A BIOGEOCHEMICAL STUDY OF THE RECENT CALCITE DEPOSITS ALONG THE LUCERO UPLIFT, VALENCIA COUNTY, NEW MEXICO

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By

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

ABSTRACT

A study was conducted to ascertain the mechanism of precipitation of $CaCO_3$ from the water discharging from the springs along the eastern slope of the Lucero Uplift.

Three possible mechanisms were identified; physical depressurization, bacterial sulfate reduction, and photosynthetic CO_2 assimilation.

A typical reach of stream was sampled from January, 1974 through April, 1974 for various chemical and biological parameters. The carbonate system was studied employing the methods of equilibrium geochemistry. Estimates of the intensity of biological activity were compared to the calculated changes in the carbonate species.

The activity of sulfate reducing bacteria had no measurable effect on the carbonate equilibria. Consumption of CO_2 by photosynthetic organisms increased the rate of approach of the solution to equilibrium.

The half-life of the excess CO_2 in solution was calculated for each sampling trip. The shortest half-lives occurred during January and February concurrent with the

bloom of a cold weather alga. The rate of CO_2 consumption was increased by roughly a factor of two during the algae bloom.

A condition of equilibrium defined by Henry's Law and the dissociation constant of $CaCO_3$ was attained after which, there was no further, measurable change in the system.

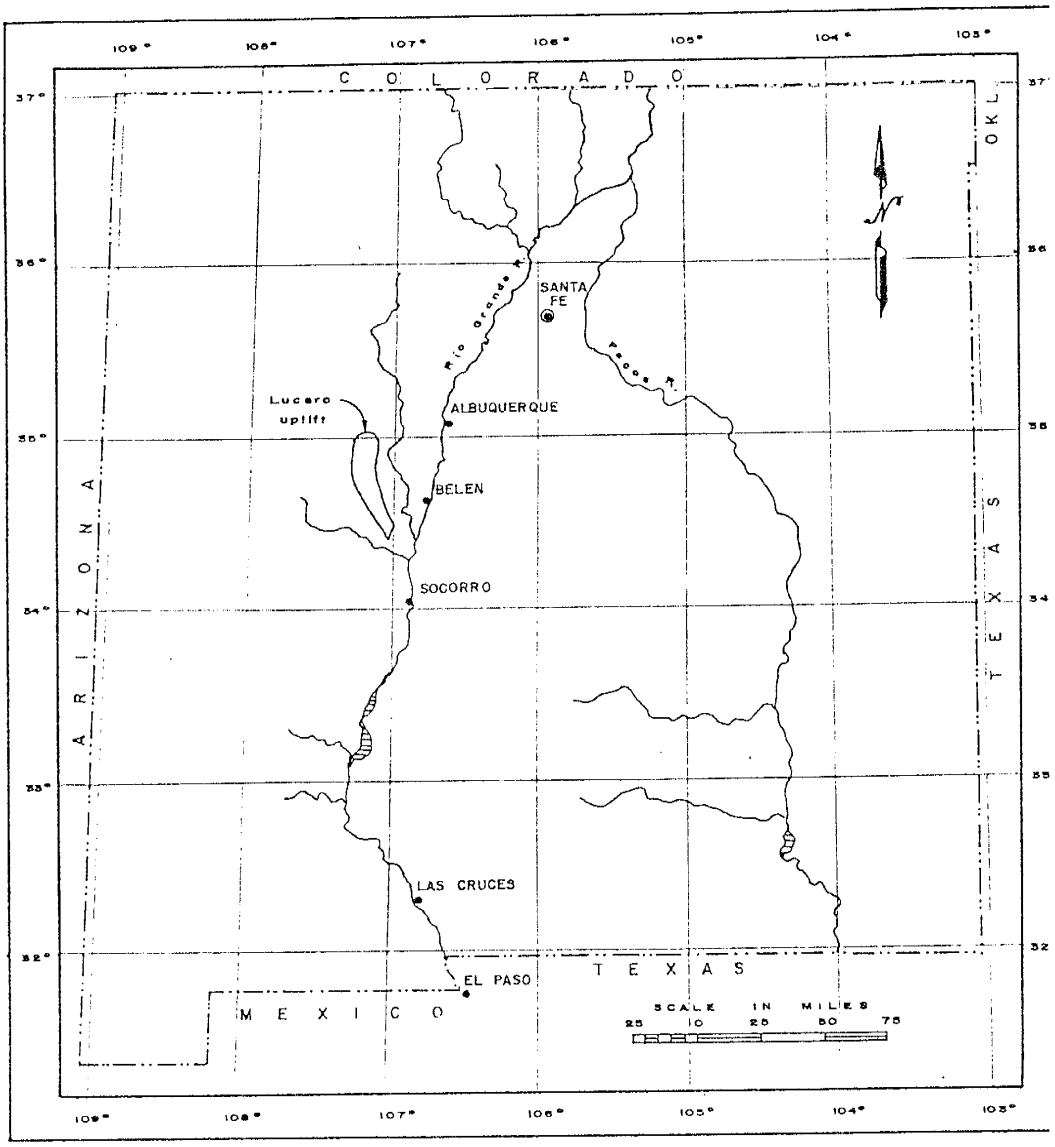
INTRODUCTION

The Lucero Uplift is located in Valencia County, New Mexico approximately 25 miles west of Belen. (See Figure 1.) The highly faulted eastern side of this uplift is the site of deposition of many thousands of cubic yards of calcium carbonate. The amount of material deposited is large enough that at one time, this rock was quarried and sold as decorative building stone. The occurance of these deposits upon the surface of the earth brought to mind the question of their origin.

The geologic features of the area give some indication of the origin and transportation of the calcite but the precise mechanism of deposition was not clear.

A zone of intense faulting along the eastern side of the uplift known as the Comanche Thrust Belt provides channels to the surface for ground water which is traveling eastward into the Rio Puerco-Rio Grande Basin. The recharge area for this water is probably the high central mesa of the uplift known as Mesa Lucero. High concentrations of sulfate, carbonate and calcium in the water suggest that it first percolates

FIGURE 1



INDEX MAP OF NEW MEXICO, SHOWING LOCATION OF THE LUCERO UPLIFT

through the evaporite beds of the Yeso formation and down through the Abo formation into the Madera limestone. The water then travels east through fractures in the Madera until it encounters the Comanche Thrust Belt where it is forced to the surface along the fault planes, (Titus, 1963).

Many of the canyons which have been cut into the eastern slope of the uplift have perennial streams flowing in them, fed by springs which surface along the canyon floors.

Certain geochemical and biological processes which occur are common to most of the streams. The most obvious is the precipitation of calcium carbonate which forms small dams and terraced ponds in the stream channel. These dams are typically one to three feet high and crescent shaped in plan view. The areas of precipitation are usually on the order of 500-1000 feet downstream from the springs. The release of gas from solution is evidenced by the presence of bubbles rising in the springs.

During certain times of the year, massive algal blooms choke the stream channel. The physical characteristics of the algal blooms such as color, morphology and distribution change with the seasons. There are also large accumulations of black sulfidic mud present in the terrace ponds and the odor of hydrogen sulfide gas can, at times, be quite strong.

Each of these observations suggest a process to which the precipitation of calcium carbonate could be attributed. All eight of the canyons visited on the uplift, exhibited the same geochemical phenomena; formation of terrace ponds caused by the building of calcite dams across the stream channel, and large accumulations of calcareous material classified by Pettijohn (1957) as calcareous tufa.

PHYSICAL DEPRESSURIZATION MODEL

Classically, the mechanism of saturation with respect to calcite is explained by the hydrogeologist in terms of physical unloading of the hydrostatic pressure as ground water enters a well bore or a rock fracture and travels upward to the earth's surface. This depressurization is the same phenomenon experienced when opening a carbonated beverage can. Carbon dioxide bubbles form and the gas is released to the atmosphere until a state of equilibrium is attained between the solution and the atmosphere. This final equilibrium state can be described with the application of Henry's Law. The loss of carbon dioxide, which behaves as an acid in aqueous solution, results in an increase in pH. This increase in pH causes a shift in the carbonate system to favor the

formation of the $CO_3^=$ ion. As $CO_3^=$ ions are produced, the point of saturation with respect to calcite can be reached, if there is any calcium in solution. When the saturation level is exceeded with respect to calcium carbonate the solid precipitate will begin to form. The reader is referred to Appendix A for a detailed discussion of the carbonate system.

CONTROL BY PHOTOSYNTHESIS

The presence of living organisms in all natural aquatic systems generally complicates the otherwise straightforward geochemical picture defined in terms of purely physical variables.

The geologist describes the earth in terms of the lithosphere, the hydrosphere and the atmosphere. The biologist adds to this the biosphere which extends into all realms of the physical world.

The most common biogeochemically active elements are carbon, nitrogen, sulfur, hydrogen and oxygen. Iron, phosphorous and manganese also can be included but are of lesser importance (Stumm and Morgan, 1970). The activities of living organisms in aquatic systems often exert the dominant control on the Eh-pH regime of those systems (Bass Becking and others, 1960).

Photosynthesis is the trapping of light energy and its conversion to chemical bond energy. The products of photosynthesis are in reduced states of higher free energy and thus nonequilibrium concentrations of carbon compounds are common. The element carbon acts as the link between the inorganic and organic world. The activity of the earth's photosynthetic organisms could almost deplete the atmosphere of carbon dioxide in a short time if it were not for the respiration of heterotrophic organisms which return CO_2 to the atmosphere, (Stumm and Morgan, 1970).

The consumption of CO_2 by photosynthetic organisms is one of the proposed mechanisms which can result in calcite precipitation. This mechanism has been referred to in the limnologic as well as geologic literature by Hem (1970), Otsuki and Wetzel (1974) and others. The process is the same chemically as the purely physical depressurization model. The important difference between the two is that photosynthetic organisms can drive a system below atmospheric CO_2 equilibrium resulting in an increase in the pH of the solution. An increase in pH can bring about the precipitation of calcite from a system which is otherwise physically stable.

BACTERIAL SULFATE REDUCTION

The third mechanism for $CaCO_3$ precipitation is also a biologically mediated redox reaction. Accumulations of organic matter undergo decomposition with the resulting consumption of oxygen. As the rate of oxygen diffusion into a system falls below the rate of consumption, the system becomes anaerobic. When this happens, organisms must find a substitute for oxygen, which functions as a terminal electron acceptor. Some organisms are specifically adapted to this sort of environment. They use the sulfate ion as a terminal electron acceptor instead of oxygen. This is known as anaerobic respiration.

The process of respiration produces chemical energy for synthetic reactions by enzymatically catalyzing a series of stepwise redox reactions within a living cell. At each step energy is derived from the reaction as the electrons are transferred to levels of lower potential energy. The final transfer is to a substance which can be discharged from the cell. Higher organisms use O_2 for this purpose. Anaerobic sulfate reducing bacteria use the sulfate ion, $SO_4^=$. Although the reduction of $SO_4^=$ to H_2S is thermodynamically favored in

some anaerobic environments, the reaction does not usually proceed in the absence of a biological catalyst (Berner, 1971). The production of H_2S then must be accompanied by the reduction of $SO_4^{=}$ concentration in the environment.

If an aqueous system is at equilibrium with respect to sypsum, and $SO_4^{=}$ is being consumed by sulfate reducing bacteria, then more $CaSO_4 \cdot 2\ H_2O$ will dissolve, if it is present. This process can eventually produce calcium concentrations which in the presence of natural HCO_3^{-} and $CO_3^{=}$ can result in saturation with respect to $CaCO_3$.

The three proposed mechanisms for $CaCO_3$ precipitation are depressurization, photosynthesis and bacterial sulfate reduction. The objective of this project was to determine which one mechanism or what combination of the three is responsible for exerting the dominant control on the carbonate system at Lucero.

METHODS

Fresh water systems such as lakes and streams commonly exhibit fluctuations in biological and chemical parameters due to seasonal variations of temperature, sunlight intensity and photoperiod. A succession of events characterizing the warming trend of oncoming summer quite often culminates in mid-summer with intense photosynthetic and metabolic activity (Odum, 1971). A reversal of this succession is also common as temperatures drop and daylight hours diminish with the approach of winter.

In the harsh, high desert environment of the Lucero Uplift, it seems safe to say that both the middle of winter with sub-freezing temperatures and the heat of mid-summer would bring biological activity to a minimum in a shallow stream. With this in mind, it was decided that the changes in certain chemical and biological parameters would be monitored from January of 1974 through June of that year. The effects of changes in those parameters upon the carbonate equilibria would be evaluated. Water samples for chemical analysis and samples of algae and bacteria were collected during biweekly trips to the field.

Four attempts were made to assess the level of photosynthetic activity by monitoring diurnal fluctuation in the chemical parameters.

DESCRIPTION OF STUDY AREA

The site chosen for the study was a small canyon named Arroyo Salado which is the location of some of the more extensive calcite deposits. The location of the study area is; T6N, R3W, Sec. 35 and 36.

The rate of discharge of the spring appeared to remain relatively constant; in the neighborhood of 100 gpm. The width and depth of the reach of stream chosen varies significantly in 1200 feet of run. The general tendency is a widening of the channel as dams and ponds are formed by calcite precipitation. At the mouth of the spring, the stream width is approximately 2 feet with a depth of about six to eight inches. At the farthest downstream sampling point, the stream is up to 15 feet wide but only an inch or two deep. This condition results in a decrease in flow velocity as the distance from the spring increases.

ESTABLISHMENT OF SAMPLING STATIONS

Six stations were chosen along a 1200 foot reach of stream which was thought to be representative of all the springs observed along the uplift. These stations were chosen after several preliminary visits to the canyon, on the basis of pH and temperature measurements. The discharging ground water has a relatively consistent pH value ranging from 6.50 to 7.00 and a temperature essentially constant at 10°C. The pH increases downstream from the spring to a value near 8.0 and then remains constant.

The stations were numbered 1 through 6. Station number 1 was the spring itself which was a depression almost five feet in depth and approximately ten feet across. There was no sign of calcite precipitation in the spring. Station 1a was at the confluence of the discharging spring water and the water flowing down the canyon from various other small seeps upstream. Stations 2, 3 and 4 were intermediate sampling points along the stream. Station 5 was the site of a small seepage area along the bank. A station was established there to monitor the effects of that discharge on the stream. Station 6 was the farthest downstream station (1200 feet from the spring) and the point at which no further change in pH was measurable.

The reach of stream chosen was thought to be adequately representative of the other streams observed on the uplift. It was hoped that the six sampling stations would supply the data necessary to characterize, in detail, the mechanism of formation of the large calcite deposits.

DEFINITION OF CHEMICAL BACKGROUND

To present a complete picture of an aqueous system, the concentrations of all the major dissolved constituents must first be determined. This information can significantly affect the interpretation of the data generated for the species of interest, especially when a rather high total dissolved solids content is anticipated. Chemical analyses of each sample were made to establish the chemical background of the system to aid in estimation of complex ion formation and the solubility effects related to ionic strength.

Each sample of solution collected was analyzed for Na^{+}, K^{+}, Mg^{++}, Ca^{++}, Cl^{-}, $SO_4^{=}$, and HCO_3^{-} - $CO_3^{=}$. Temperature, pH and dissolved oxygen measurements were also made.

FIELD METHODS OF ANALYSIS

pH

The singularly most important parameter to be measured in a natural aquatic system is pH. The pH of the solution

was measured in situ at the time of collection of each sample. An Orion 407 Ionalyzer with a combination pH-reference electrode was used for this measurement.

Before each pH measurement was made, two buffer solutions bracketing the range to be measured were placed in the stream to bring them to the temperature of the stream. The pH meter was then standardized with the two buffers prior to each measurement. The temperature corrected pH values of the buffers were used in the standardization of the pH meter.

Temperature

Temperature is also one of the more fundamental environmental parameters which profoundly affects the type and intensity of the biological activity of the system. The rates of most chemical reactions are also usually quite temperature dependent. The temperature of the solution was measured with the YSI Model 54 oxygen-temperature meter.

Dissolved Oxygen

As an indication of the level of photosynthetic activity, the dissolved oxygen concentration was measured using the same YSI Model 54. This instrument was calibrated prior to each measurement in a calibration chamber which is held in the solution to be measured to obtain the same temperature while still remaining in contact with the atmosphere.

Alkalinity

The common way to measure the amount of inorganic carbon in a natural system is by means of an alkalinity titration. Alkalinity is exactly what the name implies, acid neutralizing capacity and measures all species which accept hydrogen ions (Stumm and Morgan, 1970). The underlying assumptions upon which this method is based are two. The first assumption is that the only basic components in the system are the carbonate and bicarbonate ions. This is usually true in most natural waters. The second assumption is that the initial pH of the sample is greater than 7.5. If the pH of the solution is less than 7.5, then a significant part of the dissolved carbonate concentration is not measured because it is in the form of carbonic acid or dissolved carbon dioxide.

The second requirement could not be met when dealing with the surfacing ground water of Arroyo Salado. The initial pH at the springs ranged from 6.3 in some areas to 7.0 in the study area.

To compensate for this condition the sample was pipetted directly from the stream into a beaker in which a premeasured amount of standardized sodium hydroxide had been

added. The presence of the NaOH increased the pH into the ten to twelve range and thus converted any non-dissociated carbonic acid to carbonate and bicarbonate ions. The titration was then carried out using a pH meter to determine the two equivalence points as the standard acid was added. The quantity of acid added between the two equivalence points is a direct measure of the total carbonate in the sample. Then using the initial pH of the sample, the proper distribution of carbonate species can be determined (See Appendix A).

On the first two trips to the site, this modified alkalinity titration was performed immediately after each sample was collected to determine the total carbonate concentration in the solution. This procedure was discontinued for reasons given further on in this paper.

LABORATORY METHODS OF ANALYSIS

The samples of water collected in the field were acidified and then filtered upon returning to the laboratory. The concentrations of the common major ground water constituents were then determined.

Sodium, Magnesium and Potassium

The sodium, magnesium and potassium concentrations were determined by atomic absorption spectrophotometry. The

instrument used for these three assays was a Perkin-Elmer Model 303.

Calcium

The determination of the calcium ion concentration was made by an EDTA complexometric titration using the calcein modified indicator.

Chloride

The chloride ion concentrations were obtained by the use of the mercuric nitrate titration.

Sulfate

Sulfate concentrations were measured by the gravimetric method, using barium chloride to precipitate the sulfate.

All of the above methods were those currently being used by the New Mexico Bureau of Mines and Mineral Resources metallurgical assay lab, and were performed by the author in that laboratory.

TREATMENT OF DATA

Saturation of a solution with respect to calcite is readily evaluated by use of the dissociation constant of $CaCO_3$. The constant, K_{EQ}, is defined as the product of the equilibrium activities of the calcium and carbonate ions.

The term activity is used to describe the ideal or thermodynamically defined concentration of an ion or compound. If the product of the activities of these two ions, called the Ion Activity Product (IAP), is equal to K_{EQ} then the system is at equilibrium. At equilibrium the rate of solution equals the rate of precipitation and the activities of calcium and carbonate remain constant. If the ion activity product is less than K_{EQ} then the solid, calcite, will tend to dissolve until the IAP is equal to K_{EQ}. When the IAP is greater than K_{EQ}, a condition of supersaturation exists and the solid can begin to form spontaneously from solution.

Each water sample was analyzed to determine whether calcite was actively dissolving or precipitating at that sample point. The determination of the ion activity product for Ca^{++} and $CO_3^{=}$ at each station was the fundamental task of the project. It was hoped that precisely describing the carbonate system would uncover the controlling mechanism.

Estimation of Activity Coefficients

In a laboratory beaker at 20°C, many simplifying assumptions can be made which are not valid in the natural environment. A sizable part of the work done was directed toward evaluating the nonideality of this system. The most common

simplification afforded to the laboratory chemist is that of infinite dilution. When studying the solubility of one compound, it is common to isolate the reactants to try to eliminate the effects of other ions in solution which do not directly participate in the reaction of interest. The ionic composition of ground water rarely meets this criterion. Weak long range attraction of oppositely charged ionic species for each other, ion-dipole interactions with the water in which they are dissolved, along with other weak interactions result in nonideal behavior of ions in solution. The fact that ions in solution at a given concentration are separated by finite distances suggests that the condition of infinite dilution cannot be met. The interactions of ions in a solution at some concentration alters the effectiveness of an ion to quantitatively behave as an independent entity. The result is that the ions in a real solution have both an actual and an effective concentration. The effective or ideal concentration is termed the ion's activity. These two quantities are related by a factor known as the activity coefficient which is represented by the greek letter gamma.

$$a_i = \gamma_i m_i \qquad (1)$$

Where a_i = the activity of specie i

m_i = the actual molal concentration of specie i

γ_i = the individual ion activity coefficient of specie i

The true utility of this type of correction factor becomes apparent as the concentrations of electrolytes increase. With increasing concentration γ_i decreases and the effective concentration of species i is often much less than the actual analytical concentration. The magnitude of the factor γ_i is dependent upon a quantity known as ionic strength which is defined by the following equation

$$I = 1/2 \quad \sum m_i Z_i^2 \tag{2}$$

Where I = the ionic strength of a given solution

Z_i = the valence of ion i

m_i = the molal concentration of ion i

The evaluation of the solubility of a compound in a real solution must include an estimate of ionic interactions. The value of K_{EQ} is calculated from thermodynamic data and implicitly assumes ideal conditions. The concentrations of ions

measured analytically are actual concentrations not activities, so the IAP of $CaCO_3$ must be written as:

$$IAP = (Ca^{++})\,(CO_3^{=}) = \gamma_{Ca^{++}}\,[Ca^{++}]\;\gamma_{CO_3^{=}}\,[CO_3^{=}] \qquad (3)$$

Parentheses are used to designate activity while square brackets represent the analytically determined concentration of the enclosed species.

A thorough discussion of the deviations from ideality and the effects of ionic strength can be found in the book by Garrels and Christ, (1965, ch. 2).

Ion Pair Formation

The next correction that must be made is for more short range ionic interactions which are likely to occur as electrolyte concentrations increase. The formation of ion pairs and complex ions has a tendency to broaden the gap further between the actual and effective concentrations of dissolved ions. The association of ions in solution increases the solubility of solid ionic compounds by tying up the free ions with which the solid must equilibrate. The extent to which two ions will associate can be quantitatively evaluated by the application of the correct association constant.

The association constant is the ratio of the activities of the free and associated ions. In this case also, the individual ion activity coefficients for all the ions must be obtained first.

The effects of ion pair formation were estimated using an iterative calculation which is most clearly outlined in the article entitled "A Chemical Model of Sea Water at 25°C and One Atmosphere Total Pressure" by Garrels and Thompson, (1962).

The symbol $\dot{\gamma}$ is used herein to represent the stoichiometric ion activity coefficient. This factor takes into account the effect of both ionic strength and ion pairing. The final analysis of the solubility of $CaCO_3$ must include an assessment of those departures from ideality.

The chemical data from the field and the laboratory analyses are tabulated in Appendix B in Tables B-1 through B-7.

The detailed description of the changes in the chemical composition of the solution as it traveled from the spring to station 6 over the six-month period was compared for each sampling trip. It was thought that a study of the fluctuations in chemical composition would ellucidate the controlling mechanism. The chemical changes with time were compared with estimates of the intensity of biological activity made during each visit to the site.

The biological work done in conjunction with the chemical evaluation of the problem was performed by C.J. Fisher and was submitted to Dr. James Brierley. The final report of that part of the project is included in this paper as Appendix C.

RESULTS

CHEMICAL DATA

Sampling trips were scheduled every two weeks from late January of 1974 through June of that year. Sampling was discontinued in May when the spring stopped flowing. It was thought that exploration drilling in the vicinity with its associated water requirements caused the interruption in the spring discharge.

The sampling consisted of taking one liter of solution from each of six stations for chemical analysis. Samples of algae and bottom sediment samples for bacterial determinations were also collected.

Certain chemical parameters such as pH, alkalinity, temperature and dissolved oxygen were measured at each station at the time of sample collection. It was felt that the in situ measurement of those parameters was important.

The major constituents of the solution as can be seen in Table 1 are sodium and chloride. The concentrations of these two ions are more than an order of magnitude greater than the concentrations of the other major ions found in the

TABLE I

THE COMPOSITION OF SEA WATER, ARROYO SALADO WATER AND AVERAGE RIVER WATER.

ION	PRESENT OCEAN	ARROYO SALADO	AVERAGE RIVER
Na^{+}, m	0.47	0.23	2.7×10^{-4}
K^{+}, m	1.0×10^{-2}	2.47×10^{-3}	5.9×10^{-5}
Ca^{+2}, m	1.0×10^{-2}	1.16×10^{-3}	3.8×10^{-4}
Mg^{+2}, m	5.4×10^{-2}	1.75×10^{-2}	3.4×10^{-4}
Cl^{-}, m	0.55	0.19	2.2×10^{-4}
SO_4^{-2}, m	3.8×10^{-2}	3.58×10^{-2}	1.2×10^{-4}
AlK, EQ/L	2.3×10^{-3}	1.83×10^{-3}	9.6×10^{-4}
I, m	0.65	0.33	
pH	7.89	8.11	

solution, with the exception of the sulfate ion. The average sodium ion concentration of the spring water is 0.23 M/1 and the average chloride ion concentration is 0.19 M/1. As a comparison, Table 1 also lists the concentrations of the major constituents of sea water and the average river (Stumm and Morgan, 1970). It is interesting to note that the composition of the solution in the study area resembles that of sea water much more closely than that of the average river. The order of magnitude of the concentration of most ions listed for Arroyo Salado are very close to those of sea water. The values for pH, Ca^{++} and alkalinity listed for Arroyo Salado are the averages of the equilibrium values.

The complete chemical analysis of each sample taken on regularly scheduled trips to the field are listed in Tables B-1 through B-7 in Appendix B. As can be seen, although calcium carbonate was apparently precipitating from solution, the calcium values varied only slightly and in most cases not at all. At the same time, the pH increased by at least one whole unit.

During the first two sampling trips a modified alkalinity or C_t titration was done for each sample immediately after each sample was collected. The results of those titrations were

thought to be of paramount importance because the alkalinity titration is the only direct measurement of the bicarbonate and carbonate ions in solution. These data also showed little or no change as the distance from the spring increased. (See Table 2.) The values given in Table 2 are C_t values as defined in Stumm and Morgan, (1970):

$$C_t = [H_2CO_3^*] + [HCO_3^-] + [CO_3^=] \quad (4)$$

After the first two sampling trips the alkalinity titration was discontinued. The difficulty with this method is that alkalinity is always conserved, even as the CO_2 is bubbling off (Stumm and Morgan, 1970). The folling reaction shows the conservation of alkalinity.

$$2HCO_3^- = H_2O + CO_2 + CO_3^= \quad (5)$$

The loss of CO_2 either biologically or strictly chemically will cause an increase in the concentration of carbonate ions, and an upward shift in the pH. If the system is at equilibrium with $CaCO_3$ then the increase in $(CO_3^=)$ will bring about the formation of solid $CaCO_3$ from solution. The colloidal size particles of $CaCO_3$ are titrated along with the free HCO_3^- and $CO_3^=$.

The samples for chemical analysis were acidified and filtered upon returning to the lab. This practice has some

TABLE 2

C_T' VALUE FOR STATIONS 1 TO 6 FOR SAMPLING TRIPS 1 AND 2, IN MOLES / LITER

STATION NUMBER	DATA SET 1 1-26-74	DATA SET 2 2-9-74
1	.023 m/l	.021 m/l
2	.023 m/l	.020 m/l
3	.021 m/l	.020 m/l
4	.020 m/l	.018 m/l
5	.019 m/l	.021 m/l
6	.021 m/l	.021 m/l

$$'C_T = \left[H_2CO_3^*\right] + \left[HCO_3^-\right] + \left[CO_3^{=}\right]$$

inherent problems, when trying to study a nonequilibrium system. Any calcite that was formed is redissolved with the addition of the acid. If the samples are not acidified, there is the problem of trying to hold each sample in a nonequilibrium state until the time for analysis, and when the bottle is opened the loss of CO_2 is unavoidable. The calcium titration using EDTA also will measure suspended colloidal calcium which is in the form of solid $CaCO_3$.

