



7-1969

Solution Geochemistry of the Water of Limestone Terrains

Digital Object Identifier: <https://doi.org/10.13023/kwrrri.rr.19>

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**SOLUTION GEOCHEMISTRY OF THE WATER
OF LIMESTONE TERRAINS**

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Lexington, Kentucky**

**Project Number A-009-KY; Agreement
Number 14-01-001-911; May 1966 - June 1969**

**Completion Report
July 1969**

**The work upon which this report is based was supported by
funds provided by the United States Department of the In-
terior, Office of Water Resources Research, as authorized
under the Water Resources Research Act of 1964.**

ABSTRACT

Limestone groundwater flows mainly in openings it has solutionally enlarged, thus an understanding of the water's state of saturation relative to calcite (the principal mineral component of limestone) is fundamental to an understanding of the nature and evolution of the limestone aquifer. This study investigated the Mammoth Cave-Sinkhole Plain (MCSP) and Cave Hollow (CH) aquifers in Kentucky, both in Mississippian limestones.

Both aquifers were always undersaturated with calcite. Except for completely ventilated vadose flows (usually) and some vadose seepage (occasionally), all recharges sampled (sinking streams, vadose flows, and vadose seepage) were also undersaturated. The lack of saturation in the MCSP aquifer was due to the introduction of carbon dioxide into the water in amounts difficult to explain by the carbon dioxide content of the above recharges. In both vadose flows and seepage, undersaturation tended to correlate directly with flow volume, and there was an inverse correlation between the amount of carbon dioxide and calcite saturation in most of the waters sampled. In vadose seepage this relationship was so strong as to suggest seasonal invariance of carbon dioxide content of the water prior to out gassing.

Results suggest solutional enlargement is greatest near recharge points in "ventilated" aquifers (CH) but the carbon dioxide introduction phenomenon (MCSP) allows solution over wide areas in "unventilated" aquifers.

KEYWORDS - *geochemistry/*limestone aquifer/*groundwater/quality of

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INTRODUCTION

This project was begun in the summer of 1966, and represents a major phase of a continuing line of research by the principal investigator into the chemistry and hydrology of natural waters in limestone terrains.

Although this document is a completion report on the project as funded by the Office of Water Resources Research, U. S. Department of the Interior, under the provisions of PL 88-379, it is anticipated that work in this general area will continue and that the techniques established and data gathered for this study (and herein reported) will be used for future research and publication.

The field and laboratory analyses of the Cave Hollow area were performed by David P. Beiter for use as a thesis for the Master of Science degree in Geology. Substantial assistance in the study of the Mammoth Cave - Sinkhole Plain area was furnished by Michael T. Osolnik and Rober H. Postley, MS candidates in Geology. Other graduate students, in Geology except as otherwise indicated, who assisted with aspects of the study, were William M. Mitchell, Leonard N. Plummer, James R. Riddell (Zoology), Richard C. Worley, and Robert D. Zwicker (Physics).

Sincere appreciation is expressed to John A. Aubuchon, former Superintendent of Mammoth Cave National Park, for granting permission for phases of the study to be undertaken in Mammoth Cave, and to the many members of the National Park Service staff for their assistance and cooperation. I would also like to acknowledge the courtesy of the various landowners in allowing access to their property.

I further wish to thank Robert V. Cushman and others of the Louisville Office of the United States Geological Survey for their assistance.

Portions of the Cave Hollow area study were performed with funds received from a Ralph W. Stone Research award from the National Speleological Society to David P. Beiter.

The Mammoth Cave - Sinkhole Plain portion of the study was facilitated by the use of the field laboratory of the University of Kentucky Institute of Speleology at Mammoth Cave.

Finally, I acknowledge my most sincere appreciation of the cooperation and assistance of Dr. Robert A. Lauderdale, Director of the University of Kentucky Water Resources Institute.

Statement of Problem

Limestone aquifers are widely recognized as possessing significant qualitative differences from aquifers in granular rocks or unconsolidated material. These differences include the localization of permeability along discrete openings, rather than in intergrain pores, with resulting significant variations in well yields over short distances; and the fact that flow is often rapid in large openings, anisotropically distributed, which renders many of the usual assumptions made in ground water studies invalid or highly suspect. These assumptions include the linear proportionality of flow velocity and potential difference and the use of a single value for the hydraulic permeability.

Although limestone aquifers share with other "fracture" aquifers the above characteristics, they are distinct from such aquifers in silicate rocks (such as shale, granite, basalt, etc.) in that the limestone is soluble to such a degree in slightly acid water that nearly all the openings in limestone have been solutionally produced (or enlarged) by the water that has flowed through them.

Largely as a consequence of this solubility of limestones, many limestone aquifers have become so permeable, at least locally, that the entire surface drainage of an area is captured by the aquifer, causing the land forms described as karst topography, and resulting in extreme interactions between groundwater and surface drainage. An important, but little appreciated, consequence of this is that the aquifer in such situations becomes the

principal route by which solid, as well as dissolved, products of weathering are transported from the land surface.

It is apparent, therefore, that any real understanding of the nature of the limestone aquifer requires knowledge of the ability of the various waters of a limestone terrain to dissolve the rock. Limestone is made up largely of the mineral calcite (CaCO_3) and, with one exception, all of the other mineral constituents are usually present in such small amounts (and contribute so little to the structural integrity of the rock) that they can be ignored. The one exception is the mineral dolomite ($\text{CaMg}(\text{CO}_3)_2$) which, as an acid-soluble carbonate, behaves similarly to calcite. In the areas studied in Kentucky, dolomite is absent or present in only small amounts in the limestone.

Research into the solution of limestone which is not significantly dolomitic may, therefore, be validly cast into the framework of an investigation into the solution of the mineral calcite. The solution of calcite by natural waters may, in turn, be studied in a number of ways. The thermodynamic state of saturation with respect to calcite may be determined. The rates of solution of calcite may be examined, either in the field or in the laboratory, by investigation the kinetic processes of solution. Alternatively, the rates of solution may be determined in the field by mass-balance considerations.

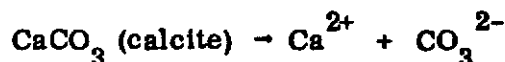
The emphasis of the present study was on the first of these approaches; that of the state of saturation with respect to calcite of natural waters within or associated with the limestone aquifer. The data gathered may also be used

in the mass balance approach, and some preliminary work in this direction has been initiated. No real attempt was made to investigate the solution kinetics problem, although some of the results of the study casts doubts on some tentative conclusions that have been drawn in this area, as will be discussed.

The thermodynamic state of saturation approach was felt to be an essential first step in the understanding of the problem, and most of the research effort was directed towards obtaining data of this kind.

Method of Investigation

The state of saturation of a water sample relative to calcite may be determined by investigating the products of the reaction



by comparing the ion activity product A_c with the (thermodynamic) solubility

product K_c , where $A_c = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}$ in the sample and $K_c = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}$ at saturation, and where a_i is the activity of species i . The comparison of

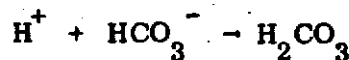
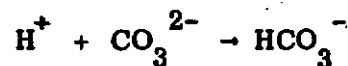
A_c and K_c is conveniently made by forming the saturation coefficient $S_c = A_c / K_c$

for each sample. A value of $S_c < 1$ (or $\log S_c < 0$) indicates the water is

undersaturated with respect to calcite; $S_c = 1$ (or $\log S_c = 0$) indicates

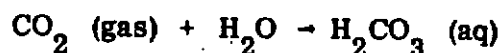
saturation; and $S_c > 1$ ($\log S_c > 0$) indicates supersaturation.

Because the amount of CO_3^{2-} ion in solution, and hence S_c , is reduced by presence of an acid through the reactions

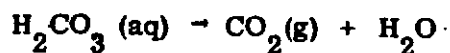


the acidity of the waters is of prime concern in determining the degree of saturation with respect to calcite.

The principle acid-producing substance which acts on the waters of limestone terrains is carbon dioxide, via the reaction



with the carbonic acid formed dissociating to form the bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and H^+ ions. Because of its importance, the amount of carbon dioxide in the water was determined for all samples. It is expressed as the partial pressure of carbon dioxide (P_{CO_2}) in an atmosphere with which the water is apparently in equilibrium; and is determined from the Henry Law solubility of CO_2 for the summary reaction



It should be noted that a convenient property of P_{CO_2} as a measure of the CO_2 content of water is its lack of temperature dependence. P_{CO_2} of the normal atmosphere is usually taken as 3×10^{-4} atm ($\log P_{\text{CO}_2} = -3.52$).

The parameters S_c and P_{CO_2} (and others) were determined for natural waters associated with two different limestone aquifers over a period of about 18 months, from July 1967 to December 1968, although no one site was sampled over the entire period. In the Mammoth Cave-Sinkhole Plain (MCSP) aquifer, the following operations were performed for each sample (details are given in Appendix 1): In the field at the time of sampling, pH, alkalinity, temperature and electrical conductivity were measured, flow rate

was estimated, and a 50 to 250 ml sample was filtered, acidified and returned to the laboratory, where analyses were performed for total calcium, magnesium, and sodium by atomic absorption spectroscopy, and for Cl^- and SO_4^{2-} by spectrophotometry. In some cases redeterminations were made and analyses for other ions were performed where change imbalances or lack of agreement between measured and calculated conductivities suggested that the analytic results were in error or that other ions might be present.

Calculations were performed on an IBM 360/50 computer at the University of Kentucky Computing Center using a program written for the purpose. Briefly stated, the program computes the activities of the various ions, and calculates parameters such as S_c and P_{CO_2} by determining activity coefficients (by the Debye-Hückel relationship) and concentrations of complex ions in solution.

Approximately the same procedure was followed for the Cave Hollow aquifer, except that complete analyses were not run for all samples. The principal effect of this was to underestimate the ionic strength of the solutions, and hence, overstate the Debye-Hückel activity coefficients. The small error thus introduced is considered in the discussions and tables which follow.

Although an attempt was made to sample both aquifers periodically, this was only achieved during the latter two-thirds of the 18-month study period, due to analytic and logistic difficulties in the first six months.

Mammoth Cave-Sinkhole Plain Area

The sites sampled (excluding those associated with White Mills and Terhune Springs, which lay some distance to the north) were concentrated at 5 localities extending south from the Green River a distance of about 25 kilometers in Edmonson, Barren, and Warren Counties, Kentucky (Figure 1). These localities lie within the boundaries of three quadrangles recently published as Geologic Quadrangle Maps by the U. S. Geologic Survey, and the discussion which follows will be based on these maps. Sites 9-14 and 21-23 are on the Mammoth Cave Quadrangle (Haynes, 1964); Sites 2, 5-7, and 20 are on the Park City quadrangle (Haynes, 1962); and sites 3 and 4 are on the Smiths Grove Quadrangle (Richards, 1964).

Structure

In this area, the Green River forms the approximate boundary between the Illinois Basin, which is generally underlain by rocks of Pennsylvanian age, to the north; and a limestone region underlain by rocks of Mississippian age to the south. About 10 kilometers south of the northern edge of the limestone region (and the Green River) is the prominent south-facing Chester or Dripping Springs Escarpment (Figure 1).

All of the rocks of the area are nearly flat-lying, with a general regional dip to the north of about 10 meters per kilometer, but with variations which may be significant for the purposes of this study. In the vicinity of the escarpment, the dips are somewhat steeper, about 20 meters per kilometer

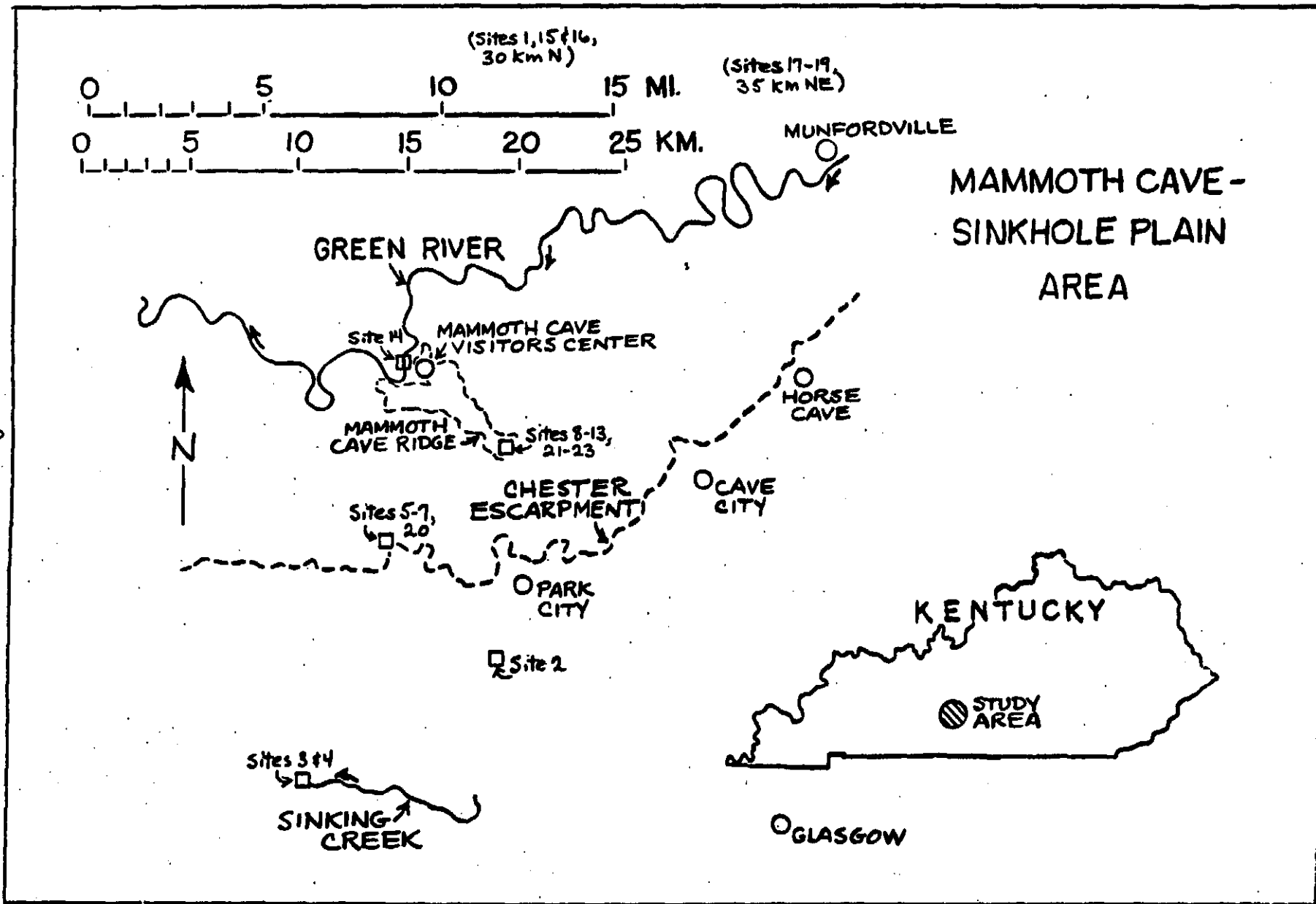


Figure 1. Map of Mammoth Cave:- Sinkhole Plain Area

near Park City. Also, there are areas where the regional dip is more nearly west than north, most noticeably in the vicinity of sites 3 and 4 and just to the northwest of sites 5-7 and 20 (Figure 1). There is structurally a rather flat area between Park City and Sites 8-13 and 21-23 (including a few small closed highs), but little else in the way of structural complications. There are no faults mapped in the vicinity of or between the sites sampled.

Geomorphology

Topographically, the Chester Escarpments divides the area into a relatively flat plain to the south and a dissected plateau area to the north. The southern plain, known as the Sinkhole Plain, is a typical karst, with few surface streams and, in most parts, a very high density of sinkholes. The average altitude is about 220 meters (750 feet) with an average local relief of about 20 meters (65 feet). The relief is fine textured; a characteristic sinkhole diameter being 100 meters (300 feet).

The plateau area north of the escarpment is also a karst south of the Green River, but of a significantly different form. The average altitude of the plateau tops is about 260 meters (850 feet) and that of the intervening sinkholes is 200 meters (650 feet). The local relief is thus three times that of the sinkhole plain. The texture is much coarser with an average sinkhole diameter of about 1 km. North of the Green River the relief and texture is similar, but the area is not karst.

The limestone plateau between the Chester Escarpment and the Green River consists of irregularly arranged plateau areas and intervening sinks. The general pattern is one of a narrow plateau along the escarpment with finger-like extensions reaching north to the river which are separated by roughly linear compound sinks. One of these finger plateaus, Mammoth Cave Ridge, is shown in Figure 1.

In both the Sinkhole Plain and the limestone plateau region north of the escarpment, there is essentially no surface drainage in a band of karst which extends from the Green River to a line at least 10 km south of the river; the only surface streams are those which flow from a ridge to the nearest sinkhole where they disappear below the surface. South of this band is another of similar dimensions in which sinkholes are relatively uncommon, but whose surface streams drain generally north and west and sink at the margin of the karst band.

Within the boundaries of the karst band are numerous caves, of which the largest (both in passage diameter and linear extent) are in the plateau area north of the Chester Escarpment. The largest of these are Mammoth Cave in Mammoth Cave Ridge and the Flint Ridge System in the next finger plateau to the north and east of Mammoth Cave Ridge. In the Sinkhole Plain south of the escarpment the caves (known to the writer) are much smaller and shorter.

Stratigraphy

No attempt will be made at a complete discussion of the sedimentary rocks of the area; detailed stratigraphic descriptions may be found in Haynes

(1962, 1964) and Richards (1964). In gross outline, the stratigraphic section may be characterized by a nearly unbroken sequence of Mississippian limestones more than 200 meters (600 feet) thick overlain by an even thicker sequence of upper Mississippian and Pennsylvanian sandstones with thin limestone units near the base (Figure 2). In ascending order the limestone units are the Salem-Warsaw, St. Louis, Ste. Genevieve, and Girkin Limestones. Although there are textural differences and variations in the amount of chert, dolomite, and clay in the various units (Haynes, 1962, 1964; Richards, 1964), the contacts are usually gradational and difficult to recognize. There appears to be little reason to consider them separately in a study of the groundwater hydrology.

Ground Water Hydrology

Studies of the ground water within the MCSP area include the Hydrologic Investigations Atlas of the central Mississippian Plateau region by Brown and Lambert (1962), a report on the entire Mississippian Plateau region, also by Brown and Lambert (1963), a report on the water supply for Mammoth Cave National Park (Cushman, Krieger, and McCabe, 1965), a study of the groundwater hydrology of the Mammoth Cave area (Brown, 1966), a discussion of the hydrology of the Mammoth Cave-Sinkhole Plain area by Watson (1966), and a report of investigations into the groundwater hydrology of the Sinkhole Plain by Cushman (1968).

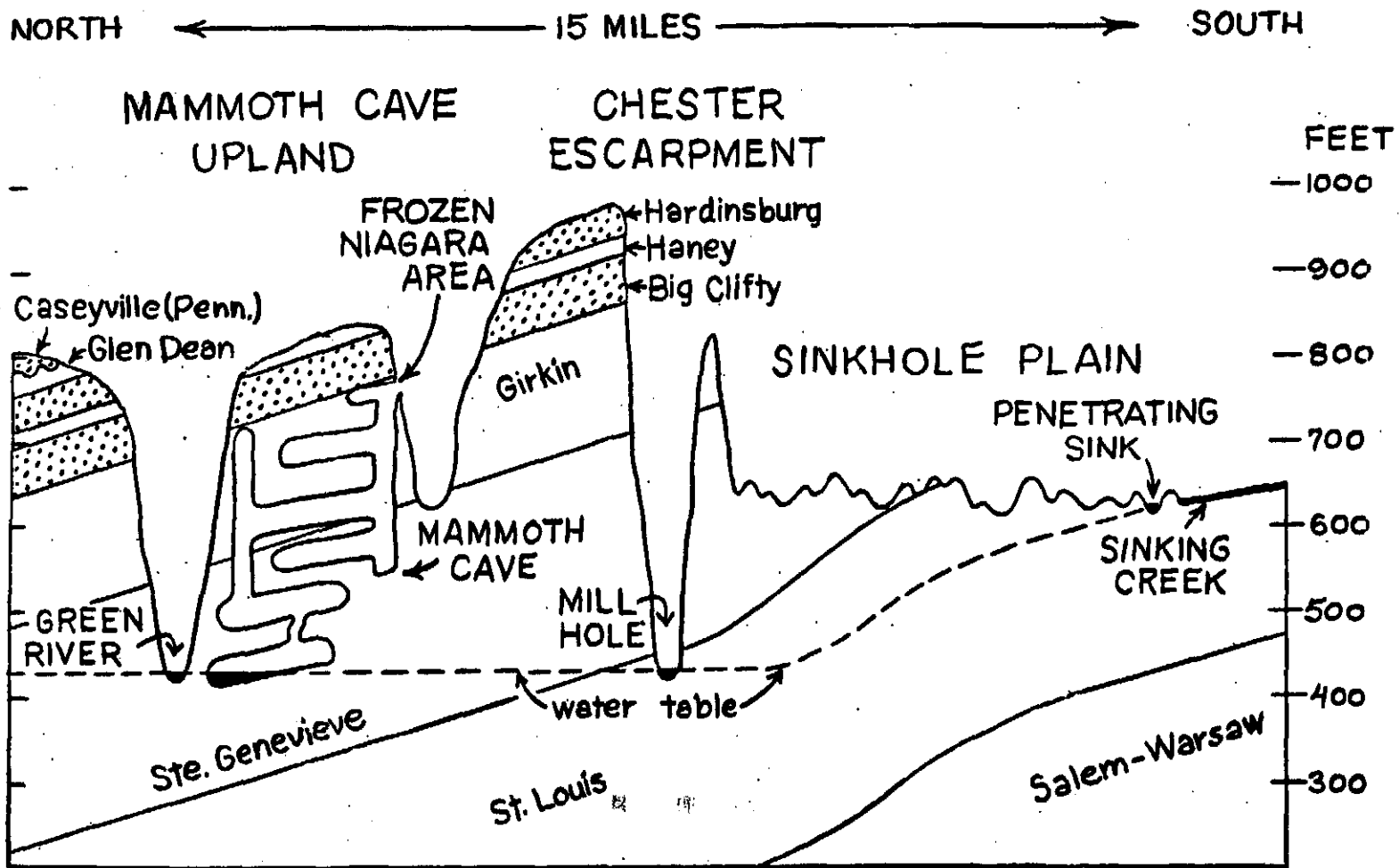


Figure 2. Diagrammatic Cross Section of Mammoth Cave - Sinkhole Plain Area

Cushman's (1968) water table map shows a continuous aquifer beneath the Mammoth Cave Upland and the Sinkhole Plain. The water table configuration shown on Figure 2 is essentially that proposed by Cushman (1968).

Cave Hollow Area

The sites sampled in this area were in a small valley (Cave Hollow) in Lee County, Kentucky about 10 km (6 miles) west of the town of Irvine. Cave Hollow lies within the boundaries of the Cobhill quadrangle, which has not yet been mapped on a large scale. The comments on the structure and stratigraphy which follow are based on reconnaissance of the area and on the Clay City Geological Quadrangle Map (Simmons, 1967) which adjoins the northwest corner of the Cobhill quadrangle.

The valley is about 2.5 km (1.5 miles) long and averages 1 km (0.6 miles) wide. Figure 3 shows a plain view of the lower part. The valley floor is composed of a series of coalescing sinks whose bottoms lie at an average altitude of about 260 m (850 feet). The altitude of the surrounding divides are about 370 m (1200 feet). Except for small streams which flow off the divides in wet weather, the only flowing stream emerges from a spring near the mouth of the valley. All of the drainage of the valley, including both the trunk stream and the lower portions of its tributaries, is underground upstream from the spring.

The sedimentary rocks of the area are nearly flat-lying, and no major structural elements (faults or large folds) were noted. The ridges which

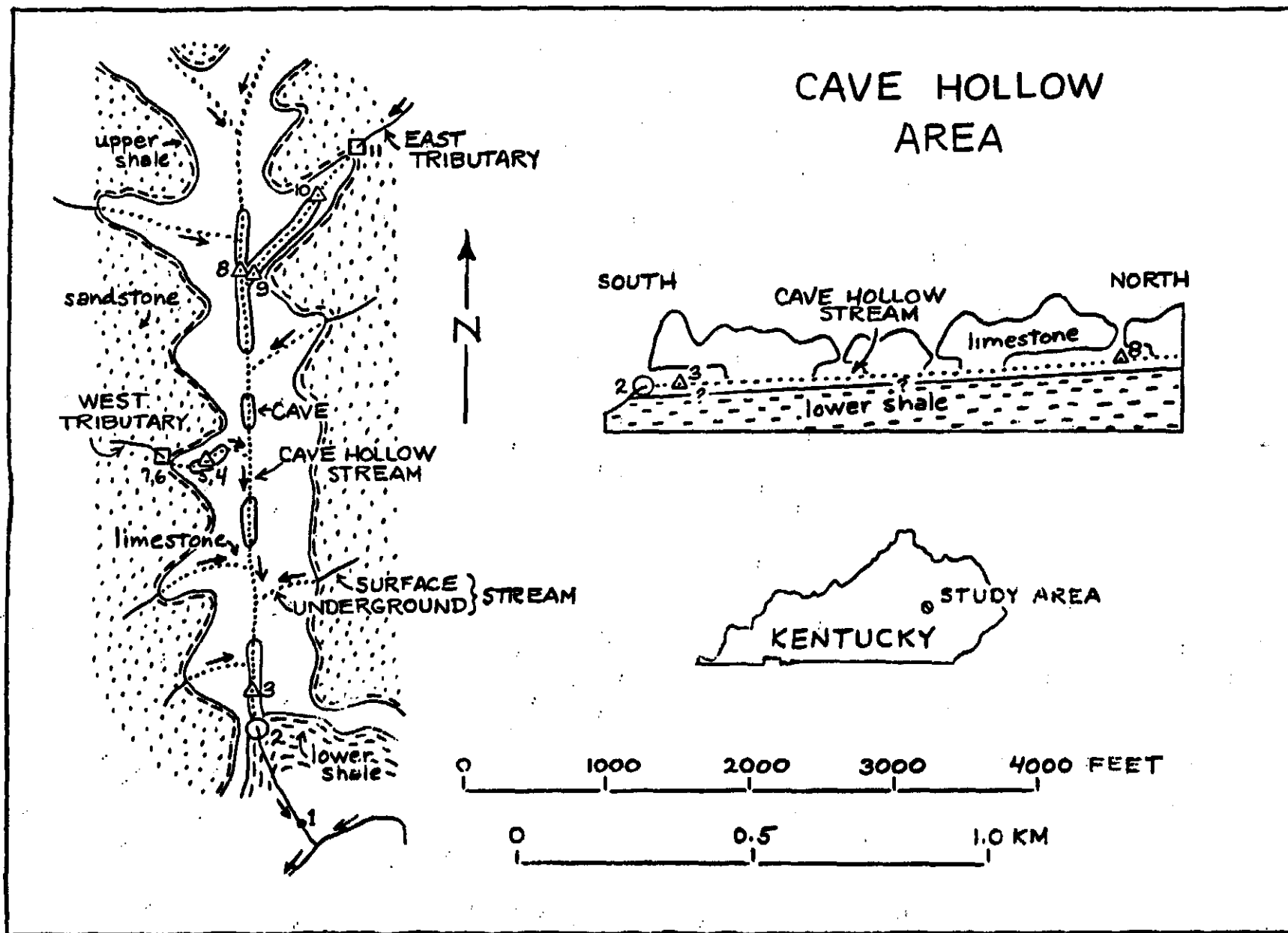


Figure 3. Map and Diagrammatic Cross Section of Cave Hollow Area

surround Cave Hollow (except at its lower end) are underlain by clastics of the Pennsylvania Lee Formation. These are underlain by a thin (about 5 m thick) Pennsylvania or Mississippian shale. The shale is underlain by the Mississippian Newman Limestone, which is correlative with the St. Louis, Ste. Genevieve, and limestones above the Ste. Genevieve in the MCSP area. The Newman at Cave Hollow is about 50 meters thick, and is underlain by shaly limestones of the Mississippian Borden Formation.

