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The Waters of Mystery Cave

Forestville State Park, Minnesota

Mystery Cave Resources Evaluation (Groundwater)

TECHNICAL REPORT

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[redacted]

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CHAPTER 1

INTRODUCTION

MYSTERY CAVE RESOURCES EVALUATION

This is the technical portion of the final report for the LCMR project **Mystery Cave Resources Evaluation (Groundwater)** and is one part of the Mystery Cave Resource Evaluation. Funding for this project was approved by the Minnesota Legislature M.L. 91, Chapter 254, Article 1, Section 14, Subd. 3(1), as recommended by the Legislative Commission on Minnesota Resources (LCMR), from the Future Resources Fund.

This part of the resources evaluation provides a technical analysis of the hydrology and chemistry of Mystery Cave in Forestville State Park. A summary of major findings is covered in a separate Interpretative Report. A separate Management Report contains recommendations for the protection of water quality; it also suggests directions for future research within the context of a resources evaluation. Additional recommendations for research of a more academic bent are included in this Technical Report.

LOCATION AND OPERATION OF MYSTERY CAVE

Mystery Cave is the largest cave in Minnesota and is in Fillmore County in the heart of southeast Minnesota's karst land (Figure 1.1). It is a joint-controlled network maze (Milske and others, 1983). A network maze consists of a net of intersecting passages with closed loops that formed more or less contemporaneously (Palmer, 1975; 1991). Over 13 miles of passage have been surveyed in sections known as Mystery I, II, and III (Figures 1.2 and 1.3). Mystery Cave has two entrances (Mystery I and II) and is owned and managed by the Minnesota Department of Natural Resources as part of Forestville State Park. The State Park staff conducts tours through the commercial parts of the cave from May to September.

PURPOSE AND GENERAL STUDY DESIGN

The groundwater portion of the Mystery Cave Resource Evaluation has five primary objectives:

(1) Inventory water chemistry and water quality throughout the cave,
(2) Identify the sources and sinks of cave waters,
(3) Measure the response of cave waters to recharge and other events,
(4) Measure the response of cave waters to human activities, and
(5) Identify seasonal hydrologic and chemical trends.

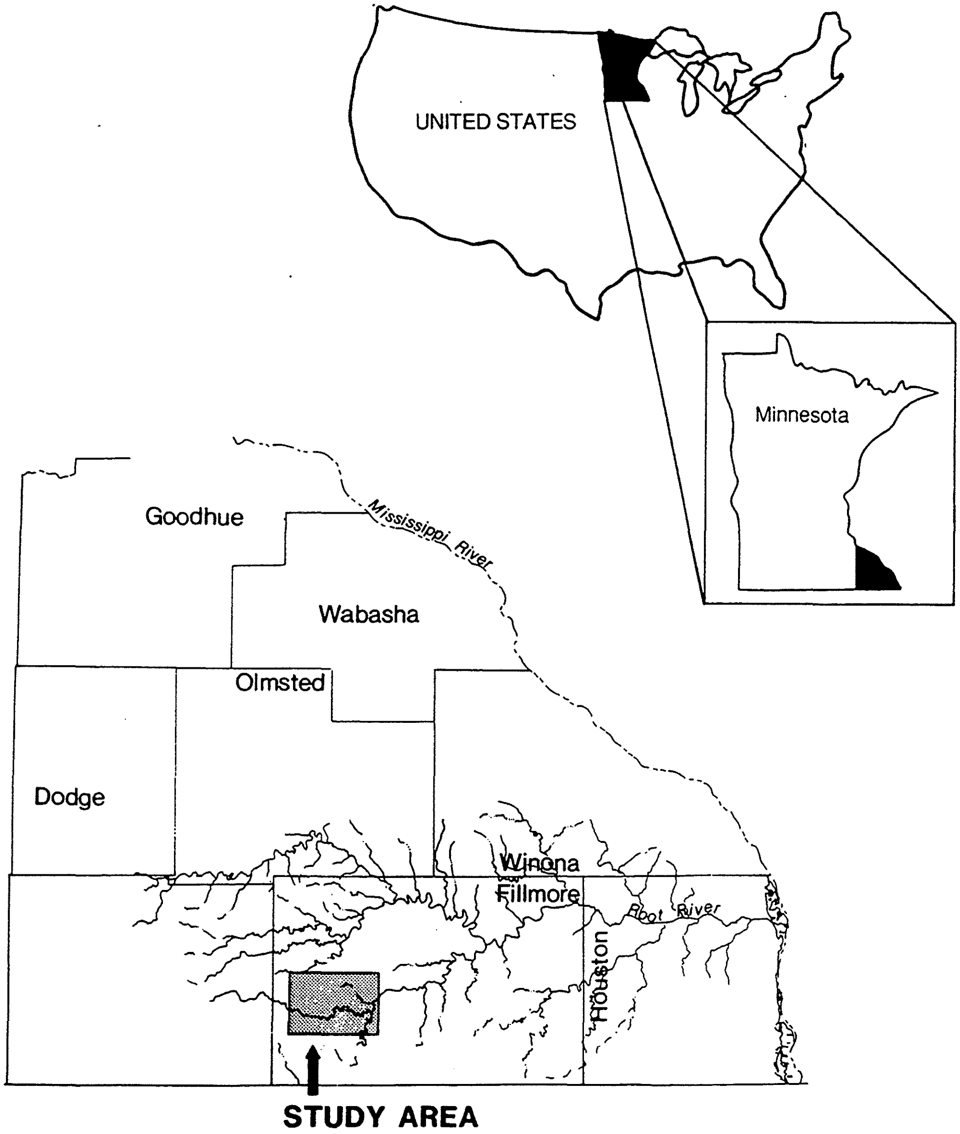
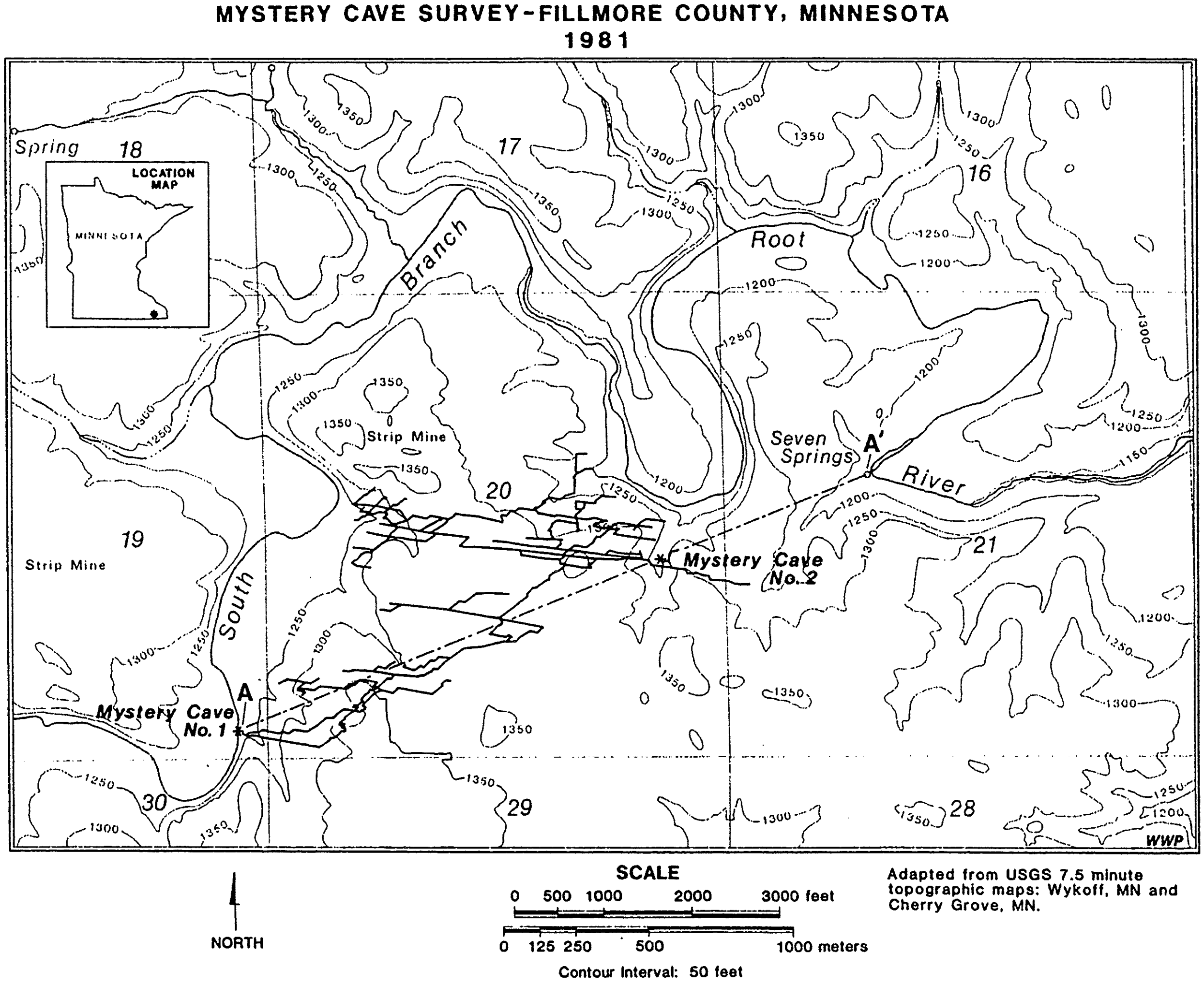


Figure 1.1. Location of Mystery Cave. From Mohring and Alexander (1986).



MYSTERY CAVE SURVEY-FILLMORE COUNTY, MINNESOTA
1981

Adapted from USGS 7.5 minute topographic maps: Wykoff, MN and Cherry Grove, MN.

Figure 1.2. Topographic setting of Mystery Cave. From Milske (1983).

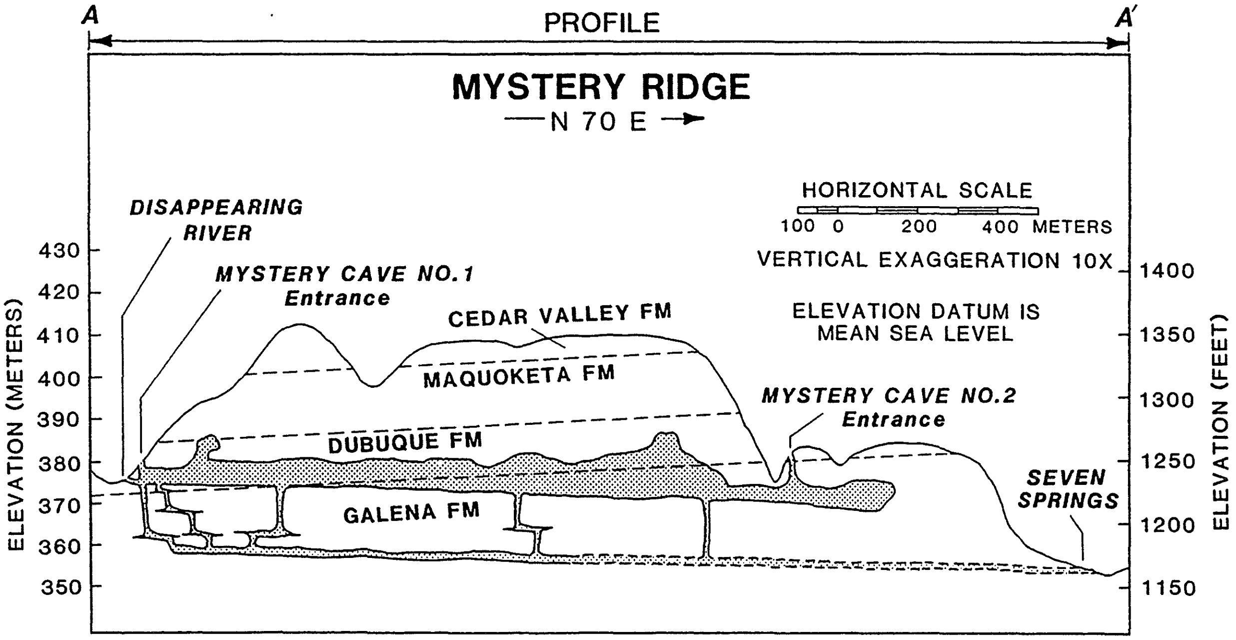


Figure 1.3. Profile of Mystery Cave. From Milske (1983).

To accomplish these objectives, we:

(1) Surveyed water chemistry and water quality (field parameters, major cations and anions, zinc, fecal coliform bacteria, atrazine, and volatile organic compounds) at 48 sites, including cave, well, spring, and surface waters,

(2) Sampled 11 cave water sites (pools, streams, waterfalls, flowstone flows, stalactite drips) on a periodic basis for selected water quality parameters,

(3) Measured precipitation and air temperature at a weather station on the South Branch of the Root River near the Mystery I entrance, for comparison with stage of a cave pool and a stream, and for comparison with drip rates at several drip sites,

(4) Measured stage of the Root River near the weather station,

(5) Measured stage, drip rates, water and air temperature, and conductivity at a cave stream, a cave pool, and a drip site, on a continuous basis for varying periods from March, 1992, through May, 1993, and

(6) Measured evaporation and condensation rates at selected sites.

ACKNOWLEDGMENTS

This project would not have been possible without the aid of a large number of people. The Minnesota Speleological Survey contributed cave maps. Without the thousands of hours their members spent exploring and surveying, we would know little of the extent of the cave. Without cave explorers and mappers, scientific studies in caves would be greatly impoverished, were they indeed even feasible.

Warren Netherton ably managed the project, providing services that went far beyond the call of duty. Warren made sure we had access to the cave, even at inconvenient times, and served as a surface contact person responsible for initiating rescue procedures in case we ran into trouble or stayed beyond projected return times. Warren kept us informed when storms disrupted power to our equipment, or when flooding threatened the weather station and other installations. Warren along with Mark White and other Mystery Cave and Forestville State Park staff helped save the weather station during the March 30-April 2 flood of 1993, even after waters had already crested the banks and risen part way up the weather station's support legs.

Art and Peggy Palmer provided preliminary results of their leveling surveys and helped measure the height of silt and sand deposits left by floodwaters at Flim Flam Creek. They also helped measure conductivities at different water levels during high-water stands at Blue Lake. Discussions with them, and later with Stein Erik Lauritzen, sharpened our interpretations.

A number of students at the University of Minnesota helped with sampling. Special thanks go to Rebecca Seal, Steve Mullen, and Paul Cutler. We benefited from questions posed on field trips by students of Roger Hooke's Geomorphology classes and Olaf Pfannkuch's hydrogeology classes. Their questions, and the questions

submitted by the 1993 Mystery Cave guides and staff, continually reminded us of the need to keep things clear and accessible to the public, even while attending to the details of the science.

We appreciate the ongoing permissions of the Jerry Rollie family to visit the resurgence springs of the Disappearing River. Numerous local landowners have tolerated, with varying degrees of humor, the often bizzare activities of karst hydrogeologists. This local support has been very valuable to our project.

CHAPTER 2

SAMPLING DESIGN AND METHODOLOGY

Much of the geochemistry of groundwater in karst is determined by processes operating on water in the soil, in the subcutaneous zone, or in the vadose zone of bedrock above the water table. Caves provide a unique opportunity to intercept and study these waters on their path to the phreatic zone. A major cave such as Mystery Cave allows flowing, dripping, seeping, or standing waters to be directly sampled and monitored at numerous sites without the necessity and expense of installing piezometers, drilling wells, or pumping water out of the ground. A variety of fundamental geochemical and hydrologic processes are then accessible for study.

CONSTRAINTS

While the cave environment provides significant opportunities to the geochemist, Mystery Cave imposes certain constraints. The waters can be sampled only where they are accessible and when they are accessible. Accessibility is limited by requirements of cave management, by physical and seasonal constraints, and by time and financial constraints.

Waters can be sampled and monitoring equipment can be installed only at locations where such activities do not negatively impact on cave resources, diminish the cave experience for visitors, or otherwise interfere with commercial operations. Mystery Cave is operated commercially from late May through early September. From about early October to early May, bats are in hibernation and are not to be disturbed. Sites near clusters of hibernating bats (or beyond them) are not accessible. Many sites along the commercial tour routes are accessible only to grab sampling during off hours. A number of sites that we would have liked to study in detail are inappropriate for monitoring that would require installation of equipment: such equipment would have been aesthetically displeasing or interfered with the movement of visitors. During the first year of the project, an extensive construction project in Mystery I limited access to some waters and prevented other waters from being sampled in a natural, unaltered state.

Many hydrologic sites in Mystery Cave are impractical to sample on a regular basis. They require too much effort and time to reach, pose relatively large risks to the health and safety of personnel, or expose equipment to damage during transport. Examples include sites that are relatively inaccessible past crawls or tight squeezes, sites beyond narrow vertical fissures that require technical climbing to negotiate, or sites that require lengthy trips with bulky equipment.

Additional constraints are imposed by weather conditions. During the winter, snow and ice limit access to cave entrances. The lower levels of the caves are subject to flooding and are accessible only during dry weather. The lower levels of the cave also have cave streams with water temperatures as low as about one degree Celsius in the winter and as high as about twenty degrees Celsius in the summer. In general, however, wet areas require the use of wet suits or other protection from hypothermia. Many of the wet areas are at or below the estimated deep cave temperature of 8.7°C most of the year.

All of the above considerations, as well as time and financial constraints, limited what could be studied. Because Mystery Cave is in an isolated rural setting, travel time and field time also posed significant constraints. Appendix 1 provides details on activities needed to prepare for field work and describes activities on a typical two-day trip to the cave.

The above constraints, and other considerations discussed below, made it necessary to modify a few sampling or monitoring techniques considered standard for studies of well or surface waters. It also was necessary to limit study parameters. For example, it was not practical to study discharge of the Root River, Flim Flam Creek, or Blue Lake; instead, we had to limit ourselves to measurements of stage. The detailed descriptions of sampling protocols and methodology are provided below so that results of this study can be properly interpreted and compared with results of other workers.

WATER SAMPLING DESIGN

Initial Sampling

An initial set of sampling locations was chosen in consultation with Mystery Cave and DNR staff in the summer of 1991. The purpose of the initial round of sampling was (1) to survey water quality at relatively accessible locations, with particular emphasis on waters visible along tour routes, and (2) to identify any waters of special concern. Later rounds of sampling in 1991 added additional sites that extended survey coverage of water quality to most major sections of cave and all major water types.

Periodic Sampling Locations

From the initial samplings, a set of ten periodic sampling locations was chosen with sites in Mystery I (3 sites), II (7 sites), and III (1 site). These sites were sampled roughly once a month from the fall of 1991 to May, 1993. As the project progressed, one of these sites was discontinued (Enigma Pit in Mystery III), due to difficulties with accessibility. One site in Mystery I was added (Lower Level Stream), so that there would be at least two periodic sampling locations for each major water type.

Periodic sampling locations were chosen (1) to give maximum coverage of all major water types; (2) to track zinc leaching from galvanized steel bridges on the Mystery I tour route; and (3) to obtain chemical data that could be correlated with other physical and chemical data. Four periodic sampling sites were selected for correlation of water chemistry with continuous measurements of stage, drip rates, water temperature, and water conductivity; these measurements were recorded on three data loggers, one serving each site (except at Blue Lake and Blue Lake Drips, where one logger served both sites). Continuous measurements of the stage of the

Root River and precipitation and air temperature at the surface Weather Station (near the Mystery I entrance) were also obtained for correlations with water chemistry and other parameters at periodic sampling sites in the cave.

As the project continued, additional sampling was undertaken to increase the coverage to sites not previously sampled, and to survey water quality at selected surface and other sites, including surface streams, a well, and springs draining Mystery Cave.

Screening for Environmental Parameters

To screen for potential contamination, a limited number of sites were sampled for fecal coliform bacteria, pesticides, and volatile organic compounds. Sites were chosen in consultation with Mystery Cave and DNR staff, to cover as much of the cave as possible (within budgetary constraints), particularly at sites deemed susceptible to contamination. Fecal coliform bacteria were sampled in summer and winter to check for seasonal variations at 18 sites in Mystery Cave and one site on the South Branch of the Root River. Atrazine was sampled in spring, summer, and winter to check for seasonal variations at 28 sites in Mystery Cave and one site on the Root River. Alachlor was also analyzed at 23 sites during the summer sampling. Volatile organic compounds were analyzed once (spring, 1993) at five locations. Further information on sampling design for environmental parameters is found in discussion of the results in Chapter 4.

SAMPLE LOCATIONS AND TERMINOLOGY

Water samples were collected at 38 sites in Mystery Cave, one site in Old Mystery Cave, the South Branch of the Root River at Mystery I, a surface stream at Mystery II, the House well at Mystery I, and at six springs on the South Branch of the Root River. Lists of all sample locations appear in Tables 2.1 and 2.2. Maps of the sample locations appear in Figures 2.1-2.3. Brief descriptions of sample sites in Mystery Cave are in Table 2.1.

Reference to the full names of sampling sites and individual samples rapidly becomes cumbersome in text, tables, and figures. To simplify references, the following terminology is used in this report.

Field sample ID. For Mystery Cave, usually a four digit identifier consisting of the abbreviation MC followed by a unique two digit sample location number. Example: MC01, which means Mystery Cave sample location number 1, which is at Turquoise Lake (Table 2.1). For other sites, which follow a similar scheme, see Table 2.2.

Sample designator and map ID. A two or three digit abbreviation for the sample location. Examples: TL, which means Turquoise Lake (Table 2.1); Sb, which means spring Sb of the Saxifrage Spring Cluster on the South Branch of the Root River (Table 2.2).

Table 2.3 provides a list of sampling sites (for Mystery Cave only) classified by water types , using the abbreviated sample designators of Table 2.2. A complete list of

Table 2.1. Mystery Cave Water Sample Locations.

Sample ID	Sample Designator	Sample Location	Mystery Location	Description
* MC01	TL	Turquoise Lake	I	Large pool behind concrete dam; originally a natural pool
* MC02	FFP	Frozen Falls Pool	I	Pool with flowstone; fed by Frozen Falls Drips, Drips Across Bridge, Pipe Organ, Across from Pipe Organ
* MC03	FFD	Frozen Falls Drips	I	Waterfall from ceiling joints and stalactites
MC04	EP	Enigma Pit	II	Waterfall over bedrock ledges
* MC05	RC	Rimstone Creek	III	Stream in basal fissures, flowing over silt and flowstone
* MC06	WWD	Wishing Well Drips	II	Waterfall from ceiling joints
MC07	BP	Boofer Pool	II	Small pool in Straddle Gallery
* MC08	BL	Blue Lake	II	Large pool; fast filling but slow draining through sediments and Blue Lake Spring
* MC09	GG1	Garden of the Gods 1	II	Stalactite drips
* MC10	BLD	Blue Lake Drips	II	Flowstone drips beneath flowstone mound near Blue Lake
MC11	CL	Coon Lake	II	Pool over silt and trail fill; fed by Coon Lake Drips
MC12	DJL	Dragon's Jaw Lake	III	Large pool
MC13	TP	Tar Pits	III	Small pool
MC14	LPL	Lily Pad Lake	III	Long shallow pool with flowstone floor
* MC15	CLD	Coon Lake Drips	II	Flowstone drips and stalactite drips
MC16	GG2	Garden of the Gods 2	II	Stalactite drips
MC17	GG3	Garden of the Gods 3	II	Drips from ceiling joint
MC18	GG4	Garden of the Gods 4	II	Drips from ceiling joint
MC19	NE	Needles Eye Drips	I	Stalactite drips
* MC20	LL	Lower Level Stream	I	Stream in basal fissures, flowing over silt
MC21	SSD	Sand Source Drips	III	Waterfall from ceiling joints
MC22	FRC	Formation Route Creek	III	Stream in basal fissures
* MC23	FFC	Flim Flam Creek	II	Stream in basal fissures
MC24	BLS	Blue Lake Spring	II	Springs in cave floor draining BL as overflow
MC25	PO	Pipe Organ	I	Drips from flowstone and stalactites; some flow from joints
MC26	DAB	Drips Across Bridge	I	Stalactite drips
MC27	BD1	Bedrock Drops 1	I	Hanging drops on underside of bed at Mystery I entrance staging area
MC28	BD2	Bedrock Drops 2	I	Hanging drops on underside of bed at start of passage to Formation Room in Mystery I
MC29	SL	Sugar Lake	II	Small shallow pool
MC30	APO	Across from Pipe Organ	I	Sheet flow and drips down flowstone; from joint on wall
MC31	CB	Ceiling Bar	I	Drops on painted metal bar on ceiling at Mystery I entrance staging area
MC32	BSS	Beyond Sand Source	III	Drips on flowstone from flow out of a wall joint
MC33	ID	Iron Drips	III	Stalactite drips
MC34	DJ1	Dragon's Jaw 1st Lake	III	Long shallow pool with flowstone
MC35	POP	Pipe Organ Pool	I	Small shallow pool below Pipe Organ
MC36	BCJ	Bridge Ceiling Joint	I	Waterfall from ceiling joints over the first bridge in Mystery I
MC37	RS	Ramp Stream	II	Shallow stream feeding intermittent pools at base of ramp in 5th Avenue
MC38	TLS	Turquoise Lake Source	I	Sheet flow from flowstone at end of Turquoise Lake

* Designates periodic sampling location

Table 2.2. Water Sample Locations in Old Mystery Cave, Surface Streams, and Springs.

Sampling Location in Old Mystery Cave

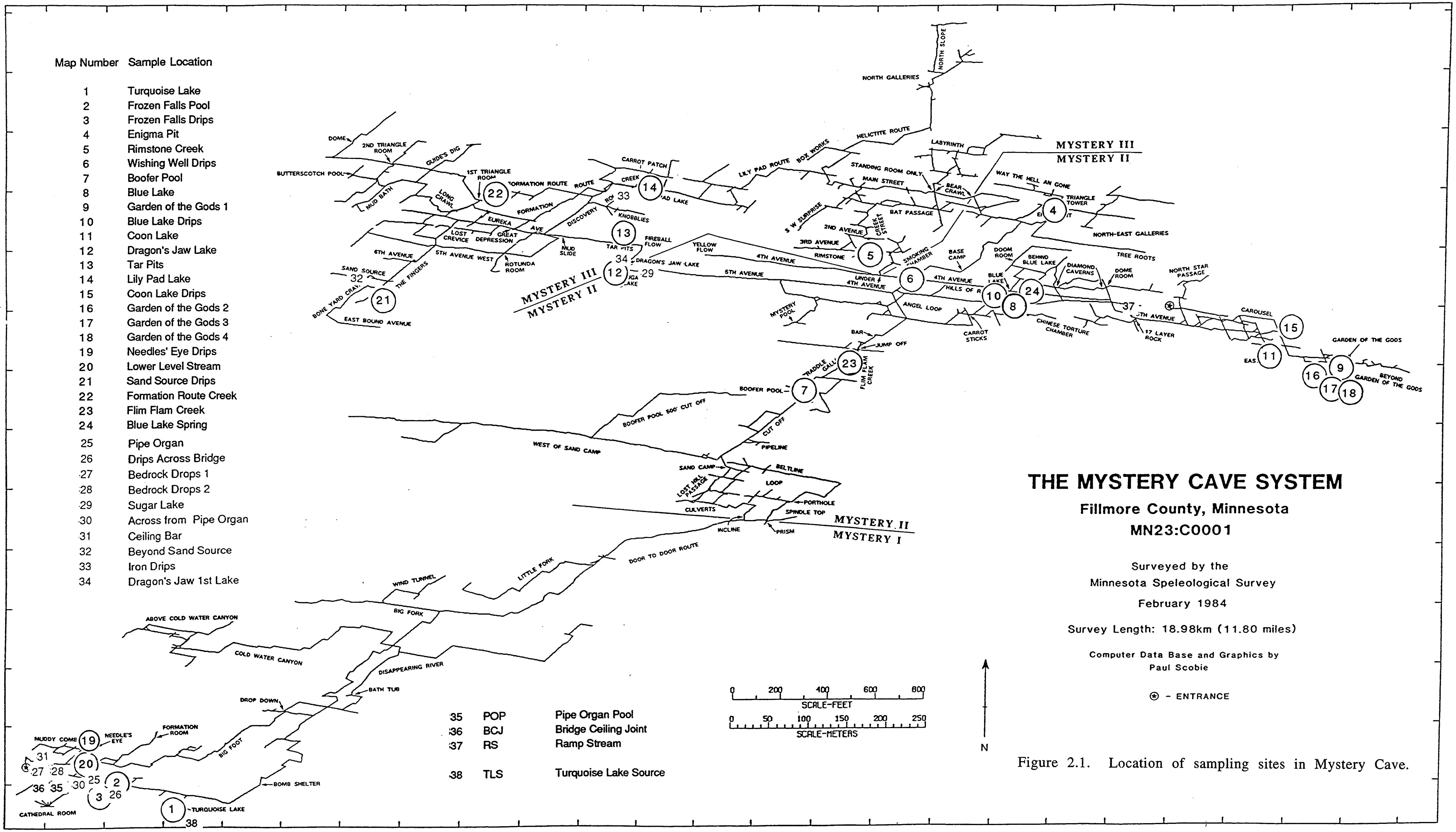
Sample ID	Sample Designator	Sample Location	Description
OM01	WOM	Old Mystery	Waterfall from ceiling joint in Old Mystery Cave

Surface Sampling Locations near Mystery Cave

Sample ID	Sample Designator	Sample Location	Description
HW01	HW	House Well at Mystery I	Well at Manager's residence at Mystery I
SB01	SB	S. Branch Root River	Root River at Mystery I entrance
SS2	SS2	Surface stream at Mystery II	Surface stream in gully at Mystery II entrance

Springs at the Rise of the South Branch of the Root River

Field Sample ID	Map ID (see Figure)	Location	Spring Cluster
DS2	Sb	S. Branch Root River	Saxifrage Springs
DS6	Sf	S. Branch Root River	Saxifrage Springs
DS9	Si	S. Branch Root River	Saxifrage Springs
DS11	Sk	S. Branch Root River	Saxifrage Springs
SS2	S3	S. Branch Root River	Seven Springs
Crayfish	CS	S. Branch Root River	Crayfish



Map Number	Sample Location
1	Turquoise Lake
2	Frozen Falls Pool
3	Frozen Falls Drips
4	Enigma Pit
5	Rimstone Creek
6	Wishing Well Drips
7	Boofer Pool
8	Blue Lake
9	Garden of the Gods 1
10	Blue Lake Drips
11	Coon Lake
12	Dragon's Jaw Lake
13	Tar Pits
14	Lily Pad Lake
15	Coon Lake Drips
16	Garden of the Gods 2
17	Garden of the Gods 3
18	Garden of the Gods 4
19	Needles' Eye Drips
20	Lower Level Stream
21	Sand Source Drips
22	Formation Route Creek
23	Flim Flam Creek
24	Blue Lake Spring
25	Pipe Organ
26	Drips Across Bridge
27	Bedrock Drops 1
28	Bedrock Drops 2
29	Sugar Lake
30	Across from Pipe Organ
31	Ceiling Bar
32	Beyond Sand Source
33	Iron Drips
34	Dragon's Jaw 1st Lake

35	POP	Pipe Organ Pool
36	BCJ	Bridge Ceiling Joint
37	RS	Ramp Stream
38	TLS	Turquoise Lake Source

THE MYSTERY CAVE SYSTEM

Fillmore County, Minnesota
MN23:C0001

Surveyed by the
Minnesota Speleological Survey
February 1984

Survey Length: 18.98km (11.80 miles)

Computer Data Base and Graphics by
Paul Scobie

⊛ - ENTRANCE

Figure 2.1. Location of sampling sites in Mystery Cave.

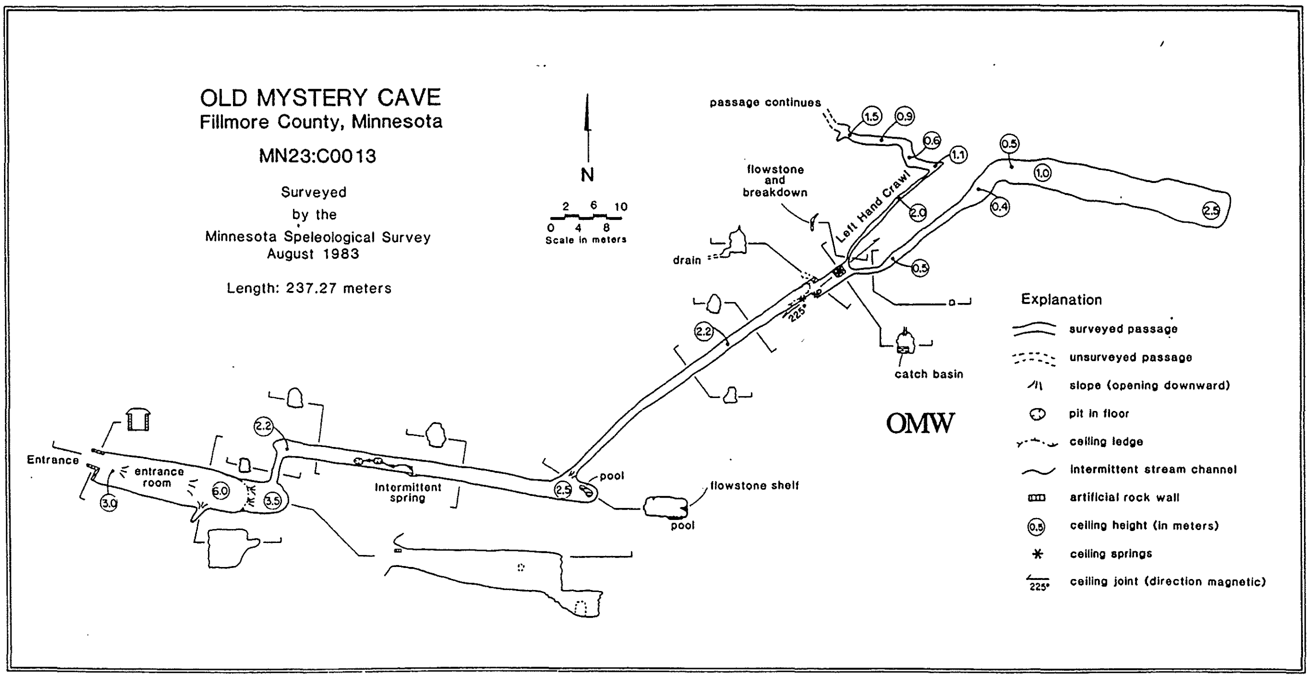
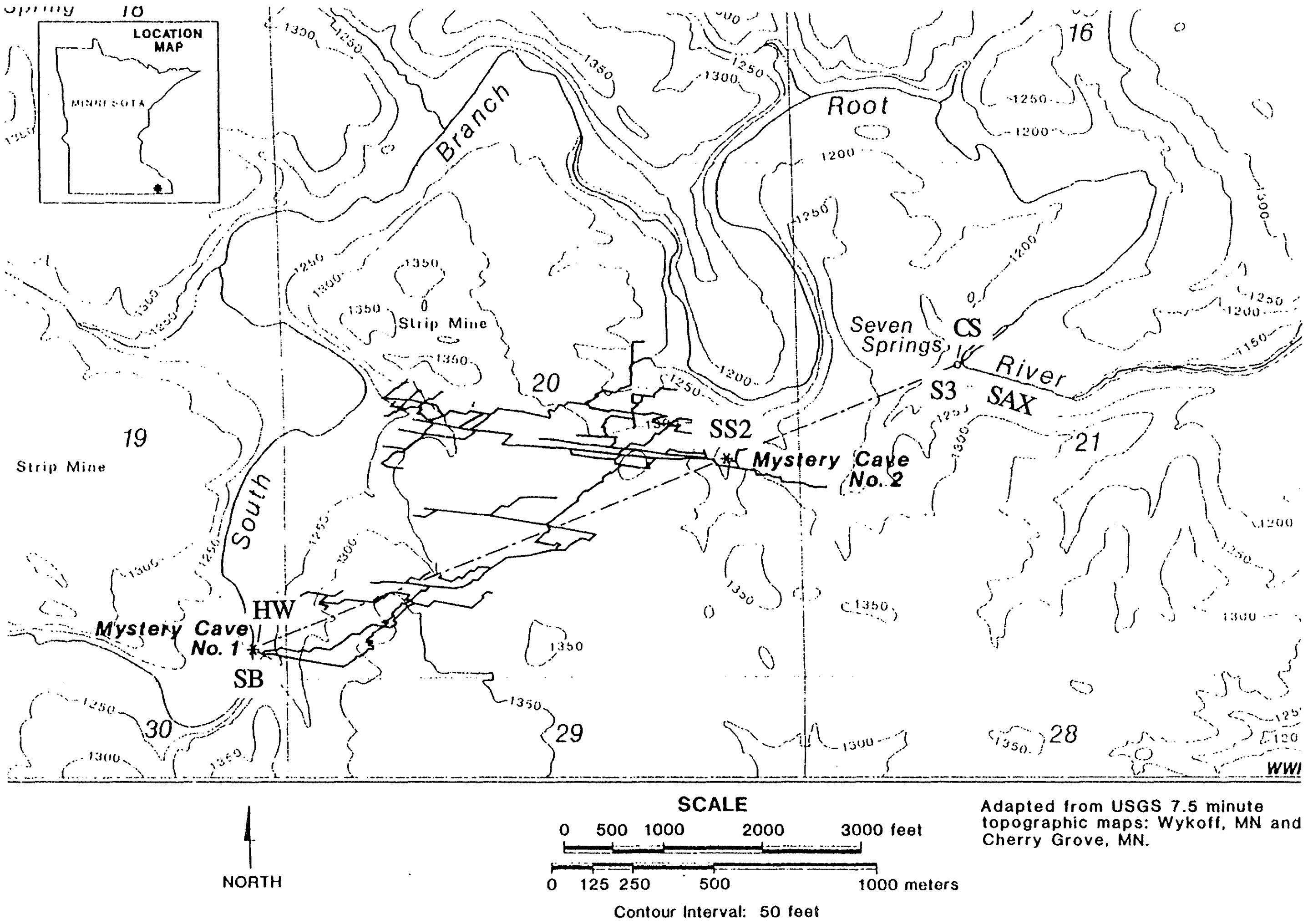


Figure 2.2. Location of sampling site in Old Mystery Cave. Sample site OMW, Old Mystery Waterfall, is at the catch basin.



Adapted from USGS 7.5 minute topographic maps: Wykoff, MN and Cherry Grove, MN.

Contour Interval: 50 feet

Figure 2.3. Location of surface sampling sites. SB = South Branch of the Root River, near Mystery I. SS2 = Surface stream at Mystery I (the intermittent stream below the entrance building). HW = House well at Mystery I. CS = Crayfish South spring. S3 = spring 3 of the Seven Springs cluster. SAX = generalized location of Saxifrage spring cluster. See Figure 3.5 for details of spring clusters.

sampled cave waters classified by water type, is in Table 2.4. Rationale for the classification of water types (into waterfalls and ceiling drips, streams, pools, flowstone drips and flows, stalactite drips, bedrock drops, and cave springs) appears in Chapter 4. Table 2.5 lists other sampled waters by type as wells, springs, or surface streams.

FIELD AND LABORATORY METHODS AND EQUIPMENT

Standard groundwater field methods and analytic procedures used in the Department of Geology and Geophysics at the University of Minnesota are explained in Appendix 2. These methods and procedures evolve as analytical protocols are improved and new equipment is acquired. Most of the methods and procedures are applicable in any ground water and many surface water investigations. However, as previously noted, there are certain practical constraints imposed by caves that alter procedures normally used for sampling wells. This section describes details of the actual field and laboratory methods and equipment used to investigate the hydrochemistry and hydrology of Mystery Cave.

Field Measurements and Sample Collection

Temperature, conductivity, and pH were measured in the cave. Temperature was measured on site with ASTM traceable (Method 63C) mercury glass thermometers designed for total immersion. These thermometers have smallest divisions of 0.1°C. To prevent breakage, thermometers were transported in one inch-diameter PVC pipe lined with foam rubber.

Conductivity was measured with Cole-Parmer 1483-40 conductivity meters or with YSI Temperature-Level-Conductivity (T-L-C) meters. Conductivity meters were calibrated with KCl standard solutions. At Flim Flam Creek, direct access to the stream was not usually feasible, because the stream is at the base of a deep (47 ft) narrow fissure. Therefore, temperature and conductivity were measured by lowering the YSI meter probe to the stream, which also allowed measurement of depth to water from a datum on the wall of the fissure. Some difficulties were encountered with performance of Cole-Parmer conductivity meters during early stages of the project. New meters were subsequently acquired and calibrated, and early conductivity measurements considered unreliable are not reported.

All pH measurements were conducted with Orion SA-210 pH meters and Orion 91-06 pH electrodes, with calibration by pH 7 and pH 10 buffers before and after measurements. Measurements of pH were made as close to the sample site as feasible, immediately following sample collection. Some sampling sites (*e.g.*, Lower Level Stream in Mystery I,; Flim Flam Creek, Enigma Pit, Rimstone Creek, Boofer Pool, Dragon's Jaw Lake, Tar Pits, Lily Pad Lake, and various other locations in Mystery III) are at relatively inaccessible locations past crawls or fissures through which it is not practical to transport the pH meter. In such cases, samples for pH measurement were collected in polyethylene bottles and transported to the pH meter, which was set up in a convenient central location. In Mystery I, the pH meter was usually set up near the Pipe Organ. Sampling sites were sufficiently close that pH could be measured within a few minutes of collection, except for samples from the Lower Level Stream, which were measured within 15-30 minutes of sampling. In Mystery II, the pH meter

Table 2.3. Water Types in Mystery Cave.

		Pools					
Waterfalls	Streams	Large Pools	Small Pools	Flowstone Drips & Flows	Stalactite Drips	Hanging Drops	Springs
FFD	FFC	TL	BP	BLD	GG1	BD1	BLS
EP	RC	FFP	CL	CLD	GG2	BD2	
WWD	FRC	BL	TP	GG3	NE	CB	
SSD	LL	DJL	SL	GG4	DAB		
BCJ	RS	LPL	POP	PO	ID		
	TLS	DJ1		APO			
				BSS			

Table 2.4. Sampled Cave Waters by Type.

	Sample Designator	Sample ID
Mystery Cave		
Waterfalls and Ceiling Drips		
Frozen Falls Drips	FFD	MC03
Enigma Pit	EP	MC04
Wishing Well Drips	WWD	MC06
Sand Source Drips	SSD	MC21
Bridge Ceiling Joint	BCJ	MC36
Streams		
Flim Flam Creek	FFC	MC23
Rimstone Creek	RC	MC05
Formation Route Creek	FRC	MC22
Lower Level Stream	LLS	MC20
Ramp Stream	RS	MC37
Turquoise Lake Stream	TLS	MC38
Pools		
Turquoise Lake	TL	MC01
Frozen Falls Pool	FFP	MC02
Blue Lake	BL	MC08
Dragon's Jaw Lake	DJL	MC12
Lily Pad Lake	LPL	MC14
Dragons Jaw 1st Lake	DJ1	MC34
Boofer Pool	BP	MC07
Coon Lake	CL	MC11
Tar Pits	TP	MC13
Sugar Lake	SL	MC29
Pipe Organ Pool	POP	MC35
Flowstone Drips and Flows		
Blue Lake Drips	BLD	MC10
Coon Lake Drips	CLD	MC15
Garden of the Gods 3	GG3	MC17
Garden of the Gods 4	GG4	MC18
Pipe Organ	PO	MC25
Across From Pipe Organ	APO	MC30
Beyond Sand Source	BSS	MC32
Stalactite Drips		
Garden of the Gods 1	GG1	MC09
Garden of the Gods 2	GG2	MC16
Needle's Eye	NE	MC19
Drips Across Bridge	DAB	MC26
Iron Drips	ID	MC33
Bedrock Drops		
Bedrock Drops 1	BD1	MC27
Bedrock Drops 2	BD2	MC28
In-cave Springs		
Blue Lake Springs	BLS	MC24
Old Mystery Cave		
Waterfalls		
Old Mystery Waterfall	OMW	OM01

Table 2.5. Classification of Other Sampled Waters.

	Sample Designator	Sample ID
Wells		
House Well at Mystery I	HW	HW01
Springs		
Crayfish Springs		
Crayfish South	CS	CS01
Seven Springs Cluster		
Seven Springs 3	S3	SS3
Saxifrage Springs		
Saxifrage Sb	Sb	DS2
Saxifrage Sf	Sf	DS6
Saxifrage Si	Si	DS9
Saxifrage Sk	Sk	DS11
Surface Streams		
South Branch Root River	SB	SB01
Surface Stream at Mystery II	SS2	SS2

was usually set up at (1) the Smoking Chamber (for Flim Flam Creek, Enigma Pit, Rimstone Creek, Wishing Well Drips, and samples from Mystery III); (2) Blue Lake (for Blue Lake and Blue Lake Drips); and (3) the bench near the entrance (for Coon Lake, Coon Lake Drips, and the Garden of the Gods samples). Generally, it was possible to measure pH within 15 minutes of sample collection, except for the samples transported from Mystery III, which were measured within a few hours. On several occasions, difficulties with the pH meter or electrode prevented field determinations of pH on one or two samples. pH was then remeasured in the lab on all samples with an aliquot of the alkalinity sample, and a correlation of lab vs field pH was used to estimate field pH for the missing values.

Before conducting pH measurements, buffers and the pH electrode were brought into thermal equilibrium with the sample. Where possible, sufficient water sample was collected to immerse buffers and electrode in a bucket with 3-4 quarts of sample, so that the buffers were at the same temperature as the original sample temperature. This procedure was not always feasible for samples with temperatures significantly above or below the deep cave ambient temperature of 8.7°C. For example, some cave streams (Flim Flam Creek, Formation Route Creek, the Lower Level Stream) have temperatures as cold as about 1°C in winter and as warm as 20°C in summer. These streams are at relatively inaccessible locations, thus precluding pH measurement at the original sample temperature. Such samples were warmed or cooled in buckets of available cave water and pH was usually measured at 8-9°C.

Samples for analysis of anions and cations were collected in polyethylene bottles from June to December, 1991, after which teflon bottles were used for nearly all cation analyses. Teflon bottles were substituted for polyethylene bottles for cation analysis so that sampling for zinc also could be performed on the same sample. (For a more complete discussion of the need for teflon bottles, see the section on zinc.) Cation samples were acidified in the field to an approximate pH of 2.5 with several drops of reagent grade HCl (initially) or HNO_3 (after the switch to teflon bottles) to retard precipitation of cations. Samples for analysis of alkalinity (300-500 ml) were collected in polyethylene bottles.

At streams and pools, samples were collected directly in the bottles. At waterfall-, ceiling drip-, and stalactite drip sites, samples were collected in plastic bags placed over five quart plastic buckets. An attempt was made to minimize collection times so that waters not in equilibrium with local cave conditions would remain close to their original temperatures and would change as little as possible chemically. In most cases sufficient water was available to triple rinse bottles before collecting the final sample. During the fall and winter, low drip rates at some stalactite and flowstone drip locations (*e.g.*, Garden of the Gods) precluded triple rinsing, and as much as 6-12 hours were required to obtain sufficient water for measurement of field parameters and complete filling of sample bottles. At Flim Flam Creek, a 250 ml polyethylene bottle was used to collect water samples, which were poured into regular sample bottles after pulling up the 60-ft line used to raise and lower the collection bottle. Samples of sessile drop waters on bedrock (bedrock drops) were collected with a syringe and filtered with 0.45 micron glass fiber filters. All other waters were collected unfiltered unless they were turbid.

Samples were stored in ice chests upon removal from the cave, then stored at 4°C in the lab pending analysis.

Alkalinity was measured in the field, or as soon as possible upon returning to the lab, generally within 24-36 hours of collection. Duplicate samples titrated in the field and in the lab at varying times up to several weeks later showed no significant differences in alkalinity. Alkalinity was measured by colorimetric titration using 1.600 N H_2SO_4 and a Bromcresol Green-Methyl Red indicator to pH 4.5, using a Hach digital titrator. Titrations were normally performed three times on weighed samples of about 100 g and averaged. At several sites (mostly Rimstone Creek samples during higher flows) color interferences were observed; Gran plots were then made to obtain alkalinity.

Analysis of Cations, Anions, and Trace Metals

Cations were measured by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) in the Geochemistry Lab at the University of Minnesota by a Perkin-Elmer/Sciex Elan 5000 ICP-MS. Anions were measured by ion chromatography using a Dionex Series 4000I, following EPA method 300.0, "The Determination of Inorganic Anions in Water by Ion Chromatography." Further details appear in Appendix 2.

Fecal Coliform Bacteria

Samples were collected in polyethylene bottles provided by the Olmsted Community Health Center Environmental Lab at Rochester, Minnesota. Pool and stream waters were collected by carefully immersing the bottles directly in the water, taking care not to touch the bottle lip or cap, or to touch the bottle lip against bedrock or sediment. Drip and waterfall waters were collected in new plastic bags opened over plastic buckets. When sufficient water was obtained, the bags were carefully closed, removed from the buckets, and then punctured with a clean knife to provide a thin stream that could be directed, after a suitable cleaning period, into the sample containers. Sampes were cooled on ice and delivered the same evening for next-day analysis by the Environmental Lab. Total coliform bacteria were analyzed following procedures in Standard Methods for the Analysis of Water and Waste Water, 16th Edition (1985).

Pesticide Sampling and Analysis

Samples for analysis of pesticides were collected in 30 ml glass vials with teflon lined caps, following a triple rinse of the bottle. Samples were stored on ice in the field and at 4°C in the lab. Samples were analyzed within one week of collection.

Atrazine and alachlor were analyzed in the Hydrogeochemistry Laboratory at the University of Minnesota. We used enzyme linked immunosorbent assay (ELISA) techniques, using RaPID Assay ® tests developed by Ohmicron. According to the manufacturers data sheets (Ohmicron, 1992), the atrazine test detects atrazine and related triazines including various metabolites, or degradation products of atrazine. Cross reactivity of the test with triazine analogues is known for ametryn, propazine, prometryn, prometon, simazine, terbutryn, terbutylazine, desethyl atrazine, desisopropyl atrazine, cyanazine, and 6-hydroxy atrazine. Although the test is stated to have an estimated minimum detectable concentration of 46 ppt (parts per trillion, 10^{-12} g/g), a reasonable practical detection limit for the waters of this study, based on our experience, is 0.1 ppb (part per billion, 10^{-9} g/g).

The alachlor test detects alachlor and related chloroacetanilides. Cross reactivity of the test with chloroacetanilide analogues is known for metolachlor, butachlor, and propachlor. Although the test is stated to have an estimated minimum detectable concentration of 50 ppt, a reasonable practical detection limit for the waters of this study, based on our experience, is 0.1 ppb.

Volatile Organic Compounds

Samples for analysis of volatile organic compounds were initially collected in special unacidified amber glass vials. The water was then poured into pre-acidified amber glass vials so as to completely fill them and eliminate headspace. The vials were provided by Twin Cities Testing Corporation. Acidified bottles normally used for sample collection of well or surface waters were not used for initial collection because of the danger of introducing concentrated HCl into the cave waters. Samples were cooled on ice immediately upon collection (in the cave) and delivered to the Twin Cities Testing Corporation lab in Minneapolis. Samples were analyzed according to Minnesota Department of Health (MNDH) Method 465C.

DIGITAL DATA ACQUISITION SYSTEMS

Digital data acquisition systems were installed at one surface and four cave sites. The surface site, the Root River Weather Station, was installed in cooperation with Richard Lively of the Minnesota Geological Survey, to measure weather data and stage on the South Branch of the Root River. The weather station is located on a flood plain on the west side of the river, about 100 yards upstream of the Mystery I entrance. Monitored cave sites include Blue Lake, Flim Flam Creek, and Coon Lake Drips in Mystery II; these were installed to monitor hydrologic and chemical parameters at a cave pool, several drip sites, and a stream in the lower level of the cave. A stalactite drip site at the Needle's Eye in Mystery I was also monitored briefly in January, 1993, to test equipment used to measure drip rates. Further details on installations appear below and in discussions of results at each site.

Equipment, Programming, and Data Retrieval

Equipment at each site was run by a programmable Campbell CR10 data logger, which also recorded the data. At the Weather Station, air temperature and relative humidity were measured with a Vaisala HMP35C sensor. A Texas Electronics TE-525 tipping bucket rain gage (inch version) with a 6.064 in diameter collector ring was used to measure precipitation. A Druck pressure transducer was used to record stage. Data were collected at one minute intervals and stored as 30 minute samples (temperature and relative humidity), totals (precipitation), or averages. Further details of the instrumentation and programming at the Weather Station are given by Lively and Krafthefer (1993).

At the cave sites, air and water temperatures were measured with thermistor wires. Druck pressure transducers were used to measure stage. Texas Electronics TE-525 tipping bucket rain gages (metric version) with 9.664 in diameter collector rings were used to measure drip rates. Conductivity was measured as a resistance voltage with Cole-Parmer conductivity probes. Data loggers were programmed to initiate measurements and record data on time schemes that varied with the measurements and station. For Blue Lake and Flim Flam Creek, all data were collected at 1 minute intervals and stored as 15 minute averages. For the drip sites, data were collected as tips over 5 or 10 minute intervals (Coon Lake Drips, Needle's Eye Drips) or 15 minute intervals (Blue Lake Drips), and then converted to discharge as liters per hour.

The data loggers were installed in a metal ammunition can at the Weather Station and in plastic boxes at all other other sites. Commercial dessicants were used to prevent acumulation of moisture in the containers.

Data loggers at the Weather Station, Blue Lake, and Flim Flam Creek were initially run off line power from electrical lines specifically installed for this project (in cooperation with Richard Lively and the Radon and Meteorology portion of the Mystery Cave Resource Evaluation). Power supply units converted line power to 12 volt direct current. However, when power is interrupted, the data loggers loose both their programs and all recorded data. Line power was lost several times early in the project. Therefore, the cave systems were reconfigured to run off 12 volt gel cell batteries connected to trickle chargers run by the line power. Initially, 1.2 amp hour cells were used, but these proved unreliable in the 8.7°C cave, so they were replaced with 1.9 amp hour cells. At the weather station, the system was reconfigured to run off a 12 volt deep cycle marine battery. The battery was placed in an insulated box next to the station. To keep the battery warm in the winter, a pipe heating coil was installed inside the box. The heating coil had a thermostat set for 35°F.

Data were downloaded onto storage modules for transport to the lab, where data were then transferred to IBM compatible computers. Downloading was performed each time the cave was visited, which varied from roughly one to six weeks.

Equipment Used at Each Site

The following equipment was used in the hydrologic study:

1. Root River Weather Station

   data logger
   tipping bucket rain gage for precipitation
   probe for air temperature and relative humidity
   pressure transducer for stage

2. Blue Lake

   data logger
   tipping bucket rain gage for drip rates at Blue Lake Drips
   pressure transducer for stage
   thermistor wire for air and water temperature
   conductivity probe for water conductivity

3. Flim Flam Creek

    data logger
    pressure transducer for stage
    thermistor wire for air and water temperature
    conductivity probe for water conductivity

4. Coon Lake Drips
    data logger
    siphon-action rain gage for drip rates (initially)
    tipping bucket rain gage for drip rates

5. Needle's Eye Stalactite Drips
    data logger
    siphon-action rain gage for drip rates

Calibration of Stage on the Root River

The set up at the Weather Station includes a stilling well on the west bank of the Root River. The stilling well is connected to the river via a steel pipe that extends 10 feet into the water. At normal flows, the stream is about 1.5-2 ft deep in the vicinity of the pipe.