The aforementioned complications made accurate description of the flowing, dynamic system impossible using conventional analytical techniques and sampling methods.

The only concrete piece of data by which the carbonate system could be described was the in situ measurement of the pH. A look at the data in Appendix B shows a consistent increase in pH along the stream, for each sampling trip. The change in pH between Stations 1 and 6 is usually at least one whole unit. The pH values at Stations 4 and 6 rarely exceed 8.10.

The ratios of the activities of the three carbonate species can be readily obtained from an accurate measurement of the pH. A complete description of the carbonate system is

possible if the concentration of only one other of the species related to the carbonate system can be quantified.

At this point it is appropriate to mention that for a detailed discussion of carbonate equilibria, the reader is once again referred to Appendix A.

The problem became finding some measurement of the quantity of inorganic carbon in solution, by a means other than the classical acid-base type of titration. The modified alkalinity titration done at the spring gave a measure of the total carbonate, C_t. The value of C_t is good only at the spring where the water first reaches the surface. The C_t titration at all points downstream becomes increasingly inaccurate as the amount of suspended $CaCO_3$ increases. Any suspended $CaCO_3$ is also titrated by the acid.

It was estimated that the solution was probably saturated with respect to solid $CaCO_3$ while still underground. If saturation could be demonstrated then the problem could then be solved.

High concentrations of dissolved solids usually indicate that the water had been traveling as ground water for a very long time. A knowledge of the rates of ground water flow, usually less than 20 feet per year, also would bring

one to the conclusion that the water had been in contact with the minerals of the aquifer for a very long period of time. A quote from Hem, (1971) summarizes the reasoning which might lead one to test the assumption that the solution was at equilibrium with $CaCO_3$. "Presumably, any reaction that reasonably could be expected to reach equilibrium would do so in the usual aquifer system." The aquifer system that is discussed here is the Madera Limestone formation. It does seem reasonable then, to assume that the discharging ground water was at equilibrium with respect to $CaCO_3$.

To test this assumption the IAP of $CaCO_3$ was calculated using the pH, $[Ca^{++}]$ and C_t values obtained at the spring during the first two sampling trips. The carbonate concentration from the C_t titration must first be converted to an activity. This must also be done for the calcium concentration. The value of the IAP is calculated using Equation (3)

$$IAP = (Ca^{++})\ (CO_3^{=}) = \gamma_{Ca^{++}}\ [Ca^{++}]\ \gamma_{CO_3^{=}}\ [CO_3^{=}] \qquad (3)$$

The IAP's thus calculated for Station 1 using the C_t titration and $[Ca^{++}]$ for the first and second sampling trips on 1/26/74 and 2/10/74 were $10^{-7.85}$ and $10^{-8.12}$ respectively.

The two values both indicate that the solution was slightly oversaturated with respect to $CaCO_3$ at the time the sample was collected. The equilibrium constant for $CaCO_3$ is $10^{-8.35}$ from Jacobson and Langmuir, (1974). Similar calculations were also made for $CaSO_2 \cdot 2H_2O$. Equilibrium was also established between that compound and the solution.

The demonstration of equilibrium of the solution with $CaCO_3$ at the spring made it possible, using the pH and $[Ca^{++}]$, to calculate the activities of all of the carbonate species. The total carbonate and partial pressure of CO_2 could also be obtained for the water at Station 1.

Evaluation of the state of the system at the stations downstream requires only two adjustments. First a new value for alkalinity must be calculated from the alkalinity value at the first station using Equation 6.

$$[Alk_2] = [Alk_1] - 2[CaCO_{3ppt}] \qquad (6)$$

where: $[Alk_1]$ = Alkalinity at Station 1, eqv./l.

$[Alk_2]$ = Alkalinity at Station 2, eqv./l

$[CaCO_{3ppt}]$ = Quantity in M/l of $CaCO_3$ precipitated between Stations 1 and 2

The second quantity to be adjusted is the $[Ca^{++}]$ at the second station which is defined by Equation 7.

$$[Ca^{++}]_2 = [Ca^{++}]_1 - [CaCO_{3\ ppt}] \tag{7}$$

where: $[Ca^{++}]_1$ = Calcium concentration at Station 1

$[Ca^{++}]_2$ = Calcium concentration at Station 2

A complete discussion of the method of calculation of the carbonate species and calcium ion concentrations at each station can also be found in Appendix A.

Using the pH and $[Ca^{++}]$ values at the spring in conjunction with the average C_t value from Table 2 of .0207 M/1, the distribution of species was calculated. From those data and the pH taken at each station the activities of all of the carbonate species were calculated along with the Ca^{++} activities. The final state of equilibrium was defined by two conditions; the partial pressure of CO_2 in solution equal to that in the atmosphere, $10^{-3.5}$ atm. and the IAP of Ca^{++} and $CO_3^{=}$ equal to the dissociation constant for $CaCO_3$. The results of these calculations are tabulated along with the other chemical data in Appendix B, Tables B-8 through B-14. All the values listed in Tables B-8 through B-14 are activities except for alkalinity

which is defined in terms of concentration. The activity coefficients were calculated using the Davies equation and an average ionic strength of 0.33 M/l. The high sodium, chloride and sulphate levels simplified the calculation of the activity coefficients. These three species form the supporting electrolyte solution which practically fixes the values of the individual ion activity coefficients.

The additional effect of ion pair formation is included in the stoichiometric ion activity coefficient, which was used in the calculation of the values in Tables B-8 through B-14. The only ion pair which affected the calculations was $NaHCO_3^o$. The average values used for the stoichiometric ion activity coefficients for Ca^{++}, $CO_3^=$ and HCO_3^- were 0.301, 0.301 and 0.625 respectively.

The most useful results of this study were the calculated activity values. Figures B-1 through B-7 are graphs of those data showing the changes in the activities of Ca^{++}, $CO_3^=$, $H_2CO_3^*$ and pH versus distance of flow from the spring. The symbol $H_2CO_3^*$ is used to designate the combination of the two species, CO_2 (aq.) and H_2CO_3. The use of this symbol is discussed in Appendix A. There is a consistent drop in pH and ($H_2CO_3^*$) along with a small increase in ($CO_3^=$). The

decrease in (Ca^{++}) indicated by the calculated values is not apparent in Tables B-1 through B-7 which are the analytically determined values. The calculated (Ca^{++}) data shows a fifty percent decrease while the chemically determined values show practically no change at all. The data from Station 5 was not used in the calculations. Although the pH did fluctuate in the marshy area around that station it had no measurable effect on the main stream due to an extremely small volume of flow.

The question of whether calcium is actually precipitated and in colloidal form or in a supersaturated state is difficult to answer. It was assumed here to be in the solid form but as very small particles. It was thought that the turbulence of the running water would disrupt any supersaturated condition. Three interesting papers by Berner, (1967), Bischoff, (1968) and Raistrick, (1949) discuss the stabilization of supersaturated solutions of $CaCO_3$ in the presence of the Mg^{++} ion and ions possessing O-P-O-P-O chains respectively. It is clear from those papers that the problem still merits investigation.

The use of a Ca^{++} specific ion electrode could have answered this question. Unfortunately, an electrode of that type was not available at the time.

BIOLOGICAL RESULTS

The samples collected for biological determinations were examined for various types of bacteria known to be associated with sulfate rich waters and sulfidic sediments. The bacteria thought to be potentially responsible for the precipitation of calcite via the conversion of sulfate to sulfide were analyzed for. Samples of bottom sediments at numerous locations showed the presence of anaerobic Gram-negative vibrios that were capable of production of hydrogen sulfide. The difficulties involved in culturing and counting strict anaerobes made detailed population and rate studies too difficult to be done within the time frame of the project. The cell morphology, trophic requirements and environmental conditions gave all indications of the presence of the originally sought after bacterium, Desulfovibrio desulfuricans. Despite the presence of sulfide rich sediments and D. desulfuricans, the data in Appendix B show no significant decrease in sulfate downstream and no source of solid calcium sulfate could be found along the stream channel.

Further bacterial work demonstrated the presence of three species of the genus Thiobacillus which are aerobic

sulfur oxidizing bacteria. The presence of these bacteria indicate complete biological cycling of sulfur compounds in the upper centimeter or two of the sediment layers.

The details of the biological work done as part of this project were presented in a report to Dr. James Brierly in the form of a directed study conducted by Carla J. Fisher. That report in its entirety is included in this paper as Appendix C.

The second biological mechanism described in the Introduction is the effect of massive algal blooms, which had been observed during the six month period prior to the study. The details of this phase of the study are also best described in Appendix C.

Two periods of rather high productivity were observed and samples of algae were collected. The rate of carbon dioxide assimilation and concomitant oxygen production were estimated. The periods of estimated high productivity were during the month of February and late April.

Four attempts were made to determine if there were any measurable diurnal fluctuations in CO_2 and O_2 content of the solution. Two of the four attempts on 2/27/74 and

4/16/74 were successful. The results of those two experiments show a somewhat slower increase in pH downstream and lower concentration of dissolved O_2 after sunset than during the daylight hours.

DISCUSSION

The objective of this study was to ascertain the mechanism by which calcium carbonate was being precipitated from the streams on the Lucero Uplift. The data collected according to accepted sampling methods provided a rather confusing picture, so a theoretical approach was taken. The activities of the key chemical species were calculated from a few basic pieces of data. Using the methods of equilibrium geochemistry and making the necessary corrections for complexing and ionic strength, a data base was developed. It is these data that have been used in the final assessment of the system under consideration.

The first mechanism that was looked at was the precipitation of calcite caused by the activity of sulfate reducing bacteria. The proposed mechanism is represented by one of the following chemical reactions depending upon the pH of the system (Berner, 1971).

$$2CH_2O + SO_4^{=} = 2HCO_3^{-} + H_2S \qquad (8)$$

or

$$2CH_2O + SO_4^{=} = HCO_3^{-} + HS^{-} + CO_2 + H_2O \qquad (9)$$

An increase in the (HCO_3^-) as shown above, in the presence of dissolved Ca^{++} could bring about the precipitation of $CaCO_3$. (A convenient way to represent organic material in the form of carbohydrates is CH_2O.)

The bacterial conversion of $SO_4^{=}$ to $S^{=}$ can also cause the dissolution of solid $CaSO_4$ which would increase the activity of Ca^{++} in solution. This would imply that the solution is already saturated with respect to $CaSO_4$ and that a source of gypsum exists nearby. The following reaction is a representation of that mechanism.

$$CaSO_4 + 2CH_2O = H_2S + H_2CO_3 + CaCO_3 \qquad (10)$$

A brief scan of the $SO_4^{=}$ assays in Tables B-1 through B-7 shows no decrease as the water traveled downstream, and if anything, a slight increase. If the above mechanism was at work, then it was at least not measurable.

The small increase in $SO_4^{=}$ concentration in some of the data sets seemed to indicate that $CaSO_4$ was dissolving and replenishing the Ca^{++} in solution as fast as it was being precipitated as $CaCO_3$. This idea was rejected because

for every 100 grams of $CaCO_3$ deposited, 172 grams of gypsum would have to dissolve; for every cubic yard of $CaCO_3$ deposited, two cubic yards of gypsum would have to dissolve. There are no apparent, large sources of gypsum in the area of any of the $CaCO_3$ deposits.

The second of the biologically related reactions deals with the consumption of CO_2 by the massive algal blooms observed in the stream.

It can be seen in the next two reactions:

$$Ca^{++} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O \qquad (11)$$

$$CO_2 + H_2O + \text{Solar Energy} \xrightarrow{\text{Photosynthesis}} CH_2O + O_2 \qquad (12)$$

that the consumption of CO_2 by intense photosynthetic activity could bring about precipitation of $CaCO_3$. It has been noted in the literature by Hem, (1970) and particularly Otsuki and Wetzel, (1974) that photosynthetic utilization of CO_2 by algae is the dominant mechanism for the precipitation of $CaCO_3$ in hard water lakes. Although the body of water under consideration is not a lake, it was thought that the flowing aspect of the system would not negate the effect of

this mechanism. Occurrances of pH values between 9 and 10 are common at midday during algal blooms in the lake systems referred to above (Otsuki and Wetzel, 1974). The same lake may have a pH in the neighborhood of 8.0 during the predawn hours. A pH of approximately 8.0 is what might be expected for a body of water at equilibrium with both atmospheric CO_2 and solid $CaCO_3$. High pH values, above 8.5 represent an under saturation of the solution with respect to CO_2. That type of situation in the presence of an algae bloom clearly represents photosynthetically controlled precipitation of $CaCO_3$. The algal activity actually drives the system beyond equilibrium to an undersaturated condition with respect to CO_2.

The major difference between Arroyo Salado and hard water lakes is that at no time was there any apparent undersaturation of CO_2. A look at the calculated data for each sampling trip in Tables B-8 through B-14 and the graphs of that data in Figures B-1 through B-7 show a steady asymptotic approach to a condition which is represented by a relatively constant pH. The calculated activities of $H_2CO_3^*$ which correspond to the final pH values at Station 6 always closely

approach the equilibrium $H_2CO_3^*$ activities. The equilibrium ($H_2CO_3^*$) values are included in Figures B-1 through B-7. The equilibrium value varies with the water temperature.

The algal community apparently did not drive the system beyond the point of atmospheric equilibrium with the solution. The calculated values for the ($H_2CO_3^*$) in all cases indicated a slight oversaturation with CO_2. The average oversaturation was approximately 0.5 mg/l of $H_2CO_3^*$. For all practical purposes the solution was at equilibrium. It appears that there was no undersaturation and only an arrival of the system at a predictable state of thermodynamic equilibrium.

Although the algae bloom did not seem to affect the final composition of the solution, its presence appeared to have affected the rate at which the system approached equilibrium.

The data obtained during the two diurnal studies indicate that during the daylight hours the rate of increase in pH was greater, (Appendix C). The change in pH and ($H_2CO_3^*$) are proportional so the pH was used as an indicator of the rate of change of the ($H_2CO_3^*$). Those data are plotted in Figures C-9 and C-10.

Dissolved O_2 was also measured as an index of photosynthetic activity. The O_2 data were plotted as percent saturation in Figures C-11 and C-12.

Figures C-9 through C-10 show that the rate of change of pH and the percent of saturation of O_2 are greater during the daylight hours when the rate of photosynthetic activity should be the highest.

The data from the regular sampling trips were analyzed to determine whether any correlation could be made between the rate of change of the ($H_2CO_3^*$) and the intensity of photosynthetic activity.

To make a meaningful comparison it was assumed that there were only two processes that affect the rate of equilibration of CO_2. The two processes were photosynthetic CO_2 consumption and diffusion of that gas from solution.

The rate of diffusion of a gas from the solution to the atmosphere can be described by Fick's First Law. This law states that the rate of diffusion is directly proportional to the concentration gradient (Daniels and Alberty, 1966).

$$J = D \left(\frac{dC}{dx} \right) \tag{13}$$

where:

J = The flux of a substance through a plane perpendicular to the direction of diffusion in units of moles per unit of time through a unit area.

D = The diffusion coefficient, a proportionality constant which has units of cm^2 per sec.

C = Concentration, moles/l

x = Distance of flow, cm

This equation is analogous to Ohm's Law in physics and Darcy's Law in ground water hydrology.

The observed rate of decrease of CO_2 was thought to be a result of the combination of both mechanisms. This reasoning led to the assumption that the rate of physical diffusion was a constant. This assumption is probably not entirely valid because there are so many variables that affect diffusion of a gas from a natural, flowing system. It does appear to be a necessary assumption if any sort of comparison is to be made. Any increases in rate from one time to another was then attributed to photosynthetic activity.

The next step was to construct an idealized stream channel. Various assumptions also had to be made here. First a regular, rectangular cross-section was assumed for the stream. The dimensions of the channel were assumed to

be constant, as was the flow velocity. Those assumptions must be made to make a quantitative comparison possible. The actual channel characteristics do at least remain constant with time.

Figure 2 is an illustration of the idealized system which was used to estimate the rate of attainment of equilibrium. The volume of flow is represented by V which is assumed to be constant. The term x is the distance of flow from the spring and W is the width of the channel.

Using this model, a mass balance can be set up for CO_2, assuming steady state conditions along the length of the stream during the sampling period. (Geankoplis, 1972 and Daniels & Alberty, 1966).

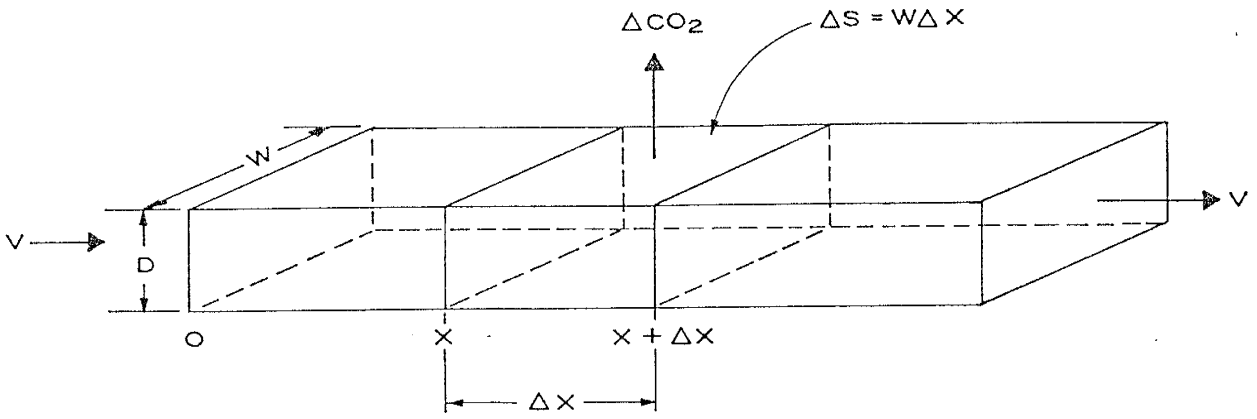
The moles of CO_2 flowing in at x per unit of time minus the moles of CO_2 flowing out at $x + \Delta x$ per unit of time is equal to the moles of CO_2 diffusing through the surface ΔS per unit of time. In equation form the system is described as follows:

$$Q_x - Q_{x+\Delta x} = \bar{R}W \quad \Delta x \tag{14}$$

where

FIGURE 2

IDEALIZED STREAM CROSS SECTION



V = SPRING DISCHARGE, 100 GPM OR $3.79 \cdot 10^5 CM^3/MIN.$

W = CHANNEL WIDTH, 10 FT. OR 305 CM

D = CHANNEL DEPTH, 2 IN. OR 5 CM

X = DISTANCE FROM SPRING IN FT. OR CM

Q = (volume of flow) $(H_2CO_3^*)$

$\bar{R}$ = average rate of diffusion between x and $x+\Delta x$

According to Fick's Law, the rate of diffusion is proportional to the concentration gradient ΔC_x.

$$\Delta C_x = (\text{Conc. of } CO_2 \text{ at Dist. x}) - (\text{Conc. of } CO_2 \text{ at equilibrium}) \tag{15}$$

The concentration gradient changes continuously downstream as does the rate of diffusion R. Equation 14 can be rearranged to:

$$\frac{(-Q_{x+\Delta x} - Q_x)}{\Delta x} = \bar{R}W \tag{16}$$

and if Δx is made infinitely small to approach the limit 0,

$$\lim_{x \to o} -\frac{(Q_{x+\Delta x} - Q_x)}{\Delta x} = \lim_{x \to o} [\bar{R}W] \tag{17}$$

$$= -\frac{dQ}{dx} = RW \tag{18}$$

The result is the definition of a derivative (Purcell, 1965 and Batschelet, 1971).

The quantity Q is defined as the volume of flow times the concentration of $H_2CO_3^*$ and can be written as:

$$Q = V \triangle C_{CO_2} \tag{19}$$

If R is proportional to the concentration gradient $\triangle C_x$, then

$$R \propto \triangle C_x$$

or

$$R = k \triangle C_x \tag{20}$$

Substituting Equations 19 and 20 into form 18, the final equation is a first order separable, differential equation.

$$-V \left(\frac{dC}{dx}\right) - kW \triangle C_x = 0 \tag{21}$$

This equation is solved by separating variables and integrating (Ross, 1966).

$$\int_{C_o}^{C_x} d \frac{\triangle C}{\triangle C} = \frac{-kW}{V} \int_o^x dx = \tag{22}$$

$$= \frac{\triangle C_x}{\triangle C_o} = e^{\frac{(-kWx)}{V}} \tag{23}$$

Converting to common logarithms results in Equation 24

$$\log \quad \triangle C_x = \frac{(-kWx)}{V} \quad \frac{1}{2.303} + \log \ \triangle C_o \qquad (24)$$

Equation 24 is identical to a first order, reaction rate equation, and if a plot of log $\triangle C$ vs. $\frac{Wx}{V}$ is a straight line then the slope of the line is k, the proportionality constant (Daniels and Alberty, 1966).

Figures B-1 through B-7 in Appendix B are, in fact, log activity vs. distance curves. If the flow velocity can be considered constant then the graphs are log activity vs. time curves. From these data log $\triangle C$ values can be calculated and plotted against distance or time. Figures B-8 through B-14 also in Appendix B are plots of log $\triangle(H_2CO_3^*)$ vs. $\frac{Wx}{V}$ for the seven sampling trips. The slopes of those lines are equal to -k/2.303. The quantity k is the mass transfer coefficient for each set of data. A more appropriate name for this application would be a consumption coefficient for CO_2. It is analogous to resistance in Ohm's Law.

Visual inspection of Figures B-1 through B-7 and B-8 through B-14 indicate that there were different mechanisms at work at different times. The plots of Data Sets 1 and 3

seem to deviate from the first order rate relationship and as Figures B-15 through B-17 in Appendix B show, give a straight line on log-log plot. Data Sets 4, 5 and 6 on the other hand give a straight line on the log-normal plots, Figures B-8 through B-14. The log-log plots indicate a more rapid decrease in ($H_2CO_3^*$) with increasing distance of flow. The data in Sets 2 and 7 seem to lie somewhere between the two distributions.

The major application of a log-log distribution is the graphical representation of a power function (Batschelet, 1971). For example:

$$y = ax^n \tag{25}$$

The common way to deal with this sort of equation is to make a logarithmic transformation which yields a linear relation with the exponent n, of the power function as the slope. Taking the logarithms of Equation 25

$$\log y = \log a + n \log x \tag{26}$$

and substituting in new variables and constants

$$Y = \log y,\ X = \log x,\ B = \log a$$

The result is,

$$Y = nX + B \tag{27}$$

a linear relation. Figures B-15 through B-17 are log-log plots of the ($H_2CO_3^*$) from Tables B-8 through B-10. Data Sets 1 and 3 seem to fit this type of plot well.

The two types of distribution make comparison difficult. To make a comparison possible the log-normal distribution with the half-life calculation was used.

Estimates of the rate of photosynthetic activity from Appendix C describe a period of high productivity coincidental with the first three sampling trips during late January and February. That period of time was characterized by a prolific bloom of a cold water alga known as Ulothrix which literally filled the stream channel from Station 1 to Station 3. It is pertinent to note that the Ulothrix bloom extended only as far as Station 3. It would appear that some factor became limiting at that point. The bloom terminated abruptly between 2/23/74 and 3/9/74.

The next period of high algal productivity occurred at the end of the study period around the time of sampling trip 7.

Using only the first part of the curves, from Stations 1 to 3, for Data Sets 1 and 3 gives a fairly good estimate of the rate of algal CO_2 utilization. The values of k

calculated from the slopes of the log $\triangle(H_2CO_3^*)$ versus $\frac{Wx}{V}$ were then used in the calculation of half-distances and half-lives of the excess CO_2 in solution for all seven sets of data. The method is outlined in detail in the chapter dealing with chemical kinetics in the book by Daniels and Alberty, (1966).

The half-distance $x_{1/2}$, is the distance from the source traversed at a constant velocity, at which $\triangle C_x / \triangle C_o = 0.5$. The half-life of the concentration gradient, $t_{1/2} = x_{1/2}/u$ where u = the velocity of flow.

The half distances were calculated from Equation (24).

$$\log \frac{\triangle Co}{\triangle C_x} = \frac{kWx}{2.303\ V} \tag{24}$$

$$x_{1/2} = 2.303 \log \frac{1}{1/2} \quad \frac{V}{k\ W} \tag{28}$$

$$x_{1/2} = 2.303\ (.301) \quad \frac{V}{k\ W}$$

The volume discharge of the spring was estimated to be 100 gallons per minute or 3.79×10^5 cm^3/min. The value of W was chosen 10 ft or 305 cm. The resultant velocity was about 250 cm per minute.

Table 3 lists the half-lives and half-distances for ($H_2CO_3^*$) for the seven sets of data. Figure 3 is a plot of the half-lives versus time in months. Figure 3 is the culmination of all the work done on this project. It shows the rate of equilibration of CO_2 with time. It is an estimate of the seasonal variation of the carbonate system.

From Figure 3 it can be seen that the half-life of ($H_2CO_3^*$) was significantly shorter during January and February than later on in the season. The effect of the algae is thought to be the shortening of the half-lives. Another way to state it is that the algae functioned as accelerators of the chemical process which resulted in the precipitation of $CaCO_3$. The effect is roughly a doubling of the rate of CO_2 loss from solution.

It is also of interest to note that the period of highest biological activity occurred during the coldest part of the year and not in late spring as was originally hypothesized. This was due to the presence of the cold water alga Ulothrix. A late spring bloom may have occurred had the flow not been interrupted.

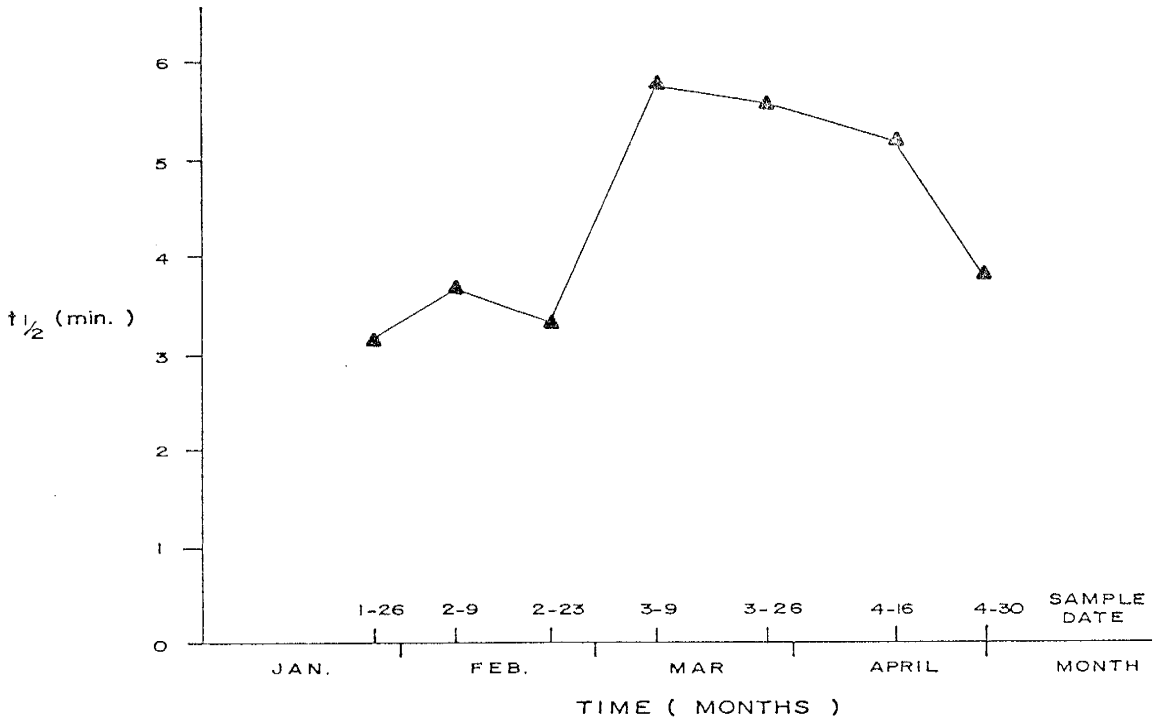
TABLE 3

HALF-LIVES $t_{1/2}$, & HALF-DISTANCE $X_{1/2}$

DATA SET	SAMPLE DATE	SLOPE	k	$X_{1/2}$ (CM)	$t_{1/2}$ (MIN)
1	1-26-74	-0.47	1.08	797	3.18
2	2-9-74	-0.41	0.94	916	3.66
3	2-23-74	-0.44	1.01	852	3.40
4	3-9-74	-0.26	0.60	1434	5.74
5	3-26-74	-0.27	0.62	1388	5.55
6	4-16-74	-0.29	0.67	1285	5.14
7	4-30-74	-0.40	0.92	935	3.74

FIGURE 3

HALF - LIFE OF (H_2CO_3*) VS TIME IN MONTHS



SUMMARY AND CONCLUSIONS

SUMMARY

Three processes were studied to determine the most probable mechanism for the precipitation of $CaCO_3$ in the canyons along the Lucero Uplift.