The stratigraphy of the CH area is broadly similar to that of the MCSP area, but differs in that the thickness of relatively pure limestone is less (50 m at CH area versus 200 m at MCSP area), that the upper limit of the massive limestone is near the base of the Pennsylvania section rather than some distance below it as in the MCSP area, and that a less soluble unit (Borden) underlies the massive limestone at moderate depths in the CH area.

As noted earlier, all of the streams in Cave Hollow are underground, at least in their lower reaches. Although numerous small streams flow off the divides in wet weather, they sink at or just below the contact of the shale and underlying limestone. They then flow in caves to the center of the valley where they join the main CH stream, which is also flowing underground. This stream emerges from a spring at the mouth of the valley, probably near the upper contact of the Borden shaly limestones. Although most of the underground courses of the main stream and its numerous tributaries are inaccessible to exploration, a sufficient number of the caves through which

streams are flowing have been entered and mapped to indicate the general outline of the drainage (Figure 3).

Although there is little evidence one way or the other, it seems likely that the main stream and the tributaries are flowing on saturated rock (and are thus "water table streams") except possibly at their extreme upstream ends. Whether or not significant porosity exists in the limestone below (or between) the streams is not known, but the relative flow volumes of the tributaries, the main stream, and the spring suggest that there is little flow other than in cave streams. Nevertheless, since the flow is underground under conditions not known to be vadose, the term Cave Hollow aquifer will be used. The aquifer is probably best visualized as confined to the Cave Hollow drainage and is perched on the underlying Borden shaly limestones.

Figure 3 shows the relationships which have been discussed, together with the various water sampling sites.

RESULTS OF PROJECT

Geochemistry of Limestone Terrains

Saturation relationships in surface streams

Samples were collected from two surface streams in the Mammoth Cave Sinkhole Plain area (Sinking Creek and Mt. Vernon Stream) and two in the Cave Hollow area (West and East tributaries). Figures 4 and 5 show plots of $\log S_c$ and $\log P_{CO_2}$, respectively, versus season; and $\log P_{CO_2}$ is plotted against $\log S_c$ in Figure 6. All of the streams were undersaturated with respect to calcite ($\log S_c < 0$) and in equilibrium with a P_{CO_2} greater than that of the normal atmosphere ($\log P_{CO_2} > -3.52$) at all times.

Although both Sinking Creek and Mt. Vernon Stream were occasionally dry, the mean flow of Sinking Creek ($1.6 \times 10^5 \text{ cm}^3 / \text{sec}$) was about 1000 times as great as that of Mt. Vernon Stream ($1.4 \times 10^2 \text{ cm}^3 / \text{sec}$) when water was present. Other than discharge, there were no obvious differences between the streams in temperature, nature (other than size) of the drainage basin, or source of water. The drainage basin of both streams is entirely underlain by the St. Louis Limestone. It is of interest to note, therefore, the considerable difference in S_c of the two streams (Figure 4), with the smaller being nearly 100 times less saturated with respect to calcite than the larger. Equilibrium P_{CO_2} , however, was nearly the same for both streams (Figure 5).

The two streams in the Cave Hollow area were small, with flows comparable to Mt. Vernon Stream. Both drained areas of sandstone and shale,

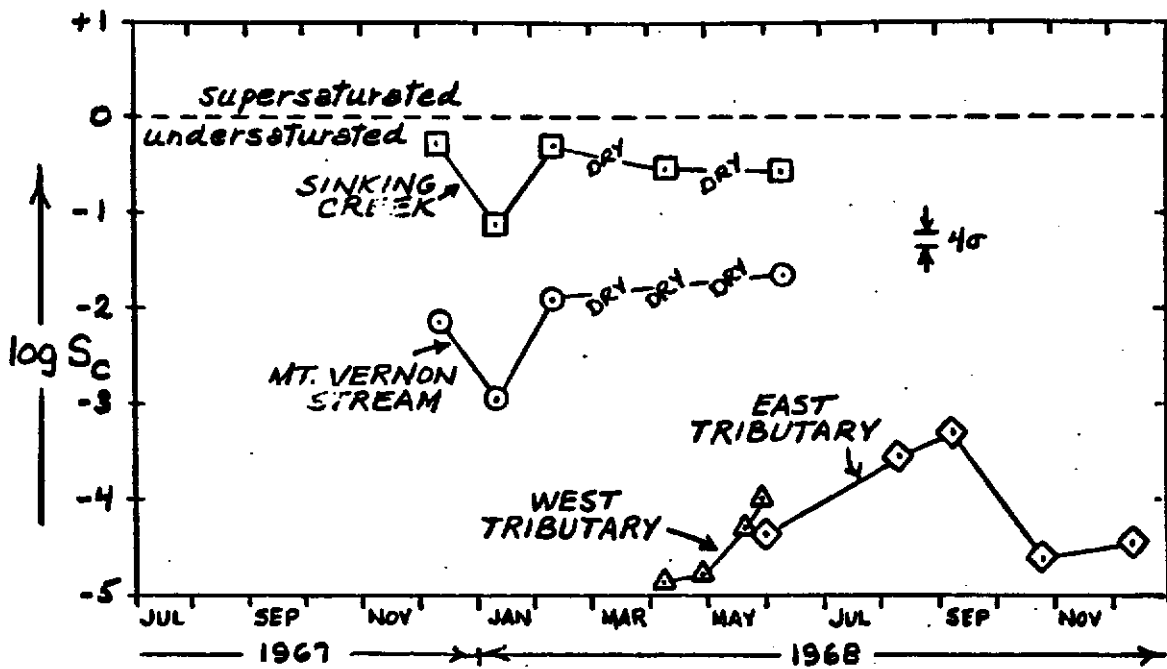


Figure 4. Log Calcite Saturation Coefficient (S_c) versus Date in Surface Streams

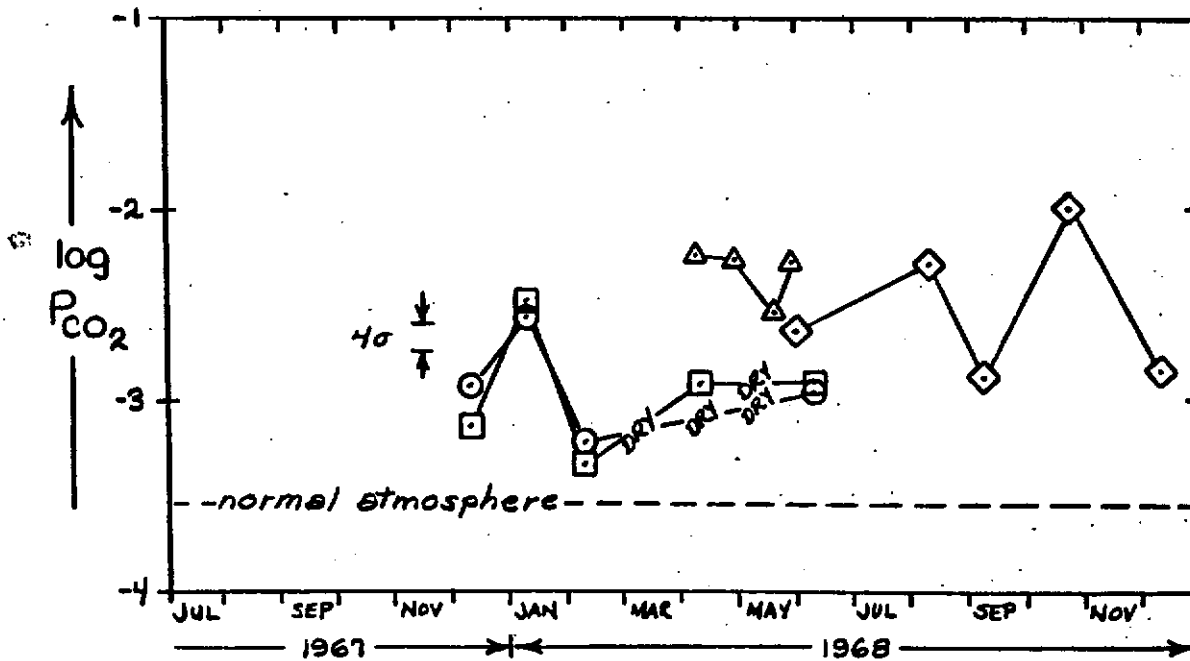


Figure 5. Log Equilibrium Carbon Dioxide Partial Pressure (P_{CO_2}) versus Date in Surface Streams. Symbols for streams same as in Figure 4.

and it is unsurprising that their values of S_c were so low, (Figure 4). Their generally higher values of P_{CO_2} relative to the MCSP area streams (Figure 5) might also be explained by their lack of opportunity to dissolve calcite, except that the MCSP stream data suggest that calcite solution is not controlling the P_{CO_2} of these streams.

Although there seems to be a general tendency in the MCSP area for S_c to be low and P_{CO_2} to be high in both streams during the winter (Figures 4 and 5), the correlation is weak. Comparison, by simple inspection, of these variables with discharge or temperature showed even less correlation. In January and February, for example, Mt. Vernon Stream showed large changes in both S_c and P_{CO_2} , but the water temperature was the same in these months and the flow varied only moderately.

The variations in S_c in the CH area, on the other hand, appear to correlate reasonably well with season, or with some seasonally related variable such as temperature or flow. Although there are insufficient data to draw any but tentative conclusions, the surface stream waters tend to be more undersaturated during the period April-June.

There appears to be a moderate to good correlation between $\log S_c$ and $\log P_{CO_2}$ for a single source, with the various samples tending to plot along a line with unit negative slope (Figure 6). This correlation is best for the sites with higher values of S_c . This correlation will be discussed further in the section on vadose seepage.

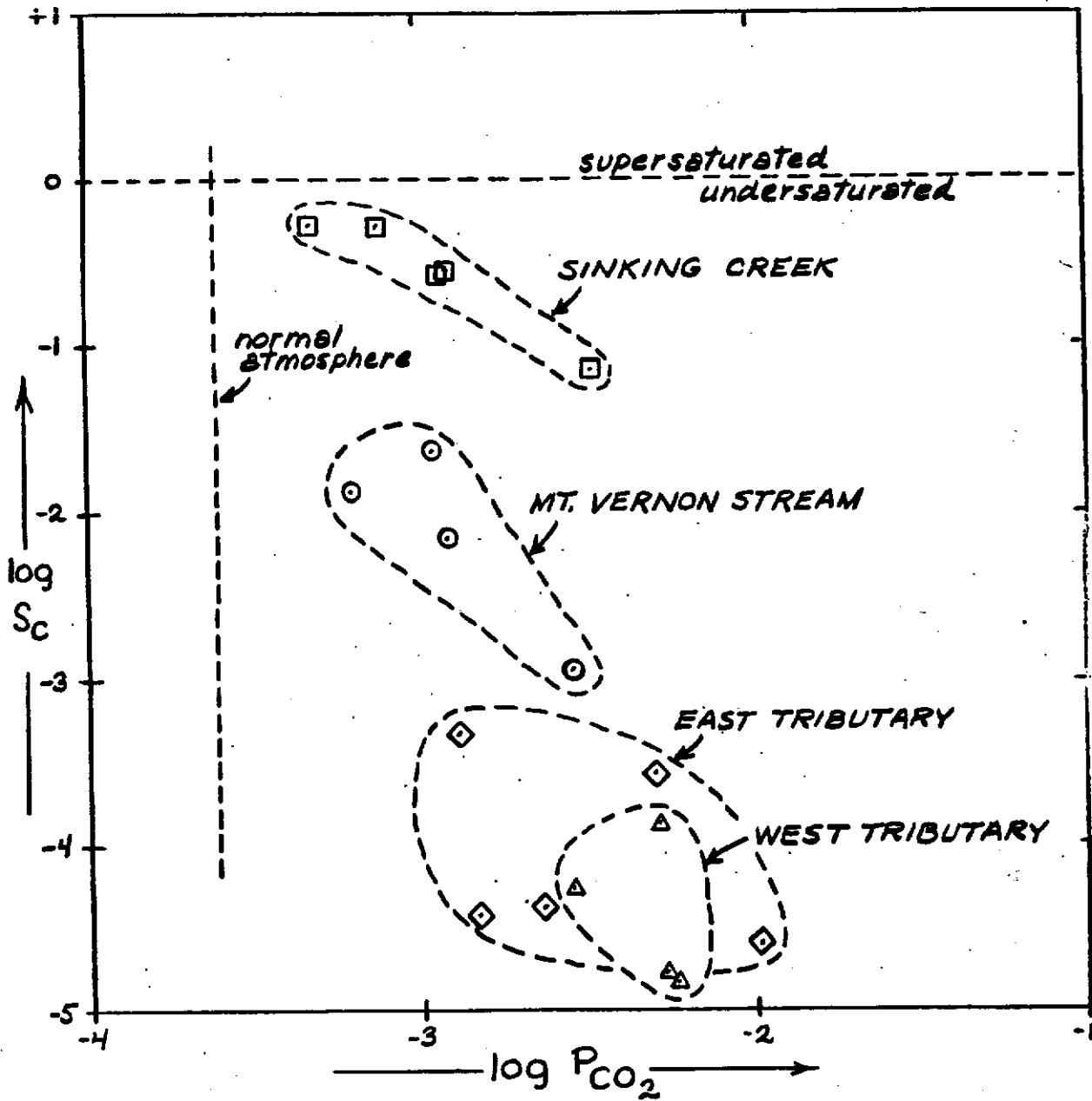


Figure 6. $\log S_c$ versus $\log P_{CO_2}$ for Surface Streams.

There are few data in the literature on the state of saturation with respect to calcite of surface streams in limestone terrains, and no data were found on equilibrium carbon-dioxide pressures. Sweeting (1964) and Sweeting et al (1965) determined the calcium concentrations and field pH of surface streams from several limestone regions and made semi-quantitative estimates of the state of saturation with respect to calcite. The way in which the data are presented make comparisons with the results of the present study difficult, however.

Sinking stream - aquifer relationships

Water believed to be part of the Mammoth Cave - Sinkhole Plain aquifer was sampled from flows which cross the bottoms of two deep sinks. One of these, here termed Penetrating Sink, is only a few hundred meters from the usual swallow point of Sinking Creek. The other, referred to as Mill Hole Stream, is a large flow across the bottom of Mill Hole, a deep sink 12 km north of the Sinking Creek swallow and 8 km northwest of the Mt. Vernon Stream swallow (Figures 1 and 2).

The flow in Penetrating Sink is almost surely that of Sinking Creek, as evidenced by the close correspondence between their temperatures and flow volumes. The presence of a flow in Penetrating Sink on one occasion when Sinking Creek was dry at the sampling site can probably be explained by Sinking Creek being swallowed further upstream than usual.

There is no information as to the source of the flow in Mill Hole. In all probability, it represents a "sample" of the water from the various stream

swallows at the south edge of the Sinkhole Plain (two of which are Mt. Vernon Stream and Sinking Creek) and of other recharge from the Sinkhole Plain itself. It may be that part of the flow from both Mt. Vernon Stream and Sinking Creek appear at Mill Hole; but it is equally likely that water from neither of these sources is represented.

The ultimate discharge of the Mammoth Cave-Sinkhole Plain is almost certainly the Green River, in springs such as Turnhole, Echo River, and Pike, as well as others concealed by the river. Water which represents MCSP aquifer water may at times be present in parts of Mammoth Cave. Because the water at the springs and in Mammoth Cave are mixed to an unknown degree with Green River water, they were not sampled during the study.

The water table of the MCSP aquifer is thought to be reached in at least two other deep sinkholes in the area (or in caves connected with them). One of these, Cedar Sink, lies north of Mill Hole near the Green River. The other, Hidden River Cave is in the town of Horse Cave (Figure 1). Neither of these were sampled. A number of wells in the area are believed to penetrate the aquifer (Cushman, in press, and Brown, 1966). No wells were sampled during the study, partly for logistic reasons and partly because the water so obtained would (unless the well was known to have a large capacity) bear unknown chemical affinities to the major circulation of the aquifer.

As stated in the introduction, the cave streams in the Cave Hollow area are considered to represent flow near the water table of the CH aquifer, for which the Cave Hollow Spring is virtually the sole discharge.

Figure 7 shows diagrammatically the flow relationships between the various sampling points (including sinking streams) in the MCSP and CH aquifers.

Aquifer saturation relationships-general

Seasonal variations in S_c of both the MCSP aquifer, as represented by the Mill Hole Stream water, and the CH aquifer, as represented by the Cave Hollow Spring water, are shown on Figure 8, together with the sinking stream data transferred from Figure 4. Figure 9 shows the seasonal variations in P_{CO_2} for the same waters, with the sinking stream data from Figure 5.

Insofar as the chemistry of the aquifers is represented by these samples, they were always undersaturated with respect to calcite with S_c ranging from 0.65 to 0.014.

The median saturation (probably a better measure than the mean) of the MCSP aquifer was .25; that of the CH aquifer was .44. Other than having comparable median undersaturations, the two aquifers had little in common. The median P_{CO_2} of the MCSP aquifer was 5.6×10^{-3} atm, that of the CH aquifer was 6.6×10^{-4} atm, almost an order of magnitude lower and near that of the normal atmosphere (3×10^{-4} atm).

The most striking differences between the two aquifers were in the apparent chemical evolution of the water relative to the sinking streams. The saturation of the MCSP aquifer was about the same as that of Sinking Creek, but higher than Mt. Vernon Stream; and the CH saturation was always higher

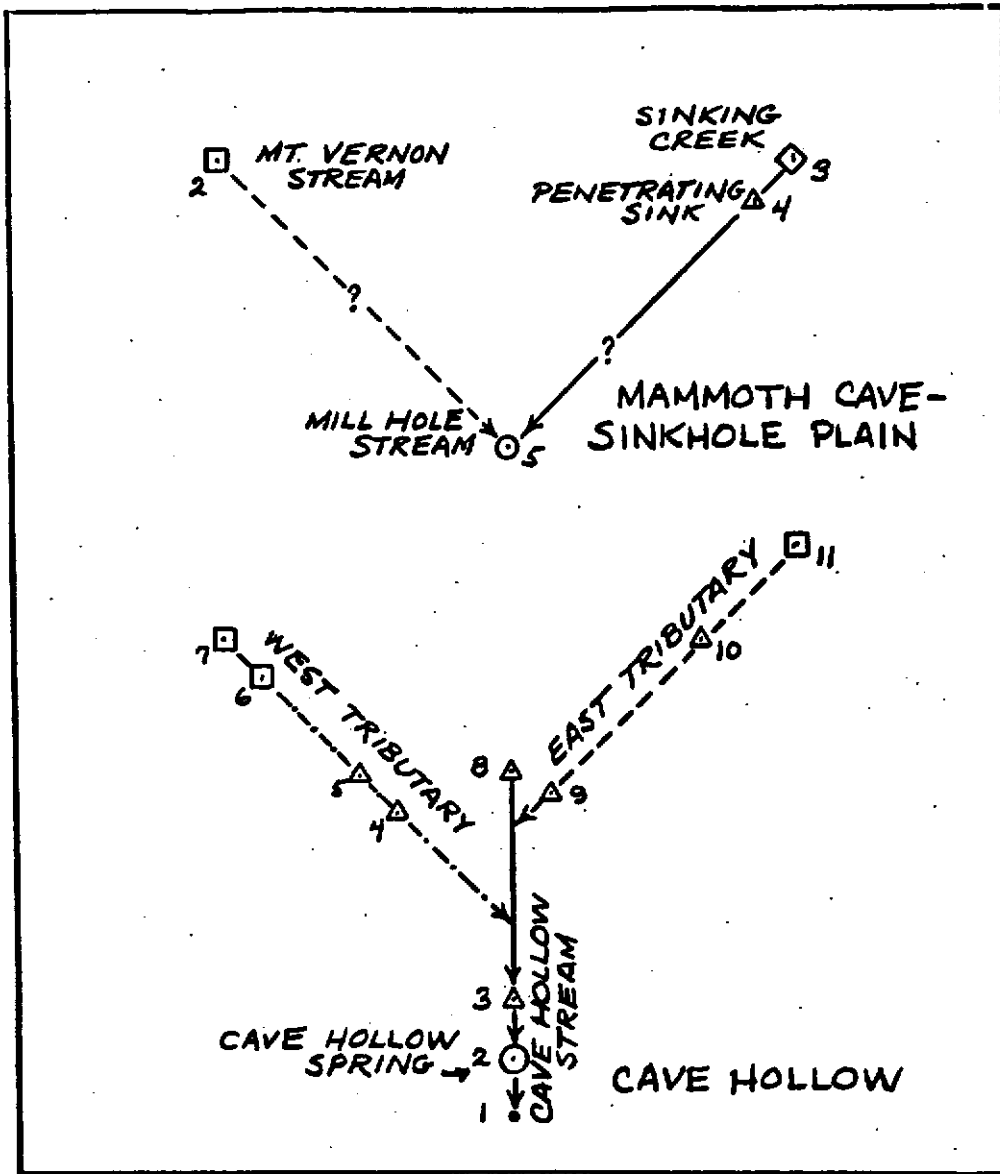


Figure 7. Diagrammatic Flow Paths in Mammoth Cave - Sinkhole Plain and Cave Hollow Aquifers.

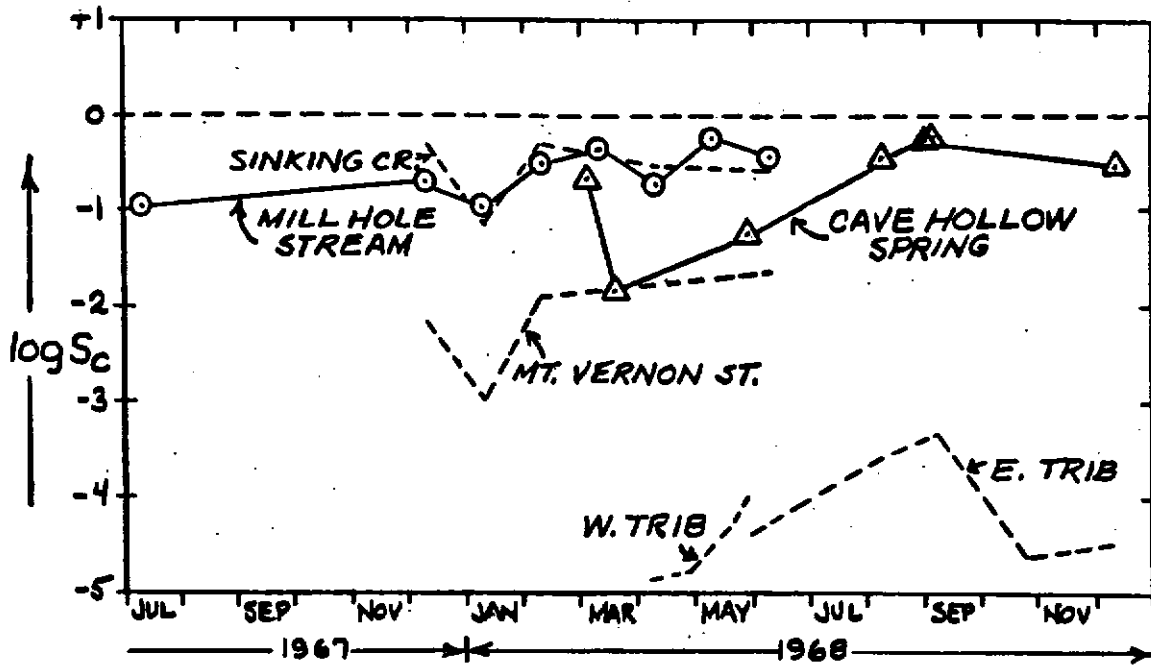


Figure 8. $\log S_c$ versus Date in Aquifers. Data for recharging surface streams plotted for comparison.