Calibration of stage was performed by linear regression of water levels in the stilling well (relative to the top of the stilling well) versus logger measurements. Water levels in the stilling well were most easily varied by rapidly filling the well with about 20 gallons of water, and then measuring declining water level with a fiberglass tape. This task required two operators, one at the logger and one at the well, and fast measurements of stage. The task had to be repeated numerous times to obtain sufficient data for a reliable calibration.

No attempt was made to convert stage to discharge. Discharge measurements would have been more useful than stage alone but insufficient field time and funding were available to perform the requisite flow measurements under varying flow conditions. In addition, there is the problem of obtaining discharge measurements when the river is iced over.

During a typical winter, the Root River freezes at the top during much of December and all of January. In cold years, the river is covered with ice throughout February and much of March. The river may well be completely frozen during the coldest periods. To prevent freezing of the water in the stilling well, and possible damage to the pressure transducer, a heat source consisting of a light bulb was installed several feet below the top of the well. That bulb was regularly checked and replaced by DNR staff during the winter of 1992, but was not successful in preventing freezing during the colder periods. When stage was calibrated after the March 30-April 2 flood, the pressure transducer functioned reliably, even though it may have been frozen in January or February and clearly was overpressured during the flood.

When the river is not iced over, the pressure measured by the pressure transducer depends on the depth of water alone. Calibrations of stage versus logger readings could be used reliably to transform logger readings into stage. However, when the river is iced over, the normal calibrations cannot reliably be applied. One simply does not know what conditions obtain: the water can be confined under pressure and it is not clear when such confining conditions operate. Nonetheless, a pressure response is recorded, and interesting (though poorly understood) results were obtained during the winter of 1992. The question is, how are they to be interpreted, and how are the data to be treated?

Considering the response of the transducer as a pressure response, there are two situations to evaluate:

(1) *The water pressure increases beneath the ice.* This is recorded as a rise in apparent stage, if the normal calibrations are used. A rise in water pressure could occur if additional snow and ice deposition depressed the ice cover. A rise in water pressure could also occur if water began to flow over the top of the ice, as occurs during periods of melting.

(2) *The water pressure decreases beneath the ice.* This is recorded as a fall in apparent stage, if normal calibrations are used. A fall in water pressure could occur abruptly if the ice cover cracked, releasing confined water. A fall in water pressure could also occur if the air temperature decreased significantly and discharge and water level decreased, so that water was no longer confined beneath the ice. If the ice cover were strong enough to support its load of snow, and did not appreciably sag, then the water level might fall significantly below the level of the ice.

In both cases, there are difficulties in deciding how to treat the data. The simplest approach, which was followed here, is to apply the normal calibration throughout the year. In interpreting the data, we then carefully note when the river was frozen over, based on (1) air temperature and (2) the observed pressure response. For the periods in which the river was thought to be frozen, the resulting stage readings are considered to be a kind of modified stage. These readings are therefore labeled with the term **equivalent stage**. In using this term, we do not mean to imply that the readings actually record stage, or a stage equivalent to a given static pressure that would be recorded were there no ice cover. We simply have a set of equivalent data. In other words, the "stage" data have been generated as if the measured pressures were generated by the normal calibration technique in which pressure readings are converted to stage by varying stage in the stilling well and correlating that stage with pressures recorded by the data logger.

Stage at Blue Lake and Flim Flam Creek

For Blue Lake and Flim Flam Creek, calibration of stage was based on linear regression of monthly logger measurements of water pressure (at the time of data downloads) with independent measurements of stage by fiberglass tape or YSI T-L-C meter. At Blue Lake, zero datum was set at the top of the third rail post from the west end of the bridge. Measurements were made by tape to the nearest 0.01 ft.

For Flim Flam Creek, datum was set as the center of an expansion bolt on an east-west cross fissure in the Straddle Galleries. Measurements were by the YSI T-L-C meter, as a depth to water, which was read to the nearest 0.01 ft. However, the uncertaintly in the measurement is somewhat larger (perhaps 0.02-0.04 ft), for several reasons. First, the fissure is not precisely vertical. Because measurements were always taken from the same place, with a hanging probe, this matters little;

instead of a precise vertical distance, we have a curved distance along the fissure wall, plus a free-hanging vertical distance. More important, the procedure at the top of the fissure is extremely cumbersome for one person. Nearly all visits to the site had to be made alone. It was then necessary to (a) hold the meter in the left hand while (b) leaning out over the fissure to wedge the meter against the opposite fissure wall. Simultaneously, (c) the right hand was used to raise and lower the probe (on about 46 ft of wire), while (d) checking for a positive electrical signal (as conductivity) indicating immersion of the probe. Next, fingers on the right hand had to (e) mark the point on the wire corresponding to the center of the bolt. This position had to be maintained while moving back onto the ledge to a safe spot where (f) the marked spot could be measured against a ruler on the back of the meter.

Blue Lake and Flim Flam Creek Stations: Installation and Maintenance

Relatively little routine maintenance of probes was performed at Blue Lake. The water at Blue Lake is normally clear. Although a scum (possibly derived from contact with two creosote-impregnated posts) is occasionally visible, along with floating calcite rafts, turbidity is low. The pool undergoes long periods of declining stage, punctuated by brief fill events (about one per year) triggered by storms that can raise stage 8-9 ft in a week or so. Initial installation at Blue Lake was during a period of extreme high stage. As water level declines below about 10 ft below the top bridge rail, the pool breaks up into smaller, shallow pools. The pressure transducer was installed within a PVC pipe and suspended so as to rest about 4 in above the pool floor, which consists of up to 4 in of mud overlying breakdown and speleothems (mostly fragments of raft cones). Purely by chance, the pressure transducer hangs in a low spot that includes a pool at low stage; water level has yet to fall below the pressure transducer. The conductivity probe and thermistor wire were initially hung together (attached by electrical tape) from the bridge adjacent to the PVC pipe, at a depth slightly higher than the pressure transducer. During low stage in the late summer and early fall of 1992, the pool level fell below the conductivity and water temperature probes. These were then rehung to remain within the pool at low stage. Because of the low turbidity, only occasional cleaning of the conductivity probe was deemed to be necessay. In addition, the thermistor wire is relatively brittle, and should not be bent or handled more than necessary, so the two wires were otherwise moved only to perform temperature and conductivity calibrations.

Flim Flam Creek flows within a narrow fissure in the Straddle Galleries, about 100 feet beyond a passage location known as The Bar. The data logger was installed about 43 ft above normal water level, on a ledge within the Straddle Galleries. A set of PVC pipes was used to protect the pressure transducer, the conductivity probe, and the thermistor wire, from damage by sediment and fast moving water during floods. The PVC pipes are 6 inches in diameter at the bottom, and are perforated to allow free movement of water. Higher sections of pipe are of smaller diameter (4 and 1.5 in). The pipes are attached by braided nylon cord to two chalkstones within the fissure, one about 11 ft, and the other about 23 ft above the stream floor. The pipes were attached in ten foot sections. Although the pipes are securely attached, they have limited strength, particularly at the joints. Consequently, they do not extend all of the way up the fissure. The pressure transducer was protected only in the basal 10 ft of one pipe. The conductivity probe and and thermistor wire were taped together and run in a second pipe that rises to about 25 ft. Regular maintenance was initially intended to include monthly cleaning of the conductivity probe, and regular but less frequent calibrations with KCl standards. However, it proved to be so difficult to move the conductivity and thermistor wires, and to replace them within the pipe, that checks were performed less frequently.

Air and Water Temperature Calibration at Blue Lake and Flim Flam Creek

When loggers were downloaded, independent measurements were usually made of water temperature and conductivity with mercury thermometers or YSI T-L-C meters for comparison with values on data loggers. Air temperature was recorded much less frequently with mercury thermometers, because of technical difficulties in obtaining reliable measurements. The thermistors and mercury thermometers are extremely sensitive to heat radiation by humans, or by carbide lamps normally used for illumination. To ensure thermal equilibrium between them, the bulb end of the thermometer was suspended adjacent to the end of the thermistor wire, and left for a period of at least several hours. Upon returning, a flashlight was used for illumination, and a value quickly read on the thermometer from a distance of about one meter. The logger was then checked for the current thermistor air temperature.

More extensive calibrations of water and air temperature probes were also conducted. In the cave, the water and air temperature probes were placed in containers of heated or cooled distilled water. A mercury thermometer was used to measure the temperature of the distilled water as the water approached thermal equilibrium with the cave. To ensure thermal equilibrium between distilled water, probes, and thermometer, the water was stirred vigourously for about one minute. Then the thermometer and logger temperatures were quickly read. Linear regression was used to obtain equations to correct logger readings.

Calibration of Conductivity Probes

Use of KCL standards. Golterman and others (1978), list the following conductivities for standard molalities of KCl, if distilled water of very low conductivity (not greater than 2 uS/cm at 25°C) is used for preparation of standards:

Solution	**KCl (Molality)**	**Conductivity (uS/cm at 25 deg C)**
1	0.0001	14.94
2	0.0005	73.9
3	0.001	147
4	0.005	717.8
5	0.01	1413
6	0.02	2767
7	0.05	6668
8	0.1	12900
9	0.2	24820

Conductivities of the waters of Mystery Cave range from well under 200 uS/cm at 25°C for dilute meltwaters in cave streams to over 1100 uS/cm at 25°C for some more concentrated drip and pool waters. Linear regression of molality vs. conductivity for KCl solutions within this range (solutions 1 to 5) gives

Equation 1 $$C_{25} = 1.3838 \times 10^5 (m_{KCl}) + 11$$

where

C_{25} = conductivity (µS/cm at 25°C), and
m_{KCl} = molality of KCl

with a correlation coefficient R of 0.999.

Standard solutions of KCl (about 100-2000 µS/cm at 25°C) were gravimetrically prepared using distilled water and oven-dried reagent grade KCl. Equation 1 was used to calculate the conductivities of the KCl standard solutions. Usually we prepared five to eight solutions and a distilled water control solution. The solutions were prepared and stored in 500 ml or 1 liter polyethylene bottles. These bottles were transported to the cave and stored overnight for equilibration to ambient cave temperature before commencing calibrations of probes at Blue Lake and Flim Flam Creek, or calibrating the portable Cole Parmer and YSI conductivity meters.

Available freshly prepared distilled water had a conductivity between about 5 and 10 µS/cm at 25°C. The conductivity of distilled water was observed to increase after preparation to about 20 to 25 µS/cm at 25°C in the same polyethylene bottles used for KCl standards. Similar increases were noted for the standards themselves. A possible interpretation is that carbon dioxide absorption (through container walls) raised conductivity. Because calibrations were to be conducted under field conditions, it was not feasible to maintain conductivities of distilled water under 2 µS/cm at 25°C, as recommended by Golterman and others (1978) for laboratory conditions. To correct for the excess conductivity, a Cole Parmer meter was used to measure the conductivity of the distilled water at a temperature close to 25°C. This conductivity was added to the values obtained by use of equation 1 to obtain a corrected conductivity for the standards.

The corrected standards were used to compare conductivities measured by the various conductivity probes on data loggers and the field meters. Let Cc_{25} = corrected conductivity of the standards at 25°C, and D = the difference between Cc_{25} and the conductivity measured by the instrument, corrected to 25°C (Ci_{25}). Then $D = Cc_{25} - Ci_{25}$. The closer D is to zero, the greater the agreement between the instrument and the KCl standards.

For comparison, it is most convenient to plot Cc_{25} vs D. A typical set of results is shown in Figure 2.4 for a Cole-Parmer and two YSI meters. The plot shows (1) relatively good agreement between corrected standards and D for conductivities less than 300 uS/cm at 25 °C. The plot also shows (2) an increase in D as Cc_{25} increases. Finally, the plot shows some differences between meters. The Cole Parmer meter agrees better with the standards, but differs from the YSI meters. The YSI meters performed similarly, except at the highest conductivity measured. Similar results were obtained for calibrations on other dates. However, results varied sufficiently to suggest that the calibrations of meters varied over time. For the most accurate work, it appears that conductivity meters ought to be calibrated against standards in the field each time they are used.

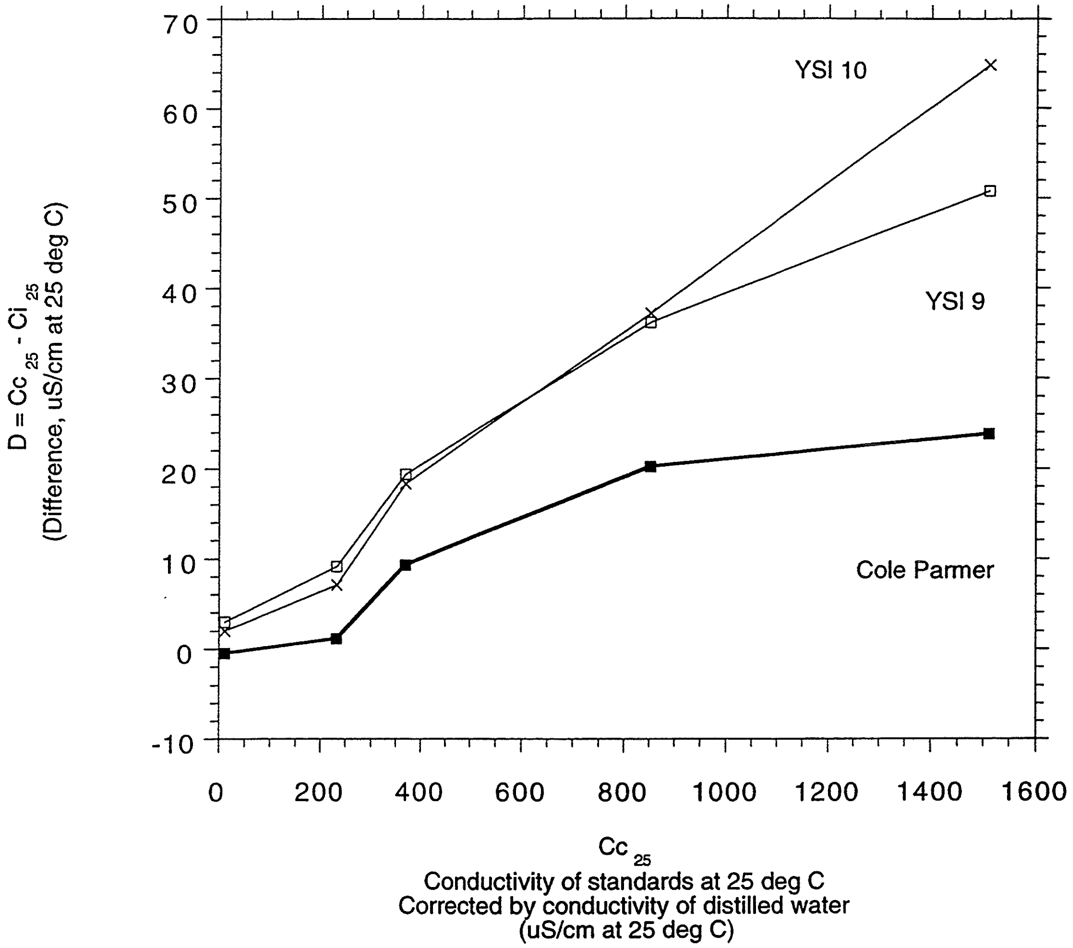


Figure 2.4. Plot of C_{c25} vs D for three conductivity meters. CP = Cole Parmer 1483-40 meter. YSI 9 and YSI 10 are YSI Temperature-Level-Conductivity (T-L-C) meters.

Conductivities measured by the three field meters on a variety of natural water samples also showed differences of 10-100 uS/cm at 25°C when measuring individual samples. Because these meters were used on a variety of projects, it was not possible to make all measurements with just one meter. Moreover, differences between the meters made it helpful to use both YSI and Cole Parmer meters. The Cole Parmer meters are smaller, and more useful for transport to far reaches of the cave. However, those meters had only short probes (4 ft), so could not be used at Flim Flam Creek or to measure conductivity at varying depths in deep pools. The YSI meter, which is designed for use in wells, was ideal for measurements of conductivity and water temperature at Flim Flam Creek and for measurements of conductivity in deep pools.

Despite these dificulties, linear regression of Ci_{25} vs Cc_{25} for each instrument (e.g., Figure 2.5) gave high correlation coefficients (R aproximately 0.9999) on each calibration date. This suggested that it might be reasonable to correct conductivity measurements made by different instruments, so as to minimize instrument variations. Therefore, measured field conductivities of water samples were later corrected by linear regression to reflect the varying responses of the instruments to measurements of the conductivity of the KCl standards. These corrected field conductivities were then used for analysis of the conductivity of water samples. Values of the original field measurements are given along with corrected values in the chemistry data tables (Appendix 3).

Correction of conductivity to a standard temperature. Conductivity is a strong function of the water temperature and the total dissolved solute load, and to a lessor extent for natural waters, the specific composition of the solutes (Hem, 1982; Miller and others, 1988). For most applications, conductivity is measured to obtain a rough estimate of the solute load.

To estimate the solute load in the field, temperature corrections must be made to approximate conductivity at a standard temperature. Most often the standard temperature used is 25°C, but many European studies use 20°C. Glaciologists work with waters close to 0°C, and some glaciologists use uncorrected conductivities (Collins, 1977; Fenn, 1987). However, meltwaters may vary by as much as about 10°C over a day at positions near the glacier, so corrections are often needed. This has prompted Smart (1992) to recommend correction to a low standard temperature of 0°C, to minimize errors resulting from compensations over large temperature ranges.

A variety of formulas have been used to correct conductivities to a standard temperature; all must be considered approximations to be tested for applicability in the specific study. Comprehensive reviews of temperature compensation are provided by Sorensen and Glass (1987), Miller and others (1988), and Smart (1992).

Many commercially available conductivity meters employ an approximate correction factor of about 2% $°C^{-1}$. Some employ a polynomial correction formula obtained by measuring conductivity of KCl standards over a range of temperatures. The latter approach was adopted in this study.

Miller and others (1988) derived the following equation to express the relationship between conductivity at 25°C (Ks) and the temperature of 0.01 N KCl solutions:

Equation 2 $$Ks = 774.1 + 23.54\,T + 0.07680\,T^2$$

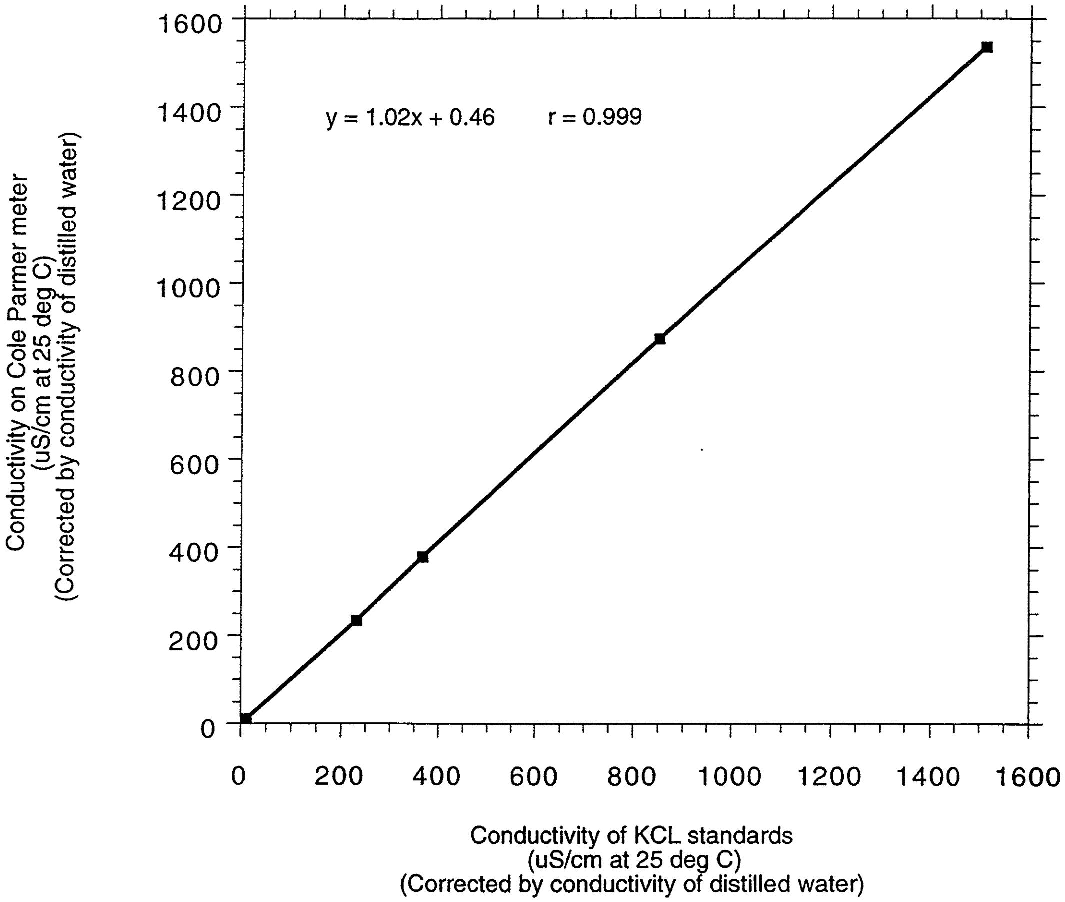


Figure 2.5. Linear regression of Ci_{25} vs Cc_{25} for a typical instrument calibration.

where

Ks = conductivity (µS/cm at 25°C), and
T = temperature (°C).

From this they derived a set of correction factors to convert conductivity at ambient temperature (K) to conductivity at 25°C (Ks), presented as their Table 4 (Miller and others, 1988, p. 7). From that table it is possible to derive the following polynomial:

Equation 3 $$f = 1.797 - 0.0468\ T + 0.000604\ T^2$$

where

f = correction factor, and
T = temperature (°C).

The correction factor f was used in this study to convert conductivity at ambient temperature to conductivity at 25°C:

Equation 4 $$C_{25} = C_a * f$$

where

C_{25} = conductivity (µS/cm at 25°C), and

C_a = conductivity (µS/cm at ambient temperature, 25°C).

Calibration of Conductivity Probes at Blue Lake and Flim Flam Creek. The conductivity probes used at Blue Lake and Flim Flam Creek were obtained from older-model Cole Parmer meters previously used in well studies. They were wired into Campbell CR10 data loggers in the lab and calibrated at about 25°C with KCl conductivity standards. As wired, they measured a ratio of resistances that was recorded in millivolts. At a constant temperature in the lab, the electrodes appeared to perform well with a 2500 mv excitation voltage. Regression of conductance voltage (1/resistance voltage) vs the corrected conductivity of KCl standards (C_{c25}) gave polynomial equations that appeared to adequately convert voltage to conductivity.

In the field, the probes initially also appeared to perform adequately. However, careful field calibration revealed inconsistencies that did not emerge until late in the project. These inconsistencies have been partly resolved but difficulties remain. Consequently, the readings from the data loggers are reported as conductance voltages (1/voltage reading on the data logger) rather than as conductivities per se. The conductance voltages can be interpreted along with other data to yield a coherent hydrochemical picture at Blue Lake and Flim Flam Creek, but the data are probably best considered a semi-quantitative surrogate for continuous measurements of conductivity.

When the problems were diagnosed, new conductivity probes were acquired and installed at Blue Lake and Flim Flam Creek in July, 1993. These probes performed much better and gave results consistent with KCl standards and the readings obtained independently from Cole Parmer and YSI conductivity meters. Data obtained with these newer probes confirms many of the results obtained with the probes before July, 1993. The newer data have been interpreted in an interim report (Jameson and Alexander, 1994a) and will be discussed in greater detail in a later report in which we will return to these calibration issues.

Evaporation and Condensation Rates

Evaporation and condensation rates were measured between September, 1992 and March, 1994. Fifteen evaporation pans were set at nine locations in Mystery II. One pan was briefly used at a single site in Mystery I. Pans with a surface area of about 305 cm^2 were covered with side-slotted baskets with solid bases. The baskets were turned upside down. The solid bases served as a roof to prevent drips from falling in. The slotted sides allowed free circulation of air. A-mass based technique was used to measure the amount of water in the pans at the start and end of one-month periods. Details of the technique are presented in Chapter 11.

CHAPTER 3

HYDROGEOLOGIC SETTING OF MYSTERY CAVE

PREVIOUS HYDROLOGIC STUDIES

Studies on the karst of southeastern Minnesota and northern Iowa have (1) delineated karst drainage basins through dye tracing (Mohring, 1983; Mohring and Alexander, 1986); (2) investigated variations in water chemistry at several sinking streams, major springs, and caves (Grow, 1986; Mullen, 1993a, b); and (3) applied methods of morphometric analysis and other techniques to study the distribution, genesis, and hydrology of sinkholes (Palmquist and others, 1976; Palmquist, 1979; Dalgleish and Alexander, 1984; Dalgleish, 1985). Additional studies on the hydrogeology of southeastern Minnesota's karst are reviewed by Mohring and Alexander (1986), and include studies by Broussard and others (1975), Giammona (1973), Wopat (1974), and Alexander (1980).

Major efforts are now in progress by several groups. These include the Minnesota Geological Survey/Minnesota Department of Natural Resources Fillmore County Geologic Atlas program. As part of that effort, Calvin Alexander's group at the University of Minnesota is making an inventory of the springs and stream sinks of Fillmore County, delineating karst drainage basins through dye tracing, inventorying and studying the distribution of sinkholes, and surveying the geochemistry and residence times of Fillmore County waters.

Milske (1982) and Milske et al. (1983) studied clastic sediments in Mystery Cave. They discuss modern flow paths in the lower levels of Mystery Cave and identify paleoflow paths. However, they say little about modern flow in the upper levels or recharge to the upper levels. Numerous dye traces (Mohring, 1983; Mohring and Alexander, 1986; Foster and others, 1990, and more recent unpublished traces) provide information on the complex primary flow system. Water sinks on the Root River, as described in detail later in this chapter, and flows through the cave's lower levels to base-level springs (Seven Springs, Crayfish Springs, Saxifrage Springs). Precise boundaries for several parts of the flow system have yet to be determined. Additional traces under very high- and very low-flow conditions would help to better define the flow boundaries and the range of travel times.

Before the onset of this study, few hydrochemical data were available for the Mystery Cave and surrounding flow systems. Grow's (1986) study included monthly samplings of water chemistry on the Root River at Mystery I and at Moth and Grabau springs, but did not survey waters in Mystery Cave. Water samples were collected in Mystery Cave by Tarun Sethi in 1991 as part of an Undergraduate Research Opportunity study at the University of Minnesota; these unpublished data were obtained from Sethi and are included in Appendix 4.

GEOMORPHIC SETTING AND LAND USE

Mystery Cave is in the Central Lowlands geomorphic province, in the drainage basin of the South Branch of the Root River in eastern Fillmore County (Figure 3.1a, b). The Root River drains east to the Mississippi River, dissecting an upland underlain by Paleozoic sedimentary rocks (Austin, 1972). Much of this upland consists of a mantled fluviokarst. Sweeting (1973) introduced the term fluviokarst to describe a karst terrane produced by a combination of fluvial and karst processes. A mantled karst has an extensive surface covering of unconsolidated deposits. In Fillmore County, loess is a major component of that mantle.

The Iowan Erosion Surface and the Loess Border

The South Branch of the Root River heads in Mower County on a part of the upland mantled by thin (<1 m) deposits of the Peoria loess (Figure 3.2a, b). Mason (1992) interprets this and a region to the north and west as a northern extension of the Iowan Erosion Surface. The Iowan Erosion Surface, as described by Mason et al. (1994, p. 44-45) is "a complex of erosion surfaces cut in pre-Illinoian glacial sediments during extensive and severe late Wisconsinian hillslope erosion (Ruhe et al., 1968; Ruhe, 1969)". West of the Iowan Erosion Surface is the eastern margin of Late Wisconsinian deposits of the Des Moines Lobe (Figure 3.2a).

The eastern margin of the Iowan Erosion surface is the loess border. The loess border is a region of abrupt thickening of the loess. Mason (1992) measured thicknesses of Peoria loess up to nearly 8 meters along the loess border in Fillmore County. The loess fines and to some extent thins to the east, indicating a source area from the west (Mason et al., 1994). The loess border extends southeast-northwest. At the scales of Figure 3.2a and 3.2b, the loess border is drawn as a distinct boundary and small outliers of loess >1 m or inliers of loess <1 m are not shown. At the scale of topographic maps, many small outliers and inliers may be mappable. Mason (1992) placed the loess border about one half mile south of most of Mystery Cave except for a section of thick loess just upslope of passages near Coon Lake Drips and the Garden of the Gods. Exposures of thick loess in gullies extending over parts of Mystery II and III (Figure 3.3), combined with hydrologic and chemical data, suggest that thick loess is more widely distributed near Mystery Cave. Much of Mystery Cave, particularly that part beneath the upland away from the Root River, apparently lies beneath the thicker loess. A more detailed mapping of the distribution and thickness of the loess would be helpful in sorting out hydrologic and chemical relationships, and might also help in further deciphering the sedimentologic and geologic history of Mystery Cave.

Topographic Setting

Mystery Cave lies beneath an upland plateau and the margins of the plateau along the Root River (Figure 1.2.). The elevation of the flat part of the upland above Mystery Cave is at 1330-1350 ft. Maximum local relief is less than 200 ft. The highest hilltops are at about 1370 ft. The sinkpoints near the Mystery I entrance are at about 1225 ft. The springs draining Mystery Cave and surrounding regions are spread out

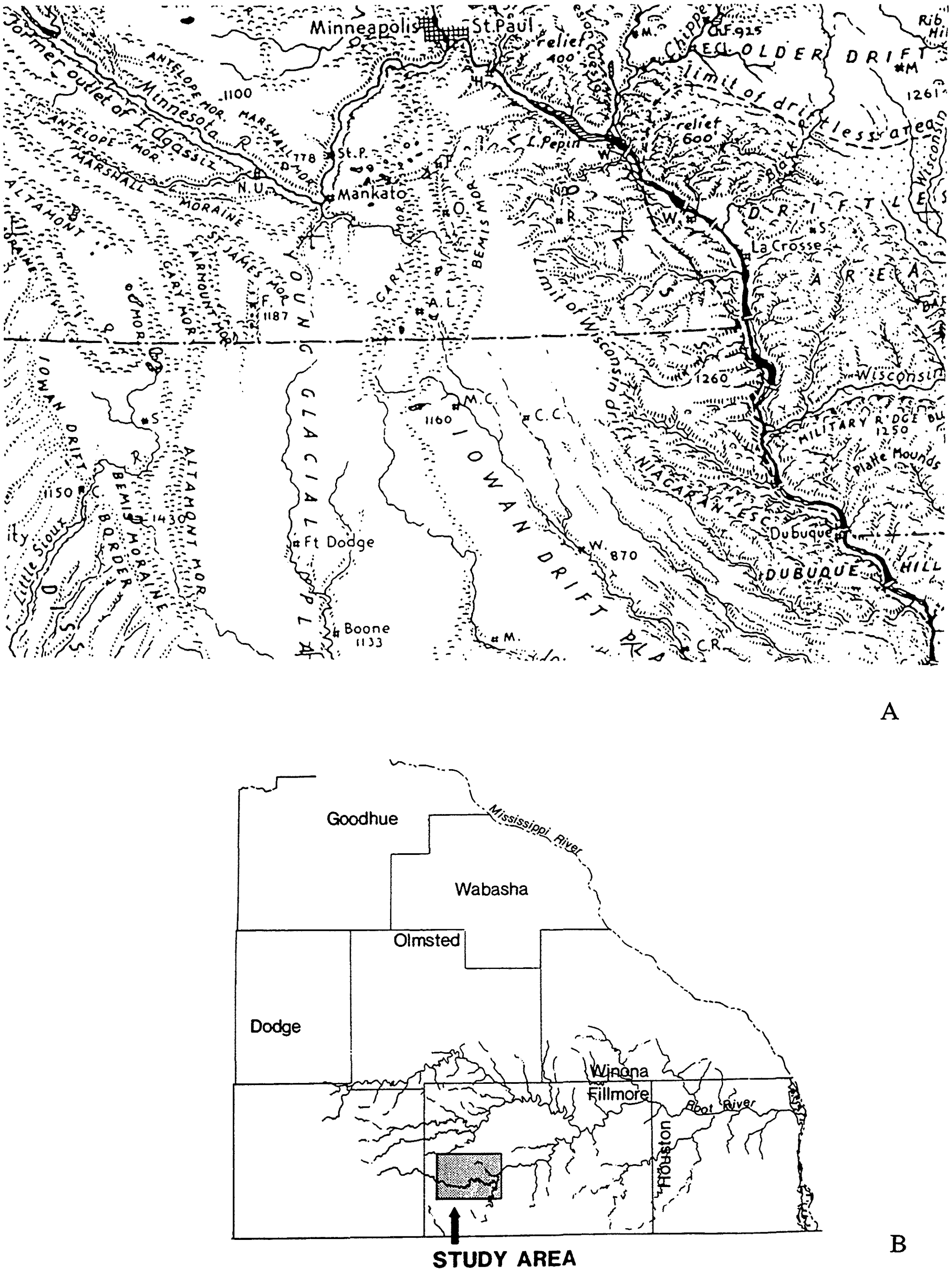
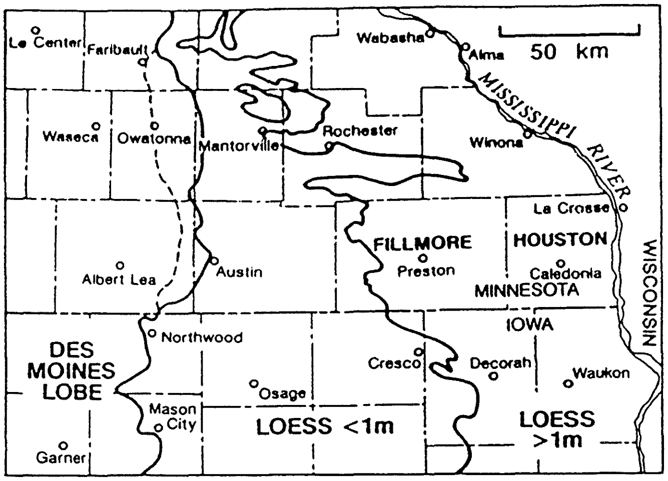


Figure 3.1. Geomorphic setting of the Root River in southeastern Minnesota. a. Geomorphology of southeastern Minnesota (from Raisz, 1957). b. Drainage basin of the Root River (from Mohring and Alexander, 1986).



A

FIG. 1. Map showing regional setting of the study area. Late Wisconsinan glaciation was limited to the area designated "Des Moines Lobe." This area lacks a distinct loess mantle, except east of the dashed line, where loess forms a nearly continuous mantle <1 m thick. The area beyond the late Wisconsinan glacial limits is subdivided according to typical loess thickness on wide upland summits. Several outliers of thick loess in Iowa are not shown. Based on Leverett (1932), Ruhe (1969), Hobbs and Goebel (1982), and field observations by the authors.

B

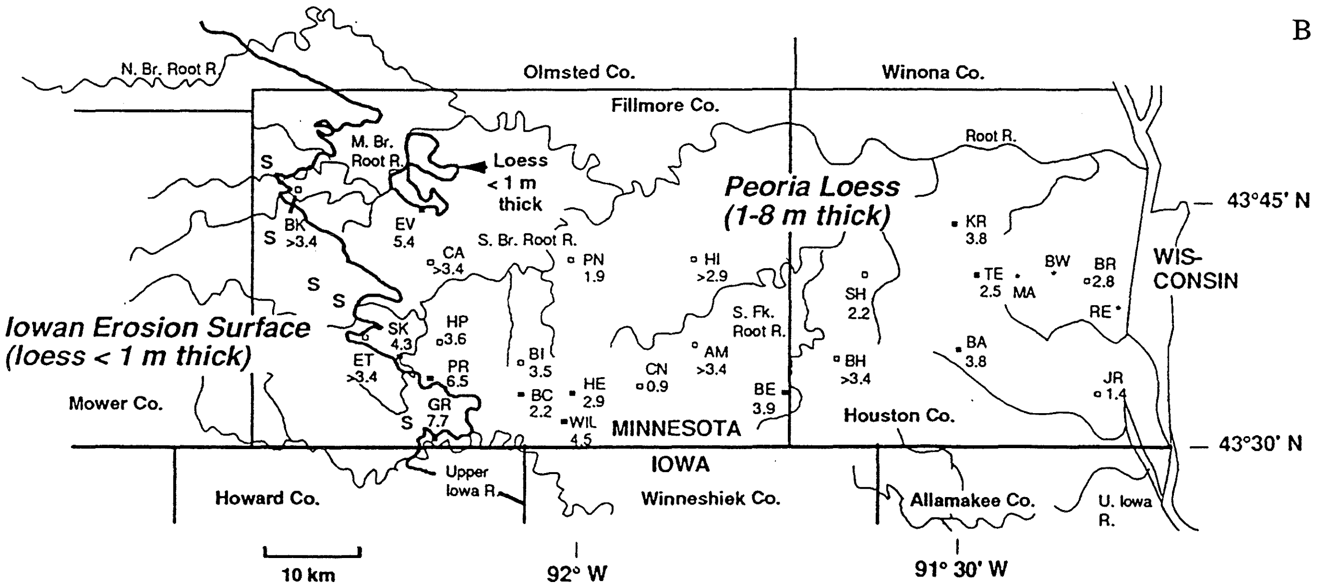


FIG. 2. Map of the study area, showing sampling sites, and the distribution of thick Peoria Loess. Solid squares are sites where intact cores were collected; open squares indicate sites where sampling was by hand auger. Sites are labeled with abbreviated designations used in text; individual cores are referred to in the text by these abbreviations plus a number (e.g., "PR-1"). Measured thickness of Peoria Loess at each site is also shown. Note that there is an inlier of thin loess just north of site EV. Occurrences of linear bodies of fine and medium sand west of the thick loess border are indicated by the letter S.

Figure 3.2. Glacial deposits in southeastern Minnesota. a. The Des Moines Lobe, the Iowan Erosional Surface (loess <1m), and the region of thick loess (>1 m). b. Distribution of Peoria loess in Mower, Fillmore, and Houston counties. Both figures are from Mason et al., 1994.

over a lengthy stretch of the Root River (see below) and are about 55-65 ft lower in elevation.

To the south of Mystery Cave, the upland is a gently rolling plateau. The plateau is extensively farmed. On the plateau margins, steep forested hillslopes lead down to intermediate benches or to floodplains along the Root River. Forested hillslopes appear along the river and in re-entrant valleys. Forested hillslopes tend to have a thinner soil and loess cover; often the loess is absent. Bedrock is exposed on the hillslopes, especially near the river, where bedrock bluffs are common.

Land Use

The bulk of the plateau near Mystery Cave is in agricultural production. Row crops are planted in corn and soy bean rotations. Alfalfa is also cropped. A few dairy farms have extensive pastures and hayfields. Relatively little of the total farmed area is used as pasture or for non-row crop agriculture.

Figure 3.3 shows land use above Mystery Cave. Four primary land uses are distinguished: (1) forest and non-agricultural grassland, (2) agricultural grassland, (3) crops, and (4) residential areas. *Forest and non-agricultural grassland* (darkest stipling) are deciduous forests or a mixture of grass, brush, and scattered trees. Non-agricultural grasslands apparently were used for grazing but have been abandoned for those purposes in recent times and are slowly reverting to the forests which they bound. *Agricultural grasslands* (intermediate stipling) are used primarily for grazing or for production of hay. *Croplands* (blank areas) were mostly in corn during the study, with scattered soy beans, alfalfa, and marginal grass strips. The grass strips are apparently used for production of hay or are left fallow; they are not fenced separately from surrounding crops. *Residential areas* (enclosed blank areas with buildings) include private residences, the buildings and trailer at the Mystery I commercial operation, and all farm buildings and grounds.

The Mystery I entrance area (Figure 3.3) is on a forested hillslope adjacent to the Root River. The commercial passage lies beneath the hillslope and a nearby forested reentrant valley. Almost all of the central part of Mystery Cave (past the Bomb Shelter along the Door-to-Door Route) lies beneath cropland. During the time of the study, nearly all of that land was planted in corn.

The Mystery II entrance area and parts of 5th and 4th Avenues nearly as far west as Blue Lake (BL on Figure 3.3) lie beneath forested hillslopes. Blue Lake lies beneath a marginal grass strip near the crop/forest boundary.

The passages leading east from the Mystery II entrance to Coon Lake Drips (CLD) and the Garden of the Gods (e.g., stalactite drip GG1 on Figure 3.3) lie beneath forested hillslopes and nonagricultural grassland.

Western Mystery III near the Root River is beneath forested hillslopes and pasture. Parts of northern Mystery III are beneath pasture; the rest is beneath forested hillslopes and re-entrant valleys. Rimstone Creek (RC) and Enigma Pit (not labeled on Figure 3.3; see Figure 2.1) lie beneath forested hillslopes.

LAND USE AND RECHARGE AT SELECTED SITES

The relation between land use and recharge deserves explicit discussion for several important hydrologic sites in Mystery I and II.

Mystery I

The passages of Mystery I trend east, directly away from the Root River. All sampled hydrologic sites in Mystery I are beneath forested hillslopes. Most water sources are believed to be local from the forested hillslopes, except for the Lower Level stream, which is partly derived from the Root River. Some waters near the Mystery I entrance and in adjacent passages may receive inputs from the intermittent stream within the re-entrant valley (Figure 3.3).

The surface immediately above Turquoise Lake is forested. The waters in Turquoise Lake are affected by the South Branch of the Root River only by backflooding through the commercial passages in the largest floods. The clarity of the lake and the stability of its chemical and physical properties suggest a relatively diffuse source area. The relatively high nitrate level in Turquoise Lake argues for impact by waters from agricultural areas.

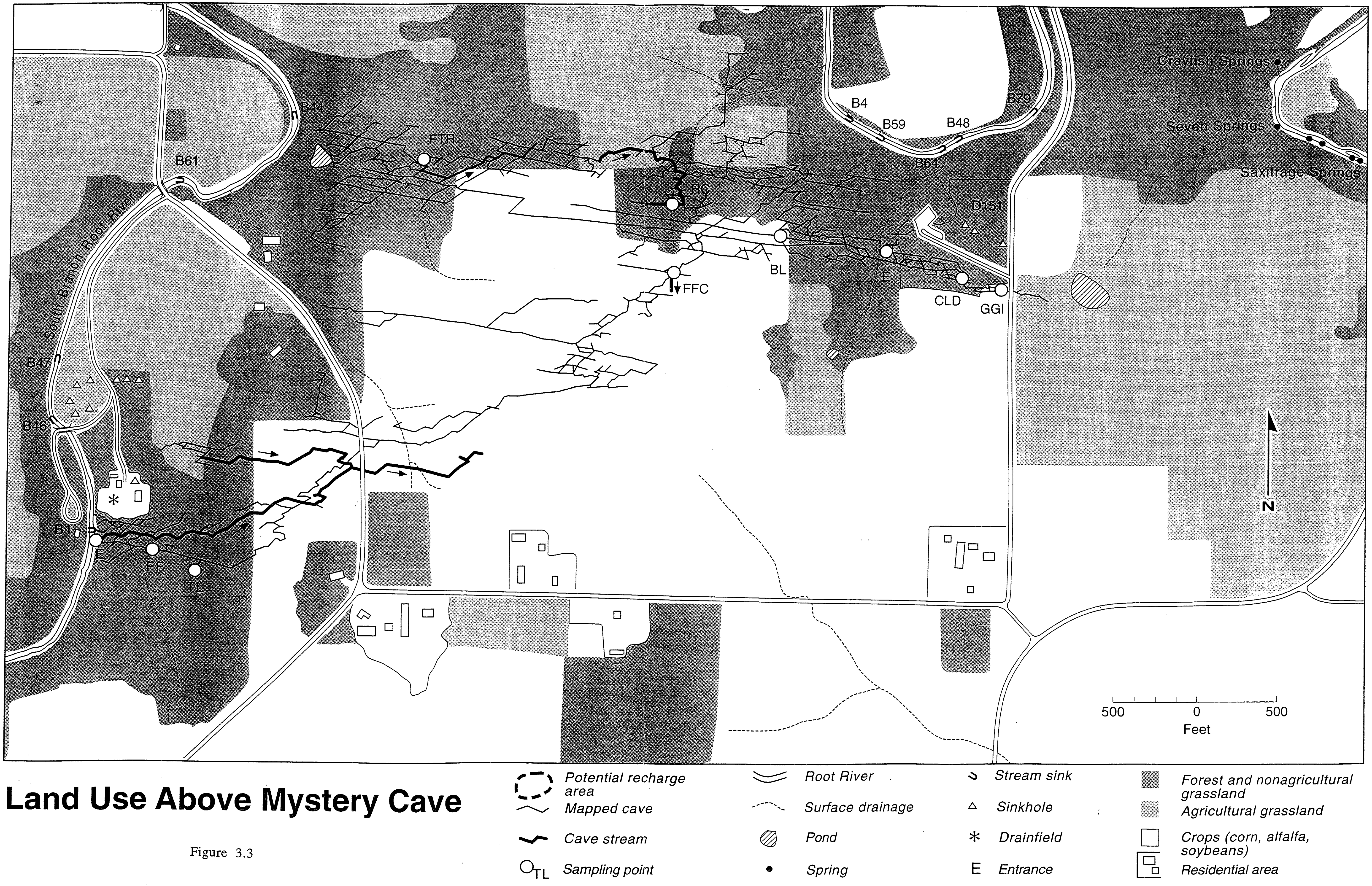
The local dip of the Dubuque Formation is northwest (Palmer and Palmer, 1993a). Groundwater in the Dubuque probably flows downdip toward the Root River. This interpretation is supported by the observation that water enters Turquoise Lake (and the springs in Old Mystery Cave) along the updip (southeast) side. (Note: the flow in the Disappearing River in the Stewartville crevices below Turquoise Lake is to the northeast---at 90° to the flow in the Dubuque.) An estimate for the recharge area contributing to the upper levels of Mystery I is shown in Figure 3.4.

The recharge that feeds the Frozen Falls area includes the forested slopes and ravine that overlie Mystery I. The greater variability of the chemical and physical properties of the Frozen Falls waters and their rapid response to precipitation events indicate a direct surface recharge in addition to a recharge component with a high nitrate and chloride composition similar to that seen in Turquoise Lake.

Mystery II

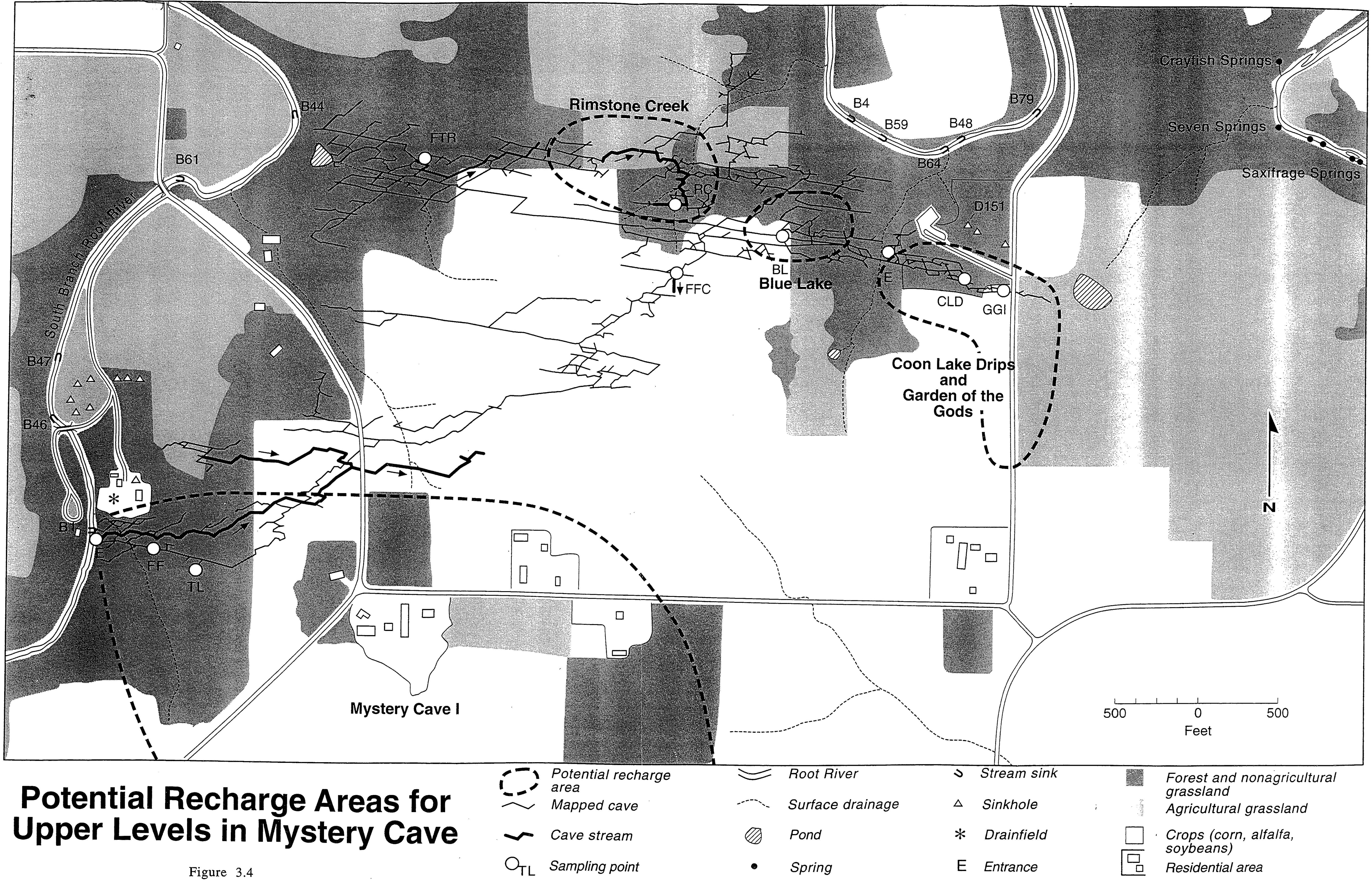
The eastern end of 5th Avenue near the Mystery II entrance lies beneath a forested hillslope. Just east of the entrance area, 5th Avenue and adjacent passages lie beneath a brush- and grass-covered hillslope (shown as forest and non-agricultural grassland on Figure 3.3). The hillslope supports a colony of gophers, as shown by numerous mounds of soil with accompanying burrows. Coon Lake Drips lie beneath this area; its source area may be restricted to the grassy hillslope or perhaps includes part of the adjacent cropland (with a marginal grass strip and alfalfa and soybeans) to the south.

Farther east, near the Garden of the Gods, Fifth Avenue and adjacent passages pass beneath the lower end of a field usually planted in corn. Palmer and Palmer (1993b) used seismic methods to estimate a depth to bedrock as 22 ft above the Garden of the



Land Use Above Mystery Cave

Figure 3.3



Potential Recharge Areas for Upper Levels in Mystery Cave

Figure 3.4

Gods. This depth must include soil, the Peoria loess, and any additional glacial materials above the sediment/bedrock interface. The Peoria loess must overlie Coon Lake Drips and its source area, but the loess thins to less than half a foot in the forested hillslope near the Mystery II entrance. Beyond the Garden of the Gods, the passages pass beneath a gravel road near the entrance gate for the driveway leading into the Mystery II parking area. The upland at the top of the hillslope above Coon Lake Drips is usually planted in grass or alfalfa for hay production. Near the Garden of the Gods, the upland was planted in corn during the period from 1991-1994. The potential recharge area for Coon Lake Drips and the Garden of the Gods is shown in Figure 3.4

As noted above, Blue Lake is below a marginal grass strip near the crop/forest boundary (Figure 3.3). The grass is adjacent to corn fields. The northern ends of the fields locally slope toward the forested hillslope. Farther west, several fields drain to a major ravine that threatens to erode into the fields. To minimize erosion, granite boulders have been placed in the upslope ends of the ravine. The ravine feeds a larger drainage system (another major tributary heads on a marginal grass strip) that passes through the forested hillslope to a lower bench of extensive pasture land nearer the Root River. Locally the ravines have steep walls with a maximum height of at least six feet. The walls are cut into the Peoria loess. In many places, sands and gravels line the ravine floors. The gravels include quartz, granite, and other pebbles indicative of a glacial origin. The ravines converge downslope to form one ravine within the forest. From the lower pasture land, the ravine drains a short distance through forest down to the Root River. In the lower reaches of the drainage system the loess is thin or absent and carbonate bedrock is exposed in the intermittent streambed.

Within the upper forested area, the ravines pass directly over parts of Rimstone Creek. At their closest, the ravines are 500 ft west of Blue Lake. Leakage from the ravines could feed Rimstone Creek and the ceiling flow at the Smoking Chamber.

Although not directly observed during this study, the flow into Blue Lake is reported to be from passages to the north. This report is consistent with the massive flowstone on the north wall of the passage west of Blue Lake. The flow at Enigma Pit, a few hundred feet from Blue Lake, also enters from the north side of an east-west passage. The recharge area for Blue Lake is, therefore, probably the area bounded by 4th Avenue on the south, Tree Roots (or possibly the passage containing Enigma Pit; see Figure 2.1) on the north, the Mystery II entrance valley on the east, and the former commercial passage that extends northeast from the Smoking Chamber on the west. (It is not clear why the Dubuque flows in this part of Mystery do not seem to be downdip on the shale beds.) The potential recharge area for flow into Blue Lake is shown in Figure 3.4.

SINKHOLES, SURFACE DRAINAGE, AND RECHARGE

Subsidence sinkholes are widespread on the karstic uplands of southeastern Minnesota (Dalgleish, 1985), and are often well-developed with widths of up to a few hundreds of feet and depths up to 30 ft. Because they have steep sides, they are rarely cultivated. Literally thousands are known. Many are readily recognizable as circular clumps of trees sticking out of pastures or croplands. Twenty-nine sinkholes have been mapped near Mystery Cave or on the surrounding upland (Figures 3.3-3.4, 3.6-3.7). No sinkholes have been located over known cave passages. The nearby sinkholes are small and do not appear to have functioned as points of concentrated recharge during early stages of cave development, or to have provided long-term sources of concentrated recharge, as is common for branchwork caves (see Palmer, 1991).

Sinkholes do not appear to serve as major points of concentrated recharge today. Much of the water that falls on the plateau either infiltrates the soil and loess, evaporates, or is transpired. However, surface drainage patterns (Figure 3.6 and 3.7) are sufficiently well developed to indicate that a significant quantity of water (particularly during snowmelt and spring storms) leaves the top of the plateau as surface runoff.

THE SINKS, UNDERGROUND RIVERS, AND SPRINGS NEAR MYSTERY CAVE

As noted above, Mystery Cave functions as a meander cutoff for the South Branch of the Root River. Surface water in the South Branch drains underground through parts of Mystery Cave, short-circuiting the longer surface course (Figures 1.2 and 1.3).