A representative study area was chosen and was sampled every two weeks from January until May of 1974.

Chemical analyses were performed on samples taken from six stations. From these analytical results a body of theoretical data was generated based primarily upon the pH of the solution. Using that data in conjunction with the biological work done by C. J. Fisher, a comparison was made of the state of the chemical system and the level of biological activity.

CONCLUSIONS

The effect of sulfate reducing bacteria was not measurable and is thought not to be significant. The aqueous sulfate concentration varied only slightly.

The presence of massive algal blooms caused an increase in the rate of change of the concentration of CO_2 but did not seem to affect the final composition of the solution

It was concluded that the actual controlling parameters of the final composition of the solution were the partial pressure of CO_2 in the atmosphere and the solubility of $CaCO_3$. In all observed cases the system came to a state of chemical equilibrium, after which there was no measurable change.

Conventional sampling and analytical procedures used for the study of natural waters proved to be inapplicable to this system, so a theoretical approach was taken. The application of the concepts and methods of equilibrium geochemistry was used to accurately describe the natural, aqueous system which has produced the anomalous deposits of $CaCO_3$ on the Lucero Uplift.

APPENDIX A

CARBONATE EQUILIBRIA

The various forms of inorganic carbon found associated with aquatic systems are CO_2 (gas), CO_2 (aq), H_2CO_3, HCO_3^-, $CO_3^=$ and $CaCO_3$(c).

THE CLOSED SYSTEM

At first it is convenient to ignore the presence of the gaseous phase and consider an aqueous system isolated from the atmosphere.

The carbonate species which occur in this system are H_2CO_3, HCO_3^- and $CO_3^=$. It is apparent that both the bicarbonate ion, HCO_3^- and the carbonate ion, $CO_3^=$ are produced by the loss of hydrogen ions from carbonic acid. The degree of dissociation of an acid can be quantified by the application of the proper dissociation constants. Carbonic acid is a diprotic acid, having two hydrogen ions (protons) available for transfer. These two transfers occur in a stepwise fashion. Each transfer has a thermodynamically derived constant which characterizes the reaction quantitatively.

The products of the first dissociation are the bicarbonate ion and one hydrogen ion. The dissociation constant for the reaction

$$H_2CO_3 = H^+ + HCO_3^-$$

is

$$K_1 = \frac{(H^+)\ (HCO_3^-)}{(H_2CO_3)} \qquad \text{(a-1)}$$

The second dissociation constant, for the reaction

$$HCO_3^- = H^+ + CO_3^=$$

is given in Equation (a-2)

$$K_2 = \frac{(H^+)\ (CO_3^=)}{(HCO_3^-)} \qquad \text{(a-2)}$$

All quantities enclosed in parentheses represent the activities or ideal concentrations of those species. Square brackets will be used to designate analytical concentration of a given substance.

(i) = the activity of substance i

[i] = the analytically determined concentration of substance i

Using the two dissociation constants, the relative amounts of the three aqueous species can be determined, if the pH of the solution is known. The actual concentration of each species can be calculated if the concentration of one of the carbonate species can be defined. Another useful quantity, ΣCO_2 is defined as the total of all the carbonate species in solution. As defined in Equation a-3

$$\Sigma CO_2 = (H_2CO_3) + (HCO_3^-) + (CO_3^=) \qquad \text{(a-3)}$$

C_t is used to represent the analogous quantity in terms of concentration. Using Equations (a-1), (a-2), and (a-3), all the quantities in this system can be obtained if just two of the five quantities, pH, ΣCO_2 (H_2CO_3), (HCO_3^-) or $(CO_3^=)$ are known.

A graphical method to represent aqueous acid-base systems has been developed by Sillen (1959). Figure A-1 is a log activity pH diagram of the carbonate system closed to the atmosphere at 25°C. ΣCO_2 has been arbitrarily set at 10^{-2} M/l.

At any pH the concentrations of H_2CO_3, HCO_3^- and $CO_3^=$ can be obtained directly from the graph. Figure A-1 also shows that the ratios of the concentrations of the three species are totally dependent upon pH no matter how ΣCO_2 is varied.

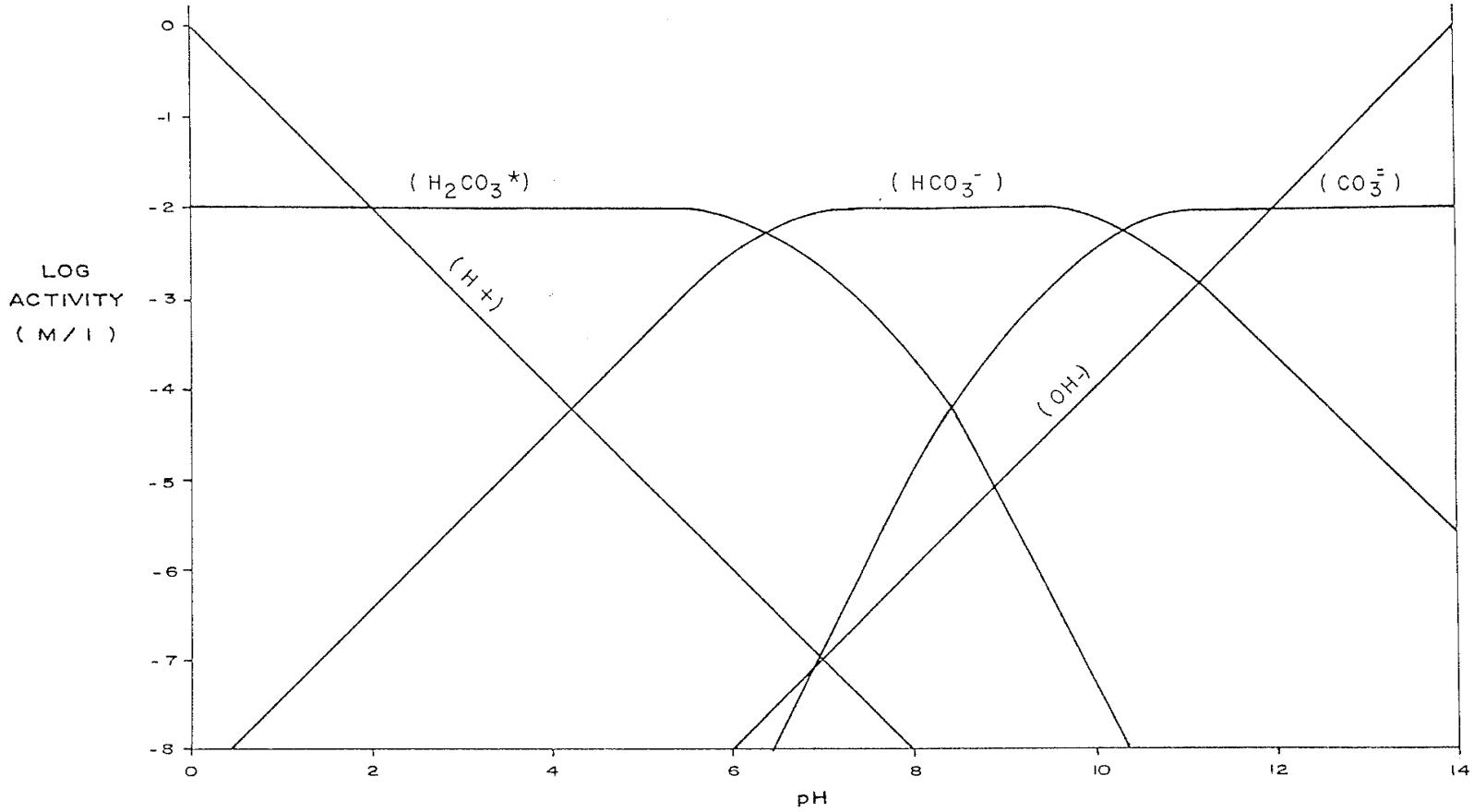
FIGURE A-1

LOG ACTIVITY

VS

pH DIAGRAM FOR THE CARBONATE SYSTEM ISOLATED FROM THE ATMOSPHERE

$\Sigma CO_2 = 10^{-2}$ TEMP = 20° C



THE OPEN SYSTEM

The next carbonate system to look at is the system open to the atmosphere. Figure A-2 is a log activity - pH diagram of the three carbonate species at equilibrium with the atmospheric partial pressure of CO_2, which is approximately $10^{-3.5}$ atm. at sea level.

The notation $H_2CO_3^*$, (Stumm and Morgan 1970) is used to represent the sum of the activities of both $CO_2(aq)$ and H_2CO_3. This approach is commonly used to simplify the discussions of carbonate equilibria. Using this simplification necessitates the use of a composite acidity constant.

It is not commonly discussed in most ground water literature but the true first dissociation constant of carbonic acid given by Fischer and Peters, (1968) for the reaction

$$H_2CO_3 = H^+ + HCO_3^-$$

is actually

$$K_1 = \frac{(H^+)\ (HCO_3^-)}{(H_2CO_3)} = 10^{-3.76} \qquad \text{(a-4)}$$

The value commonly used for K_1 is in the neighborhood of $10^{-6.35}$ at 20°C, which is the composite acidity constant for the first dissociation of carbonic acid. The composite value

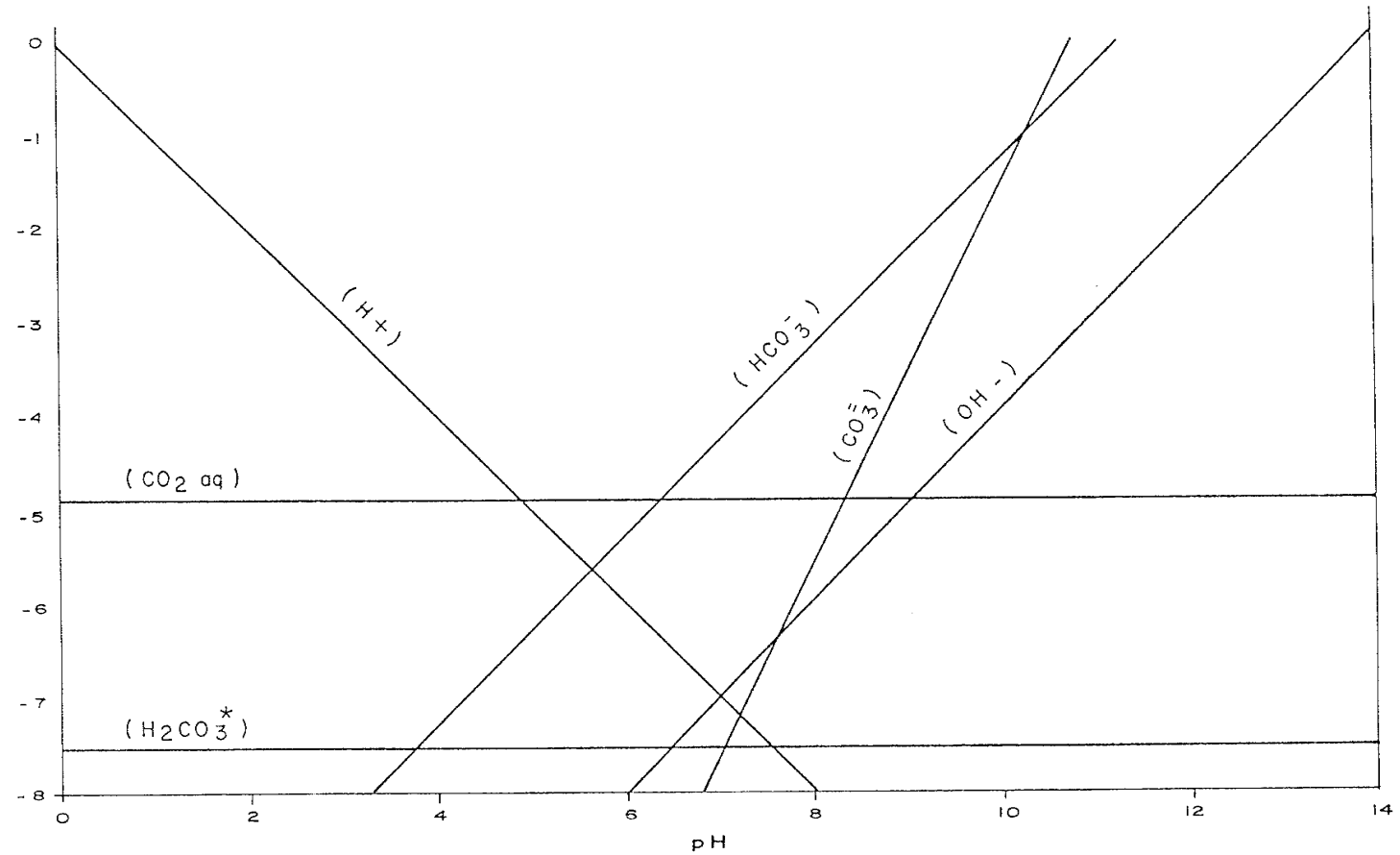
FIGURE A - 2

LOG ACTIVITY

VS

pH DIAGRAM FOR THE CARBONATE SYSTEM OPEN TO THE ATMOSPHERE

$pCO_2 = 10^{-3.5}$ atm TEMP = 20°C



will be used in conjunction with the symbol $H_2CO_3^*$ to distinguish it from the value given in Equation (a-4). The composite acidity constant is actually derived from two reactions

$$CO_2\ (aq) + H_2O = H_2CO_3$$

$$K_H = \frac{(H_2CO_3)}{(CO_2\ (aq))} = 10^{2.59} \qquad \text{(a-5)}$$

and Equation (a-4) from above.

Upon combining the two reactions we have:

$$H_2O + CO_2 = H_2CO_3 = H^+ + HCO_3^-$$

The constant for this combined reaction is

$$\frac{(H_2CO_3)}{(H_2O)\ (CO_2(aq))} \qquad \frac{(H^+)\ (HCO_3^-)}{(H_2CO_3)} = 10^{-6.53} \qquad \text{(a-6)}$$

which is the value most commonly used for the first dissociation constant for carbonic acid. This also shows that H_2CO_3 is a much stronger acid than it is usually thought and that the dominant species in solution is actually CO_2 (aq) and not H_2CO_3. It is for this reason that the notation $H_2CO_3^*$ from Stumm and Morgan, (1970) is used. Equation (a-4) will be written as Equation (a-7) and the composite constant will be used for K_1.

$$K_1 = \frac{(H^+)\ (HCO_3)}{(H_2CO_3^*)} = 10^{-6.35} \qquad \text{(a-7)}$$

bearing in mind that actually

$$(H_2CO_3^*) = (H_2CO_3) + (CO_2\ aq) \qquad \text{(a-8)}$$

Figure A-2 shows the open system without the use of the composite constant. CO_2 (aq) and H_2CO_3 are shown as they actually occur. Although CO_2 (aq) is the dominant species of the two it must be converted to H_2CO_3 before it can dissociate to HCO_3^-. It is this step which is commonly ignored.

The actual differences in the closed and open systems can be seen by comparing Figures A-1 and A-2 where ΣCO_2 was held constant in Figure A-1, $H_2CO_3^*$ is held constant in Figure A-2 and ΣCO_2 varies as a function of pH.

In actuality (H_2CO_3) is a function of the $(CO_2$ (aq)) according to Equation (a-5), and the $(CO_2$ (aq)) is dependent upon the partial pressure of CO_2 in the atmosphere. The equilibrium concentrations of gaseous and aqueous CO_2 are determined by Henry's Law which is written as

$$p_i = H_i\ f_i \qquad \text{(a-9)}$$

where:

p_i = to the partial pressure of solute i in the gaseous phase in atmospheres

f_i = the mole fraction of solute i in the liquid phase.

H_i = the Henry's Law constant for the solute i in atmospheres per mole fraction.

At 20°C, the value of H_{CO2} is $10^{3.15}$ from Foust and others (1960), and the value of pCO_2 is about $10^{-3.5}$ atm. at sea level.

The activity of CO_2 (aq) is calculated as follows:

$$\frac{10^{-3.5} \text{ atm}}{10^{3.15} \frac{\text{atm.}}{\text{mole fraction}}} = 10^{-6.65} \qquad \text{(a-10)}$$

$$(10^{-6.65})\ (10^{1.74} \text{ m/l } H_2O) = 10^{-4.91} \text{ m/l } CO_2 \text{ (aq)} \qquad \text{(a-11)}$$

Figure A-2 shows how ΣCO_2 increases as a function of pH at a constant pCO_2 of $10^{-3.5}$ atm or $(H_2CO_3^*) = 10^{-4.91}$ moles per liter. Equation (a-12) is the combined form of Equations (a-8) and (a-9)

$$K_H = \frac{(H_2CO_3^*)}{pCO_2} \qquad \text{(a-12)}$$

which relates Henry's Law to the composite first dissociation constant for carbonic acid, as in Equation (a-5).

Figures A-1 and A-2 show that the carbonate system in contact with the atmosphere as in a stream or lake, behaves differently than in the closed system which describes more closely a confined ground water system.

$CaCO_3$ SOLUBILITY

The addition of calcium to either system further complicates the calculations but also imposes a boundary on the system. This boundary is the saturation point of $CaCO_3$.

$$(Ca^{++})\ (CO_3^{=}) = K_{EQ} \qquad \text{(a-13)}$$

Equation (a-13) clearly states that at equilibrium if either (Ca^{++}) or $(CO_3^{=})$ is known, then the other value is fixed. A further extension of this line of thought brings about the realization that if the activity of Ca^{++} and pH are known for a system at equilibrium with $CaCO_3(s)$ all other species can be calculated if either ΣCO_2 or pCO_2 are known. Combining Equations (a-2), (a-3), (a-7), and (a-13) yields Equation (a-14) for the closed system where ΣCO_2 is held constant.

$$\sum CO_2 = \frac{K_{EQ}}{(Ca^{++})} \quad \frac{(H^+)^2}{K_1K_2} + \frac{(H^+)}{K_2} + 1 \qquad \text{(a-14)}$$

Equations (a-15), (a-16), and (a-17) define $(H_2CO_3^*)$, (HCO_3^-) and $(CO_3^=)$ respectively for the closed system at equilibrium with $CaCO_3(s)$

$$(H_2CO_3^*) = \frac{K_{EQ}\ (H^+)^2}{(Ca^{++})\ K_1K_2} \qquad \text{(a-15)}$$

$$(HCO_3^-) = \frac{K_{EQ}\ (H^+)}{(Ca^{++})\ K_2} \qquad \text{(a-16)}$$

$$(CO_3^=) = \frac{K_{EQ}}{(Ca^{++})} \qquad \text{(a-17)}$$

Equation (a-18) can be used for a solution at equilibrium with solid calcite and an atmosphere with some partial pressure of CO_2.

$$(Ca^{++}) = \frac{K_{EQ}\ (H^+)^2}{K_1K_2\ K_HpCO_2} \qquad \text{(a-18)}$$

Equation (a-18) is the combined form of Equations (a-2), (a-7), and (a-12). Equations (a-15), (a-16) and (a-17) once again can be used to calculate $(H_2CO_3^*)$, (HCO_3^-), and $(CO_3^=)$, as in the closed system. The utility of Equations (a-14) and (a-18)

becomes most apparent when trying to define an aqueous carbonate system in terms of easily obtainable analytical data. If equilibrium with $CaCO_3$ can be demonstrated, then to define the entire system only two parameters need to be determined analytically. The activity of the hydrogen ion can be accurately determined with a standard pH electrode, ΣCO_2 can be obtained from an alkalinity titration and (Ca^{++}) is readily measured with a simple EDTA titration. The partial pressure of CO_2 is most often calculated from the pH and alkalinity titration.

The important boundary condition for these equations is saturation with respect to $CaCO_3$. This turns out to be an easily met condition for ground water traveling through a limestone formation.

The application of Equations (a-14) and (a-18) to natural systems requires that the distinction between activity and concentration be taken into account.

The quantity that is commonly used as a measure of the concentration of inorganic carbon in a solution is the alkalinity. Alkalinity is defined as acid neutralizing capacity of a solution. The dominant basic components of most natural

systems are usually assumed to be HCO_3^- and $CO_3^=$. In such cases alkalinity is defined as,(Stumm and Morgan, 1970):

$$[Alk] = [HCO_3^-] + 2[CO_3^=] + [OH^-] - [H^+] \qquad (a\text{-}19)$$

Equation (a-19) shows that [Alk] is not affected by changes in $[H_2CO_3^*]$. The alkalinity of a carbonate solution is conserved as CO_2 is lost or gained, as indicated by the following reaction.

$$2HCO_3^- = H_2O + CO_2 + CO_3^=$$

A change in $[H_2CO_3^*]$ does not affect the charge balance upon which [Alk] is defined.

Another quantity which is defined strictly in terms of concentration is C_t.

$$C_t = [H_2CO_3^*] + [HCO_3^-] + [CO_3^=] \qquad (a\text{-}20)$$

The use of either of these two concentration equations in conjunction with Equations (a-1) and (a-2) or (a-14) and (a-18) necessitates the calculation of activity coefficients which are defined by Equation 1 in the text. The quantities in (a-19) and (a-20) can be written in terms of activity with the application of the proper activity coefficients.

$$C_t = \frac{(H_2CO_3^*)}{\gamma_{H_2CO_3^*}} + \frac{(HCO_3^-)}{\gamma_{HCO_3^-}} + \frac{(CO_3^=)}{\gamma_{CO_3^=}} \qquad \text{(a-21)}$$

$$[Alk] = \frac{(HCO_3^-)}{\gamma_{HCO_3^-}} + \frac{2\ (CO_3^=)}{\gamma_{CO_3^=}} \qquad \text{(a-22)}$$

The activities of the carbonate species can be calculated from Equation (a-22) and Equation (a-2) if the pH of the solution is known. No correction is needed for the pH because it is a measure of the hydrogen ion activity. For an in depth discussion of carbonate equilibria, see Garrels and Christ, (1965) and Stumm and Morgan, (1970).

METHOD OF CALCULATION

The calculated activity values listed in Tables B-8 through B-15 were obtained using the following iterative process.

The initial $[Ca^{++}]$ and C_t are known for the first station. The pH is measured at each station.

Step 1. Assuming equilibrium with respect to $CaCO_3$ calculate $(CO_3^=)$.

$$K_{EQ} = (CO_3^=)\ [Ca^{++}]\ \gamma_{Ca^{++}} \qquad \text{(a-23)}$$

$$(CO_3^=) = \frac{K_{EQ}}{[Ca^{++}]\ \gamma_{Ca^{++}}} \qquad \text{(a-24)}$$

Step 2. At given pH find (HCO_3^-), $(H_2CO_3^*)$, C_t and [Alk] for the first station using the following relations.

$$(HCO_3^-) = \frac{(CO_3^=)\ (H^+)}{K_2} \qquad (a\text{-}2)$$

$$(H_2CO_3^*) = \frac{(CO_3^=)\ (H^+)^2}{K_1K_2} \qquad (a\text{-}25)$$

$$C_t = \frac{(H_2CO_3^*)}{\gamma_{H_2CO_3^*}} + \frac{(HCO_3^-)}{\gamma_{HCO_3}} + \frac{(CO_3^=)}{\gamma_{CO_3}} \qquad (a\text{-}21)$$

$$[Alk] = \frac{(HCO_3^-)}{\gamma_{HCO_3^-}} + \frac{2\ (CO_3^=)}{\gamma_{CO_3^=}} \qquad (a\text{-}22)$$

Step 3. From Equations (a-1), (a-2), (a-22) and (a-23), calculate the carbonate species for the next station downstream, Station n+1.

To do this, first assume that no $CaCO_3$ is precipitated from solution. Then since alkalinity is conserved, although CO_2 is lost from the system, the alkalinity before precipitation of $CaCO_3$ is the same at Station n+1 as it was at Station n.

Using the value of pH for Station n+1, a value for (HCO_3^-) can be calculated from the [Alk] using Equation (a-26).

$$(HCO_3^-) = \frac{[Alk]\ (H^+)\ \gamma_{HCO_3^-}\ \gamma_{CO_3^=}}{CO_3^=\ (H^+) + 2\ K_2\ \gamma_{HCO_3^-}} \qquad \text{(a-26)}$$

Using $(HCO_3^-)_{n+1}$ from Equation (a-26), calculate $(H_2CO_3^*)_{n+1}$ and $(CO_3^=)_{n+1}$ for station n+1 with Equations (a-1) and (a-2).

Step 4. Test IAP and adjust (Ca^{++}) and $(CO_3^=)$. The value of $(CO_3^=)_{n+1}$ is then substituted into Equation (a-13) along with the (Ca^{++}) from station n.

$$(Ca^{++})_n\ (CO_3^=)_{n+1} = IAP_{n+1} \qquad \text{(a-13)}$$

If the IAP is greater than K_{EQ}, equimolar amounts of Ca^{++} and $CO_3^=$ will precipitate until IAP = K_{EQ}. The amount of each species precipitated is calculated by setting up a quadratic equation and solving it for X where X = [CaCO] precipitated from solution.

$$(Ca^{++} - X)\ (CO_3^= - X) = K_{EQ} \qquad \text{(a-27)}$$

The values of $(Ca^{++})_{n+1}$ and $(CO_3^=)_{n+1}$ can be recalculated by subtracting X from the original value which assumed no precipitation.

The precipitation of $CO_3^=$ causes a shift in the activity ratio of $CO_3^=$ and HCO_3^-. Using this new ratio calculate the pH of the system. This pH will be almost the same as pH_n.

Step 5. Using the values for $(HCO_3^-)_{n+1}$, $(CO_3^=)_{n+1}$ and $(H_2CO_3^*)_{n+1}$ calculate a new adjusted value for [Alk] and C_t using Equations (a-19) and (a-20) respectively.

Using the new adjusted value for [Alk] and the actual measured pH at station n+1, return to Step 3.

This iterative process should be continued until the pH calculated from the activity ratio in Step 4 is equal to pH_{n+1}.

The final set of conditions for a station n+1 are defined by:

$$(Ca^{++})_{n+1}\ (CO_3^=)_{n+1} = K_{EQ} \qquad \text{(a-13)}$$

and

$$-\log \frac{(CO_3^=)_{n+1}}{(HCO_3^-)_{n+1}\ K_2} = pH_{n+1} \qquad \text{(a-28)}$$

Those two tests were made in Step 4.

The calculated values of the carbonate species and calcium ion activities were all derived from the above calculation.