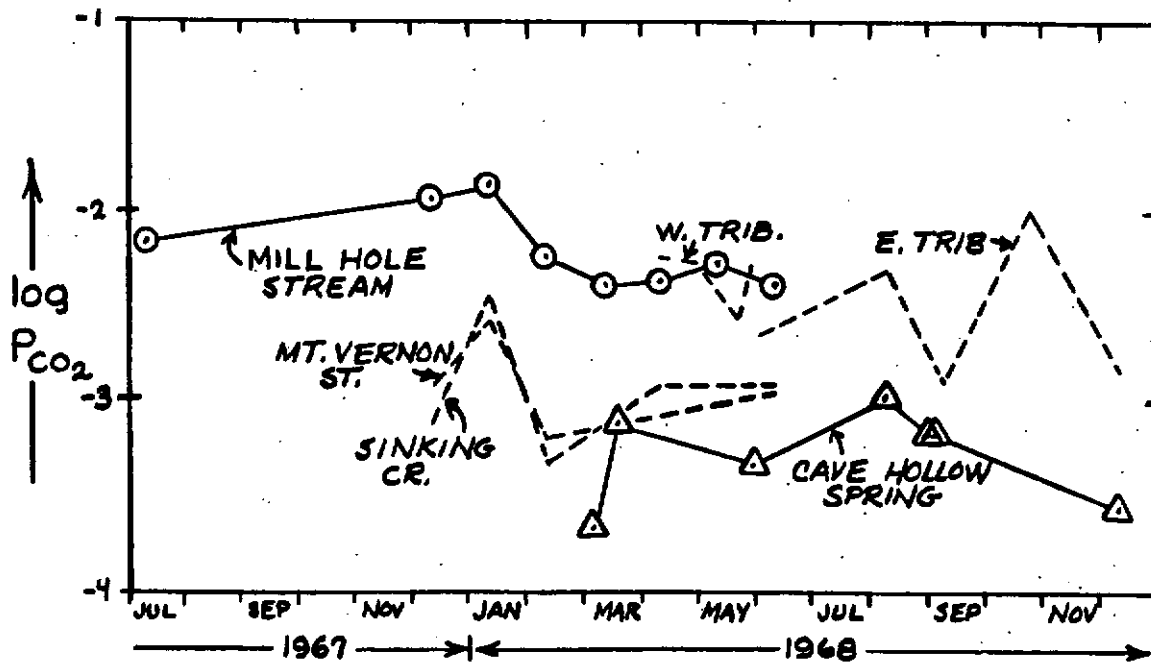


Figure 9.- $\log P_{CO_2}$ versus Date in Aquifers. Data for recharging surface streams plotted for comparison.

than its recharging streams. The P_{CO_2} of the corresponding sinking streams was markedly and consistently lower than that of the CH aquifer, but higher than that of the MCSP aquifer.

Although the median state of saturation in the MCSP aquifer was nearly the same as that of Sinking Creek, the median calcium content of the former was nearly twice as great as the latter (49.0 ppm versus 28.7 ppm - from data in Table 1, Appendix 4). This reflects the considerably higher P_{CO_2} content of the aquifer water (Figure 9). Only a few previous studies have been made of the state of saturation of waters of limestone aquifers relative to calcite or of their equilibrium P_{CO_2} . Moore (in Hostetler, 1964) found the water in a deep lake in a California cave to be approximately saturated with respect to calcite and to be in equilibrium with a P_{CO_2} of about 4×10^{-3} atm. Hanshaw, et al (1965) and Back, et al (1966) reported the waters of the Floridian limestone aquifer to be generally supersaturated with respect to calcite (S_c from 1.07 to 1.49) with one sample undersaturated ($S_c = 0.83$). In a study comparing the Floridian and Yucatan limestone aquifers, Back and Hanshaw (in press) indicate the range of S_c in Florida to be from 0.35 to 1.92, and in Yucatan from 0.21 to 3.11. Finally, Langmuir (1969) in a study of limestone groundwaters in Pennsylvania found a range of S_c from 0.7 to 2.5 and of $\log P_{CO_2}$ from -2.7 to -1.6.

Aquifer saturation relationships - Cave Hollow

In addition to the sinking stream and Cave Hollow Spring sites, one or more samples were collected at six different sites in caves "within" the CH aquifer. The S_c and P_{CO_2} data for these sites (as well as for the sinking streams and the spring) are plotted on Figures 10 and 11. The locations of these sites are shown on Figures 3 and 7.

The increase in S_c which takes place between the sinking streams and the spring appears to occur soon after the water sinks, since the saturation of the cave streams tends to resemble that of the spring much more than the saturation of the surface streams (Figure 10). Usually the greatest amount of CO_2 loss occurs in the same interval, except possibly during the summer months (Figure 11).

The chemistry of the cave streams is probably profoundly influenced by the fact that they are in accessible and partially ventilated caves whose atmosphere is probably only moderately higher in CO_2 than the normal atmosphere.

Aquifer Saturation Relationships - Mammoth Cave - Sinkhole Plain

In addition to the "principal" aquifer sampling site at Mill Hole Stream, water was also sampled at Penetrating Sink. As stated earlier, this water is believed to be that of Sinking Creek, whose swallow point is only a few hundred meters distant (Figures 1 and 2). The geometric flow relationships are shown on Figure 7, and Figures 12 and 13 show variations in S_c and P_{CO_2} , respectively, between the various sampling sites.

log

Fig

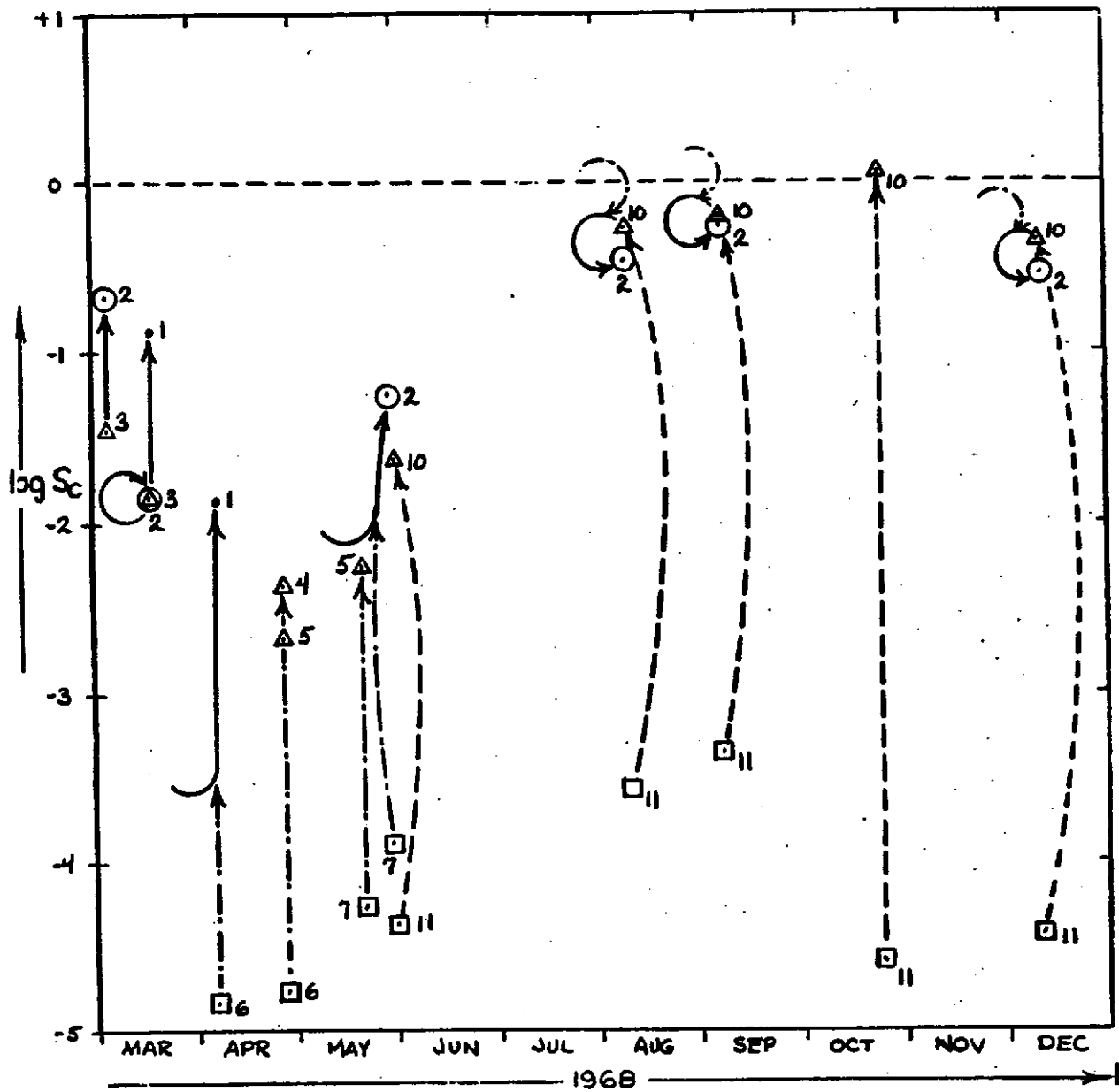


Figure 10. $\log S_c$ versus Date for Cave Hollow Aquifer Sites. See Figures 3 and 7 for geometry of flow paths.

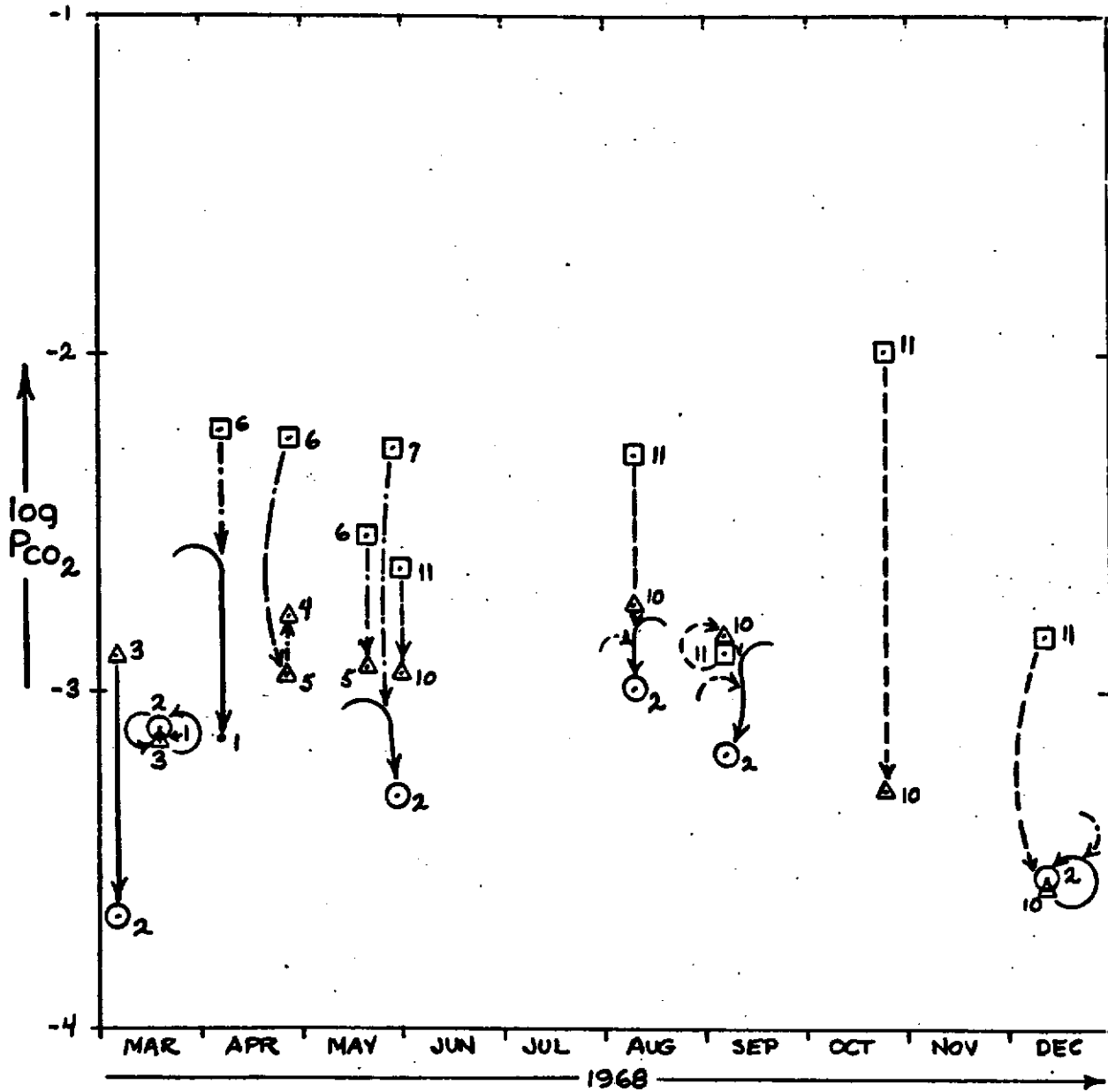


Figure 11. Log P_{CO2} versus Date for Cave Hollow Aquifer Sites. See Figures 3 and 7 for geometry of flow paths.

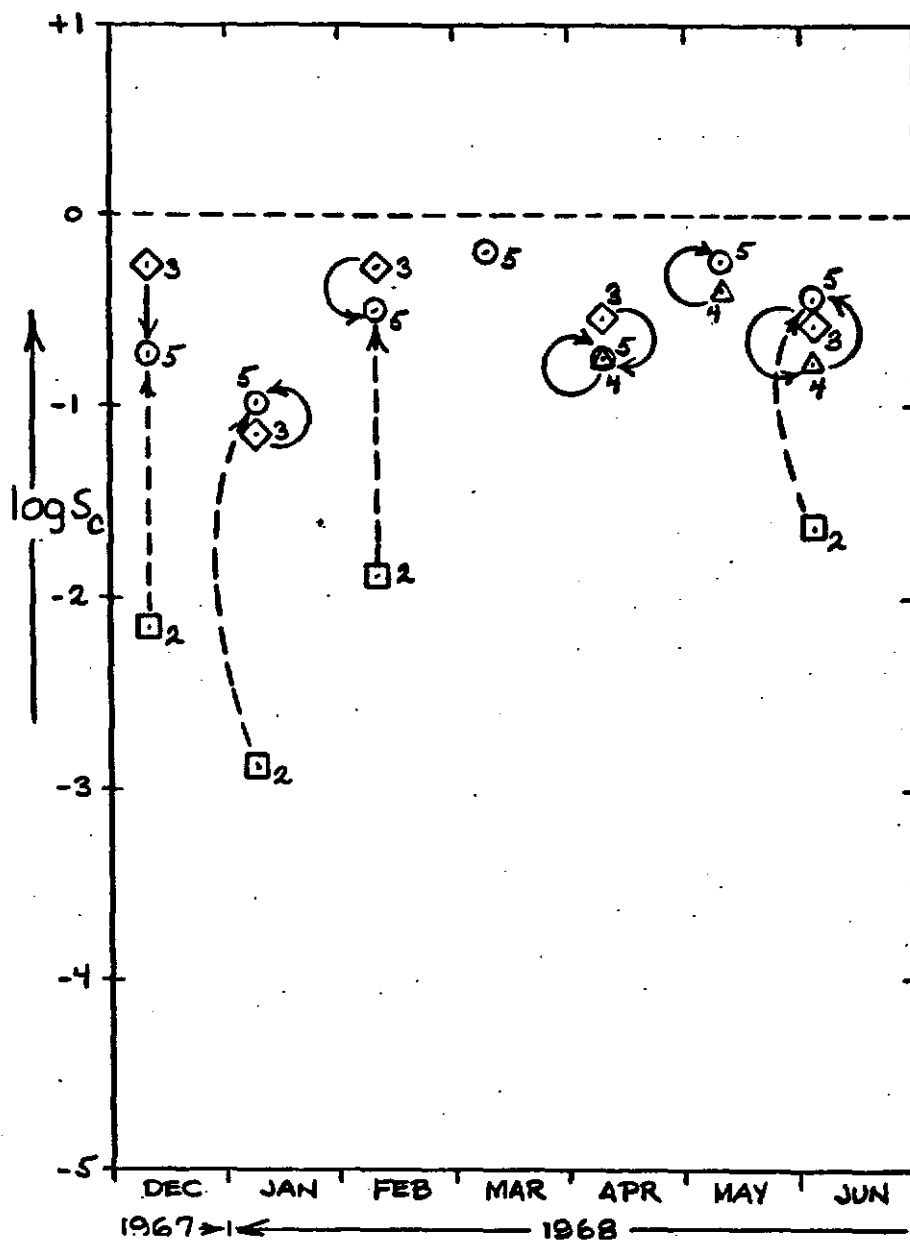


Figure 12. $\log S_c$ versus Date for Mammoth Cave - Sinkhole Plain Aquifer Sites. See Figures 1, 2, and 7 for geometry of flow paths.

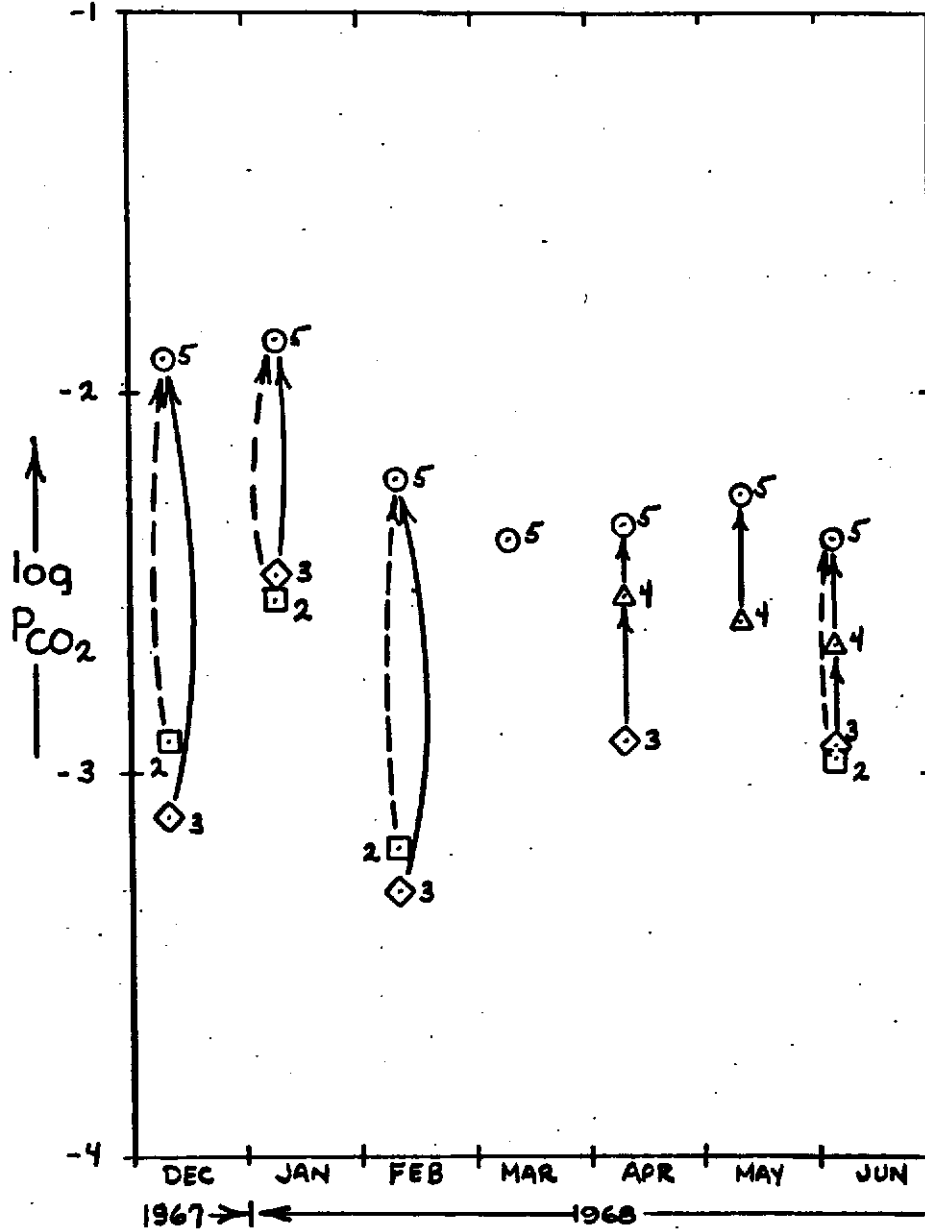


Figure 13. $\log P_{CO_2}$ versus Date for Mammoth Cave - Sinkhole Plain Aquifer Sites. See Figures 1, 2, and 7 for geometry of flow paths.

The general chemical changes apparently taking place along the major flow routes have already been discussed. The major process apparently operating within the aquifer is a "carbon-dioxide pump" which raises the equilibrium P_{CO_2} of the water as it flows through the aquifer. Thus the water apparently remains somewhat undersaturated at all times of the year even though it is dissolving significant amounts of calcite.

The data for Penetrating Sink provide additional information on this process. In April and June samples were taken of both Sinking Creek and Penetrating Sink. As shown on Figure 13, the equilibrium P_{CO_2} of the Penetrating Sink water was significantly higher than that of Sinking Creek, and accounted for about one-half (or more) of the increase in P_{CO_2} between the sinking streams and Mill Hole in the less than 400-meter distance separating the swallow point of Sinking Creek and Penetrating Sink. Although the total calcium content of the Penetrating Sink water was about 2ppm higher than the corresponding samples from Sinking Creek during these months (see table 1, Appendix 5), the increase in P_{CO_2} was even greater, resulting in a slight decrease in S_c (Figure 12).

Completely ventilated vadose flows

The samples which are believed to represent the water chemistry of limestone aquifers or of streams which recharge the aquifer essentially "at grade" with the water table have been discussed in the sections above. The most important recharge, however, is water which descends through the region between the soil zone and the water table, known as the vadose zone.

It is believed (Thraillkill, 1968) that water descending through the vadose zone in limestones may conveniently be separated into two categories: discrete flows of water, termed vadose flows, and disseminated seepage, termed vadose seepage.

A water source in the MCSP area interpreted as a vadose flow was sampled repetitively at two sites at a spring which emerges from a cave mouth on the side of Mill Hole sink. The stream so fed flows to the bottom and joins Mill Hole Stream near its swallow point. The water from the spring was sampled at the mouth of the cave and at a point about 15 meters downstream from the cave mouth.

The most obvious process taking place in the flow from this spring (termed Mill Hole Spring) is the escape of carbon dioxide as the water emerges, resulting in an equilibrium P_{CO_2} for the downstream sample that is lower at all times of the year than that measured at the mouth of the cave (although for February and March the difference was within the analytic error), as shown on Figure 14. As would be expected, the water emerging from the spring, being in equilibrium with a P_{CO_2} higher than that of the normal atmosphere, loses carbon dioxide rapidly to the atmosphere. The very slight difference in February and March may be ascribed to the low flow volume. The spring flows from the mouth of an open cave which has been dammed at the entrance for a water supply. During low flow conditions, a considerable amount of equilibration could take place in the open cave before the water flows out the mouth.

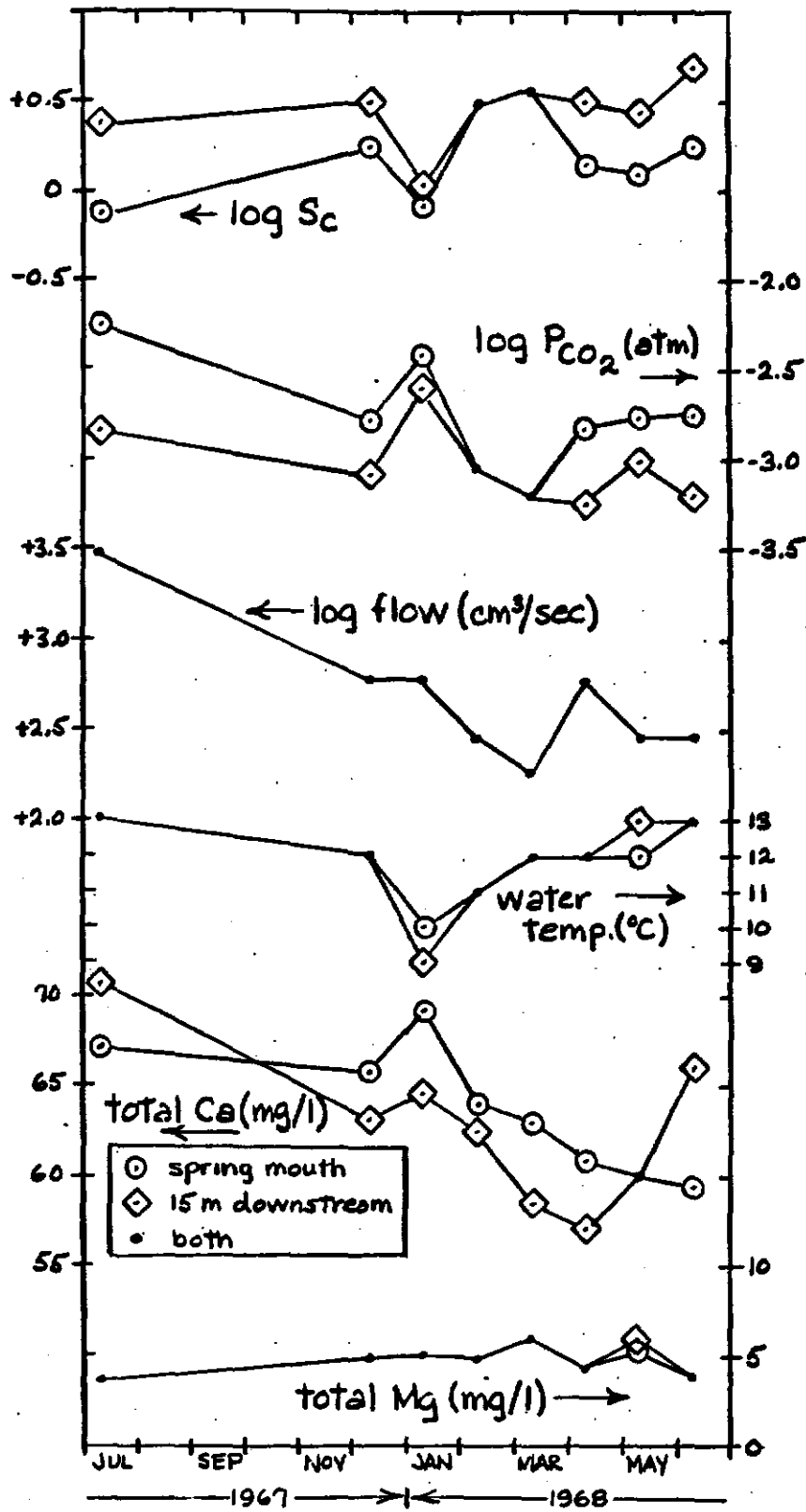


Figure 14. Various Parameters versus Date for Completely Ventilated Vadose Flow.