Sinks

At the Mystery I entrance the river locally flows north and the entrance is on the east side of the river. Water sinks at discrete points which start near the entrance and appear in the riverbed for several miles downstream. The sink points are vertical joints that have been solutionally enlarged and filled with sediment. The sink points have a collective capacity to accept surface water. When the flow in the river exceeds that capacity, water continues to flow through the entire surface reach of the South Branch near the cave. As the flow in the river recedes toward and then below the capacity of the sink points, a terminal sink develops on the South Branch. This terminal sink migrates upstream as the flow in the river decreases. During all but the wettest years several miles of the South Branch are dry during much of the summer and fall. The permanent flow in the South Branch resumes at Seven Springs about 1.5 miles east-northeast of the Mystery I entrance and about 0.5 miles east-northeast of the Mystery II entrance (Figure 3.5).

The location of the terminal sink of the South Branch is complicated by the existence of two semi-perennial streams. One stream is fed by springs A854 and A86 (Figure 3.6) and empties into the South Branch just east of A86. A second stream, fed by springs A76, A77, A78, and A79, empties into the South Branch about 200 ft upstream, to the southwest of Matheson Sink (B3 on Figure 3.6). Under low flow, the stretch of river shown in Figure 3.6 can have three sequential terminal sinks. For the rest of this discussion, unless otherwise specified, "the terminal sink" refers to the first, most upstream sink.

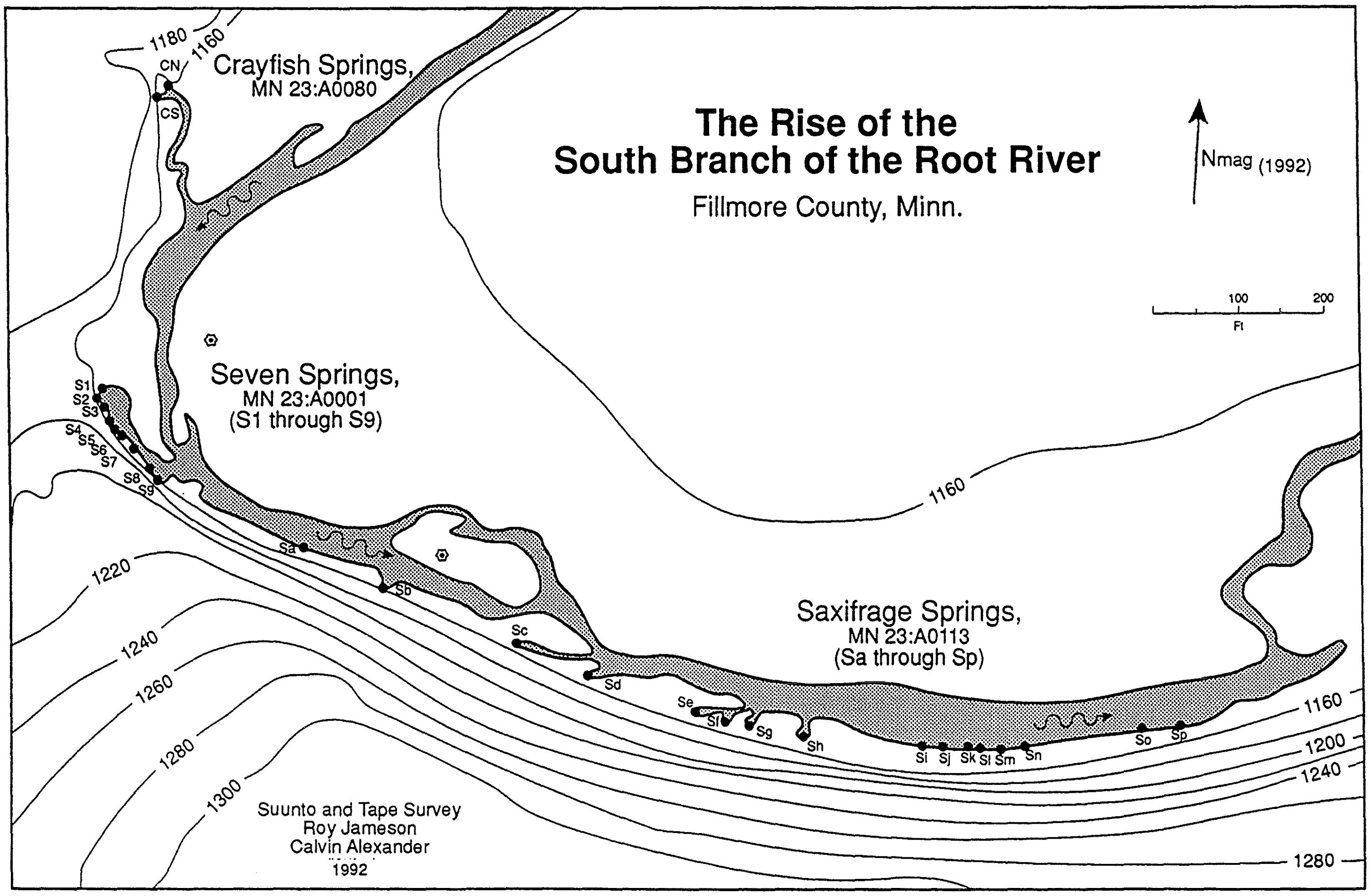
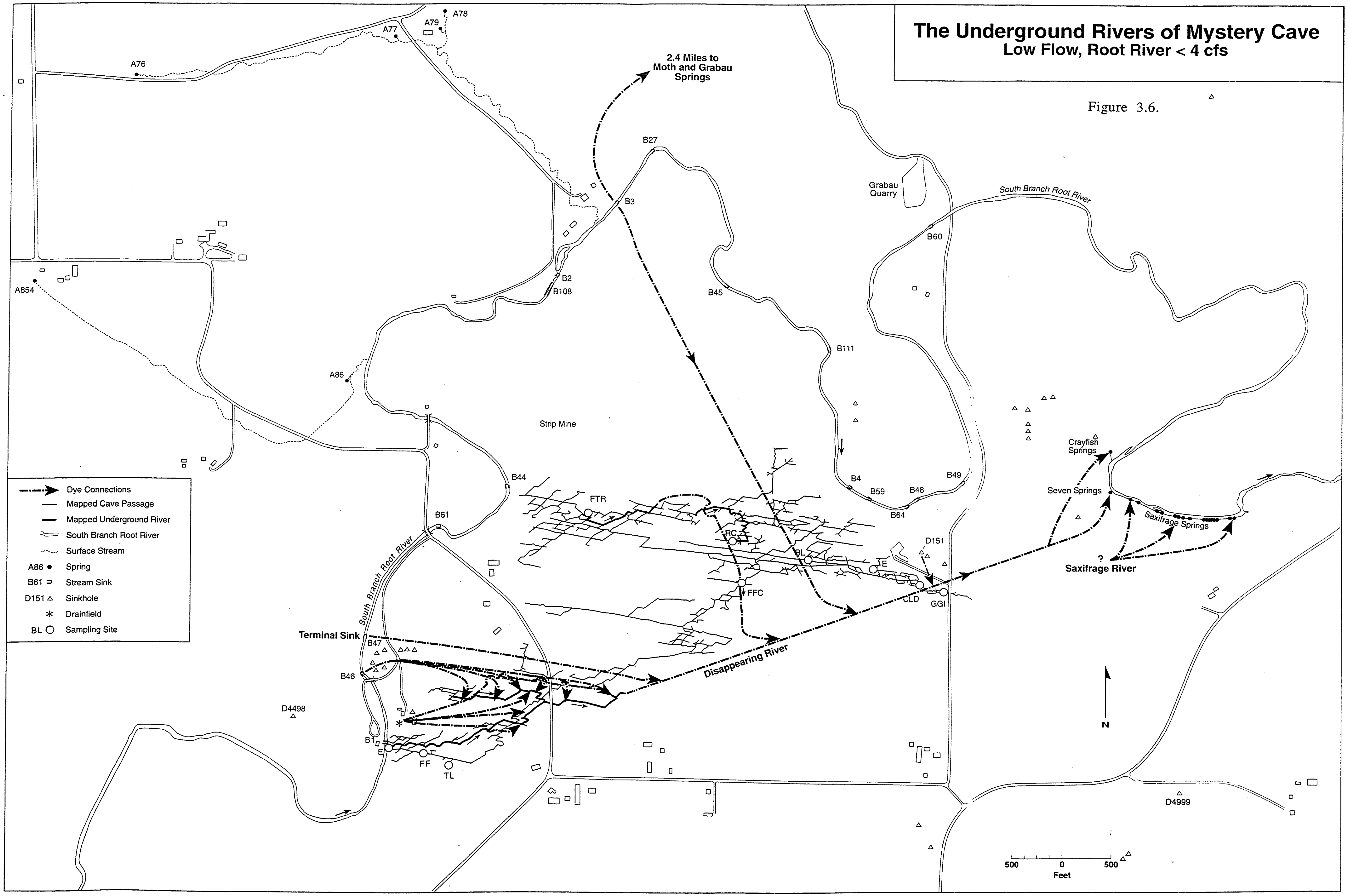
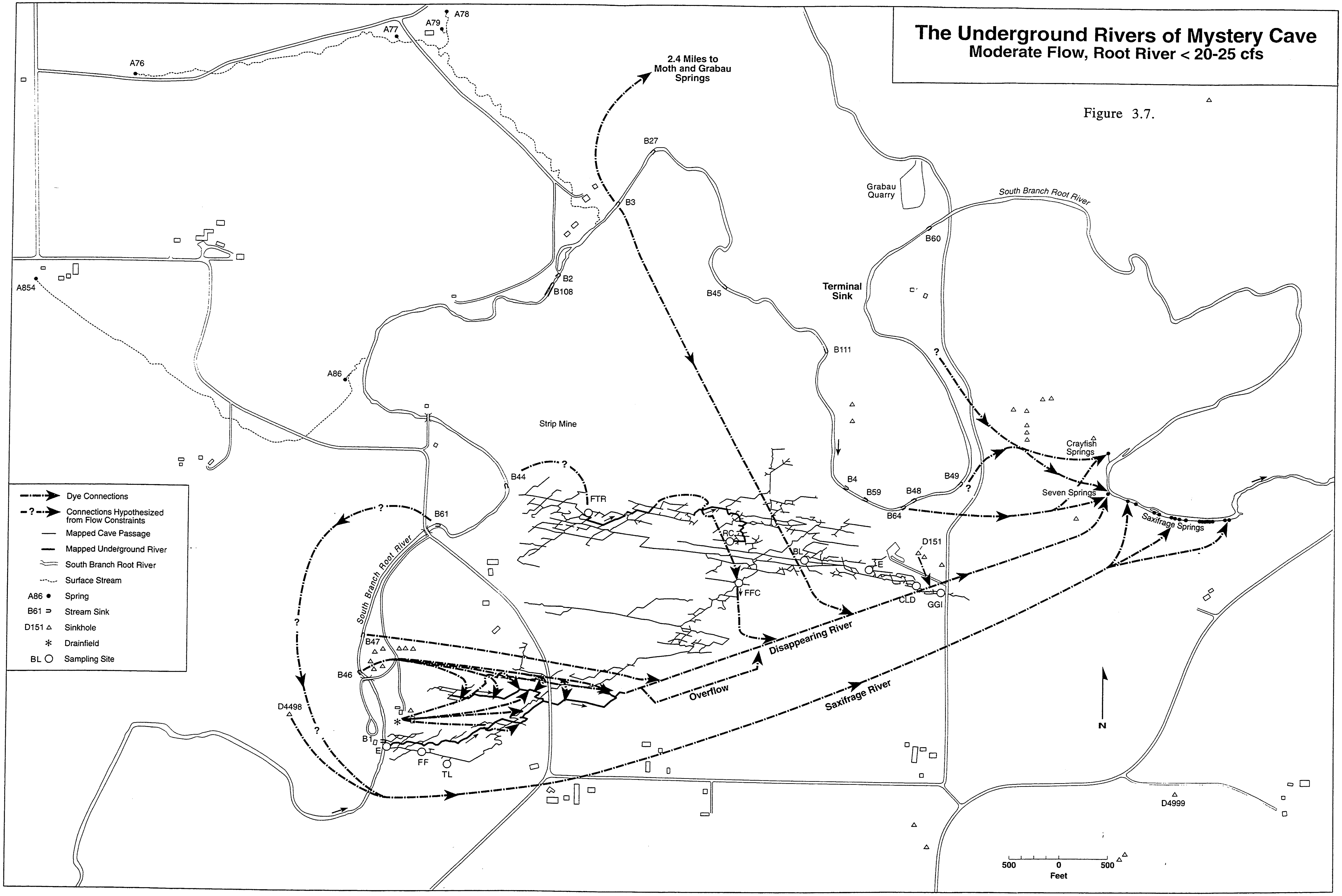


Figure 3.5. The Rise of the South Branch of the Root River.



The Underground Rivers of Mystery Cave
Low Flow, Root River < 4 cfs

Figure 3.6.



The Underground Rivers of Mystery Cave
Moderate Flow, Root River < 20-25 cfs

Figure 3.7.

Springs

Seven Springs is one of three spring clusters (Figure 3.5); the others are Crayfish Springs and Saxifrage Springs. The *Crayfish Springs* (Figures 3.5 and 3.6) are ephemeral---they dry up when the terminal sink of the South Branch retreats upstream of the river bed immediately north of the Mystery II entrance. *Saxifrage Springs* are volumetrically the largest of the springs much of the year, but may also decrease in discharge when the terminal sink has retreated above the bridge at the east end of the Mystery I driveway. *Seven Springs* are the most perennial of the three complexes. Seven Springs actually has more than seven springs. When surveyed in September, 1992, nine springs were identified (Figure 3.5).

The number of springs in each cluster probably varies seasonally with flow conditions; it also may vary over longer time spans because of changing sedimentologic conditions on the Root River. Many of the springs are at the bases of bedrock cliffs. Rock falls from collapses periodically block individual spring orifices or divert water so that flow is from two or more orifices. Most of the springs issue from joints or bed-joint intercepts, but some issue from rubble piles so that it is uncertain whether flow is actually from a single solutionally-enlarged fracture or several.

The flow from all three spring complexes is dominated by water from the sinks of the South Branch. The water temperature in all three spring complexes varies seasonally indicating relatively short underground residence times. On any given day the temperatures and conductivities in all three spring complexes are similar, but not identical. Stream flow measurements made above the start of the sinks at Mystery I and below Saxifrage Springs confirm that, within the errors of conventional stream-flow measurements, nearly all of the water resurging at the three spring complexes could be sinking flow from the South Branch. Cave mapping, dye tracing, flow measurements, and careful observation of spring behavior relative to river flow and the position of the terminal sink, have begun to reveal a detailed picture of the underground plumbing system that flows beneath the ridge containing Mystery Cave.

Results from Dye Tracing

Early Traces. By the mid-1970's, it was common knowledge in the local caving and southeast Minnesota karst communities that the resurgence of the Mystery Cave system was Seven Springs. The concept was simple. The South Branch sank to form the Disappearing River which flowed through the lower levels of Mystery Cave and resurged at Seven Springs. Quantitative dye tracing in and around Mystery Cave in the late 1970's and early 1980's documented that the Disappearing River system did indeed resurge at Seven Springs (Mohring, 1983; Mohring and Alexander, 1986).

Mohring discovered that the situation was complicated, however. During high flow in particular there was strong evidence that a second source of water contributed to the flow at the northwest end of the Seven Springs group. Mohring hypothesized that a separate groundwater basin existed north of Mystery II, but he never caught the flow conditions right to do a trace from that area. Mohring also demonstrated that water which sinks at Matheson Sink, B3, splits underground---part of it resurges at Seven Springs while most of it flows into the Forlorn River system and resurges at Moth and Grabau Springs on Forestville Creek. This meant that: (1) whenever the terminal sink of the South Branch was below Matheson Sink, part of the South Branch's flow is diverted into the springs heading Forestville Creek through a third groundwater basin, and (2) the hypothesized second groundwater basin could not extend very far to the west or north. Mohring and Alexander were unaware of the existence of Crayfish Springs and Saxifrage Springs during much of their early tracing work.

Crayfish Springs (Figure 3.5 and 3.6) were recognized in 1981 during a trace of the entire South Branch of the Root River (Alexander, 1987). Crayfish Spring is the major outlet of Mohring's postulated second groundwater basin. That groundwater basin was named the Crayfish River Basin and its general location is shown in Fig. 10 of the 1984 MSS Corn Feed Guidebook (MSS, 1984). During the 1980s, several traces were conducted through the Disappearing River system into the Seven Springs/Crayfish Springs complex. These traces demonstrated that under low flow conditions water from the Disappearing River system reached Crayfish Springs and dominated Seven Springs, but under high flow conditions the flow from the Crayfish River Basin pushed the Disappearing River flow to the southeast part of Seven Springs. The boundary between the Crayfish River Basin and the Disappearing River Basin is mobile and moves in response to varying flow conditions.

In the late 1980s, it was recognized that under most flow conditions a lot of water emerges from a series of springs along the south bank of the South Branch in the quarter mile downstream from Seven Springs---more even than emerges from Seven Springs proper. This complex was named Saxifrage Springs after the Nature Conservancy's Saxifrage Hollow Preserve that starts a few feet uphill from the springs. (The Preserve protects the rare and endangered plant and animal species that inhabit the aligific talus slopes immediately above the springs. The Preserve is totally closed. Visitors to the springs should refrain from walking on or disturbing the slope above the springs.) The number of discrete springs in the Saxifrage Springs group is a matter of judgment, but 16 separate rise points are designated on Figure 3.5.

1989 Dual Dye Trace. In October, 1989 a dual dye trace was run through Mystery I (Foster et al., 1992). With the assistance of DNR personnel and volunteers from the Minnesota Speleological Survey, charcoal detectors were placed and retrieved at a number of sites along the Disappearing River and Coldwater Canyon sections of the lower stream level. Two dyes were introduced: one (Fluorescein) was poured into a toilet to flow through through the septic system at the residence at Mystery I; the second (Rhodamine WT) was poured into sink B46.

The Rhodamine WT introduced at B46 was detected at nine feeder joints, mainly along the north side of Cold Water Canyon and the Disappearing River downstream of its confluence with Cold Water Canyon. The Fluourescein poured in the toilet was recovered at nine feeded joints along both sides of the Disappearing River and Cold Water Canyon. Both dyes resurged in about 17 hours at Seven Springs. Most of the dye from the residence was retained by the septic tank but that portion that got through did so very rapidly.

1991 Triple Trace and the Saxifrage Basin. In October, 1991 a triple-trace was performed in and around Mystery Cave during relatively high flow. The terminal sink of the South Branch was between Steve Landsteiner's house and the ford to the Grabau Quarry. Rhodamine WT was introduced into Ground Hog Sink (D4998) about 350 m west northwest of the Mystery I entrance. Fluorescein was introduced in Cold

Air Sinks (B64) in the South Branch just in front of Cold Air Cave down the ravine from the extended Mystery II parking lot. Sodium bromide was introduced into a dry sinkhole (D151) immediately adjacent to the parking lot at Mystery II. The bromide ions reached Seven Springs in about two and a half hours with a pattern of increasing concentration toward the high numbers (the downstream or east end of the Seven Spring group). That pattern is diagnostic of flow through the Disappearing River system under relatively high flow conditions. None of the bromide was detected at Crayfish Springs or at the western-most of the Saxifrage Springs.

The fluorescein came out the middle of the Seven Springs group (S4 under the existing flow conditions) in about two hours and did reach Crayfish Springs but was not detected at any of the Saxifrage Springs. This pattern confirms the existence of the hypothesized Crayfish River underground basin immediately north of Mystery II. This basin feeds Crayfish Springs and the west (low numbered) end of Seven Springs under high flow conditions. Under low flow conditions when the terminal sink of the South Branch is upstream from the Mystery II area, the Crayfish River Basin is essentially dry, Crayfish Springs stop flowing, and all of the flow from Seven Springs comes from the Disappearing River Basin.

The Rhodamine WT was detected in the Saxifrage Springs, in the east end of Seven Springs at S8, but was not detected in Crayfish Springs. This represents, to our knowledge, the first documented trace into the Saxifrage Springs and is the first evidence of a fourth, independent groundwater basin in the area of Mystery Cave. This new basin is named the Saxifrage River Basin.

Chemical analyses of water samples collected at Crayfish and several of the Seven Springs and Saxifrage Springs in July, 1992 (Appendix 3), indicates that water in the three springs is very similar and suggests that it comes from the South Branch. The temperatures in the Seven Springs and the Saxifrage Springs were similar and well above normal groundwater temperatures, indicating that the waters in both springs come from the same surface source and have spent comparable, short periods of time underground.

Results of Flow Measurements on the Root River. On July 29 and 30, 1992, with the assistance of DNR personnel, we measured the flow in the South Branch at several places above and below Mystery Cave. Starting at the upstream end, the flow at the bridge between sections 25 and 26 (T102N, R13W, two miles west of Mystery I) was 14.8 cfs. The flow in Etna Creek where it crosses County Road 14 was 5.7 cfs. At the bridge between section 26 and section 30 (T 102N, R12W) about one mile west of Mystery I, the flow was 21.5 cfs. The flow at Mystery I was 22.9 cfs. The river seems to be gaining flow all the way to Mystery I.

The flow from Seven Springs was 5.4 cfs. The flow immediately downstream from the end of Saxifrage Springs was 19.3 cfs. If about 3.6 cfs were lost near B3 to the Moth and Grabau springs drainage, these numbers yield a consistent picture. Under these flow conditions, about 60% of the Root River's flow at Mystery I resurged at Saxifrage Springs, 25% resurged at Seven Springs, and 15% resurged through Moth and Grabau springs.

These flow data create a major problem. Where does the South Branch water that resurges in Saxifrage Springs sink? None of the traces from sinkpoints in the river have yet been detected in Saxifrage Springs. All of the river sinkpoints traced resurge in Seven Springs/Crayfish Springs and/or Moth and Grabau springs.

There are some anecdotal observations that may be relevant to this question. During a very low flow period in the summer of 1988, the terminal sink of the South Branch retreated to Blakeslee Sink, about 100 meters downstream from the new culverts into the Mystery I parking area. DNR personnel measured the stream flow immediately upstream of Mystery I and downstream from Seven Spring and those two flows were the same at about 3 cfs. At that time DNR personnel were unable to find the Saxifrage Springs---that is, the springs may have been dry at that time.

During the late summer and early fall of 1992, the most upstream terminal sink of the South Branch was the sink Beaver Sinks, which is a few meters east of the Township Road bridge near the start of the driveway to Mystery I. Under those flow conditions the Saxifrage Springs were reported to be flowing. Taken at face value, the 1988 and 1992 observations would indicate that water sinking at Beaver Sink or immediately upstream is the source of the Saxifrage Springs. If that area is the source of the Saxifrage Springs, that flow must either: (1) cross the Disappearing River system, or (2) flow west, then south, then back east around the west end of the Disappearing River system. We currently favor option (2) but option (1) is still possible.

Mystery Cave's Underground Rivers

The dye tracing, mapping, and flow data outlined above can be integrated into a diagramatic presentation of the underground rivers around Mystery Cave. The flow system in Mystery varies with the volume of water moving through the cave. It is convenient, therefore, to present the results as a low flow map (Figure 3.6) and as a moderate flow map (Figure 3.7).

Low Flow Conditions. Figure 3.6 is consistent with all of the low-flow information. (Flow conditions low enough for the terminal sink to retreat to B47 do not occur most years. Flows this low occur only during unusually dry periods.) Water that sinks at B1, B46, B47 and other unmapped sinks between these sinks flows through the Disappearing River and Cold Water Canyon and resurges at Seven Springs. Although the river would be dry downstream of B47 under these conditions, water stored in the unsaturated zone will maintain a low flow in Formation Route Creek. That water flows through Flim Flam Creek and resurges at Seven Springs.

Water from the small springs north of the river will reach flow to sinks between A86 and B27. The water that sinks at B3 flows in part under Mystery II or III and resurges at Seven Springs. Most of that water resurges in Moth and Grabau springs, however.

Infiltrating waters over the east end of Mystery III near D151 will also contribute to the flow to Seven Springs. Crayfish Springs will be very low and part of the Disappearing River flow reaches Crayfish Springs.

The behavior of Saxifrage Springs under these flow conditions is not documented. The springs may dry up. Alternately, a low flow may be maintained by infiltration waters from the area south of Saxifrage.

Moderate Flow Conditions. Figure 3.7 outlines the flow conditions that occur at moderate flows of 20-25 cfs. Under these flow conditions the terminal sink is between B79 and B60, north of the Mystery II parking lot. Under these conditions all of the flows shown in Figure 3.6 will be operative except the Disappearing River no longer contributes to Crayfish Springs.

Crayfish Springs flow strongly under these conditions from water sinking near B79 and farther downstream. The flow through time here is only three or four hours. This flow also feeds the north (low numbered) end of Seven Springs.

Water sinking at B64 resurges at the middle of Seven Springs but not via the Disappearing River system. The boundary between the Disappearing River Basin to the south and the Crayfish River Basin to the north is very fuzzy and mobile.

There is a high level overflow in the Disappearing River somewhere upstream of the confluence of the Formation Route Creek/Flim Flam Creek tributary. Under high flow conditions (Mohring, 1983), a dye pulse from B1 was split into double peaks but a dye pulse from the First Triangle Room (FTR, west end of Mystery III; see Figure 3.7) on Formation Route Creek remained a single peak.

Water sinking near B44 is probably the source of Formation Route Creek. This connection has not, however, been proven with a dye trace.

Finally, Figure 3.7 hypothesizes that the bulk of the flow to Saxifrage Springs originates from water sinking in the vicinity of B61.

STRATIGRAPHY, PASSAGE CHARACTER, AND THEIR INFLUENCE ON FLOW PATTERNS

Mystery Cave is primarily in the dolomite of the Stewartville Formation, and in the limestone, dolomite, and shale of the overlying Dubuque Limestone (Figure 3.8). Some of the highest parts of the cave are near-surface breakdown rooms in dolomite and shale of the lower part of the Maquoketa Formation (Milske, 1982; Palmer and Palmer, 1993a). Many passages appear to have originated as vertical fissures at or near the Dubuque/Stewartville contact, then enlarged upward by a combination of collapse with dissolution and downstream transport of the debris. Most of the present void space of the explored passages is in the Dubuque Formation.

Passages in the Dubuque Formation tend to be tubular with rectangular or elliptical cross sections. There is abundant breakdown from wall collapse and upward collapse of thin alternating shales, limestone, and dolomite. Collapse has produced blocky but arched cross sections and passage widenings that produce small rooms; the rooms have ceilings that resemble the breakout domes of caves in the eastern United States and are produced by the same processes (collapse and solutional removal and downstream transport of the debris). Such locations can be described as incipient breakout domes, for few such locations are fully developed with both domes and conical debris piles. Passages in the Dubuque formation have so much breakdown that they have irregular, ungraded floor profiles. Passage cross-sectional area can abruptly change from about 10 square ft (5 ft wide by 2 ft high) to hundreds or, at the extreme, even a thousand square feet (20 ft wide by 50 ft high). Sites of greater cross-sectional area imply more efficient removal of the collapse debris. Usually these sites can be correlated with underlying fissures in the Stewartville Formation that allowed lower level streams direct access (often during flooding) for removal of the breakdown.

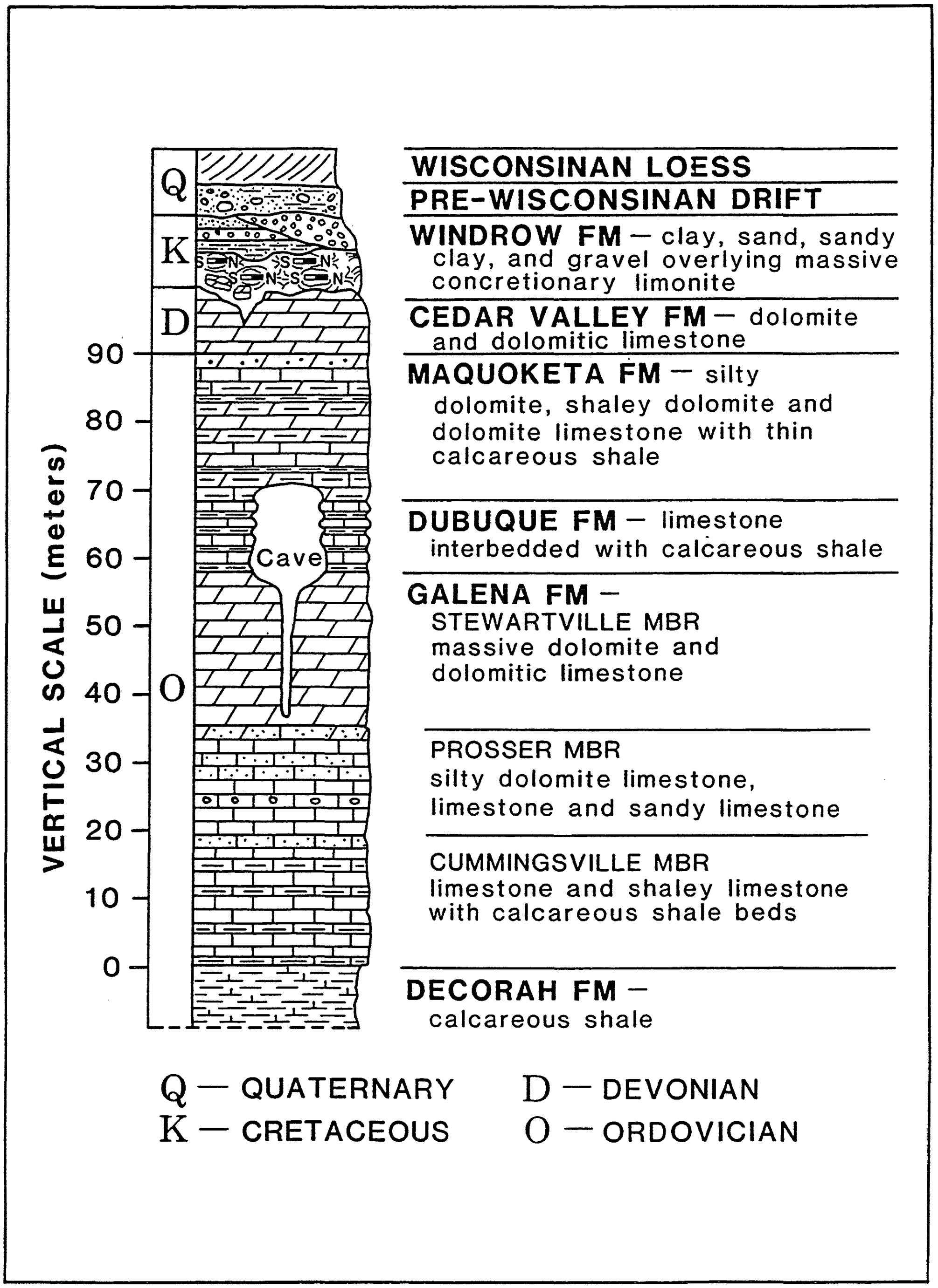


Figure 3.8. Stratigraphy at Mystery Cave. From Milske, 1982.

Most of the current water movement in the Dubuque Formation is vertically downward along the steepest available paths, which are joints. Above the cave there may be some significant lateral movement along solutionally enlarged joints and bedding planes, but such movement is unlikely to exceed a few hundreds to a thousand feet. Water tends to enter cave passages as (1) drips and falls out of ceiling joints, or (2) as seeps and flows out of joints in walls or as seeps from horizontal shale partings. Many of the smaller seeps and flows from walls issue from the bases of vertical joints at locations where the joints die downward at contacts with bed partings or shaly interbeds. (A prominent example in Mystery I is the flow issuing from the joint at the sampling site APO, or Across from Pipe Organ.) No stream entering a Dubuque passage can be expected to be followable a significant distance horizontally today, because the stream would disappear downward in breakdown and enter joints or fissures in the Stewartville Formation. Nearly all of the movement of water in the Dubuque passages thus has a strong vertical component of flow.

Passages in the Stewartville dolomite are often narrow fissures or are keyhole shaped as tubes over fissures. The larger passages, such as parts of 5th Avenue, are tubular with arched or rectangular cross sections, but sediments hide fissures in the floor. Thus the actual shape of the lower part of the primary solutional void may be obscured. Consequently, it is not entirely clear whether deep floor fissures are universal in the Stewartville passages. Silt, and silt and gravel fills (see Milske et al., 1983) are common in passages developed in the Stewartville Formation; in places silt and gravels overlie breakdown or are interbedded with breakdown. Many fissures in the Stewartville are extensively filled with silt, which perches small streams that are incapable of removing the silt. Perching by silt limits water contact with bedrock, thus impeding bedrock dissolution and preventing more direct downward vertical movement of water to the water table.

In many areas, Mystery Cave has two levels: an upper level of tubular shape, and a lower level in the Stewartville fissures (Figure 1.3). The primary cave streams (Disappearing River, Formation Route Creek, and Flim Flam Creek) obtain most of their discharge by recharge from the streambed of the Root River; they flow laterally through the cave within the lower level fissures. None of the streams is normally visible along the tour routes, although Flim Flam Creek has been known to flood sufficiently high (e.g., July, 1993) to be visible at the Bar in Mystery II.

RECHARGE AND WATER FLOW PATTERNS

Recharge to Mystery Cave takes both diffuse (dispersed) and concentrated forms. *Diffuse recharge* occurs through the soil and loess. This water moves vertically downward and collects in discrete zones at the regolith/bedrock contact, to then follow joints downward. Lateral movement of the diffuse recharge within the soils and loess is probably extremely limited on the flat parts of the upland above Mystery Cave, for there are few surface depressions or major sinkholes to funnel overland flows and interflows toward central drains with perched water tables. On hillslopes there may be much more lateral movement via interflows in the soil, but water probably cannot flow laterally more than a few dozens of feet before encountering surface drainages or being shunted down open joints on rocky slopes.

The most important *concentrated recharge* takes place, as previously noted, along the South Branch of the Root River, where occluded joints transmit water down to the lower levels of Mystery Cave. Minor amounts of concentrated recharge are also important in some near-surface sections of cave, such as the Mystery I and II entrance areas. At these locations, concentrated recharge must take the form of flow into open joints on hillslopes with exposed bedrock, or flow into macropores in thin soil and loess. For example, at Mystery I, direct connections to the forested hillslope surface are indicated by: (1) rapid response to rainfall, (2) water temperatures that reflect surface-water temperatures only slightly modified, and (3) increases in turbidity and decreases in conductivity in response to storms. These responses are characteristic of such drip and waterfall locations as Frozen Falls Drips, Drips Across Bridge, and the Pipe Organ. At Mystery II, similar responses are found at drip sites in the entrance passage and in the stairwell. Water gushes out of cracks in the concrete stairwell following storms or during winter snowmelt events. Similar responses also appear at the Ramp stream in Mystery II. This stream occasionally (e.g., much of the wet summer of 1993) has a discharge sufficient to leave the ramp area past 17 Layer Rock and spread out over the floor, inundating a 50 ft stretch of 5th Avenue.

CHAPTER 4

HYDROCHEMISTRY

INTRODUCTION

Major Influences on the Chemistry of Karst Waters

Troester and White (1986, p. 476) present the following conceptual equation to describe major influences on the carbonate chemistry of karst springs:

[chemistry] = [hydrogeology of aquifer] + [short-term storm-related events] +
[seasonal variations] + [long-term climatic influences].

In this equation, the hydrogeology of the aquifer is considered to be a function primarily of lithology, the chemical composition of the bedrock, and the type of permeability and flow (diffuse flow in pores and fractures or conduit flow in solutional voids). The primary seasonal variation is the cycle of carbon dioxide pressure, which is tied to the growing season in temperate climates but can be absent in low-elevation tropical karsts.

A similar conceptual equation can be devised to describe the chemistry of waters in Mystery Cave:

[chemistry] = [surficial anthropogenic influences] +
[hydrogeology of the soil and loess aquifer] +
[hydrogeology of the bedrock above and adjacent to the cave] +
[in-cave anthropogenic influences] +
[natural in-cave geochemical changes] +
[influence of short-term storm-related recharge events] +
[influence of short-term snowmelt-related recharge events] +
[influence of seasonal variations] +
[long-term climatic influences].

The inclusion of the environmental terms (surficial and in-cave anthropogenic influences) is necessary because we are concerned with the broader context of Mystery Cave's hydrochemistry, and not just with the carbonate chemistry. The division of the aquifer term of Troester and White (1986) into two terms (hydrogeology of the soil and loess aquifer and hydrogeology of the carbonate aquifer) is suggested by the analysis of the hydrogeologic setting in Chapter 3. Natural in-cave geochemical changes---primarily changes in carbonate chemistry that change the compositions of precipitating solutions---are ubiquitous in caves, and we discuss evidence for some of these changes for Blue Lake in Chapter 7. The division of short-term events into storm-related events and snowmelt-related events is necessary because there can be significant differences in hydrologic response or in physical and chemical parameters of infiltrating waters in the two cases. In addition, they obviously need not occur together. Examples of these differences are discussed below in Chapter 8 for Coon Lake Drips and in Chapter 9 for Flim Flam Creek. However, for the purposes of a generalized conceptual equation, these two terms could just as easily be combined into one term by defining it as the "influence of short-term recharge events".

One of the advantages of studying the bulk chemistry of springs is that springs provide an integrated measure of all of the chemical sources, chemical sinks, and geochemical processes that occur within an aquifer. Many waters from varying environments have mixed by the time they reach the springs, but they mix in proportion to their volumetric significance. Thus, even though there is an effective averaging of many aquifer properties, there is some assurance that an overall chemical picture for the basin will be possible, if the springs are monitored for sufficiently lengthy periods and at a sufficient frequency. Even for springs that exhibit the most uniform behaviour, there are chemical and physical variations that allow inference of aquifer properties and chemical sources and sinks upflow of the springs.

In studying the chemistry of cave waters, we are at each site subject to the same primary restriction---the sampled waters are mixtures of upflow tributary waters. Nonetheless, for many cave waters, the averaging of properties and processes is less extreme. There is generally a shorter flow distance from recharge sites to sampling sites, and it can be easier to distinguish differences in the chemistries of waters from different environments.

Concept of Hydrochemical Facies in Carbonate Aquifers

A number of workers have contributed to the developing concept of hydrochemical facies, or distinct water types in karst. According to Hess and White (1993, p. 196), Back (1966) "quantified" the concept of hydrochemical facies by identifying "the chemical variation along a flow field, and within different rock types". (Changes in the bulk chemistry of groundwater occur, for example, as water moves from one rock type to another.)

Within karst settings, waters have been found to exhibit different chemistries depending on their location and hydrogeologic setting, usually based on derived parameters rather than bulk chemistry or measured parameters. Drake and Harmon (1973), e.g., first classified central Pennsylvania karst waters into *a priori* hydrogeological groups (allogenic surface recharge, soil water, conduit springs, diffuse springs, well water, and basin surface runoff). They then used linear discriminant analysis of the measured variables pH, HCO_3, Ca, Mg, water temperature, and specific conductance, along with the derived variables SI_C, SI_D, and P_{CO_2}, in a stepwise procedure to determine which, if any variables might separate their hydrogeological groups at a statistically significant level. They found that SI_C, SI_D, and P_{CO_2} were successful discriminants, and that these parameters could be used to demonstrate the chemical evolution of waters along flow paths. More recent studies have also relied on hardness (sum of Ca and Mg, expressed as $CaCO_3$) in distinguishing karst water types.

This is a relatively narrow concept of hydrochemical facies in karst, being based on only part of the carbonate chemistry. However, it is useful within its realm and has received additional support in studies by Harmon et al. (1975) and more recently by Troester and White (1986) and by Hess and White (1989, 1993). To the list of the six waters of Drake and Harmon (1973), Troester and White (1986) add cave drip waters and vertical shaft waters (the latter based primarily on Brucker et al., 1972), but limit their study of three tropical Puerto Rico basins to the composite waters that they label surface streams, large cave streams, and springs.

There have been many other geochemical studies in carbonate aquifers that identify geochemical types. These range from studies of diffuse-flow systems in chalk (see, e.g., the reviews by Lloyd, 1993 and Price, 1993) to studies of mixed-flow systems in limestone and dolomite (see, e.g., Thrailkill, 1972; Scanlon, 1989, 1990) to studies that include predominantly conduit-flow aquifers in a variety of temperate-zone and tropical settings (e.g., Fish, 1977; Miller, 1981; Worthington, 1991; Troester, 1994). In these, and many other studies, there has been little tendancy to explictly distinguish water types for **each karst hydrogeologic setting**, or to attempt to do so for **each potential cave water type** if cave waters were sampled instead of primarily surface streams, wells, and springs.

One of the difficulties that arises in any attempt to classify waters is that there is a certain arbitrariness to *a priori* groupings. One can distinguish any number of water types based on one's imaginative ability to distinguish potentially significant karst environments or combinations of environments and specific chemical processes. What strikes us the most, at the present time, however, is that the study of karst geochemistry is still very much in its infancy. We simply do not know what hydrogeological water types correspond most usefully to objectively identifiable chemical water types. Thus, at the beginning of this study, the waters of Mystery Cave were classified according to physical water types (see below). This classification was not expected to correspond to karst chemical water types---it was merely a convenient way of grouping the data in a fashion that we hoped would not too obviously bias results by predisposing us to identify the same chemical water types distinguished in previous studies or to relate them merely to the same *a priori* hydrogeological water types (surface streams, wells, diffuse-flow springs, conduit-flow springs, etc.), no matter how advantageous that might seem. (Also, our scope was primarily limited to cave waters, whose classification into physical and chemical water types has received much less attention.) Some of the early ground-breaking studies, particularly by researchers who would consider themselves part of the mainstream karst community, relied on chemical analyses that were restricted to only a few measured and derived parameters. With the advances in scientific instrumentation that allow relatively inexpensive analysis of a whole suite of major, minor, and trace elements, we today have a much broader data base to work with. We also have a broader appreciation of the possibilities of more-or-less objective "classification" or "assignment" of water types, based on statistical techniques whose application to geological and hydrologic topics has lagged behind applications in other fields, such as the social and life sciences, but which is rapidly advancing. (See Davis, 1986, and the highly useful compilation by Rock, 1988. Incidentally, Rock, 1988, p. 275, distinguishes classification from assignment as follows: "If we take a series of measurements on, say, an assemblage of conodonts, and, without pre-conceived paleontological criteria, attempt to assess relationships *purely* from these measurements, we are *classifying*. If, by contrast, we assign the conodonts to known species by comparing them with established species, we are *assigning*. Classification is a 'suck-it-and see', exploratory approach with no *a priori* framework; assignment is a follow-up approach where some established framework already exists.")

Purpose and Scope

This chapter discusses selected aspects of the hydrochemistry of Mystery Cave. It covers only part of the conceptual equation introduced above. To prevent the analysis from becoming a purely academic discussion of carbonate and environmental chemistry---which in any case would require a more complete analysis of the data than it yet has been possible to accomplish---we concentrate on four things. First, we provide an enumeration and discussion of the physical water types. In a sense, this just sets the stage; but it also allows us to synthesize much of the relevant hydrologic information and to illustrate the range of water types present in Mystery Cave. Second, we discuss, mostly at an elementary level, a few of the measured field and analytical parameters (water temperature, conductivity, etc.) along with several derived parameters (saturation indices, P_{CO_2}). This allows us to answer some very specific questions posed by DNR and Mystery Cave staff: e.g., what are typical values of various constituents? It also allows us to point out the significance of some of these parameters, and to discuss their implications for understanding certain aspects of the cave's geomorphology. For example, it allows us to explain why there are no vertical shafts (of the kind found in the eastern U.S., or in western alpine settings) in Mystery Cave. Third, we discuss, at a more advanced level, the results of the environmental chemistry. This consists primarily of discussions of nitrate, chloride, zinc, fecal coliform bacteria, volatile organic compounds, and the pesticides atrazine and alachlor. Fourth, and last, we return to the topic with which we opened this chapter: what kinds of waters are there in Mystery Cave, and what do they tell us about the hydrologic system as a whole?

WATER TYPES AND WATER SAMPLING

Water types in Mystery Cave are classified in Table 4.1. Five of these waters (streams, pools, waterfalls and ceiling drips, stalactite drips, and flowstone flows) were sampled on a periodic basis at about a dozen sites for field parameters and major ions. For convenience, these waters will be referred to collectively as the "five main water types" or "five water types." Two additional waters (bedrock drops and in-cave springs) were sampled only a few times, bringing the number of sampled cave water types to seven. Water types listed as "other waters" in Table 4.1 (interstitial waters in clastic sediments, diffuse flows that seep out of bedrock surfaces, and condensation waters) lie outside of the scope of the project and were not sampled. In addition to the sampling for major ions, several water types were sampled for zinc, fecal coliform bacteria, pesticides, and volatile organic compounds at selected sites, as discussed later in this chapter.

The classification is based on the form of the water, its discharge, the type of flow, and its setting or location within Mystery Cave. For pools, the residence time and pool volume are also important. Human influences can be significant, so a distinction is made between natural and artificial pools. Like all classifications, this one is arbitrary in the sense that other classifications could be used depending on the purpose and scope of the discussion. A description of these water types follows.

*1. **Streams.*** As on the surface, streams consist of flowing water in pool and riffle sequences. However, in a cave there is a roof and flow can completely fill the conduit. Most of the streams are derived from the South Branch of the Root River. The

Table 4.1.
Water Types of Mystery Cave

Five Main Water Types

1. **Streams**
    - Derived from the Root River
    - Derived from areas over Mystery Cave
2. **Pools**
    - Natural
        - Isolated pools
        - Flowstone pools
    - Artificial pools (in present configuration)
3. **Waterfalls and ceiling drips (from joints)**
    - Falls from ceiling and wall joints or open fissures
    - Drips from ceiling and wall joints or open fissures
4. **Stalactite drips**
    - Drips from tips of stalactites
    - Drips and flows from outer surfaces of stalactites
5. **Flowstone flows and drips**
    - Drips and flows on surfaces of flowstone

Other Waters

6. Bedrock drops and films
7. In-cave springs (from Blue Lake at high water stands)
8. Interstitial waters in clastic sediments
9. Diffuse flows and seeps from interstitial pores in bedrock
10. Condensation drops and films

major streams sampled include one of the tributaries to the Disappearing River, the Lower Level Stream in Mystery I; Formation Route Creek in Mystery III; and Flim Flam Creek in Mystery II.

As described in Chapter 3, water infiltrates sediment-filled fissures in the bed of the Root River and rapidly descends to the lower levels in the Stewartville Formation. It then flows near-horizontally to springs. Close to the Root River, flow is in solutionally-enlarged joints and air-filled passages, but short sumps (closed-conduit flow) within joints are also probable. Farther from the river, all of the streams sump. Flim Flam Creek sumps but reappears downstream in lower-level passages before sumping again. Streams derived from the Root River vary considerably in discharge and physical and chemical parameters. This is an expected result, since their primary recharge is derived from rapidly infiltrating river waters whose discharge and other physical and chemical characteristics rapidly respond to rainfall or snow melt.

Two primary cave streams do not fit this flow pattern; they in fact occupy different positions within the hydrologic system and exhibit different hydrologic and chemical characteristics. One is the stream feeding Turquoise Lake in Mystery I. Known as the Turquoise Lake Source stream (TLS), it apparently flows a significant distance laterally within the Dubuque Formation from an area beneath agricultural lands and forested hillslopes to the southeast of Turquoise Lake (Figure 3.4). Its discharge is on the order of a liter to perhaps five-ten liters per minute. The other stream is Rimstone Creek in Mystery III; it flows over 500 ft laterally within the Dubuque Formation and probably receives recharge from several ravines that drain corn fields (Figure 3.4). The discharge of Rimstone Creek is similar to that of Turquoise Lake, but larger discharges are common after major recharge events. Also, a more variable water chemistry indicates a more direct connection to surface recharge.

All of the primary cave streams appear to be perennial. In general, their discharge diminishes during dry periods in the summer. During the winter, discharge can fall very low at Rimstone Creek and Turquoise Lake once the ground is frozen and blanketed with snow. At such times, most of their discharge must be derived from slow drainage from soil and loess into the fractured bedrock above the cave, and physical and chemical parameters are relatively stable. In contrast, the lower-level streams remain active even when the Root River freezes at the top. Discharge often falls abruptly following extreme cold spells (see discussion of Flim Flam Creek in Chapter 9). Physical and chemical parameters in the lower level streams are relatively stable during the coldest periods of the winter, but only a minor amount of melting is needed to produce significant changes in temperature, conductivity, and chemistry.

*2. **Pools.*** A pool is a reservoir with a volume and shape (under conditions of free-surface flow) that ensures a relatively long residence time for its water compared to the local residence time of inflowing or outflowing waters. "Local residence time" refers to the residence time for short reaches of flow path, just upstream or downstream of the input and outputs points to the pool. No quantification of residence time is attempted here, but it is useful to give a qualitative ranking of residence times for various types of pools, because of the role of residence time in carbonate chemistry. Those pools with a long residence time tend to have active deposition of calcite, particularly as calcite rafts, at least at some times of the year. The category of pools, as used here, does not include pools within pool and riffle sequences of the lower-level streams: all such waters are considered stream waters.

Pools can be natural or artificial. For Mystery Cave, we distinguish artificial pools and two subtypes of natural pools: isolated pools and speleothem pools.

Isolated pools. These are mostly small, shallow pools fed by low-discharge sources such as stalactite drips and seeps out of joints or bed partings. Isolated pools include Sugar Lake and the Tar Pits in Mystery III. A few larger isolated pools, such as Dragon's Jaw Lake, apparently receive occasional abrupt inflows from joints following major recharge events. Isolated pools are not normally fed by, nor are they drained by the primary cave streams. Their water slowly accumulates and is then lost by seepage into clastic sediments and joints or is lost by evaporation. The waters of isolated pools have relatively long residence times compared to those of most speleothem pools, the pools within streams, or such artificial pools as the Wishing Well Drips pool. Isolated pools may have extensive speleothem linings.

Flowstone pools. Most of these are small, shallow pools (<1 to perhaps 100 ft^3) on flowstone. This group includes the Pipe Organ Pool and the unnamed pools of the Rock Garden in Mystery I. It also includes the many pools of Lily Pad Lake in Mystery III. Flowstone pools are generally fed by persistent seeps and drips, and are drained by flowstone flows up to perhaps a liter per minute. The smaller flowstone pools (e.g. the Pipe Organ Pool) have very short residence times, whereas the larger ones (Lily Pad Lake; some of the unnamed pools of the Rock Garden) have longer residence times and more persistent presence of calcite rafts.

Artificial pools. Includes Turquoise Lake, Blue Lake, Frozen Falls Pool, and Coon Lake. These pools are artificial in their present configuration, which has been modified for commercial purposes. Turquoise Lake and Blue Lake are at sites that have long supported pools, as shown by extensive deposits of subaqueous speleothems. Turquoise Lake (which has a constant volume that can only roughly be estimated as 1200-1500 ft^3) and Frozen Falls Pool (about 200-250 ft^3) are perennial. Blue Lake (<100 ft^3-about 10,000 ft^3) may be perennial, but dramatically decreases in volume from about May to November in a typical year (see Chapter 7). By November it usually has broken up into a number of small shallow pools (as little as a few inches deep). Unlike the other pools, Blue Lake does not have a perennial source. All of the artificial pools have input waters or actual pool waters that are in contact with materials that could influence their chemistry. Such materials include concrete (used as retaining walls, or as cement holding limestone blocks in place), steel and galvanized steel (bridges and railings), wiring and light fixtures (adjacent to, and in some cases within pools), and creosote-impregnated pilings (used as bridge support).

3. Waterfalls and ceiling drips from joints. This group includes Frozen Falls Drips, Wishing Well Drips, and the waterfall at Enigma Pit. These waters enter via joints or fissures developed on joints; they are vertically descending waters following the steepest available paths through the vadose zone. In all probability, there is little lateral component of flow within the bedrock above their entry points into Mystery Cave. Some of these waters run down the sides of stalactites to drip and fall points; although they must mix with stalactite drip waters, their greater volume results in a mixture at the cave floor whose physical and chemical character derives only minimally from water dripping out of the stalactites. Discharge ranges from much less than a liter per minute to perhaps ten-fifteen liters per minute. Discharge was usually less than 500 ml per minute during the middle of the winter at the periodic sampling sites.

4. Stalactite drips. This group includes drips from stalactite GG1 and other nearby drips at the Garden of the Gods in Mystery II, and the Iron Drips in Mystery

III. Stalactite drips, narrowly conceived, would consist only of waters that flowed through the stalactites. In practice, stalactite drips were sampled by collecting all of the water that fell into containers placed below drip points. During higher flows, water could be seen to flow down the outsides of some stalactites. Such flows probably emerge from joints feeding the stalactites or from other nearby joints. However, these waters can originate from different flow paths and have very different physical and chemical characteristics, as well as different residence times underground, than the "true" stalactite drip waters. Discharges at sampled stalactite drip sites ranged from a few drops per minute to perhaps ten-fifteen liters per hour (at GG2).

5. ***Flowstone flows and drips.*** These waters enter via joints (or bed-joint intercepts at some locations) and spread out as thin films and flows over flowstone on walls, ledges, and floors. This group includes Coon Lake Drips in Mystery II and the drips and flows at the Pipe Organ and Across from Pipe Organ in Mystery I. These waters are low-discharge flows with discharges ranging from drops per minute to liters per hour. As with stalactite drips, the waters flowing across flowstone can have more than one nearby upstream source. At the Pipe Organ, e.g., there are at least two sources. One is the normal source (derived from slow flow or diffuse recharge) and the second is a faster, concentrated source that mixes with the first and carries both a temperature and a turbidity signal from the surface.

6. ***Bedrock drops and films.*** Drops and films occur on bedrock at numerous locations in Mystery Cave. They can originate as seepage water from joints or other fractures, as seepage water from interstitial porosity, and from condensation. A few samples of bedrock drops were taken in Mystery I near the entrance; these did not have an unequivocal origin, but probably were condensation waters. Bedrock drops at a site in the passage leading to the Needle's Eye (BD2) could have been water condensing on bedrock with disseminated pyrite in the Dubuque Formation, but their very high sulfate content and location suggests that these are seepage waters perhaps augmented by condensation.

7. ***In-cave springs.*** These are artificial springs in the gravel trail bed east of Blue Lake. They are active only when water level at Blue Lake is high, and have a chemistry similar to that of Blue Lake.

8. ***Other waters.*** A variety of other types of waters are present in caves. They occur in small quantities or have low fluxes. They have little impact on water quality of the primary flowing waters. They may, however, be important in speleothem deposition or in cementation processes that consolidate clastic sediments. These waters include (1) interstitial waters in clastic sediments, (2) diffuse flows and seeps from interstitial pores in bedrock, and (3) condensation drops and films. In Mystery Cave, clastic sediments are rarely well cemented, so evaporation of interstitial waters from clastic sediments may not be important, as it is in many caves in the eastern U.S., e.g., in the caves of the Greenbrier karst of West Virginia. Diffuse flows and seeps from interstitial pores in bedrock is undoubtedly important in Mystery Cave, as shown by aragonite and other crusts lining lower walls in 5th Avenue and elsewhere (see Chapter 11). Condensation waters are widespread near entrances and lower-level streams in Mystery Cave, but are not volumetrically significant, nor do they have significant associated dissolutional and depositional forms such as drop dents or rills (see Jameson, 1986; Jameson and Alexander, 1989; Jameson and Alexander, 1990).