APPENDIX B

TABLE B-1

DATA SET 1 JANUARY 26, 1974

MEASURED CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

STATION	Na^+ M/l	K^+ M/l	Mg^{++} M/l	Ca^{++} M/l	Cl^- M/l	$SO_4^=$ M/l	pH	O_2 mg/l	TEMP. °C
1	0.225	0.0043	0.0193	0.0142	0.218	0.0320	7.02	6.97	8.0
2	0.269	0.0049	0.0186	0.0148	0.203	0.0327	7.50	8.5	6.5
3	0.276	0.0049	0.0185	0.0153	0.211	0.0317	7.89	8.1	7.7
4	0.266	0.0048	0.0183	0.0146	0.214	0.0337	7.97	8.6	5.0
5	0.273	0.0069	0.0183	0.0142	0.202	0.0338	7.80	7.5	4.5
6	0.269	0.0045	0.0179	0.0125	0.217	0.0347	8.03	8.5	5.5

TABLE B-2

DATA SET 2 FEBRUARY 9 , 1974

MEASURED CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

STATION	Na^+ M/l	K^+ M/l	Mg^{++} M/l	Ca^{++} M/l	Cl^- M/l	$SO_4^=$ M/l	pH	O_2 mg/l	TEMP. °C
1	0.208	0.0030	0.0164	0.0113	0.173	0.0326	6.95	7.9	4.2
2	0.202	0.0030	0.0168	0.0118	0.175	0.0331	7.67	9.2	3.7
3	0.205	0.0026	0.0170	0.0118	0.180	0.0337	7.70	8.2	4.8
4	0.202	0.0026	0.0173	0.0112	0.181	0.0356	7.75	9.6	0.2
5	0.216	0.0027	0.0173	0.0105	0.194	0.0354	7.75	8.05	1.2
6	0.222	0.0027	0.0180	0.0115	0.198	0.0363	8.05	8.5	0.2

TABLE B-3

DATA SET 3 FEBRUARY 23, 1974

MEASURED CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

STATION	Na^+ M/l	K^+ M/l	Mg^{++} M/l	Ca^{++} M/l	Cl^- M/l	$SO_4^=$ M/l	pH	O_2 mg/l	TEMP °C
1	0.205	0.0021	0.0166	0.0103	0.175	0.0347	6.93		4.0
2	0.211	0.0021	0.0159	0.0100	0.177	0.0338	7.75		3.3
3	0.197	0.0021	0.0158	0.0098	0.172	0.0317	7.97		5.3
4	0.206	0.0022	0.0163	0.0098	0.171	0.0354	8.05		5.5
5	0.216	0.0019	0.0164	0.0090	0.176	0.0348	7.50		5.5
6	0.223	0.0022	0.0176	0.0098	0.197	0.0348	8.05		5.0

TABLE B-4

DATA SET 4 MARCH 3 , 1974

MEASURED CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

STATION	Na^+ M/l	K^+ M/l	Mg^{++} M/l	Ca^{++} M/l	Cl^- M/l	$SO_4^=$ M/l	pH	O_2 mg/l	TEMP. °C
1	0.213	0.0029	0.0159	0.0103	0.183	0.0343	6.75	6.1	7.2
1a	0.211	0.0027	0.0159	0.0098	0.176	0.0346	6.87	7.3	9.7
2	0.216	0.0027	0.0165	0.0102	0.186	0.0335	7.21	8.9	12.2
3	0.218	0.0028	0.0164	0.0100	0.193	0.0351	7.73		15.2
4	0.206	0.0028	0.0164	0.0097	0.180	0.0359	8.02	7.3	14.0
5	0.216	0.0028	0.0163	0.0092	0.185	0.0355	7.15	4.1	9.5
6	0.217	0.0029	0.0166	0.0090	0.200	0.0364	8.10	6.1	15.0

TABLE B-5

DATA SET 5 MARCH 26, 1974

MEASURED CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

STATION	Na^+ M/l	K^+ M/l	Mg^{++} M/l	Ca^{++} M/l	Cl^- M/l	$SO4^=$ M/l	pH	O2 mg/l	TEMP °C
1	0.210	0.0033	0.0185	0.0100	0.186	0.0364	7.08		9.0
1a	0.241	0.0036	0.0187	0.0100	0.195	0.0369	7.20		11.0
2	0.229	00036	0.0191	0.0106	0.197	0.0351	7.40		15.0
3	0.239	0.0036	0.0193	0.0102	0.194	0.0370	7.80		16.0
4	0.236	0.0030	0.0192	0.0099	0.194	0.0367	8.07		11.5
5	0.240	00028	0.0187	0.0092	0.190	0.0353	7.30		12.0
6	0.259	0.0030	0.0195	0.0091	0.197	0.0363	8.10		11.0

TABLE B-6

DATA SET 6 APRIL 16, 1974

MEASURED CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

STATION	Na^+ M/l	K^+ M/l	Mg^{++} M/l	Ca^{++} M/l	Cl^- M/l	$SO_4^=$ M/l	pH	O_2 mg/l	TEMP °C
1	0.230	0.0022	0.0173	0.0096	0.189	0.0374	6.98	7.3	10.0
1a	0.233	0.0020	0.0170	0.0098	0.188	0.0364	6.96	7.3	13.0
2	0.237	0.0021	0.0172	0.0101	0.192	0.0371	7.30	8.4	13.0
3	0.236	0.0020	0.0171	0.0100	0.188	0.0372	7.78	8.3	12.4
4	0.252	0.0021	0.0176	0.0093	0.197	0.0400	8.04	7.7	12.5
5	0.241	0.0022	0.0165	0.0089	0.193	0.0376	7.10	3.3	15.0
6	0.262	0.0025	0.0192	0.0084	0.223	0.0400	8.03	7.9	12.7

TABLE B-7

DATA SET 7 APRIL 30 , 1974

MEASURED CONCENTRATIONS OF MAJOR CATIONS AND ANIONS

STATION	Na^+ M/l	K^+ M/l	Mg^{++} M/l	Ca^{++} M/l	Cl^- M/l	$SO_4^=$ M/l	pH	O_2 mg/l	TEMP °C
1	0.239	0.0028	0.0173	0.0100	0.194	0.0375	7.26	6.7	12.0
1a	0.245	0.0024	0.0172	0.0096	0.192	0.0375	7.33	6.9	16.0
2	0.238	0.0024	0.0168	0.0100	0.187	0.0373	7.43	8.2	19.7
3	0.232	0.0021	0.0171	0.0101	0.187	0.0366	8.07	7.3	22.3
4	0.297	0.0022	0.0183	0.0096	0.206	0.0400	8.29	6.4	19.5
5	0.257	0.0023	0.0174	0.0091	0.197	0.0385	7.43	3.5	17.7
6	0.304	0.0023	0.0213	0.0083	0.245	0.0485	8.35	6.9	21.0

TABLE B-8

DATA SET 1 JANUARY 26, 1974

CALCULATED ACTIVITY VALUES FOR CARBONATE EQUILIBRIA

STATION	pH	LOG [ALK] M/l	LOG (HCO_3^-) M/l	LOG ($CO_3^=$) M/l	LOG ($H_2CO_3^*$) M/l	LOG (Ca^{++}) M/l
1	7.02	-1.75	-2.26	-5.87	-2.70	-2.48
2	7.50	-2.44	-2.64	-5.77	-3.56	-2.58
3	7.89	-2.78	-2.98	-5.72	-4.29	-2.63
4	7.97	-2.85	-3.06	-5.72	-4.45	-2.64
6	8.03	-2.91	-3.11	-5.71	-4.57	-2.64

TEMPERATURE, H_2O = 0°-5° C

EQUILIBRIUM LOG ($H_2CO_3^*$) = -4.60 m/l

LOG K_1 = -6.579

LOG K_2 = -10.625

TABLE B-9

DATA SET 2 FEBRUARY 9, 1974

CALCULATED ACTIVITY VALUES FOR CARBONATE EQUILIBRIA

STATION	pH	LOG ALK M/l	LOG (HCO_3^-) M/l	LOG ($CO_3^=$) M/l	LOG ($H_2CO_3^*$) M/l	LOG (Ca^{++}) M/l
1	6.95	-1.93	-2.13	-5.81	-2.51	-2.54
2	7.67	-2.44	-2.64	-5.60	-3.73	-2.75
3	7.70	-2.46	-2.67	-5.60	-3.79	-2.76
4	7.75	-2.50	-2.71	-5.59	-3.88	-2.77
6	8.05	-2.75	-2.96	-5.54	-4.43	-2.82

TEMPERATURE, H_2O = 0°-5° C

EQUILIBRIUM LOG ($H_2CO_3^*$) = -4.60 m/l

LOG K_1 = -6.579

LOG K_2 = -10.625

TABLE B-10

DATA SET 3 FEBRUARY 23, 1974

CALCULATED ACTIVITY VALUES FOR CARBONATE EQUILIBRIA

STATION	pH	LOG [ALK] M/l	LOG (HCO_3^-) M/l	LOG ($CO_3^=$) M/l	LOG ($H_2CO_3^*$) M/l	LOG (Ca ++) M/l
1	6.93	-1.84	-2.04	-5.67	-2.46	-2.68
2	7.75	-2.25	-2.46	-5.27	-3.69	-3.08
3	7.97	-2.37	-2.58	-5.17	-4.03	-3.19
4	8.05	-2.41	-2.62	-5.13	-4.15	-3.22
6	8.05	-2.41	-2.62	-5.13	-4.15	-3.22

TEMPERATURE, H_2O = 5.0° C

EQUILIBRIUM LOG ($H_2CO_3^*$) = -4.68 m/l

LOG K_1 = -6.517

LOG K_2 = -10.557

TABLE B-II

DATA SET 4 MARCH 9, 1974

CALCULATED ACTIVITY VALUES FOR CARBONATE EQUILIBRIA

STATION	pH	LOG [ALK] M/l	LOG (HCO_3^-) M/l	LOG ($CO_3^=$) M/l	LOG ($H_2CO_3^*$) M/l	LOG (Ca^{++}) M/l
1	6.75	-1.84	-2.04	-5.79	-2.33	-2.57
1a	6.87	-1.93	-2.13	-5.76	-2.54	-2.60
2	7.21	-2.15	-2.36	-5.64	-3.11	-2.71
3	7.73	-2.53	-2.73	-5.50	-4.00	-2.86
4	8.02	-2.75	-2.97	-5.44	-4.52	-2.91
6	8.10	-2.87	-3.03	-5.43	-4.67	-2.93

TEMPERATURE, H_2O = 10 - 15° C

EQUILIBRIUM LOG ($H_2CO_3^*$) = -4.76 m/l

LOG K_1 = -6.464

LOG K_2 = -10.490

TABLE B-12

DATA SET 5 MARCH 26, 1974

CALCULATED ACTIVITY VALUES FOR CARBONATE EQUILIBRIA

STATION	pH	LOG [ALK] M/l	LOG (HCO_3^-) M/l	LOG ($CO_3^=$) M/l	LOG ($H_2CO_3^*$) M/l	LOG (Ca^{++}) M/l
1	7.08	-2.03	-2.23	-5.65	-2.85	-2.71
1a	7.20	-2.11	-2.32	-5.61	-3.05	-2.74
2	7.40	-2.25	-2.45	-5.55	-3.39	-2.81
3	7.80	-2.52	-2.73	-5.43	-4.07	-2.93
4	8.07	-2.73	-2.94	-5.37	-4.55	-2.99
6	8.10	-2.75	-2.96	-5.36	-4.60	-2.99

TEMPERATURE, H_2O = 10 - 15° C

EQUILIBRIUM LOG ($H_2CO_3^*$) = -4.76 m/l

LOG K_1 = -6.464

LOG K_2 = -10.490

TABLE B-13

DATA SET 6 APRIL 16, 1974

CALCULATED ACTIVITY VALUES FOR CARBONATE EQUILIBRIA

STATION	pH	LOG [ALK] M/l	LOG (HCO_3^-) M/l	LOG ($CO_3^=$) M/l	LOG ($H_2CO_3^*$) M/l	LOG (Ca^{++}) M/l
1	6.98	-1.98	-2.18	-5.66	-2.73	-2.70
1a	6.96	-1.98	-2.18	-5.66	-2.73	-2.70
2	7.30	-2.19	-2.40	-5.53	-3.28	-2.87
3	7.78	-2.51	-2.72	-5.37	-4.08	-2.98
4	8.04	-2.70	-2.91	-5.30	-4.53	-3.05
6	8.04	-2.70	-2.91	-5.25	-4.53	-3.11

TEMPERATURE, H_2O = 10 - 15° C

EQUILIBRIUM LOG ($H_2CO_3^*$) = -4.76 m/l

LOG K_1 = -6.464

LOG K_2 = -10.490

TABLE B-14

DATA SET 7 APRIL 30, 1974

CALCULATED ACTIVITY VALUES FOR CARBONATE EQUILIBRIA

STATION	pH	LOG [ALK] M/l	LOG (HCO_3^-) M/l	LOG ($CO_3^=$) M/l	LOG ($H_2CO_3^*$) M/l	LOG (Ca ++) M/l
1	7.26	-2.16	-2.37	-5.49	-3.25	-2.87
1a	7.33	-2.21	-2.41	-5.47	-3.36	-2.89
2	7.43	-2.27	-2.48	-5.43	-3.53	-2.92
3	8.07	-2.69	-2.90	-5.21	-4.59	-3.14
4	8.29	-2.84	-3.06	-5.15	-4.97	-3.20
6	8.35	-2.89	-3.11	-5.14	-5.08	-3.21

TEMPERATURE, H_2O = 15 - 20° C

EQUILIBRIUM LOG ($H_2CO_3^*$) = -4.95 m/l

LOG K_1 = -6.381

LOG K_2 = -10.377

TABLE B-15

CALCULATED LOG ($H_2CO_3^*$) & LOG ΔC VALUES

STA	LOG ($H_2CO_3^*$)	LOG ΔC
SET 1		
1	-2.70	-2.71
2	-3.56	-3.60
3	-4.29	-4.53
4	-4.45	-4.84
6	-4.56	-5.20
SET 2		
1	-2.51	-2.51
2	-3.73	-3.80
3	-3.79	-3.86
4	-3.88	-3.98
6	-4.42	-4.91
SET 3		
1	-2.46	-2.46
2	-3.69	-3.74
3	-4.03	-4.15
4	-4.15	-4.31
6	-4.15	-4.31
SET 4		
1	-2.33	-2.33
1a	-2.54	-2.54
2	-3.11	-3.12
3	-3.99	-4.08
4	-4.52	-4.52
6	-4.67	-5.40

STA	LOG ($H_2CO_3^*$)	LOG ΔC
SET 5		
1	-2.85	-2.85
1a	-3.06	-3.06
2	-3.39	-3.41
3	-4.07	-4.17
4	-4.55	-4.96
6	-4.60	-5.12
SET 6		
1	-2.73	-2.73
1a	-2.73	-2.73
2	-3.23	-3.30
3	-4.08	-4.18
4	-4.52	-4.91
6	-4.52	-4.91
SET 7		
1	-3.25	-3.25
1a	-3.36	-3.38
2	-3.53	-3.55
3	-4.59	-4.87
4	-4.97	0
6	-5.08	0