The lack of similar equilibration during low-flow conditions in May and June is difficult to explain, but might be due to initially higher equilibrium P_{CO_2} values.

All of the downstream samples were supersaturated with respect to calcite, and all but two of the spring mouth samples were also supersaturated, suggesting that considerable CO_2 loss had already occurred before the water emerged at the spring. Figure 14 also shows a plot of total calcium for the two sampling sites. Throughout most of the year Ca was lower at the downstream site, indicating deposition in response to this supersaturation. It is not known why the July and June samples show an increase in Ca, since the plot of total Mg (Figure 14) does not show a similar increase (due, for example, to evaporation). In general, it appears that the water can maintain a supersaturation of about 3 ($\log 3 = +0.480$).

As is evident on Figure 14, the January sample is somewhat anomalous. The air temperature was the lowest ($-4^{\circ}C$) measured during the year, but the February air temperature ($-2^{\circ}C$) was nearly as low. The January samples were collected following a week of high snowfall. No firm explanations can be offered at this time for the high P_{CO_2} and total calcium values obtained.

The summary, the chemistry of Mill Hole Spring was about as expected, and represents a recharge to the aquifer of low P_{CO_2} , high S_c water.

Partially ventilated vadose flows

Two other vadose flows were sampled during the study. These flows were of water spilling from the edge of the impermeable clastic caprock

(Big Clifty) of Mammoth Cave Ridge. Such flows are responsible for the excavation by solution of deep vertical shafts, called domepits (Bretz, 1942; Pohl, 1955; Thrailkill, 1968) and are thus presumably undersaturated with respect to calcite. They represent a major source of recharge to the MCSP aquifer. When sampled in the cave, such flows are in contact with an atmosphere which has a P_{CO_2} slightly higher than that of the normal atmosphere, as measured with a gas detector (See Appendix 1) and shown in Table 1.

Table 1

Direct P_{CO_2} determinations			
Date	Location	P_{CO_2} ($\times 10^4$ atm)	$\log P_{CO_2}$
26 Oct. 67	Frozen Niagara (cave)	6.0	-3.22
"	Frozen Niagara (cave)	7.0	-3.15
9 Dec. 67	White Mills Sp. (surf.)	3.5	-3.54
"	Mill Hole Sp. (surf.)	3.5	-3.54
"	Frozen Niagara (cave)	6.5	-3.19
10 Feb. 67	Frozen Niagara (cave)	6.5	-3.19

The P_{CO_2} environment of the Frozen Niagara section of Mammoth Cave thus appears to be relatively stable and, if 6.5×10^{-4} atm is taken as representative, slightly more than twice that of the normal atmosphere (3×10^{-4} atm). Thus the vadose flows sampled in the cave are considered to be partially ventilated.

Two such flows were sampled in the Frozen Niagara Section of Mammoth Cave. One, known as the Showerbath, falls from the ceiling of a passage near the trail. The other, here termed Hidden Pool, was an almost inaccessible flow nearby which was sampled from a shallow pool it formed before cascading down a domepit.

Both of these flows were always undersaturated with respect to calcite and maintained remarkably constant equilibrium P_{CO_2} slightly higher than that of the cave atmosphere (Figure 15). Hidden Pool water was always more nearly saturated with respect to calcite than that of the Showerbath, and had a slightly lower equilibrium P_{CO_2} (although the difference in April was too small to plot).

The variations in S_c of both flows correlate almost perfectly with variations in flow volume of the Showerbath. They would presumably show an equally good correlation with flow volume of the Hidden Pool, but variations of this flow could not be estimated with any degree of certainty, due to its inaccessibility, and are not shown on Figure 15.

The analyses of these two flows essentially document the chemical evolution of partially ventilated vadose flows outlined in Thrallkill (1968). Water draining off the clastic cap of the plateau is in equilibrium with a fairly high P_{CO_2} and greatly undersaturated with respect to calcite. As it falls nearly vertically through the vadose zone, it actively dissolves vertical shafts (domepits). If these shafts intersect cave passages in which the P_{CO_2}

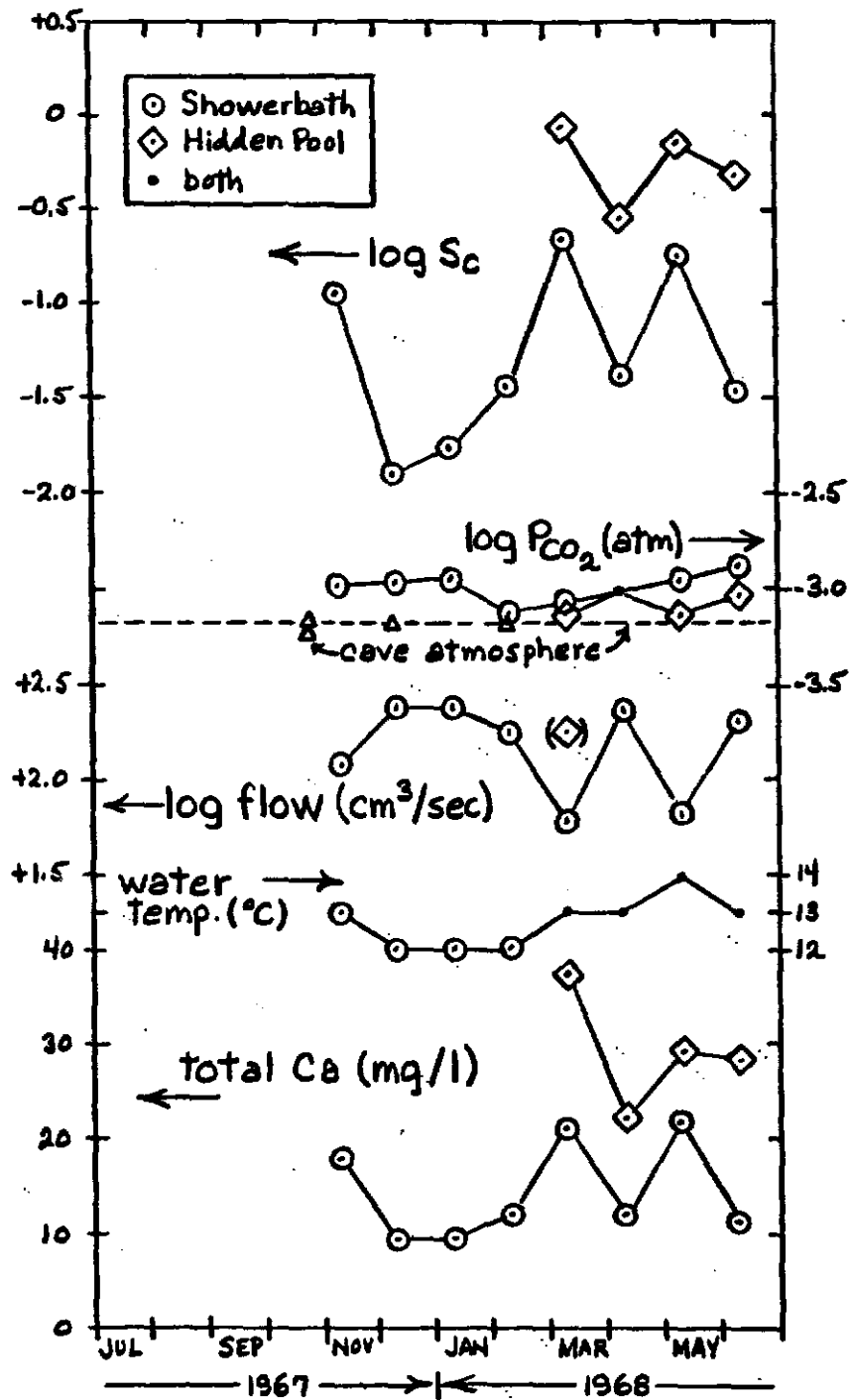


Figure 15. Various Parameters versus Date for Partially Ventilated Vadose Flows

is lower than that of the water, outgassing of CO_2 will occur. Thus two processes act concurrently to raise S_c in this water: calcite solution and CO_2 outgassing. Whether or not the water is undersaturated with respect to calcite when it reaches the water table depends on the speed of these processes relative to the transit time of the water in the vadose zone.

The data collected indicate that CO_2 outgassing is rapid relative to calcite solution. This implies that the degree of ventilation is a critical factor in the state of saturation of the vadose flows when they arrive at the water table. Additional factors of importance are the volume of flow and the residence time in the vadose zone. Although nothing is known about the path of either the Showerbath or Hidden Pool flows above the point at which they were sampled, it seems reasonable that the consistently higher S_c (and total calcium content) and lower P_{CO_2} of the Hidden Pool water reflects a longer residence time in the vadose zone. The residence time of the water is difficult to relate to its distance from the surface for several reasons. Flows down small domepits tend to be as a moving film down the walls. As the domepit is solutionally widened by this process, a critical diameter is reached and the water will fall free from the walls. Other factors, such as ponding on top of an insoluble bed or on a clastic fill (which may account for the higher saturation of the Hidden Pool water) also will affect the travel time of these flows through the vadose zone.

No data on the state of calcite saturation or equilibrium P_{CO_2} of vadose flows (either completely or partially ventilated), which are clearly identifiable

as such, has been found in the literature. Some of the sites sampled by Langmuir (1969) may have been flows above the major aquifer. Holland, et al (1964) sampled from pools in Indian Echo Cave and Carpenter Cave, Pennsylvania, but since the slight flow was derived from stalactite drips, this water is here considered vadose seepage. A somewhat larger flow sampled by the same authors in Luray Caverns was of water piped in from the surface (Holland, et al, 1964).

Vadose seepage

As stated earlier, water which seeps down through the vadose zone in small openings (vadose seepage) was thought to be chemically distinct from the larger flows of water discussed above. Four such seepages were sampled in Mammoth Cave. Although such water rapidly ventilates when it enters a cave, it was possible to measure the alkalinity and conductivity, which change rather slowly, within a few minutes after the water entered the cave passage. Tests showed a negligible change in these parameters in this time. The property that changes most rapidly is pH, and a sequence of readings on one sample showed an increase of 0.5 pH units in the first 5 minutes after the water emerged. Accordingly, the pH determinations used in calculations were taken on single drops of water as they appeared on the wall or stalactite tip.

The four drips sampled were all in the Frozen Niagara section of Mammoth Cave, and the names used here were derived from their location or

some characteristic. Table 2 gives approximate location and notes on the deposits associated with each drip.

Table 2

Vadose Seepage Sampling Sites

Name	Location	Deposits
Seven Second drip	Drip impacts on slope about 1/2 m to left (going down) of lowest flight of stairs to Drapery Room about 1/2 of the way down	Drip falls from small stalactite on large drapery. No apparent recent deposition (or solution) of stalactite, some recent-looking flowstone at impact point was calcite with trace of aragonite by x-ray diffraction.
Radio Room drip	Drip from top of recess above ledge at entrance to Radio Room (about 3 meters below trail at Frozen Niagara).	Drip falls from short (~ 3 cm) tubular stalactite. Appears to be actively depositing. Stalactite was calcite by x-ray diffraction.
Onyx Colonnade drip	Rapid drip from short stalactite a few cm behind wire at end of Onyx Colonnade nearest Frozen Niagara Entrance.	Rapid drip from stub of broken stalactite. Little or no recent deposition on stalactite, considerable recent flowstone at impact point was calcite by x-ray diffraction.
Leaky Ceiling drip	Area to right of trail going toward Grand Central Station near first view of stairs leading to College Heights.	No evidence of any deposition (recent or otherwise).

Two of the drips (Seven Second and Leaky Ceiling) were undersaturated at all times during the period sampled (November or December through June). The other two were occasionally supersaturated by amounts up to 2.6 times saturation, but were usually undersaturated (Figures 16-19). Equilibrium P_{CO_2} of the drips varied widely, and on two occasions appeared to fall as low as that of the cave atmosphere for one drip (Leaky Ceiling). The pH of this drip was hard to measure, however, and the water was usually exposed to the cave atmosphere for several seconds before a determination could be made.

The calcium content of a single drip was essentially constant within the analytic precision whenever sampled. This is illustrated on Figure 16 where total calcium is plotted for the Seven Second drip. The range in total calcium is only 3.3 ppm, which is less than half the (2σ) analytic uncertainty of about 7 ppm for these samples (Table 1, Appendix 4). There is a similar narrow range for total magnesium, also shown on Figure 16. This constancy (which since it is within the analytic error, could be absolute) of calcium and magnesium is shown graphically on Figure 20.

The inverse relationship between $\log S_c$ and $\log P_{CO_2}$ for surface streams was noted earlier (Figure 6). A similar plot for the four vadose seepage samples (Figure 21) is striking and has interesting implications. The nearly perfect inverse correlation between $\log S_c$ and $\log P_{CO_2}$ which can be seen on Figures 16-19 is quite apparent on Figure 21. Samples from a single source tend to lie along a line with unit negative slope, here termed a variation

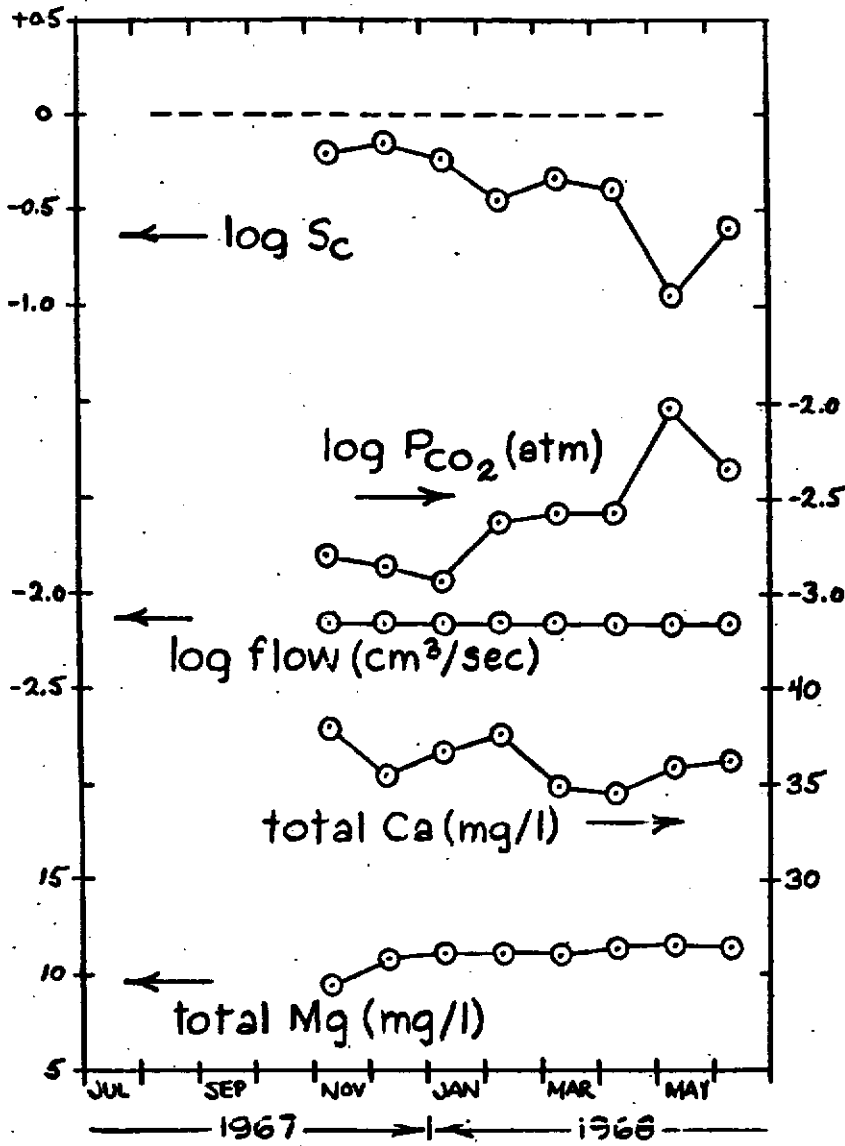


Figure 16. Various Parameters versus Date for Seven-Second Drip.

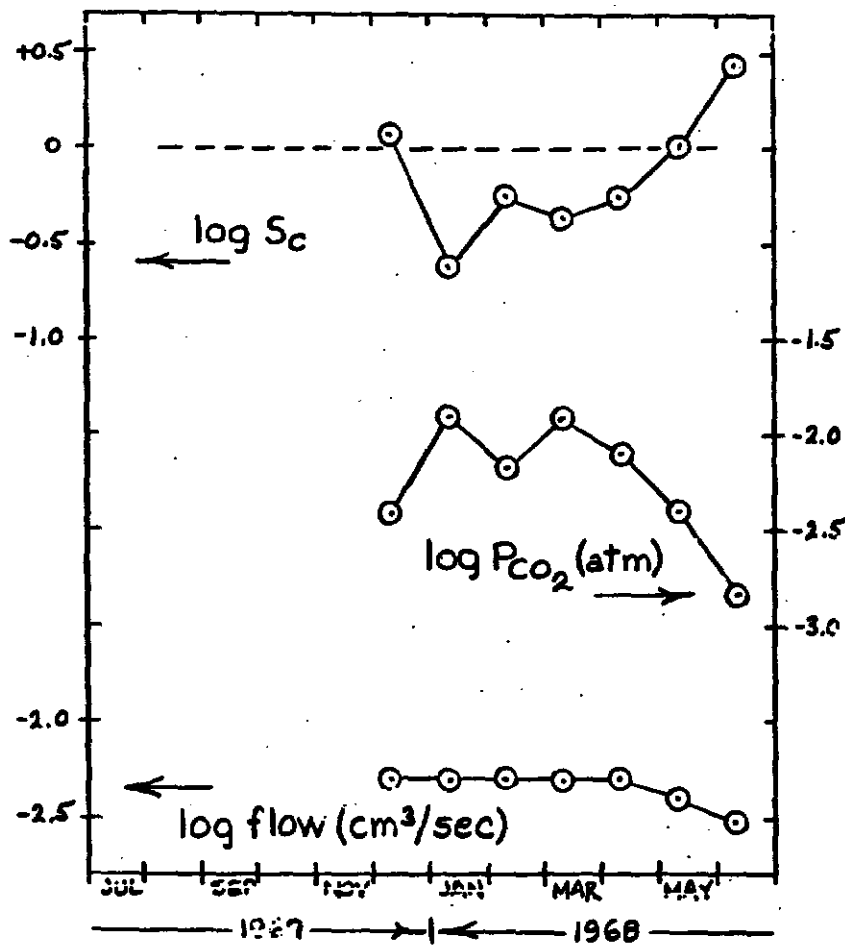


Figure 17. Log S_c, Log P_{CO₂}, and Log Flow versus Date for Radio Room Drip.

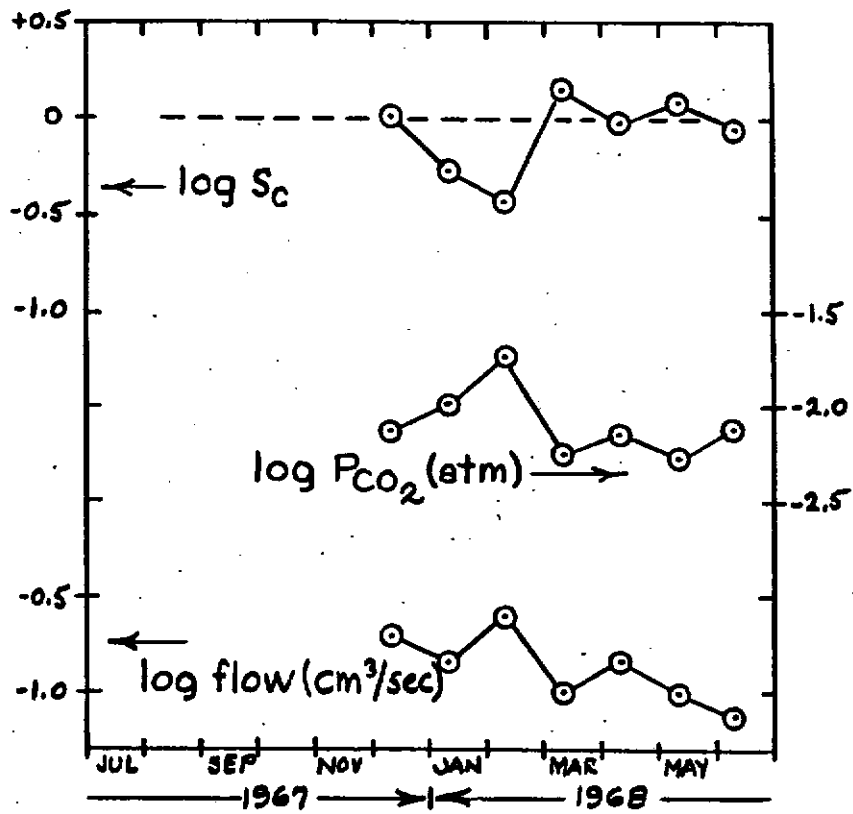


Figure 18. Log S_c, Log P_{CO₂}, and Log Flow versus Date for Onyx Colonnade Drip.

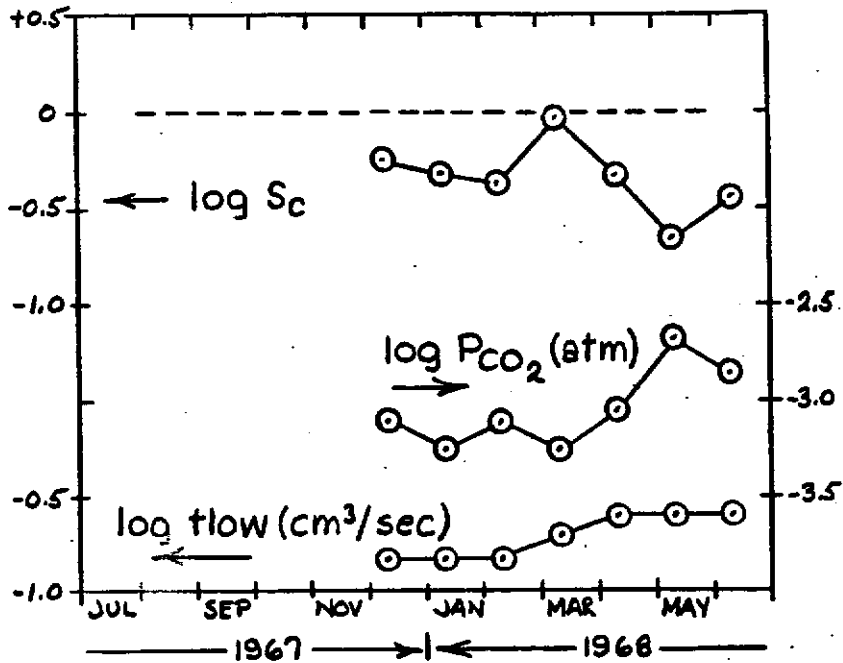


Figure 19. Log S_c , Log P_{CO_2} , and Log Flow versus Date for Leaky Ceiling Drip.

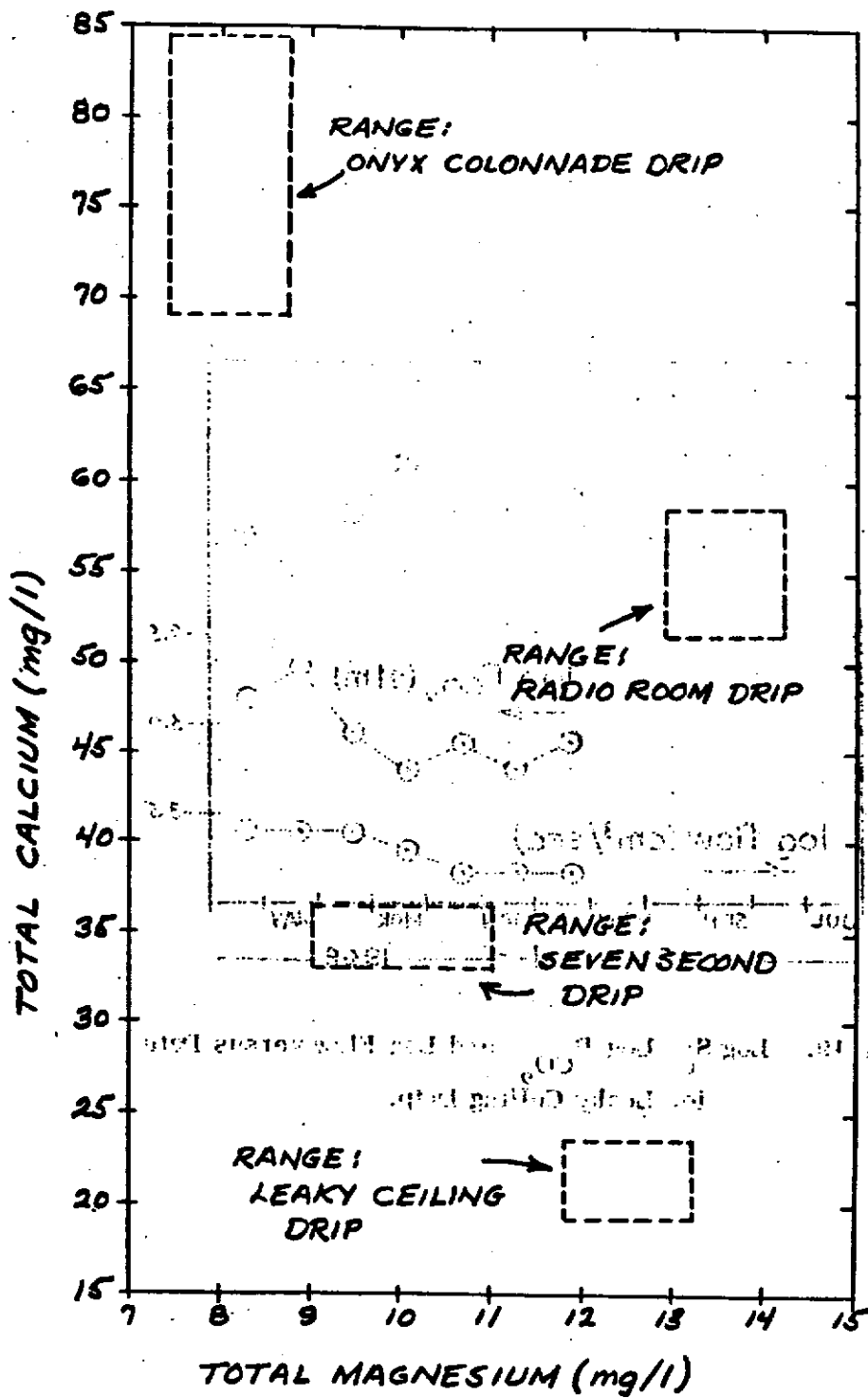


Figure 20. Calcium versus Magnesium for Vadose Seepage.