WATER TEMPERATURE

Estimation of Deep Cave Temperature

The mean temperature of a cave might be considered to be the average of temperature at all points within the cave air, water, clastic and chemical sediments, and a representative small volume of surrounding bedrock (e.g., the bedrock forming such speleogens as flutes or bedrock bridges). Such a definition might be formally correct, but it is operationally useless. It can have little significance in cave studies.

As an alternative, the average cave temperature might be conceptualized as the measurable air or water temperature at isolated "deep" sites within the cave. Such sites could be assumed to be sufficiently isolated and distant from entrances and primary sources of surface air-exchange or surface water-recharge as to allow the assumption that a long-term thermal equilibrium had been established between air, water, clastic and chemical sediments, and surrounding bedrock. Isolated dead-end passages far from entrances would offer the best candidates for sites to estimate deep cave temperature.

In the presence of a uniform geothermal gradient reflecting heat transmission from beneath the cave, deep cave temperature would be approximately equal at all "deep" sites at equal subsurface elevations. This assumes, of course, that overburden and bedrock are sufficiently thick above and to the side of the cave that the thermal damping depth has been exceeded---that is, that diurnal and seasonal temperature signals (passing as heat conduction from the surface through the soil and bedrock) do not extend that far. (See, e.g., Jury et al., 1991 and Hanks, 1992. See also Lange, 1954a, b for a mathematical analysis showing that surface thermal signals can produce temperature excesses as far as 20 m beneath a horizontal surface in response to annual insolation cycles and 175 meters for climatic cycles with a period of 100 years.)

The deep cave temperature also would be constant over time, assuming that neither the local geothermal gradient nor the climate were to change. It would be approximately equal to (but actually slightly higher than) the mean annual surface temperature, if the cave were sufficiently close to the surface but had a very limited vertical extent. So defined, the deep cave temperature would fundamentally be *a single* rock and sediment temperature shared by the air and water also present at the isolated "deep" site. Deviations from deep cave temperature, which would occur at all other "nondeep" cave sites, would mostly result from heat exchange with advecting air or water, or from absorption or release of latent heat associated with phase changes (such as the condensation of water near entrances or warm-water cave streams; see Chapter 11). If the cave had a significant vertical range, then there would be more than one possible deep cave temperature.

Mystery Cave has a limited vertical range (roughly 100 ft) but a highly variable "overburden" depth (here only, overburden depth is the sum of the thicknesses of soil, loess, and bedrock above the cave; this ranges from a few feet at entrances to about 100 ft beneath the upland). More importantly, Mystery Cave has a significant airflow between entrances and significant heat exchange from or to lower level streams (depending on the season). Heat exchange from advecting water and air is sufficient to make it exceedingly difficult to estimate a deep cave temperature based on available data, which consist of water temperature measurements. Thus no isolated deep cave site was explicitly identified and investigated during this study. However, two hydrologic sites, Blue Lake and Turquoise Lake, come close in having remarkably stable water temperatures.

Deep cave temperature in Mystery is estimated to lie within the range of 8.5-8.8°C. It possibly is close to 8.7°C (47.7°F). This conclusion is based in part on measurements of water temperature with ASTM Method 63C mercury glass thermometers at Blue Lake and Turquoise Lake. These sites had mean temperatures and standard deviations of 8.72 ± 0.06°C (Blue Lake, n=20) and 8.67 ± 0.06°C (Turquoise Lake; n=16 if the single anomalous temperature of 8.25°C due to the March 30-April 3 flood is disregarded). The conclusion is also based on water temperature and air temperature measurements from continuous data recorded at Blue Lake. (However, see below and also the discussion of water temperature for Rimstone Creek in Chapter 5.)

Turquoise Lake has a large, essentially constant volume (somewhere in the range of 1200 to 1500 ft^3 as noted above, but hard to estimate) with a greater water-rock contact surface area than an air-water surface area. It is somewhat isolated in that it is in a dead-end side passage about 30 ft from the commercial trail. It probably has only limited air flow over it, but is visited by tourists and has a minor internal heat source consisting of a submerged lamp, along with several nearby external heat sources also consisting of lamps. Turquoise Lake is relatively near an entrance (about 750 ft). The adjacent commercial route has a significant air flow. Its air temperatures (as measured at the Bomb Shelter) show a much subdued correlation with outside air temperatures, ranging from about 9.62°C in the summer to 9.38°C in the winter (Lively and Krafthefer, 1993b, Figure D-8). Apparently, however, these heat sources are ineffective at modifying water temperature. Mean water temperature is lower at Turquoise Lake than at Blue Lake. This is an unexpected result if heat transfer from air or the lamps were important. Air temperature at Blue Lake (8.65°C; see below) is consistently cooler than what air temperature should be near Turquoise Lake, based on air temperature at the Bomb Shelter. (It should be cautioned that the minor difference in water temperatures measured at the time of water sampling at TL and BL is not statistically significant. To investigate this question more rigorously, monthly water sample data is not adequate; data loggers would be needed at both sites, given the small differences in temperatures involved.)

Blue Lake is farther from a cave entrance (about 900 ft) in what can be regarded as a side passage (with regard to primary air exchange) and receives much less visitation. It has no lights and the heat from the nearby data logger is apparently negligible. Air temperature is nearly constant at about 8.65°C. The volume of Blue Lake ranges from less than 100 ft^3 to about 10,000 ft^3, however, so there is considerable variation in the ratio of the air-water to water-rock contact surface areas. Airflow across the lake into or from Mystery III is probably significant, and may contribute slightly to declining water level by evaporation. Moreover, there is a minor amount of variation in water temperature, as recorded by the Blue Lake data logger. This temperature variation is associated with the influx of slightly cooler water; that water causes temperature recorded by the data logger to fall about 0.03-0.05°C (see Chapter 7).

Thus neither pool is free of variations in water temperature. Neither can be considered truly isolated in a thermal sense, but these pools provide the best available data for estimating deep cave temperature.

Other water types at other sites (for example, stalactite drips at apparently isolated locations) might normally be considered more suitable than large cave pools for determining deep cave temperature---if the estimation is to use water temperature. However, we suspect that it would be better to estimate deep cave temperature by burying temperature sensors in sediments at isolated sites far from entrances.

Sampled waters at sites other than Turquoise Lake and Blue Lake had water temperatures that are deemed implausible candidates for deep cave temperature. This conclusion is based on a number of reasons. First, at some sites there are inconsistencies in the data due to the method of data collection. For example, Wishing Wells Drips might have been a good site because its relatively stable chemistry suggests a long residence time, which might allow for thermal equilibrium between infiltrating water and bedrock. But its water was allowed to collect for variable amounts of time, which depended on flow rate. Even though the water temperature was read to the nearest 0.05°C, the measured temperature is unlikely to be representative of the water temperature at its entry point into the cave. Heat exchange may have taken place within the sampling container as it filled, warming the water. It is also conceivable that measured water temperatures were influenced by the effects of falling 40 ft from the ceiling; evaporation has a tendency to cool the water that does not evaporate. At WWD, mean temperature was 8.84 ± 0.26°C, with a range of 8.60 to 9.50°C for n = 18. The higher temperatures are undoubtedly a result of heat exchange during the period water was allowed to collect before sampling.

Other reasons for excluding other periodically sampled sites include the following. At some sites, water temperatures simply varied too greatly for the sites to be plausible candidate deep cave sites. At other sites, water temperatures even appeared to be correlated with seasonal surface air temperature or surface water temperature. In each case, we infer that water temperatures were influenced by advecting air or water.

Temperature Distribution of Sampled Waters

Water infiltrates at a temperature determined by conditions at the time and location of recharge. Most water infiltrates at a temperature different from mean cave temperature. Heat exchange occurs as the water passes through overburden and bedrock to enter and flow within cave passages. The water is warmed or cooled. During the summer, waters at Mystery Cave usually are cooled. During the winter and the spring melt, waters are warmed.

For water, deviations from deep cave temperature will depend on such factors as (1) the temperature of recharge; (2) the length of subsurface flow; (3) the type of flow or relative proportion of different flows (porous media flow vs. open- or closed-conduit flow) in mixed flows ; (4) the contact areas of the water/solid and air/water interfaces; (5) the flow velocity; (6) the temperature gradient between the water and materials with which it comes into contact; and (7) the heat capacity, thermal conductivity, and thermal diffusivity of those materials. We shall make no attempt to discuss these factors, or sort out their influences on the temperatures of the various water types; it will suffice here to consider only the most broad trends in water temperatures for the entire data set and for the different water classes.

Temperature ranged 1.3 to 16.4°C, with a mean of 8.95°C, for 231 water samples collected in Mystery Cave. Figure 4.1a presents these data as a histogram. Figure 4.1b

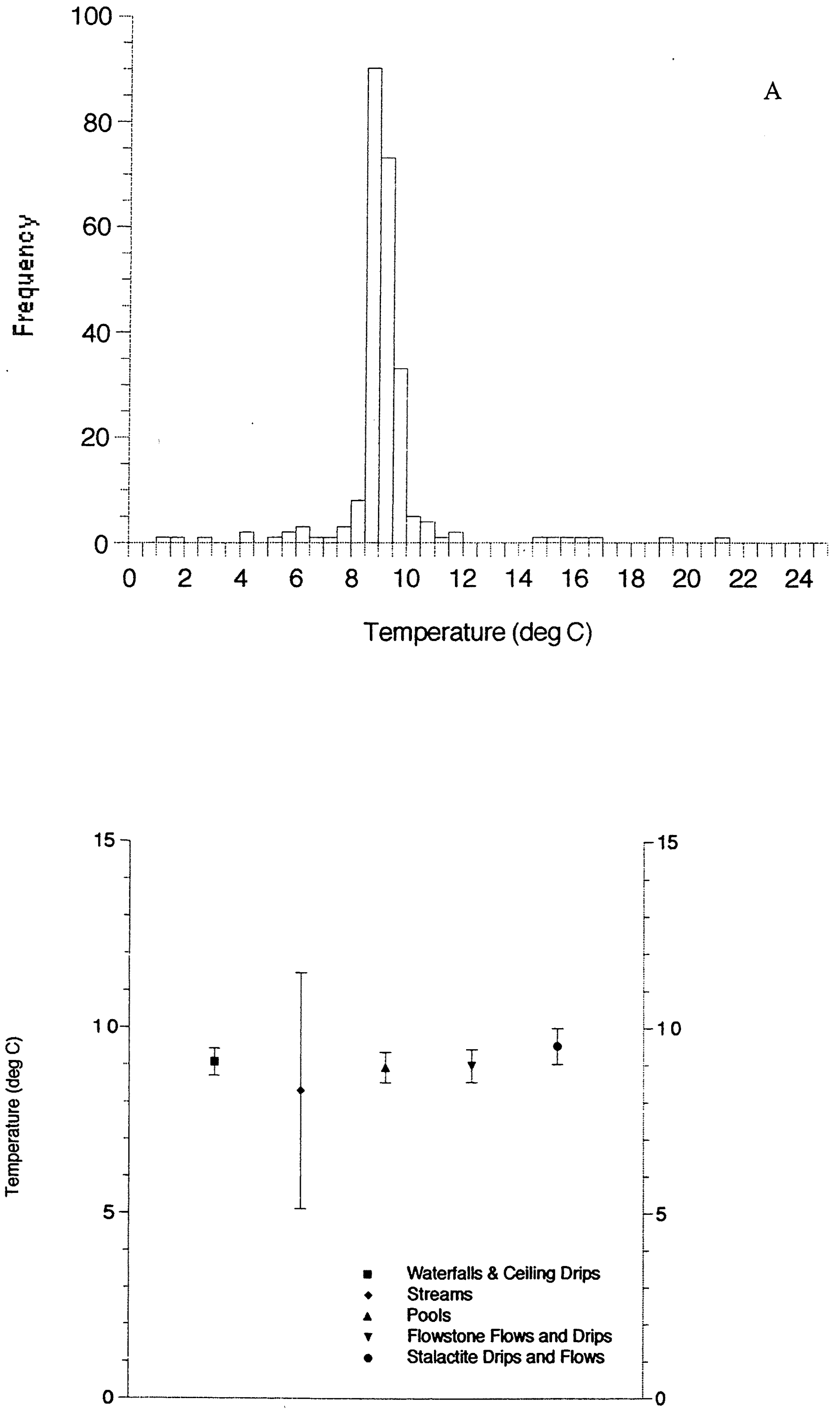


Figure 4.1. a. Histogram of temperature of sampled waters in Mystery Cave. b. Means and standard deviations of water temperature. Bars show one standard deviation above and below the mean.

shows mean temperatures and standard deviations for each of the five primary water types sampled.

Waters with temperatures significantly different from about 8.7°C are most likely to be waters with relatively short transit times and much warmer or colder infiltration temperatures. Such waters are mostly cave-stream waters. Some waterfall and ceiling drip waters in passages near entrances in Mystery I also fall in this category. In fact, all water temperatures below 7°C and above 11°C in Figure 4.1 are temperatures of streams. Of the five water types, streams thus exhibit the greatest range of water temperature (Figure 4.1a). Additionally, the data logger at Flim Flam Creek has recorded temperature as high as 21°C in the summer and as low as 1.2°C in winter. Flim Flam Creek is about 2560 ft in a straight line from its postulated source area on the Root River. Since heat is lost in summer and gained in winter along the flow path, the actual range of water temperatures for cave streams (e.g., for parts of streams nearer sink points) must be somewhat greater than those recorded at lower level stream-water sampling sites (Flim Flam Creek, Formation Route Creek, and the Lower Level Stream).

It is notable that all of the main water types except streams have mean temperatures greater than 8.7°C. This is probably an artifact of the location of sampling sites. Sampling sites are biased toward near-surface locations (e.g., all sampling sites in Mystery I are within 800 ft of the entrance). It is also possible that there is a slight seasonal bias in the water temperatures beyond that evidenced for streams. Relatively fewer sampling trips were made in the winter than in other seasons. A full analysis of this question, however, would not consider seasons alone. It would have to consider a variety of other factors, including surface weather immediately before and during sampling. It also would have to consider the timing of the fall and spring overturns in air flow---what is important here is the time of transitions of mean air temperatures on the surface to temperatures above and below mean cave temperatures, and changes in airflow patterns that might affect local passage temperatures generally, and water temperatures in particular. (See Lively and Krafthefer, 1993a.)

The high mean temperature of stalactite drips (9.5°C) is an artifact of both location and sampling procedures. Most of the sampled stalactite drips were at drips GG1 and GG2 in the Garden of the Gods, a section of the cave that probably has a mean air temperature of about 9.2°C, based on occasional air temperature measurements. (In is worth noting that data collected by a water temperature probe installed after June, 1993 at the Coon Lake Drips site, closer to the entrance than the Garden of the Gods, had a temperature of about 9.0°C. That probe sits in a container that holds about 0.75 l and the CLD water is constrained to flow through it at rates that vary naturally from about 0.25-14 l/hr, without, however, exhibiting a significant temperature variation. Evidently, water that passes as diffuse flow through soil, loess, and fractured bedrock to emerge in this area of the cave is relatively warm, warmer than the estimated 8.7°C for a deep cave temperature.) The drips at the Garden of the Gods stalactites were collected in plastic bags over time periods that varied with discharge from less than one to more than 10 hours, allowing time for incoming water to warm to local cave temperature. Further, water temperatures for GG1, at least, were apparently increased due to sampling procedures adopted to maximize sample size (see the discussion of sites at the Garden of the Gods in Chapter 5).

In summary, the "deep" cave temperature is estimated to be about 8.7°C. Major deviations from it are present in lower level streams, whose temperatures reflect in a subdued fashion the temperature of the Root River. Minor deviations from deep cave temperature in water samples are ubiquitous near entrances in the summer and winter. Water temperatures of small pools and low-discharge drips and flows is influenced by advecting surface air, particularly in passages within a few hundreds of feet of entrances. The temperature of condensation moisture and seepage moisture (mostly drops) on bedrock surfaces is also affected; in the summer, the water and outer bedrock are warmed, and in the winter the water and outer bedrock are cooled.

CONDUCTIVITY AND SOLUTES

Ordinary distilled water from our lab (not deionized) that has equilibrated with atmospheric carbon dioxide has a conductivity of about 20 µS/cm at 25°C. The conductivity of water slowly melted (at room temperature) from snow collected from the flood plain of the Root River is about 30-40 µS/cm at 25°C. The conductivity of rain water was not sampled during this study. It probably is as low or lower than that of snow melt at this rural location but probably also varies a good bit from storm to storm as its solute load varies. As a conservative estimate, conductivities larger than about 50 µS/cm at 25°C for natural waters at Mystery Cave should reflect solute uptake between the time of precipitation and the time of sampling.

Conductivity ranged 303 to 954 µS/cm at 25°C for 196 water samples collected in Mystery Cave. Figure 4.2a presents these data as a histogram with three peaks. This suggests the possibility of distinct chemical groups discriminated by conductivity. Figure 4.2b shows mean conductivities and standard deviations for each of the five primary water types. The mean conductivities of two groups (waterfalls and ceiling drips, and pools) are somewhat higher than those of the other groups, but there is considerable overlap in the conductivities that fall within one standard deviation of the mean. From these plots, it appears unlikely that conductivities correlate in any simple way with the five physical water types.

The range of conductivities in Mystery Cave is rather large, over 600 µS/cm at 25°C. This could reflect (1) a variety of natural and anthropogenic chemical processes involved in solute uptake between infiltration and arrival at the sampling site, (2) a large range of contact times for interactions between water and substrate, and (3) variable amounts of mixing between waters that follow different flow paths. Another complication is that water types with long residence times at the sampling sites, such as the waters of isolated pools, can undergo processes (e.g., precipitation) that further modify the chemistry and affect conductivity, at least within limited ranges. Another point to make is that we did not sample waters on the Root River or Flim Flam Creek during major snow-melt events or precipitation events. At these times, dilution effects could be expected to be most extreme and conductivities would be expected to be lowest for those cave waters that received a significant component of rapid recharge. Thus the range of conductivities expected for Mystery Cave waters is actually somewhat greater than the reported range. In fact, conductivities measured more recently with continuous data acquisition systems (winter melt events of February, 1994) indicate that conductivity can drop as low as about 180 µS/cm at 25°C on the Root River for 4-5 days and as low as 140 µS/cm at 25°C for several days at Flim Flam Creek.

As noted in Chapter 2, conductivity is a function of solute concentrations as well as water temperature. Many authors (e.g., Hem, 1985) have related conductivity to solute concentrations in surface and groundwaters, obtaining linear relationships between conductivity and hardness or other solute measures. White (1988) reports a

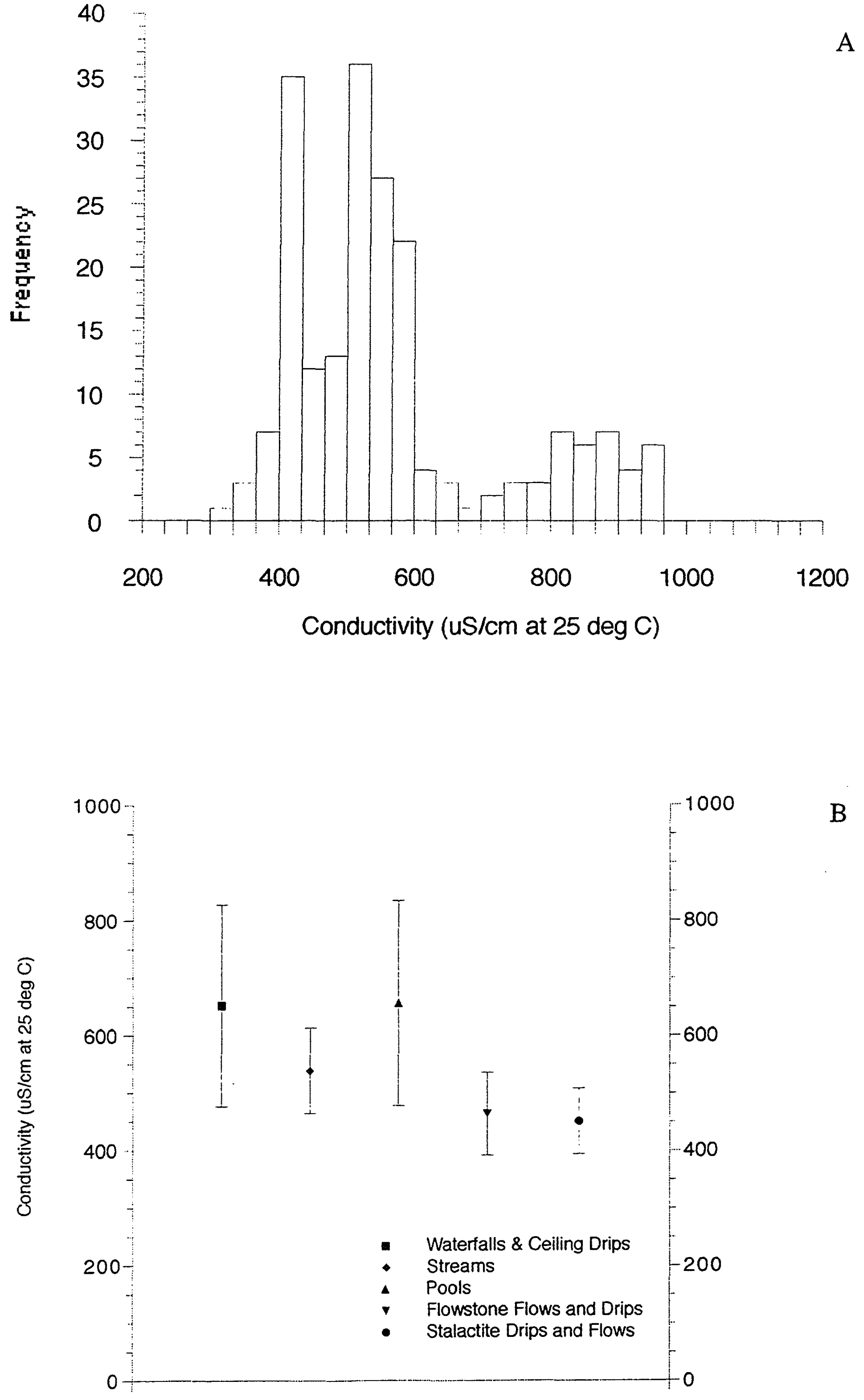


Figure 4.2. a. Histogram of conductivity of sampled waters in Mystery Cave. b. Mean conductivities and standard deviations for each of the five primary water types. Bars show one standard deviation above and below the mean.

relationship between conductivity (in Siemens/meter at 25°C) and hardness (Hd = sum of Ca and Mg, expressed as $CaCO_3$) for well and spring waters in the mixed limestone and dolomite terrane of central Pennsylvania, using data from Langmuir (1971). That relationship (White, 1988, p. 136, eqn. 5.42) may be modified to give

$$C_{25} = 1.70 \text{ Hd} + 50$$

in which C_{25} is conductivity in µS/cm at 25°C. Similarly, Jacobson and Langmuir (1970) obtained

$$I = 1.88 \times 10^{-5} C_{25}$$

in which I is ionic strength. For Mystery Cave waters, we obtained

$$C_{25} = 1.79 \text{ Hd} - 9.2 \quad (r = 0.97)$$

and

$$I = 1.65 \times 10^{-5} C_{25} \quad (r = 0.98)$$

as shown in Figure 4.3a and b. Although there is a strong linear relationship between conductivity and hardness, it is not generally useful for interpretive purposes to convert conductivities measured by the data loggers into estimated hardnesses by rearranging the equation above. Figure 4.3a shows that there actually is a large amount of scatter about the regression line. The scatter increases as conductivity and hardness increase. Part of the scatter is a function of uncertainties in conductivity, which increase as conductivity increases and also increase as the sampling temperature deviates from 25°C (see Chapter 2). (The uncertainty in the Ca and Mg concentrations is probably negligible by comparison.) But much of the scatter is a result of the varying concentrations of other ions, such as SO_4 and Cl, which also contribute to conductivity.

pH AND P_{CO_2} OF CAVE WATERS

The pH ranged 7.17 to 8.39, with a mean of 7.91 for 231 sampled waters in Mystery Cave. Figure 4.4a presents these data as a histogram with a near-unimodal distribution about the mean. Figure 4.4b shows the mean pH and standard deviations for each of the five primary water types sampled.

The mean pH is relatively high. pH values are higher, in fact, than those found in cave waters in many temperate-zone karsts, such as in the eastern U.S., in which most cave waters are unsaturated with respect to calcite and dolomite. The pH of karst waters depends on a number of factors, beginning with the amount of available carbon dioxide for production of carbonic acid and its seasonal variation.

In Minnesota's mantled karst, in which waters infiltrate through a thick soil and loess cover, waters potentially have a long contact time with materials in which carbon dioxide is being produced. However, there is only a short growing season for primary carbon dioxide production in the soil and loess. If downward transport of organic materials were significant, then there might be some additional CO_2 production beyond the growing season, in the zone beneath the frozen soil and

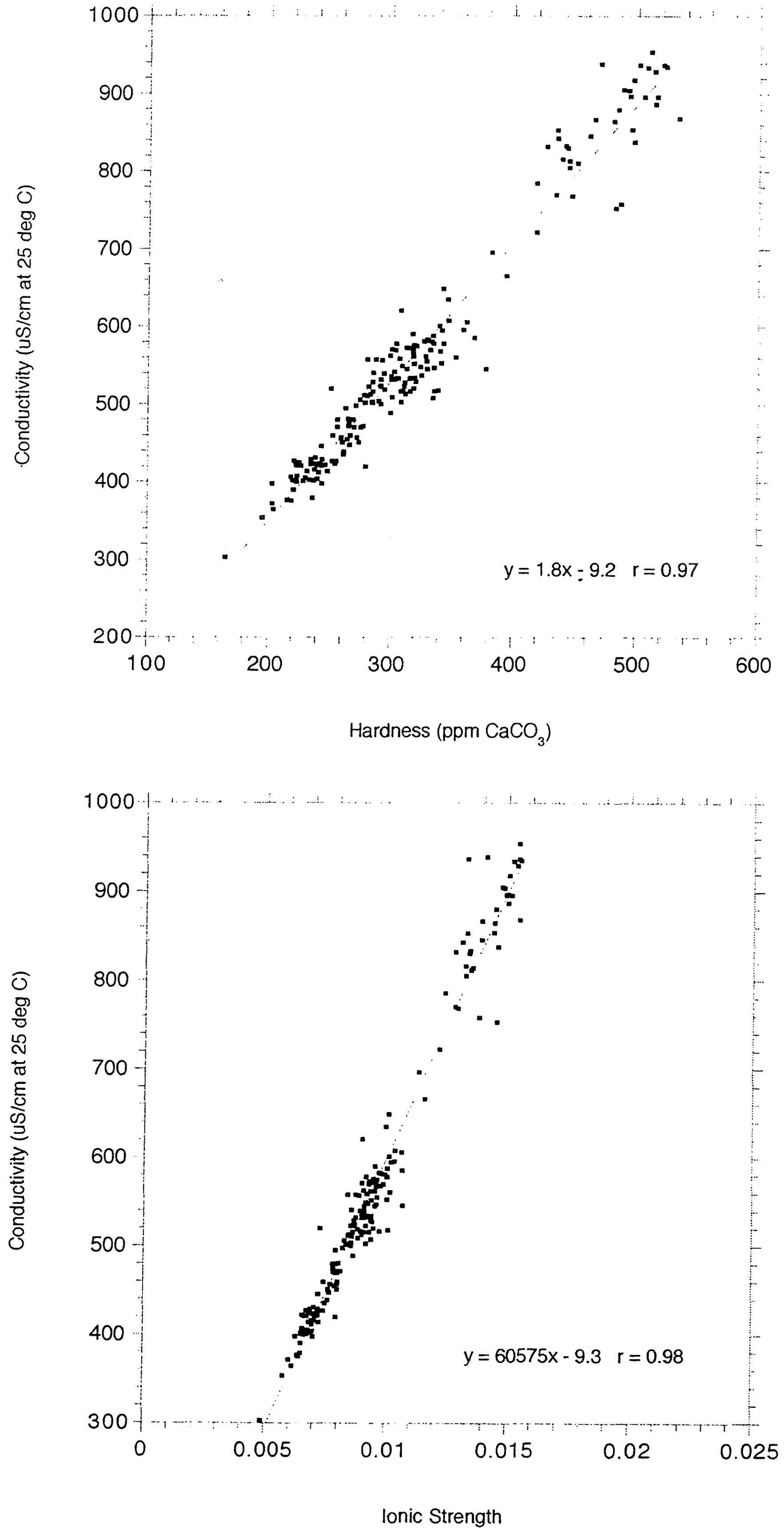


Figure 4.3. Relationships between conductivity, hardness, and ionic strength for Mystery Cave waters. a. Conductivity vs. hardness. b. Conductivity vs. ionic strength. Some waters, such as BD2, which has an ionic strength of about 0.02, are not included, because conductivity was not measured.

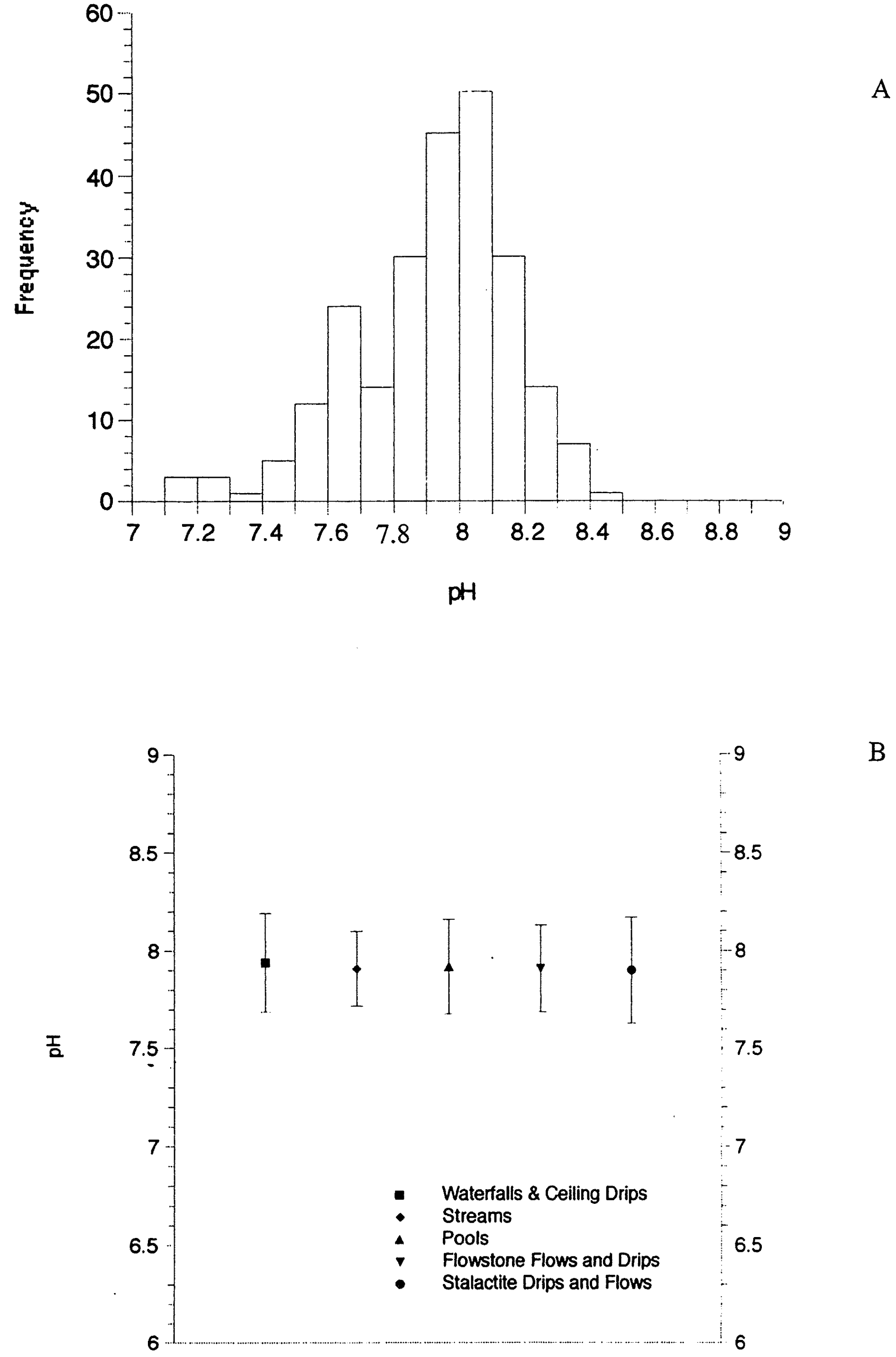


Figure 4.4. pH in Mystery Cave waters. a. Histogram of pH. b. Means and standard deviations for the five water types. Bars show one standard deviation above and below the mean.

upper loess, as organic materials were altered by biological activities. We have no direct evidence to support or contradict this idea, though seasonal signals in P_{CO_2}, discussed below, would suggest that any such effect is minimal.

Surface waters at Mystery Cave should be equilibrated with atmospheric P_{CO_2} of about $10^{-3.5}$ atmospheres. This is about 350 ppm by volume (or .035%) and it was increasing at about 1.8 ppm/year in 1990. Anthropogenic activities have increased the P_{CO_2} of the Earth's atmosphere to about 350 ppm from a pre-industrial revolution value of about 270-280 ppm, and from a value of about 315 ppm since 1958, as measured in Hawaii (see Elsom, 1992).

No direct measurements of CO_2 have been made in soils or loess at Mystery Cave. It is probable that values of P_{CO_2} are much higher than atmospheric values most of the time throughout the soil zone and within the loess. Near but below the soil surface, P_{CO_2} should be close to but slightly higher than atmospheric P_{CO_2} due to upward diffusion of CO_2. Published P_{CO_2} values for cave atmospheres are usually higher than atmospheric values, due to downward diffusion of CO_2 from topsoil and from soils filling solutional voids in the subcutaneous zone (e.g., Troester and White, 1984; White, 1988; see also the review by Ford and Williams, 1988). Lively and Krafthefer (1993a) measured atmospheric CO_2 levels of 1700 to 1850 ppm in Mystery Cave, and 1200 ppm at the Mystery II Entrance, with a Riken portable CO_2 monitor in May, 1991.

For karst waters in which pH is "determined" primarily by limestone (or dolomite) dissolution, at a given temperature, pH is a function of the available CO_2 and the contact time for reactions. In the following we assume sufficient time for reactions to go to equilibrium. We further assume CO_2 values typical of surface, soil, or cave atmospheres.

If CO_2 is constantly replenished by an atmospheric reservoir, then we have an open system (also called coincident; see Drake, 1983). More calcium and bicarbonate will be in solution at equilibrium in an open system than in a closed system for a given atmospheric P_{CO_2}. In the closed system, there is an initial amount of CO_2, but then that CO_2 is used up in dissolution and is not replenished. (This is also known as a sequential system.) Waters in contact with the surface atmosphere are under open system conditions. Waters that infiltrate into the soil and loess and pass downward into fractured bedrock without coming into contact with an open atmosphere (the fractures are completely filled with water) are in closed-system conditions. When they enter open fractures and solutionally-enlarged fractures and enter the cave, then they once again are in open-system conditions. However, those subsurface open system conditions are likely to be different from surface open-system conditions, in addition to being different from the closed-system conditions which the water so recently left.

The pH of a water at equilibrium is lower as the available CO_2 increases. Stated alternately, an increase in atmospheric CO_2 (in the soil or cave atmosphere, e.g.) results in a lower equilibrium pH. For the open case, the initial amount of local atmospheric CO_2 is the same as the final amount of local atmospheric CO_2. As CO_2 is used up in dissolution, more CO_2 dissolves into the water and solute concentrations can continue to increase toward equilibrium values. For the closed case, the initial

CO_2 is used without being replenished, solute concentrations do not rise as high, and the resulting pH at equilibrium is higher.

With the preceeding in mind, it is now possible to make sense out of the statement that the pH of Mystery Cave waters is relatively high. Most of the sampled waters evolved under conditions that were predominantly closed (in the lower soil, loess, and upper fractured bedrock). The amount of time those conditions were maintained was relatively long, so equilibrium was approached or attained.

The P_{CO_2} of cave waters at equilibrium can be estimated from field measurements of pH and from HCO_3^- (obtained from alkalinity) as:

$$P_{CO_2} = ([HCO_3^-][H^+]) / (K_1 K_{CO_2})$$

in which square brackets denote activities, K_1 is the first dissociation constant for carbonic acid, and K_{CO_2} is the bulk equilibrium constant for neutral carbon-bearing species (see White, 1988). The P_{CO_2} so estimated is the theoretical carbon dioxide pressure of the coexistent gas that would be in equilibrium with the water sample. This does not mean that the gas phase is actually present, or that the atmosphere that is present has that amount of CO_2.

P_{CO_2} ranged about $10^{-1.7}$ to $10^{-0.3}$ for 231 sampled waters in Mystery Cave. Figure 4.5a presents these data as a histogram with a bimodal distribution about the mean. Figure 4.5b shows mean P_{CO_2} and standard deviations for each of the five primary water types sampled. As with conductivity and temperature, the pH and P_{CO_2} do not correlate with the five physical water types identified at the start of this project.

SATURATION INDICES AND P_{CO_2}

The degree of saturation of waters is commonly quantified in terms of the Saturation Index, SI, for each mineral. In Mystery Cave it is useful to consider the saturation state of the waters with respect to calcite, aragonite, dolomite, and gypsum. The dissolution of these minerals is described, in part, by the following reactions:

Calcite

$$CaCO_3 \text{ (calcite)} = Ca^{+2} + CO_3^{-2}$$

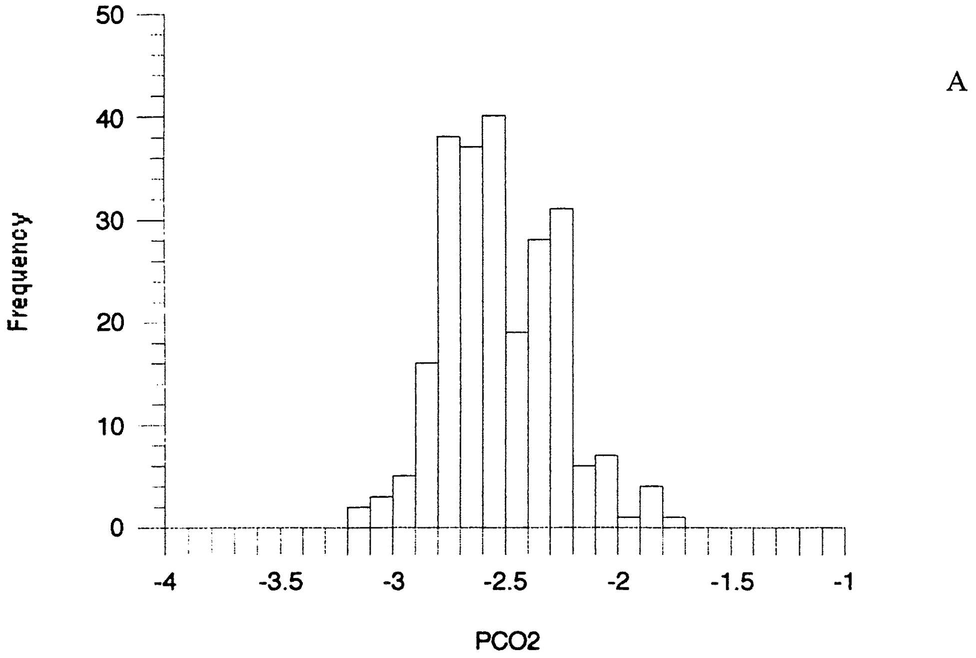
$$SIC = \log([Ca^{+2}]\,[CO_3^{-2}] / Kc)$$

where Kc is the equilibrium constant for calcite and brackets denote activities of the enclosed chemical species.

Aragonite:

$$CaCO_3 \text{ (aragonite)} = Ca^{+2} + CO_3^{-2}$$

$$SIA = \log([Ca^{+2}]\,[CO_3^{-2}] / Ka)$$



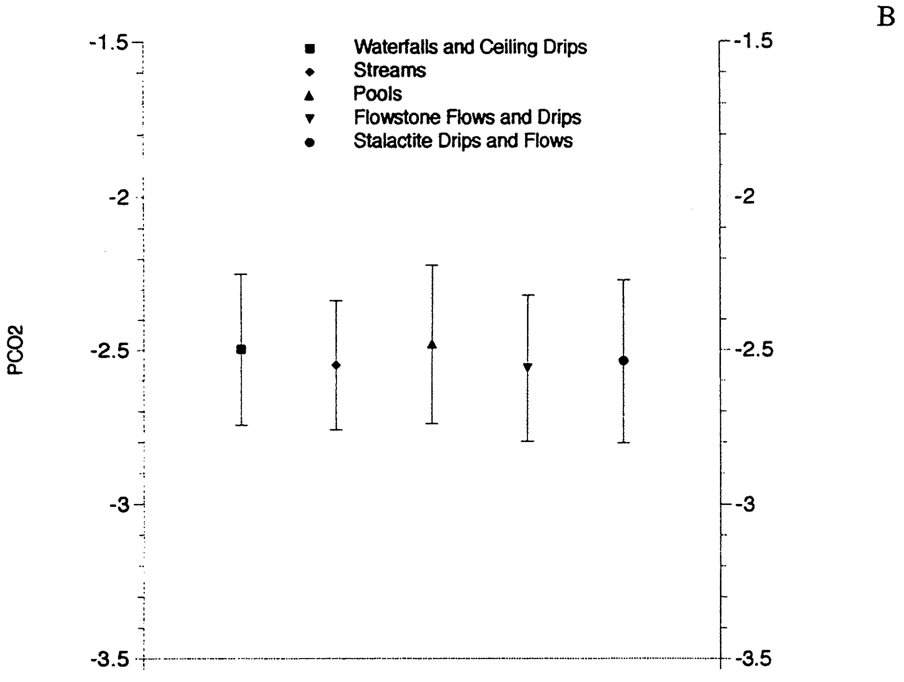


Figure 4.5. P_{CO_2} in Mystery Cave waters. a. Histogram of P_{CO_2}. b. Means and standard deviations of P_{CO_2} for the five water types. Bars show one standard deviation above and below the mean.

where Ka is the equilibrium constant for aragonite.

Dolomite:

$$CaMg(CO_3)_2 = Ca^{+2} + Mg^{+2} + 2\ CO_3^{-2}$$

$$SID = \log([Ca^{+2}]\ [Mg^{+2}]\ [CO_3^{-2}]^2 / Kd)$$

where Kd is the equilibrium solubility product for dolomite. Alternately, SID is defined as the square root of the expression in parentheses on the right side; this allows comparison of SIC and SID in terms of equal numbers of moles of CO_3^{-2} (White, 1988; Hess and White, 1989).

Gypsum:

$$CaSO_4 \cdot 2H_2O = Ca^{+2} + SO_4^{-2} + 2\ H_2O$$

$$SIG = \log([Ca^{+2}]\ [SO_4^{-2}] / Kg)$$

where Kg is the equilibrium constant for gypsum.

A saturation index equal to zero indicates saturated conditions. SI greater than zero indicates supersaturated conditions. SI less than zero indicates unsaturated waters which are capable of dissolving additional quantities of the mineral. Note that saturation indices are on a log scale. A value of 1 is ten times saturation, 2 is 100 times saturation, etc. Although pH does not appear explicitly in the equations above, the pH measurement is critical in determining the saturation indices for calcite, aragonite, and dolomite, because CO_3 is not directly measured; it is estimated in part on the basis of the pH measurement. pH values are accurate, at best, to about 0.02 pH units, though they are measured to the nearest 0.01 pH units on a digital ouput on most pH meters. The uncertainty in pH is the single most important measurement determining the uncertainty in saturation indices. Generally, the uncertainty is sufficient that waters within 0.1 SI units of zero are considered to be at saturation.

Figures 4.6-4.9 show histograms of SIs and mean SIs and standard deviations for each of the five sampled water types for calcite, aragonite, dolomite and gypsum. The SIs do not correlate with the water types.

Nearly all of the waters sampled in Mystery Cave are saturated or supersaturated with respect to calcite. Almost as many are saturated with respect to aragonite and dolomite. These waters are incapable of dissolving bedrock without undergoing additional processes that renew their capacity for dissolution.

Many of the waters seen in the upper levels of Mystery Cave are vertically descending waters. They issue from joints and either drip and fall to the floor, or they flow as films and sheets down walls. There are almost no vertically-oriented dissolutional features associated with these waters. Vertical shafts of the type described by Brucker et al. (1972) are absent. Breakdown on the floor lacks dissolutional flutes or corings, nor are there vertical dissolutional features on cave walls. To those accustomed to alpine caves of the western U.S., or caves characteristic of the Appalacians or the interior lowlands of the east, the absence of these features

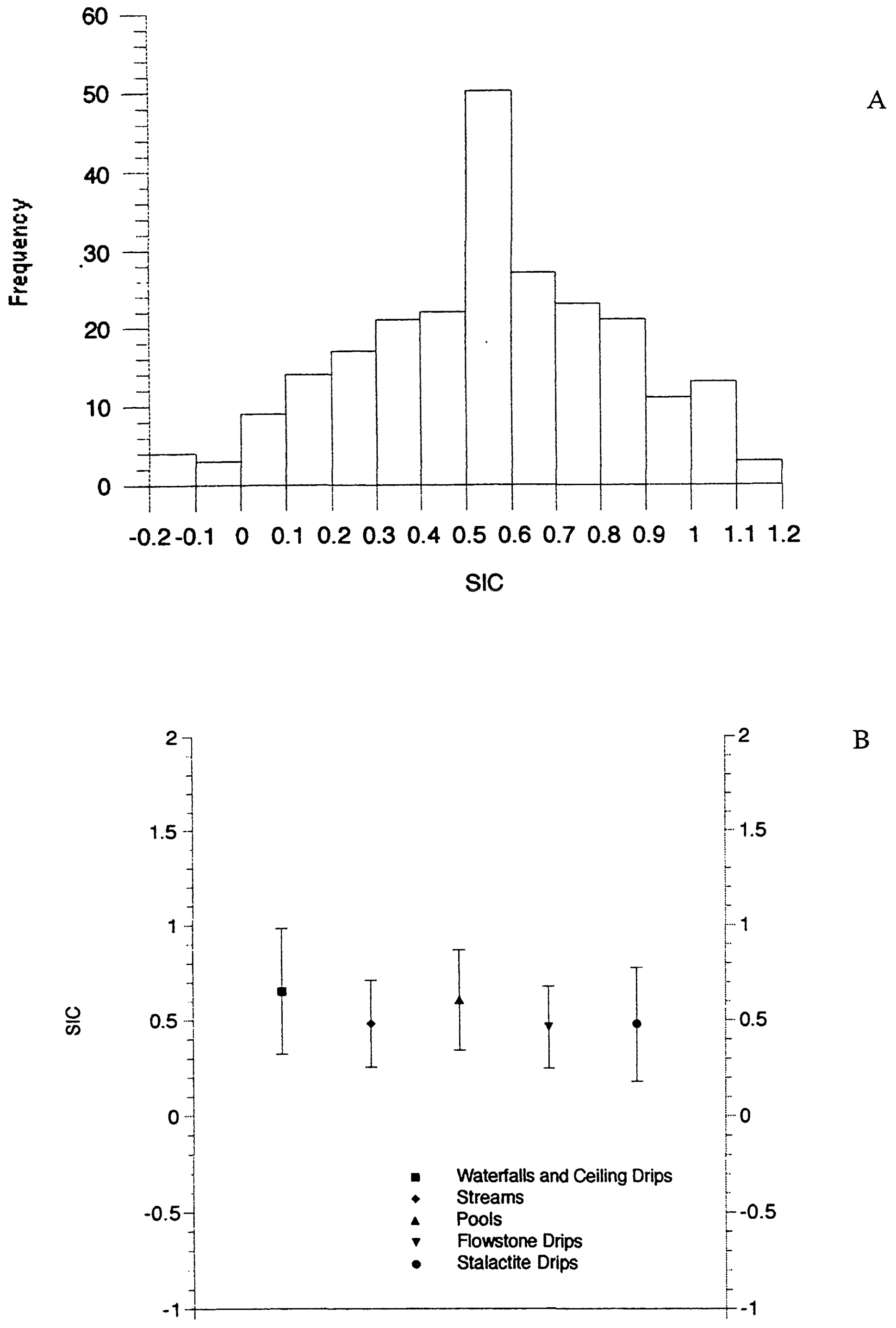


Figure 4.6. SIC in Mystery Cave waters. a. Histogram of SIC. b. Means and standard deviations of SIC for the five water types. Bars show one standard deviation above and below the mean.

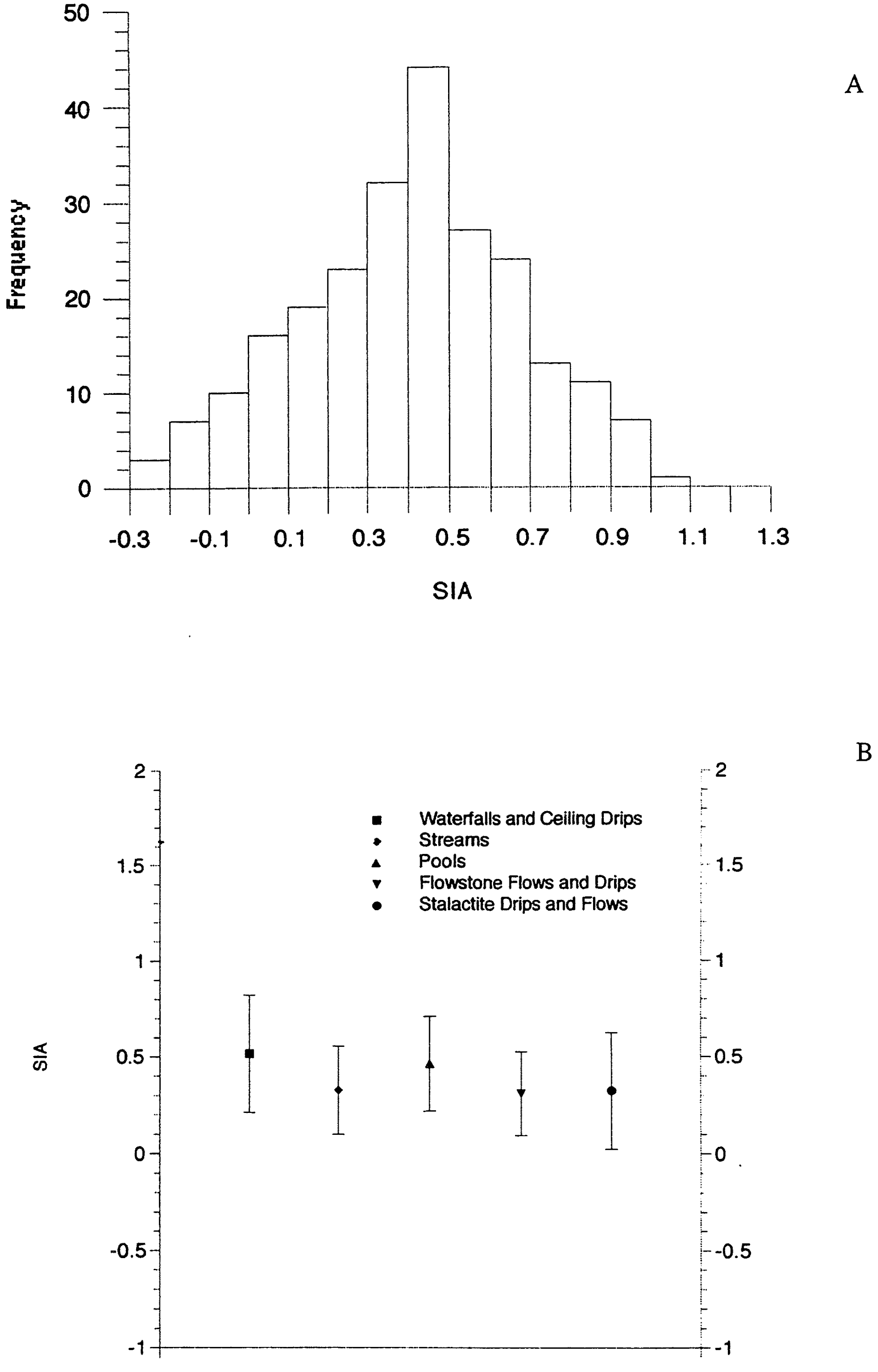


Figure 4.7. SIA in Mystery Cave waters. a. Histogram of SIA. b. Means and standard deviations of SIA for the five water types. Bars show one standard deviation above and below the mean.

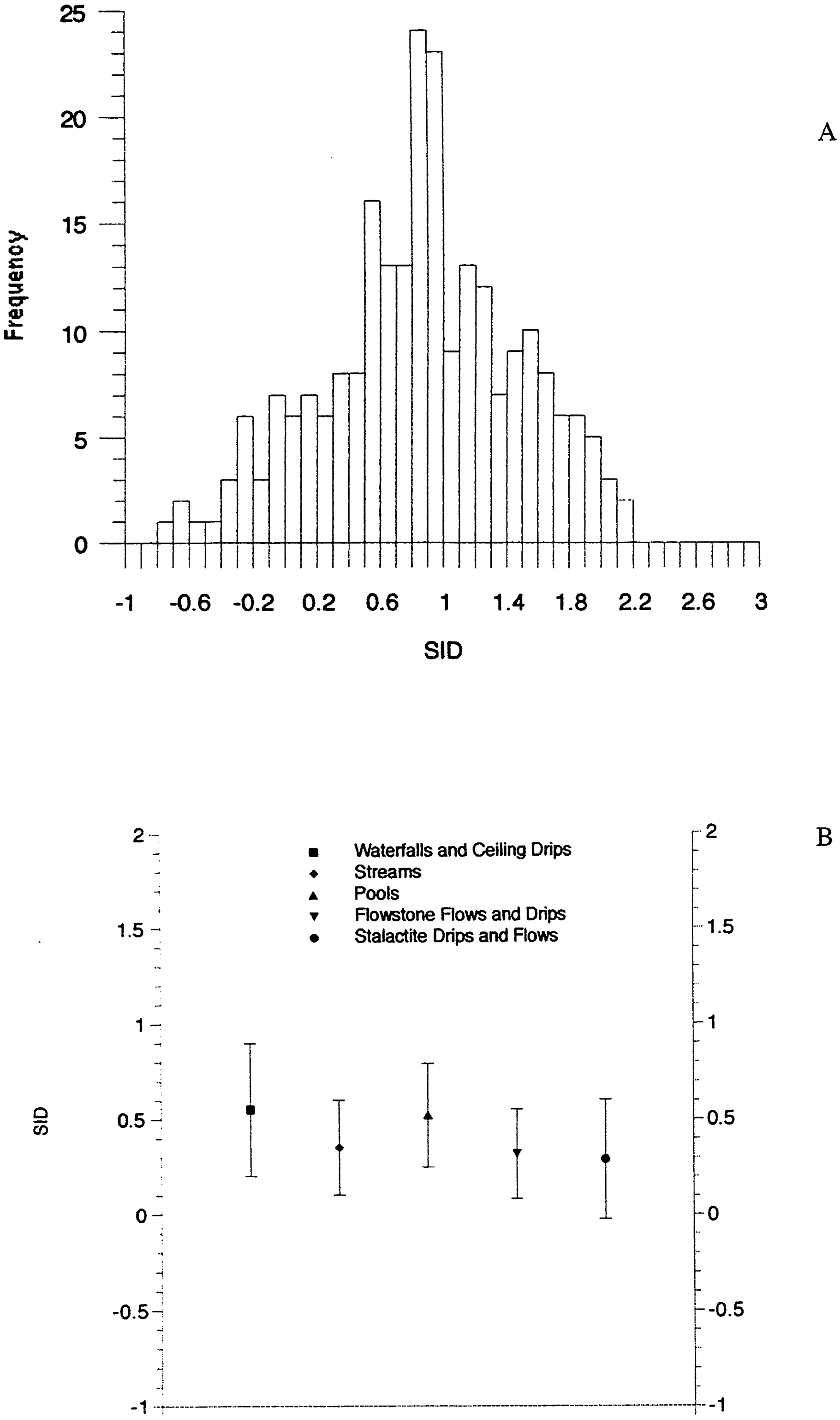


Figure 4.8 SID in Mystery Cave waters. a. Histogram of SID. b. Means and standard deviations of SID for the five water types. Bars show one standard deviation above and below the mean.