FIGURE B - 1

LOG ACTIVITY VS DISTANCE

DATA SET 1 1-26-74

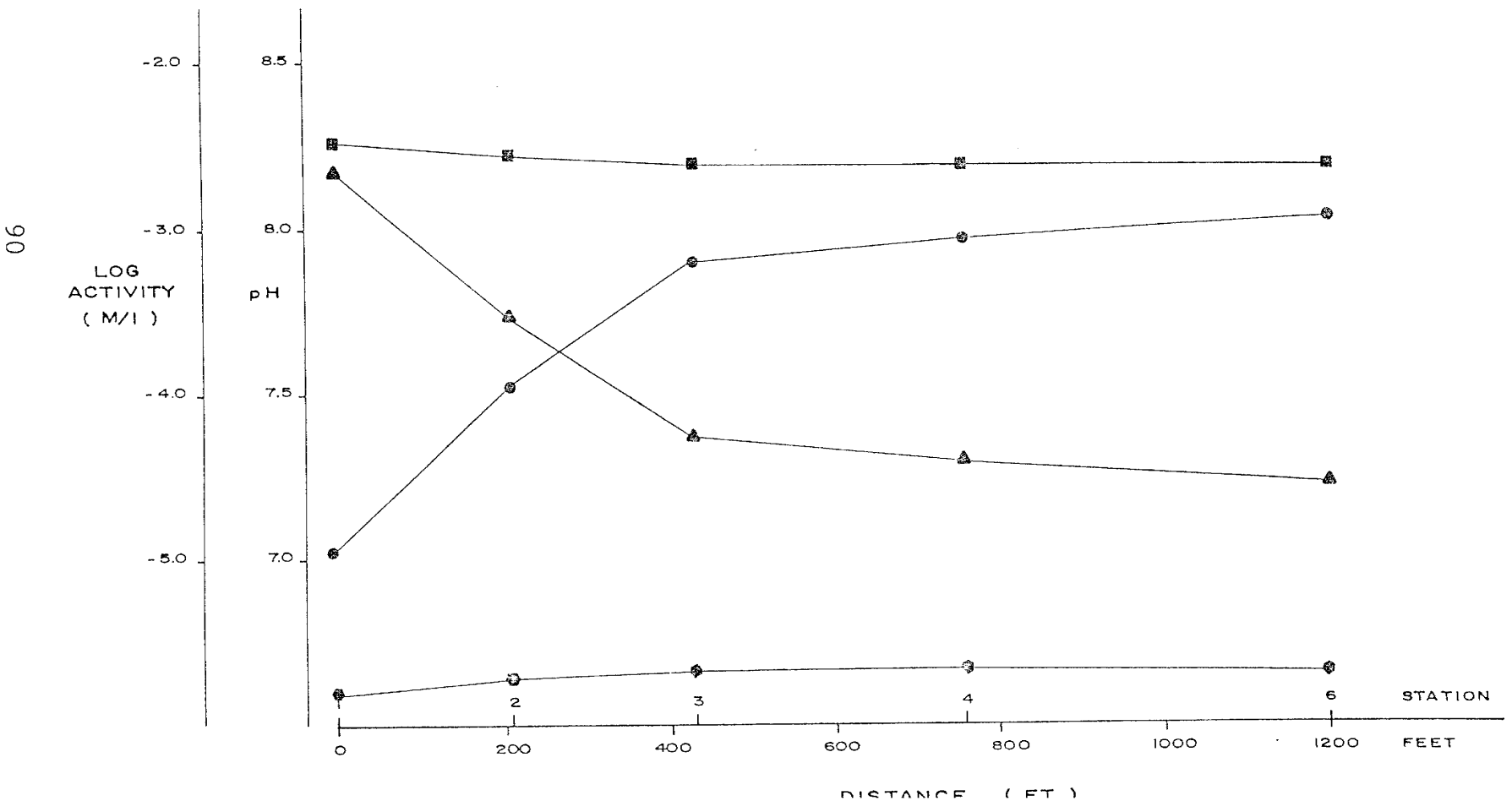


FIGURE B - 2

LOG ACTIVITY VS DISTANCE

DATA SET 2 2 - 9 - 74

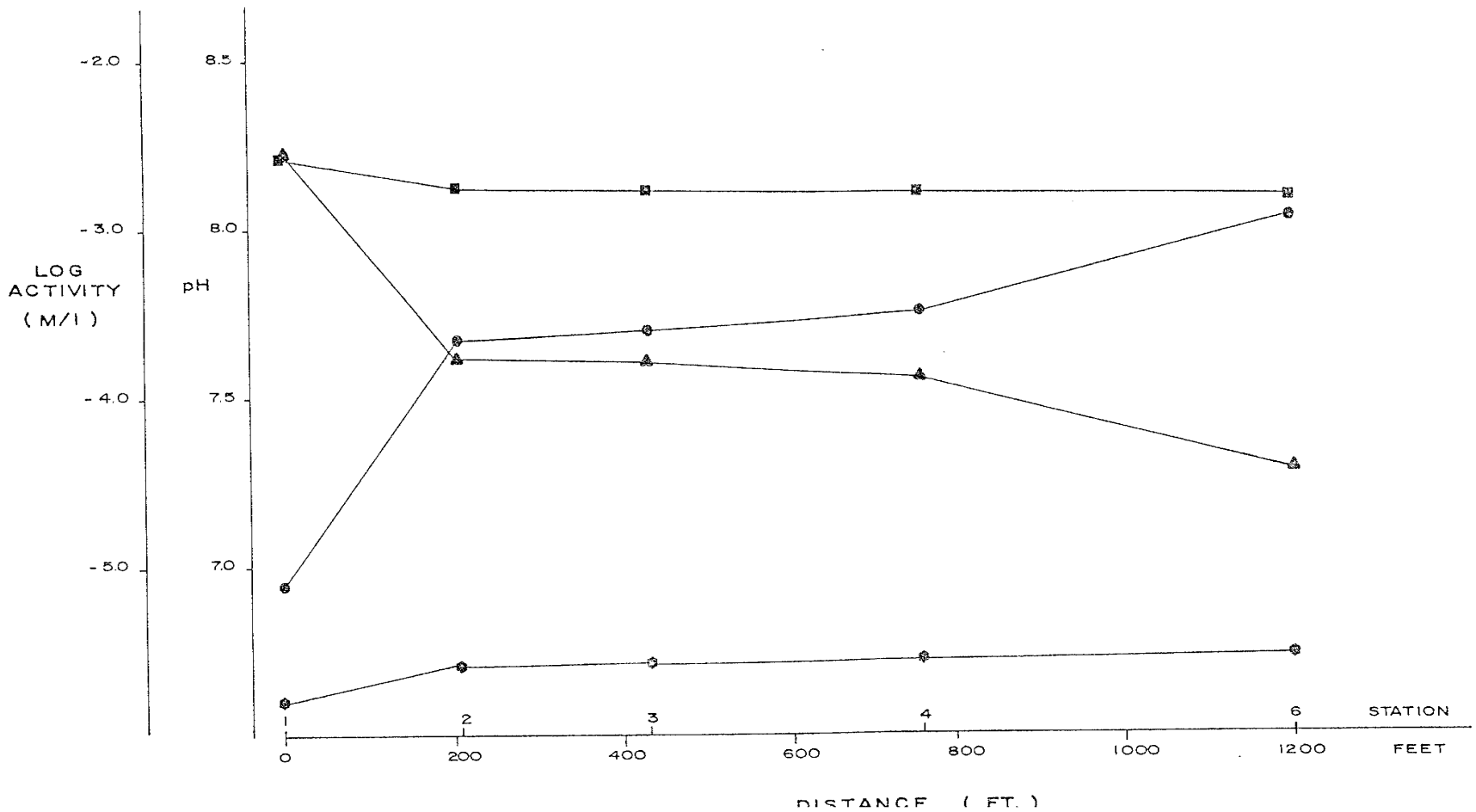


FIGURE B-3

LOG ACTIVITY VS DISTANCE

DATA SET 3 2-23-74

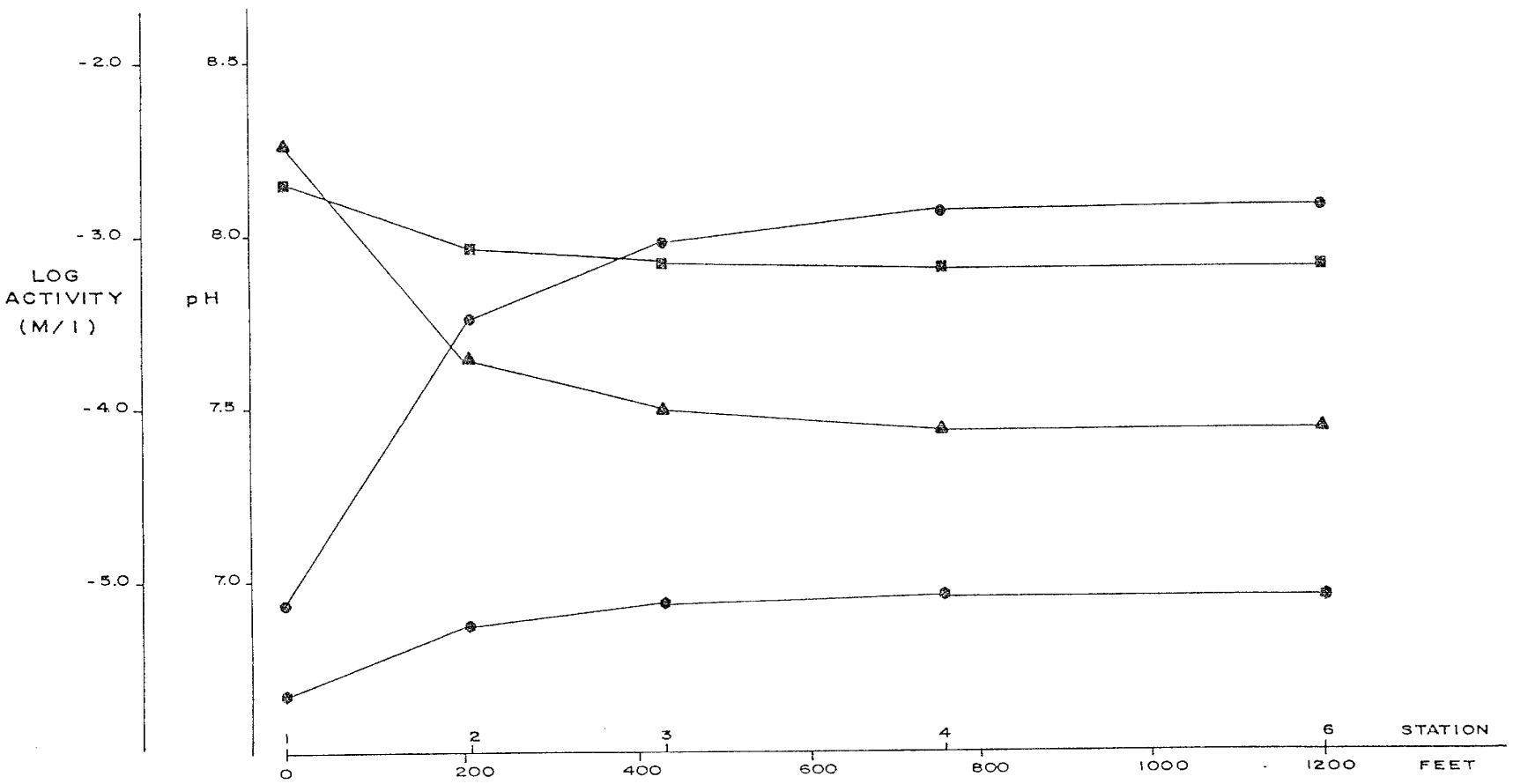


FIGURE B-4

LOG ACTIVITY VS DISTANCE
DATA SET 4 3-9-74

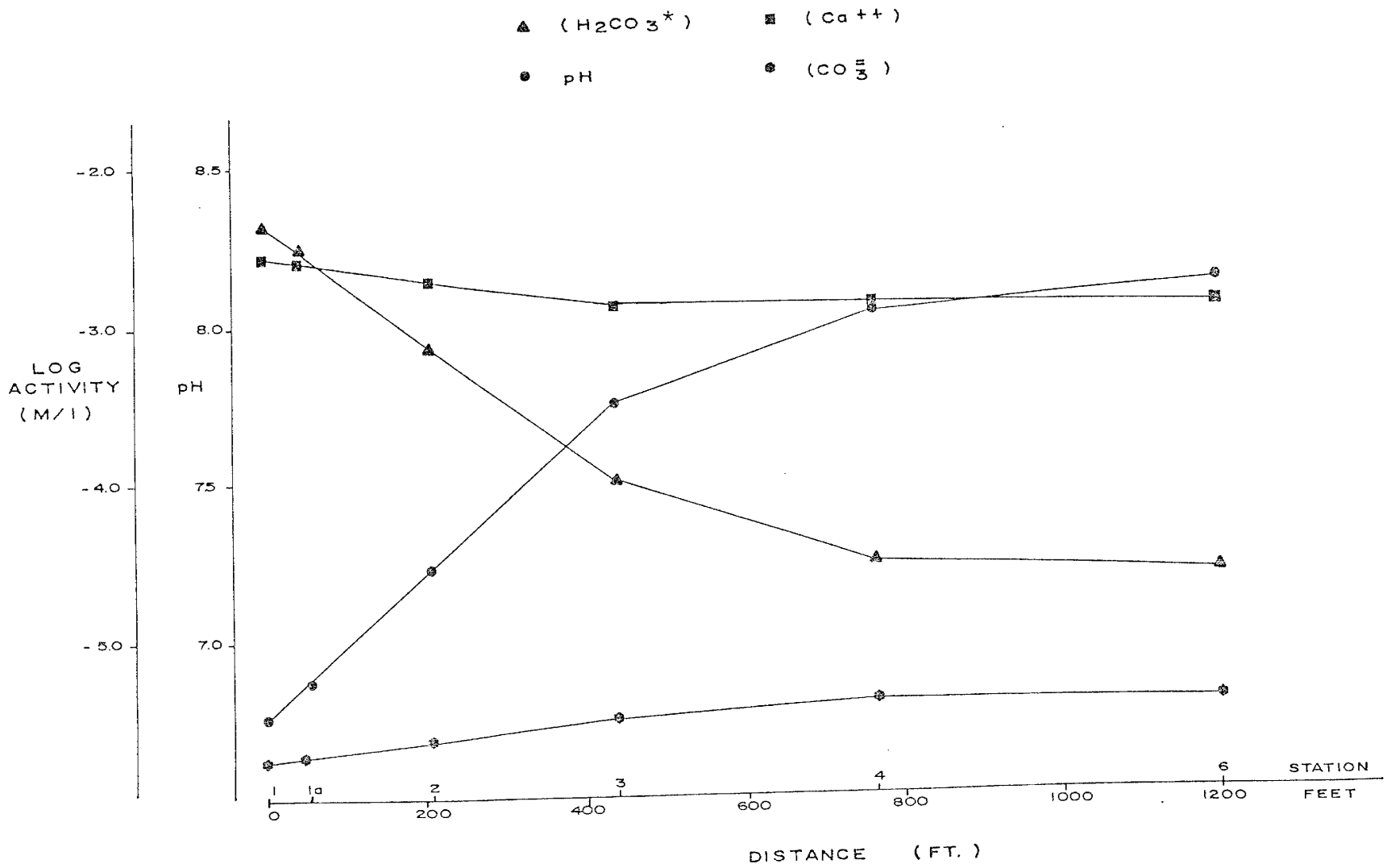


FIGURE B-5

LOG ACTIVITY VS DISTANCE
DATA SET 5 3-26-74

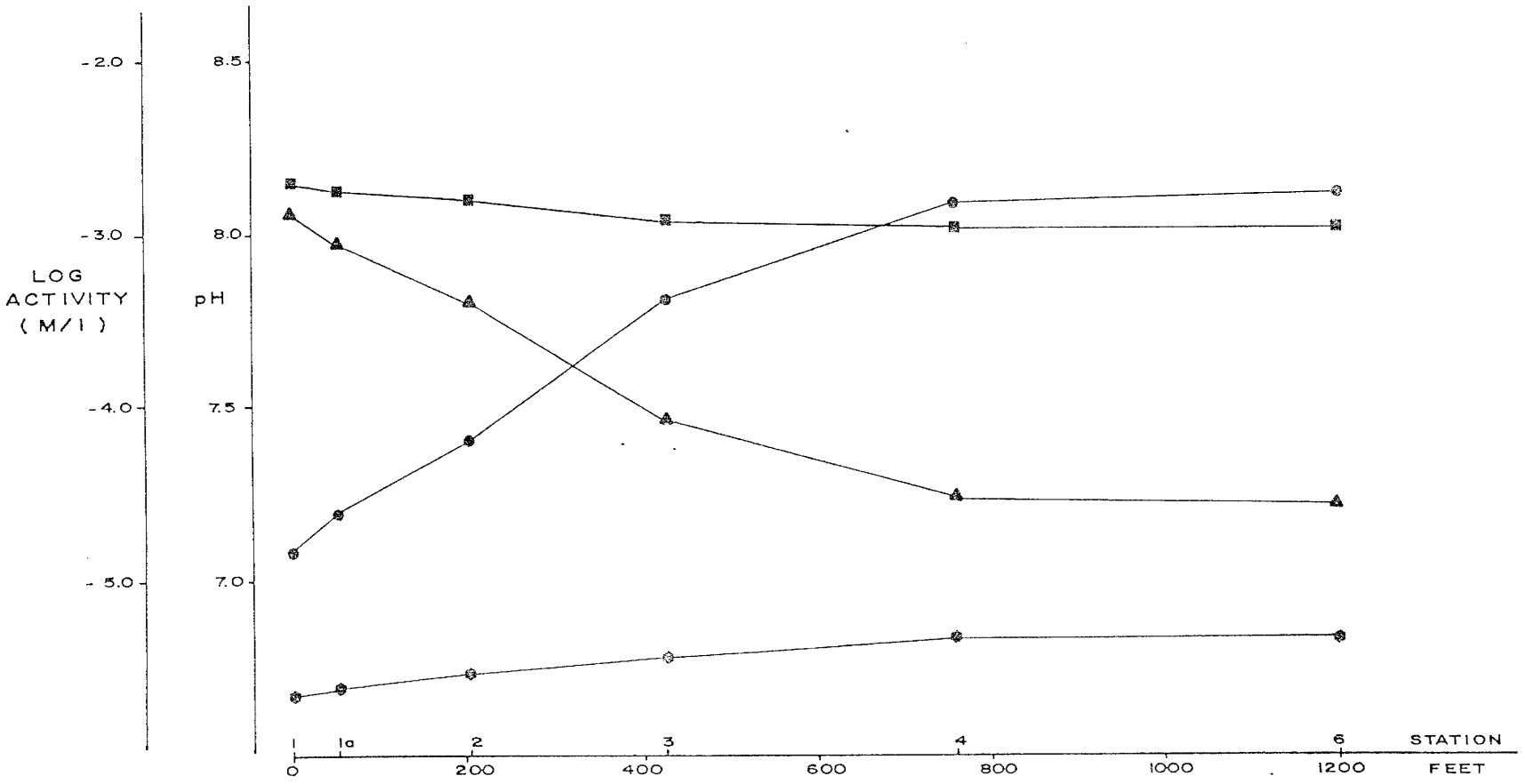


FIGURE B-6

LOG ACTIVITY VS DISTANCE

DATA SET 6 4-16-74

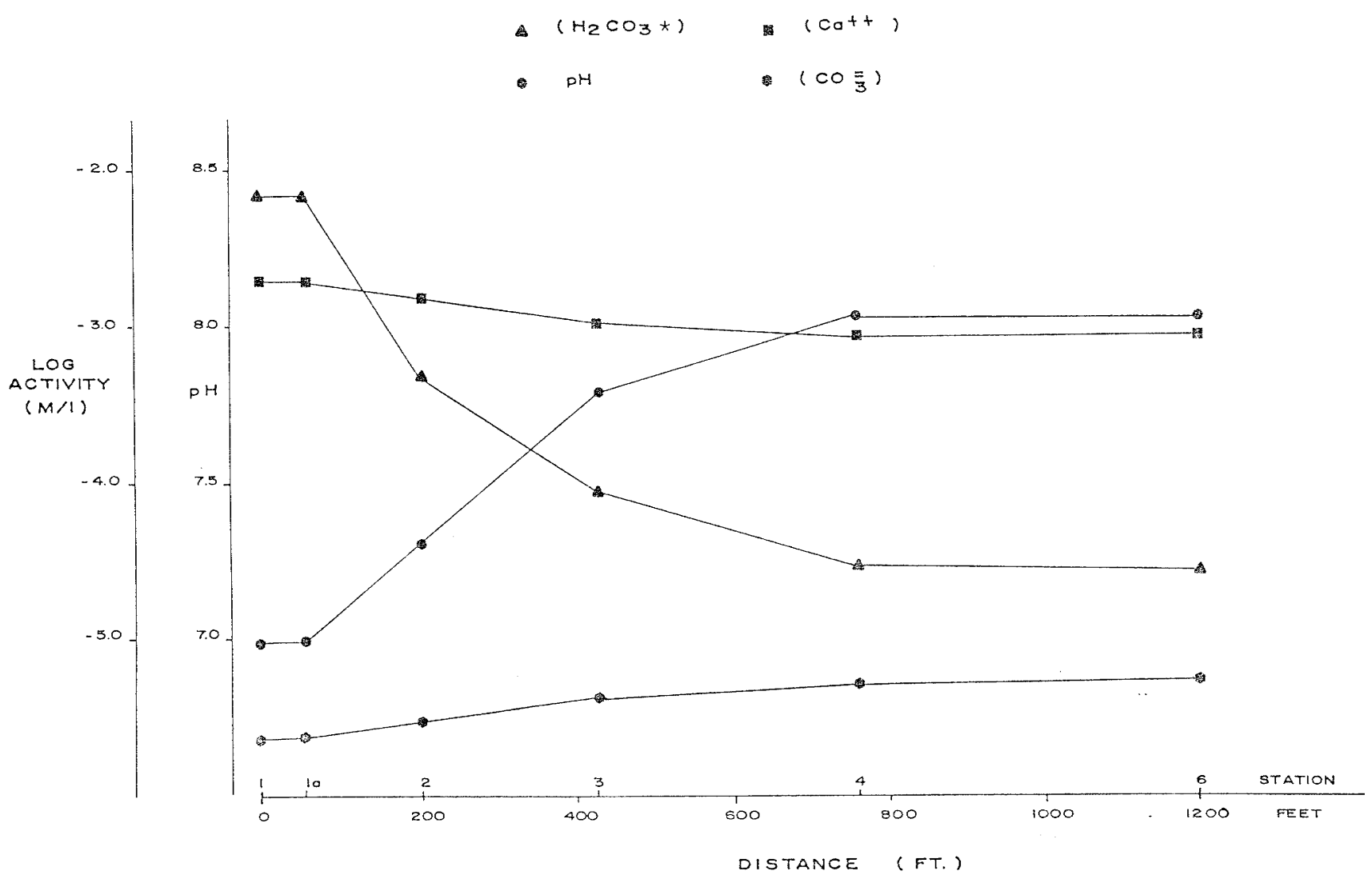


FIGURE B-7

LOG ACTIVITY VS DISTANCE

DATA SET 7 4-30-74

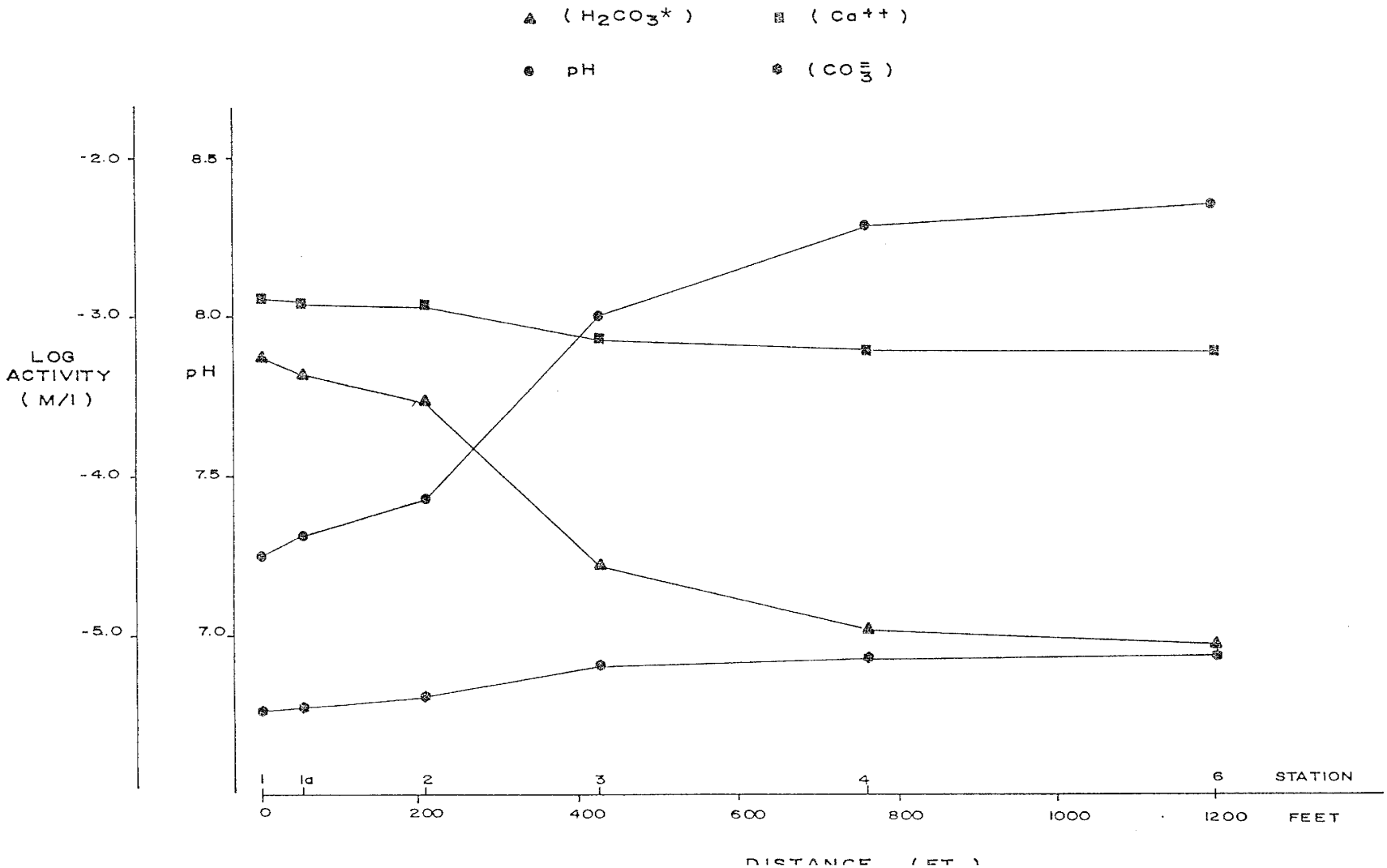


FIGURE B-8

DATA SET 1

LOG ΔC VS $\frac{Wx}{V}$

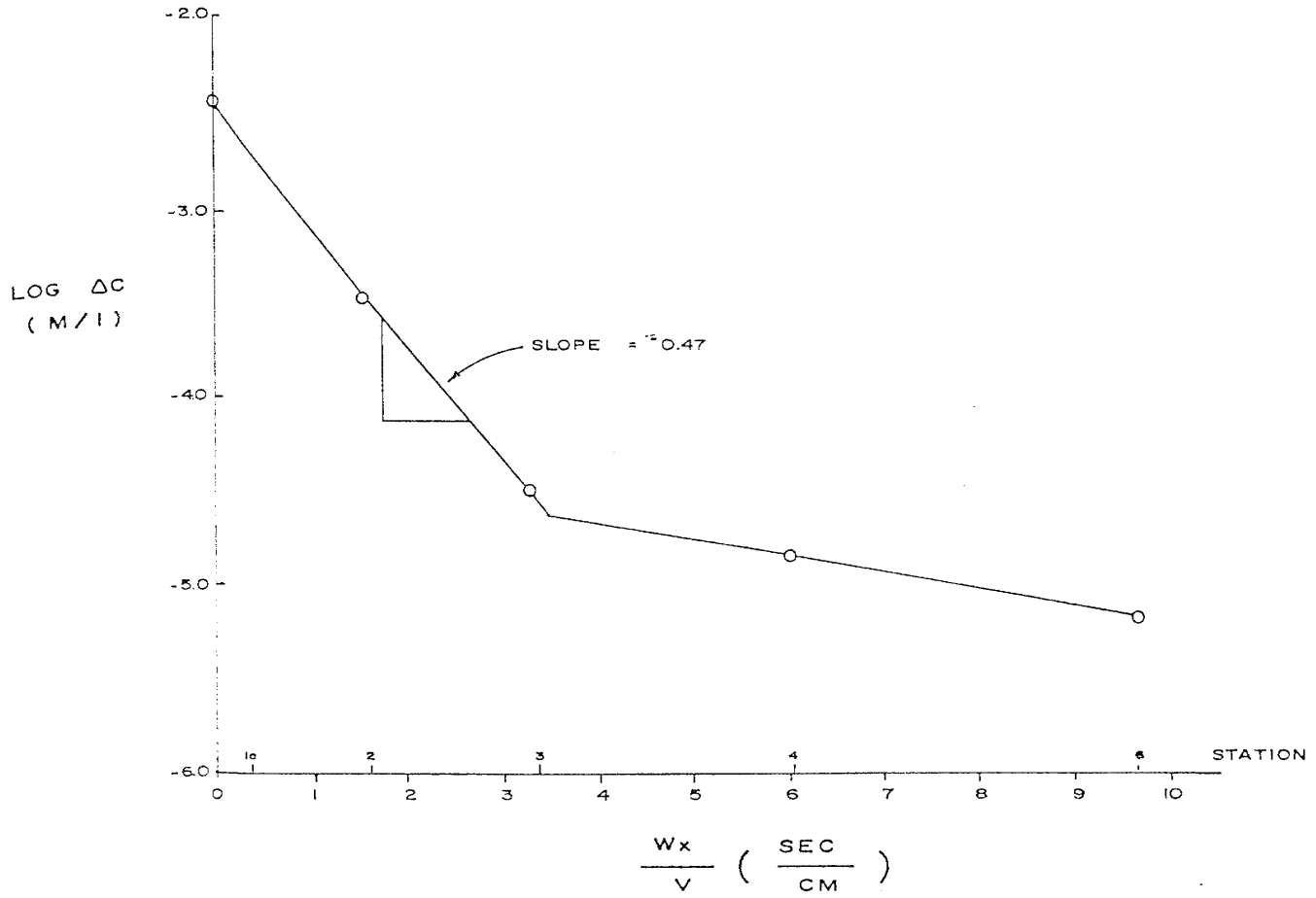


FIGURE B-9

DATA SET 2

LOG ΔC VS $\frac{Wx}{V}$

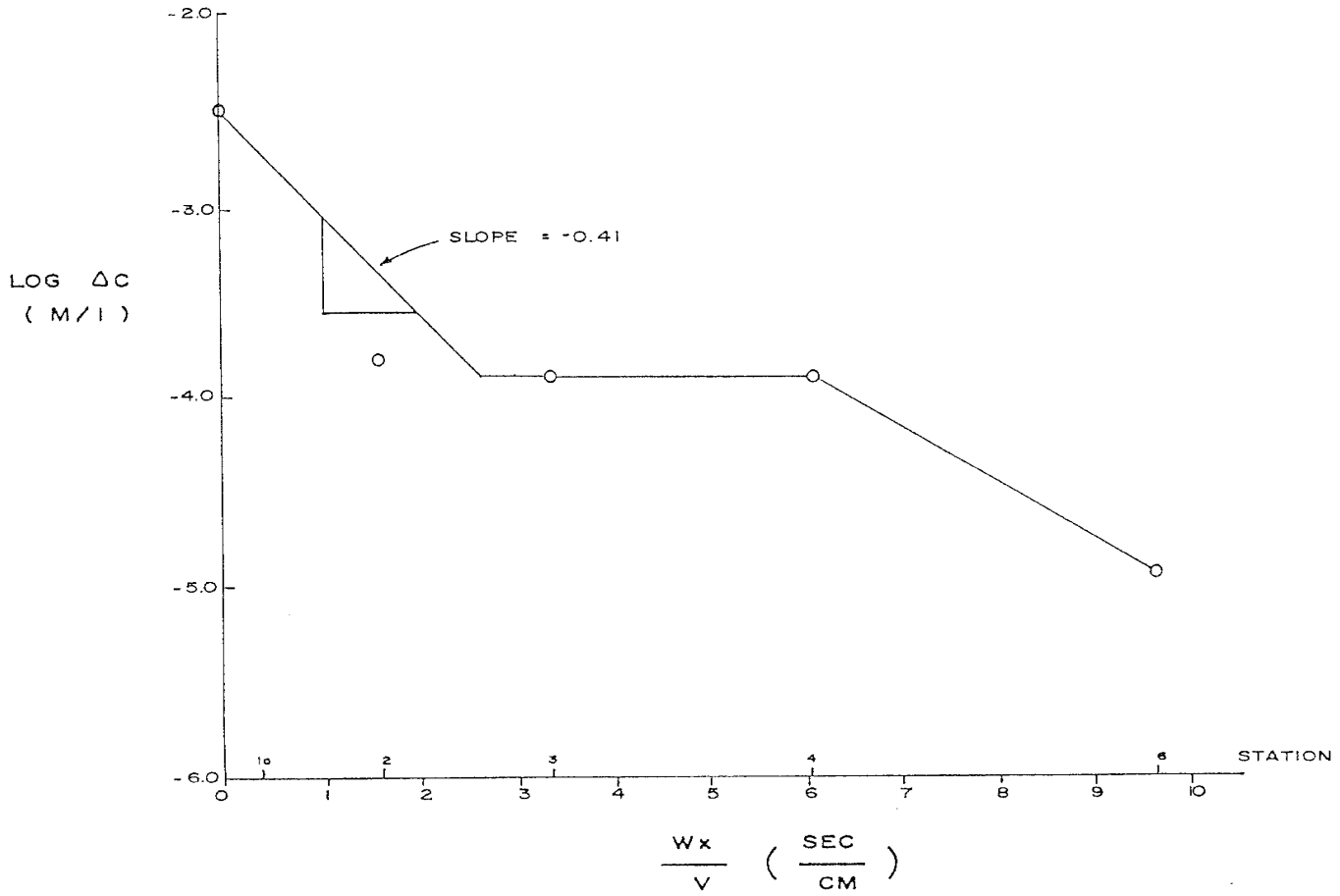


FIGURE B-10

DATA SET 3

LOG ΔC VS $\frac{Wx}{V}$

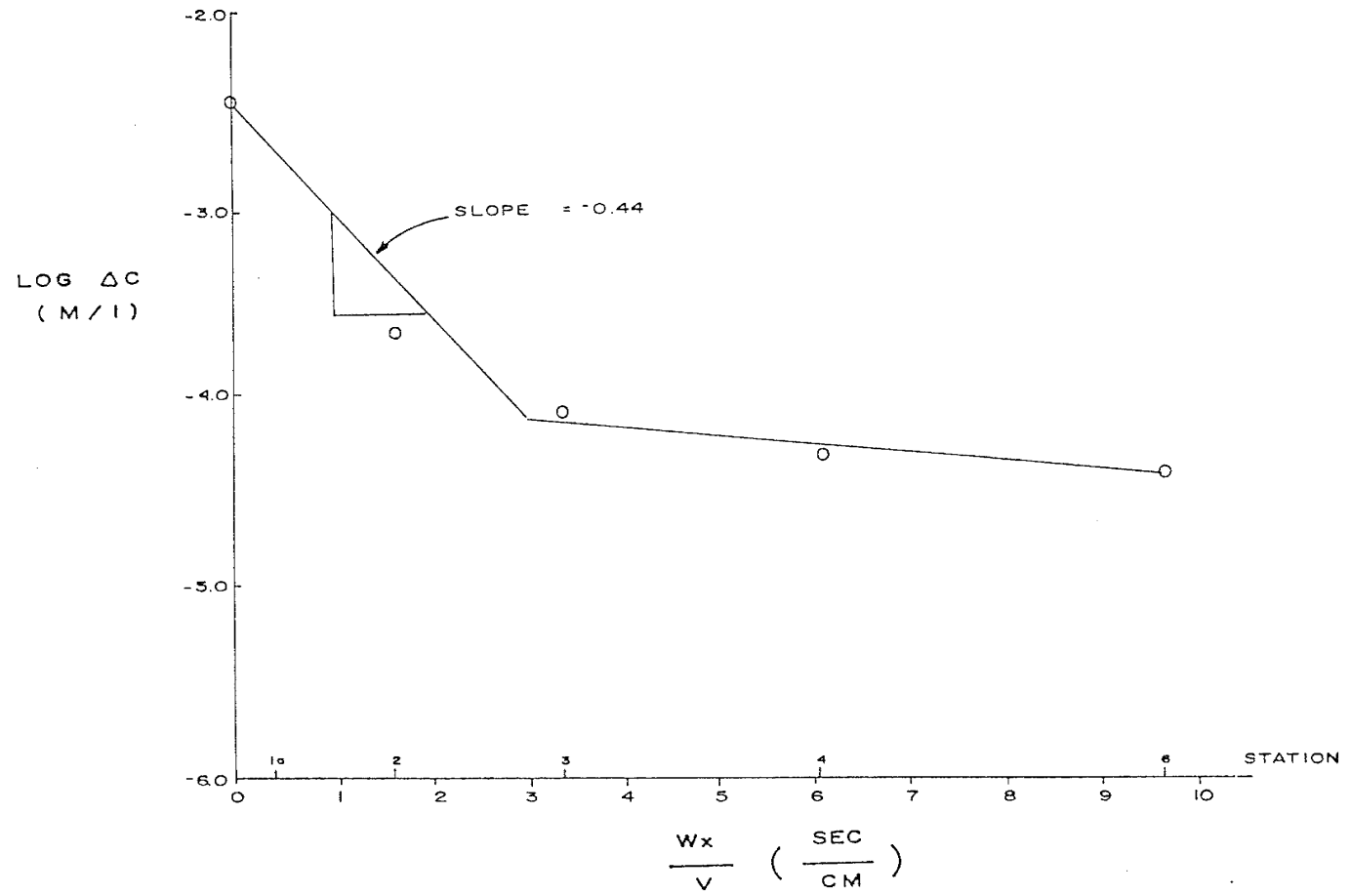


FIGURE B-11

DATA SET 4

LOG ΔC VS $\frac{Wx}{V}$

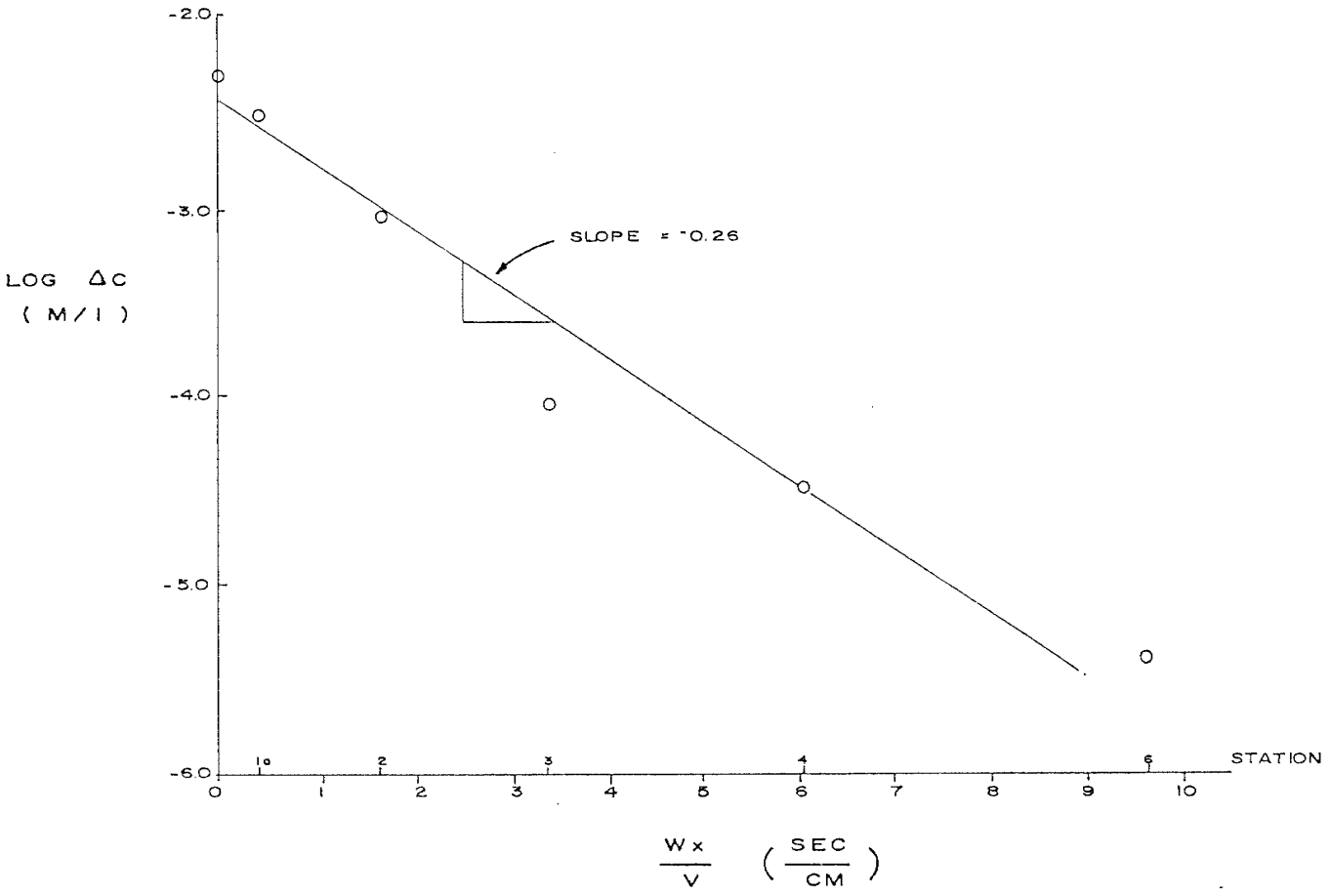


FIGURE B-12

DATA SET 5

LOG ΔC VS $\frac{Wx}{V}$

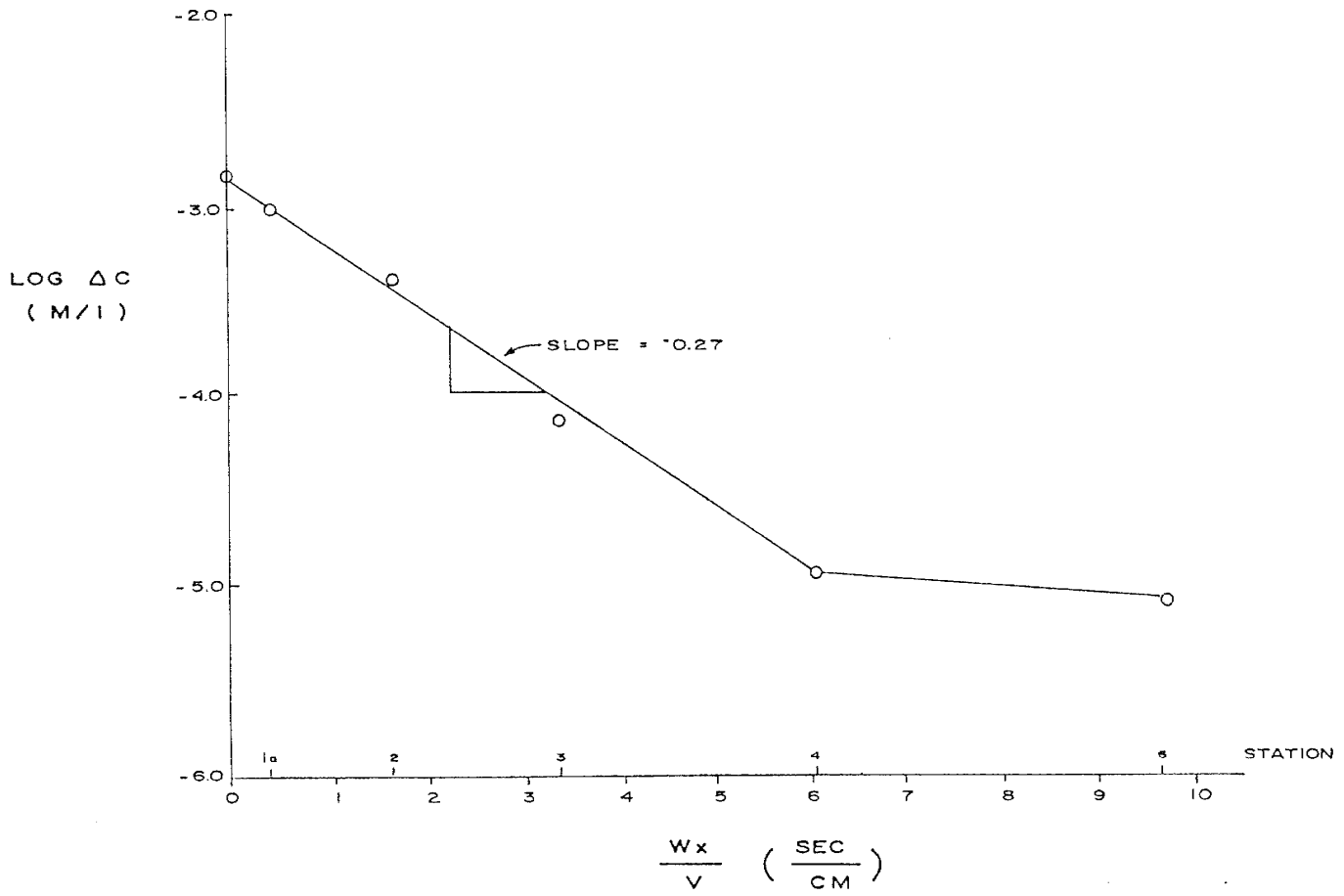


FIGURE B - 13

DATA SET 6

LOG ΔC VS $\frac{Wx}{V}$

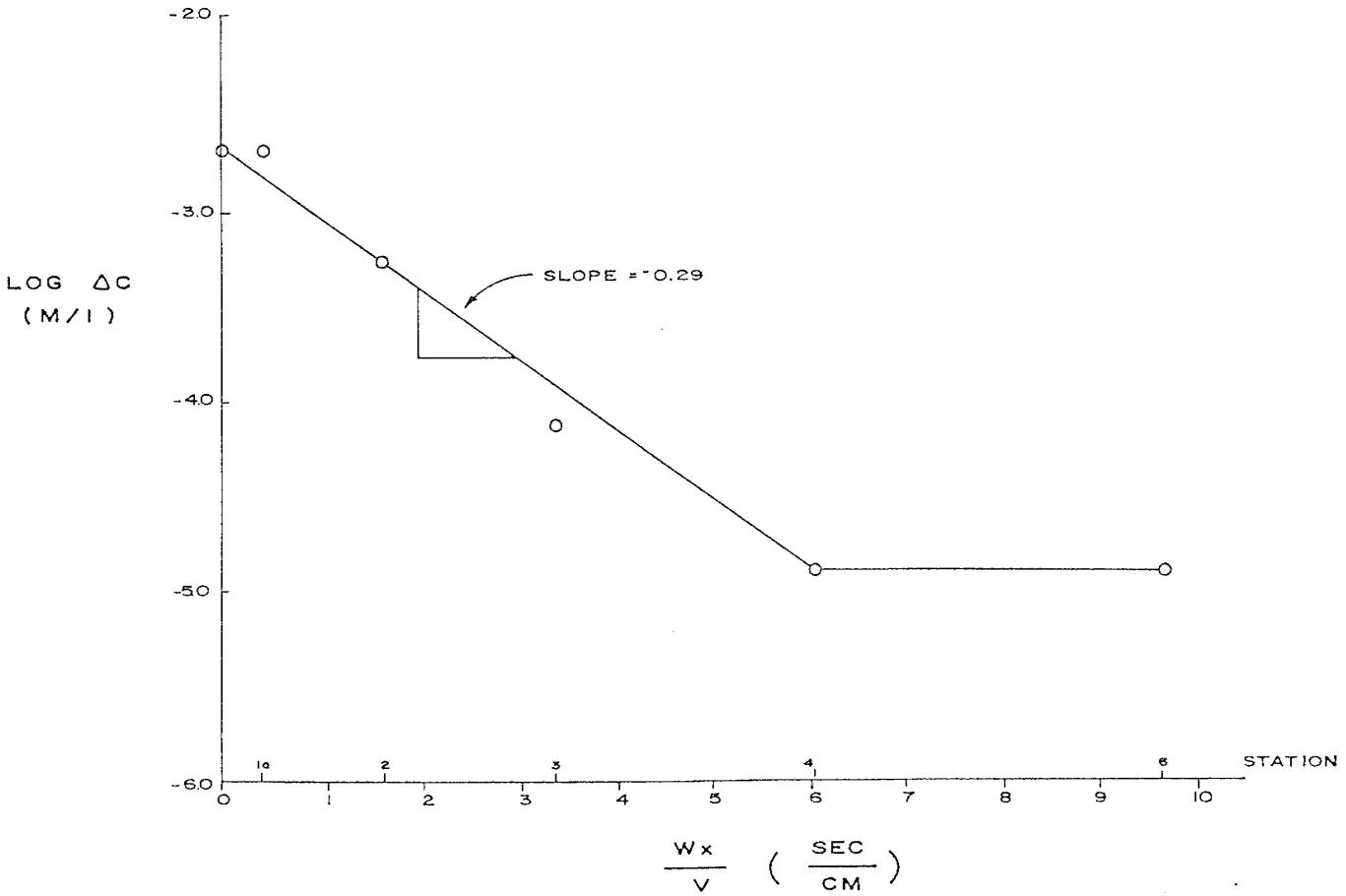


FIGURE B-14

DATA SET 7

LOG ΔC VS $\frac{Wx}{V}$

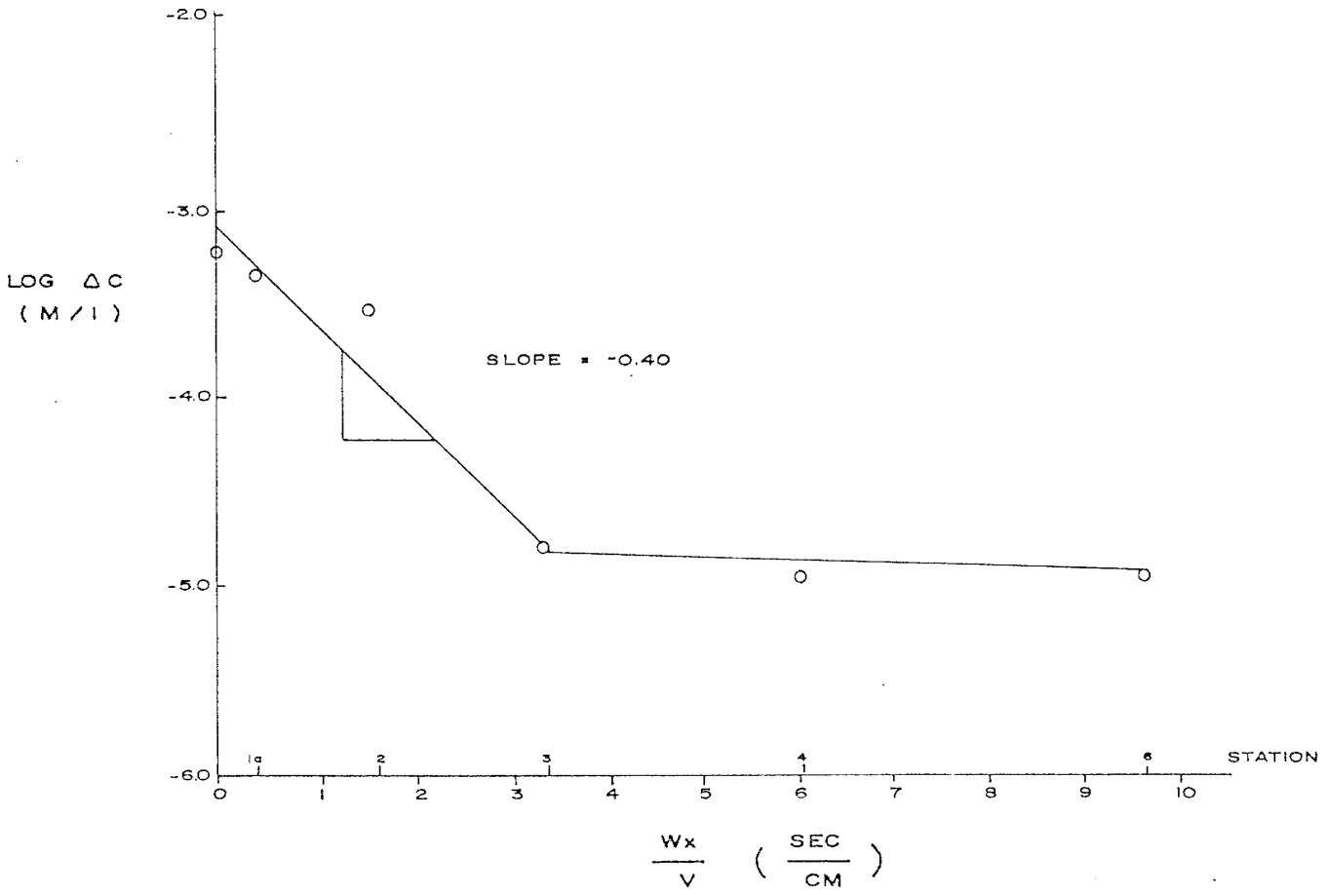


FIGURE 8 15

DATA SET 1

LOG ($H_2CO_3^*$) VS LOG DISTANCE

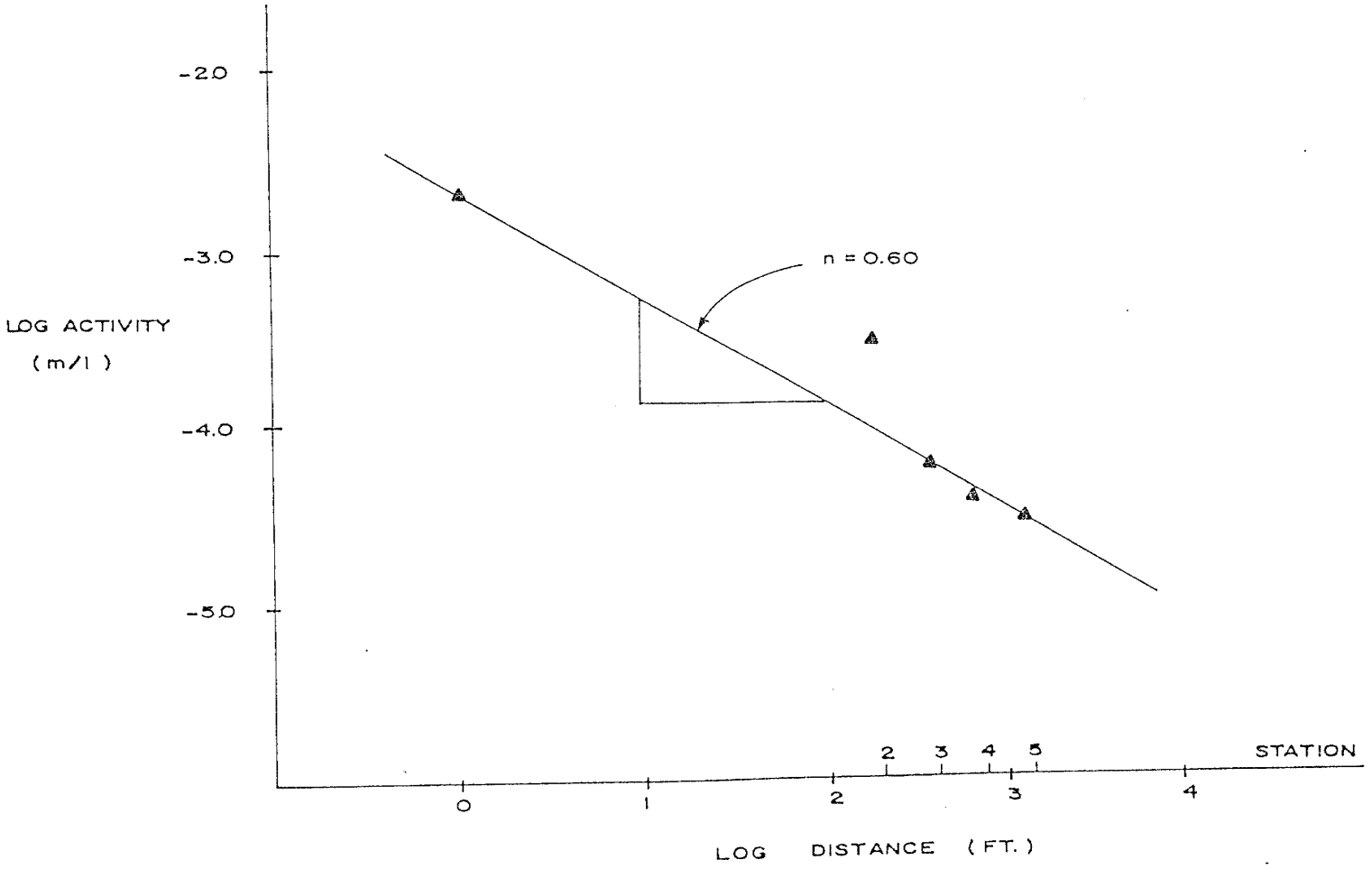


FIGURE B 16

DATA SET 2

LOG ($H_2CO_3^*$) VS LOG DISTANCE

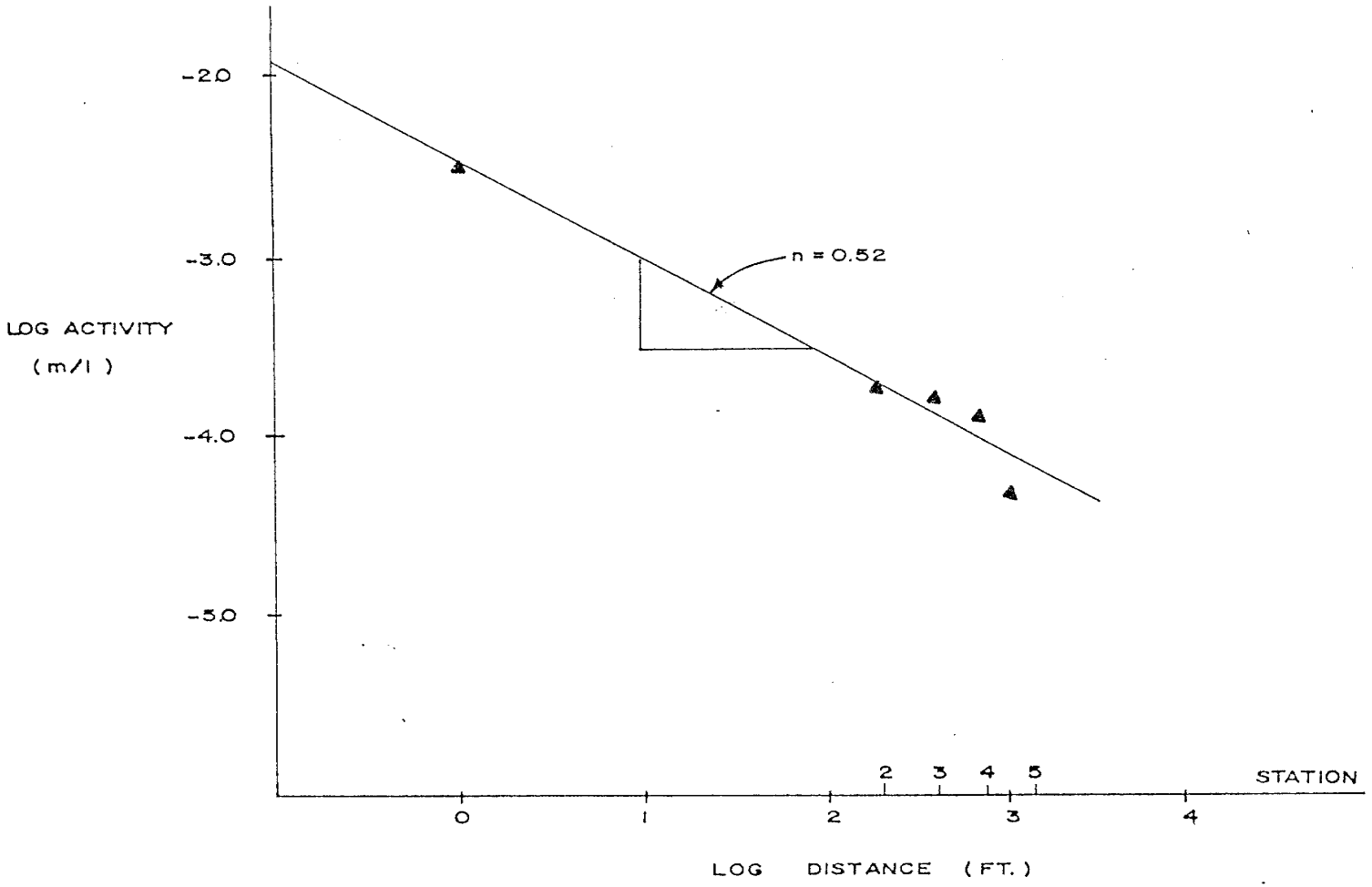
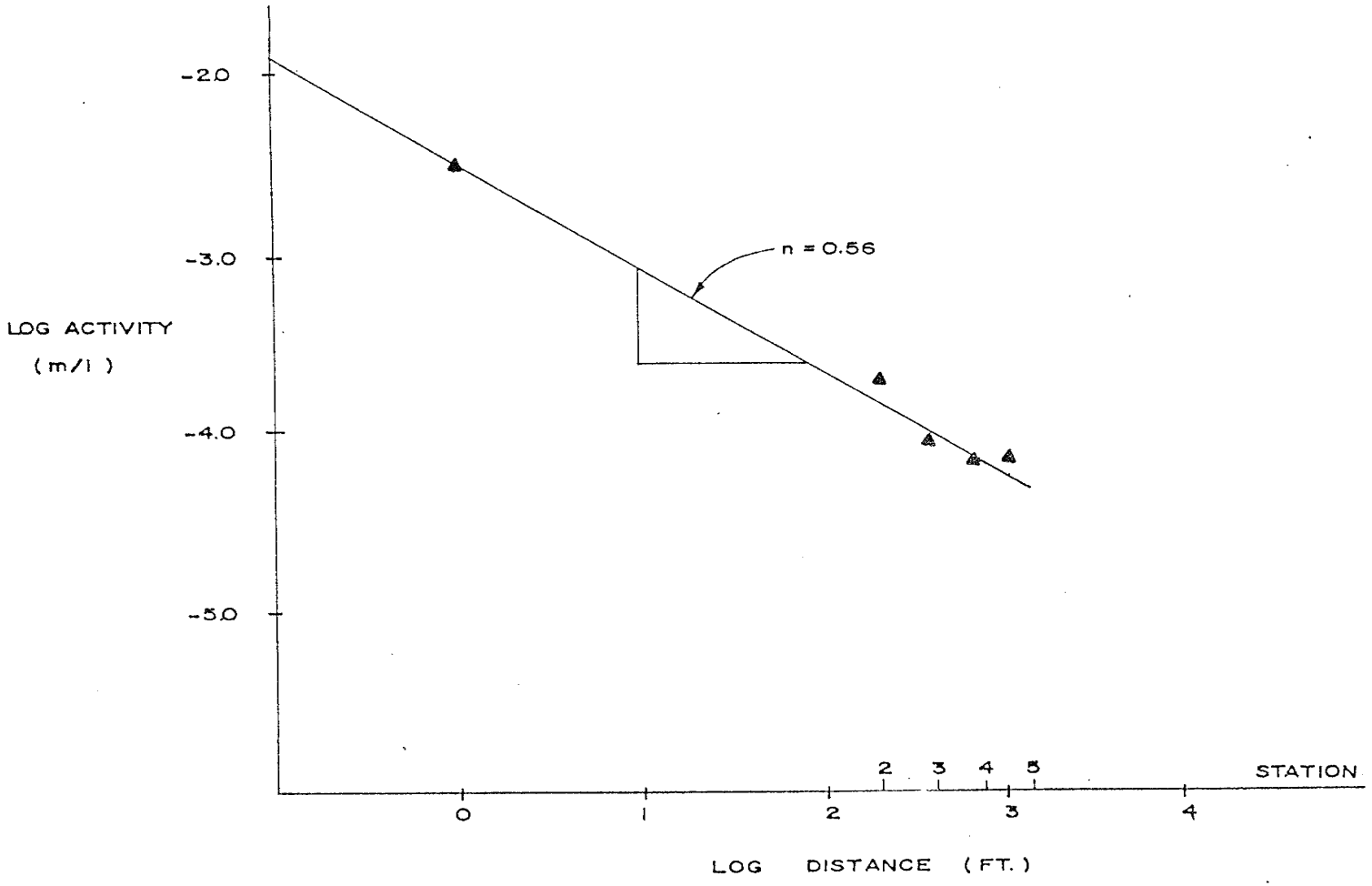


FIGURE B 17

DATA SET 3

LOG ($H_2CO_3^*$) VS LOG DISTANCE



APPENDIX C

THE BACTERIA AND ALGAE OF ARROYO SALADO, VALENCIA COUNTY, NEW MEXICO, AND THEIR RELATION TO THE AQUEOUS CARBONATE AND SULFATE SYSTEMS

By

Carla Fisher

October 7, 1974

Acknowledgments

This work was supported by the New Mexico Bureau of Mines and Mineral Resources. I would also like to thank Dr. James Brierley of the Dept. of Biology, New Mexico Tech, for his guidance and the use of his laboratory, and Ms. Corale Brierley of the New Mexico Bureau of Mines and Mineral Resources for her assistance.

THE BACTERIA AND ALGAE OF ARROYO SALADO, VALENCIA COUNTY, NEW MEXICO, AND THEIR RELATION TO THE AQUEOUS CARBONATE AND SULFATE SYSTEMS

SUMMARY

An alkaline, saline spring system was studied to determine the mechanisms of calcium carbonate deposition. Biological parameters evaluated in this study were compared with the physical and chemical parameters studied simultaneously by Fisher (7). Biological factors included the presence of a sulfate-reducing bacterium (Desulfovibrio desulfuricans), and three sulfur oxidizing bacteria (Thiobacillus novellus, T. thioparus, and T. neapolitanus). These bacteria theoretically affect the cycling of $CaCO_3$ and $CaSO_4$ in the system. It was found, however, that their effect was negligable.