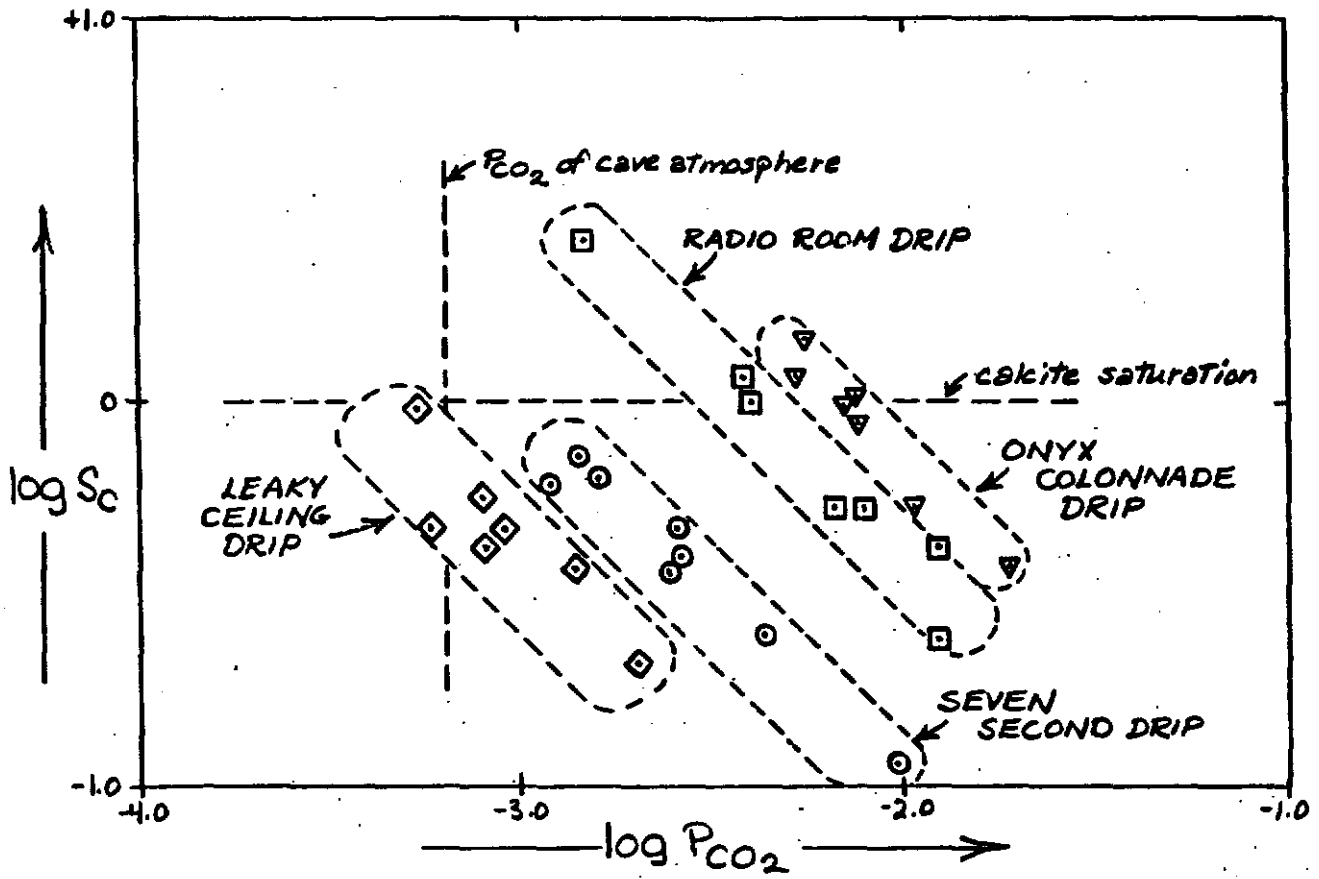


Figure 21. $\log S_c$ versus $\log P_{CO_2}$ for Vadose Seepage.

path, and each source has its own intercept. Although there are several models which probably could result in this configuration (combinations of solution and evaporation, for example), the simplest interpretation is that each source is derived from a reservoir with a unique equilibrium $P_{CO_2} - S_c$ combination, and that varying degrees of CO_2 outgassing have occurred, since simple outgassing of CO_2 will cause movement upward and to the left on Figure 21 along the observed variation path.

Although this appears to be the most straight forward explanation, the implied existence of such a reservoir with a constant $S_c - P_{CO_2}$ value throughout the year under both wet and dry conditions is surprising, to say the least. Although it is not possible to explore all the ramifications of the concepts suggested by these observations at this time, two observations may be of interest. First, a single sample would have been sufficient to determine the variation path for that source. Second, whether or not a drip of water can ever become supersaturated with respect to calcite and cause deposition depends on the intercept of its variation path. As shown in Figure 21, the Leaky Ceiling drip reaches equilibrium with the P_{CO_2} of the cave atmosphere before it reaches saturation and cannot therefore, deposit calcite, while the Seven Second drip will be slightly supersaturated when it is ventilated to the P_{CO_2} of the cave atmosphere and a small amount of deposition may result. Drips plotting farther to the right (Radio Room and Seven Second drips) are not so restricted and will begin to deposit long before they reach the CO_2 of the cave atmosphere.

Vadose seepage is certainly an important, and very likely the most important, source of recharge to the aquifer. It has generally been thought that, because such seepage moves so slowly through, and is in such intimate contact with the rock, that it must be very nearly saturated by the time it reaches the water table (Thraillkill, 1968). These data, however, indicate something quite different. Not only is the seepage usually undersaturated with respect to calcite, but some seepage sources (such as the Leaky Ceiling drip) have an $S_c - P_{CO_2}$ relationship such that they do not become saturated even when the water is semi-ventilated. Such water would presumably remain undersaturated even though it flows through open caves and fissures in the vadose zone as it descends to the water table. It may be that these relationships extend to other sources of recharge to the water table, such as the disappearing streams shown on Figure 6.

It is not known whether the variation paths for the Leaky Ceiling and Onyx Colonnade drips shown on Figure 21 represent the extreme values for these paths, but there seems to be no reason to believe that vadose seepage with a path to the left of the Leaky Ceiling drip does not exist. Such water could experience CO_2 outgassing even down to the P_{CO_2} of the normal atmosphere without becoming saturated (assuming the absence of evaporation or other processes, of course). The factors which determine the position of the variation path of a single source are likewise unknown, although the order of variation paths of increasing P_{CO_2} at calcite saturation is probably the order of

decreasing thickness of rock plus soil overlying the drips in Mammoth Cave. The Leaky Ceiling drip, which is farthest into the cave, is the farthest beneath the surface while the Onyx Colonnade drip is nearest the Frozen Niagara Entrance and probably closest to the surface.

There is no clear correlation between the position of a given sample along its variation path and any of the variables measured, but there is a tendency for equilibrium P_{CO_2} to increase (and S_c to decrease) with increasing flow, as shown on Figure 22. The Seven Second drip had a constant flow rate at all times (one drop every seven seconds), which might be explained by some mechanism which diverted a constant amount from a larger (and undiscovered) varying flow.

Other limestone waters

Sampling was done at a number of sites other than the ones which have been discussed. With one exception, each site was sampled only once during the early phases of the study. These sites were the Green River at Mammoth Cave Ferry (Site 14); Terhune spring, Larue County, (See Van Couvering, 1962, for location), Sites 17-19; the stream which flows from Mill Hole Spring some distance below the spring (Site 20); Crystal Lake in the Frozen Niagara section of Mammoth Cave (Site 21); and a small pool in the Fox Avenue section of Mammoth Cave (Site 22).

A sequence of samples (Sites 1, 15, 16) was taken at White Mills Spring in Hardin County, Kentucky (location described in Van Couvering, 1962).

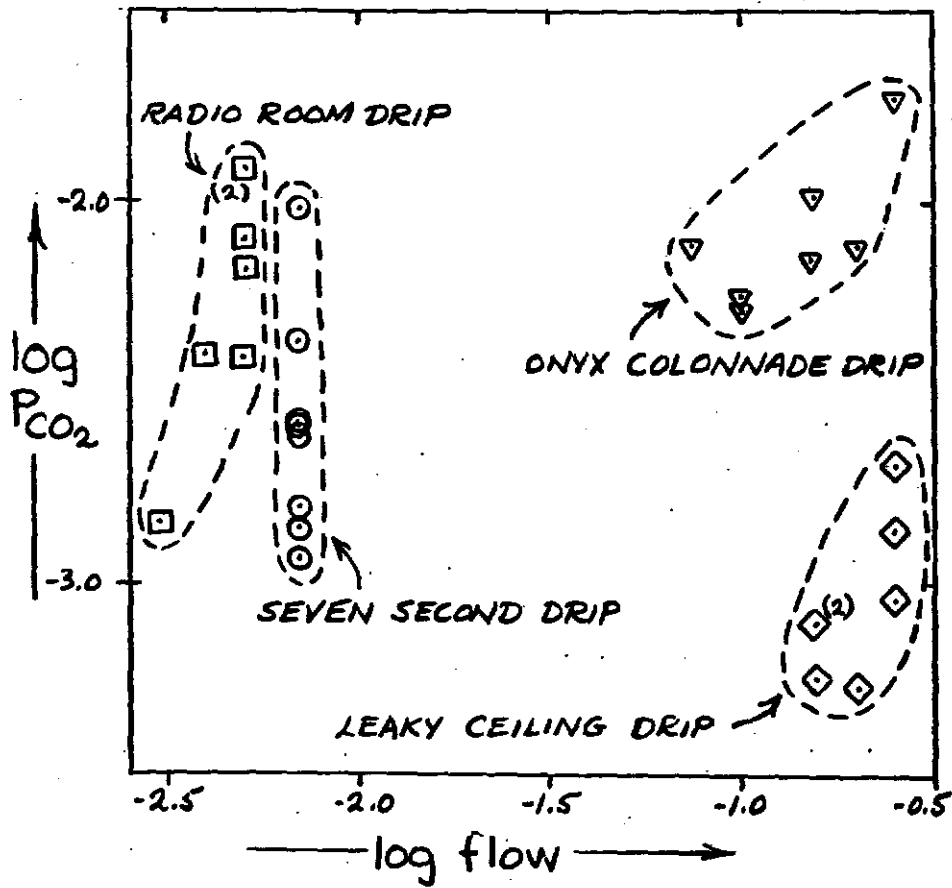


Figure 22. $\log P_{CO_2}$ versus Log Flow for Vadose Seepage.

Although some distance north of the MCSP area, this is one of the largest springs in Kentucky, and issues from the north bank of the Nolin River sufficiently above river level to prevent contamination by river water. It was hoped that it would yield valuable information on the chemistry of discharge from a limestone aquifer. Its temperature was found to follow the air temperature closely, and it showed none of the chemical characteristics usually associated with aquifer water. Finally, when a spring sample (#69) was found to be essentially identical chemically with a sample of Nolin River water (#71) collected at the same time, it was concluded that the flow from White Mills Spring is merely a diversion of Nolin River Water. Data for all the above samples is presented in Appendix 4.

Water Supply and Other Implications of Study

It is believed that the findings of this study have some interesting and at least potentially valuable implications regarding the nature of limestone aquifers and the solution of problems of groundwater supply in these aquifers. Before discussing these implications, however, a brief outline of current concepts of the limestone aquifer is in order.

First, it should be made clear that the term "limestone aquifer" is applied to aquifers in which the porosity and permeability are largely due to the presence of openings which have been created or substantially enlarged by solution. Hence aquifers in limestones in which the voids are mainly intergranular, and these are not uncommon, are not "limestone aquifers" in the

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sense used here, nor are aquifers in which the voids are simple fractures unmodified by solution. Unless solution has played a major role in creating the voids, there is no reason to believe the flow parameters are qualitatively different from those in aquifers in sandstones (in the intergranular case) or granites (in the fracture case). Conversely, the term limestone aquifer may be applied to aquifers in the rock dolomite (or any mixture of limestones and dolomites) if the origin of the voids is mainly by solution.

Prior to the development of the "typical" limestone aquifer, the limestone has a very low porosity and permeability, probably largely in fractures (joints and bedding planes). The water it contains is original sea water whose composition has undergone many changes (usually in the direction of greatly increased salinity) since its initial intrapment. Although this water is probably nearly static, it has enlarged the initial openings by solution to an extent and by processes which are largely unknown.

The initial development of the aquifer usually starts as this saline water is replaced by meteoric water infiltrating from the base of a soil zone. This water is apparently capable of and responsible for accelerated solution of the rock, resulting in sufficient integration of the voids to allow their draining in periods of low infiltration. This allows the development of a vadose zone overlying a thin zone of fresh water. Further integration permits this water to circulate slowly through the solutionally enlarged openings to discharge at or near the level of surface streams.

At this point, the limestone aquifer might be said to be in its initial stage. It can be characterized by a rather steep water table, which fluctuates widely with infiltration rate, and the virtual absence of fresh ground water during low infiltration periods. The possibilities of deriving water supplies of more than a few gallons per minute from any well into such an aquifer would appear to be slight.

Because areal variations both in the available infiltration and in the permeability of infiltration paths through the vadose zone usually exist, however, the initial stage of the aquifer described above is unstable. Some paths will transmit more water than others, and if this water is chemically as capable (or more capable) of dissolving limestone than the rest of the infiltrating water, these paths will be preferentially enlarged. Once such paths are established, the nature of the aquifer changes markedly. Within the thin layer of fresh water constituting the aquifer, paths will be dissolved out which carry these concentrated flows to discharge points. The great increase in permeability causes the water table to fall in the vicinity of these conduits.

Concurrently with the underground development of these flow paths, modifications of the surface topography take place. The high flow paths through the vadose zone capture subsoil drainage and experience accelerated subsoil solution near the upper ends, causing sinkholes to develop. As the sinkholes increase in size, more of the diffuse seepage is diverted to the discrete flows through the vadose zone, resulting in further enlargement of the

aquifer conduits if the water is undersaturated and capable of dissolving limestones.

The limestone aquifer may now be considered as having reached a developed stage. Much of the flow in the aquifer is concentrated in discrete conduits, and the water table is nearly flat, at least in the vicinity of these conduits. Since a major part of the surface drainage is into sinkholes (karst topography), the total amount of water entering the aquifer is large. The aquifer is still relatively thin, but even during dry periods may be several meters thick, since conduits are apparently developed some distance below, as well as at, the water table.

In a developed limestone aquifer, most wells will have capacities little higher than in the initial aquifer, since most of the aquifer is, essentially, still in the initial stage. Wells which intersect one or more of the flow conduits, however, may have very large capacities. It is obviously highly desirable to have some way of predicting the location of these conduits when siting wells. In addition, pollution originating on the surface will follow these conduits, and information on their paths is essential for the evaluation and control of such pollution beyond the point of origin.

Early in the development of the limestone aquifer, the conduits follow paths of high initial permeability, most notably joints. Since some joints are often visible on topographic maps or aerial photographs as vague linear features, called fracture traces, wells drilled on these features are often more successful than average (Lattman and Parizek, 1964).

As the limestone aquifer develops, the system of drainage conduits becomes more and more integrated. Certain conduits become major "trunk" conduits and may transport the aquifer flow for a large area. It appears that the processes which result in this enlargements of certain conduits are of some complexity, and involve chemical and hydraulic factors to a considerable degree. Much of our information on the nature of these trunk conduits comes from study of caves, of which the larger are often such trunk conduits now abandoned by a regionally falling water table. These conduits are seen to be not simply widened joints, but are often tubular passages several meters in diameter whose general course is not controlled by the degree of jointing. Further, their location is not easily predictable by surface topography. In the moderately developed Cave Hollow aquifer the trunk passage follows the bottom of the valley, but in more highly developed aquifers (such as Mammoth Cave - Sinkhole Plain) there appears to be a tendency for the trunk passages to migrate toward the ridges. This phenomenon is understandable, since the ridges are capped by nearly impermeable rock which prevents any infiltration into the aquifer beneath them. The water table therefore must slope away from the intervening valleys where recharge is occurring and the conduits would tend to migrate down this slope beneath the ridges.

It is within this conceptual framework that the study here reported was conceived and conducted. Earlier work by the principal investigator and others had suggested certain chemical properties of limestone waters, as

follows: (1) vadose seepage is probably usually saturated or supersaturated with respect to calcite (Holland, et. al, 1964); (2) vadose flows may be quite undersaturated with respect to calcite (Thraikill, 1968, on theoretical grounds only); and (3) aquifer water is usually supersaturated with respect to calcite but may be occasionally be undersaturated (Back, 1963; Thraikill, 1968 on theoretical grounds), although Back (1963) found water in the Florida aquifer which had remained unsaturated for long periods.

It is clear that the state of saturation of the aquifer water and its various recharges is a fundamental control in the solutional development of the limestone aquifer, and hence the present study was undertaken. Briefly, it was found that (1) the vadose seepage sampled was nearly always undersaturated with calcite, in contrast with point 1 above; (2) vadose flows were in some cases undersaturated, but one at least was in equilibrium with such a high P_{CO_2} that it became supersaturated after complete ventilation (see point 2 above); and (3) the MCSP aquifer water was not only undersaturated, but that the undersaturation was due to some process which introduces carbon dioxide into the aquifer.

As often seems to be the case, the situation has been complicated rather than simplified by this new data. It is certainly not possible to rule out any major source of recharge as being unable, because of its state of saturation with respect to calcite, to participate in the conduit-dissolving process. It is believed that these findings and further study of the data will result in significant

advances of our knowledge of the limestone aquifer. The principal immediate conclusions which can be reached, however, are that (1) there is little reason to consider that aquifer permeability, and hence potential well capacity, associated with any one type of recharge (sinking stream, vadose flow; or vadose seepage) is significantly greater than any other recharge source; and (2) the ability of aquifer water to remain undersaturated for large distances from major recharge sites suggests that solution, and therefore, average well quality, is not limited to the neighborhood of recharge points.

Publications and Other Project Results

Publications, reports, or papers

- (1) Thrailkill, John, Progress report of OWRR Project No. A-009-KY,
Solution geochemistry of the water of limestone terrains, Report
of the University of Kentucky Water Resources Institute for FY
1966, p. 129-133, 1966.
- (2) Thrailkill, John. Progress report of OWRR Project No. A-009-KY.,
Solution geochemistry of the water of limestone terrains, Report
of the University of Kentucky Water Resources Institute for FY
1967, p. 109-123, 1967.
- (3) Thrailkill, John. Progress report of OWRR Project No. A-009-KY,
Solution geochemistry of the water of limestone terrains, Report of
the University of Kentucky Water Resources Institute for FY 1968,
p. 51-56, 1968.
- (4) Belter, D. P., and John Thrailkill, Calcite saturation of karst streams,
in eastern Kentucky (abstract), Geol. Soc. American Programs for
1969, Part 6, p. 2, 1969.
- (5) Thrailkill, John, M. J. Osolnik and R. H. Postley, Calcite saturation
relationships in a Kentucky limestone aquifer (abstract), Geol. Soc.
America Programs for 1969, Part 6, p. 49, 1969.
- (6) Thrailkill, John. Progress report of OWRR Project No. A-009-KY,
Solution geochemistry of the water of limestone terrains, Report of
Univ. of Kentucky Water Res. Institute for FY 1969, p. 33-42, 1969.

The following report results from equipment acquired or techniques developed in connection with this project.

- (7) Thrailkill, John. Calcium-magnesium ratios in spring waters from the Curdsville Limestone, in Factors controlling porosity and permeability in the Curdsville Member of the Lexington Limestone, by W. C. MacQuown, Jr., University of Kentucky Water Resources Institute, Research Report No. 7, p. 62-65, 1967.
- (8) Thrailkill, John. Deposition in caves - a review (abstract), Nat. Speleo. Soc. Bull., v. 29, p. 112, 1967; Geol. Soc. America Spec. Paper 101, p. 455-456, 1968.
- (9) Thrailkill, John. Dolomite cave deposits from Carlsbad Caverns, Journal Sed. Petrology, v. 38, p. 141-145, 1968.

Talks presented

- (1) Belter, D. P., Calcite saturation of karst streams in eastern Kentucky, presented at North-Central Section of Geol. Soc. America, Columbus, Ohio, May 1969 (see publication 4).
- (2) Thrailkill, John. Calcite saturation relationships in a Kentucky limestone aquifer, presented at North-Central Section of Geol. Soc. America, Columbus, Ohio, May 1969 (see publication 5).
- (3) Thrailkill, John. Solution geochemistry in the Mammoth Cave - Sinkhole Plain area, seminar presented at Western Kentucky State University, Bowling Green, Kentucky, May 1969.

The following reported results from equipment acquired or techniques developed in connection with this project, or discussed results of the project in addition to other topics.

- (4) Thraikill, John. Deposition in caves-a review, presented at national meeting of American Association for the Advancement of Science, Washington, D. C., December 1966 (see publication 8).
- (5) Thraikill, John. Solution chemistry and precipitate mineralogy in Carlsbad Caverns, presented at Gordon Research Conference (Geochemistry), New Hampton, New Hampshire, August 1966.
- (6) Thraikill, John. Three approaches to limestone hydrology, presented at Midwest Ground-Water Conference, Lexington, Kentucky, December 1969.
- (7) Thraikill, John. Cave development in the Mississippian Plateau, presented at Annual Kentucky Geological Survey - U.S. Geol. Surv. Meeting, Park City, Kentucky, January, 1970.

Training accomplished

Eight graduate students participated in aspects of the study and received training in the techniques involved. Five of these (W. M. Mitchell, L. N. Plummer, J. R. Riddell, R. C. Worley, and R. D. Zwicker) were employed for brief periods during the first year of the study (FY 1967). Due to the small numbers of graduate students available during this first year, and the short lead time between the notice of funding and start of the year, no graduate

students could be obtained for "full-time" research assistance, and it was necessary to use a number of students for short periods to work on the analytic aspects of the study (the principal goal of the first year).

Two graduate assistants participated in the program during the second year (FY 1968). Both of these began theses connected with the project, but one (M. J. Osolnik) was drafted at the end of the year and the other (R. M. Postley) dropped out of school. The project was extended for a third year (FY 1969) with funds sufficient to furnish support for M. S. thesis research on the Cave Hollow aquifer by D. P. Belter. This thesis is currently in the writing stage.

Since the conclusion of the project, two other graduate students have begun theses dealing with aspects of limestone groundwater. These will probably be at the M.S. level and are unsupported by OWRR funds.

During the period of the project, courses at the graduate level in Hydrogeology and Advanced Low-Temperature Geochemistry have been developed and taught by the principal investigator.

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APPENDIX 1

ANALYTIC TECHNIQUES

Field Techniques

Alkalinity: Alkalinity of each sample was determined by titration with standardized H_2SO_4 to a pH of 4.5 using one of the two pH meters described below which had previously been calibrated with buffers. Titrations were generally performed at the sampling site within 1 to 5 minutes of collection. When surface temperatures were below freezing, delays of up to 15 minutes occurred while samples were transported for analysis, but tests indicated no significant change in alkalinity. In every case care was taken to prevent any change in temperature in the period between sampling and analysis. Titration equipment consisted of a Class A buret and reservoir in a shock resistant case.

pH: Measurements of pH were made with a Beckman Model G battery-operated pH meter and a Beckman 39182 flat-bulb combination electrode. Some of the later determinations were checked with an Orion Model 401 Specific ion meter with Beckman 39182 or 39142 electrodes. In every case the meter was calibrated to temperature corrected buffers. Because operating difficulties were encountered when the ambient temperature was below freezing, some samples were transported for analysis with delays of up to 15 minutes. Care was taken to maintain the sample temperature during transport and the samples so transported were generally not those in which the pH was changing rapidly.

Conductivity: The electrical conductivity (=1/resistivity) was measured at the sampling point with a Beckman RB3 Solu-Bridge conductivity meter and Beckman BB1 cell. In most cases, conductivity was read both for the sample temperature and for 25°C.

Sample Preservation: Most samples were pressure filtered through millipore 0.45 μ filters at the time of collection. A few of the earlier samples were rough filtered only (Whatman No. 2). After filtering, about 1 drop of 40% acetic acid and 2 drops of formaldehyde were added for each 50 ml of sample. The acid was added to prevent the precipitation of calcium carbonate and the formaldehyde served to prevent the growth of algae. Tests showed that neither additive had a significant effect on later laboratory determinations.

Other Field Determinations: Temperatures were measured with a thermometer which had previously been calibrated against a Bureau of Standards certified thermometer. A few direct measurements were made (mainly in Mammoth Cave) of relative humidity and the partial pressure of carbon dioxide. Humidity measurements were made with a Bacharach sling psychrometer and the P_{CO_2} determinations were made with a Kitagawa gas detector (Union Industrial Equipment Company Model 400) and carbon dioxide low-range tubes. This device consists of a 100 cc syringe which, while filling, passes air through a glass tube. The contained carbon dioxide produces a color change in an absorbant in the tube.

Laboratory Techniques--Atomic Absorption

General: Equipment used was a Beckman DB-G Spectrophotometer-Atomic Absorption Accessory with Laminar Flow Burner and recorder. The principal variable affecting the analytic ranges is the optional operation of a heated mixing chamber which concentrates the sample before it enters the flame ("Hot Mode" versus "Cold Mode"). Other important parameters are the delivered pressure in pounds per square inch of air ("Air") and acetylene ("Acet."), slit width in millimeters ("Slit"), wavelength in $m\mu$ ("λ"), burner elevation in inches below point where burner head intercepts beam ("Elev."), and lamp current in milliamperes ("Lamp").