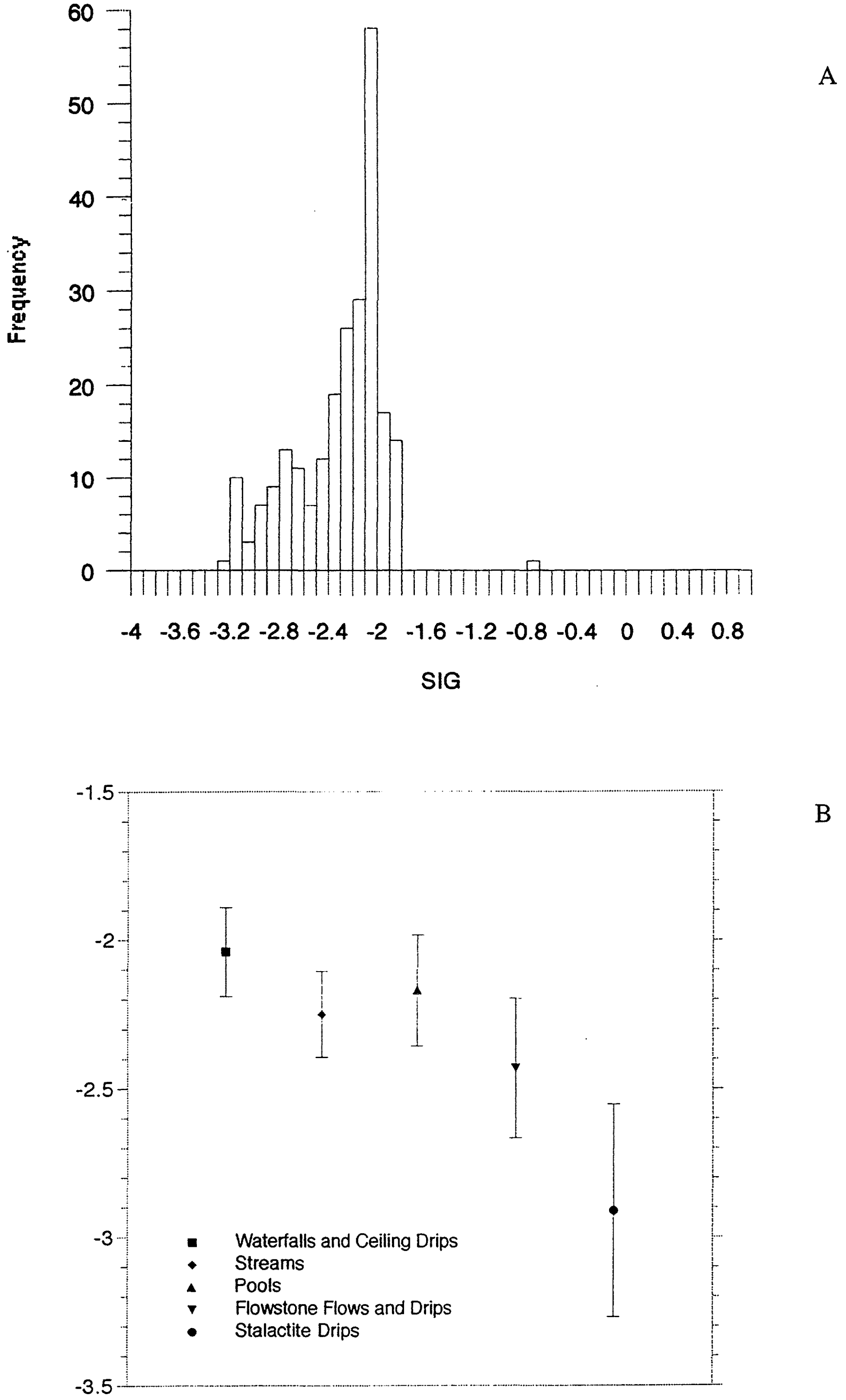


Figure 4.9. SIG in Mystery Cave waters. a. Histogram of P_{CO_2}. b. Means and standard deviations of SIG for the five water types. Bars show one standard deviation above and below the mean.

striking. Were undersaturated waters available, one would expect to see vertically oriented dissolutional features. At the most, there are dissolutional pockmarks and fretting associated with just a few sites, such as the Enigma Pit site (which is not a vertical shaft site, despite the name). We know of no vertical shafts in Mystery Cave. The nearest cave with an unequivocal vertical shaft (with an accompanying retreating waterfall and an associated solution canyon) is Niagra Cave, about 10 mi south-southeast of Mystery Cave in a setting that receives direct surface runoff.

Mystery Cave has probably had a preponderance of saturated waters in its upper levels for a very long time. This is evident from the lack of vertical dissolutional features (such as vertical shafts and flutes) that are so characteristic of caves with vertically descending waters that are undersaturated.

The supersaturated waters are responsible for the ongoing deposition of speleothems in many areas of Mystery Cave. An indication of the rapidity with which supersaturated waters can deposit speleothems is visible along the left (north) side of the commercial trail of Mystery I, near the Rock Garden, an area of flowstone ledges with abundant calcite rafts. At floor level, white deposits of calcite (up to nearly 1/2 in thick) already cover part of the cement walkway installed during 1992.

All of the waters tested in Mystery Cave had gypsum saturation indices significantly less than zero. The sole sample with a SIG greater than about -1.8 was BD2, a sessile drop water with an SIG of -0.70 (Figure 4.9).

Ca, Mg, and HCO_3

The waters of Mystery Cave are predominantly calcium-magnesium-bicarbonate waters, with varying amounts of nitrate, chloride, and sulfate. Most of the nitrate and chloride are from anthropogenic sources, as discussed in later sections. Part of the sulfate is anthropogenic, but part is also derived from oxidation of pyrite included in the carbonate bedrock. In many respects, the carbonate chemistry is typical of karst regions with mixed dolomite and calcite bedrock. However, some of the carbonate chemistry may be determined above the bedrock in the soil zone and loess, which contain both calcite and dolomite.

Histograms of Ca, Mg, and HCO_3 concentrations are in Figures 4.10-4.12. The distribution of Ca is distinctly bimodal with one outlier, sessile bedrock drop BD2. The distribution of Mg is more or less trimodal in detail, but bimodal at a coarser scale. The distribution of HCO_3 is strongly bimodal. Comparisons of these histograms with those for total dissolved solids (TDS) and ionic strength (Figure 4.13) suggest that it might be useful to distinguish two classes of carbonate waters at Mystery Cave. One group has relatively high concentrations of Ca, Mg, and HCO_3; the other has lower concentrations, but their range is narrower. The notion of two rough concentration groups receives additional support from the histogram for conductivity (Figure 4.2), which is coarsely bimodal although---as with Mg and TDS---apparently trimodal in detail.

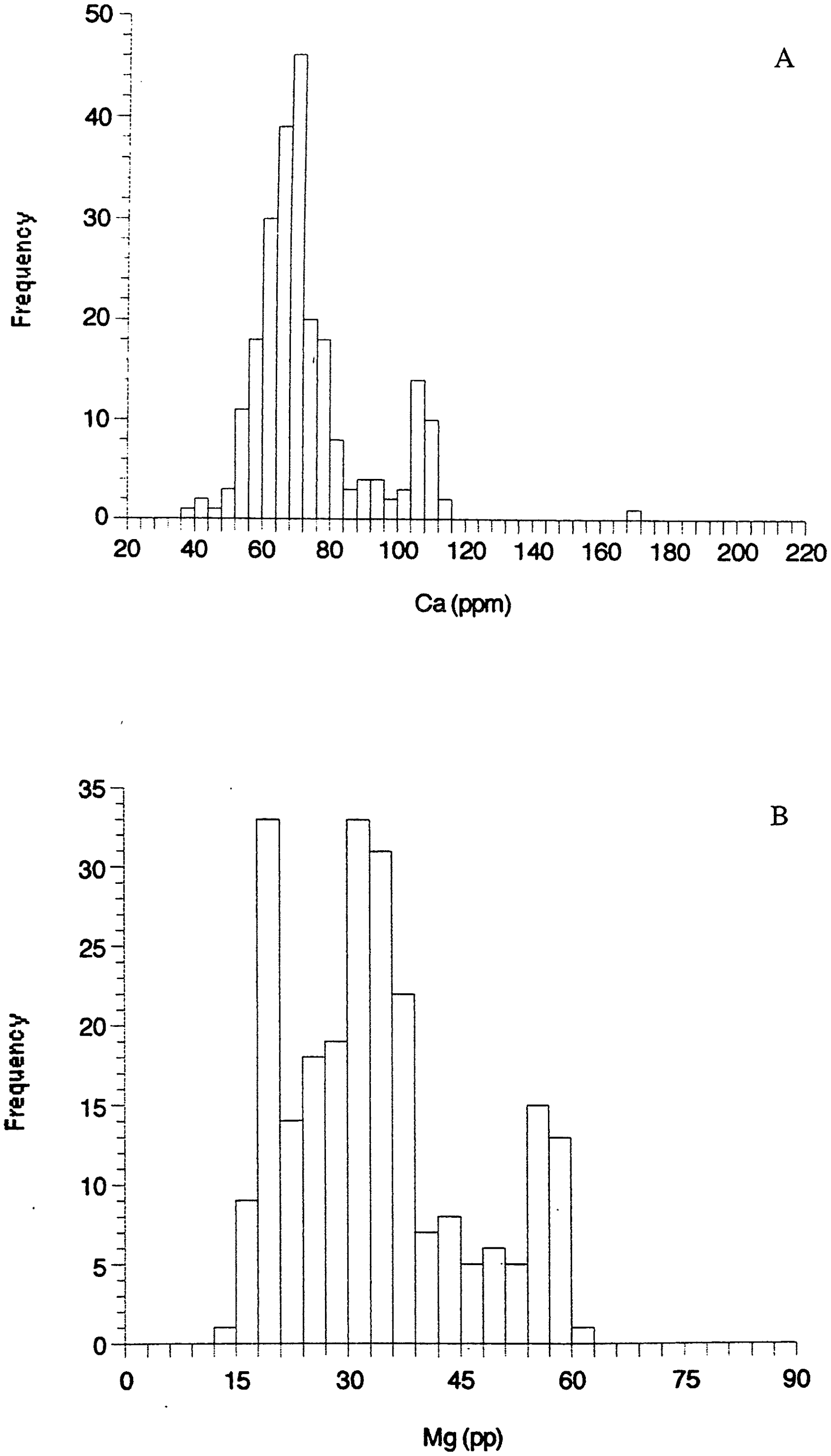


Figure 4.10. Ca and Mg in Mystery Cave waters. a. Histogram of Ca. b. Histogram of Mg.

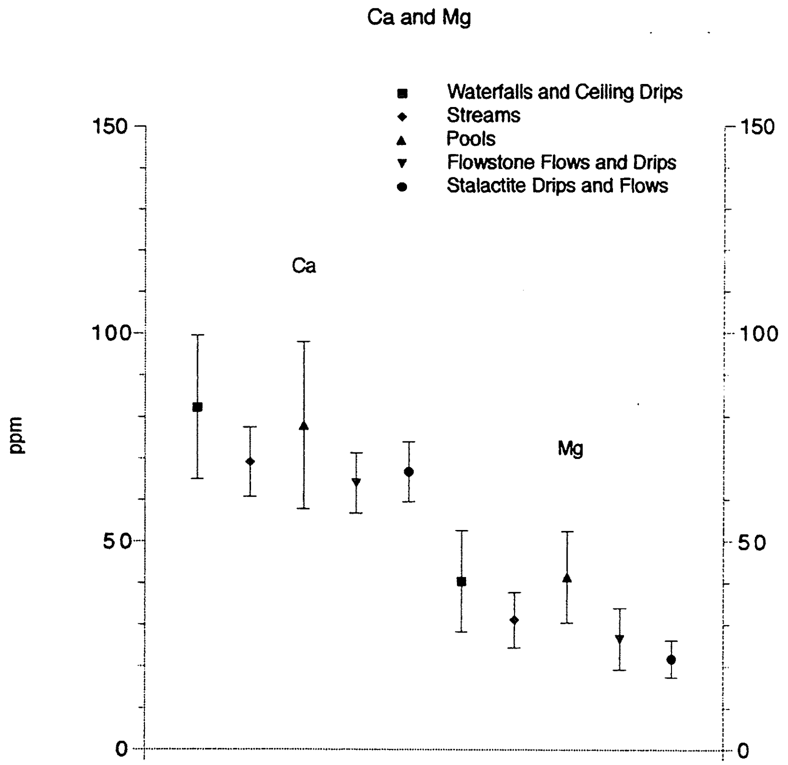


Figure 4.11. Ca and Mg means and standard deviations. Bars show one standard deviation above and below the mean.

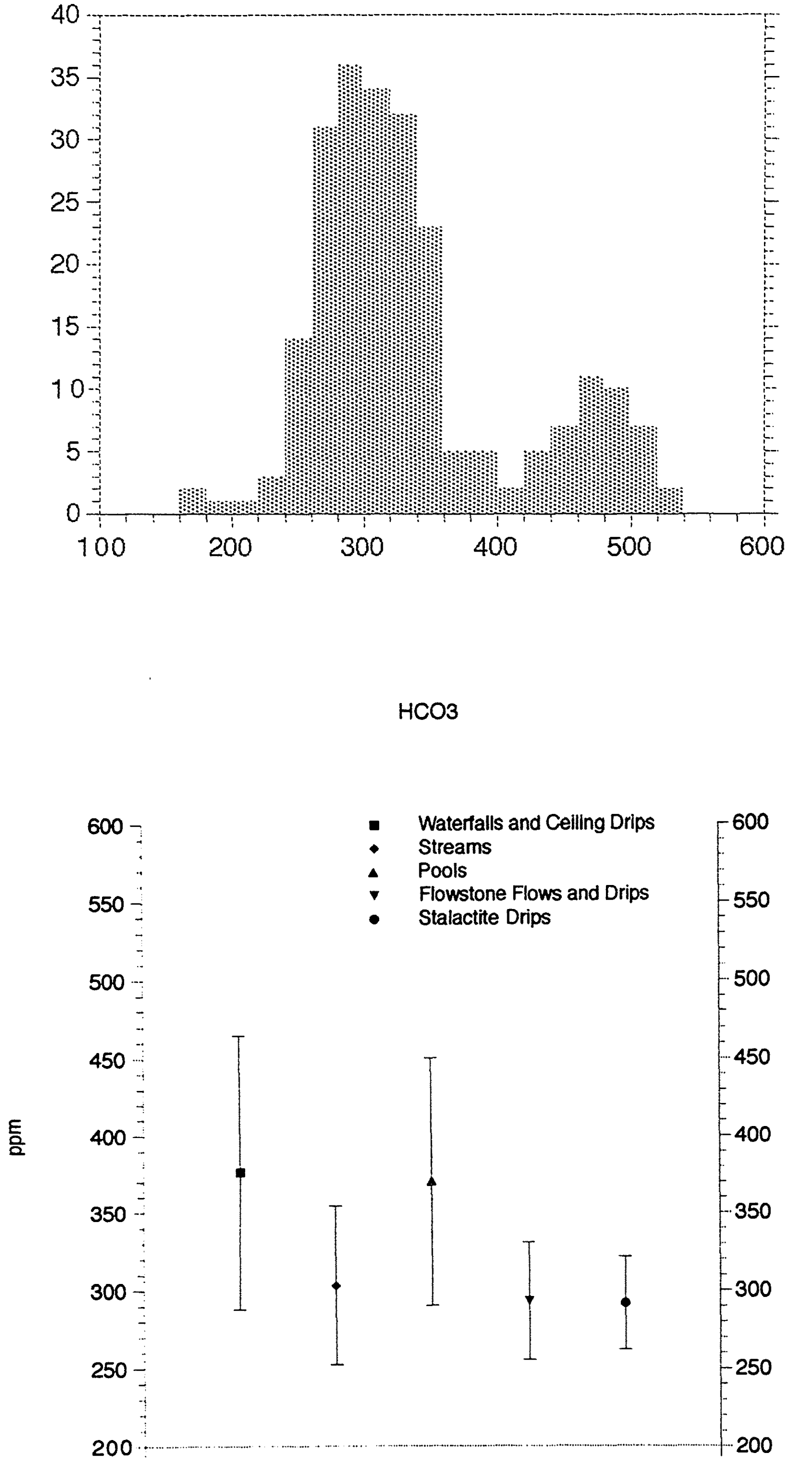


Figure 4.12. HCO_3 in Mystery Cave waters. a. Histogram of HCO_3 . b. Means and standard deviations of HCO_3 for the five water types. Bars show one standard deviation above and below the mean.

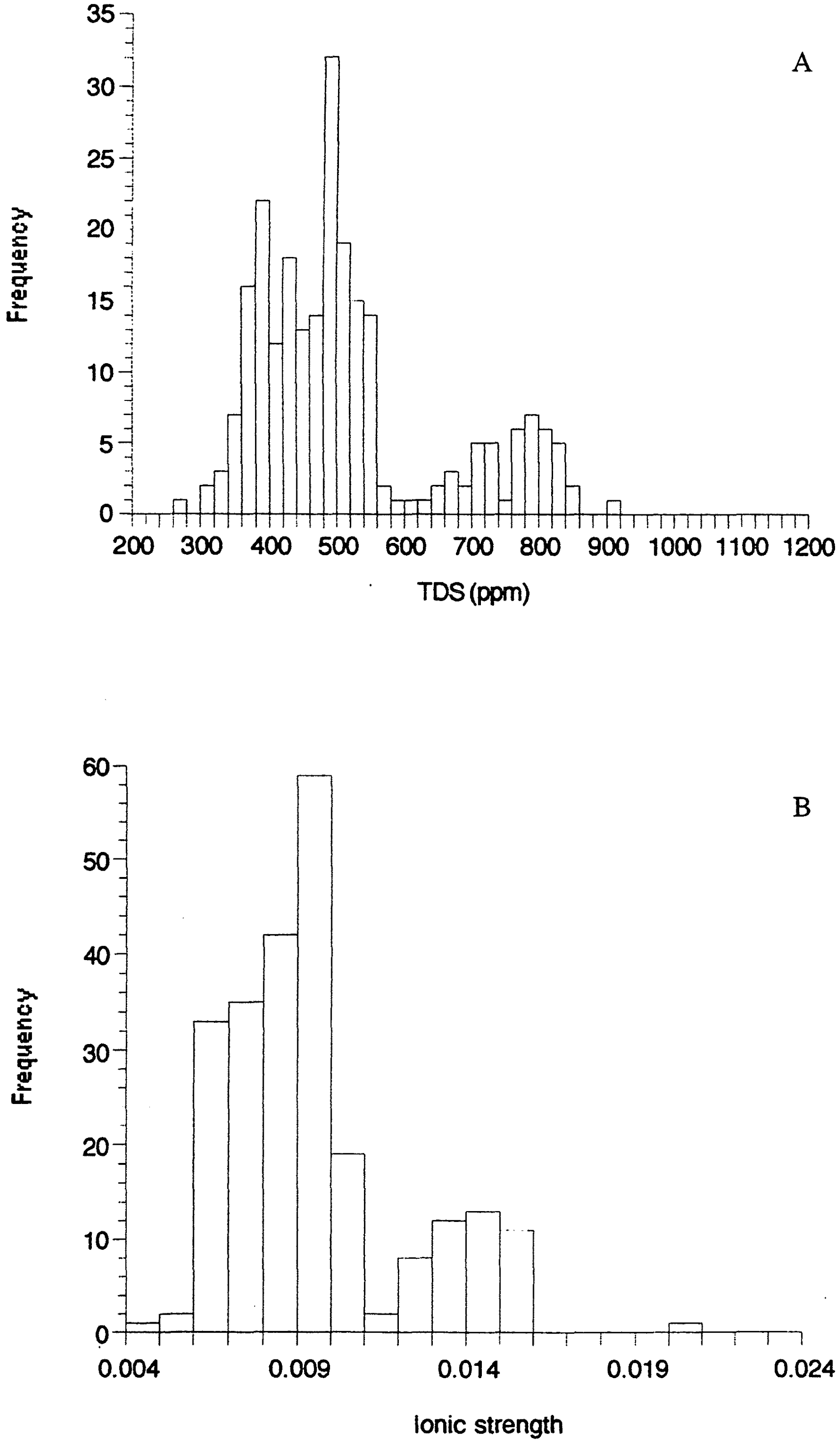


Figure 4.13. TDS and ionic strength in Mystery Cave waters. a. Histogram of TDS (total dissolved solids). b. Histogram of ionic strength.

The Mg/Ca Ratio

Figure 4.14 plots Mg versus Ca in meq. (meq = milliequivalents per kilogram, which compares the numbers of atoms present.) Lines for Mg/Ca ratios of 1.0 and 0.8 are included as convenient references. By equilibrium calculations, the Mg/Ca ratio is about 0.8 (at 25°C) for waters saturated with respect to both dolomite and calcite according to Appelo and Postma (1993). (We use their ratio of 0.8 at 25°C here solely for convenience, as a first approximation; other thermodynamic data give a slightly different ratio.) Waters in contact with pure dolomite would have a Mg/Ca ratio of about 1.0 at equilibrium. Even pure calcite limestones contain some Mg substituting for Ca, so Mg/Ca ratios of natural karst waters will not approach zero. Typical Mg/Ca ratios from source areas on limestone in the eastern U.S. range from 0.125 to 0.20 (1/8 to 1/5; see Hess and White, 1989).

The 0.8 line in Figure 4.14 runs through the middle of the Mystery Cave array. The points that lie above the 1.0 line correspond to samples richer in Mg than Ca. Most of the Mg-enriched samples are pool waters; these may be enriched in Mg due to precipitation of calcite in cave pools. Waters that plot below the 1.0 line are enriched in Ca relative to Mg. The vast majority of the waters of Mystery Cave plot below the 1.0 line.

Waters that plot below the 0.8 line have an excess of Ca relative to the Mg/Ca ratio that would be present were the waters produced entirely by dissolution of dolomite. Almost all of the stalactite drips and many of the flowstone flows plot below the 0.8 line. Many of the stream waters and both of the bedrock drop waters plot below the 0.8 line. The bedrock drop waters were collected as sessile drops on limestone bedrock; their enrichment in Ca supports an interpretation that their bulk chemistry was locally determined, on the bedrock surface or nearby within the bedrock if they consist of seepage in addition to condensation moisture. The remaining waters below the 0.8 line apparently received some Ca from sources other than dolomite. Such sources could include calcite in the limestone of the Dubuque Formation, above the cave in the fractured bedrock, or in the cave itself. They also may include Ca removed from clay minerals and other sources in the soil and loess, particularly if ion exchange of K from KCl fertilizers is releasing Ca and thereby augmenting Ca concentrations in the cave waters (see below and the discussion of the chemistry at the Garden of the Gods stalactite drips sites in Chapter 5).

The inverse of the Mg/Ca ratio of 0.8 is the Ca/Mg ratio of 1.25. Figure 4.15 shows a histogram of the Ca/Mg ratio and means and standard deviations for all five water types. As with Ca, Mg, and HCO_3, there is a bimodal distribution. The larger peak is close to a ratio of 1.25.

The Ca/Mg Ratio and Conductivity

Figure 4.16 plots the conductivity vs the molar Ca/Mg ratio for all seven sampled water types. A number of interesting features are visible in Figure 4.16:

(1) most stalactite drips have low conductivities (300-550 µS/cm) and relatively high Ca/Mg ratios (1.4-2.2).

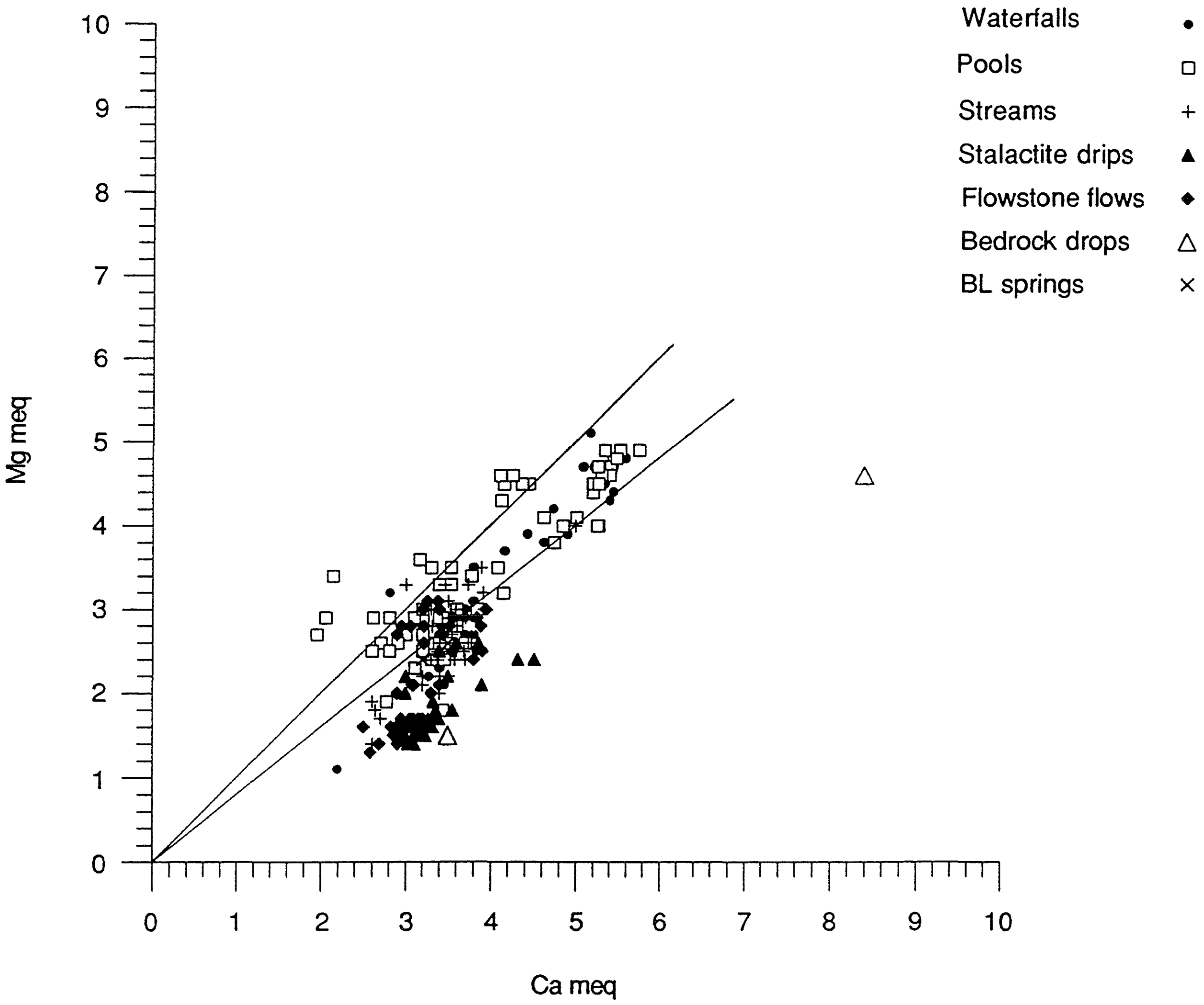


Figure 4.14. Mg vs Ca for Mystery Cave waters.

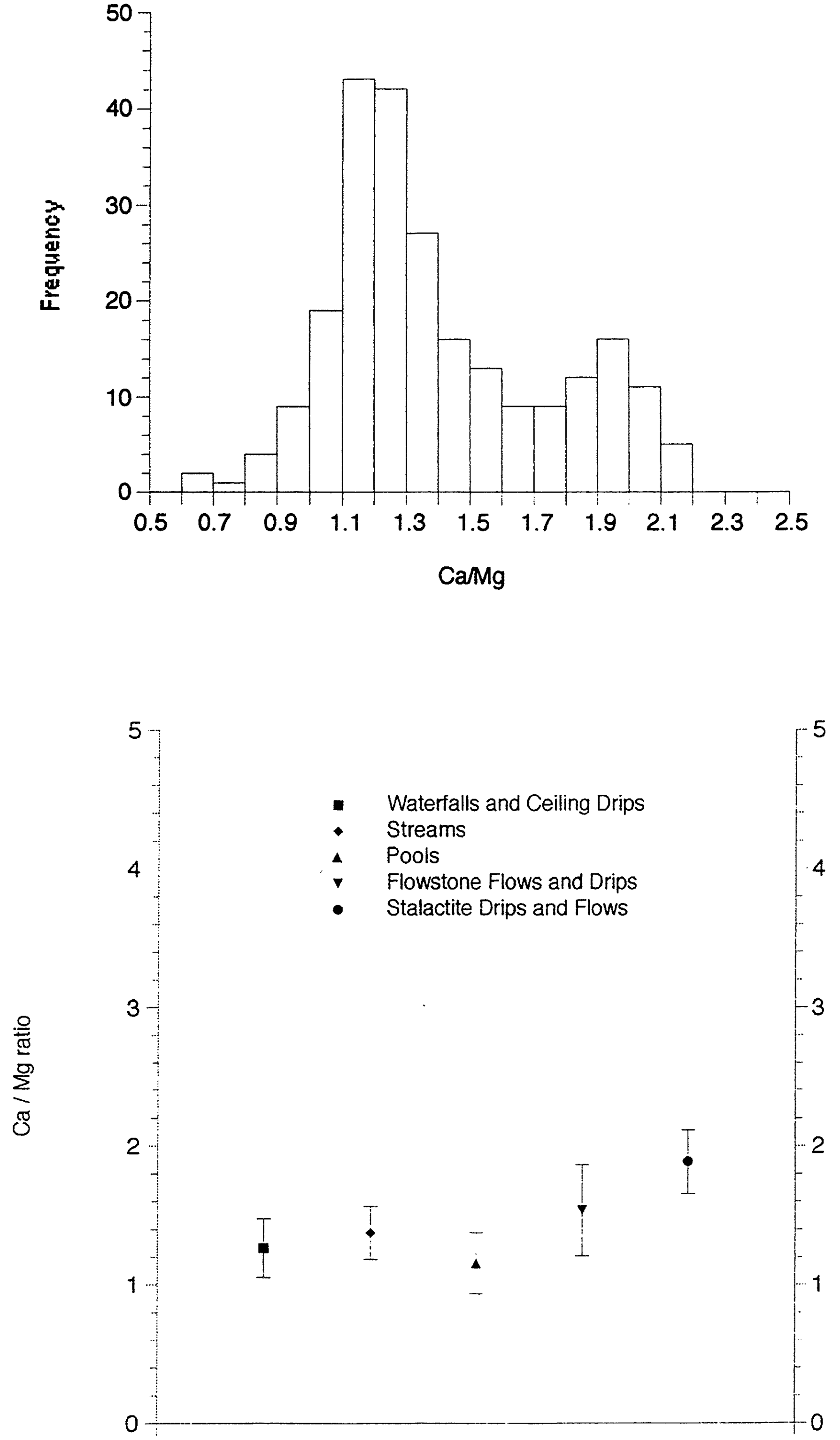


Figure 4.15. Ca/Mg ratio in Mystery Cave waters. a. Histogram of Ca/Mg ratio. b. Means and standard deviations for the five water types.

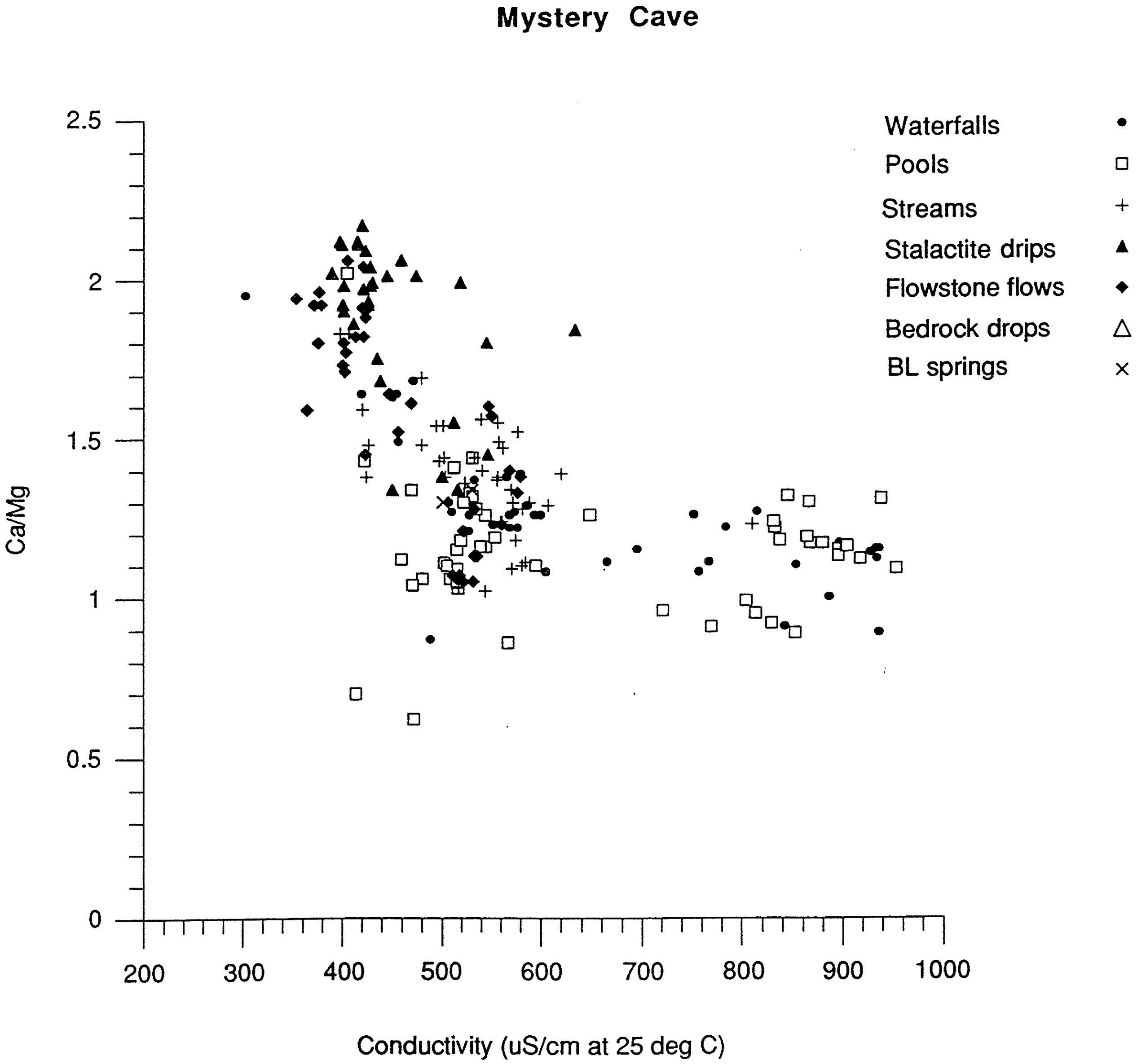


Figure 4.16. Ca/Mg ratio vs conductivity for Mystery Cave waters.

(2) both pools and waterfalls seem to divide into two populations, one with low conductivities (450-620 µS/cm) and one with higher conductivities (700-950 µS/cm). The groups have similar low Ca/Mg ratios (0.8-1.4).

(3) streams have low conductivities (400-600 µS/cm) except for Turquoise Lake Source, which has a higher conductivity (847 µS/cm). The streams have intermediate Ca/Mg ratios (1.0-1.8).

(4) flowstone flows seem to divide into two populations, one with low (350-450 µS/cm) conductivity and high Ca/Mg ratios (1.4-2.1) and one with slightly higher (500-600 µS/cm) conductivities but lower Ca/Mg ratios (1.0-1.5).

The relatively low conductivities of stalactite drips compared to other waters is unusual. In most temperate-zone caves, the waters actively depositing stalactites are low-discharge flows. They move slowly as a diffuse flow on fractures and have had long contact times following exposure to high CO_2 partial pressures in the soil. They have a relatively high solute load compared to other cave waters, leading to high conductivities. Stalactite drips in many caves are less likely to contain contaminants derived from human activities on the surface than are other cave waters which have a point-source recharge and exhibit rapid flow-through times.

Two stalactite drips, GG1 and GG2 at the Garden of the Gods, were sampled a sufficient number of times to examine their range of behavior with respect to conductivity. The drips varied considerably in behavior, despite a close proximity. Drip GG1 and GG2 are about 15 ft apart, and lie on different joints of the same trend. Drip GG2 varied little in conductivity (416-460 µS/cm) or other chemical parameters but varied more in discharge than GG1. Drip GG1 varied much more in conductivity (390-635 µS/cm). GG1 received inputs of elevated chloride, calcium, and other ions following recharge events that significantly increased discharge and conductivity. All three conductivities greater than 500 µS/cm for GG1 are associated with anthropogenic inputs, apparently from the overlying corn field.

In short, the high solute load and high conductivity of stalactite drips in many caves is produced by source areas with high carbon dioxide concentrations and long contact times for bedrock dissolution. However, the stalactite drips in Mystery Cave have relatively low conductivities compared to other cave waters. Conductivity should be lowest and Ca/Mg ratios highest in dilute waters that have had relatively little contact with bedrock, soil, or loess, and have had short residence times underground. At this point, the stalactite drips in Mystery Cave exhibit a behaviour that is enigmatic.

The high conductivity group of pool, waterfall, and stream (just Turquoise Lake Source) samples are all in Mystery I. The low conductivity group includes all of the streams directly fed by the South Branch, all pools and waterfalls in the rest of the cave, and some of the pool and waterfall samples from the sites in Mystery I that yielded high conductivity samples at other times. The low but variable conductivity values in the streams fed by the South Branch are expected. Conductivity should be low in melt waters and precipitation runoff sampled on the Root River. Spot checks of conductivity in the South Branch during the melt off in late March and April of 1992 and 1993 showed values of about 300 mS/cm at 25°C. The lowest conductivities recorded around or in the cave were at Flim Flam Creek during the winter melt off. Conductivity also should be relatively low for rapid run-in waters at waterfalls or pools fed by waterfalls during major recharge events, depending on the precise time of sampling relative to the event and the relative mixing of different waters.

SEASONAL SIGNALS IN THE CARBONATE CHEMISTRY

Seasonal signals in the calcium and magnesium concentrations and in SIC, SIA, SID, and PCO_2 were noted for a number of sites; at others, seasonal signals are present but are masked, apparently by mixing effects. At still others, no seasonal signals are evident in time series plots of the raw data, though they may appear if plots are transformed by smoothing procedures (moving averages). We provide one example here, for Coon Lake Drips (Figure 4.17), more by way of an exhibit than an analysis. At this site PCO_2, shows a distinct cyclicity tied to the growing season. For example, there is a rise in PCO_2 during June, 1992 and a peak in September, lagging somewhat behind the peak of the growing season. During the late fall and winter, PCO_2 declines. (The rise shown for early April, 1993, however, does not signal the onset of a new growing season---this is a result of the major flood discussed in later chapters.) During part, but not all of the cycle, Ca and Mg concentrations rise and fall. SIC and SID also rise and fall, but their rise is lagged and the fall is evident only for the flood event.

Figure 4.18 plots SID vs PCO2. This kind of plot is often used to distinguish water types from different hydrochemical environments (e.g., Drake and Harmon, 1972; Hess and White, 1989, 1993). For sites at which there are seasonal trends in PCO_2 and in saturation indices, these plots may exhibit linear arrays with negative slopes. When an entire data set is plotted on one diagram, as is done here, there may be an overlapping of arrays (one per site, e.g.) that causes a blurring of the different water classes. However, it is possible to distinguish two separate groups of arrays in Figure 4.18. The upper group consists of all of the samples from Turquoise Lake, most of the samples from Frozen Falls pool, and a few other samples from Mystery I. This is the same group of samples that formed the high conductivity group in Figure 4.16. The lower group consists of everything else.

Seasonal signals are readily detected by measurements of conductivity. So are signals resulting from dilution events, in which ion concentrations decline. So also are flushing events, in which stored waters with high solute concentrations (or stored contaminants) are expelled from the soil or loess. Conductivity is therefore a useful parameter with which to monitor the bulk chemistry of the water and can be combined with digital measurements of drip rates, discharge, stage, and water temperature. Continuous monitoring of conductivity at Blue Lake, Coon Lake Drips, and Flim Flam Creek has been instrumental in deciphering the hydrology and chemistry of Mystery Cave. We have learned much from these sites, and expect to learn more in the future. We recommend that such monitoring be continued, and if possible, be expanded to include additional sites discussed in Chapter 5, particularly the sites at the Garden of the Gods in Mystery II and near Frozen Falls in Mystery I.

NITRATE AND CHLORIDE

Nitrate and chloride are extremely mobile species in surface- and ground waters. Nitrate has the more complex chemistry because of its participation in redox

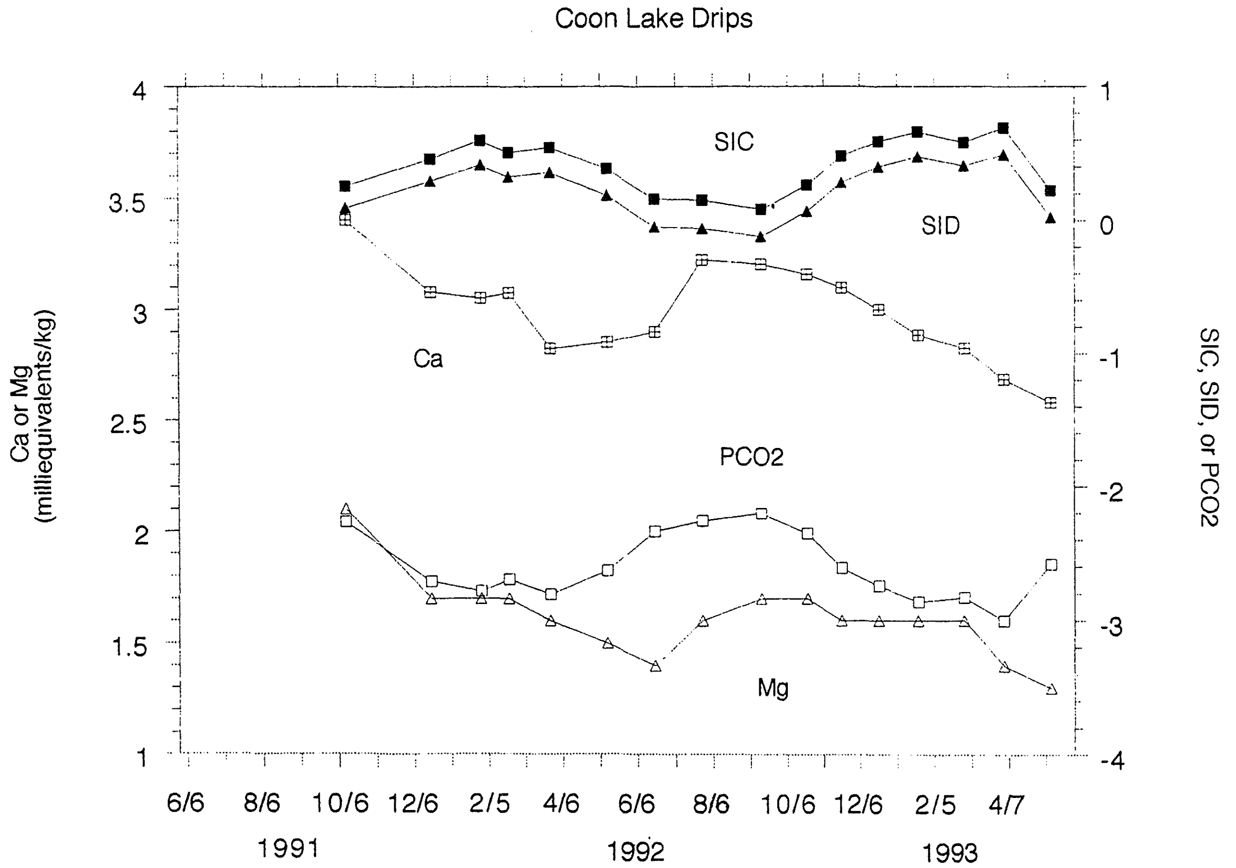


Figure 4.17. Seasonal signals in SIC, SID, PCO2, Ca, and Mg at Coon Lake Drips.

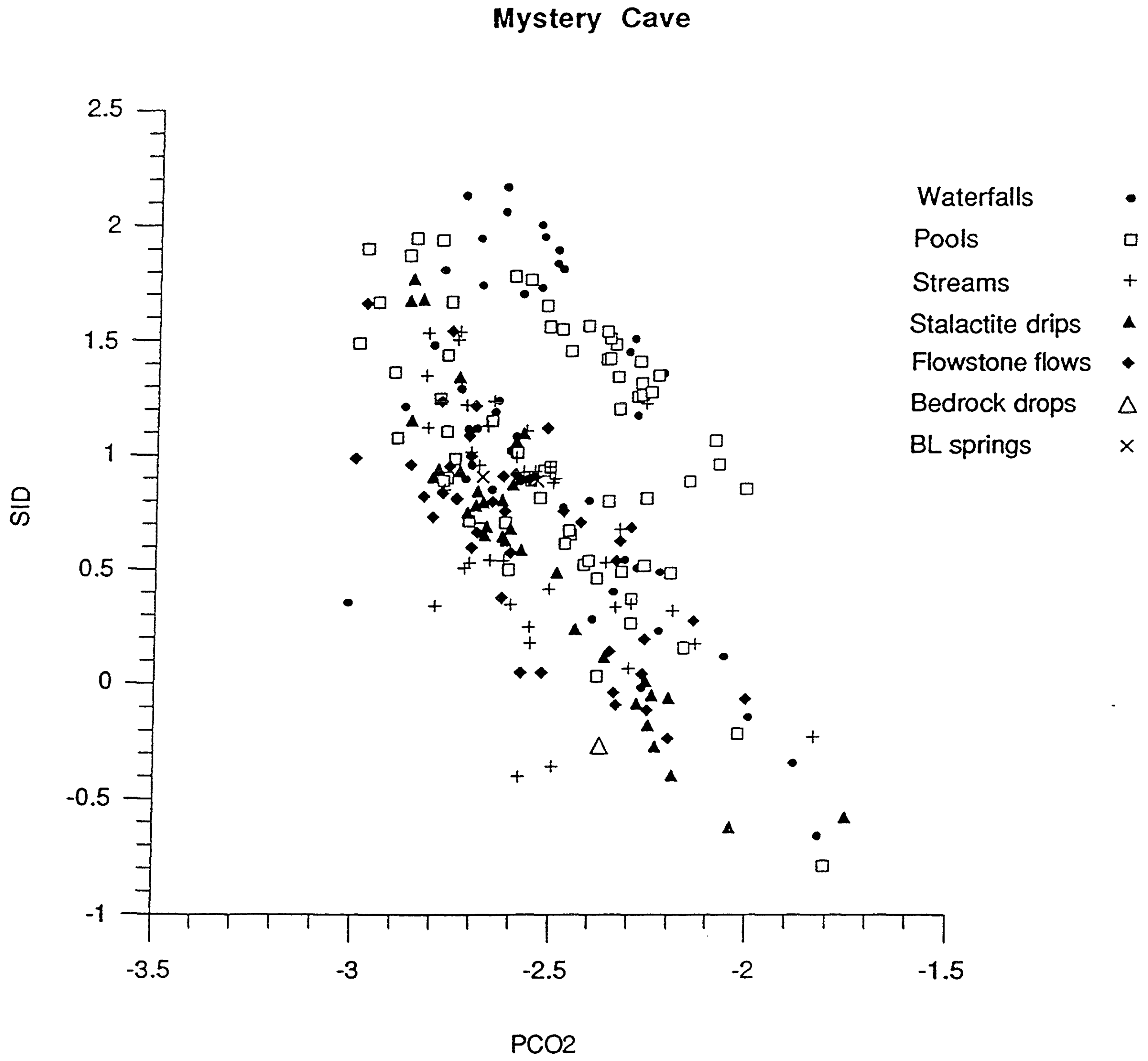


Figure 4.18. SID vs P_{CO_2} for waters in Mystery Cave.

reactions that produce transformations between atmospheric nitrogen (N_2), ammonia (NH_4), nitrite (NO_2^-), nitrate (NO_3^-), and other species. Most such reactions are bacterially mediated. At Mystery Cave, this mediation could occur in the soil, the loess, in waters as they pass through fractured bedrock to reach the cave, or in the cave itself. Study of these transformations was beyond the scope of this project, which was confined to analyses of NO_3^- and NO_2^- in selected cave and surface waters. Only a few samples had measurable NO_2^-, so NO_2^- is not discussed. All samples had measurable NO_3^-. NO_3^- is often expressed as NO_3-N in ground-water studies. This practice is followed here, but the discussion employs both sets of terms. Values of NO_3^- (mg/l or ppm) can be approximated by multiplying NO_3-N (mg/l or ppm) by 4.4268 Both sets of numbers appear in the data tables of Appendix 3.

Sources of Nitrate and Chloride

The natural NO_3^- content of limestones is so low that bedrock can be excluded as a significant source of natural NO_3^-. Natural NO_3^- produced by bacterially-mediated reactions in the soil is much more important. Anthropogenic sources of NO_3^- include fertilizers and animal and human wastes (outhouses, septic systems, feedlots, manure spreading). Atmospheric deposition can also contribute anthropogenic NO_3^-.

In continental karst aquifers, Cl in connate brines is typically removed by the circulation of meteoric waters during relatively early stages of aquifer development, long before major conduit-flow systems become integrated to form caves. Anthropogenic sources of Cl include fertilizers (e.g. fertilizer with KCl components), road salts, and septic systems. Atmospheric deposition can also contribute natural or anthropogenic Cl, but is unlikely to be a major contributor to Cl in the waters of Mystery Cave.

Elevated concentrations of NO_3^- and Cl are useful indicators of anthropogenic inputs to water chemistry. Elevated concentrations of NO_3^- and Cl can indicate the presence of open, high permeability pathways that directly transmit surface waters into the cave. (As described in Chapter 2, the main components of open pathways at Mystery Cave are open joints on hill slopes with thin soil and loess, macropores in soil and loess, animal burrows, and occluded fractures in the bed of the Root River.) However, both NO_3-and Cl can be stored on the surface or in subsurface reservoirs (soil, loess, subcutaneous zone, bedrock fractures) with low fluxes, particularly during prolonged dry periods. They can then be transmitted, weeks or months later, into the cave during major recharge events. Thus, the identification of flow paths characterized by rapid flow should not be based solely on the interpretation of NO_3^- and Cl concentrations. Other physical and chemical parameters, including water temperature, conductivity, fecal coliform bacteria, and pesticide concentrations, must be considered.

Nitrate

NO_3-N ranged from less than 1 to 12.3 ppm for 253 samples in Mystery Cave (Figures 4.19 and 4.20). The mean concentration was 3.4 ppm. The coefficient of variation was 97%.

The distribution of NO_3-N, as shown by the histogram of Figure 4.19, is strongly skewed, with breaks at 1 and 3 ppm. The histogram suggests that concentrations of NO_3-N >3 ppm, and probably >1 ppm, indicate the presence of significant anthropogenic components.. The inverse, however, in not necessarily true: individual samples with less than 3 (or 1) ppm NO_3-N are not necessarily from natural sources of NO_3-N or free from anthropogenic contamination. Dilution from precipitation or snow melt can lower NO_3-N concentrations. Denitrification is a common process in aquifers (see, e.g., the review by Appelo and Postma, 1993). Although natural high-nitrate concentrations in clastic sediments is common in saltpeter caves of the southeastern U.S. (Hill, 1981) and high nitrate concentrations in drop waters have been reported by Jameson and Alexander (1990) from a cave in West Virginia, no high nitrate waters or saltpeter-bearing sediments are known from Minnesota caves. There is no evidence that any of the elevated nitrate levels measured in Mystery Cave waters are from natural sources.

Mean NO_3-N concentrations for the five waters and the South Branch of the Root River are shown in Figure 4.21. The highest mean concentration was in the Root River (7.2 ppm for $n = 5$), which receives considerable nitrate loading from agricultural lands. Cave streams, pools, and waterfalls and ceiling drip waters all had mean concentrations above the 3 ppm break on the histogram of NO_3-N for all waters. Only flow stone drips and stalactite drips had lower values of mean NO_3-N. The cave waters, although clearly impacted by anthropogenic nitrate, serve to dilute the nitrate levels in the South Branch water that flows through the lower level streams in Mystery Cave.

NO_3-N often approached (and occasionally exceeded) EPA drinking water limits of 10 mg/l at several sites. These include sites along tourist trails, such as Turquoise Lake, Frozen Falls Drips, and Frozen Falls Pool in Mystery I (see Chapter 5).

Sethi (unpublished data, see Appendix 4) obtained a NO_3-N value of 8.1 ppm at Turquoise Lake in December, 1990. In this study, Turquoise Lake (Figure 5.x) showed a consistent and long-term rise in NO_3-N from 8.7 to 12.0 ppm between June of 1991 and April of 1993. The April sampling was a few days after flushing by water from the Root River during a major flood. NO_3-N did not decrease significantly, as did Cl, SO_4, and other anions (Figure 5.xxx and the major cations Ca, Mg, and Na. When most recently sampled (May, 1994), the NO_3-N level in Turquoise Lake had declined slightly to 10.9 ppm. The high concentration of NO_3-N, its slow variation on the time scale of years, and the lack of response to major recharge events is consistent with the diffuse response of karst aquifers to wet and dry cycles on the time scale of years. The water entering Turquoise Lake is fed mostly by diffuse infiltration through agricultural lands. These lands provide a major source of nitrate (or other nitrogen species that are transformed into nitrate). The chemical interactions between that source and the ground water are relatively unaffected by short-term recharge events.