Algal blooms and diurnal changes were monitored to determine their effect on the equilibration with the atmosphere, of a water supersaturated with CO_2. It was observed (Fisher, 1978) that the algae hasten this equilibration, but do not drive the system beyond an equilibrium point.

Conclusions are that the biological mechanisms in this stream do not drive the system but hasten a process which would occur without them.

INTRODUCTION

Arroyo Salado is located on the Lucero Uplift in central-western New Mexico. It is comprised of several small springs and seeps which contribute to the local flow down the canyon. This is a narrow desert canyon, through which strong winds blow at least fifty percent of the time.

After observing the entire stream, a representative segment was chosen by using a pH meter and a temperature probe to determine major changes in these parameters. It was found that wherever a spring entered the drainage the pH was low (6.5) and as the water flowed downstream from the spring the pH would increase to a maximum of about 8.0 just above the entry of another spring. A constant temperature of 8-10°C was also observed at each spring while in the remainder of the stream water, the temperature varied according to the weather conditions and the time of day. The segment was chosen for its consistancy with other segments and its lack of large secondary seeps which in some areas made the exact definition of a spring impossible.

The study segment, is headed by a spring with a low pH that suggested that it might be supersaturated with CO_2. This is a plausible assumption because before surfacing, the ground water flows through the Madiera Limestone while under hydrostatic pressure, which would allow supersaturation of CO_2.

Downstream from the spring was a dense algae bloom. Since CO_2 concentration is possibly a limiting factor for algal growth, a high level of CO_2 could produce euthrophic conditions and an abnormally high rate of productivity. About 128 meters downstream the algae bloom suddenly ceased and did not reappear for the remainder of the segment. Throughout the algae bloom there was little deposition of calcium carbonate. With the ceasing of the bloom, terraces and ponds began to form, comprised of accumulations of $CaCO_3$. Black patches were observed in the bottom muds of these ponds, which when a sample was removed had a strong odor of hydrogen sulfide gas. From this it was hypothesized that sulfate reducing bacteria were present.

The objectives of this study were to describe the bacteria present which might effect complete sulfur cycling,

to observe the occurance of algal blooms throughout the spring and early summer, and to test for downstream and diurnal changes in water chemistry as related to productivity and the carbonate equilibrium system.