The atomic absorption instrument used has the capability of tripling the length of the light beam in the flame by folding the light path, but the approximately 2x sensitivity gain which results is at the expense of increased light absorption, and this feature was little used. Similarly, it was possible to employ a larger capillary feed tube to increase the sensitivity, but the increase was found to be so small relative to the increased rate of sample consumption that the small capillary was used for all determinations.

Calcium: In Cold Mode with no additives the approximate linear ranges is 0-12 ppm. Absorbance for 12 ppm was 0.29 for the last samples analyzed. No blank correction with twice-distilled - deionized water. Satisfactory operating parameters are Air: 18-20; Acet.: 3; Slit: 0.50; λ: 285; Elev.: 0.2; Lamp: 12.

As has been reported by several workers, Na^+ and K^+ enhance absorbance, but effect is easily controlled by adding excess Na^+ . Cl^- , NO_3^- , and especially SO_4^{2-} and PO_4^{2-} interfere by complexing with calcium. Strontium or lanthanum, alone or in combination with EDTA (ethylenediaminetetraacetate ion) have been suggested as additives to control this interference, but investigation showed that EDTA alone was satisfactory for natural water samples. Final procedure was to make final solution 10 mM in Na_2EDTA and 1 mM in NaOH (to stabilize the solution). Such solutions show a reduction in absorbance of about 5%, but the linear range is relatively unchanged. Small variations in the amount of EDTA above 5 mM and in NaOH above .5 mM do not affect absorbance. Acetate ion in small amount (the water samples were acidified at the time of collection to prevent precipitation) does not interfere.

In Hot Mode, the range 0.5 (absorbance \approx 0.19) to 2 (abs. \approx 0.61)ppm is the most nearly linear, but the entire calibration curve is noticeably curved. Absorbance appears to be somewhat sensitive to the amount of Na_2EDTA and NaOH added.

Magnesium: In Cold Mode with no additives the approximate linear range is 0-3 ppm. Absorbance for 3 ppm \approx 0.40. No blank correction necessary. Satisfactory operating parameters are Air: 18-19; Acet.: 3; Slit: 0.25; λ : 285; Elev.: 0.2; Lamp: 12. Na^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} show interferences similar to calcium, but effects are controlled

with the same $\text{Na}_2\text{EDTA-NaOH}$ addition used for calcium. Reduction in absorbancies and other comments same as for calcium.

Due to the extreme sensitivity, little work was done with Hot Mode; linear range is probably in the 0-0.2 ppm range or less.

Sodium: With vapor discharge (Osram) lamp in cold mode with no additives the approximate linear range was 0-11 ppm. Absorbance for 11 ppm \approx 0.75; no blank correction necessary. Suitable operating parameters are Air: 18; Acet.: 3-3.5; Slit: 0.15; λ : 589; Elev.: 0.15; Lamp: 500.

Ca^{2+} , Fe^{2+} , PO_4^{3-} , SO_4^{2-} , NO_3^- and acetate ion do not interfere. K^+ and Mg^{2+} interfere slightly, but both interferences may be eliminated by adding 100 (or more) ppm K^+ which enhances absorption slightly, but does not affect the linear range. The Cold Mode sensitivity was high enough for all analyses undertaken and Hot Mode operation was not investigated in detail.

As shown in Appendix 4, the sensitivity of the sodium analysis was considerably lower than that for calcium and magnesium (as discussed in Appendix 3), which was probably due to the gas discharge lamp. In addition, various operating difficulties were encountered with this lamp, which failed near the end of the project. It was replaced with a hollow cathode lamp which was used for analyses of samples 92-113. There was a significant increase in stability, ease of operation, and precision with the hollow cathode lamp, with the following operating parameters: Air: 18; Acet: 2.5; Slit: 0.15; λ : 589; Elev.: 0.15; Lamp: 7.2. The approximate linear range was 1-4 ppm with absorbance for 4 ppm \approx 0.45.

Potassium: Little work was done on potassium, and the same instrument parameters were used as for sodium. No major interference were believed to exist, and undiluted samples were analysed.

Laboratory Techniques - Spectrophotometric

Chloride: Mercuric chloranilate procedure was modified after that described by Bertolacini and Barney (Anal. Chem 29:281-283, 1957, and later papers). Low concentrations measured at 310 m μ in 10mm silica cells; linear range 0-55 ppm; absorbance for 5.5 ppm \approx 1.0. Higher concentrations were measured at 530 m μ in 40mm pyrex cells; linear range 0-23 ppm; absorbance for 23 ppm \approx 0.93. At 530 m μ in 10 mm pyrex cells; linear range 0-90 ppm; absorbance for 90 ppm \approx 0.97.

Cations were removed from both standards and unknown by shaking 1 gm of strong-acid cation resin with 25 gm sample for 3 hours in mechanical shaker. It was found that precision was much improved (and sensitivity to amount of mercuric chloranilate eliminated) by (a) soaking mercuric chloranilate for several hours in 50% ethylene glycol monomethyl ether solution and then drying overnight at 105^o and (b) shaking sample after addition of mercuric chloranilate in mechanical shaker for several hours.

Sulfate: Basic barium chloranilate procedure is that of Klipp and Barney (Anal. Chem. 31: 596-597, 1957). Low concentrations measured at 330 m μ in 10 mm silica cell; range 0-7.5 ppm was nearly linear (slightly concave upward); absorbance for 7.5 ppm \approx 0.97. Higher concentrations measured at 530 m μ ; linear range 10-100 ppm; absorbance for 100 ppm \approx 0.97.

Cations removed by procedure for chloride (see above). Chloride interference and sensitivity to amount of chloranilate added was eliminated by substitution of isopropyl alcohol for ethanol, mechanically shaking (overnight) samples after addition of barium chloranilate, and using 0.45 μ membrane filters for separation of unreacted barium chloranilate.

Iron and Aluminum: Procedure used was the ferron-orthophenanthroline method described in Rainwater and Thatcher (U. S. Geol. Surv. Water Supply Paper 1454: 97-100, 1960).

Nitrate: Phenoldisulfonic acid method (Rainwater and Thatcher, U. S. Geol. Survey Water Supply Paper 1454: 216-19, 1960) was used.

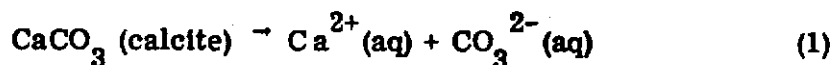
APPENDIX 2 - COMPUTATIONS

The principal information sought in this study was the state of saturation of the various waters with respect to calcite, and the partial pressure of carbon dioxide with which the water was in equilibrium.

Saturation Coefficient

The state of saturation of water with respect to calcite may be described by a saturation coefficient, S_c , which is the ratio the ion activity product, A_c and the (thermodynamic) solubility product, K_c (Table 1), or $S_c = A_c / K_c$. For a given sample, a value of $S_c = 1$ indicates saturation and values less than or greater than unity denote undersaturation or supersaturation, respectively.

For the solution reaction



The ion activity product is given by

$$A_c = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} \quad (2)$$

where a_i denotes the (thermodynamic) activity of a species, with the activity of the crystalline phase (calcite) taken to be unity.

Activity of the carbonate ion, $a_{\text{CO}_3^{2-}}$: Measured alkalinity,

expressed as $c_{\text{HCO}_3^-}$ (in ppm), is taken to be the algebraic sum of all "neutralizable" species in solution. Of these, HCO_3^- is the major one, and may be derived from the expression .

$$\begin{aligned}
m_{\text{HCO}_3^-} = & m_{\text{alkalinity}} - 2m_{\text{CO}_3^{2-}} - m_{\text{OH}^-} - m_{\text{CaHCO}_3^+} \quad (3) \\
& - m_{\text{MgHCO}_3^+} - 2m_{\text{CaCO}_3^0} - 2m_{\text{MgCO}_3^0} - 2m_{\text{NaCO}_3^-} \\
& - m_{\text{CaOH}^+} - m_{\text{MgOH}^+} + m_{\text{HSO}_4^-}
\end{aligned}$$

where m_i is the molality (moles/kg H_2O) of a species and

$$m_{\text{alkalinity}} = \frac{\text{alkalinity} \cdot 10^{-3}}{W_{\text{HCO}_3^-} \cdot [1 - (\text{total ppm dissolved solids} \cdot 10^{-6})]} \quad (4)$$

with $W_{\text{HCO}_3^-}$ = gram-formula-weight of HCO_3^- .

The activity of the hydrogen ion (a_{H^+}) was measured directly as the pH, and the activity of the CO_3^{2-} ion may be calculated from the expression

$$a_{\text{CO}_3^{2-}} = \frac{K_2 \cdot \gamma_{\text{HCO}_3^-} \cdot m_{\text{HCO}_3^-}}{a_{\text{H}^+}} \quad (5)$$

where K_2 is the second dissociation constant of carbonic acid (Table 1).

The individual ion activity coefficient for the bicarbonate ion, $\gamma_{\text{HCO}_3^-}$, was calculated from the Debye-Huckel expression:

$$-\log \gamma_1 = \frac{A \cdot z_1^2 \cdot \sqrt{I}}{1 + D_1 \cdot B \cdot \sqrt{I}} \quad (6)$$

(Garrels and Christ, "Solutions, Minerals, and Equilibria", Harper and

Row, 1965, p. 61) where A and B are temperature dependent constants

(Table 1), z is the charge on the ion, and D is the hydrated diameter of the

ion (Table 2). The ionic strength, I, is given by the expression

$$I = 1/2 \sum m_i \cdot z_i^2 \quad (7)$$

where the summation is over all ions in solution.

Activity of the calcium ion, $a_{Ca^{2+}}$: The activity of the calcium ion is evaluated by

$$a_{Ca^{2+}} = \gamma_{Ca^{2+}} \cdot m_{Ca^{2+}} \quad (8)$$

with $\gamma_{Ca^{2+}}$ from equation 6 and $m_{Ca^{2+}}$ from

$$m_{Ca^{2+}} = m_{\text{calcium}} - m_{CaHCO_3} - m_{CaCO_3^0} - m_{CaSO_4^0} \quad (9)$$

$$- m_{CaNO_3^+} - m_{CaOH^+}$$

where

$$m_{\text{calcium}} = \frac{c_{\text{calcium}} \cdot 10^{-3}}{W_{\text{calcium}} \cdot [1 - (\text{total dissolved solids} \cdot 10^{-6})]} \quad (10)$$

with c_{calcium} the measured calcium in solution. The molality of complex ions in solution are evaluated from solution of expressions such as equation 9 and from equations such as

$$m_{CaOH^+} = \frac{\gamma_{Ca^{2+}} \cdot \gamma_{OH^-} \cdot m_{Ca^{2+}} \cdot m_{OH^-}}{\gamma_{CaOH^+} \cdot K_{CaOH^+}} \quad (11)$$

where the various γ_i are obtained from equation 6 and the various dissociation constants K_i from the data in Table 2.

It is apparent that a simultaneous solution of many of these equations is required. Equation 3 requires a value obtained from equation 11; a value for total dissolved solids in equation 4 can only be obtained after a knowledge of the concentration of all species is obtained (equations such as 9 and 11); as does the correct value for the ionic strength (equation 7) and hence values for γ_i (equation 6). The diverse forms of the various equations makes it unfeasible

to solve them simultaneously, and a method of successive approximations is used which converges rather rapidly (no more than 7 iterations were required).

Carbon Dioxide Partial Pressure

The partial pressure of carbon dioxide with which the water was in equilibrium was calculated from

$$P_{\text{CO}_2} = \frac{a_{\text{H}_2\text{CO}_3^0}}{K_B}$$

where K_B is the Henry law solubility product of CO_2 relative to H_2CO_3^0 in solution (all CO_2 (aq) was considered hydrated). Values of K_B used are listed in Table 1. Values of $a_{\text{H}_2\text{CO}_3^0}$ were computed from the expression

$$a_{\text{H}_2\text{CO}_3^0} = \frac{a_{\text{H}^+} \cdot a_{\text{HCO}_3^-}}{K_1}$$

with values of K_1 from Table 1.

Other Parameters

In addition to values of solution variables needed for calculation of the two principle parameters discussed above, certain other information was calculated for completeness and later reference, or to check the accuracy of the analyses. This included calculation of saturation coefficients relative to other mineral phases of interest (see table 1 for values of K_1 used), and a calculation of the conductivity of the solution as computed from the analyses according to the "Modified Rossum Method" of Logan (Journ. of Geop. Res. 66: 2482, 1961). All calculations were carried out, using IONPAIR2, a Fortran IV program written for the project, on an IBM 360/50 computer at the University of Kentucky Computing Center.

Table 1

Constants Used-General

Values of constants used in calculations for which temperature variations are known or were estimated. Division into 5° increments involves interpolation of original data in most cases.

Temp °C	Debye-Huckel A B x10 ⁻⁸		-log K _{H₂O}	-log K ₁	-log K ₂	-log K _B	-log K _C
1-2	.4883	.3241	14.950	6.577	10.625	1.12	8.02
3-7	.4921	.3249	14.741	6.517	10.557	1.19	8.09
8-12	.4960	.3258	14.535	6.465	10.490	1.26	8.15
13-17	.5000	.3262	14.349	6.420	10.430	1.33	8.22
18-22	.5042	.3273	14.164	6.382	10.377	1.40	8.28
23-27	.5085	.3281	13.998	6.351	10.329	1.47	8.34
28-32	.5130	.3290	13.883	6.327	10.290	1.53	8.40
33-37	.5175	.3297	13.683	6.309	10.253	1.59	8.46
38-42	.5221	.3305	13.534	6.296	10.220	1.64	8.52
43-47	.5271	.3314	13.398	6.290	10.192	1.68	8.58
48-52	.5319	.3321	13.262	6.287	10.172	1.72	8.63
53-57	.5471	.3329	13.139	6.30	10.18	1.76	8.69
58-60	.5425	.3338	13.016	6.31	10.18	1.80	8.75
Source	1	1	2	3	4	3	3

Source or Note:

1. Garrels and Christ, "Solutions, Minerals, and Equilibria, 1965, p. 61.
2. Barnes, et. al., Geo. Soc. Amer. Memoir 97, p. 404, 1966.
3. Source 1, p. 89.
4. Values for 53-60° from Source 2, p. 408; others from Source 1, p. 89.

Table 2

Constants Used - Individual Ions

	Diameter $\frac{9}{\text{A}}$	Source	log Dissociation Constant (1)	Source
Ca ²⁺	6.00	2	-	-
Mg ²⁺	8.00	2	-	-
Na ⁺	4.25	2	-	-
K ⁺	3.00	2	-	-
Cl ⁻	3.00	2	-	-
NO ₃ ⁻	3.00	2	-	-
SO ₄ ²⁻	4.25	2	-	-
H ⁺	9.00	2	-	-
HCO ₃ ⁻	4.25	2	(9)	-
CO ₃ ²⁻	4.50	2	-	-
OH ⁻	3.50	2	-	-
H ₂ CO ₃ [•]	-	-	(10)	-
CaHCO ₃ ⁺	2.50	3	-1.26	11
MgHCO ₃ ⁺	3.00	4	-1.16	11
CaCO ₃ [•]	-	-	-3.20	11
MgCO ₃ [•]	-	-	-3.40	11
NaCO ₃ ⁻	4.25	5	-1.27	11
CaSO ₄ [•]	-	-	-2.31	11
MgSO ₄ [•]	-	-	-2.36	11
NaSO ₄ ⁻	3.50	6	-0.72	11
KSO ₄ ⁻	3.00	7	-0.96	11
HSO ₄ ⁻	3.50	6	-2.00	11
CaNO ₃ ⁺	2.50	3	-0.28	12
MgNO ₃ ⁺	3.00	4	0.00	12
CaOH ⁺	3.00	4	-1.30	11
MgOH ⁺	4.25	8	-2.58	11

- Source or Note:
1. K for reaction ion pair \rightarrow cation + anion
 2. Garrels and Christ, "Solutions, Minerals, and Equilibria", Harper & Row, 1965, p. 62.
 3. analogy with Rb^+ in Source 2.
 4. analogy with K^+ in Source 2.
 5. analogy with HCO_3^- in Source 2.
 6. analogy with MnO_4^- in Source 2.
 7. analogy with NaSO_4^- in Source 2.
 8. analogy with Na^+ in Source 2.
 9. see K_2 in Table 1.
 10. see K_1 in Table 1.
 11. Garrels and Christ, "Solutions, Minerals, and Equilibria," Harper & Row, 1965, p. 96.
 12. Yatsimirski and Vastl'ev, "Instability Constants of Complex Compounds", Van Nostrand, 1966, p. 113.

APPENDIX 3 - ERRORS

The reliability of the data in the Mammoth Cave Sinkhole Plain Area was evaluated (1) both as to the probable imprecision of the analyses and (2) with regard to the estimated probability of gross errors.

Probable Analytic Imprecision

Individual calculation of the analytic uncertainty of each analysis has not been performed. An attempt to assess a general imprecision for each of the analytic parameters discussed in the text was made and is outlined below. This estimate refers to samples from the 13 principal sites discussed, and overstates the error for most of the analyses. Because the analytic imprecision for some of the early analyses and a few of the very dilute samples is rather high in some cases, up to 15% (12) of the 82 analyses used in the 13 sites were eliminated in assigning an uncertainty.

In the following discussion, it is assumed that the analytic uncertainty (or uncertainty in the value of a constant) is normally distributed and independent. The notation (x) will be used for $\sigma_x \%$ (coefficient of variation). Note that the analytic uncertainties are reported as $\pm 2 \sigma$ in Appendix 4.

Saturation with respect to calcite, S_c :

This uncertainty may be expressed as

$$(S_c)^2 = (K_2)^2 + (K_c)^2 + (a_{\text{HCO}_3^-})^2 + (a_{\text{Ca}^{2+}})^2 + (a_{\text{H}^+})^2$$

(1) Second dissociation constant (K_2)

No uncertainties for K_2 were stated in the source used (Garrels and Christ, 1965, p. 89). Solutions, Minerals, and Equilibria, Harper & Row. The mantissa of $\log K_2$ was given to two figures, suggesting an uncertainty (2σ) of about 3%. The approximate change of K_2 with temperature is about the same, and a total uncertainty (2σ) of 6% was assumed, yielding $(K_2) = 3\%$.

(2) Calcite solubility product (K_c)

Values of $\log K_c$ (Garrels and Christ, 1965, p. 89) were also given to two figures in the mantissa, and the temperature variation was similar to $\log K_2$. A value of $(K_2) = 3\%$ was therefore used. It might be noted that the uncertainty in K_c whose values are based directly on solubility determinations is much less than the uncertainties associated with the (Gibbs) free energy of the solution reaction.

(3) Bicarbonate ion activity ($a_{\text{HCO}_3^-}$)

A rigorous determination of the uncertainty in $a_{\text{HCO}_3^-}$ would involve the analyses of all other ions in solution as well as many parameters used in the calculations. The uncertainty in the value of the Debye-Huckel $\gamma_{\text{HCO}_3^-}$ is probably negligible relative to the imprecision in the value of $m_{\text{HCO}_3^-}$, hence $(a_{\text{HCO}_3^-}) \simeq (m_{\text{HCO}_3^-})$. Furthermore, HCO_3^- is by far the major species comprising the measured alkalinity, and $(m_{\text{HCO}_3^-}) \simeq (\text{alkalinity})$. The uncertainty (2σ) in alkalinity is absolute and estimated to be 2 ppm (as HCO_3^-). A value of (alkalinity) of 2% overstates the imprecision for all but 9 samples (numbers 37, 43, 50, 55, 62, 66, 86, 102, and 108) and will be used for $(a_{\text{HCO}_3^-})$.

(4) Calcium ion activity ($a_{Ca^{2+}}$)

By an argument similar to that for bicarbonate ion, ($a_{Ca^{2+}} \simeq (m_{Ca^{2+}})$). Only 9 samples had an uncertainty (2σ) greater than 8% (numbers 10, 12, 37, 45, 55, 62, 66, 76, 102) and ($a_{Ca^{2+}}$) will be taken = 4%.

(5) Hydrogen ion activity (a_{H^+})

The uncertainty in pH measurements (=negative log a_{H^+}) was 0.03 pH unit (2σ), or an uncertainty in a_{H^+} of 7%. Hence (a_{H^+}) was set at 4%. Computations using these values yields (Sc) \simeq 7.4%, or a 2σ uncertainty of \pm 15%.

Partial pressure of carbon dioxide, P_{CO_2} :

The uncertainty in P_{CO_2} may be derived from

$$(P_{CO_2})^2 = (a_{H^+})^2 + (a_{HCO_3^-})^2 + (K_1)^2 + (K_B)^2$$

(1) Hydrogen and bicarbonate ion activities

From above, (a_{H^+}) = 4% and ($a_{HCO_3^-}$) = 2%

(2) First dissociation constant (K_1) and CO_2 solubility (K_B). By an analysis similar to that for K_2 above, the values of these constants (Garrels and Christ, 1965, p. 89) are believed to be uncertain by 6% and 10% respectively, yielding (K_1) = 3%, and (K_B) = 5%.

Hence (P_{CO_2}) \simeq 7.4%, or a 2σ uncertainty of 15%.

Flow:

The 2σ uncertainties with which flow could be estimated were generally large and varied considerably between sites. The values used are listed below;

Table 1

Site	2 σ
Mill Hole Spring mouth	70%
Mill Hole Spring below	70%
Hidden Pool	70%
Leaky Ceiling drip	70%
Onyx Colonnade drip	70%
Mt. Vernon Stream	60%
Showerbath	60%
Sinking Creek	50%
Penetrating Sink	50%
Mill Hole Stream	50%
Radio Room drip	50%
White Mills Spring	35%
Seven Second drip	35%

Temperature:

Temperatures were noted only to the nearest degree C and are assumed to be measured without error (a calibrated thermometer was used). The uncertainty (2 σ) is taken to be 0.5°.

Probability of Gross Errors

In addition to a statement regarding the analytic uncertainty, each water sample was examined and a judgement made as to the probability that a gross error had been made in its collection or analyses. These are described in Table 2, Appendix 4.

APPENDIX 4

MAMMOTH CAVE - SINKHOLE PLAIN AREA DATA

S:
pl
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1

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1

1

1

1

10

17

18

19

20

Table 1
Chemical Analyses and Temperatures

Figures in parentheses following data (or in column heading) represent analytic errors (2σ) in same units as data.

Note 1: Alkalinity as Mg/l HCO_3^- .