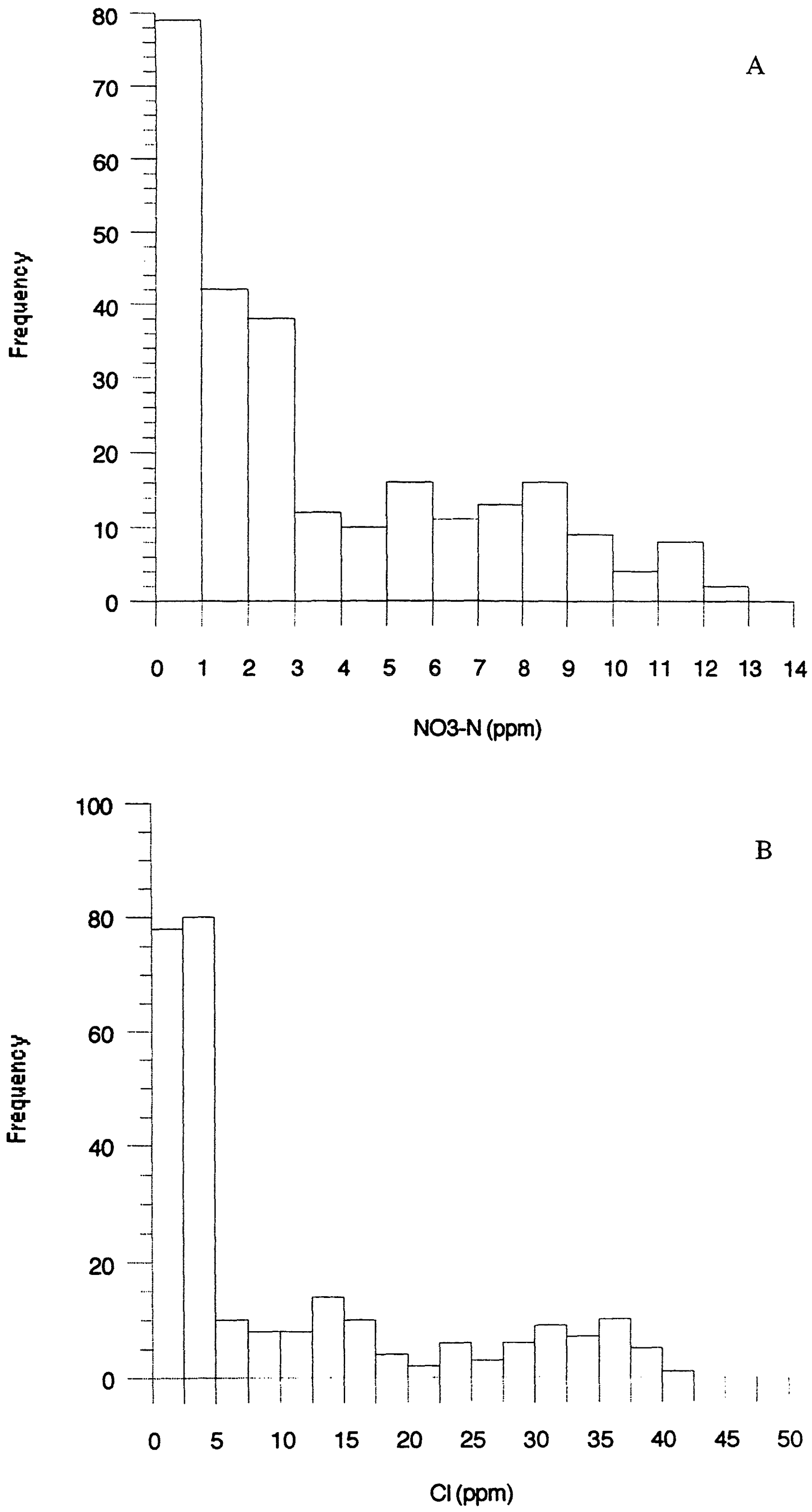


Figure 4.19. Histograms of NO3-N and Cl in waters of Mystery Cave. a. NO3-N. b. Cl.

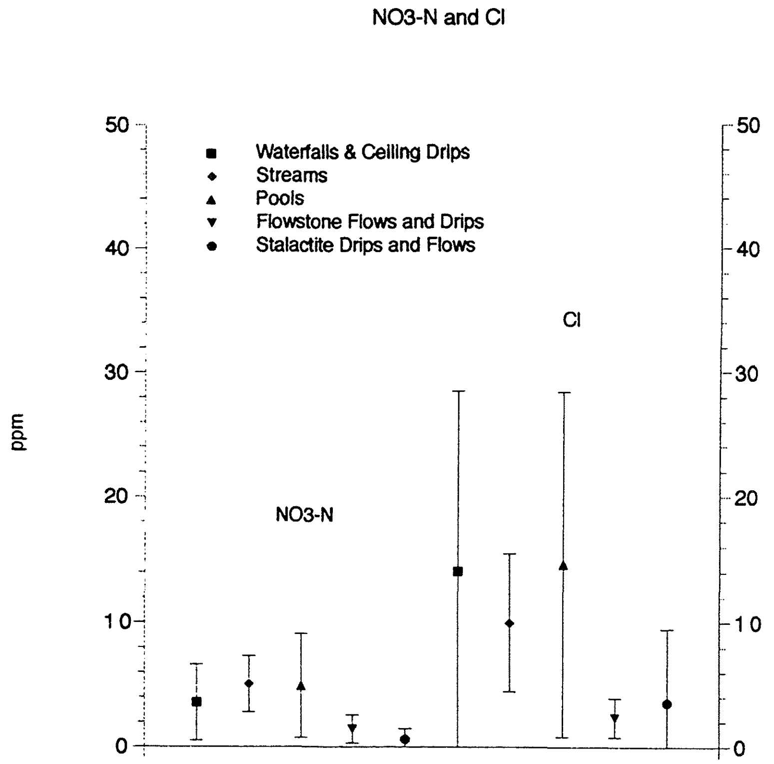


Figure 4.20. Mean NO_3-N and Cl concentrations for waters at Mystery Cave. Bars show one standard deviation above and below the mean.

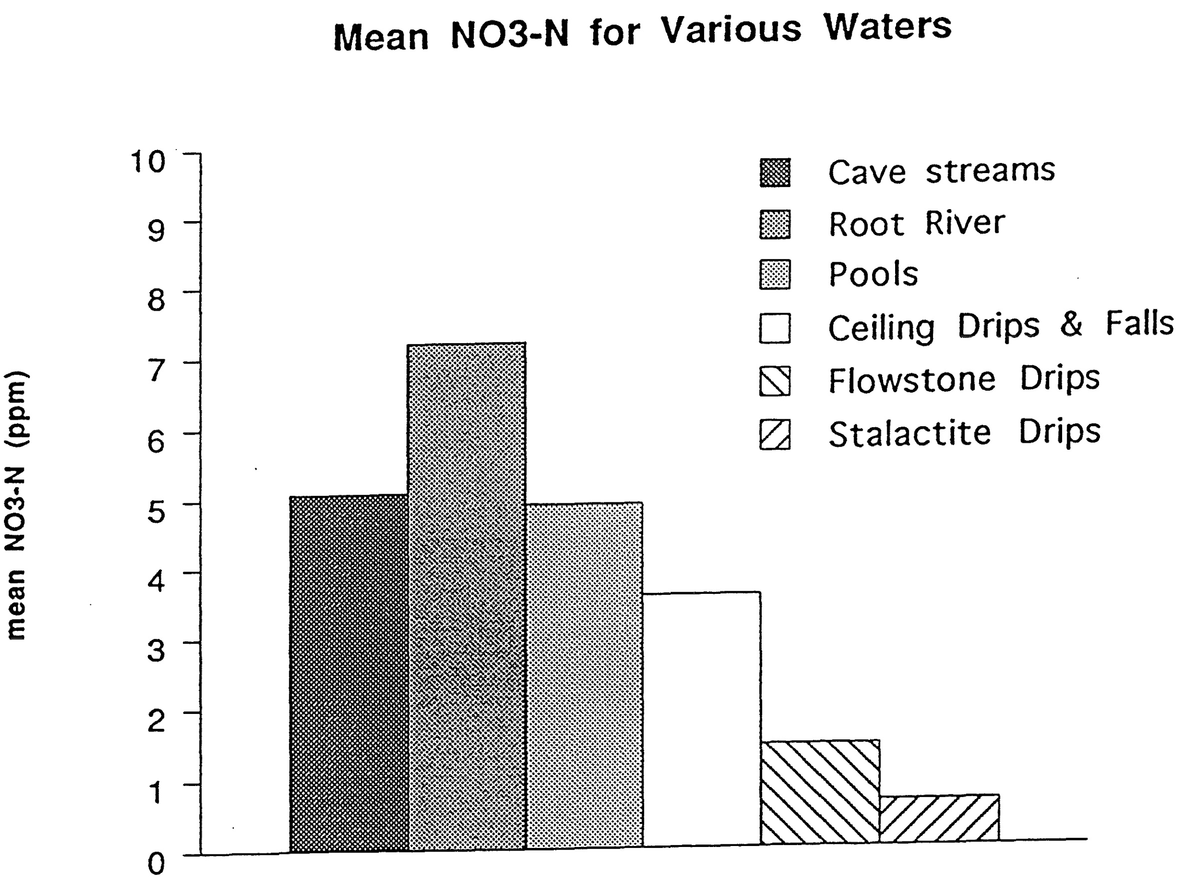


Figure 4.21. Mean NO_3-N for Mystery Cave waters and the South Branch of the Root River.

Chloride

Chloride ranged from 0.4 to 40.5 ppm for 253 sampled waters in Mystery Cave. The mean concentration was 9.9 ± 11.6 ppm. The coefficient of variation was 117%. The distribution of Cl, as shown by the histogram of Figure 4.19, is strongly skewed, with a large break at 5 ppm and a low, broad secondary peak at about 35 ppm. The histogram suggests that concentrations greater than 5 ppm Cl are above anthropogenic concentrations. A similar caution to the one for NO_3-N is in order here: individual samples of less than 5 ppm do not necessarily derive from natural sources of Cl. In fact, most chloride probably derives from KCl-bearing fertilizers or road salts. The bedrock at Mystery Cave (which should be well flushed of connate brines due in part to an extensive period of karstic groundwater circulation) is unlikely to be a natural source of Cl concentrations greater than a few ppm.

Chloride concentrations should reflect such factors as (1) the amount and temporal distribution of source material, (2) the amount of recharge that mobilizes the Cl, (3) the temporal distribution of the recharge, (4) the amount of Cl that is stored in soil, loess, the subcutaneous zone, and fractured bedrock above the cave, (5) the distance between the source and the sampling site, and (6) the amount of mixing of waters along the flow path.

Mean Cl concentrations for the cave waters and the Root River are shown in Figure 4.22. All waters except for flowstone drips and stalactite drips have mean Cl concentrations above the 5 ppm break on the Cl histogram of Figure 4.19.

The two major anthropogenic chloride sources that might affect Mystery Cave waters are chloride from potassium chloride, applied to the overlying fields as the "potash" component of fertilizers, and chloride from sodium chloride from human and animal wastes, road salt, water softening, etc. If the chloride were coming directly from a sodium chloride source it would have a characteristic Cl/Na ratio of 1.0 (in atomic concentration units). Figure 4.23 plots Cl vs Na for Mystery Cave waters. Lines corresponding to Cl/Na ratios of 1.8, 1.0 and 0.5 have been added to the figure for comparison. Figures 4.24 through 4.29 show details of the Cl vs Na relationship for pools, waterfalls, the Root River, cave streams, flowstone flows, and stalactite drips.

The most obvious cluster in Figure 4.23 has a slope corresponding to a Cl/Na ratio of about 1.8. This cluster is actually two clusters. The upper, >0.6 meq Cl, end of the apparent trend is defined by the samples from Turquoise Lake and Frozen Falls Pool (Figure 4.24), Frozen Falls Drips (Figure 4.25), and Turquoise Lake Source (Figure 4.27) and does scatter about a line with a slope of about 1.8. The lower, <0.6 meq Cl, end of the apparent trend is defined by samples from Frozen Falls Pool, Lily Pad Lake, Boofer Pool, and Dragon's Jaw Lake (Figure 4.24); the Lower Level Stream, Flim Flam Creek and Formation Route Creek (Figure 4.27); and the Root River (Figure 4.26); these scatter about a line with a slope of about 2.2. Both arrays looks like dilution trends of a waters with characteristic Cl/Na ratios by waters with much lower Cl and Na contents such as rain water or snow melt. The water with a Cl/Na ratio of about 1.8 is seen in Mystery I. The water with the Cl/Na ratio of 2.2 is seen in the Root River and in lower level streams fed by the Root River but is also seen in other several places in the cave.

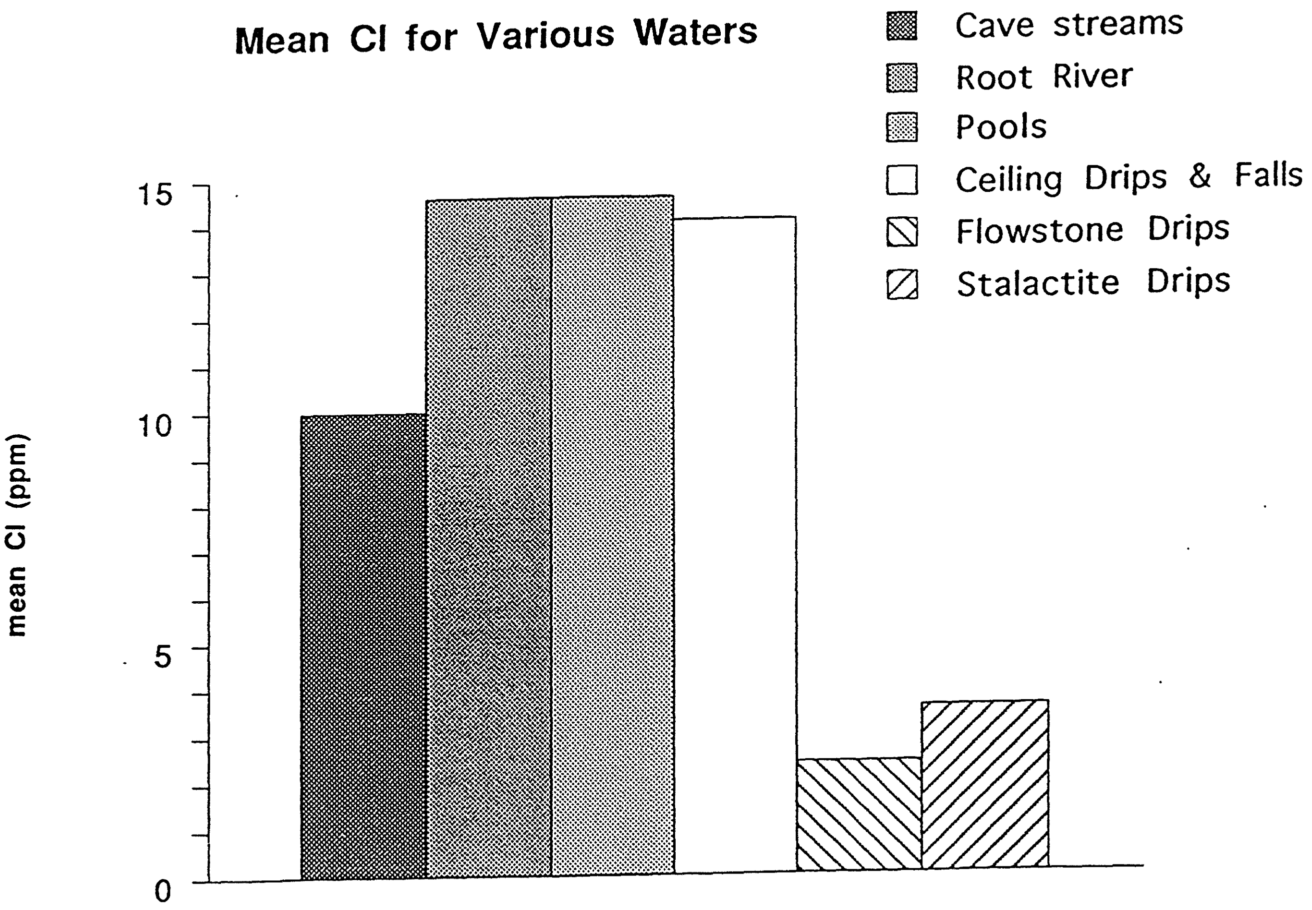


Figure 4.22. Mean Cl for Mystery Cave waters and the South Branch of the Root River.

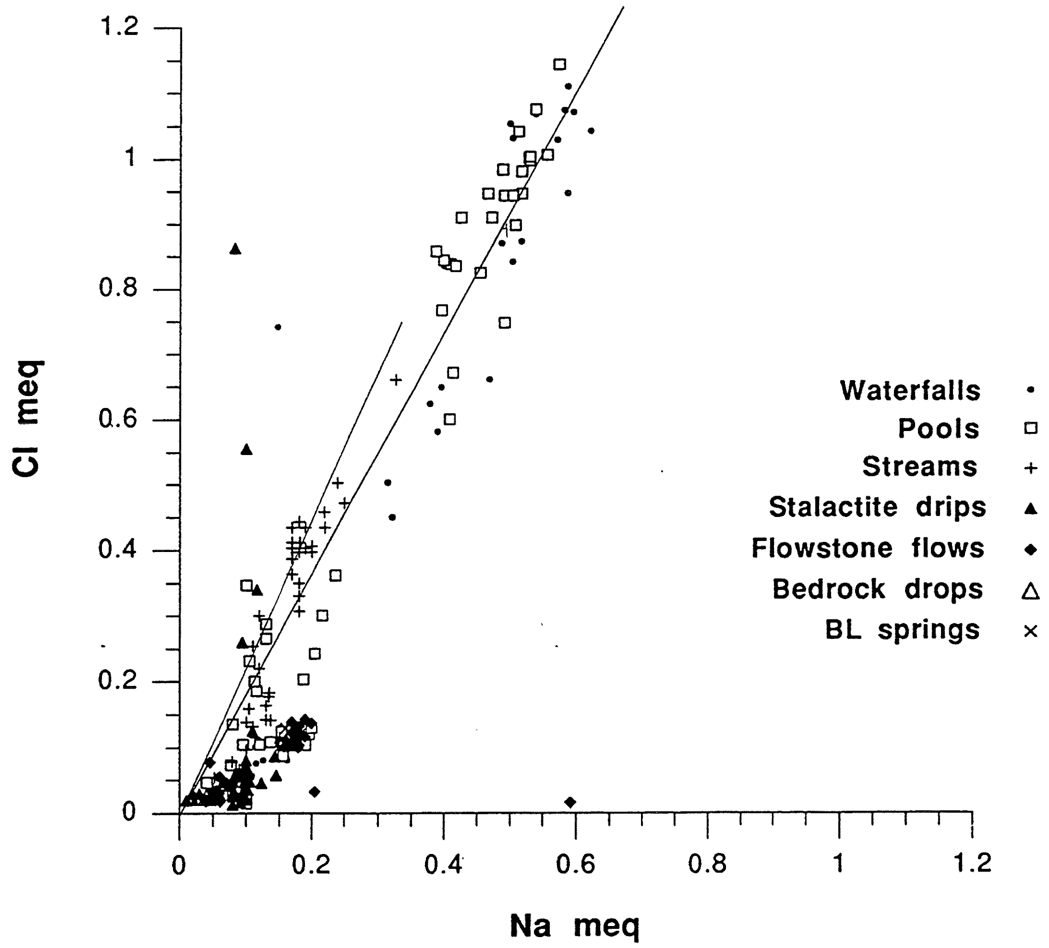


Figure 4.23. Cl vs Na for Mystery Cave waters.

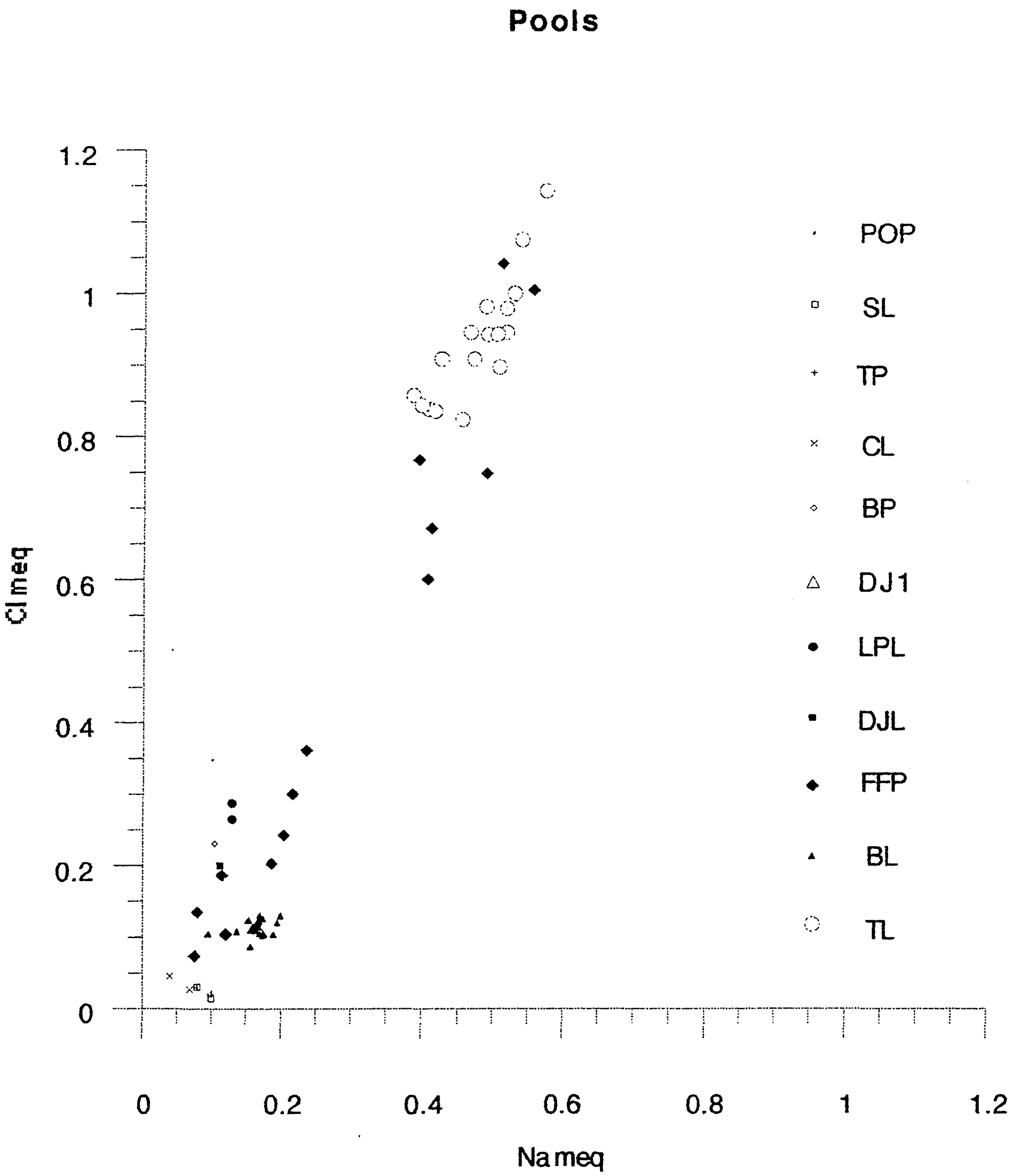


Figure 4.24. Cl vs Na for pools.

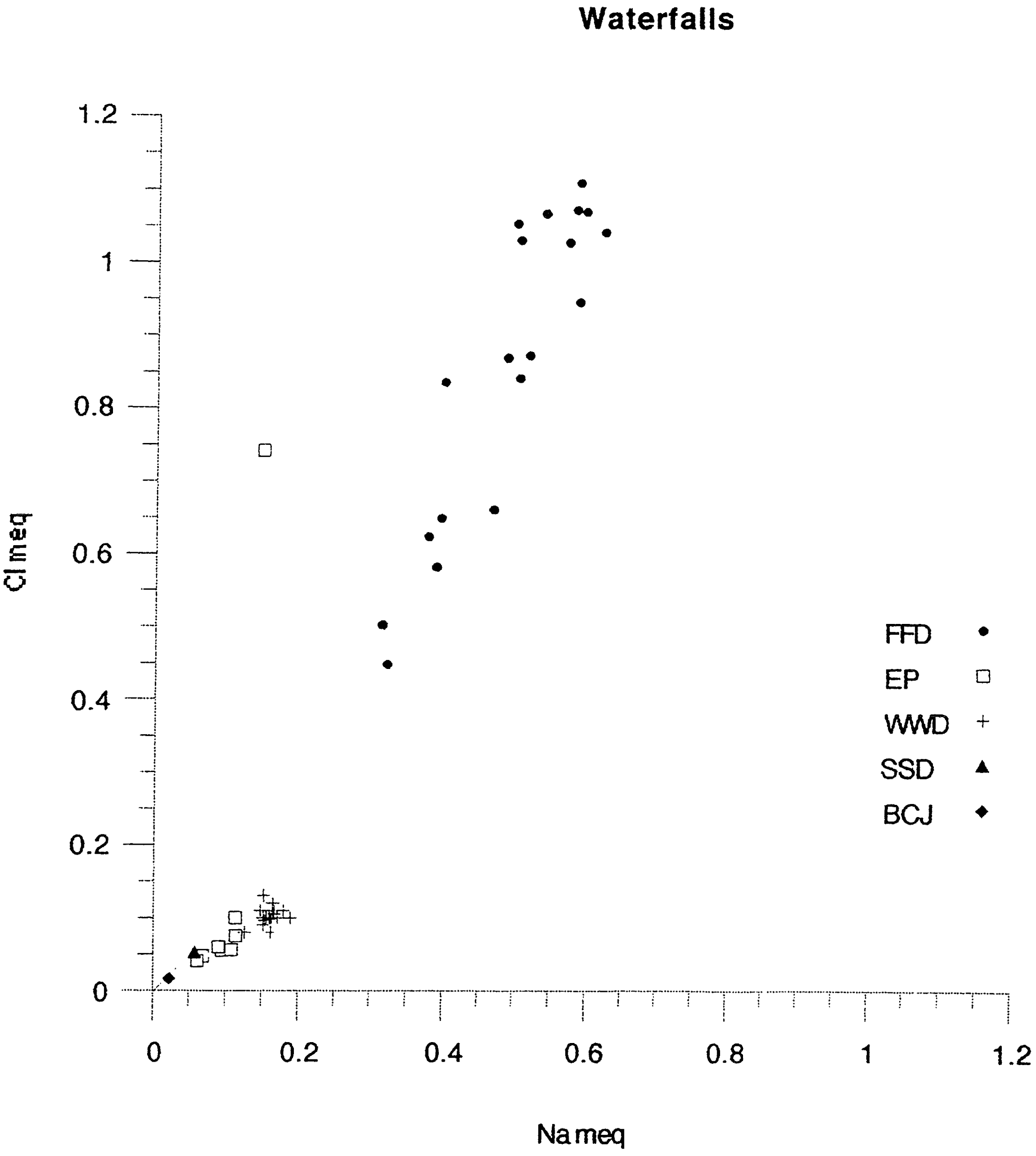


Figure 4.25. Cl vs Na for waterfalls.

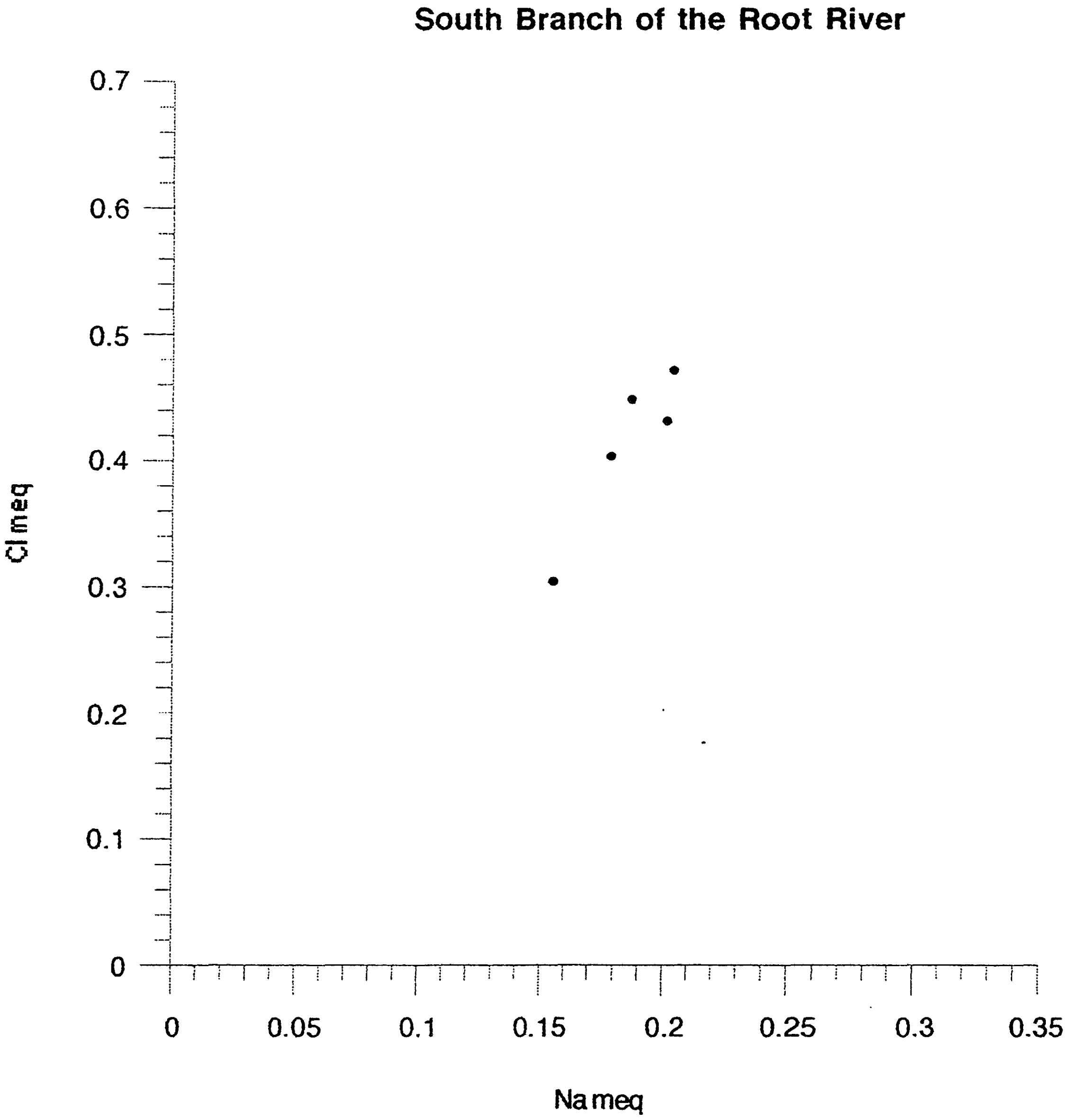


Figure 4.26. Cl vs Na for the South Branch of the Root River.

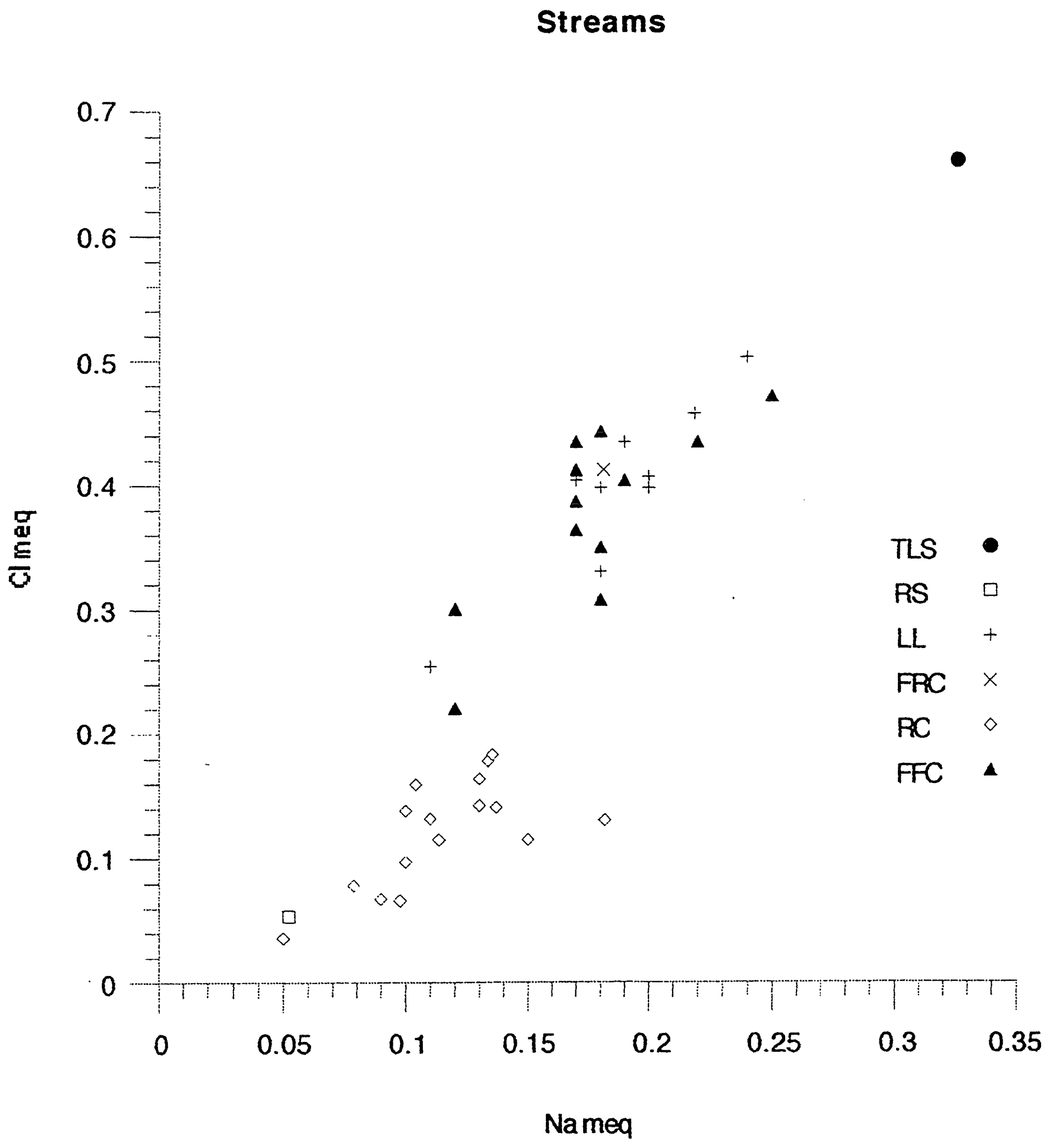


Figure 4.27. Cl vs Na for cave streams.

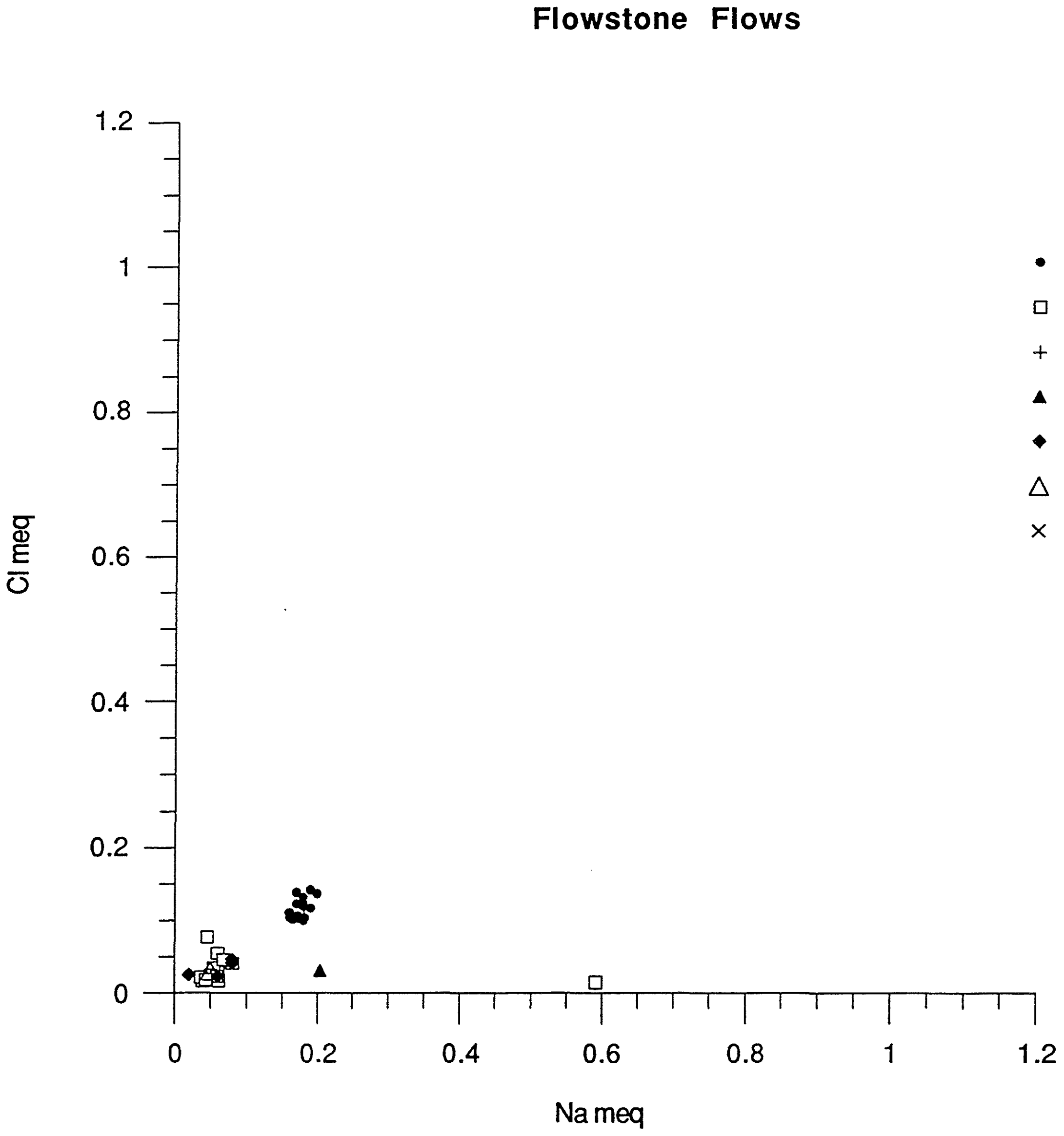


Figure 4.28. Cl vs Na for flowstone flows.

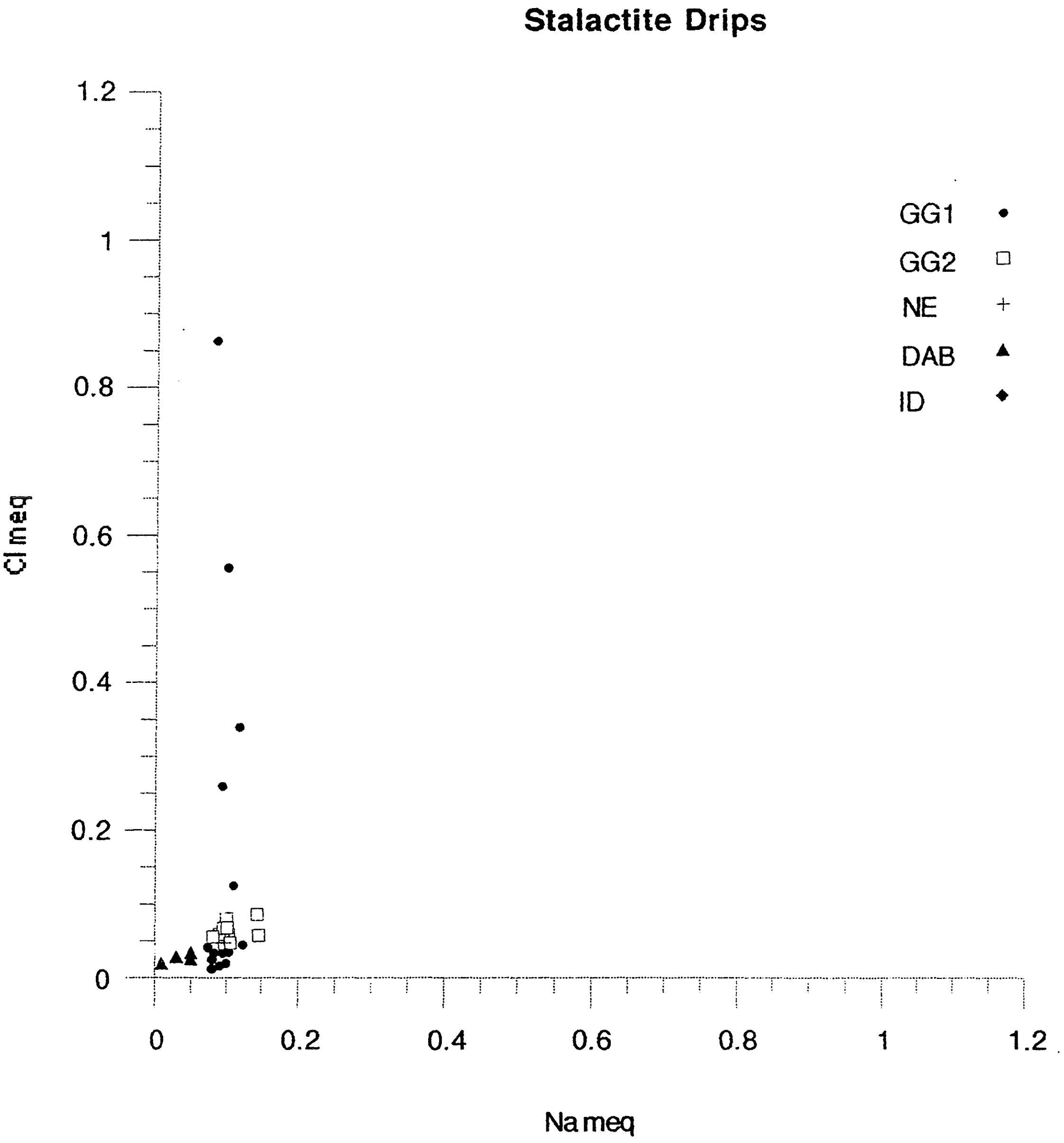


Figure 4.29. Cl vs Na for stalactite drips.

The source of these high Cl/Na components is not obvious. One possibility is that they are a mixture of Cl from NaCl sources with Cl from KCl sources (from which the K has been removed by ion exchange process in the soil.) The one Enigma Pit outlier in Figure 4.25 and the high Cl samples from Garden of the Gods 1 in Figure 4.29 probably represent a cleaner case of this latter phenomena (see discussion of GG1 samples in Chapter 5.)

The only samples that appear to have Cl/Na ratios close to 1.0 have low (<0.2 meq) Cl and Na contents (Figures 4.27, 4.28, and 4.29.) There are a few samples that have Cl/Na ratios << 1. These samples also have very low Cl contents.

Figure 4.30 compares the nitrate and chloride concentrations in Mystery Cave waters. Although both ions are generally considered geochemically conservative and mobile, they have different sources, and plots of NO_3 versus Cl often show a scatter of data with no obvious trends. At first glance, Figure 4.30 is very scattered, but on closer examination a number of interesting patterns can be seen.

The horizontal array across the bottom of Figure 4.30 contains the high Cl samples from GG1 and the one sample from Enigma Pit with elevated Cl. This array is discussed in Chapter 5.

Figures 4.31 and 4.32 show the nitrate versus chloride relationships for the pools and streams, respectively. Reference lines with slopes corresponding to NO_3/Cl ratios of 1.0, 2.0 and 3.7 are shown for comparison. In Figure 4.31 the data from Frozen Falls Pool form a clean mixing line between a component with nitrate and chloride contents of about 40 ppm and a component with nitrate and chloride values of less than 4 ppm. Turquoise Lake shows chloride concentrations > 30 ppm and nitrate values that range from 35 to 55 ppm. Lily Pad Lake, Dragon's Jaw Lake and Boofer Pool have a higher NO_3/Cl ratio of about 3.7.

In Figure 4.32, Flim Flam Creek and the Lower Level Stream scatter around a slope 2 line. Rimstone Creek seems to form a mixing line around the slope 3.7 line.

SULFATE

Sulfate is a ubiquitous component in the waters of Mystery Cave. Sulfate contents ranged from 2 to 49 ppm (Figure 4.33) with one outlier (not shown in Figure 4.33; BD2, drops of water collected from a bedrock surface near beds with disseminated pyrite in the Dubuque Formation; SO4 = 512 ppm).

Sulfate probably comes from both natural and anthropogenic sources. The major natural source is the oxidation of sulfides such as pyrite. The reactions involved in this process can be summarized as:

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{+2} + 2\ H_2SO_4$$

$$CaCO_3 + H_2SO_4 = Ca^{+2} + SO_4^{-2} + CO_2 + H_2O$$

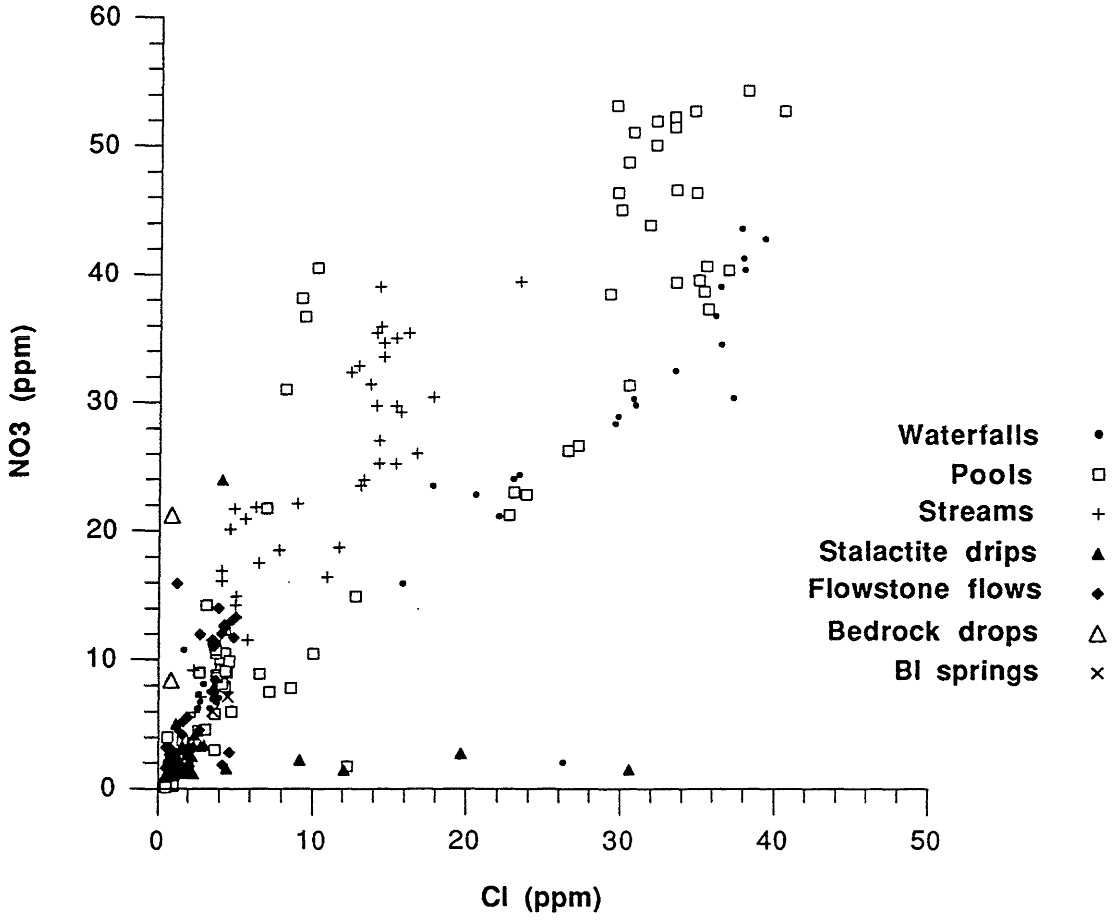


Figure 4.30. NO_3 vs Cl for Mystery Cave waters.

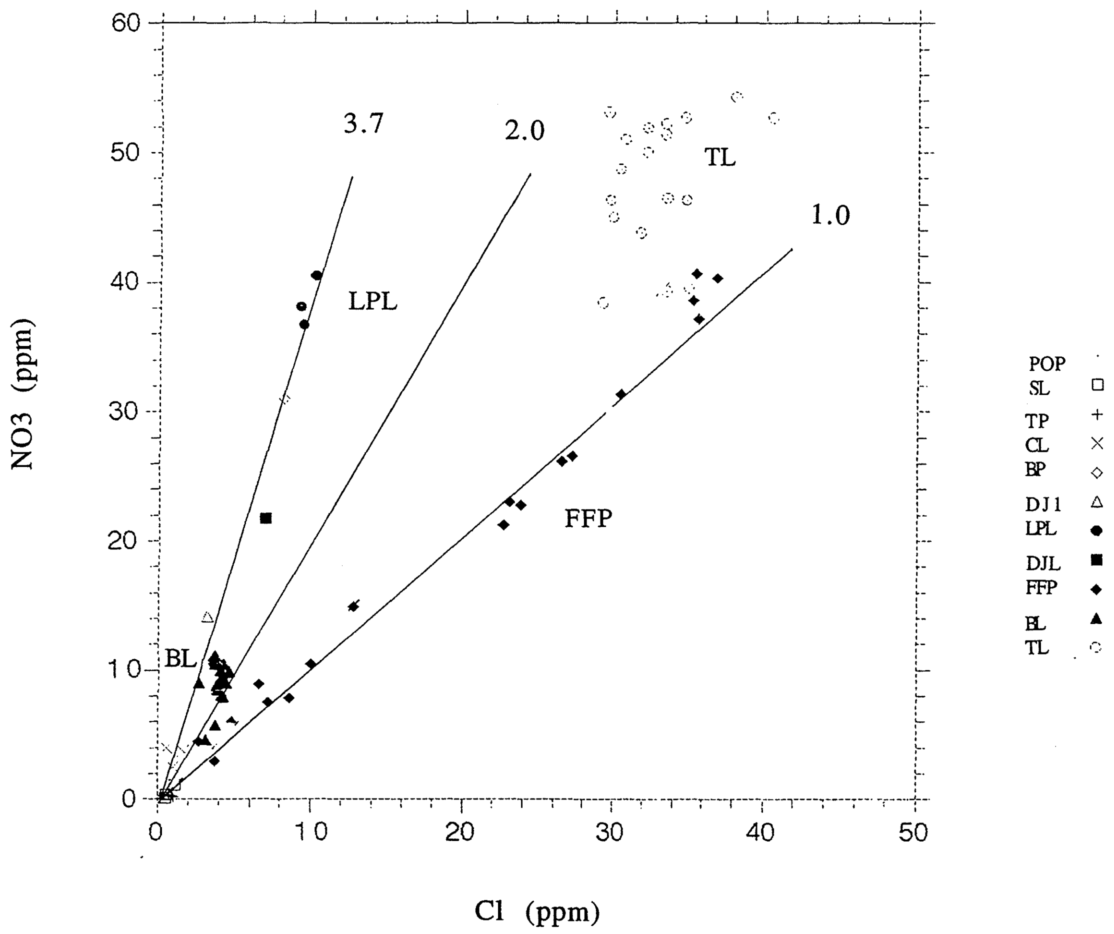


Figure 4.31. NO_3 vs Cl for pools.

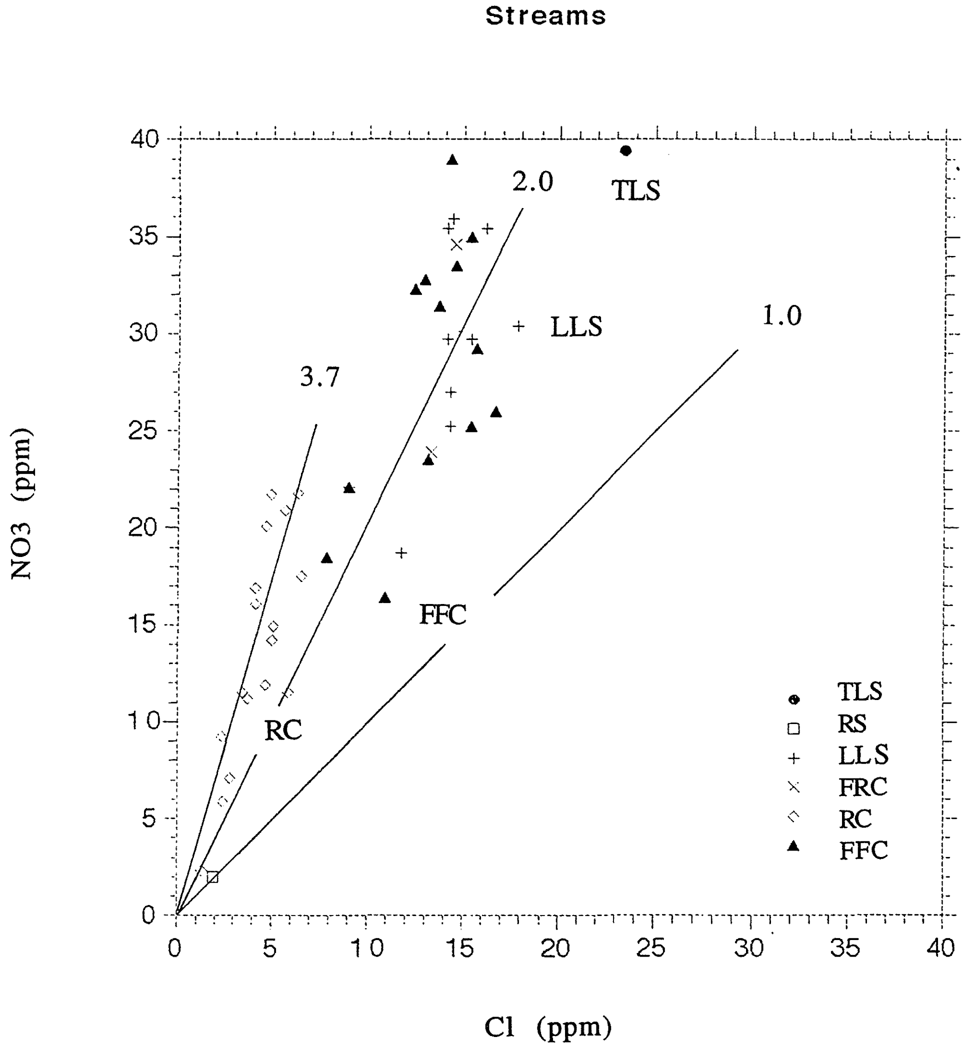
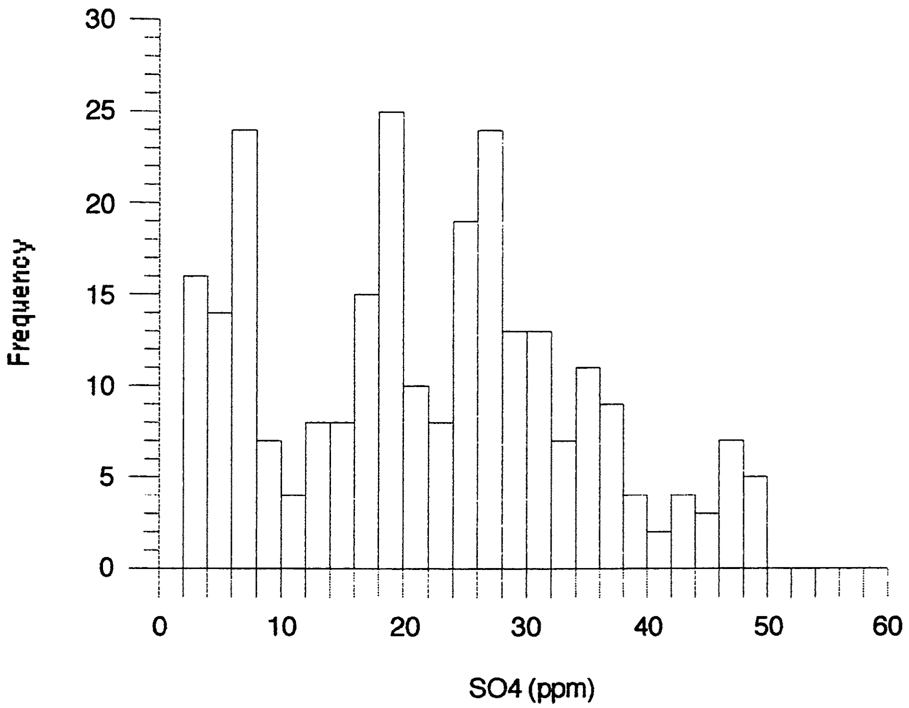


Figure 4.32. NO_3 vs Cl vs for cave streams.