BACTERIAL STUDIES

Introduction

The purpose of this segment of the study was to analyze for microorganisms known to affect the $CaSO_4$ equilibrium, which might be present in the bottom mud of the stream. The reaction considered can be illustrated by:

$$CaSO_4(s) \rightleftharpoons SO_4^{=}(aq) + Ca^{++}(aq) + CO_3^{=}(aq) \rightleftharpoons CaCO_3(s)$$

$$\begin{array}{l} \underline{\text{T. neapolitanus}} \\ \underline{\text{T. thioparus}} \\ \underline{\text{T. novellus}} \end{array} \quad \Big\uparrow \Big\downarrow \quad \underline{\text{D. desulfuricans}}$$

$$H_2S$$

When sulfate is removed, the reaction proceeds to the right, dissolving $CaSO_4$ and creating an excess of Ca^{++}. This calcium then combines with existing carbonate ions and precipitates as $CaCO_3(s)$. The presence of sulfur bacteria, therefore, would indicate that they were a mechanism of deposition of $CaCO_3$, at this point ignoring other existing buffer systems.

The mud contained two well defined zones; an upper red-brown colored aerobic or oxidized layer, and the lower black colored anaerobic or reduced layer, smelling strongly of

sulfide gas. The two types of bacteria analyzed for were aerobic sulfur oxidizers, and anaerobic sulfate reducers. Enrichments and isolation media were used for the detection and identification of the bacteria. The mud was also tested for bacteria capable of precipitating calcite crystals ($CaCO_3$) from an enrichment medium. Since this was a general survey of the microorganisms, samples were taken from several stations during the study period.

SULFUR BACTERIA METHODS AND MATERIALS

Mud samples were obtained from the bottom of ponds within the study area. Surface mud of the oxidized zone was analyzed for the presence of aerobes, and the reduced zone for anaerobes. Only sulfur bacteria that could tolerate the pH range of the water, from 6.6 to 8.1, were considered (4). For this reason emphasis was placed on confirming the existence of those Thiobacillus sp. and Desulfovibrio sp. which would exist in this pH range.

The first tests were made in February using enrichment flasks to obtain a general idea of which microorganisms were present. The media used were Medium B for the enrichment of sulfate-reducing bacteria (2), and a thiosulfate medium

for the enrichment and isolation of Thiobacillus sp. (3). pH was measured, and slide and Gram stains were made from these flasks after two weeks of incubation under standard conditions of darkness at room temperature (25°C). Representative samples of muds taken from the stream study area were used as inocula. Results of these flask cultures confirmed that the considered bacterial genera were present.

The next step was to begin plating for enumeration and identification of the proposed species. Media used for the anaerobic bacteria were Medium E (13) and A.P.I. Medium (13). Two changes in the media were made. First, filtered water from the study stream was substituted for distilled water to provide any trace elements that the bacteria might require. In addition, 0.1 g/l of Thioglycollate Medium was substituted for thioglycollic acid in Medium E due to unavailability of the acid. This chemical provided the low Eh necessary for the growth of the bacteria. Plates were poured and allowed to "cure" for at least one day at room temperature to facilitate rapid drying (5-15 min.) of the sample on the plate (13). Dilutions were made using the filtered stream water, and immediately after autoclaving the bottles were plunged into ice water. This quick cooling decreased the absorption of

O_2 back into the dilution water so that more of the anaerobic bacteria would remain viable during the dilution process. Inoculation was with 0.1 ml of the appropriate dilution by the spread plate technique. The plates were incubated in a BBL anaerobic chamber using a BBL Gas-Pack for anaerobiosis, at standard conditions for fourteen days. This procedure was followed several times during the study.

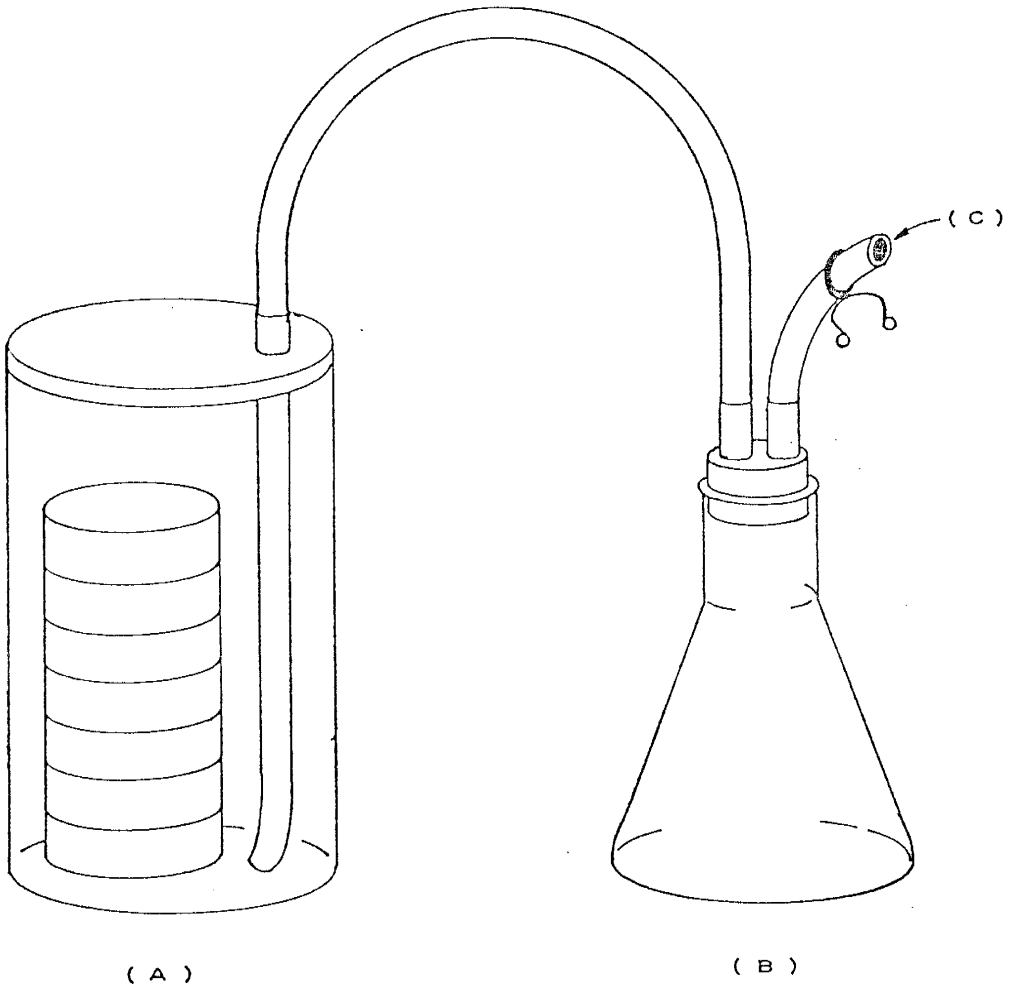
Aerobic samples were plated on a Thiobacillus thioparus Medium Agar (19) with the substitution of filtered stream water using the same reasoning as above. Dilutions were also made with the stream water but they were allowed to cool naturally. Again, 0.1 ml. of sample was spread on each plate and incubated aerobically under standard conditions for fourteen days. Gram stains were then made from representative colonies. Growth on these plates included all Thiobacillus species.

In order to differentiate between the Thiobacillus species the following was considered: T. novellus is a facultative autotroph that can utilize thiosulfate and organic compounds as energy sources. T. thioparus is a strict autotroph that uses thiosulfate but will not grow

on organic media, and T neapolitanus is a strict autotroph that utilizes thiosulfate, tetrathionate, and hydrogen sulfide. The following steps were taken for isolation. First, random colonies composed of all three species from the aerobic plates described in the previous section were streaked on Nutrient Agar plates with organic matter as the sole energy source, and incubated under standard conditions for four days. Colonies were then chosen at random from these plates and streaked on Nutrient Agar slants, giving pure cultures of the organotroph. These slants were incubated for four days under standard conditions. The final step involved plating these colonies on T. thioparus Medium Agar to confirm their ability to utilize thiosulfate.

One last culture was made to determine if T. neapolitanus was present in the aerobic samples. A BBL chamber was set up to provide an atmosphere of hydrogen sulfide gas. The system used is shown in Figure C-1. Plates were prepared using a Minimal Agar Medium, one without a thiosulfate or organic nutrient source. These were innoculated with 0.1 ml. of the appropriate dilution, and placed in the chamber (A). In flask B, (Figure C-1) were placed 0.0105g of sodium bicarbonate and 0.0125g of zinc sulfide. After the system

FIGURE C-1



HYDROGEN SULFIDE GENERATING INCUBATION SYSTEM

(A) CHAMBER CONTAINING INNOCULATED PLATES

(B) CHEMICAL MIXING FLASK

(C) CHEMICAL ADDITION PORT

was closed to the atmosphere ten ml. of concentrated HCl were added through tube C. This was calculated to give a maximum concentration of CO_2 and 1000 ppm H_2S. The plates were then incubated for fourteen days at standard conditions and Gram stains made of the resultant colonies.

RESULTS

By the use of isolation and enrichment techniques as described above, bacteria of the species T. novellus, T. thioparus, and T. neapolitanus were proven to be present in the samples. This conclusion is based on the fact that T. thioparus and T. neapolitanus must have elemental sulfur or thiosulfate as an energy source, and will not grow on organic media, whereas T. novellus will grow on both organic and mineral media (4). When colonies were transferred randomly from the T. thioparus Medium Agar to the Nutrient Agar plates, 8 out of 11 plates or 67% showed growth. This indicated that the remaining three plates or 33% were innoculated with colonies of T. thioparus and/or T. neapolitanus which could not grow on organic media. Retransfer of the colonies from the 8 plates with growth back to T. thioparus Medium Agar resulted in growth. All were thus proven to be Gram negative rods that could utilize either organic or inorganic media, and could be called T. novellus.

The results are shown below in Table C-1, and indicate the relative proportions of the three bacteria as observed from the aerobic plating of samples taken on 4/16/74. This indicates that the majority of sulfur oxidizing bacteria present in the sample are of the species T. novellus. These figures are in general agreement with the 67% of T. novellus found during isolation plating as described in the above paragraph.

A test was also run to determine the presence of T. neapolitanus. The highest tolerance level of bacteria to H_2S is around 1200-1400 ppm (6) so an atmosphere of 1000 ppm H_2S was used. The results were the growth of a Gram negative rod on the medium, with the dilution of 10^{-1} producing an average of 36 colonies and 10^{-2} an average of 6.5 colonies per plate. It can be inferred that the bacteria producing the growth were T. neapolitanus although further isolations and enrichment should be done for confirmation.

Tests were run for the presence of sulfate reducing bacteria of the species Desulfovibrio desulfuricans. Culturing was successful in most cases although enumeration was not, due to the problem of maintaining anaerobiosis. The surface drop method (13) and the spread plate technique

TABLE C-1

DILUTION	AVERAGE COUNTS		%	
	T. novellus	T. thioparus & T. neapolitanus	T. novellus	T. thioparus & T. neapolitanus
Control	0	0	0	0
10^{-1}	287.5	80	78.2	21.8
10^{-2}	118.5	11	91.5	8.5
10^{-3}	9.5	0	100	0

THIOBACILLUS SP. PRESENT IN LUCERO SAMPLES

4-16-74

were both tried with only the latter being successful. In enumeration, only the colonies that remained black after one hour of exposure to air were counted, these colonies were Gram negative vibrios. It was thus inferred that D. desulfuricans, with an optimum pH of 6- 7.5, was present.

CALCITE BACTERIA MATERIALS AND METHODS

Attempts were made to isolate and culture bacteria from the bottom mud of Arroyo Salado which were capable of producing calcium carbonate crystals from the solutes in a B-4 Solid Medium (5). Samples of the oxidized mud from Station 1 were innoculated on B-4 Medium and incubated under standard conditions for fourteen days. Representative crystal producing colonies were transferred to plates of Nutrient Agar for isolation of the specific bacteria. These were incubated for four days. Nutrient Agar isolation was repeated. Colonies were then streaked on the B-4 Medium and incubated for fourteen days for confirmation of their calcite producing capabilities.

RESULTS

Four types of bacteria were thus isolated: a Gram negative cocci, a Gram positive cocci, a large, chain forming

Gram positive rod, and a spore forming Gram positive cocci. These were not further identified because of a lack of time.

The majority of the calcite crystals were rhombohedral. Crystals were found in the medium below and in concentric rings around the colonies. Two samples of T. thioparus were also plated and found to produce crystals on the B-4 Medium.

This confirms the study of Boquet (5), who found that most bacteria and some algae and fungi, are capable of producing changes in concentrated medium so that calcite crystals are deposited. This may indicate that calcite crystal formation can be a function of medium composition and not necessarily a result of any unusual physiological capabilities of the organism.

SULFUR AND CALCITE BACTERIA DISCUSSION

The bacteria found in this study represent a microlayer in the stream where complete cycling of sulfur is occurring. There are sufficient nutrients, organic and inorganic, available within the system for the bacteria to metabolize at a maximum rate within their temperature limits. It was observed that the occurrance of black sulfide areas in pools

increased with higher water temperatures of spring and summer. The extensive deposits of sulfide mud appear to be a function of both the high amounts of $SO_4^{=}$ and sufficient amounts of organic matter.

However, in this fast flowing stream, the effect of the $CaCO_3$- buffering system is so strong that little can be done to quantitatively determine the effect of sulfur bacteria on the sulfate equilibrium. The chemical analyses showed, if anything, a slight increase in $SO_4^{=}$ downstream, instead of a decrease which would result if sulfate reduction was occurring at a significant rate with respect to the volume of discharge of the spring.

PHYCOLOGY STUDY

Introduction

The purpose of the algal portion of the study was to determine what effect algal populations had on the $CaCO_3$ equilibrium of the stream. Preliminary observations inferred that the discharging spring water was supersaturated with CO_2. If this was true, then this would promote prolific algae blooms. It was hypothesized that the algae would affect the equilibration of the water with atmospheric CO_2 as the water progressed downstream from the spring, and thus be a major factor in the deposition of $CaCO_3$. The system can be illustrated by the following:

$$\begin{array}{l} CO_2(g) \\ \updownarrow \quad \text{Algae using } CO_2(aq) \\ CO_2(aq) + H_2O = H^+ + HCO_3^- = 2H^+ + CO_3^{=} + Ca^{++} = CaCO_3(s) \end{array}$$

This assumes the only buffering system to be the carbonate system. Algae use CO_2 and drive the pH up, favoring the formation of the carbonate ion. Since carbonate is extremely unstable in the presence of calcium, the excess formed by the increase in pH will precipitate as calcium carbonate.

The hypothesis was tested by identifying the genera of algae present, taking population counts and species diversity, wet and dry weights of the algae blooms, diurnal studies of various chemical parameters, and evaluating the relation of stream productivity to CO_2 usage.

MATERIALS AND METHODS

Identification of algae present in the stream was done in December and January. After that an alga was identified as it appeared. Representative samples were collected, placed in a small bottle and kept in the stream to maintain a constant temperature until they were brought to the laboratory. There the samples were placed in an open petri dish and refrigerated at approximately 1.0°C. until they could be identified. No preservatives were necessary. A Nikon light microscope was used for observation. Identification was done only to a generic level (16)(17), except where only one species is present in the United States. Attempts were made to clean the diatom samples with sulfuric acid (15) for easier identification, but it was found that freezing the sample produced better results.

Biomass was determined within the blooms by the use of dry weights. Two squares of plastic screen (5 cm x 5 cm) were weighed along with a plastic bag and a closing wire for each sample. Samples were collected by placing one piece of screen above and one piece of screen below the algae mat and then clipping the excess algae from the periphery of the screens, allowing excess water to drain for fifteen seconds and placing it in the preweighed bag. The final weight was determined and the tare weight subtracted to obtain an algae weight. Samples were then removed from the bag and allowed to dry with the screens and reweighed to determine dry weight. This was believed to be a fairly accurate method of comparing different periods within the bloom.

Diversity and population counts were accomplished by taking representative samples of all types of algae at each of the sampling stations. These were taken to the lab and refrigerated until needed. The procedure was to mix the sample with a stirring rod until it was homogeneous, place a drop on the slide and count the various individual algae present, repeating the procedure at five different positions on each slide. This gave approximate proportions of the individuals present per unit volume. This was done for five

sampling periods with a total of thirty-one samples. The percent of each genus per sample was calculated, and totals were then computed for all the samples of that date. This information was then presented graphically to show dominent species changes with respect to time (14)(15)(10).

Diurnal studies were successful on two dates; 2/27/74 which is defined by three sets of data and 4/16/74 with four sets of data. Each data set included pH taken with an Orion pH meter and a combination electrode, water and air temperature measured with a Y.S.I. Model 54 oxygen meter, dissolved oxygen and time. Alkalinity was titrated (7). Productivity was calculated using the results of the diurnal studies. CO_2 data was obtained from calculations by Fisher (7).

RESULTS AND DISCUSSION

The identified algae are presented in Table C-2. Most of these were present during the entire study. The exceptions are the cold weather filaments, Ulothrix and Oscillatoria. The first bloom in early spring was composed entirely of Ulothrix filaments. Ulothrix is a cold water filament, with microzoospores that disintegrate if the water temperature is above 10°C.

Table C-2

Algae of Arroyo Salado

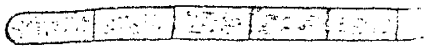
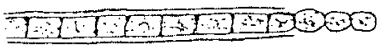
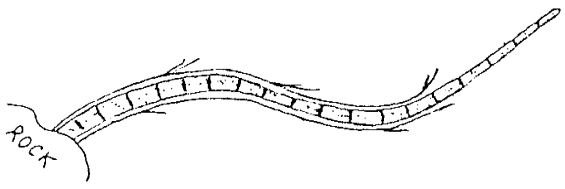
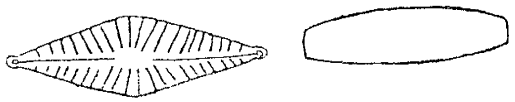
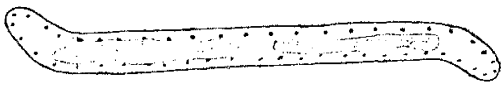
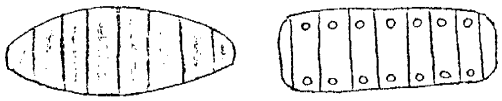
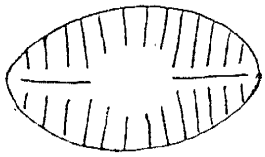
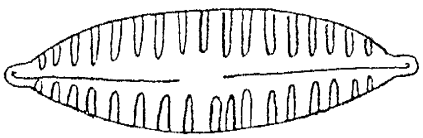
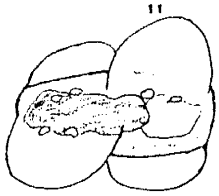
Genus	Division	Description
Ulothrix 	Chlorophyta	A bright green non-branching alga which appears in cold weather, spring and fall. This was the spring bloom alga.
Oscillatoria 	Cyanophyta	Bright green filaments, no branching No visible sheath, found only in December.
Epichrysis 	Chrysophyta	An epiphytic alga. Only one species in U.S. Found only in December samples.
Lyngbya 	Cyanophyta	No branching, green to yellow-brown with a definite sheath. Grows attached to rocks, present all year.
Calothrix 	Cyanophyta	Brownish-yellow or green with brown-yellow sheaths. False branching and tapering at apex. Grows attached to rocks in main flow channel and found all year round, Appears black. Crystals found in solution with alga after sitting a few days in refrigerator.

Table C-2 (Cont.)

Genus	Division	Description
Navicula	Bacillariophyta 	The most prolific alga in the stream. Several sizes found but all with the same raphe design.
Nitzschia	" 	A long diatom with carinal dots along both sides. Second most abundant diatom.
Denticula Thermalis	" 	Motile, gray-green. Only one species found in this country.
Diploneis	Bacillariophyta 	Occasionally found in samples.
Pinnularia	" 	Occasionally found in samples.
Amphiprora ornata	" 	A very ornata diatomata. Never very abundant. Only fresh water species in the United States
?	" 	This alga was found in the samples but could not be identified. It appeared with the diatoms.

The diatoms were present year-round in one of the upstream springs. This sheltered spring maintains a constant temperature throughout the year and it appeared to be from this point that the diatoms spread when the downstream portions become thermally suitable. This is believed why there were always a few diatoms in other algal samples at any time of the year. The total population in this spring was Navicula sp. with Nitzschia sp. and Denticula sp. found in rare instances. Jackson (9) states that in natural eutrophic springs the dominant diatom species are Achnanthres sp., Navicula sp., Nitzschia sp, and Synedra sp. Since our springs contain two of these indicator species, we can postulate that they are euthrophic.

The late spring bloom was composed entirely of diatoms. By far the dominant genus was Navicula. Its concentration was always greater than 90% of a sample. Diatoms formed thick mucillaginous mats that would fill with gas, presumably oxygen, and rise to the surface of the stream. As the mats aged they would dry at the surface and become encrusted with a thick layer of evaporite.

Calothrix sp. was present year-round. It formed a black coating on the bottom rocks in the flow channel. As temperature increased in the spring this alga became more prolific, appearing on rocks just below the surface of the water at the edge of the stream.

Biomass can be expressed as g/m^2 of dry weight or ash free dry weight (10). In this case the former was chosen so that further examination could be made of the sample. One of the samples was digested in HCl to find the weight of diatom shells in g/m^2. The result showed that in a diatom mat 41% of the weight is due to the silicon shells. Dry weights can be seen in Table C-3. There is a good comparison using dry weights within the diatom bloom, or within any one bloom of constant algal composition, but the dry weights of two different blooms of different composition cannot be used to estimate rates of productivity or other parameters which are not directly related to biomass. The diatoms bloom and the Ulothrix blooms cannot be compared using dry weight alone. First, the Ulothrix bloom was not vertically as thick as the diatom bloom. Second the diatoms may weigh

TABLE C-3. Algal Dry Weight

Sample Date	Average Biomass From Dry Weights	Remarks
2-25-74	109.5 g/m^2	Results of only Ulothrix bloom. Bloom was not vertically as thick as diatom bloom.
3-26-74	426.6 g/m^2	Beginning of diatom bloom.
3-26-74 Sample C	69.6 g/m^2	Dry wt. of sample.
	28.6 g/m^2	Wt. of diatom shells after digestion. Amount to 41% of total dry wt. of sample.
4-16-74	419.2 g/m^2	Cold weather killed some of the bloom and visibly reduced mass.
5-13-74	528.5 g/m^2	Just past the peak of the diatom bloom. Huge masses of algae mat present.

more because of their silicon shells. Thus there cannot be a direct relation to productivity unless the dominant species is constant.

Population counts were used for species diversity analyses. Graphical analyses of these counts can be seen in Figures C-2 through C-6 (14). In general, a truncated log normal curve is used to analyze for an oligotrophic condition. Oligotrophic conditions consist of an algal flora composed of a large number of species, most of which have small populations. Eutrophic conditions are demonstrated by a small number of species with some having a very large population (14). Work by R. Patrick (14) may be consulted for comparison with Arroyo Salado graphs. The graph of an unpolluted stream approximates a truncated log normal curve while that of polluted waters resembles flattened log normal curve, approaching a horizontal line. It can be readily seen that the populations that we are dealing with are existing under extremely eutrophic conditions. However, we must take into account that the sample size was low.

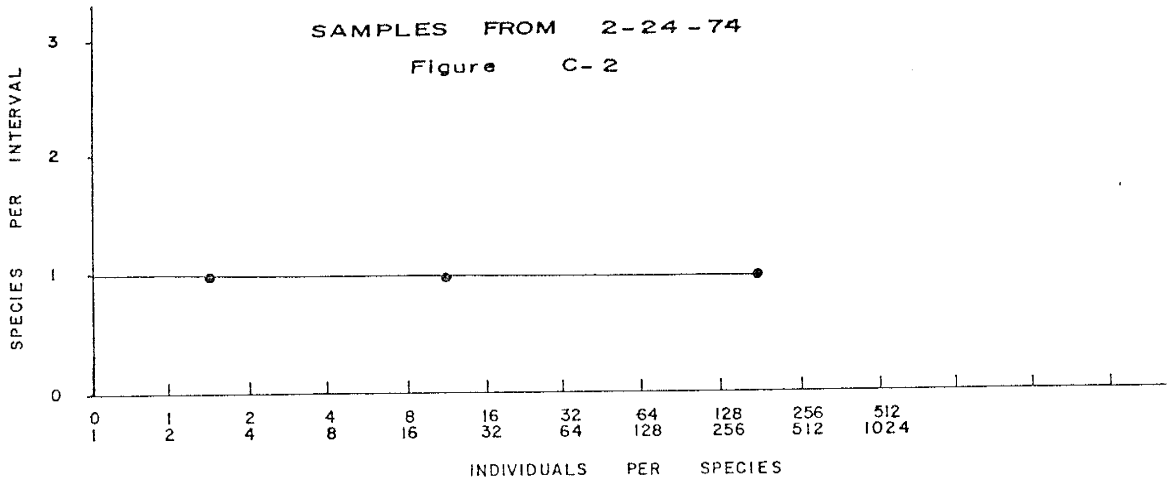
Another method for analyzing the stream conditions is the use of Shannon's Diversity Index (15)(10).