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Sam- ple	Calcium mg/l	Magnesium mg/l	Sodium mg/l	Chloride mg/l	Sulfate mg/l	Alkalinity (2.0) Note 1	pH (.03)	T °C (.5)
7	31.8(2.4)	2.67(.10)	0.67(.16)	2.50(1.0)	10.0(2.0)	96.1	8.12	13
8	33.5(2.0)	2.70(1.6)	0.52(.30)	2.70(1.0)	10.0(2.0)	96.1	7.45	15
9	37.6(2.2)	5.35(.20)	0.47(.16)	-	-	111.6	7.14	14
10	37.4(3.2)	4.10(.20)	0.64(.30)	2.70(.25)	1.20(0.5)	111.6	7.13	14
11	67.1(2.0)	3.30(.10)	0.39(.24)	1.00(.25)	7.50(2.0)	213.9	7.50	13
12	70.8(6.0)	3.36(.16)	0.64(.20)	1.40(.25)	7.50(2.0)	192.2	8.04	13
13	64.6(4.2)	3.21(.20)	0.64(.30)	1.60(.25)	8.80(2.0)	195.3	7.34	13
14	66.7(5.2)	6.31(.24)	0.74(.12)	4.35(.30)	7.00(2.0)	209.2	7.62	14
15	61.1(2.0)	6.45(.20)	0.95(.20)	4.38(.30)	7.00(2.0)	210.2	7.62	15
16	66.7(4.1)	6.42(.14)	1.28(.30)	4.87(.30)	6.00(1.5)	210.2	7.59	15
17	67.6(2.8)	6.40(.24)	0.72(.24)	4.50(.30)	6.00(1.5)	210.2	7.59	15
18	47.1(2.4)	4.75(.12)	0.77(.30)	2.25(.30)	3.00(1.0)	161.2	7.18	13
19	46.2(2.0)	4.75(.10)	0.56(.28)	2.05(.30)	3.00(1.0)	161.2	7.18	13
20	49.6(2.8)	4.77(.12)	0.65(.24)	2.70(.30)	5.00(1.5)	158.1	7.28	13

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
21	49.0(1.8)	4.70(.20)	0.97(.30)	2.08(.30)	5.00(1.5)	158.1	7.28	13
22	48.5(3.2)	4.95(.24)	0.49(.08)	2.25(.30)	6.50(1.5)	158.1	7.28	13
23	40.1(1.6)	4.90(.20)	0.62(.12)	3.00(.30)	6.50(1.5)	139.5	7.53	13
24	40.2(2.2)	4.81(.18)	0.59(.28)	3.35(.30)	6.50(1.5)	139.5	7.53	13
25	53.5(1.5)	5.90(.25)	1.92(.76)	1.88(.50)	15.0(1.0)	-	-	12
26	-	-	not analyzed		-	-	-	-
27	-	-	not analyzed		-	-	-	-
28	38.0(1.0)	9.40(.20)	2.20(.40)	2.20(.50)	6.40(1.0)	136.4	7.86	13
29	18.5(1.0)	2.20(.15)	1.75(.60)	0.94(.50)	7.30(1.0)	62.1	7.72	13
30	51.6(1.6)	6.27(.42)	2.40(.30)	3.75(.50)	7.80(1.0)	181.2	7.51	8
31	51.7(0.8)	6.37(.40)	2.70(.40)	3.94(.50)	7.80(1.0)	181.2	7.51	8
32	48.9(1.8)	9.10(.40)	5.95(.30)	11.0(.50)	9.44(1.0)	186.3	7.11	13
33	63.1(2.2)	4.55(.40)	2.70(.30)	2.57(.50)	9.30(1.0)	216.6	8.31	12
34	67.8(2.0)	4.70(.40)	1.45(.40)	2.57(.50)	9.40(1.0)	216.6	8.31	12
35	65.8(2.4)	4.80(.40)	1.45(.40)	2.50(.50)	9.40(1.0)	221.2	8.02	12
36	22.3(1.0)	2.20(.50)	1.80(.30)	1.72(.50)	7.50(1.0)	77.3	7.82	13
37	9.4(1.2)	1.40(.20)	1.90(.30)	2.13(.50)	6.60(1.0)	33.3	7.42	12
38	51.2(1.2)	6.90(.40)	4.80(.40)	3.13(.50)	19.7(1.0)	170.6	7.80	12
39	75.1(0.6)	8.35(.18)	1.20(.28)	2.47(.50)	21.0(1.0)	292.4	7.50	13
40	62.7(2.6)	13.8(.40)	1.75(.30)	1.88(.50)	12.8(1.0)	237.0	7.70	13

(8)	Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
13									
13	41	35.5(2.0)	10.8(.20)	1.40(.30)	2.72(.50)	10.3(1.0)	143.9	7.93	13
13	42	21.6(1.6)	13.5(.20)	2.20(.40)	2.10(.50)	9.10(1.0)	121.2	8.10	13
13	43	8.8(0.4)	2.10(.20)	1.75(.30)	2.66(.50)	7.80(1.0)	27.3	7.28	9
12	44	28.7(1.4)	5.87(.28)	2.15(.28)	4.70(.50)	8.40(1.0)	115.4	8.08	10
	45	18.0(4.0)	2.00(.50)	1.97(.40)	1.56(.50)	6.80(1.0)	62.1	7.72	13
-									
-	46	51.7(1.6)	6.90(.50)	4.30(.40)	6.26(.50)	12.8(1.5)	179.3	7.22	2
13	47	49.1(1.0)	9.30(.40)	9.00(.30)	11.90(.50)	12.8(1.5)	174.9	7.00	9
13	48	64.6(2.2)	4.90(.40)	1.85(.30)	2.20(.50)	12.8(1.5)	214.6	7.82	9
8	49	69.2(2.2)	5.00(.50)	1.70(.30)	2.35(.50)	11.3(1.0)	224.9	7.65	10
	50	9.5(0.4)	1.50(.10)	1.80(.30)	1.66(.50)	7.30(1.0)	38.8	7.48	12
8									
13	51	81.1(2.8)	9.40(.20)	2.20(.30)	1.94(.50)	19.1(1.0)	285.2	7.32	12
12	52	20.1(0.8)	13.3(.30)	1.90(.30)	1.56(.50)	8.10(1.0)	116.1	8.20	12
12	53	59.7(1.2)	13.9(.10)	1.55(.30)	1.66(.50)	10.3(1.0)	236.1	7.18	12
12	54	36.8(1.6)	11.0(.10)	1.80(.30)	2.13(.50)	9.10(1.0)	140.8	7.97	12
	55	5.8(1.0)	2.20(.20)	1.90(.30)	2.15(.50)	6.30(1.0)	29.4	6.90	1
13									
12	56	34.7(2.2)	5.80(.20)	2.50(.30)	2.88(.50)	6.30(1.0)	113.2	7.41	1
12	57	54.0(2.5)	6.75(.30)	2.99(.40)	4.93(.40)	10.7(1.0)	195.0	7.58	5
13	58	50.2(2.4)	9.50(.60)	6.15(.30)	10.6(.40)	9.30(1.0)	199.0	7.42	10
13	59	64.0(2.5)	4.85(.30)	1.55(.30)	3.57(.40)	12.8(1.0)	232.0	8.26	11
	60	62.5(2.5)	4.85(.30)	1.20(.40)	3.21(.40)	13.0(1.0)	217.8	8.31	11

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Sam- ple
61	91.6(4.0)	9.16(.50)	0.40(.30)	1.93(.40)	22.5(1.0)	303.6	7.10	12	
62	12.0(1.0)	1.95(.30)	1.45(.30)	1.43(.40)	6.40(.50)	42.9	7.67	12	81
63	22.1(1.4)	12.8(.20)	2.20(.50)	2.11(.40)	9.20(.50)	122.1	8.08	12	82
64	37.7(1.6)	11.0(.30)	0.29(.30)	2.78(.40)	11.8(.50)	155.8	7.70	12	83
65	58.5(2.5)	14.7(.30)	0.29(.30)	1.96(.40)	14.5(.50)	260.4	7.49	12	84
									85
66	7.4(1.2)	3.25(.30)	2.40(.30)	3.46(.40)	8.00(.50)	41.9	7.71	1	
67	29.0(1.3)	6.50(.15)	2.05(.30)	3.99(.40)	7.80(.50)	128.7	8.30	1	86
68	7.4(1.2)	3.25(.30)	3.05(.30)	3.46(.40)	8.00(.50)	41.9	7.71	1	87
69	54.5(2.5)	7.65(.30)	3.71(.30)	4.65(.30)	8.80(.40)	210.2	8.21	8	88
70	60.0(2.5)	7.55(.30)	4.04(.30)	4.75(.30)	8.25(.40)	210.5	8.28	8	89
									90
71	57.0(2.5)	7.50(.30)	4.70(.30)	5.75(.30)	8.32(.40)	204.6	8.64	10	
72	57.0(2.5)	12.8(.30)	11.4(.46)	20.0(1.0)	12.0(.40)	228.4	7.64	11	91
73	63.0(2.5)	6.00(.30)	1.45(.30)	3.70(.30)	11.3(.40)	212.1	8.40	12	92
74	58.5(1.6)	5.90(.30)	2.16(.30)	3.50(.30)	11.6(.40)	207.9	8.42	12	93
75	37.5(2.5)	8.46(.30)	3.15(.30)	4.30(.30)	17.0(.40)	112.9	8.09	13	94
									95
76	21.2(2.2)	3.00(.20)	1.87(.30)	3.00(.30)	5.58(.40)	73.3	7.87	13	
77	85.0(3.2)	8.25(.50)	1.35(.30)	2.80(.30)	19.5(.40)	283.8	7.61	13	96
78	34.8(1.6)	11.0(.20)	1.46(.30)	3.25(.30)	8.62(.40)	158.1	7.71	13	97
79	61.0(2.5)	15.0(.30)	0.35(.30)	2.55(.30)	10.2(.40)	259.4	7.24	13	98
80	24.9(1.8)	12.5(.25)	1.87(.30)	2.80(.30)	7.50(.40)	122.1	8.27	13	99

100

(8)	Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
12	81	26.0(.80)	4.42(.16)	0.70(.30)	4.52(.12)	4.58(.20)	90.6	7.80	15
12	82	28.5(1.0)	4.55(.16)	0.70(.30)	3.35(.12)	5.05(.20)	108.4	7.50	13
12	83	61.0(2.5)	4.45(.30)	1.20(.28)	2.25(.25)	11.6(.20)	193.3	8.00	12
12	84	57.0(.60)	4.08(.20)	0.42(.30)	2.00(.12)	11.7(.20)	189.4	8.41	12
	85	37.6(.60)	7.22(.22)	3.35(.30)	7.63(.12)	7.68(.20)	144.4	7.41	12
1									
1	86	12.0(.50)	2.08(.18)	1.00(.20)	2.50(.12)	5.70(.20)	44.4	7.59	13
1	87	22.5(1.2)	6.85(.14)	2.97(.20)	4.20(.12)	18.5(.20)	90.6	7.90	13
8	88	84.0(3.2)	8.58(.50)	1.15(.30)	1.25(.25)	20.6(.20)	259.8	7.48	13
8	89	22.5(1.0)	12.7(.15)	0.30(.28)	1.50(.12)	6.60(.20)	114.8	8.02	13
	90	56.3(.80)	13.7(.22)	1.00(.30)	0.80(.12)	11.6(.20)	241.3	7.40	13
10									
11	91	34.6(2.5)	11.3(.30)	1.15(.30)	2.20(.12)	8.08(.20)	145.0	7.67	13
12	92	34.5(1.0)	6.69(.10)	1.66(.12)	1.47(.12)	5.70(.25)	139.2	7.67	17
12	93	60.0(1.5)	5.18(.10)	1.18(.20)	1.25(.12)	11.1(.25)	200.6	7.95	12
13	94	60.0(1.5)	5.80(.18)	1.22(.16)	1.05(.12)	10.6(.25)	191.8	8.19	13
	95	56.0(1.5)	11.8(.15)	10.0(.20)	14.7(.50)	12.1(.25)	208.4	7.51	14
13									
13	96	29.3(1.2)	7.93(.12)	3.28(.28)	1.87(.12)	15.1(.25)	109.0	8.10	14
13	97	77.6(2.1)	8.21(.21)	0.59(.12)	0.63(.12)	19.3(.25)	259.4	7.61	14
13	98	21.8(.80)	3.35(.08)	1.78(.12)	3.18(.12)	5.38(.25)	75.8	7.78	14
13	99	21.1(.80)	13.1(.15)	0.85(.16)	2.70(.12)	5.80(.25)	117.8	7.69	14
	100	36.0(1.2)	11.4(.12)	0.50(.16)	3.40(.12)	8.75(.25)	145.3	7.11	14

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
101	56.5(1.5)	14.0(.15)	0.51(.12)	5.25(.25)	10.8(.50)	235.3	7.69	14
102	7.0(.80)	1.95(.30)	2.50(.30)	2.20(.15)	2.70(.25)	37.8	7.52	19
103	24.1(1.0)	4.05(.30)	3.30(.30)	3.43(.15)	5.58(.25)	90.3	7.82	17
104	26.2(.60)	4.05(.30)	3.05(.30)	3.05(.15)	4.75(.25)	94.8	7.57	16
105	59.3(1.0)	3.95(.30)	2.62(.30)	1.88(.15)	11.8(.25)	200.4	7.97	13
106	66.1(.80)	3.95(.30)	3.05(.30)	2.15(.15)	11.8(.25)	201.0	8.41	13
107	43.6(1.0)	7.70(.30)	8.98(.30)	6.68(.15)	9.08(.25)	158.9	7.51	15
108	11.1(.60)	1.65(.30)	2.41(.30)	1.33(.15)	6.80(.25)	42.3	7.51	13
109	81.0(.80)	7.95(.30)	1.20(.30)	1.83(.15)	20.8(.25)	262.3	7.44	13
110	28.3(.80)	5.80(.30)	6.21(.30)	3.10(.15)	17.4(.25)	103.7	7.98	13
111	21.6(1.0)	13.75(.30)	2.20(.30)	1.62(.15)	8.03(.25)	127.8	7.89	13
112	36.2(.80)	11.40(.30)	1.20(.30)	2.38(.15)	10.8(.25)	146.4	7.45	13
113	55.8(1.0)	14.45(.30)	1.83(.30)	2.00(.30)	13.8(.50)	238.8	8.12	13

Table 2

Additional Data and Quality Evaluations

(8)
14 NOTE 1: Sampling sites are (see text for complete description): 1, White
19 Mills Spring-mouth; 2, Mt. Vernon Stream; 3, Sinking Creek; 4, Penetrating
17 Sink; 5, Mill Hole Stream; 6, Mill Hole Spring-mouth; 7, Mill Hole Spring-
16 below; 8, Showerbath; 9, Hidden Pool; 10, Leaky Ceiling; 11, Seven Second
13 Drip; 12, Onyx Colonnade Drip; 13, Radio Room Drip; 14, Green River;
13 15, Nolan River; 16, White Mills Spring - below; 17, Terhune Spring-mouth;
15 18, Terhune Spring-below; 19, Stream near Terhune Spring; 20, Mill Hole
13 Spring-far below; 21, Crystal Lake; 22, Devil's Pool. Site number in
13 parentheses indicates replicate for that site (and date) judged less representative.

13 NOTE 2: Sampling dates are: 1-13, 11 July 1967; 14-24, 7 Sept. 1967; 25,
13 26, Oct. 1967; 26-29, 45, 10 Nov. 1967; 30-42, 9 Dec. 1967; 43-44, 10 Dec.
13 1967; 46-54, 8 Jan. 1968; 55-56, 9 Jan. 1968; 57-65, 10 Feb. 1967; 66-68,
11 Feb. 1968; 69-80, 9 Mar. 1968; 81-91, 13 April 1968; 92-101, 10 May 1968;
102-113, 4 June 1968.

NOTE 3: See Appendix 3 for errors in estimated flow. Units are: F, ft³/sec;
G, gallons/min; D, drops/sec.

NOTE 4: Sample characteristics are: 1, sample not filtered; 2, rough
filtering only; 3, no preservative added; 4, sample not acidified; 5, possibility
of error in pH; 6, charge imbalance exceeds 5%; 7, charge imbalance exceeds 10%;

8, calculated conductivity less than 93% or greater than 107% of measured conductivity; 9, calculated conductivity less than 85% or greater than 115% of measured conductivity, or no conductivity measured; 10, redetermination; 11, other analyses done (see Table 4, Appendix 4).

NOTE 5: Quality grades are: S, slight possibility of gross error (any of characteristics 1, 4, 5, 7, or 9); V, very slight possibility of gross error (any of characteristics 2, 3, 6, or 8); N, negligible possibility of gross error (none of characteristics 1 through 9).

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Site Note 1	Date Note 2	estim. Note 3	Flow log cm ³ /sec	Meas. conduc. T	25°C	Quality grade	Sample characteristics
7	(14)	Jul.	15000	F +8.65	-	-	S	1,3,9
8	14	"	15000	F +8.65	-	-	S	2,3,9
9	(5)	"	80	F +6.38	-	-	S	1,3,7,9
10	5	"	80	F +6.38	-	-	S	2,3,7,9
11	6	Jul	50	G +3.48	-	-	S	2,3,9
12	7	"	50	G +3.48	-	-	S	2,3,6,9,11
13	20	"	50	G +3.48	-	-	S	2,3,9
14	1	Sep	40	F +6.08	-	-	S	2,3,9,11
15	(1)	"	40	F +6.08	-	-	S	1,3,9,11
16	16	Sep	40	F +6.08	-	-	S	2,3,9,11
17	(16)	"	40	F +6.08	-	-	S	1,3,9
18	17	"	-	- -	-	-	S	2,3,9,11
19	(17)	"	-	- -	-	-	S	1,3,9
20	18	"	-	- -	-	-	S	2,3,9
21	(18)	Sep	-	- -	-	-	S	1,3,9
22	(18)	"	-	- -	-	-	S	1,3,4,9
23	19	"	-	- -	-	-	S	2,3,9
24	(19)	"	-	- -	-	-	S	1,3,9
28	11	Nov	0.14	D -2.16	-	-	S	3,5,6,9
29	(8)	"	2	G +2.08	-	-	S	1,3,4,9
30	(1)	Dec	50	F +6.18	327	-	S	3,9

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
31	1	Dec	50	F +6.18	327	-	V	3, 8
32	5	"	6	F +5.26	380	-	S	3, 9
33	7	"	10	G +2.78	405	-	S	3, 9
34	(7)	"	10	G +2.78	405	-	S	1, 3, 9
35	6	"	10	G +2.78	422	-	S	3, 9
36	22	Dec	-	- -	142	-	S	3, 5, 8
37	8	"	4	G +2.38	64	-	V	3, 6
38	21	"	-	- -	290	-	V	3
39	12	"	4	D -0.70	450	-	S	3, 5, 6, 8, 10, 11
40	13	"	0.1	D -2.30	355	-	S	3, 5
41	11	Dec	0.14	D -2.16	248	-	S	3, 5
42	10	"	3	D -0.82	202	-	S	3, 5
43	2	"	3	G +2.26	66	-	V	3
44	3	"	7	F +5.32	225	-	S	3, 9, 10, 11
45	8	Nov	2	G +2.08	-	-	S	3, 9
46	1	Jan	50	F +6.18	328	-	V	8
47	5	"	6	F +5.26	280	-	V	8
48	7	"	10	G +2.78	375	-	V	8
49	6	"	10	G +2.78	402	-	S	9
50	8	"	4	G +2.38	76	-	S	7

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
51	12	Jan	3	D -0.82	440	-	N	
52	10	"	3	D -0.82	195	-	N	
53	13	"	0.1	D -2.30	355	-	N	
54	11	"	0.14	D -2.16	248	-	N	
55	2	"	3	G +2.26	60	-	S	7
56	3	Jan	3	F +4.95	180	-	V	6, 8
57	1	Feb	60	F +6.26	288	-	N	10
58	5	"	5	F +5.18	350	-	V	8
59	6	"	5	G +2.48	310	-	V	6, 11
60	7	"	5	G +2.48	280	-	V	8
61	12	Feb	5	D -0.60	460	-	N	10, 11
62	8	"	3	G +2.26	60	-	S	9
63	10	"	3	D -0.82	198	-	N	
64	11	"	0.14	D -2.16	248	-	N	
65	13	"	0.1	D -2.30	360	-	V	6, 10
66	2	Feb	0.5	G +1.48	70	-	S	5, 7, 9
67	3	"	2	F +4.78	195	-	S	5, 6, 10
68	(2)	"	0.5	G +1.48	70	-	S	5, 7, 9
69	1	Mar	30	F +5.95	300	205	S	5, 10
70	16	"	30	F +5.95	315	215	S	5, 10

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
71	15	Mar	-	- -	310	210	S	5,10
72	5	"	4	F +5.08	400	302	S	5,10
73	6	"	3	G +2.26	315	235	N	10
74	7	"	3	G +2.26	292	222	N	10,11
75	9	"	3	G +2.26	205	157	S	7,8,10,11
76	8	Mar	1	G +1.78	117	87	V	8
77	12	"	2	D -1.00	400	310	N	10
78	11	"	0.14	D -2.16	245	187	N	
79	13	"	0.1	D -2.30	350	270	N	10,11
80	10	"	4	D -0.70	187	140	N	
81	3	Apr	4	F +5.08	162	128	N	
82	4	"	4	F +5.08	188	142	V	8
83	6	"	10	G +2.78	290	220	N	10
84	7	"	10	G +2.78	285	224	N	
85	5	"	6	F +5.26	250	190	N	
86	8	Apr	4	G +2.38	85	67	V	6
87	9	"	3	G +2.26	180	137	N	
88	12	"	3	D -0.82	410	305	N	10
89	10	"	5	D -0.60	185	145	N	10,11
90	13	"	0.1	D -2.30	350	270	N	

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
91	11	Apr	0.14	D -2.16	250	190	V	8,10
92	4	May	1.5	F +4.65	-	-	S	9
93	6	"	5	G +2.48	337	255	V	8,11
94	7	"	5	G +2.48	300	225	N	
95	5	"	5	F +5.18	375	295	N	11
96	9	May	3	G +2.26	200	157	N	
97	12	"	2	D -1.00	385	300	S	9
98	8	"	0.8	G +1.68	127	102	S	5,11
99	10	"	5	D -0.60	185	150	S	5
100	11	"	0.14	D -2.16	235	185	N	
101	13	May	0.08	D -2.40	-	-	S	9
102	2	Jun	3	G +2.26	80	70	S	6,9
103	3	"	10	F +5.48	175	155	V	8
104	4	"	10	F +5.48	185	150	V	8
105	6	"	5	G +2.48	340	255	V	8
106	7	Jun	5	G +2.48	310	240	N	
107	5	"	6	F +5.38	255	210	N	
108	8	"	3.5	G +2.32	80	65	V	6
109	12	"	1.5	D -1.13	400	300	N	
110	9	"	3	G +2.26	190	145	N	
111	10	Jun	5	D -0.60	205	150	N	
112	11	"	0.14	D -2.16	240	185	N	
113	13	"	0.06	D -2.52	-	-	S	9

Table 3

Concentrations and Activities of Major Ions

Concentration units ("ppm") are in mg/Kg H₂O

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)
	Ca ²⁺ ppm(ax10 ⁴)	Mg ²⁺ ppm(ax10 ⁴)	Na ⁺ ppm(ax10 ⁴)	Cl ⁻ ppm(ax10 ⁴)	SO ₄ ²⁻ ppm(ax10 ⁴)	HCO ₃ ⁻ ppm(ax10 ⁴)
7	30.7(6.14)	2.58(.857)	.670(.275)	2.50(.666)	8.96(.744)	94.4(14.6)
8	32.3(6.45)	2.61(.865)	.520(.213)	2.70(.718)	8.92(.739)	94.4(14.6)
9	36.6(7.23)	5.23(1.72)	.470(.192)	-	-	110.(16.9)
10	36.4(7.19)	4.00(1.32)	.640(.262)	2.70(.716)	1.05(.086)	110.(16.9)
11	63.4(11.8)	3.13(.972)	.390(.157)	.999(.261)	6.28(.482)	207.(31.5)
12	66.7(12.4)	3.16(.981)	.639(.258)	1.40(.365)	6.23(.365)	183.(27.8)
13	61.2(11.5)	3.06(.954)	.639(.258)	1.60(.418)	7.39(.571)	190.(28.9)
14	63.1(11.7)	5.99(1.85)	.739(.298)	4.35(1.13)	5.80(.443)	202.(30.7)
15	57.7(10.7)	6.12(1.90)	.949(.041)	4.38(1.14)	5.86(.450)	203.(30.9)
16	63.1(11.7)	6.10(1.88)	1.28(.515)	4.87(1.27)	3.95(.588)	203.(30.8)
17	64.0(11.8)	6.08(1.88)	.719(.290)	4.50(1.17)	4.96(.378)	203.(30.8)
18	45.2(8.69)	4.58(1.47)	.770(.313)	2.25(.387)	2.58(.205)	158.(24.2)
19	44.3(8.54)	4.58(1.47)	.560(.228)	2.05(.540)	2.59(.206)	158.(24.2)
20	47.5(9.11)	4.59(1.46)	.650(.264)	2.70(.710)	4.28(.339)	154.(23.7)
21	47.0(9.00)	4.53(1.44)	.969(.394)	2.08(.547)	4.29(.340)	155.(23.7)
22	46.4(8.90)	4.76(1.52)	.490(.199)	2.25(.592)	5.58(.442)	155.(23.7)
23	38.5(7.49)	4.71(1.53)	.620(.253)	3.00(.792)	5.67(.457)	136.(21.0)
24	38.6(7.51)	4.63(1.50)	.590(.241)	3.35(.885)	5.67(.457)	136.(21.0)
28	36.4(7.03)	9.01(2.90)	2.20(.895)	2.20(.580)	5.51(.441)	132.(20.2)
29	18.0(3.75)	2.14(.739)	1.75(.727)	.940(.253)	6.77(.587)	61.2(9.58)
30	49.0(9.29)	5.99(.189)	2.40(.972)	3.75(.983)	6.63(.519)	176.(26.9)

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)
31	49.1(9.31)	6.08(1.92)	2.70(1.09)	3.94(1.03)	6.63(.519)	176.(26.9)
32	46.5(8.71)	8.69(2.72)	5.94(2.40)	11.0(2.86)	7.96(.616)	182.(27.7)
33	58.4(10.9)	4.19(1.30)	2.70(1.09)	2.57(.671)	7.83(.603)	204.(30.9)
34	62.8(11.7)	4.33(1.34)	1.45(.584)	2.57(.670)	7.84(.601)	203.(30.8)
35	61.5(11.4)	4.49(1.39)	1.45(.584)	2.50(.652)	7.86(.602)	212.(32.1)
36	21.6(4.44)	2.13(.726)	1.80(.745)	1.72(.461)	6.89(.588)	75.8(11.8)
37	9.22(2.00)	1.37(.493)	1.90(.797)	2.13(.580)	6.31(.570)	33.1(5.24)
38	48.1(9.08)	6.49(2.04)	4.79(1.94)	3.13(.819)	16.8(1.31)	165.(25.2)
39	69.1(12.4)	7.73(2.32)	1.20(.478)	2.47(.637)	17.2(1.27)	282.(42.5)
40	58.6(10.7)	12.9(3.94)	1.75(.701)	1.88(.487)	10.5(.786)	228.(34.4)
41	33.7(6.51)	10.3(3.29)	1.40(.569)	2.72(.716)	8.88(.708)	139.(21.3)
42	20.6(4.05)	12.8(4.20)	2.20(.899)	2.10(.556)	7.98(.650)	116.(18.0)
43	8.63(1.87)	2.06(.739)	1.75(.734)	2.66(.724)	7.44(.672)	27.1(4.29)
44	27.5(5.45)	5.61(1.85)	2.15(.270)	4.70(.616)	7.48(.616)	112.(17.3)
45	17.5(3.66)	1.95(.674)	1.97(.819)	1.56(.420)	6.32(.549)	61.2(9.58)
46	49.0(9.28)	6.58(2.07)	4.30(1.74)	6.26(1.64)	10.9(.849)	175.(26.8)
47	46.6(8.74)	8.88(2.78)	8.99(3.63)	11.9(3.11)	10.8(.838)	171.(26.0)
48	60.5(11.3)	4.60(1.43)	1.85(.745)	2.20(.573)	10.7(.822)	207.(31.4)
49	65.0(12.0)	4.71(1.45)	1.70(.683)	2.35(.611)	9.38(.714)	217.(33.0)
50	9.30(2.01)	1.47(.525)	1.80(.755)	1.66(.451)	6.98(.628)	38.5(6.09)

	Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)
9)							
7)							
9)	51	75.1(13.4)	8.76(2.62)	2.20(.877)	1.94(.500)	15.4(1.14)	276.(41.4)
8)	52	19.2(3.80)	12.4(4.07)	1.90(.778)	1.56(.414)	7.13(.586)	112.(17.2)
1)	53	56.2(10.3)	13.2(4.03)	1.55(.622)	1.66(.431)	8.44(.637)	229.(34.7)
	54	35.1(6.77)	10.5(3.37)	1.80(.732)	2.13(.561)	7.80(.623)	136.(20.9)
8)	55	5.70(1.25)	2.16(.785)	1.90(.800)	2.15(.587)	6.06(.555)	29.3(4.65)
24)							
.2)	56	33.5(6.64)	5.62(1.85)	2.50(1.02)	2.88(.764)	5.52(.453)	111.(17.2)
.5)	57	51.0(9.61)	6.41(2.01)	2.99(1.21)	4.93(1.29)	9.05(.704)	190.(28.9)
.4)	58	47.5(8.89)	9.04(2.82)	6.14(2.48)	10.6(2.77)	7.85(.606)	194.(29.5)
	59	59.0(11.0)	4.44(1.38)	1.55(.624)	3.57(.930)	10.8(.825)	219.(33.2)
.3)	60	57.7(10.8)	4.44(1.38)	1.20(.483)	3.21(.837)	11.0(.843)	205.(31.1)
.0)							
29)	61	84.5(14.9)	8.51(2.52)	.399(.159)	1.93(.496)	17.9(1.30)	293.(43.9)
.3)	62	11.7(2.52)	1.91(.676)	1.45(.606)	1.43(.388)	6.05(.539)	42.4(6.69)
58)	63	21.1(4.16)	12.2(3.98)	2.20(.559)	2.01(.559)	8.08(.660)	118.(18.2)
	64	35.8(6.88)	10.4(3.33)	.290(.118)	2.78(.731)	10.1(.804)	152.(23.2)
3.8)	65	54.5(9.94)	13.7(4.18)	.290(.116)	1.96(.508)	11.9(.896)	252.(38.1)
3.0)							
1.4)	66	7.23(1.56)	3.17(1.13)	2.40(1.00)	3.46(.939)	7.62(.682)	41.6(6.56)
3.0)	67	27.6(5.48)	6.17(2.04)	2.05(.840)	3.99(1.06)	6.93(.570)	124.(19.2)
.09)	68	7.23(1.56)	3.17(1.13)	3.05(1.28)	3.46(.939)	7.62(.682)	41.6(6.56)
	69	50.8(9.51)	7.10(2.22)	3.71(1.50)	4.65(1.22)	7.44(.575)	199.(30.3)
	70	55.8(10.4)	6.99(2.17)	4.04(1.63)	4.75(1.24)	6.91(.531)	198.(30.1)

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)
71	51.9(9.73)	6.70(2.09)	4.69(1.90)	5.75(1.50)	7.02(.543)	184.(28.0)
72	53.5(9.76)	12.0(3.66)	11.4(4.57)	20.0(5.19)	9.94(.747)	221.(33.4)
73	58.1(10.8)	5.48(1.70)	1.45(.584)	3.70(.965)	9.49(.729)	197.(30.0)
74	53.9(10.1)	5.38(1.68)	2.16(.871)	3.50(.914)	9.76(.755)	193.(29.4)
75	35.6(6.89)	8.01(2.58)	3.15(1.28)	4.30(1.13)	14.7(1.18)	108.(16.6)
76	20.6(4.24)	2.92(.995)	1.87(.774)	3.00(.805)	5.12(.438)	71.8(11.2)
77	78.5(14.0)	7.65(2.28)	1.35(.537)	2.80(.721)	15.7(1.15)	272.(40.9)
78	33.1(6.37)	10.4(3.34)	1.46(.593)	3.25(.856)	7.44(.592)	154.(23.6)
79	57.1(10.4)	14.2(4.30)	.350(.140)	2.55(.660)	8.29(.620)	252.(38.0)
80	23.7(4.65)	11.8(3.84)	1.87(.764)	2.80(.741)	6.56(.533)	116.(17.9)
81	25.2(5.10)	4.29(1.44)	.700(.288)	4.52(1.21)	4.12(.346)	88.6(13.8)
82	27.6(5.52)	4.41(1.46)	.700(.288)	3.35(.892)	4.52(.375)	106.(16.5)
83	57.3(10.8)	4.18(1.31)	1.20(.484)	2.25(.588)	9.76(.756)	185.(28.2)
84	52.8(9.99)	3.74(1.18)	.419(.170)	2.00(.524)	9.96(.779)	177.(27.0)
85	36.0(6.98)	6.94(2.24)	3.35(1.36)	7.63(2.01)	6.68(.535)	141.(21.7)
86	11.8(2.51)	2.04(.721)	1.00(.418)	2.50(.678)	5.39(.479)	43.9(6.92)
87	21.4(4.29)	6.52(2.16)	2.97(1.22)	4.20(1.12)	16.6(1.38)	88.4(13.7)
88	78.0(14.0)	8.00(2.40)	1.15(.458)	1.25(.322)	16.6(1.22)	250.(37.6)
89	21.6(4.27)	12.2(3.99)	.300(.123)	1.50(.398)	5.79(.474)	111.(17.1)
90	52.8(9.68)	12.9(3.96)	1.00(.401)	.799(.208)	9.58(.725)	234.(35.4)

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)
.0)	91	33.1(6.38)	10.8(3.46)	1.15(.468)	2.20(.580)	6.96(.555) 141.(21.6)
.4)	92	33.1(6.47)	6.43(2.09)	1.66(.678)	1.47(.389)	5.00(.405) 136.(20.9)
1.0)	93	56.3(10.6)	4.87(1.52)	1.18(.476)	1.25(.327)	9.33(.722) 193.(29.3)
1.4)	94	56.0(10.5)	5.39(1.68)	1.22(.492)	1.05(.274)	8.90(.688) 181.(27.6)
3.6)	95	52.8(9.69)	11.1(3.41)	10.0(4.03)	14.7(3.82)	10.0(.759) 202.(30.6)
1.2)	96	27.8(5.48)	7.52(2.46)	3.28(1.34)	1.87(.495)	13.3(1.09) 105.(16.2)
3.9)	97	71.9(13.0)	7.64(2.31)	.589(.236)	.630(.163)	15.7(1.16) 250.(37.6)
3.6)	98	21.2(4.35)	3.26(1.11)	1.78(.736)	3.18(.852)	4.92(.419) 74.4(11.6)
8.0)	99	20.3(4.01)	12.7(4.16)	.849(.348)	2.70(.716)	5.09(.416) 115.(17.8)
7.9)	100	34.5(6.64)	11.0(3.51)	.500(.203)	3.40(.895)	7.51(.597) 142.(21.8)
3.8)	101	52.9(9.71)	13.1(4.02)	.509(4.02)	5.25(1.36)	8.87(.671) 227.(34.3)
6.5)	102	6.90(1.50)	1.92(.692)	2.50(1.06)	2.20(.599)	2.59(.235) 37.5(5.94)
8.2)	103	23.3(4.73)	3.92(1.32)	3.30(1.36)	3.43(.916)	5.06(.425) 88.4(13.7)
7.0)	104	25.4(5.13)	3.94(1.32)	3.05(1.26)	3.05(.814)	4.28(.358) 93.2(14.5)
1.7)	105	55.5(10.4)	3.70(1.16)	2.62(1.06)	1.88(.491)	9.99(.773) 192.(29.3)
5.92)	106	60.9(11.3)	3.60(1.12)	3.05(1.23)	2.15(.561)	9.87(.758) 185(28.2)
13.7)	107	41.6(7.91)	7.37(2.33)	8.97(3.64)	6.68(1.75)	7.80(.613) 155.(23.7)
37.6)	108	10.8(2.32)	1.61(.571)	2.41(1.01)	1.33(.361)	6.46(.575) 46.8(7.38)
17.1)	109	75.1(13.5)	7.41(2.23)	1.20(.479)	1.83(.472)	16.9(1.25) 253.(38.1)
35.4)	110	26.9(5.32)	5.50(1.81)	6.20(2.54)	3.10(.822)	15.6(1.28) 101.(15.5)
	111	20.7(4.05)	13.2(4.29)	2.20(.899)	1.62(.429)	7.03(.571) 124.(19.1)
	112	34.6(6.64)	10.9(3.49)	1.20(.488)	2.38(.626)	9.27(.737) 143.(21.9)
	113	51.5(9.46)	13.3(4.07)	1.83(.734)	2.00(.519)	11.4(.863) 225.(34.1)

Table 4

Additional Determinations

Figures in parentheses following data represent analytic errors (2σ) in same units as data. Asterisk indicates data used in calculation.

Sample	Potassium mg/l	Nitrate mg/l	Iron mg/l	Aluminum mg/l
12	-	0.32(0.5)	-	-
14	-	0.37(0.3)	-	-
15	-	0.48(0.4)	-	-
16	-	3.97(0.4)*	-	-
18	-	2.58(1.1)*	-	-
39	0.68(0.1)*	-	-	-
44	1.12(0.1)*	-	-	-
59	-	5.90(0.4)	0.0(0.1)	0.00(.07)
61	0.60(0.1)*	-	-	-
74	-	6.59(0.4)	0.0(0.1)	0.00(.07)
75	1.68(0.1)*	-	-	-
79	0.70(0.1)*	-	-	-
89	-	2.28(0.4)	0.0(0.1)	0.00(.07)
93	-	6.07(0.4)	0.0(0.1)	0.00(.07)
95	-	8.60(0.4)	0.0(0.1)	0.00(.07)
98	-	1.75(0.4)	0.0(0.1)	0.00(.07)

Table 5

Additional Calculations

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Sam- ple	Conductivity		Charge balance		Ionic strength ($\times 10^3$)	log S_c	log P_{CO_2}
	Calc.	Calc. as % of meas. (T)	imbal. ($\times 10^3$)	imbal. as % of tot. equiv.			
7	166	-	-.018	1	2.77	-0.74	-2.61
8	170	-	+.057	2	2.85	-0.79	-2.54
9	181	-	+.508	12	3.18	-0.98	-2.16
10	184	-	+.301	7	3.13	-0.99	-2.15
11	309	-	-.053	1	5.32	-0.14	-2.25
12	304	-	+.491	7	5.32	+0.37	-2.85
13	296	-	+.086	1	5.10	-0.35	-2.13
14	321	-	+.182	3	5.55	-0.04	-2.38
15	311	-	-.093	1	5.31	-0.07	-2.38
16	327	-	+.141	2	5.60	-0.06	-2.35
17	323	-	+.235	3	5.59	-0.06	-2.35
18	241	-	-.035	1	4.08	-0.71	-2.05
19	236	-	-.042	1	4.01	-0.71	-2.05
20	245	-	+.124	2	4.19	-0.60	-2.16
21	243	-	+.120	2	4.15	-0.60	-2.16
22	244	-	+.059	1	4.16	-0.61	-2.16
23	215	-	-.075	2	3.62	-0.48	-2.46
24	216	-	-.089	2	3.63	-0.48	-2.46

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)
28	224	-	+ .335	7	3.86	-0.20	-2.80
29	109	-	-.016	1	1.78	-0.93	-2.99
30	276	84	-.043	1	4.67	-0.43	-2.35
31	277	85	-.022	0	4.69	-0.43	-2.35
32	304	80	-.111	2	5.01	-0.72	-1.92
33	312	77	-.176	3	5.28	+0.50	-3.09
34	319	79	+ .014	0	5.48	+0.53	-3.10
35	320	76	-.150	2	5.47	+0.24	-2.79
36	129	91	-.099	4	2.09	-0.67	-3.00
37	68	107	-.077	6	1.05	-1.90	-2.98
38	286	99	+ .037	1	4.83	-0.18	-2.67
39	404	90	-.794	9	6.91	+0.01	-2.12
40	354	100	+ .137	2	6.21	+0.06	-2.41
41	231	93	+ .071	1	3.96	-0.14	-2.85
42	195	96	+ .049	1	3.32	-0.25	-3.10
43	68	102	+ .004	0	1.05	-2.16	-2.92
44	188	84	-.162	4	3.06	-0.29	-3.12
45	108	-	-.055	2	1.74	-0.95	-2.99
46	291	89	-.048	1	4.86	-0.99	-2.10
47	310	111	+ .138	2	5.08	-0.98	-1.86
48	319	85	-.139	2	5.45	+0.03	-2.60
49	334	83	-.049	1	5.73	-0.09	-2.41
50	72	95	-.159	11	1.11	-1.77	-2.97

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)
51	413	94	-.210	2	7.20	-0.27	-1.98
52	184	94	+.039	1	3.14	-0.32	-3.24
53	346	97	+.060	1	6.05	-0.61	-1.91
54	231	93	+.262	5	3.99	-0.22	-2.93
55	59	99	-.121	10	0.90	-2.94	-2.54
56	194	108	+.250	6	3.27	-1.14	-2.48
57	297	103	-.178	3	4.99	-0.44	-2.41
58	315	90	-.200	3	5.19	-0.50	-2.23
59	327	105	-.509	7	5.50	+0.48	-3.01
60	314	112	-.360	5	5.31	+0.49	-3.09
61	445	97	-.141	1	7.82	-0.42	-1.73
62	80	133	-.054	3	1.27	-1.44	-3.12
63	194	98	-.005	0	3.30	-0.38	-3.10
64	244	98	-.082	2	4.18	-0.44	-2.61
65	361	100	-.487	6	6.26	-0.27	-2.18
66	81	116	-.210	13	1.23	-1.89	-3.20
67	195	100	-.313	7	3.18	-0.28	-3.32
68	82	118	-.182	11	1.24	-1.89	-3.20
69	306	102	-.249	4	5.13	+0.33	-3.00
70	317	101	+.035	1	5.37	+0.44	-3.08

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)
71	306	99	-.023	0	5.12	+0.74	-3.47
72	385	96	-.167	2	6.26	-0.19	-2.39
73	315	100	-.095	1	5.36	+0.57	-3.20
74	303	104	-.248	4	5.12	+0.55	-3.23
75	226	110	+.422	9	3.81	-0.06	-3.12
76	127	109	-.015	1	2.06	-0.66	-3.07
77	417	104	-.157	2	7.26	+0.16	-2.25
78	239	97	-.161	3	4.04	-0.32	-2.59
79	366	105	-.223	3	6.36	-0.37	-1.91
80	197	106	+.112	3	3.36	-0.02	-3.27
81	153	95	-.016	1	2.52	-0.56	-2.91
82	169	90	-.150	4	2.78	-0.75	-2.53
83	295	102	-.010	0	5.04	+0.14	-2.82
84	278	98	-.205	3	4.73	+0.50	-3.25
85	286	94	-.125	2	3.87	-0.75	-2.35
86	82	96	-.103	6	1.29	-1.38	-3.00
87	173	96	-.172	5	2.82	-0.54	-3.01
88	400	98	+.227	3	7.06	-0.01	-2.15
89	183	99	+.119	3	3.16	-0.33	-3.04
90	340	97	-.239	3	5.90	-0.27	-2.10

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)
91	228	91	+ .097	2	3.92	-0.40	-2.58
92	207	-	- .098	2	3.48	-0.41	-2.60
93	297	88	- .081	1	5.09	+0.10	-2.76
94	291	97	+ .131	2	5.03	+0.44	-3.00
95	357	95	+ .116	1	5.89	-0.23	-2.27
96	195	97	+ .103	2	3.28	-0.16	-3.14
97	382	127	- .097	1	6.69	+0.09	-2.28
98	131	103	- .003	0	2.13	-0.73	-2.97
99	186	101	+ .043	1	3.18	-0.67	-2.69
100	234	100	+ .097	2	4.03	-0.94	-2.02
101	343	-	- .239	3	5.91	0.00	-2.40
102	63	79	- .120	9	0.95	-1.63	-2.96
103	152	87	- .013	0	2.45	-0.58	-2.93
104	157	85	+ .034	1	2.57	-0.77	-2.66
105	296	87	- .184	3	5.00	+0.24	-2.75
106	308	99	+ .157	2	5.26	+0.70	-3.21
107	269	106	+ .218	4	4.43	-0.43	-2.39
108	82	102	- .159	9	1.27	-1.47	-2.89
109	395	99	- .035	0	6.91	-0.06	-2.11
110	193	102	+ .010	0	3.15	-0.31	-3.04
111	198	97	- .003	0	3.38	-0.43	-2.86
112	237	99	- .105	2	4.07	-0.60	-2.36
113	342	-	- .205	3	5.91	+0.42	-2.84

APPENDIX 5

CAVE HOLLOW AREA DATA

Table 1

Chemical Analyses and Temperatures

Data in parentheses indicate values used in augmented analyses where no data available.

Analytic errors estimated to be similar to Mammoth Cave - Sinkhole Plain analyses.

Note 1: Alkalinity as mg/l HCO_3^- .

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Sam- ple	Cal- cium mg/l	Mag- nesium mg/l	Sod- ium mg/l	Potas- sium mg/l	Chlo- ride mg/l	Sul- fate mg/l	Alka- linity Note 1 mg/l	pH	Temp °C
1	17.5	2.29	1.73	0.21	2.54	3.9	62.6	8.30	7
2	16.6	2.08	1.39	0.21	2.49	3.5	56.1	8.31	7
3	16.2	2.06	1.35	0.21	5.82	3.5	55.4	7.66	7
4	16.3	2.08	1.38	0.21	4.27	3.3	55.3	7.54	7
5	10.6	1.55	0.65	0.19	0.92	3.1	34.7	7.58	7
6	9.98	1.47	0.67	-	0.84	2.6	34.8	7.56	7
7	9.73	1.46	0.65	-	1.08	2.7	33.8	7.58	7
8	9.41	1.48	0.66	-	2.98	2.7	32.6	7.34	7
9	8.81	1.42	0.59	-	1.06	2.7	29.4	7.52	9
10	1.14	0.67	0.52	-	0.67	3.1	7.2	6.02	9
12	13.7	1.98	0.76	0.20	1.47	-	46.3	8.15	11
15	1.90	1.46	0.60	-	1.17	-	5.7	5.95	11
16	5.21	1.88	0.58	-	0.97	-	17.8	7.14	9
17	7.94	1.96	0.55	0.22	0.92	-	26.7	7.13	9
18	1.92	1.70	-	-	0.53	-	6.3	6.58	12
19	1.88	1.41	-	-	0.57	-	6.3	6.30	13
20	5.86	1.49	-	-	0.28	-	29.0	7.32	10
21	12.5	1.63	-	-	0.60	0	41.0	7.84	11
22	1.75	1.33	-	-	0.65	-	13.9	6.38	13
23	1.51	1.27	-	-	0.65	-	6.5	6.39	12

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
24	12.9	1.82	-	-	-	-	40.9	7.48	11
25	26.6	3.09	-	-	-	-	110.2	7.94	12
26	2.01	1.98	-	-	-	-	15.4	6.47	22
27	37.9	5.41	-	-	-	-	157.4	7.85	9
28	26.8	2.90	-	-	-	-	108.7	8.12	12
29	27.3	3.07	-	-	-	-	114.0	8.13	12
30	1.76	1.56	-	-	-	-	11.0	6.91	18
31	37.7	4.96	-	-	-	-	154.1	7.93	10
32	27.4	3.07	-	-	-	-	113.2	8.16	11
36	1.70	1.38	-	-	-	-	8.6	6.88	13
37	32.8	4.27	-	-	-	-	133.8	8.33	9
38	24.8	2.74	-	-	-	-	95.9	8.21	11
39	31.0	4.23	-	-	-	-	132.0	8.38	9
40	30.3	3.92	-	-	-	-	127.6	8.23	8
41	1.23	1.12	-	-	-	-	6.4	6.56	4
42	19.9	2.58	-	-	-	-	72.7	8.35	9
43	17.8	2.03	-	-	-	-	61.3	8.25	11

Table 2

Additional Data and Calculations

NOTE 1: Sampling sites (see Text for further discussion) are: 1, Cave Hollow Stream below resurgence 15 meters above bridge on road up Big Sinking Creek; 2, Cave Hollow Spring (resurgence of Cave Hollow Stream); 3, Cave Hollow Stream at downstream limit of accessibility in Cave Hollow Cave; 4, West Tributary in West Tributary Cave; 5, West Tributary in Gurgle Pit cave 30 meters upstream from Site 4; 6, West Tributary 15 meters above swallow at base of upper shale unit; 7, West Tributary 15 meters upstream from Site 6; 8, Cave Hollow Stream at upstream limit of accessibility in East Tributary Cave a few meters above confluence of East Tributary; 9, East Tributary in East Tributary Cave a few meters above confluence with Cave Hollow Stream; 10, East Tributary near upstream limit of accessibility in East Tributary Cave; 11, East Tributary just upstream from swallow at base of upper shale unit. Site number in parentheses indicates duplicate for that site (and date) judged less representative.

NOTE 2: Gage height in inches above arbitrary datum (normalized to one location) measured at three locations on Cave Hollow Stream near Site 1. These values believed to approximate the relative stage of all streams in area.

All analyses assigned quality grade of S, "slight possibility of gross error" (see Appendix 3 and Appendix 4, Table 2, Note 5).

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Sam- ple	Site Note 1	Date (1968)	Gage Height Note 2	Conductivity Meas. (T)	Conductivity Calc.	Charge Imbal ($\times 10^3$)	Ionic Strength ($\times 10^3$)
1	1	2 Mar	-	-	106	-.035	1.70
2	2	5 "	4.7	-	98	+.004	1.57
3	(3)	5 "	4.7	-	103	-.102	1.60
4	3	5 "	4.7	-	100	-.045	1.58
5	1	17 "	15.7	72	63	+.030	1.02
6	2	18 Mar	15.0	70	60	.000	.974
7	3	18 "	15.0	-	60	.000	.958
8	(3)	18 "	15.0	69	62	.055	.961
9	1	6 Apr	10.5	61	54	+.014	.872
10	6	7 "	10.5	22	18	-.067	.256
12	1	21 Apr	7.2	99	77	+.086	1.26
15	6	27 Apr	-	30	18	+.115	.292
16	5	27 Apr	-	51	35	+.121	.585
17	4	27 "	-	66	49	+.123	.800
18	(7)	19 May	>5.1	31	17	+.118	.295
19	7	20 "	5.1	37	16	+.091	.269
20	5	20 "	5.1	69	41	-.068	.654
21	2	28 May	8.4	88	66	+.070	1.10
22	7	28 "	8.4	30	20	-.050	.320
23	11	31 "	9.2	28	15	+.055	.242
24	10	31 "	9.2	86	66	+.121	1.12
25	2	9 Aug	4.4	196	147	-.224	2.44

Sam- ple	(1)	(2)	(3)	(4)	(5)	(6)	(7)
26	11	9 Aug	4.4	40	23	+ .011	.389
27	10	9 "	4.4	270	209	- .244	3.53
28	2	2 Sep	4.0	196	145	- .209	2.41
29	2	6 Sep	4.5	200	150	- .251	2.49
30	11	7 "	4.5	32	18	+ .036	.306
31	10	7 Sep	4.5	261	205	- .239	3.45
32	3	28 "	4.9	185	150	- .237	2.49
36	11	23 Oct	5.	30	16	+ .057	.270
37	10	23 "	5.	230	178	- .203	2.99
38	2	1 Nov	4.3	175	132	- .107	2.21
39	9	1 "	4.3	235	173	- .268	2.89
40	8	1 "	4.3	225	168	- .255	2.81
41	11	11 Dec	5.4	20	12	+ .049	.206
42	10	11 "	5.4	138	106	+ .016	1.77
43	2	11 "	5.4	120	92	+ .052	1.54

Table 3

Additional Calculations

Sam- ple	(1) Ca ²⁺ ppm(a x 10 ⁴)	(2) Mg ²⁺ ppm(a x 10 ⁴)	(3) HCO ₃ ⁻ ppm(a x 10 ⁴)	(4) log S _c	(5) log P _{CO₂}
1	17.1(3.58)	2.22(.773)	60.8(9.54)	-0.63	-3.61
2	16.2(3.43)	2.03(.708)	54.5(8.57)	-0.69	-3.67
3	15.9(3.36)	2.02(.706)	54.7(8.60)	-1.35	-3.02
4	16.0(3.38)	2.04(.714)	54.7(8.59)	-1.46	-2.90
5	10.4(2.27)	1.53(.550)	34.4(5.45)	-1.80	-3.13
6	9.84(2.15)	1.45(.524)	34.5(5.47)	-1.84	-3.12
7	9.60(2.10)	1.44(.521)	33.5(5.31)	-1.84	-3.15
8	9.29(2.03)	1.46(.528)	32.4(5.13)	-2.11	-2.92
9	8.70(1.91)	1.40(.509)	29.2(4.63)	-1.87	-3.13
10	1.13(.263)	.665(.255)	7.24(1.17)	-4.83	-2.23
12	13.5(2.90)	1.95(.691)	45.3(7.14)	-0.87	-3.57
15	1.90(.439)	1.46(.557)	5.73(.921)	-4.78	-2.26
16	5.18(1.16)	1.87(.694)	17.7(2.83)	-2.68	-2.96
17	7.88(1.74)	1.95(.710)	26.6(4.22)	-2.34	-2.78
18	1.92(.443)	1.70(.648)	6.28(1.01)	-4.11	-2.85
19	1.88(.435)	1.41(.539)	6.29(1.01)	-4.27	-2.54
20	5.81(1.30)	1.48(.546)	28.9(4.60)	-2.24	-2.93
21	12.4(2.68)	1.61(.577)	40.5(6.40)	-1.27	-3.31
22	1.74(.402)	1.33(.504)	13.9(2.24)	-3.88	-2.28
23	1.51(.351)	1.27(.487)	6.51(1.05)	-4.38	-2.64
24	12.7(2.75)	1.80(.644)	40.5(6.40)	-1.61	-2.95
25	25.8(5.24)	3.00(1.01)	108.(16.7)	-0.46	-2.99

2
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1
28
34
35
39

	(1)	(2)	(3)	(4)	(5)
26	2.00(.457)	1.97(.744)	15.4(2.46)	-3.58	-2.30
27	36.3(7.11)	5.20(1.69)	153.(23.6)	-0.27	-2.75
28	25.8(5.26)	2.80(.944)	106.(16.4)	-0.28	-3.18
29	26.4(5.35)	2.96(.995)	111.(17.2)	-0.25	-3.17
30	1.75(.405)	1.56(.592)	11.0(1.76)	-3.33	-2.88
31	36.1(7.08)	4.76(1.55)	150.(23.0)	-0.20	-2.84
32	26.4(5.35)	2.96(.995)	110.(17.0)	-0.22	-3.20
36	1.70(.393)	1.38(.527)	29.8(4.81)	-4.59	-1.99
37	31.3(6.24)	4.06(1.34)	128.(19.8)	+0.08	-3.30
38	24.0(4.93)	2.65(.900)	92.8(14.4)	-0.28	-3.32
39	29.6(5.91)	4.01(1.33)	126.(19.5)	+0.10	-3.36
40	29.1(5.83)	3.75(1.25)	123.(19.0)	-0.06	-3.23
41	1.23(.288)	1.12(.432)	6.36(1.03)	-4.44	-2.84
42	19.4(4.05)	2.50(.865)	70.0(11.0)	-0.34	-3.58
43	17.4(3.68)	1.98(.693)	59.5(9.35)	-0.55	-3.55