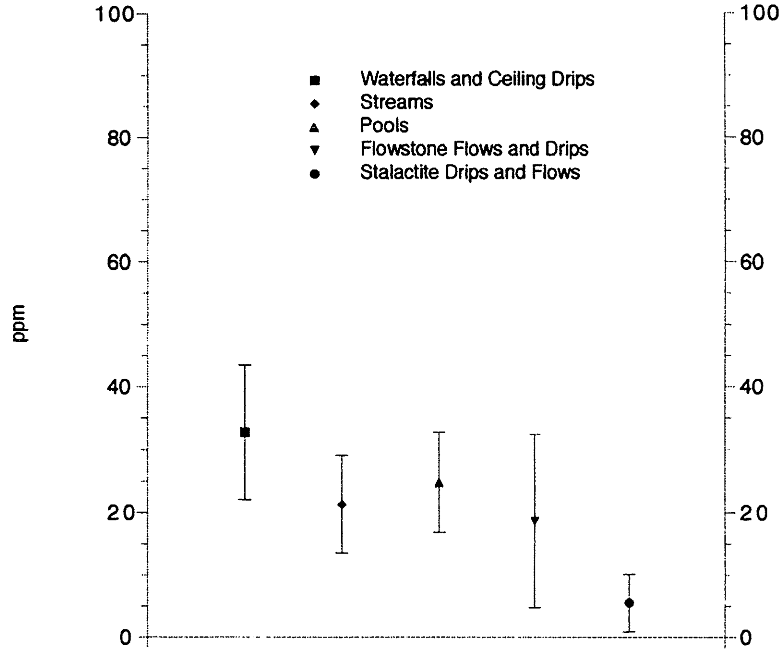


Figure 4.33. SO_4 in Mystery Cave waters. a. Histogram. b. Means and standard deviations for the five water types. Bars plot one standard deviation above and below the mean.

The pyrite oxidizes to form sulfuric acid which reacts with the surrounding limestone to form a calcium sulfate solution. The anthropogenic sources include the sulfate deposited as part of acid precipitation and sulfate applied to fields as part of fertilizers.

Figure 4.34 plots SO_4 vs Cl for waters from Mystery Cave. Three trends are evident. The horizontal group of stalactite drip samples across the bottom are the GG1 samples discussed in Chapter 5. A gently sloping array contains samples with 10 to 32 ppm sulfate and chloride contents ranging up to 40 ppm. The array consists of samples from Turquoise Lake (open squares with Cl > 30 ppm), Frozen Falls Pool (open squares with Cl < 30 ppm), Frozen Falls (solid circles with Cl > 15 ppm), and Flim Flam Creek, Formation Route Creek and Lower Level Creek (plus marks). The third array is a steeply sloping line with Cl < 6 ppm and the entire range of sulfate values.

Figure 4.35 plots the saturation index for gypsum vs P_{CO_2} for water samples from Mystery Cave. All of the samples are undersaturated with respect to gypsum (SIG < 0). The anomalous BD2 sample comes the closest to being saturated with gypsum. The rest of the samples tend to occur in horizontal bands. The waterfalls and pools are the highest. Flowstone flows and stalactite drips are the lowest. The waterfalls are formed by water that has collected from a larger area and moved horizontally within the Dubuque. This apparently leads to greater exposure to oxidizing pyrite in the Dubuque and higher sulfate contents. The pools form (in many cases) from the waterfalls. Conversely, the flowstone flows and stalactite drips apparently represent water moving more directly downward. While that water has to traverse the Dubuque, the residence time is perhaps shorter and the paths are more completely flushed of their original sulfides.

MINOR AND TRACE ELEMENTS

Sodium and Potassium

Na and K are major cations in many ground waters but tend to be fairly low in most karst waters. The waters of Mystery Cave follow this general trend. Na and K concentrations are at minor to trace levels.

Na concentrations ranged from <1 ppm to 14 ppm (Figures 4.36 and 4.37). The distribution is distinctly bimodal with one peak at about 3 ppm and a second broader peak at about 12 ppm. The broad 12 ppm peak consists of the Turquoise Lake and Frozen Falls samples that cluster in other graphs. The relationships between Na and Cl are shown in Figures 4.23-4.29 and are discussed in the section on chloride above.

The K concentrations ranged from < 0.1 ppm to 5.3 ppm (Figures 4.36 and 4.37). The distribution is unimodal with a peak between 0.5 and 0.75 ppm with a scattering of higher values.

Figure 4.38 is a plot of K vs Na for waters from Mystery Cave. The bulk of the samples cluster in the < 2 ppm K and < 5 ppm Na part of the diagram. The relatively high Na samples have about 1 ppm K and consist of the Turquoise Lake and Frozen

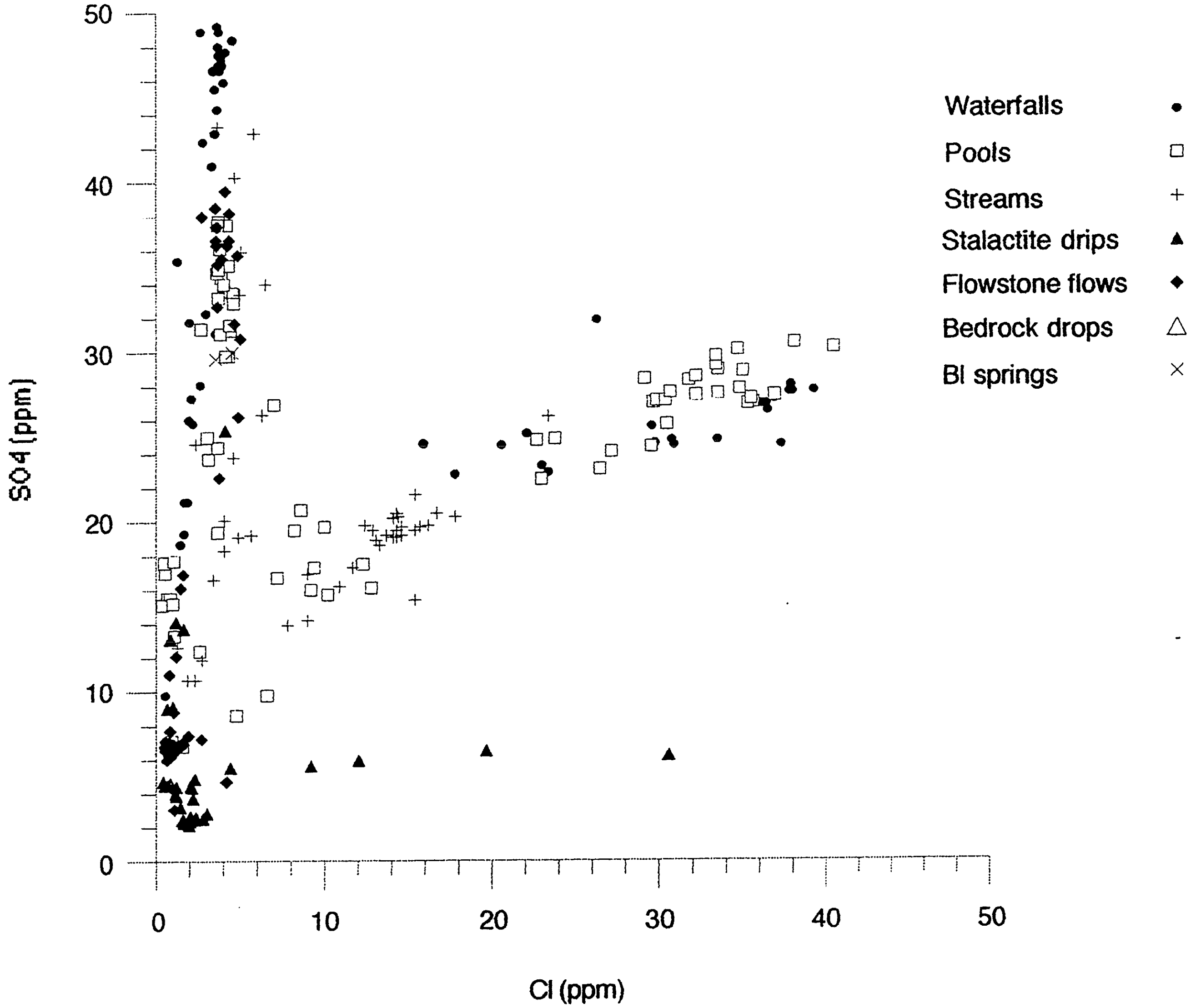


Figure 4.34. SO_4 vs Cl for Mystery Cave waters.

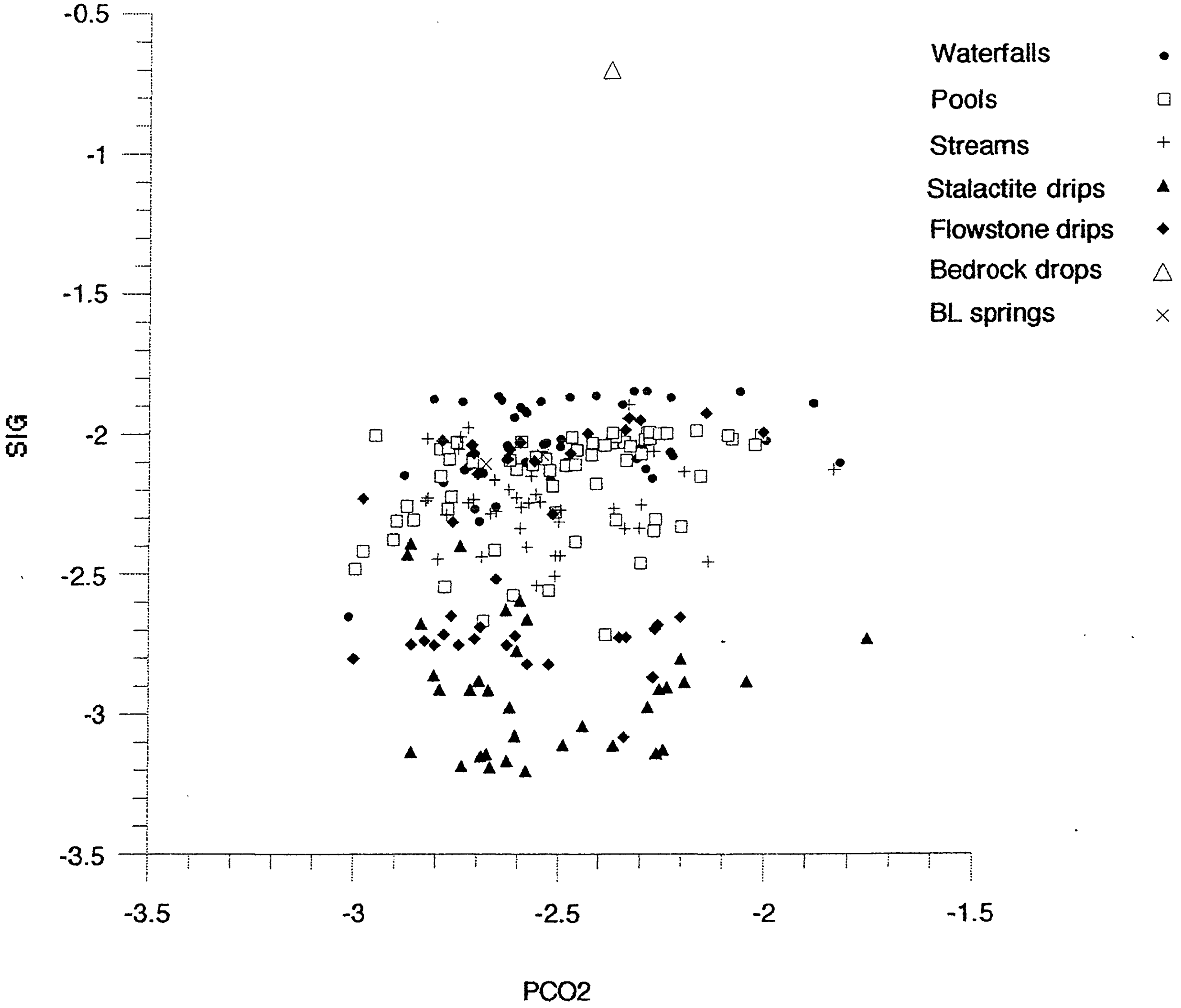
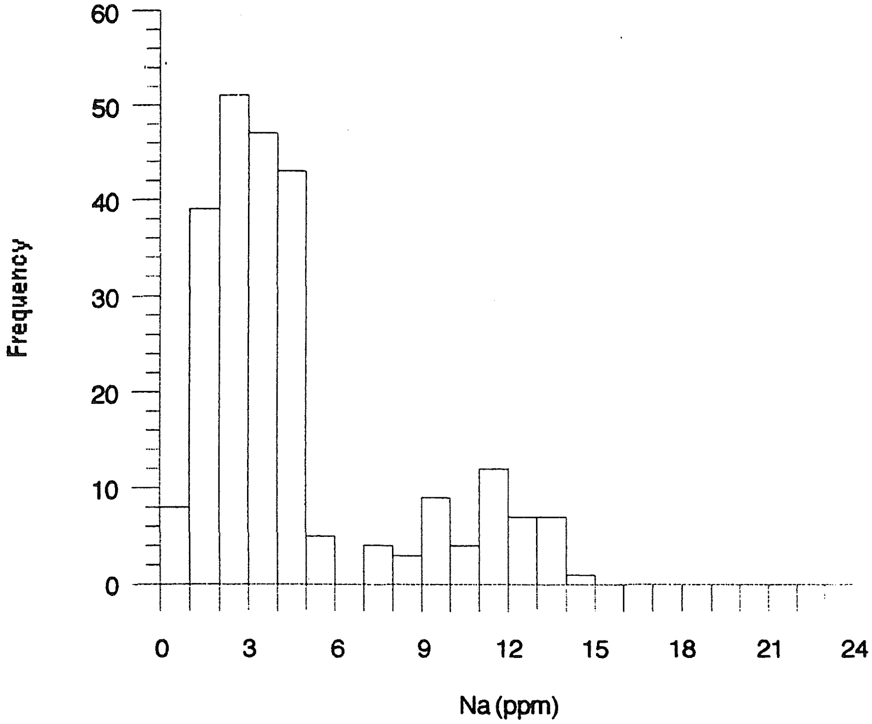


Figure 4.35. Gypsum saturation indices (SIG) vs P_{CO_2} for water samples from Mystery Cave.



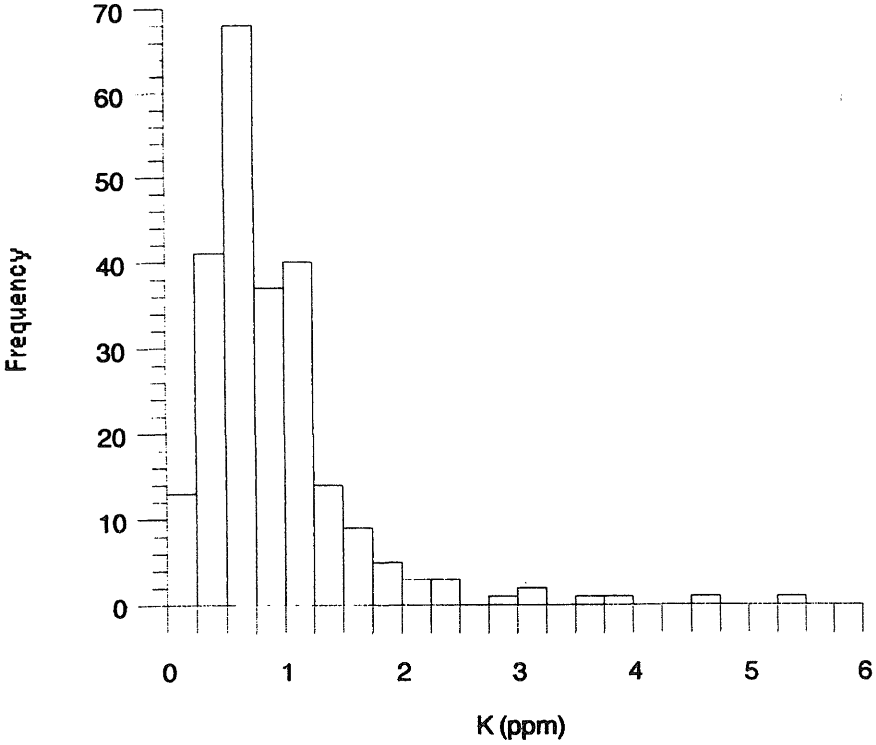


Figure 4.36. Histograms of Na and K.

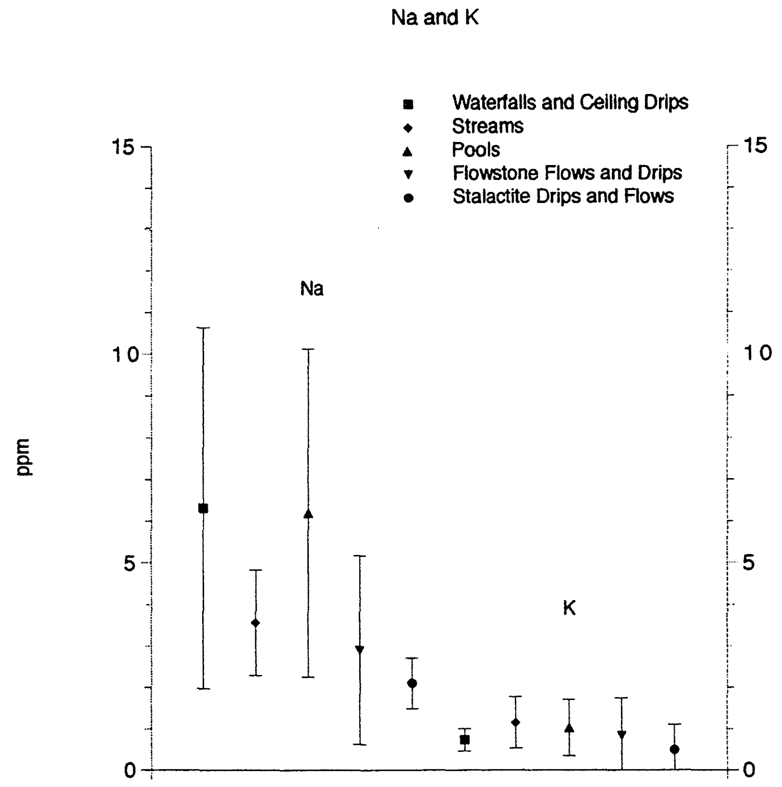


Figure 4.37. Means and standard deviations for Na and K for the five water types. Bars represent one standard deviation above and below the mean.

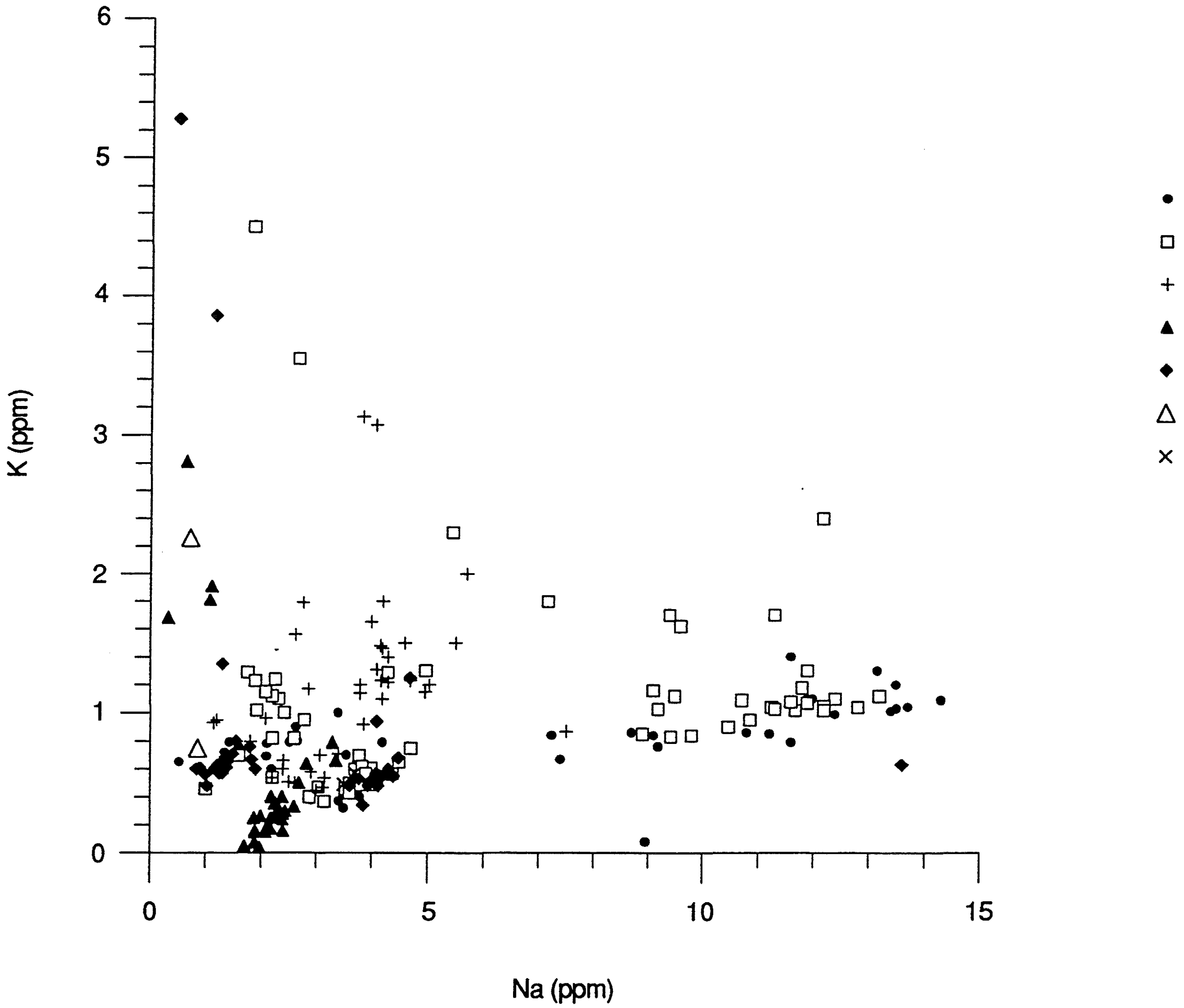


Figure 4.38. Na vs K for Mystery Cave waters.

Falls samples. The relatively high K potassium group have relatively low Na contents.

Strontium and Barium

Strontium and barium are in the same column of the periodic table below magnesium and calcium. Strontium and barium are ubiquitous trace elements in karst waters. Figure 4.39 gives histograms of the Sr and Ba contents of Mystery Cave waters. The Sr values range from 0.03 to 0.18 ppm with one outlier (BR2) at .29 ppm. The Ba values range from 0.02 to 0.16 ppm with one outlier (BD2) at 0.8 ppm. Both histograms are unimodal. Ba forms a very insoluble sulfate, barite, while all of the common Sr compounds are relatively soluble. Note that the high sulfate sample, BD2, has the highest Sr content but relatively low Ba.

Figure 4.40 plots Sr vs Ba. The data form a fan shaped array with groups of samples forming different mixing lines. The lower array has a slope corresponding to a Sr/Ba ratio of about 0.75 and contains the Turquoise Lake and part of the Frozen Falls samples. The steepest array has a slope corresponding to a Sr/Ba ratio of 5.2.

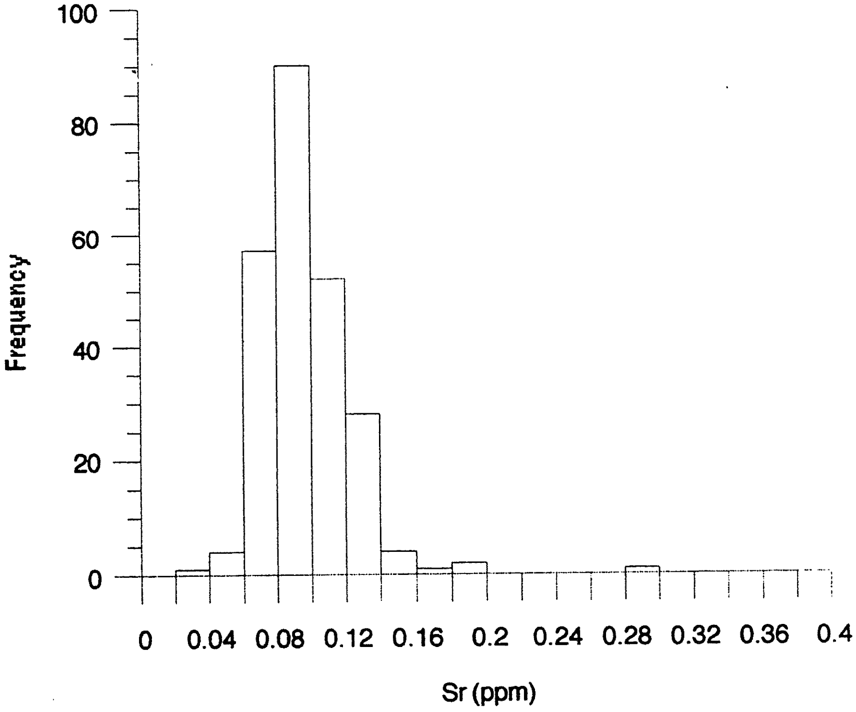
FECAL COLIFORM BACTERIA

Potential sources of fecal coliform bacteria include abandoned outhouses, septic systems, feed lots, and manure spreading. Recommended limits of fecal coliform bacteria in drinking water are zero colonies per 100 ml.

Table 4.2 shows results of winter (February 23, 1992) and summer (July 29, 1992) samplings for fecal coliform bacteria at 19 sites. The winter sampling was carried out during a cold period with an extensive snow cover; the Root River was frozen over and there was no visible runoff in surface drainages. The winter sampling was an initial survey to check for the presence or absence of fecal coliform bacteria, and was unable to quantify counts higher than 200 colonies/100 ml. Two sites (Formation Route Creek and Coon Lake Drips) had bacteria in numbers too high to count for in that sampling, in which no serial dilutions were performed. Therefore, selected samples were run with serial dilutions in the July sampling. The summer sampling was carried out one week after a 1.15 in storm on July 22; .02 in were also measured at the Root River weather station on July 23 and again on July 25.

Bacteria were not present in 16 of 28 total samples, were present in seven samples (1, 1, 1, 2, 20, 1000, and 5000 colonies/100 ml) and were too numerous to count (TNC, >100, >100, >200, and >200 colonies) in four samples. One test in the winter sampling was inconclusive.

The highest bacterial counts were in the Root River (5000 colonies/100ml). In the cave, high counts (100, and >200) were obtained for Flim Flam Creek and Formation Route Creek. The high counts in the winter sampling at Formation Route Creek suggest the possibility that fall and winter spreading of manure in fields contributes significantly to bacterial concentrations in winter surface runoff, which then reaches the cave via sinks on the Root River.



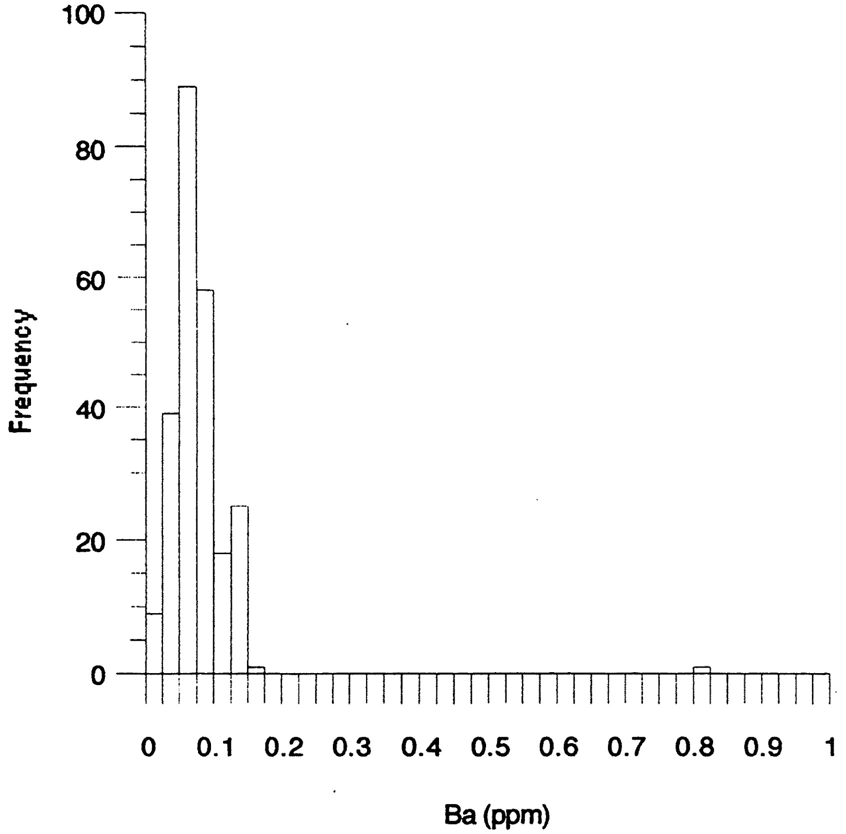


Figure 4.39. Histograms of strontium and barium.

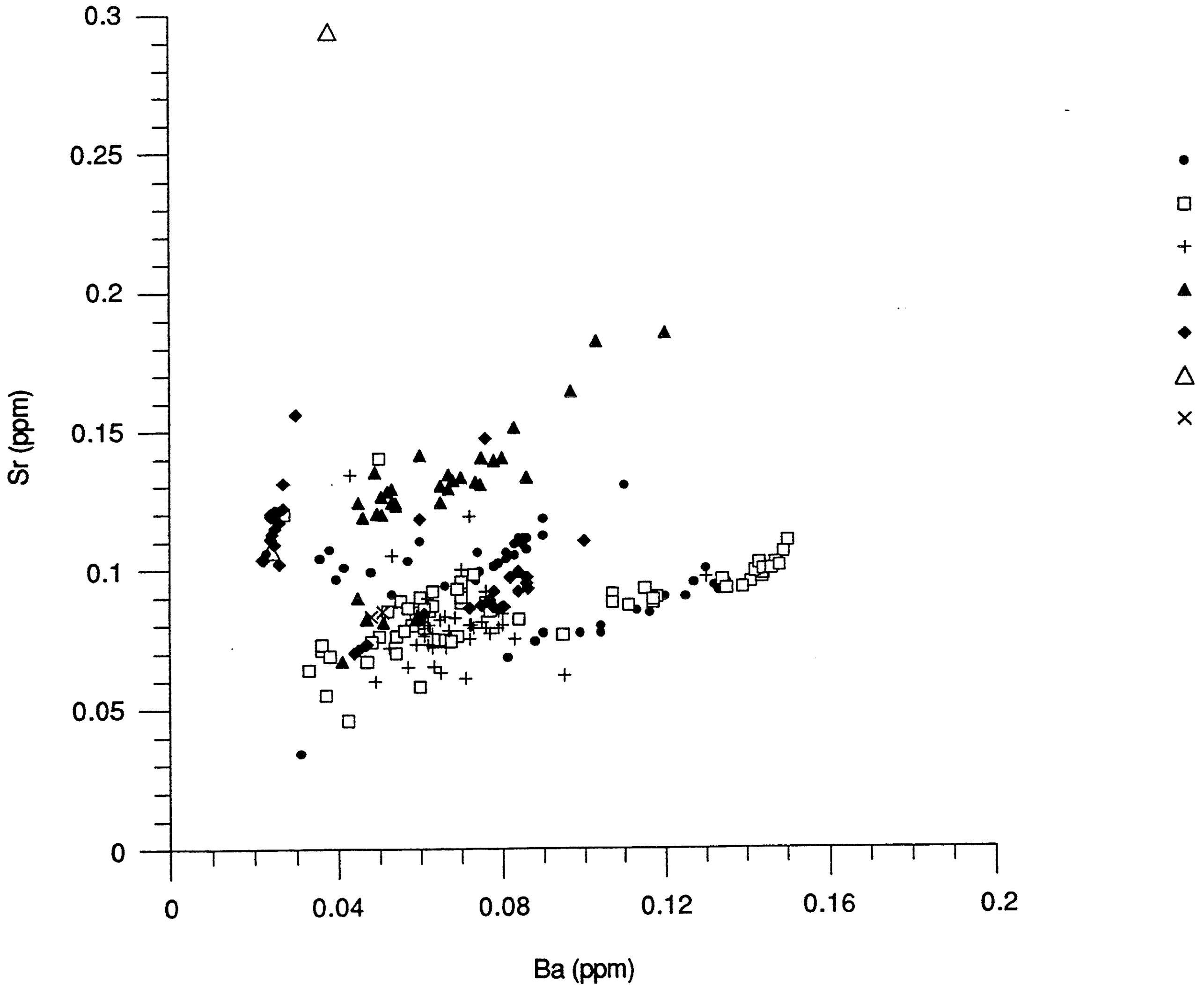


Figure 4.40. Sr versus Ba for Mystery Cave waters.

Table 4.2 Total Coliform Bacteria.

Water type	Location	Season	NO3-N (ppm)	Total Coliform Bacteria Presence	Total Coliform Bacteria Number in 100 ml
Streams					
	Rimstone Creek	winter	3.94 ± .08	Not present	
	Rimstone Creek	summer	2.65 ± .05	TNC	>100
	Formation Route Creek	winter	7.8 ± .02	TNC	>200
	Lower Level Stream	summer	6.7 ± .01	Present	20
	Flim Flam Creek	summer	6.6 ± .1	Present	100
	South Branch Root R.	summer	7.1 ± .01	Present	5000
Pools					
	Turquoise Lake	winter	10.5 ± .2	Present	1
	Turquoise Lake	summer	11.3 ± .2	Not present	
	Frozen Falls Pool	winter	5.1 ± .1	Not present	
	Frozen Falls Pool	summer	6.0 ± .1	TNC	>100
	Blue Lake	winter	2.36 ± .05	Inconclusive	
	Blue Lake	summer	2.05 ± .04	Not present	
	Coon Lake	summer	0.85 ± .02	Not present	
	Dragon's Jaw Lake	winter	4.9 ± .1	Present	1
	Tar Pits	winter	.06 ± .01	Not present	
	Lily Pad Lake	winter	9.2 ± .2	Present	2
Ceiling Drips and Waterfalls					
	Frozen Falls Drips	winter	6.8 ± .1	Not present	
	Frozen Falls Drips	summer	7.8 ± .2	Present	1
	Wishing Well	winter	1.74 ± .03	Not present	
	Wishing Well	summer	1.70 ± .03	Not present	
	Sand Source Drips	winter	0.53 ± .01	Not present	
Flowstone Drips					
	Coon Lake Drips	winter	1.25 ± .02	TNC	>200
	Coon Lake Drips	summer	1.03 ± .02	Not present	
	Blue Lake Drips	winter	2.87 ± .06	Not present	
	Blue Lake Drips	summer	2.82 ± .06	Not present	
Stalactite Drips					
	Garden of the Gods 1	winter	.37 ± .01	Not present	
	Garden of the Gods 1	summer	.29 ± .01	Not present	
	Garden of the Gods 2	winter	.77 ± .02	Not present	

TNC = Too Numerous to count

Winter sampling was on February 23, 1992

Summer sampling was on July 29, 1992

High bacterial counts (20 colonies/100 ml) were obtained at the Lower Level Stream in the summer. The Lower Level Stream is in Mystery I and is fed by the Root River.

Rimstone Creek had >100 colonies/100 ml in the summer sampling. This supports our interpretation of a source area for Rimstone Creek that includes drainage from corn fields and agricultural grasslands via the overlying gully system (see Figure 3.3). It would not surprise us to see high bacterial counts in Rimstone Creek in winter samplings following warm spells, or during the spring melt. However, no bacteria were detected in the winter sampling at Rimstone Creek.

Frozen Falls Pool in Mystery I is fed by Frozen Falls Drips, which had one colony/100 ml at the summer sampling, when Frozen Falls Pool had >100 colonies. Frozen Falls Pool is also fed by Drips Across Bridge, the Pipe Organ Drips, and the flowstone flow from a wall fracture at Across from Pipe Organ. It would be instructive to sample all five sites to attempt to locate the source(s) of fecal coliform bacteria in Frozen Falls Pool. Both Drips Across Bridge and the Pipe Organ become turbid after summer storms, indicating a direct connection to the surface. They could contribute to high bacterial counts in Frozen Falls Pool. However, Frozen Falls Drips is the most probable primary source of fecal coliform bacteria. It has a high discharge compared to the other sites, and has a more variable chemistry with periodic high inputs of NO_3-N, Cl, and SO_4.

Coon Lake Drips had high bacterial counts (>200) in the winter sampling. Bacteria were not detected in the summer sampling. The drip rate at Coon Lake Drips has been observed to fluctuate from about 0.2 l/hr in the winter, up to 13.6 l/hr following major recharge events. There is a short lag time between precipitation and the onset of increased discharge, as well as peak discharge (see Chapter 9).

PESTICIDES

Atrazine and Alachlor

Atrazine is widely used as a selective herbicide for the control of broadleaf and grassy weeds on corn and other row crops (Weed Society of America, 1989). It is also used as a nonselective herbicide for a variety of vegetation types, including noncrop lands. The maximum contaminant level for atrazine in drinking water is 3 ppb (EPA, 1991 Federal Register). Atrazine breaks down into a number of triazine metabolites (see Chapter 2, p. 20). These metabolites are also detected by the Ohmicron ELISA technique used to test for atrazine, but are not separately distinguished. For convenience, atrazine and its related triazines are referred to simply as atrazine in the following discussion.

Alachlor is used as a selective herbicide. The maximum contaminant level for alachlor is 2 ppb (EPA, 1991 Federal Register).

Sampling

Forty-five samples were collected at 27 cave sites and one surface site, the South Branch of the Root River at Mystery I for analysis of pesticides. Samples were collected on April 4, 1992, August 16, 1992, and May 12, 1993 to provide winter, summer, and spring sampling dates. Atrazine was analyzed on all 45 samples. Results are tabulated by location and date in Table 4.3, and by water type in Table 4.4. Alachlor was analyzed only on the 22 samples collected on August 16, 1992. Results appear in tables 4.5 and 4.6.

Results of Atrazine Sampling

Atrazine was below the 3 ppb EPA Maximum contaminant level for drinking water at all sites for all three samplings. Atrazine values ranged from below the 0.1 ppb detection limit to 0.8 ppb. For 38% (17 of 45) of the samples, atrazine was below the detection limit.

Samples from all five water types tested positive for atrazine (Table 4.5). Mean atrazine values (excluding atrazine < 0.1 ppb) for the five water classes are reported in Table 4.7. The mean atrazine concentration for all waters was 0.3 ppb. A summary for samples with atrazine below the detection limit is in Table 4.8. A histogram of atrazine concentrations for all samples is in Figure 4.41. Histograms comparing atrazine concentrations for each water type are in Figures 4.42 and 4.43.

Given the small number of samples from each water type, rigorous statistical comparisons between types is not warranted. However, a few observations are possible. First, the highest atrazine concentrations were in the South Branch of the Root River (0.7 and 0.8 ppb) and in cave streams partly recharged by the Root River, such as Flim Flam Creek (0.8 and 0.5 ppb), Formation Route Creek (0.5 ppb), and the Lower Level Stream (0.5 ppb). The mean atrazine concentration for all surface and cave streams was 0.5 ppb. None of the seven stream samples tested below the detection limit for atrazine (Table 4.8). All of these results are reasonable because (1) atrazine is readily transported from crop lands into surface streams, and (2) losing surface streams provide the most direct (and most continuously recharged) pathways for introduction of contaminants into the cave.

Second, the relatively high mean of 0.3 ppb atrazine for pools is largely from samples collected at Turquoise Lake (Table 4.7), which also has a postulated direct surface source on agricultural lands. Turquoise Lake consistently has elevated levels of NO_3-N and Cl with means and standard deviations of 10.8 ± 1.1 ppm and 32.9 ± 3.0 ppm. As discussed in the section on $N0_3$-N and Cl, for Mystery Cave, such elevated levels of NO_3-N and Cl suggest surface recharge from agricultural lands.

Third, it must be stressed that samples of all five types of water tested positive for atrazine at values >0.1 ppb. Atrazine is used widely in the Midwest and is ubiquitous in surface waters. Its presence in all types of cave water, including a stalactite drip sampled at low discharge (Iron Drips), and such isolated pools as Sugar Lake and the Tar Pits, testifies to a pervasive and widespread distribution in infiltrating waters that follow a variety of flow paths. Atrazine is not confined merely to the most open flow paths in the lower level streams.

Table 4.3 Atrazine Concentrations by Location and Date.

Atrazine

Sample Designator	Sample Location	Atrazine (ppb) Date 4/9/92	Date 8/16/92	Date 5/12/93
MC01	TL	0.5	0.5	0.4
MC02	FFP	<.1	0.2	-
MC03	FFD	<.1	0.3	<.1
MC04	EP	-	0.1	-
MC05	RC	-	0.1	-
MC06	WWD	<.1	0.1	0.2
MC08	BL	<.1	0.2	0.1
MC09	GG1	<.1	0.1	-
MC10	BLD	<.1	0.1	-
MC11	CL	-	0.3	-
MC13	TP	-	0.1	<.1
MC14	LPL	-	0.5	-
MC15	CLD	0.1	0.3	<.1
MC16	GG2	<.1	-	-
MC20	LL	-	0.4	-
MC21	SS	-	<.1	-
MC22	FRC	-	0.5	-
MC23	FFC	-	0.8	0.5
MC25	PO	-	-	<.1
MC26	DAB	-	-	<.1
MC29	SL	-	<.1	<.1
MC31	CB	-	*	-
MC32	BSS	-	0.1	-
MC33	ID	-	0.1	-
MC34	DJ1	-	0.2	-
MC38	TLS	-	-	0.4
MC39	MFD	-	-	0.1
MC40	PBF	-	-	<.1
SB01	SB	-	0.8	0.7

- not sampled
* suspected interference from paint on ceiling bar

Table 4.4 Atrazine Concentrations by Water Type.

Water type	Location	Season	Atrazine (ppb)
Streams			
	Rimstone Creek	Summer	0.1
	Lower Level Stream	Summer	0.4
	Formation Route Creek	Winter	0.5
	Flim Flam Creek	Summer	0.8
	Flim Flam Creek	Spring	0.5
	Root River	Summer	0.8
	Root River	Spring	0.7
Pools			
	Turquoise Lake	Winter	0.5
	Turquoise Lake	Summer	0.5
	Turquoise Lake	Spring	0.4
	Frozen Falls Pool	Winter	<.1
	Frozen Falls Pool	Summer	0.3
	Blue Lake	Summer	<.1
	Blue Lake	Winter	0.2
	Blue Lake	Spring	0.1
	Coon Lake	Summer	0.3
	Tar Pits	Summer	0.1
	Tar Pits	Spring	<.1
	Lily Pad Lake	Summer	0.5
	Sugar Lake	Summer	<.1
	Sugar Lake	Spring	<.1
	Dragons Jaw 1st Lake	Summer	0.2
Ceiling Drips and Waterfalls			
	Frozen Falls Drips	Winter	<.1
	Frozen Falls Drips	Summer	0.3
	Frozen Falls Drips	Spring	<.1
	Enigma Pit	Summer	0.1
	Wishing Well Drips	Winter	<.1
	Wishing Well Drips	Summer	0.1
	Wishing Well Drips	Spring	0.2
	Sand Source Drips	Summer	<.1
	Drips Across Bridge	Spring	<0.1
Flowstone Drips			
	Blue Lake Drips	Winter	<.1
	Blue Lake Drips	Summer	0.1
	Coon Lake Drips	Winter	0.1
	Coon Lake Drips	Summer	0.3
	Coon Lake Drips	Spring	<.1
	Pipe Organ	Spring	<.1
	Beyond Sand Source	Summer	0.1
	Milky Flowstone Drips	Spring	0.1
	Big Flowstone Pool	Spring	<.1
Stalactite Drips			
	Garden of the Gods 1	Winter	<.1
	Garden of the Gods 1	Summer	0.1
	Garden of the Gods 2	Winter	<.1
	Drips Across Brideg	Spring	<.1
	Iron Drips	Summer	0.1

Winter sampling on 4/9/92
Summer sampling on 8/16/92
Spring sampling on 5/12/93

Table 4.5 Alachlor Concentrations by Location and Date.

Alachlor

Sample Designator	Sample Location	Alachlor (ppb) Date 8/16/92
MC01	TL	<.1
MC02	FFP	<.1
MC03	FFD	<.1
MC04	EP	<.1
MC05	RC	<.1
MC06	WWD	<.1
MC08	BL	<.1
MC09	GG1	<.1
MC10	BLD	<.1
MC11	CL	<.1
MC13	TP	<.1
MC14	LPL	1.1
MC15	CLD	<.1
MC20	LLS	0.2
MC21	SS	<.1
MC22	FRC	0.8
MC23	FFC	0.8
MC29	SL	<.1
MC31	CB	*
MC32	BSS	<.1
MC33	ID	0.2
MC34	DJ1	0.4
SB01	SB	0.8

* suspected interference from paint on ceiling bar

Table 4.6 Alachlor Concentrations by Water Type.

Water type	Location	Alachlor (ppb)
Streams		
	Rimstone Creek	<.1
	Lower Level Stream	0.2
	Formation Route Creek	0.8
	Flim Flam Creek	0.8
	Root River	0.8
Pools		
	Turquoise Lake	<.1
	Frozen Falls Pool	<.1
	Blue Lake	<.1
	Coon Lake	<.1
	Tar Pits	<.1
	Lily Pad Lake	1.1
	Sugar Lake	<.1
	Dragons Jaw 1st Lake	0.4
Ceiling Drips and Waterfalls		
	Frozen Falls Drips	<.1
	Enigma Pit	<.1
	Wishing Well Drips	<.1
	Sand Source Drips	<.1
Flowstone drips		
	Blue Lake Drips	<.1
	Coon Lake Drips	<.1
	Beyond Sand Source	<.1
Stalactite Drips		
	Garden of the Gods 1	<.1
	Iron Drips	0.2

Sampling was on 8/16/92

Table 4.7. Mean Atrazine Concentrations.

Means for Atrazine Samples*

Water Type	No. Samples	Mean (ppb)	Standard Deviation
Streams	7	0.5	0.3
Pools	10	0.3	0.2
Ceiling drips and waterfalls	4	0.2	0.1
Flowstone drips and flows	5	0.1	0.1
Stalactite drips	2	0.1	0.0
Totals	28	0.3	0.2

* For samples with atrazine > detetection limit of 0.1 ppb

Table 4.8. Atrazine Samples Below the 0.01 ppb Detection Limit.

Atrazine Samples Below the O.1 ppb Detection Limit

Water Type	**No. of Samples**	**No. of samples with < 0.1 ppb Atrazine**	**% Below Detection Limit**
Streams	7	0	0
Pools	15	5	33.3
Ceiling drips and waterfalls	9	5	55.5
Flowstone drips and flows	9	4	44.4
Stalactite drips	5	3	60.0
Totals	45	17	37.8

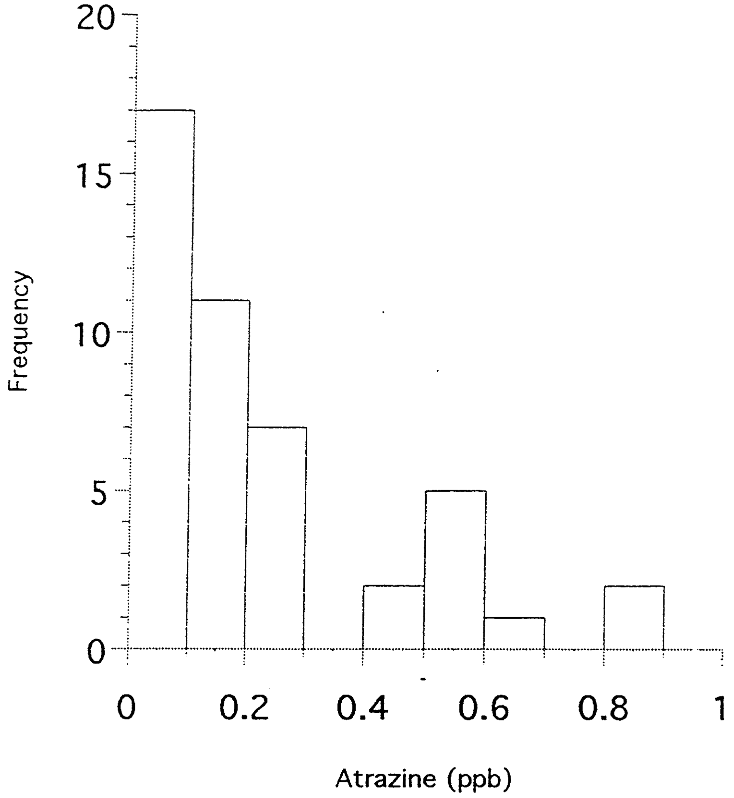


Figure 4.41. Histogram of atrazine concentrations for all waters.

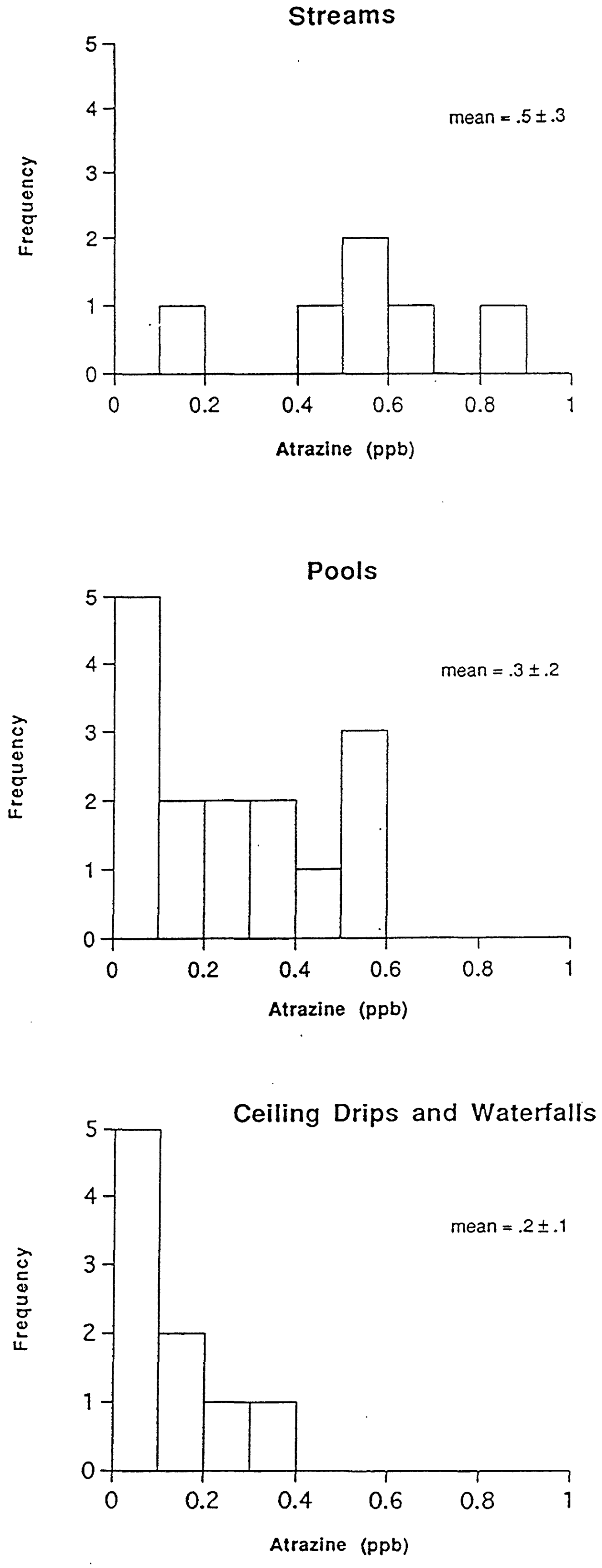


Figure 4.42. Histograms of atrazine concentrations is streams, pools, and ceiling drips and waterfalls.