$$H' = - \frac{C}{N} (N \log N + \quad n_i \log n_i)$$

SPECIES DIVERSITY ANALYSIS

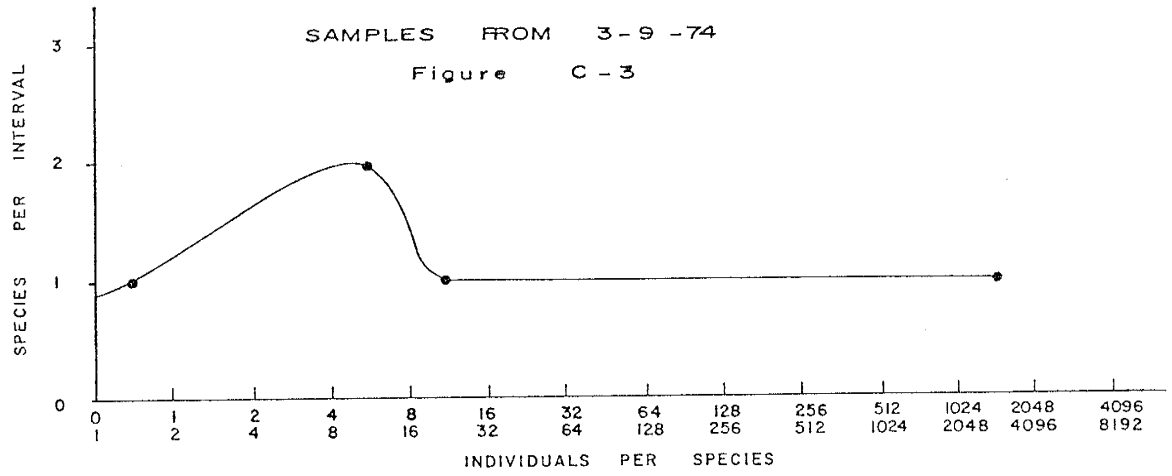
SAMPLES FROM 2-24-74

Figure C-2



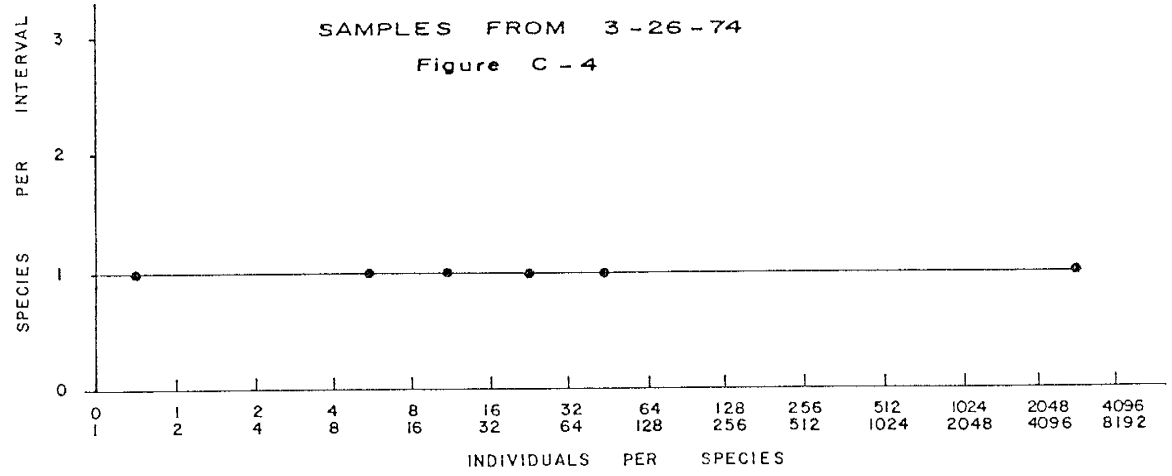
SAMPLES FROM 3-9-74

Figure C-3



SAMPLES FROM 3-26-74

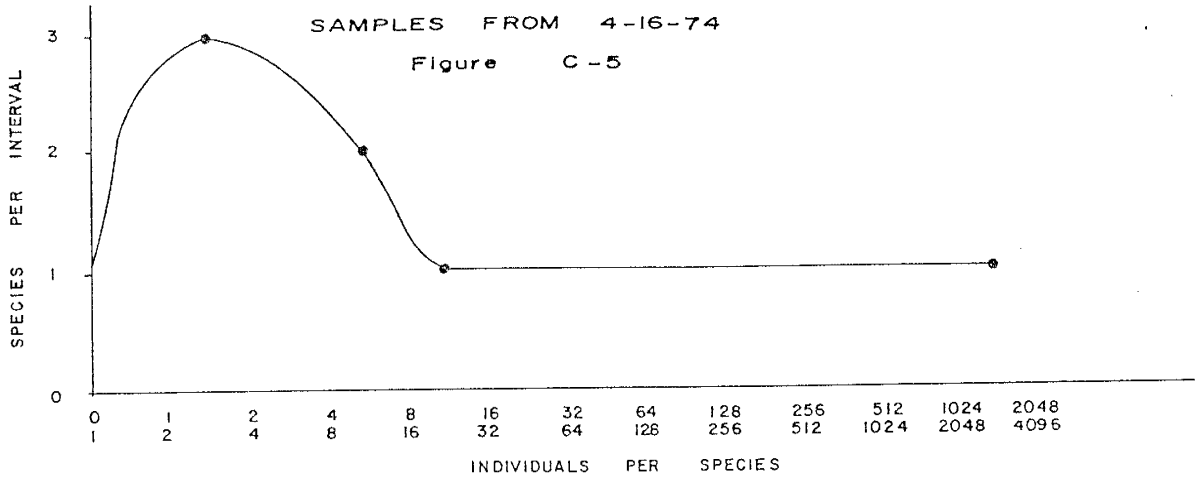
Figure C-4



SPECIES DIVERSITY ANALYSIS

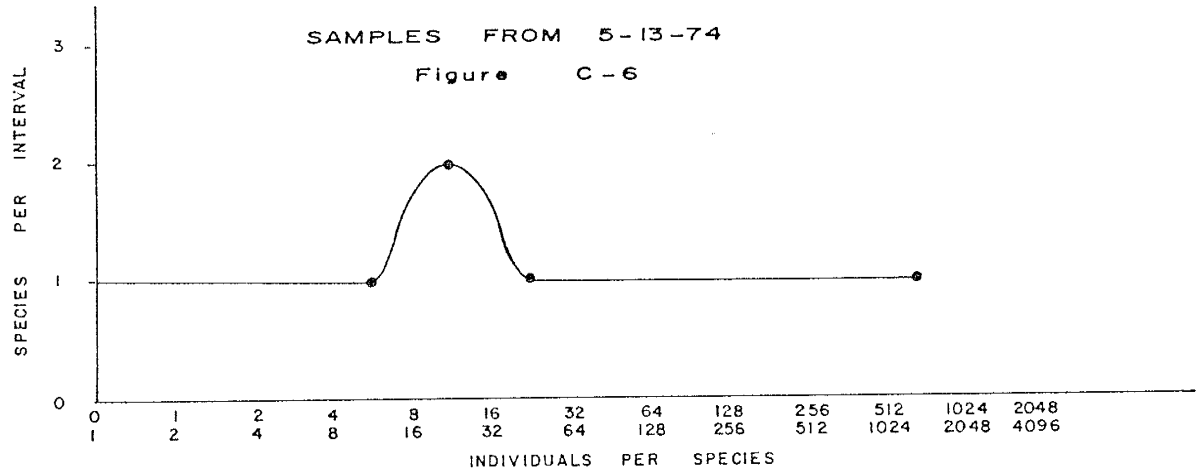
SAMPLES FROM 4-16-74

Figure C-5



SAMPLES FROM 5-13-74

Figure C-6



Where N is the total number of individuals, n_i is the number of individuals in each species, and C is 1 when using base 10 logs. Results of this calculation are given in Table C-4. Since H values of 0.7 to 1.0 indicate eutrophy (notes from Bio. 343 - Brierley) it is safe to say once again that this stream is eutrophic.

Data and graphical representations for two diurnal studies are given in Table C-5 and Figures C-7 through C-10. From these, an approximation of the impact of algae (photosynthesis) can be obtained. Although the data from 4-16-74 appears to be the most ideal, that of 2-27-74 demonstrates the general idea. The pH increases very rapidly through the first 130 meters. Although this is the bloom area it is doubtful that the algae alone cause the pH increase. The pH rise is probably due to the rapid release of CO_2 from the supersaturated water. In Figure C-8, only the differences in starting pH are significant. The higher daytime pH is probably due to algae at the spring quickening release of some CO_2 before the water proceeds down the stream. The pH readings taken at night would most clearly resemble the true pH of the spring. The decrease in pH at Station 4-Fa on the 10:30 A.M. run would be due to respiration within the algae bloom increasing the CO_2 content and thus lowering the pH.

TABLE C - 4

SHANNONS DIVERSITY INDEX

Sample Date	H'
2-24-74	.09661
3-9-74	.04389
3-26-74	.08170
4-16-74	.05800
5-13-74	.11660

DIURNAL DATA

TABLE C-5

'E	STATION	2:00 AM 100 % SATURATION / READING	2:00 AM % SAT.	2:00 AM pH	2:00 AM TEMP. °C	6:00 AM 100 % SATURATION / READING	6:00 AM % SAT.	6:00 AM pH	6:00 AM TEMP. °C	9:00 AM 100 % SATURATION / READING	9:00 AM % SAT.	9:00 AM pH	9:00 AM TEMP. °C	100 % SATURATION / READING	% SAT.	pH	TEMP. °C
-74	4 - F	7.35 / 7.42	101	6.73	9.5												
	5 - A	7.8 / 7.8	100	7.89	6.9												
	4 - Fa	7.7 / 7.9	102.5	7.23	7.7	7.5 / 7.4	98.6	6.9	8.6	7.85 / 5.95	75.8	6.85	6.3				
	4 - E	6.9 / 8.5	123.2	7.48	12.1	7.3 / 8.6	117.6	7.43	10.0	8.1 / 6.85	84.6	6.87	5.0				
	4 - D	6.6 / 7.1	107.6	7.8	14.0	7.1 / 7.5	105.6	7.83	11.3	8.1 / 8.2	101	7.62	4.5				
	4 - C	6.9 / 7.38	107	7.98	12.0	7.3 / 7.2	98.5	7.98	10.0	7.9 / 7.28	92.2	7.83	6.0				

DIURNAL DATA

TABLE C-5

E	STATION	12:30 AM 100 % SATURATION / READING	% SAT.	PH	TEMP. °C	4:30 AM 100 % SATURATION / READING	% SAT.	PH	TEMP. °C	8:30 AM 100 % SATURATION / READINGS	% SAT.	PH	TEMP. °C	10:15 AM 100 % SATURATION / READING	% SAT.	PH	TEMP. °C
-74	4-F	7.3 / 7.3	100	6.98	10	7.3 / 7.6	104	6.90	10	7.4 / 5.8	78.3	6.83	8.8	7.7 / 5.65	73.2	6.75	8.0
	4-Fa	6.7 / 7.3	109	6.96	13	6.8 / 6.8	100	6.95	12.5	7.4 / 4.8	64.9	6.85	9.0	7.7 / 5.1	66.4	6.6	8.0
	4-E	6.3 / 8.4	133.5	7.31	16.4	6.4 / 8.6	134.5	7.40	16	7.3 / 6.8	93.2	7.20	10.2	7.7 / 6.75	87.7	7.1	8.2
	4-D	7.0 / 8.3	118.5	7.78	12.4	6.2 / 7.6	122.7	7.88	17.8	6.9 / 6.75	97.7	7.90	11.7	7.35 / 7.0	95.3	7.83	9.5
	4-C	6.9 / 7.7	111.5	8.04	12.0	6.1 / 7.5	123	7.98	18.3	6.6 / 6.5	98.4	7.95	14.0	7.0 / 6.75	96.4	8.03	11.4

FIGURE C - 7

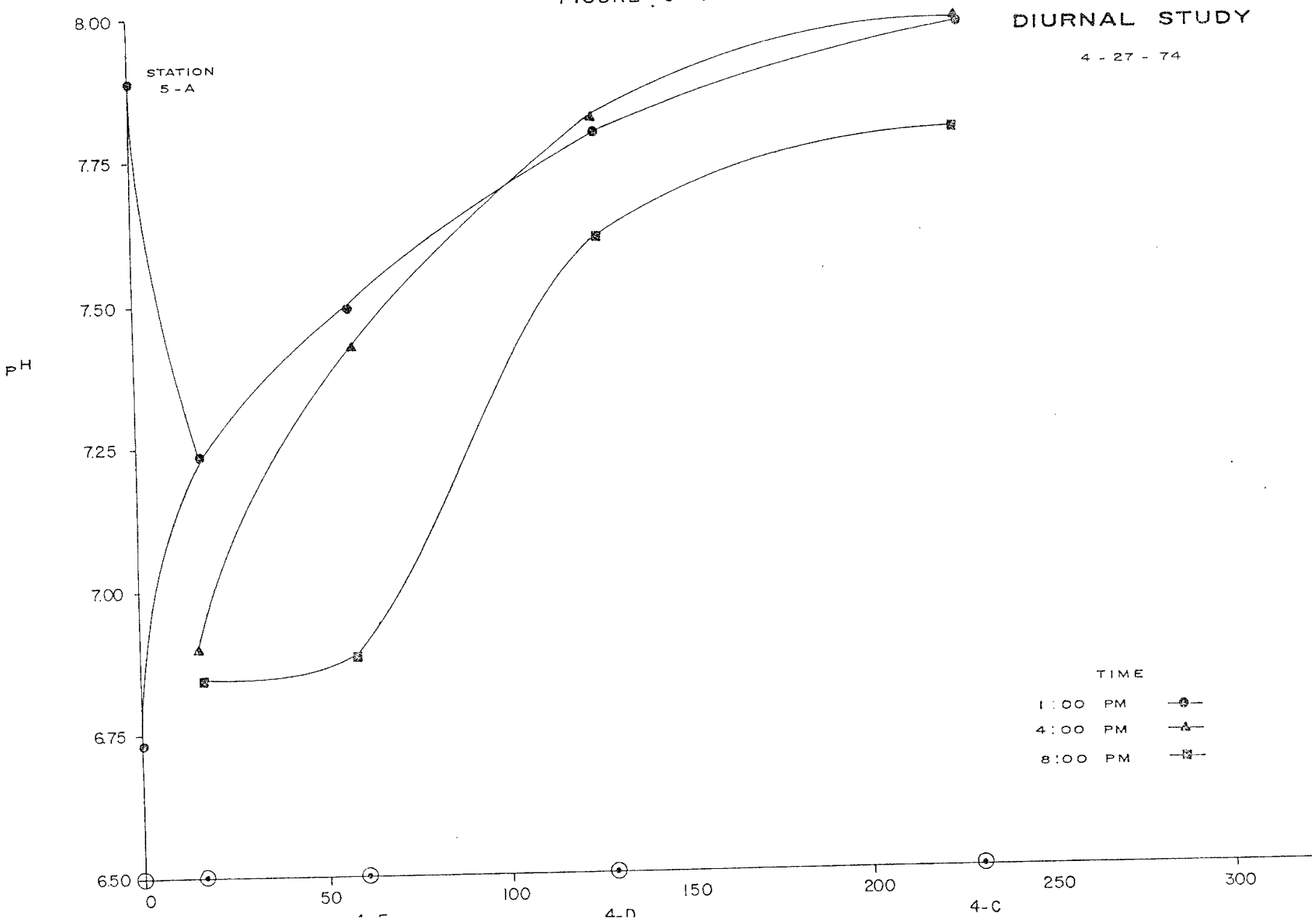

DIURNAL STUDY
4 - 27 - 74
STATION
5 - A
pH
8.00
7.75
7.50
7.25
7.00
6.75
6.50
0
50
100
150
200
250
300
4-C
TIME
1:00 PM
4:00 PM
8:00 PM

FIGURE C - 8

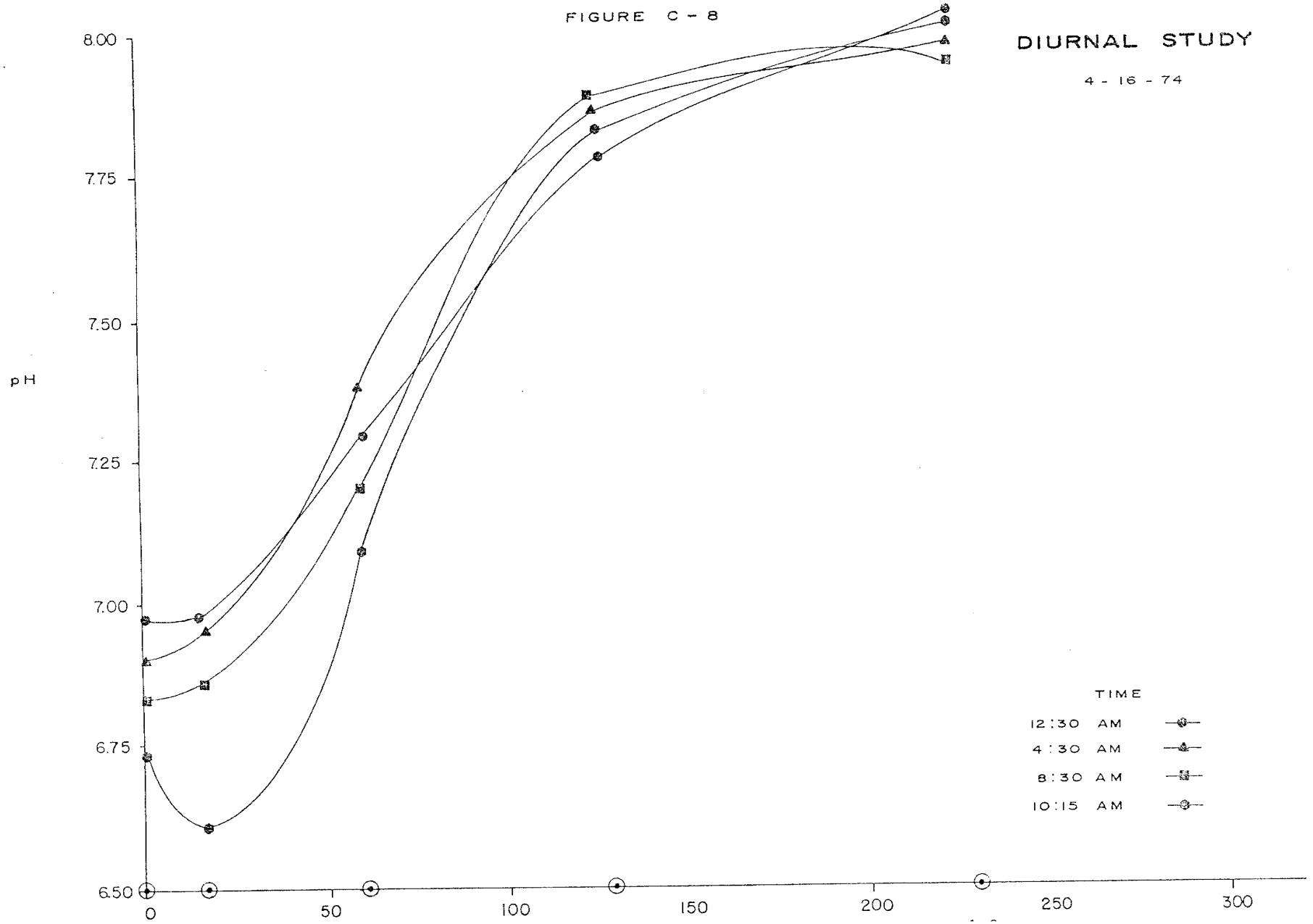

DIURNAL STUDY
4 - 16 - 74
pH
8.00
7.75
7.50
7.25
7.00
6.75
6.50
0
50
100
150
200
250
300
TIME
12:30 AM
4:30 AM
8:30 AM
10:15 AM

FIGURE C - 9

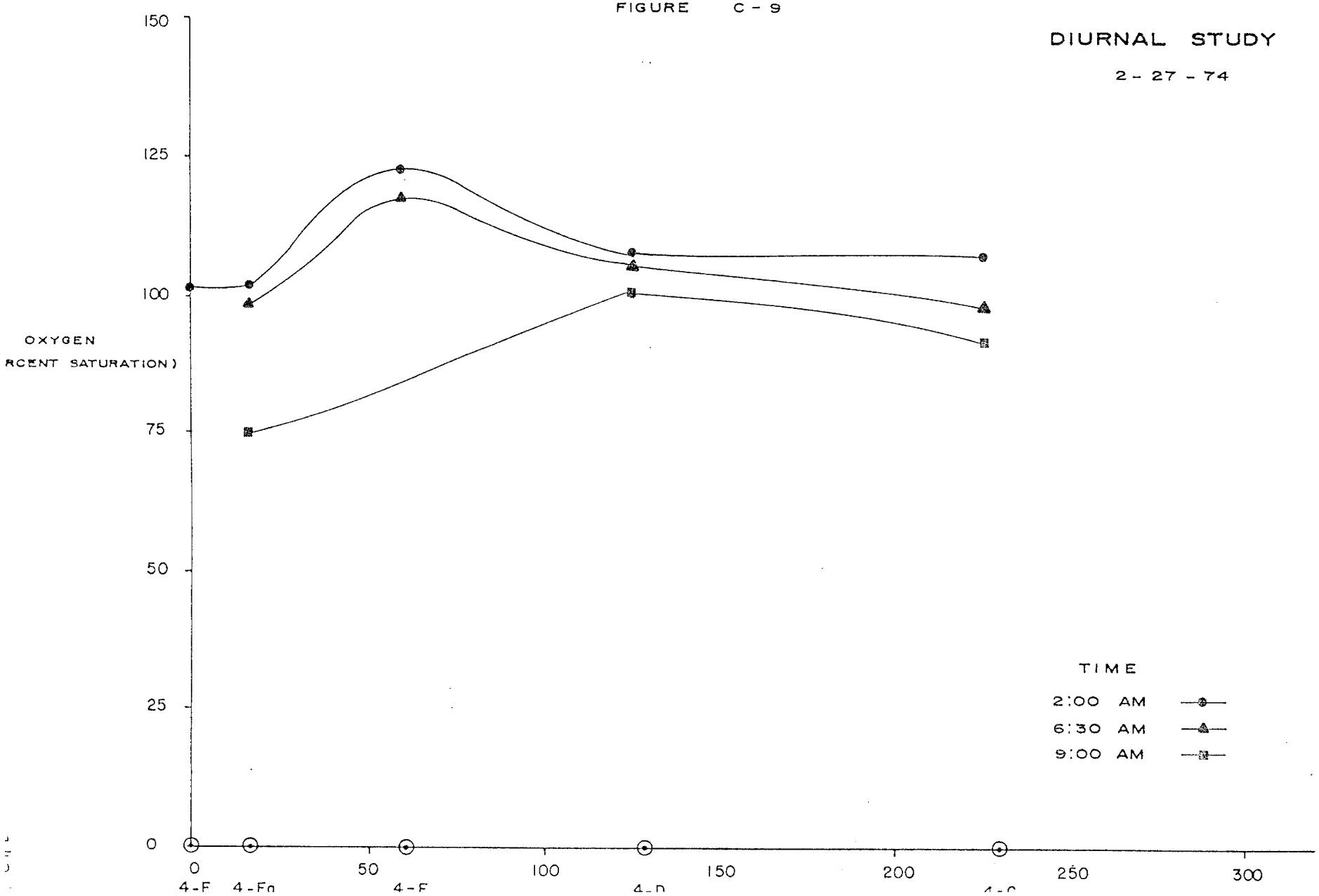
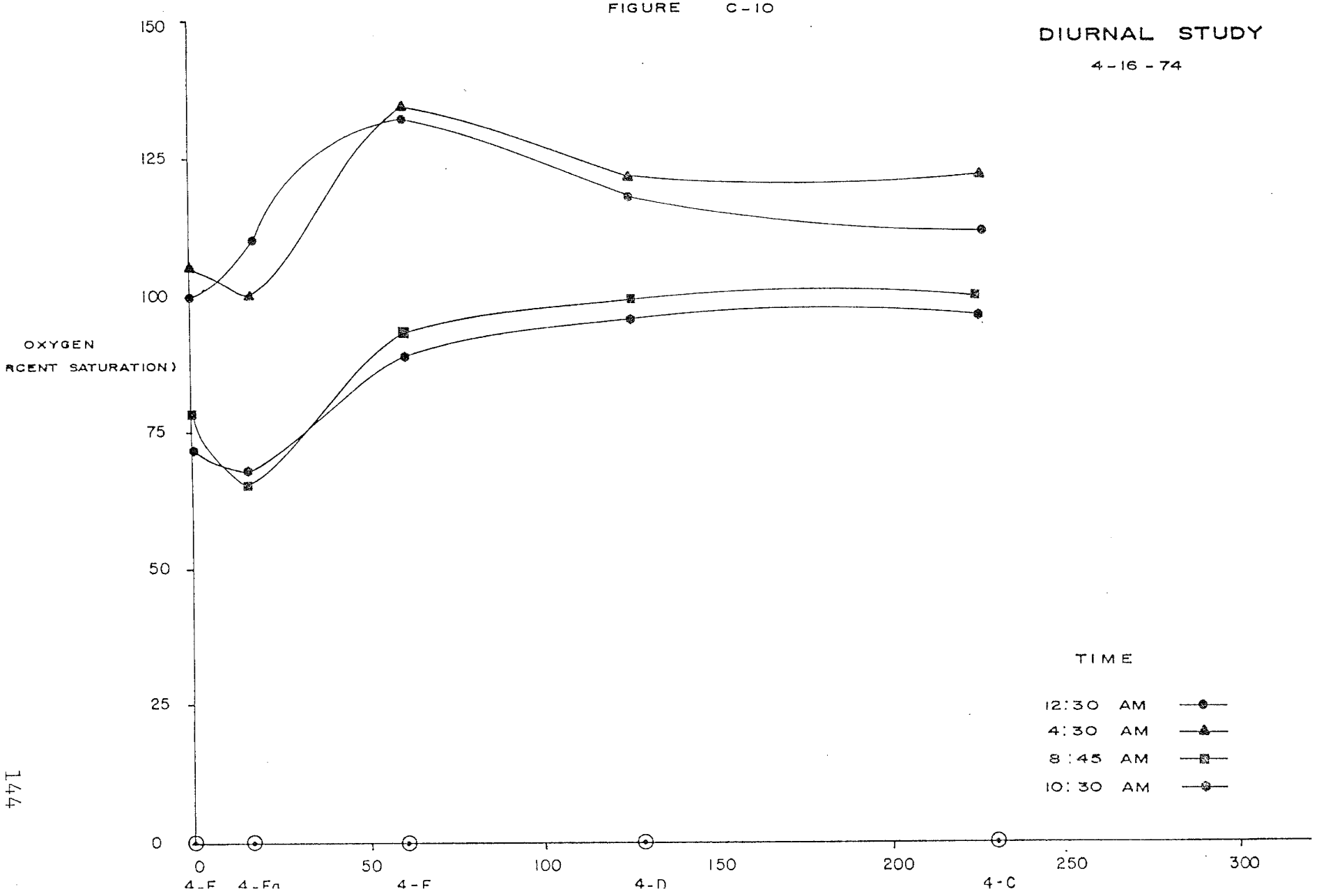

DIURNAL STUDY
2 - 27 - 74
150
125
100
75
50
25
0
OXYGEN
RCENT SATURATION)
TIME
2:00 AM
6:30 AM
9:00 AM
0
50
100
150
200
250
300
4-F
4-Fa
4-E
4-D

FIGURE C-10


DIURNAL STUDY
4-16-74
150
125
100
75
50
25
0
OXYGEN
RCENT SATURATION)
0
50
100
150
200
250
300
4-F
4-Fa
4-F
4-D
4-C
TIME
12:30 AM
4:30 AM
8:45 AM
10:30 AM

Dissolved oxygen was an important parameter in the diurnal studies. Once again Figure C-10 of sample date 4-16-74 seems to have the most complete data. Daytime readings show super-saturation of O_2 at all stations, with 4-E having the highest concentration. This agrees with observations that the greatest algae bloom mass was between 4-Fa and 4-E below which percent saturation begins to lower, presumably because of decreased oxygen production and diffusion out of excess O_2. However, maintenance of the high level of dissolved oxygen between 4-D and 4-C cannot be explained. The dip in the night readings at 4-Fa is caused by algal respiration. After leaving the bloom area the water quickly establishes equilibrium with the atmosphere, or 100% saturation.

Gross productivity, or the measurement of total primary production due to photosynthesis, was calculated using a general equation described by Odum(12). A method for the precise calculation of productivity was considered(10) but rejected because exact definition of flow rate and stream channel characteristics was not possible. An equation using CO_2 to solve for productivity was also considered(18) and is a good method but was rejected because the calculations were more rigorous and not necessary.

The equation given by Odum(12) is:

$$Q = P + D_{\text{out or in}} - R + A$$

where Q = The rate of change of dissolved oxygen per unit area

P = The rate of gross primary productivity per unit area

D = The rate of oxygen uptake by diffusion per unit area

R = The rate of respiration per unit area

A = The rate of drainage accrual

Respiration can be considered constant and thus removed from the equation. Accrual is considered zero because the only inputs to the stream are spring and upstream water. The equation is now stated:

$$P = Q + R - D - A$$

when $R = 0$ and $A = 0$,

then $P = Q - D$

The maximum oxygen production, or 2.0 ppm above saturation at 4-E date 4-16-74 was used for evaluation. This was considered to be the maximum production level within the algae bloom. The calculations and equations are given in Table C-6.

The result is P = 12.85 g m^{-2} day^{-1}. This compares with other productivity values given in Odum(12) and is found to indicate eutrophic conditions. This is not surprizing because all other methods of evaluation used have come to the same conclusion.

Figure C-13 and Table C-7 both directly from Fisher(7) present the half-life of CO_2 in solution at various sampling times in this stream. The lowest point of 1.9 minutes indicates the time of highest algal productivity and thus the most rapid release of CO_2 from the water. This corresponds to the Ulothrix bloom and increases in water and air temperature. It is not known why the high masses of algae between 4-16-74 and 5-13-74 do not produce reductions in the half-life of that time span. There may be other factors present that have not been considered.

CONCLUSION

Arroyo Salado by all definitions is a eutrophic stream. This is established by the presence of certain algae, particularly the diatoms Navicula and Nitzschia, species diversity graphs, Shannon's Diversity Index, large bacterial growths involving the sulfur cycle, and a high value for productivity.

Since there is no visible organic pollution except from allochthanous material which enters infrequently, another type of pollution must be considered. Carbon dioxide is present in abnormally high concentrations and is thus related to the prolific algae blooms. It also affects the equilibrium of all other ions in solution (7) causing many shifts. One of these effects is the deposition of $CaCO_3$. Through equilibrium equations and evaluations of the chemical reactions of the water it is concluded that CO_2 equilibration is the significant mode of $CaCO_3$ deposition(7). The biological effect is to accelerate processes that would eventually occur.

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