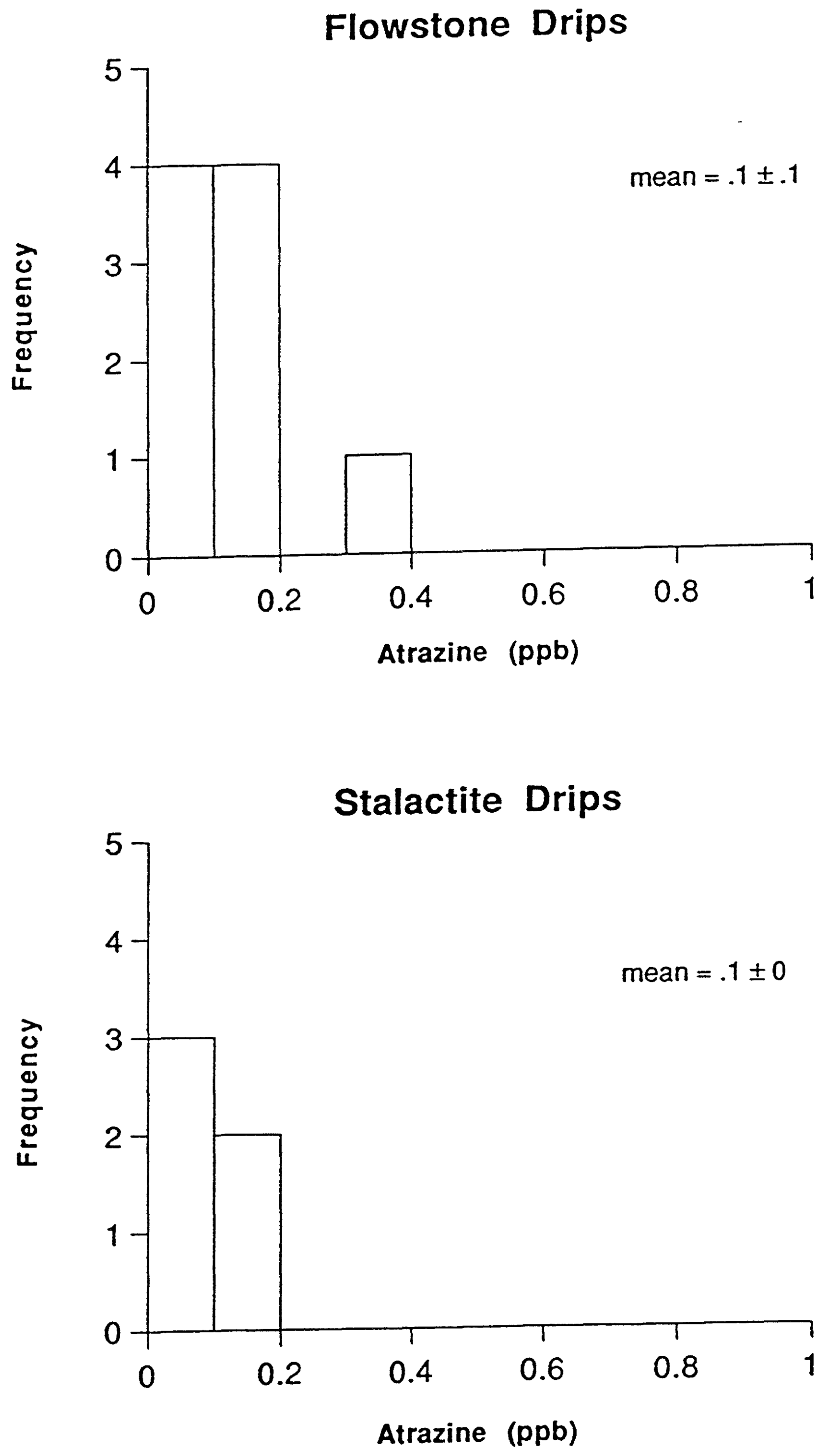


Figure 4.43. Histograms of atrazine in flowstone drips and stalactite drips.

Results of Alachlor Sampling

Alachlor was below the 2 ppb EPA Maximum contaminant level for drinking water at all 22 sampled sites (Table 4.5). The highest detected value was 1.1 ppb at Lily Pad Lake. Alachlor was below the 0.1 ppb detection limit for 68% (15 of 22) of the samples. Alachlor was detected in streams, pools, and stalactite drips (Table 4.6). As expected, alachlor was relatively high (mean = 0.65 ± 0.3 ppb) in four lower level streams. The Iron Drips stalactite had 0.2 ppb alachlor.

ZINC

Zinc and zinc-iron alloys are used in the process of galvanization. Galvanized structures were installed along the Mystery I tour route during the Mystery reconstruction project. Structures include floor grates, hand rails, and bridges. Floor grates and bridges are used to span fissures and low points in the passage floor. This allows pathways to have a low gradient and eliminates the use of stairways at many locations. Hand rails are used for safety on bridges and floor grates. Hand rails are also used as containment to separate visitors from delicate cave features.

In the humid environment of Mystery I, the galvanized steel is moistened by condensation water. At numerous locations, notably at Frozen Falls, but also at the Ceiling Joint drips, galvanized steel is wetted by dripping and splashing water. On rare occasions, when the Root River undergoes major floods, water rises from the lower level fissures and flows through parts of the tourist route. It can then wet the galvanized steel and deposit surface coatings of clays and other sediments. Although some drying occurs during winters, when the land surface is frozen and water flux through the cave is at a minimum, much of the cave never completely dries. Most galvanized steel bridges and railings are therefore in a perennially moist environment conducive to the corrosion of zinc.

The corrosion processes result in zinc compounds that can be removed by flowing water. The zinc coatings can be transferred from the railings and bridges directly onto visitor's hands, clothing, and feet. From feet, zinc can be transported throughout the cave on the concrete pathways. The walkways are occasionally washed to remove sediment deposited by turbid waters or to remove sediment carried in on visitor's feet. Zinc on walkways can be transmitted wherever washings are drained.

Within the first year of installation, brown spots on some galvanized steel were noted by Mystery Cave staff. The brown spots were interpreted by Zalk (written communication to DNR staff, 1992; see Appendix 5) as clay particles apparently deposited during construction activities. Katsoulis (written communication to DNR, 1992; see Appendix 5) interpreted rusty spots at one location (long beam of the Devil's Kitchen bridge) as being due to poor quality galvanization.

Mystery Cave and DNR staff expressed some concern about the leaching of zinc and its possible accumulation in cave waters or sediments. As with other heavy metals, zinc in high concentrations can be toxic to aquatic plants, invertebrates, and fish (Moore and Ramamoorthy, 1984). This section discusses zinc concentrations in several waters of Mystery I; the accumulation of zinc in sediments is beyond the scope of the study.

Galvanization and Zinc Surface Coatings

The process of galvanization uses zinc as a surface coating to protect underlying metals from corrosion. The zinc acts first as a physical barrier. More importantly, once the coating is breached by abrasion or deep scratches, zinc also serves as a sacrificial anode. As long as zinc is present, it is removed by corrosion in preference to the more reactive metal.

According to the American Galvanizers Association (AGA, 1989), the initial surface coating produced by hot dip galvanization consists of a series of layers of zinc and zinc-iron alloys. Pure zinc is at the surface and the percentage of iron increases from 6 to 10 to 25% with depth in coatings described by the AGA (1989).

Exposed to the environment, zinc oxidizes in air, forming a film of zinc oxide (AGA, 1989). In the presence of moisture, the zinc oxide reacts with water to form zinc hydroxide. The zinc hydroxide reacts with carbon dioxide to form a zinc carbonate layer, characterized by the AGA (1989, p. 2) as a "thin, compact and tightly adherent layer." The layer is whitish gray and conceals the zinc crystals below. The layer is considered to be relatively insoluble and weather-resistant.

Nonetheless, zinc is sufficiently soluble to be leached from galvanized steel and enter cave waters. In contact with liquids, zinc is amphoteric. It is relatively insoluble at low (< 6) and high (>12.5) pH. For the pH ranges normally encountered in karst waters (roughly 7.2-8.2), zinc tends to hydrolize, forming Zn(OH)2 at pH > 8.0 (Moore and Ramamoorthy, 1984).

Initial Sampling of Zinc

Several bridges are located near Frozen Falls, where drips splash onto the bridge from Frozen Falls Drips and from Drips Across Bridge before collecting in Frozen Falls Pool. To investigate the possibility that zinc from the bridges would affect water quality, water samples from drips at Frozen Falls and Frozen Falls Pool were collected and analyzed. To check background levels of zinc, samples were also collected at locations throughout Mystery Cave, in Mystery I and II, far from known locations of galvanized steel. Sampling began before installation of the bridges, in June, 1991, using the standard polyethylene cation bottles, and 6N HCl for sample preservation. Early analyses (e.g., August, 1991) showed higher levels of zinc in Frozen Falls Pool (.087 ppm) than in Frozen Falls Drips (.037 ppm), which supported the interpretation of leaching of zinc from the bridges. However, it was also possible that trace amounts of zinc could have been leached from the bottles, or could be derived from the preservation acid.

Therefore, on November 22, 1991, a comparison sampling test was run, using polyethylene cation and anion bottles, high-purity deionized water for blanks, and water collected at Frozen Falls Drips. For each type of bottle and type of water, one sample was acidified and one was not acidified.

The results of the comparison are shown in Table 4.9 and Figure 4.44. The deionized water blanks contained as much or more zinc as did the actual samples from Frozen Falls Drips. The acidified samples contained higher levels of zinc than did the unacidified samples. The lowest zinc contents were measured in the unacidified cave

Table 4.9.

Test of Sample Bottles and Acidification on Zinc Concentration

Sample ID	Run	Sample type	Bottle type	Preservative (6 N HCl)	Zn (ppm)
DIEX1Anion	1	DI water	Anion bottle	not acidified	0.013
DIEX1Anion	2	DI water	Anion bottle	not acidified	0.011
DIEX2Anion	1	DI water	Anion bottle	not acidified	0.021
DIEX2Anion	2	DI water	Anion bottle	not acidified	0.016
DIEX1Cation	1	DI water	Cation bottle	2 drops	0.021
DIEX1Cation	2	DI water	Cation bottle	2 drops	0.018
DIEX2Cation	1	DI water	Cation bottle	2 drops	0.032
DIEX2Cation	2	DI water	Cation bottle	2 drops	0.029
MC031191	1	FF drips	Anion bottle	not acidified	0.0003
MC031191	2	FF drips	Anion bottle	not acidified	0.00028
MC031191	1	FF drips	Cation bottle	2 drops	0.012
MC031191	2	FF drips	Cation bottle	2 drops	0.013

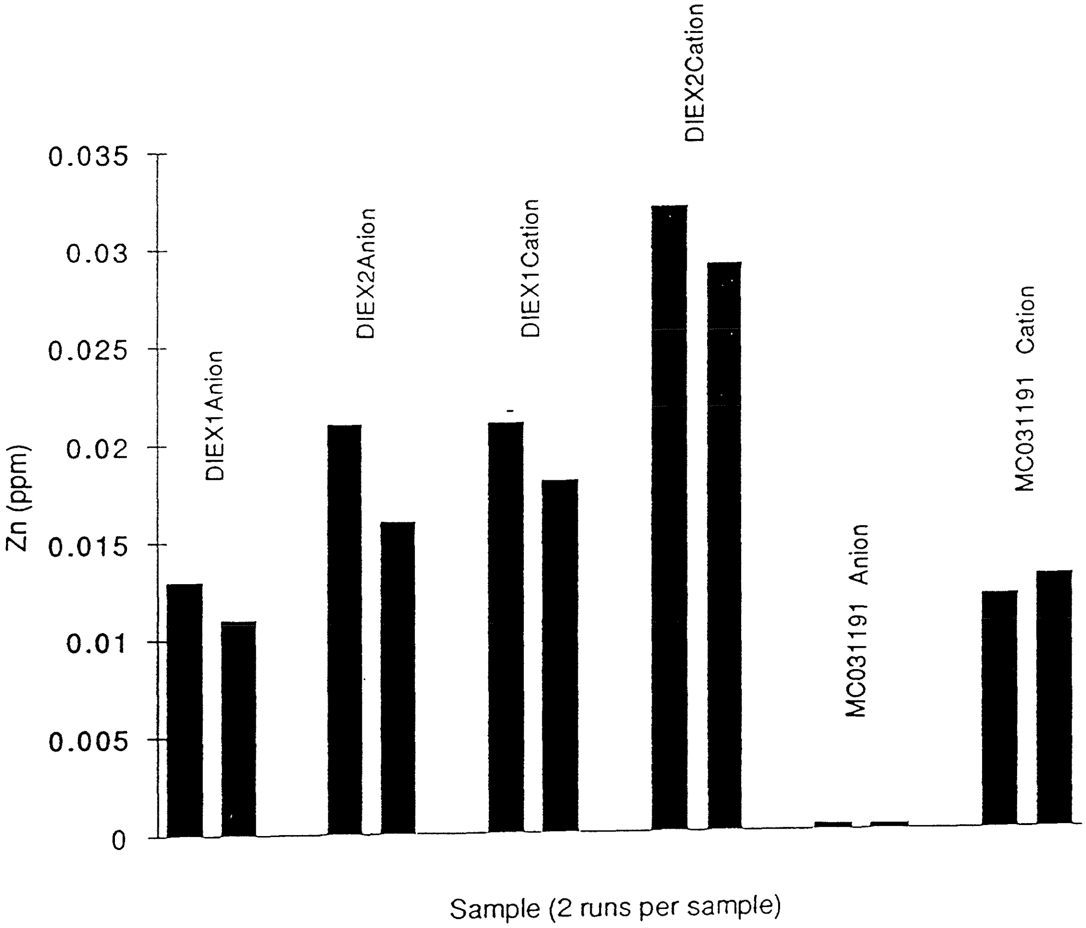


Figure 4.44. Comparisons of Zn concentrations in test.

water sample. We therefore concluded that (1) zinc present in the polyethylene bottles was leached from the bottles by deionized water. Also (2) it appeared possible that some zinc was present in the HCl. Therefore, we began collecting cation samples in teflon bottles and switched to high-purity nitric acid for sample preservation. The data obtained from the initial round of sampling (summer, 1991) is considered unreliable.

Sampling of Zinc in Teflon Bottles

Zinc was sampled at seven sites in Mystery I between November, 1991 and April, 1993. Thirty-three samples were collected from sites in the Frozen Falls area, mostly from Frozen Falls Drips and Frozen Falls Pool, and from Turquoise Lake (Table 4.10 and Figures 4.45).

The water in Frozen Falls Pool comes primarily from Frozen Falls Drips. Even at low flow in the winter, the flux from Frozen Falls Drips is greater than a few liters per hour. During storms, discharge at FFD can increase to perhaps ten liters per hour and the water may become turbid.

Zinc concentration in Frozen Falls Pool was almost always greater than that in Frozen Falls Drips (Figure 4.45); it averaged 0.023 ± .019 ppm (n=12 samples). Zinc in Frozen Falls Drips averaged 0.003 ± .003 ppm (n=13). The concentration of zinc in the pool is thus about 8 times higher than it is in the drips feeding it. Zinc in the pool is about 4 times higher than zinc in all other sampled waters (mean = 0.0053 ± .0079 ppm; n = 21) in Mystery I. Zinc thus is measurably being leached from the bridge above Frozen Falls Pool.

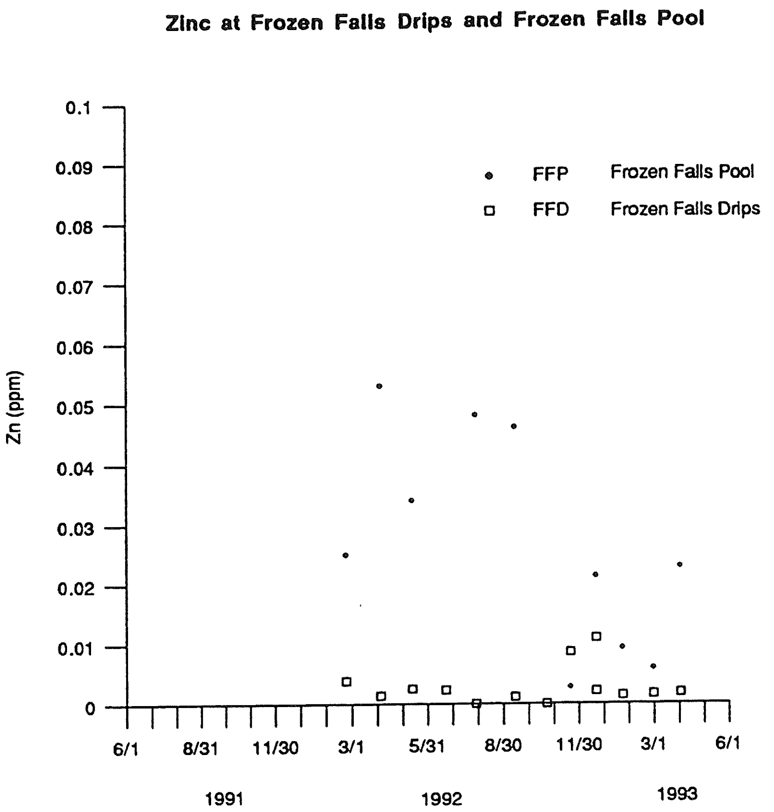
Frozen Falls Pool is also fed by drips and flows originating from Drips Across Bridge, the Pipe Organ, the Pipe Organ Pool, and the flow out the wall joint that feeds Across from Pipe Organ. These sources all exhibit low concentrations of zinc except for one sampling at Drips Across Bridge, when zinc was measured at .0360 ppm (Table 4.10). None of the waters except Drips Across Bridge appears to contact galvanized steel railings adjacent to the tourist trail. The single high zinc concentration at Drips Across Bridge was collected on a sampling date in which the drips were collected in a plastic bag-lined bucket at a level below the top rail, which allowed some splash from the rail to enter the container. Nearly all of the zinc above cave background levels in Frozen Falls Pool should originate in splash from Frozen Falls Drips and Drips Across Bridge. It is possible that some of the zinc contributing to background levels is anthropogenic. Zinc sulfate-bearing fertilizer is sometimes used as a starter for cultivation of corn in southeastern Minnesota.

The measured concentrations of zinc are not particularly high. and are unlikely to reach dangerous concentrations in pools or streams along or near the tourist trails. Although zinc appears on the list of contaminants subject to regulation under the Safe Drinking Water Act Amendments of 1986, apparently no Maximum contaminant level (MCL) or Secondary maximum contaminant level (SMCL) standards for drinking water have yet appeared. The World Health Organization has set an aesthetic water quality limit of 5 mg/l, and Canada uses a maximum acceptable concentration in drinking water of 5 mg/l (as reported in van der Leeded and others, 1990). The standards for protection of aquatic life in freshwater for total recoverable zinc set a limit of 180 microgram/l at any time, assuming a water hardness of 50 mg/l as CaCO3 (U.S. EPA, Water Quality Criteria, Federal Register, November 28, 1980).

Table 4.10.

Zinc Samples in Mystery Cave

Sample ID	Location	Zn	Date
MC011092	TL	0.0001	10/22/92
MC021291	FFP	0.0110	12/21/91
MC020292	FFP	0.0250	2/23/92
MC020492a	FFP	0.0530	4/4/92
MC020592	FFP	0.0340	5/13/92
MC020792	FFP	0.0480	7/29/92
MC020992	FFP	0.0460	9/14/92
MC021092	FFP	0.0000	10/22/92
MC021192	FFP	0.0027	11/20/92
MC021292	FFP	0.0213	12/21/92
MC020193	FFP	0.0093	1/22/93
MC020393	FFP	0.0059	3/1/93
MC020493	FFP	0.0227	4/3/93
MC031291	FFD	0.0110	12/21/91
MC030292	FFD	0.0039	2/23/92
MC030492a	FFD	0.0014	4/4/92
MC030592	FFD	0.0025	5/13/92
MC030692	FFD	0.0023	6/22/92
MC030792	FFD	0.0000	7/29/92
MC030992	FFD	0.0012	9/14/92
MC031092	FFD	0.0000	10/22/92
MC031192	FFD	0.0087	11/20/92
MC031292	FFD	0.0021	12/21/92
MC030193	FFD	0.0014	1/22/93
MC030393	FFD	0.0016	3/1/93
MC030493	FFD	0.0018	4/3/93
MC250692	PO	0.0071	6/22/92
MC251192	PO	0.0022	11/20/92
MC260692	DAB	0.0055	6/22/92
MC261192	DAB	0.0034	11/20/92
MC261292	DAB	0.0360	12/21/92
MC301192	APO	0.0126	11/20/92
MC351292	POP	0.0064	12/21/92



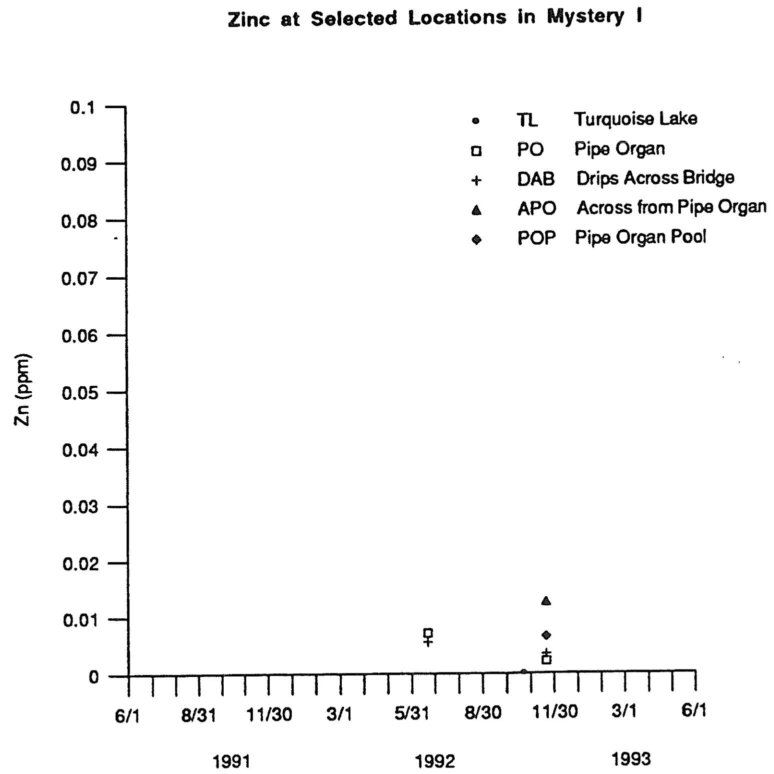


Figure 4.45. Zinc concentrations in Mystery I waters.

Effect of Flooding on Zinc Concentrations at Turquoise Lake

The flood on the Root River in late March, 1993 resulted in flooding in the main passage of Mystery I and filled Frozen Falls Pool with turbid water on March 31. Three days later, the April 3 sampling of zinc showed near-average values for Frozen Falls Pool (0.022 ppm) and Frozen Falls Drips (0.0018 ppm). It is unlikely that flooding did not alter the zinc chemistry of Frozen Falls Pool. The zinc concentrations of floodwaters derived from rain on snow should be very low (this is a reasonable, but undocumented assumption). A simple hypothesis that accounts for these observations is that after flooding ceased and water levels lowered, the flux of water into Frozen Falls Pool from Frozen Falls Drips and Drips Across Bridge was sufficiently high, and leaching rates sufficiently rapid to restore zince to "normal" bridge-influenced concentrations in the pool within three days.

The residence time for water in Frozen Falls Pool, and fluxes for its source waters, could be investigated. The volume of the pool and the water fluxes need to be determined. The residence time is calculated by dividing the pool volume by the total water flux. However, fluxes may be difficult to measure without structural modifications of the cave floor to concentate waters flowing from the Pipe Organ and from the flowstone at Across from Pipe Organ. Fluxes from Frozen Falls Drips and Drips Across Bridge could be measured with buckets suspended from bridge railings.

VOLATILE ORGANIC COMPOUNDS

An extensive list of contaminants in groundwater, with typical uses and sources, is provided by Fetter (1993, Table 1.2). Fetter's list groups contaminants under the following categories:

aromatic hydrocarbons
oxygenated hydrocarbons
hydrocarbons with specific elements
other hydrocarbons
metals and cations
nonmetals and anions
microorganisms
radionuclides

The first four categories are organic compounds. Specific contaminants within the list are used as, or are components of, such diverse substances as: pesticides, herbicides, insecticides, adhesives, solvents, degreasers, varnishes, paint removers, fumigants, wood preservatives, refrigerants, flame retardants, explosives, fuels, plastics, resins, detergents, pharmaceuticals, and dyestuffs.

Thus hundreds of organic compounds are potential contaminants in surface and ground waters. Some of these contaminants have relatively high vapor pressures and are known as volatile organic compounds (VOC's) or semi-volatile organic compounds.

In karst environments, VOC's from leaking underground storage tanks (LUST's) and from accidental spills from tank trucks, train cars, or pipelines, constitute major hazards. Where gasoline and other petroleum products leak or spill and then migrate into groundwater or into subsurface fissures, caves, or basements of houses and schools, there can be significant danger of fires or explosion (Crawford, 1984, 1986).

Other potential problems can derive from the presence of volatile organic substances in karst areas. Such substances can be harmful to subsurface aquatic or terrestrial organisms. They could pose significant health risks to the public, even where there was no danger of fire or explosion. Finally, because volatile organic substances are readily volatilized from contaminated water or soils, they can impart odors that would degrade the cave experience.

Potential Sources of Volatile Organic Compounds

In the Mystery Cave area, volatile organic compounds could derive from both surface and subsurface sources. On the surface, VOCs could be transported into the cave from the South Branch of the Root River. For example, VOCs could originate from industrial contamination at the Ironwood Sanitary Landfill, spills from farm equipment and storage tanks, spills from transportation accidents, and leakage from the oil pipeline upstream from Mystery Cave. On a more local scale, VOCs could reach the cave from parking lots at Mystery I or II, from agricultural spills, or from spills along the roads that pass over or near the cave.

In the subsurface, VOC's and related organic compounds could derive from sources over or within Mystery Cave itself. VOCs from septic systems or LUST's over the cave could be a problem. Construction materials or equipment from currentt and past commercializations are potential sources of VOCs. At Blue Lake in Mystery II, treated lumber pilings support a bridge installed during earlier commercialization activities. The pilings appear to consist of parts of two telephone or electric poles. Such poles are typically impregnated with creosote or other compounds to retard rotting. Inspection of the pilings at Blue Lake indicates that they are impregnated with a black substance with a creosote-like odor.

Among other potential sources of VOC's, there are several lighting systems. An old wiring system is largely removed from both Mystery I and II, but short sections of wire and insulators remain. It is conceivable that volatile organic compounds could be derived from more recently installed electrical equipment, for example from equipment at the lighting control system in the entrance area of Mystery I, or from recently installed wiring along commercial paths (and nearby paths not currently used) in Mystery I. In Mystery II, VOC's could be derived from electrical wiring in the entrance area, or from wiring strung through the cave as part of the groundwater or radon and meteorology parts of the LCMR Mystery Cave Resources Evaluation. In the entrance area to Mystery II, there are several electrical junction boxes. One of these leads to a wooden housing with at least 60 hand lanterns. The lanterns are used for lantern tours. Between tours the lanterns are charged in place in the housing.

Volatile organic compounds can be mobilized directly into the air from sources and be removed by circulating air. If concentrations are sufficiently high, even standing water containing VOC's can be expected to support a considerable flux into the vapor phase. Yet greater fluxes would be expected from water splashing, dripping, or otherwise moving in a turbulent flow regime.

Screening for Volatile Organic Compounds

To screen for volatile organic compounds, five sample sites were chosen in consultation with DNR staff. The sites include the South Branch of the Root River, Turquoise Lake, Flim Flam Creek, Blue Lake, and Coon Lake Drips.

Sample sites were chosen to cover a few of the most probable sources of volatile organic compounds, assuming they were present. For example, were volatile organic compounds escaping from the Ironwood Landfill into the South Branch of the Root River, then they might be detected in the Root River at Mystery I, or in Flim Flam Creek in Mystery II. Because of the proximity of Turquoise Lake to the Root River at Mystery I, it is possible, but unlikely, that volatile organic compounds might be detected at Turquoise Lake. (It is unlikely because the water at Turquoise Lake is chemically dissimilar to that of the Root River and has a different source area; water from the Root River apparently gets into Turquoise Lake only during major floods.) Were volatile organic compounds present at any of these three locations, their concentrations would depend on such factors as (1) their concentrations in the leachate, (2) the amount of dilution between the source and the sampling site, and (3) the efficacy of volalitization, degradation, or sorption processes, which would vary with the specific compound.

Were volatile organic compounds escaping from the impregnated pilings at Blue Lake, they would be expected in the water of Blue Lake itself.

Samples were collected on May 12, 1993, and analyzed by Twin City Testing Corporation for Volatile Organic Compounds according to Minnesota Department of Health(MNDH) Method 465C. This method tests for 49 compounds. All five sampling sites tested below detection limits for all 49 compounds. The list of compounds appears in Appendix 5.

Several cautions are in order. First, this sampling represents only one date at a time of high water levels present throughout an unusually wet period that began in late winter. Were volatile organic compounds escaping from the Ironwood Landfill, sustained high water levels might not represent the best circumstances to detect them. They might be flushed from that site in quantities detectable in the Root River or at Flim Flam Creek only at times of high flow following protracted dry spells.

We must stress, however, that we did not expect to see detectable concentrations of volatile organic compounds derived from the Ironwood Landfill at either site. The straight-line distance between the landfill and the cave is over 3 miles and the distance along the river is nearly 5 miles. It would probably require very large concentrations of volatile organic compounds at the landfill and significant flushing to see detectable concentrations at Mystery Cave, especially in Flim Flam Creek. It is probable, that had volatile organics been detected, that they would have come from some other, closer source, such as a farm or road spill.

A resampling for these three sites cannot be recommended. Further, we doubt that periodic (e.g., quarterly) sampling on the Root River at Mystery I would be a cost-effective means for the detection of volatile organic compounds from the Ironwood Landfill. Testing for volatile organic compounds is expensive, and cannot be recommended as a blind screening. One really ought to have a clear set of target chemicals. Some of the volatile organic and semi-volatile organic compounds in particular are very hard and expensive to detect and accurately quantify at low levels, given current technology.

A careful resampling for creosote derivatives, or other organic compounds used in treating lumber, might result in measured concentrations above detection limits at Blue Lake. The MNDH Method 465C for Volatile Organic Compounds is not the most sensitive or accurate method for detecting and quantifying creosote derivatives: apparently, the compounds of interest are best detected with a modified method.

Any VOC contamination at the cave from the river is likely to be a transient event. A possible precaution that could be taken would be to have the guides check for evidence of floating organics on the river before taking tours into the cave. Any unusual odors---for example, odors resembling gasoline or other petroleum products---would signal a need to cancel tours. It would be useful to have empty, clean VOC sampling bottles on reserve if a transient event were to develop.

Recommendation for Replacement of Wood Pilings at Blue Lake

As previously noted, treated lumber is included in the bridge materials at Blue Lake. At times of high water level, a strong, organic smell associated with that of creosote is present in the vicinity of Blue Lake (particularly to the east toward Diamond Caverns). The smell seems most strong after Blue Lake has rapidly risen from low to high levels, inundating more of the bridge pilings. At intermediate and high water levels, there has at times been a scum present on the surface of the water. This scum may be derived in part from the pilings. It does not resemble the calcite rafts that occasionally form on the water surface.

When the water level rises above about 1233 ft in Blue Lake (Palmer elevations from leveling in April, 1993) a set of springs known as Blue Lake Springs appears in the tourist trail to the east of Blue Lake (See Chapter 7). That water has a chemistry similar to that of Blue Lake, and is believed to come directly from Blue Lake via seepage and conduit flow (between the breakdown blocks and finer sediment used in trail construction). Blue Lake water thus exits the springs and then flows about 100 ft before disappearing into holes in the floor along the north wall of the passage. The water spreads out over nearly the entire width of the tourist trail near the springs, then concentrates within a side ditch downstream. This pattern of flow maximizes contact with air, and undoubtedly contributes to the stronger creosote-like smell toward Diamond Caverns.

The odor is objectionable to some people. It can be expected to be strong as far as Diamond Caverns any time Blue Lake Springs is active. Blue Lake Springs can be expected to be active roughly from late March or early April through May in most years. In wet years, such as in 1993, the springs may be active well into the summer tourist season.

We recommend the removal of the impregnated pilings. This should alleviate the odor, although it may not entirely rectify the problem. At the same time it may be necessary to replace the entire bridge. The construction of the bridge is such that removal of the pilings will be possible only during low water levels. Based on observations of water level during this study, it will probably be possible to remove the pilings during the late summer of dry years and the fall or early winter of most years. It should be noted that a persistent rain of several day's duration in

November, 1992, resulted in a partial filling of Blue Lake to a depth of several feet (see Chapter 7).

CHEMICAL WATER TYPES IN MYSTERY CAVE

The physical water types defined at the start of this chapter were convenient ways of organizing our sampling but do not correspond to chemically distinct groups. This is not surprising. The geochemical processing of water is complex as it moves through a series of chemical environments: It falls from the sky, makes its way underground, moves through the cave in the vadose zone, and then moves through a phreatic (or saturated) zone to a spring, evolving in composition throughout its transit. The geochemical processing is effected by many processes. These include: precipitation and condensation; freezing and melting; evaporation and evapotranspiration; dissolution and precipitation; redox reactions; ion exchange reactions; and the mixing of waters from different flow paths of varying chemical composition.

More or less distinct groupings are evident in the data, however. The waters of certain areas of the cave are different from those in other parts of the cave. These groupings are based on the chemical contents, physical properties, and hydrogeologic settings of the water. Given the present state of our knowledge, we make no attempt to rigidly define these groups. It is not obvious that we have yet observed their complete range of properties. Nevertheless, as a start, we identify four main water types and provide a brief account of our reasons for distinguishing them:

(1) water from the South Branch of the Root River,
(2) rapid surface recharge (exclusive of that from the Root River),
(3) diffuse flow into Mystery II and III, and
(4) diffuse flow into Mystery I.

Water from the South Branch of the Root River

These waters infiltrate from the South Branch, flow through the lower-level streams, and then resurge at Crayfish, Seven, and Saxifrage springs. Perhaps the most significant characteristic of this subsurface river water is its variability. The physical and chemical properties of the water vary on time scales down to at least minutes. The range of variability, particularly of the physical parameters like temperature, is much greater than seen in the other waters. This variability proves to be a distinctive marker. A look at the temperature record in Flim Flam Creek or Saxifrage Springs quickly convinces one that the water comes primarily from the South Branch. Conversely, the lack of short-term variability in the water quality at Turquoise Lake is evidence of the absence of any direct connection with the river.

The subsurface river waters are fundamentally moving horizontally through the cave. Only at times of extreme low flow during dry periods or extended cold periods during the winter (when the river is frozen at the top, and stage abruptly falls in cave streams, as at FFC), do lower-level stream waters exhibit a chemistry that marks them as having a major component admixed from the other chemical water types. Volumetrically, the subsurface waters of the South Branch dominate the water budget of the cave under normal conditions. During floods they overwhelm the water budget.

We sampled the Root River only a few times during this study. However, as a first approximation, we may take the major ion chemistry of Flim Flam Creek as representative of the major ion chemistry of the Root River and expect major differences between them only a small amount of the time. Thus we may state that the waters of the South Branch are Ca-Mg-HCO_3 waters. They include variable but significant amounts of Cl , NO_3 , and SO_4, much of these being of agricultural origin. They contain a variable load of other environmental components, including fecal coliform bacteria, pesticides, and herbicides.

River waters ultimately originate as precipitation. However, the water in the South Branch of the Root River---as it flows past Mystery I---does not resemble precipitation. Much of the water has already spent a significant amount of time underground. Much of the flow is derived from shallow groundwater discharge via springs upstream from the cave, and from shallow through-flows and interflows in soil or loess (some of which has been enhanced by tile drainage). The chemical properties of the river water near Mystery I are largely preconditioned by these base-flow components and integrate natural and anthropogenic conditions upstream of the cave. Only in the largest recharge events following major storms and major snow melts does direct surface runoff become the major part of the South Branch's flow. Surface runoff from precipitation or snow melt is an intermittent, second-order effect that tends to dilute the base-flow components, but that runoff itself can at times carry a significant solute or organic load into the river.

The magnitude of the base-flow components is best seen in the coldest part of the winter. Then the river is frozen over. Melting is nonexistent due to temperatures well below freezing for extended periods. All other components are minimal because the ground is frozen and there is an extensive snow and ice cover. At such times, there is still flow in the Root River beneath the ice. There is still flow in the lower-level streams of Mystery Cave. Water temperature in the Root River is less than 1°C and at Flim Flam Creek is as low as 1.4°C, conclusively showing that the primary component of flow at Flim Flam Creek is river water. However, solute concentrations and conductivity (which is in the range of 400-550 µS/cm at 25°C) are also similar, and too high to be derived primarily from waters melting at the base of the snow and ice cover---waters that would not normally be noticed as surface runoff from melting.

As shown by continuous monitoring of water temperature and conductivity from July, 1993-December, 1994, the waters of the Root River exhibit a daily (up to 4 or 5°C) temperature cycle in the warmer months. They also exhibit a seasonal temperature cycle (from less than 1°C in winter to about 25°C in the summer). They posess a seasonal weak conductivity signal apparently tied to daily biological activity, but this is seen only during the warmer months of June to August and is easily masked by precipitation events or a prolonged cloudy spell. The waters of the Root River respond to rainfall and snow melt with a significant drop in solute load but can become very turbid during these events. During part of the the spring melt off, the waters of the Root River contain an extensive organic signal, in which black and brown organics (probably derived from decaying leaves and other vegetative matter that accumulated over the fall and winter) are flushed through the surface system.

Rapid Recharge to Near-Surface Cave Sites

There are a number of places where relatively unaltered precipitation moves rapidly into Mystery Cave. This water is almost always mixed with other water types by the time is can be sampled in the cave, where it so far has been seen only at near-surface sampling sites near entrances. Waters at these sampling points (1) can respond to precipitation in minutes with a rise in discharge if the land surface is already primed for runoff; (2) may become turbid with sediments and organics derived from surface materials on the forested hillslopes; and (3) vary in temperature. The temperature either increases or decreases depending on the temperature of the recharge and its volume relative to the waters with which it mixes. A rapid surface-recharge component is sometimes distinguishable at the low-concentration end of the mixing lines observed on chemical plots. This water carries soluble components from precipitation (essentially negligible concentrations of major ions in the absence of industrial contaminants) and very quickly picks up additional dissolved components from admixed vadose waters. Admixed vadose waters include waters displaced from soil, loess, and fractured bedrock.

Rapid surface recharge is the only significant unsaturated water that we observe in the cave. It is seen both in the cave and in the river water following major recharge events. In the cave we have thus far seen it mixed with base-flow components of the waters of waterfalls and ceiling drips, flowstone flows, and cave streams.

Diffuse Flow into Most of Mystery II and III

The waters from stalactite drips, ceiling drips and waterfalls, flowstone flows, pools, and upper-level streams in most of the sampled parts of Mystery II and III are derived primarily from a diffuse flow system that regulates their flow rates. They spent a significant amount of time in the vadose (or unsaturated) zone above the cave. They are Ca-Mg-HCO_3 solutions that are supersaturated with respect to calcite, aragonite, and dolomite when sampled in the cave. They may be close to saturation within their flow paths before reaching the cave and then attain saturation or supersaturation primarily from carbon dioxide degassing in or above the cave. These waters are the most commonly seen waters in the upper levels of the cave. Because they are supersaturated, they tend to precipitate calcite or aragonite speleothems and thus continue to evolve geochemically. They typically have a near-constant temperature and a relatively restricted range of chemical compositions at specific sampling points. However, their composition varies somewhat across the cave. Such flows carry a range of values of anthropogenic chloride and nitrate, depending on the land use in their recharge area and processes (such as denitrification or mixing) that alter concentrations along the flow path. In some samples, the anthropogenic component is low; in others it is more significant. At some sites there is an additional significant sulfate component.

Diffuse Flow into Mystery I

Some of the diffuse flows into Mystery I are chemically distinct from the flows into the rest of the cave. The diffuse flows have higher levels of calcium, magnesium, bicarbonate, chloride and nitrate than the rest of the cave waters. This is seen most clearly at Turquoise Lake and, at low flow, at Frozen Falls. These Turquoise Lake and low-flow Frozen Falls samples form a distinct grouping in many of the figures in this chapter.

This contrast between the Mystery I diffuse recharge and the rest of the cave's diffuse recharge is one of the more unexpected findings of this project. The cause of this difference is not known. Two observations may or may not be relevant. The first observation concerns anthropogenic activity. Three active homesteads including a major farmstead are in the interpreted potential recharge area for upper level flows in Mystery I (Figure 3.4). No active homesteads directly lie over passages in Mystery II and III, or are above known and delimited recharge areas. There are active drain fields and manure-handling operations over Mystery I's recharge area. There are no active drain fields over Mystery II and III's recharge areas. The second point is more of a speculation. Mystery Cave lies, perhaps not coincidentally, right under the complex border between the thick loess and thin loess. Detailed mapping of the loess distribution above the cave might reveal some interesting correlations with the water chemistry.

CONCLUSION

The chemistry of Mystery Cave is dominated by the reactions between water, carbon dioxide, and the carbonate minerals calcite and dolomite. Although the cave is developed in limestone and dolomite bedrock, much of the carbonate dissolution apparently occurs in the overlying loess and soil. These contain a significant carbonate component, primarily dolomite. However, the fractured bedrock above the cave is also carbonate, so it is difficult to assess the relative importance of dissolution within each material. Nonetheless, the overall result is clear: The waters of Mystery Cave are calcium-magnesium-bicarbonate solutions. Many of their characteristics (state of saturation, P_{CO_2}, and most of the environmental chemistry) are determined above the cave, before the waters reach it.

Anthropogenically induced ion-exchange processes play a role in the carbonate chemistry. Potassium from KCl-bearing fertilizer is exchanged for calcium and magnesium in the soil and loess. Nitrogen fertilizer is applied to the overlying fields in a variety of chemical forms; it also plays a role, because its net effect (following a number of chemical interactions) is to contribute the equivalent of a calcium and magnesium nitrate to the cave waters. Both anthropogenically-induced processes increase the calcium and magnesium concentrations beyond what would be produced by dissolution of calcite and dolomite. Both processes occur where water has recharged through agricultural lands. The effects are most obvious after primary recharge events, in which subsurface solute concentrations (including Cl) increase, as stored waters are flushed from the soil, loess, and fractured bedrock above the cave, mixing with variable but unknown amounts of new event water.

Oxidation and reduction reactions play a role in the hydrogeochemistry. The nitrate component is fed by the oxidation of organic nitrogen and ammonium- and ammonia-nitrogen. The oxidation of sulfides in the bedrock provides a component of sulfate in cave waters.

The waters of Mystery Cave receive anthropogenic inputs of sulfate (from fertilizers), coliform bacteria (from animal and human wastes) and pesticides (from agricultural activities), in addition to the calcium, magnesium, chloride, and nitrate components noted above. Within the cave, there are two additional anthropogenic influences on water quality. Zinc is being leached at low rates from recently-installed galvanized steel bridges. Volatile organic compounds are being leached from creosote-impregnated lumber at a bridge installed during an earlier phase of commercialization.

CHAPTER 5

WATERS AT SELECTED SITES IN MYSTERY CAVE

This chapter synthesizes hydrologic and chemical observations made at selected sites in Mystery Cave. The sites include Turquoise Lake, various sites in the Frozen Falls area, the Lower Level Stream, Wishing Well Drips, Rimstone Creek, and the drip sites at the Garden of the Gods. Many of these sites were sampled periodically for chemical parameters throughout the project. That sampling provided sufficient data to form a picture of general aspects of each site's hydrogeochemical behavior. However, none of the sites was instrumented continuously for discharge, conductivity, or water temperature. Also, many of the chemical data were collected before installation of the Weather Station on the Root River in June, 1992. This severely limits the number of recharge events that can be interpreted. Some supplementary precipitation data (see Chapter 6) are available for Spring Valley, which is about 6 miles north-northwest of Mystery Cave. Inclusion of these data allow us to make tentative interpretations of several events recorded in the earlier (summer 1991 to spring, 1992) parts of time series plots of chemical parameters. Because of the synthetic nature of these discussions, there is much overlap with material covered elsewhere within this report. To minimize repetition, we therefore reference other sections as needed.

TURQUOISE LAKE

Plots for the field parameters, cations, anions, saturation indices, and P_{CO_2} vs saturation indices at Turquoise Lake appear in Figures 5.1-5.5.

Turquoise Lake (TL) is in Mystery I on the commercial tour route, in a side alcove about 30 ft south of the main passage (Figure 2.1). The pool is about 800 ft west of the South Branch of the Root River.

In its present configuration, Turquoise Lake is an artificial pool. Its depth is controlled by a concrete dam. During the 1991-1992 recommercialization project (when the first ten periodic samplings were made) a pump was used to control water level and direct flow to a drain into floor joints. The pump turned on when the water rose above a stage of about 9 inches below the crest of the dam. The pump was several feet from the sampling site. It probably had a negligible influence on water chemistry.

Turquoise Lake is fed by a free-surface stream, Turquoise Lake Source, with a normal flow of a few liters per minute. The stream enters via a joint, traverses a small room behind the pool, and then spreads out over flowstone. From the flowstone, the water drips and flows into the back of Turquoise Lake. Sources of the stream have not been determined by dye tracing and it would be difficult to do so due

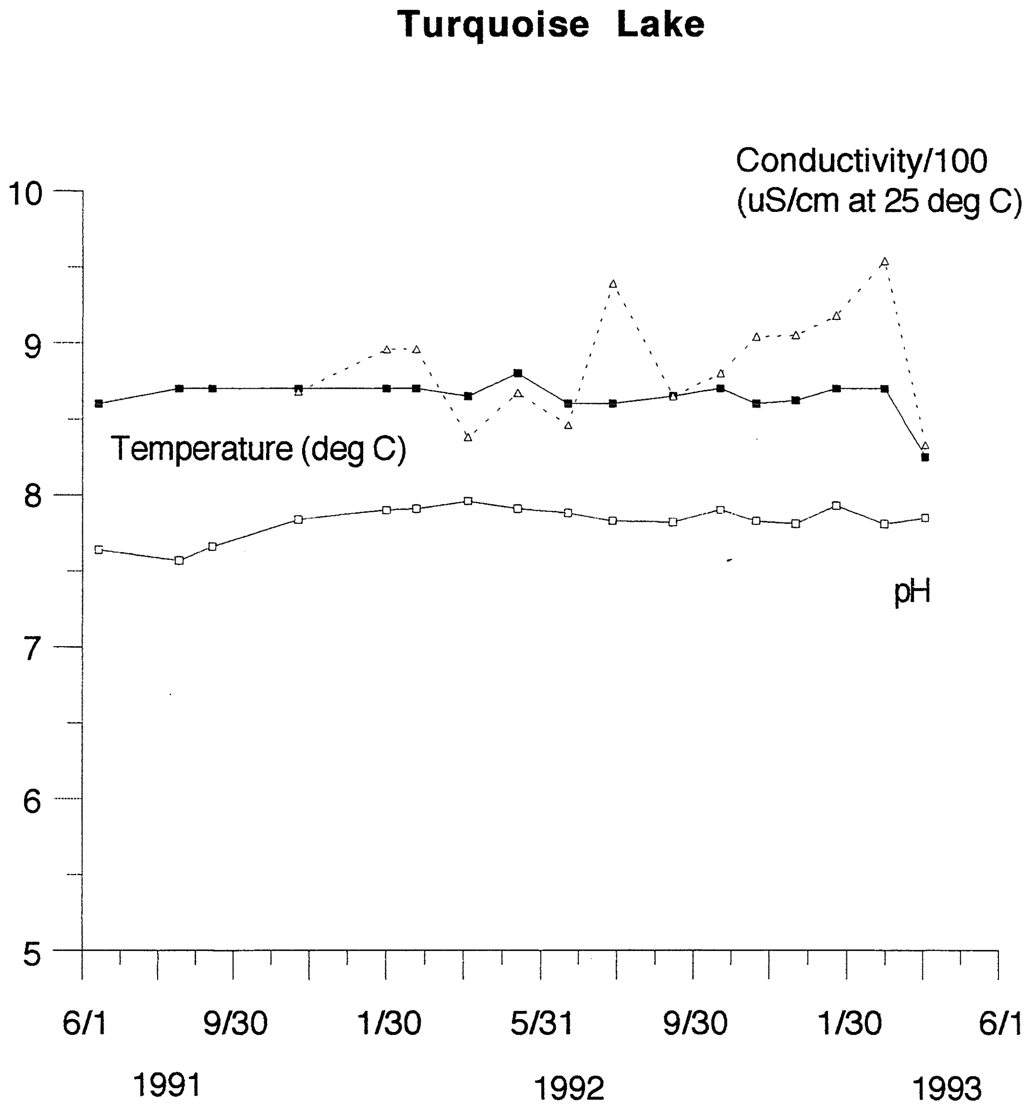


Figure 5.1. Field Parameters at Turquoise Lake, 1991-1993.

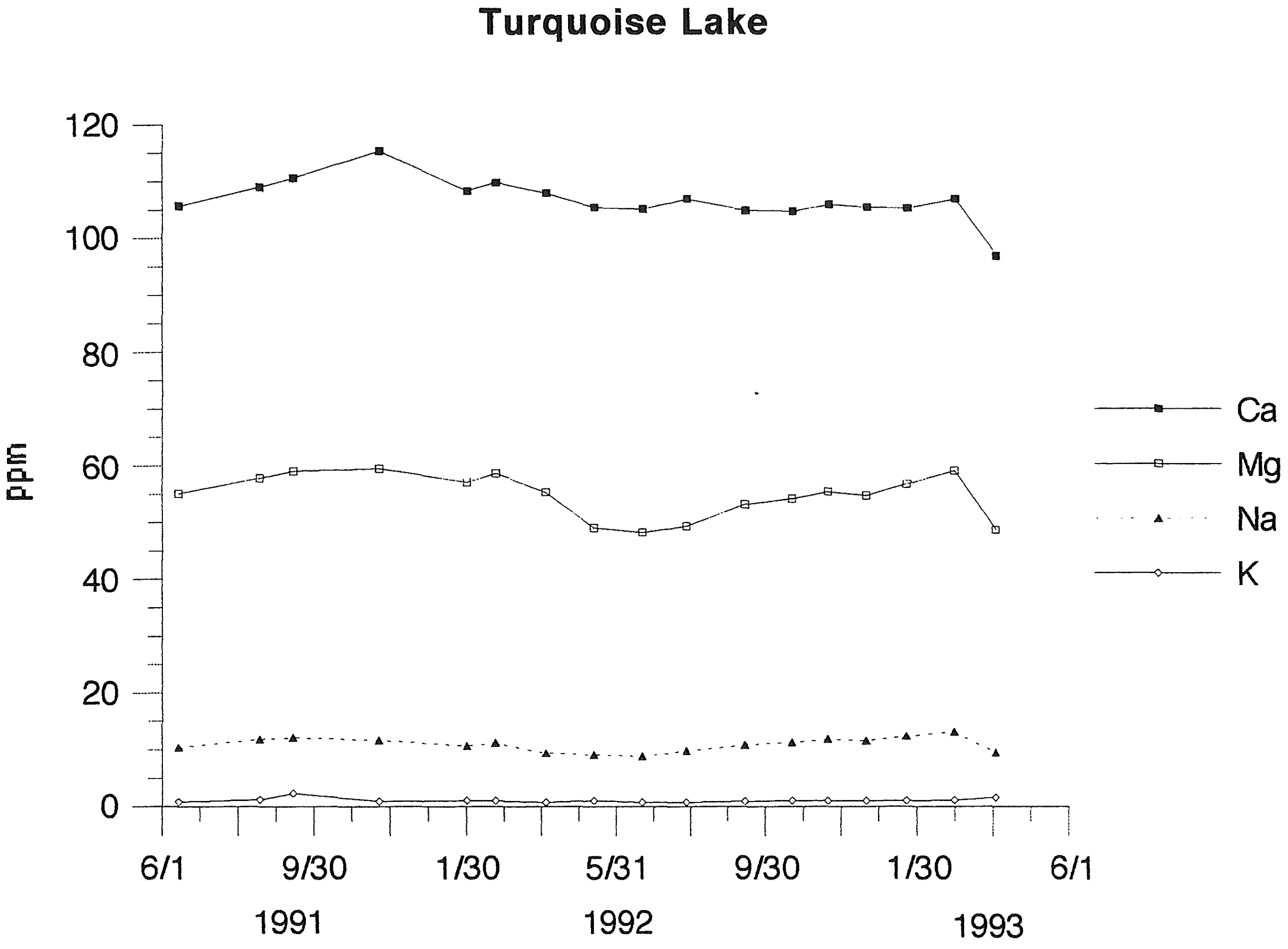


Figure 5.2 Cations at Turquoise Lake, 1991-1993.

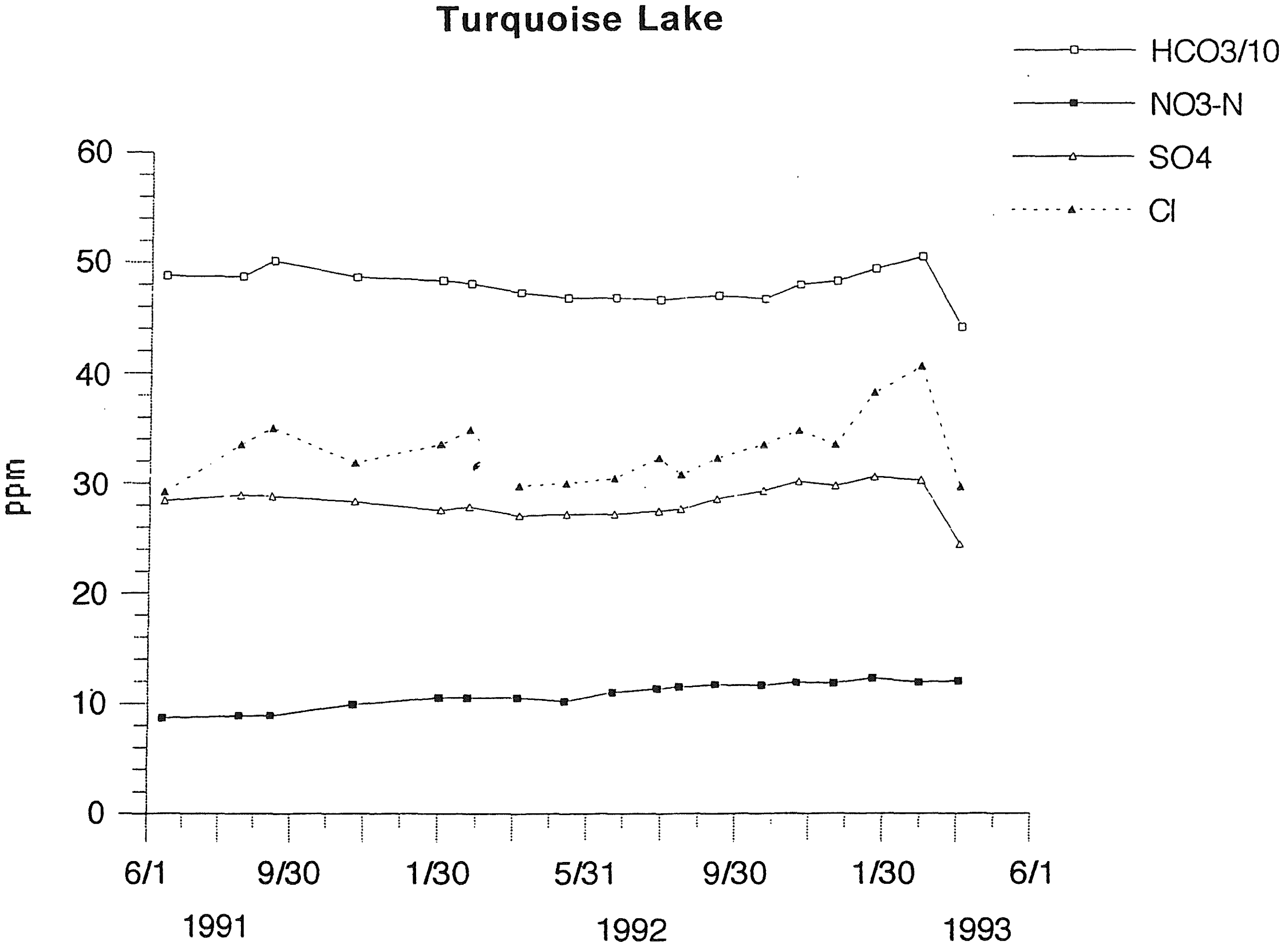


Figure 5.3. Anions at Turquoise Lake, 1991-1993.

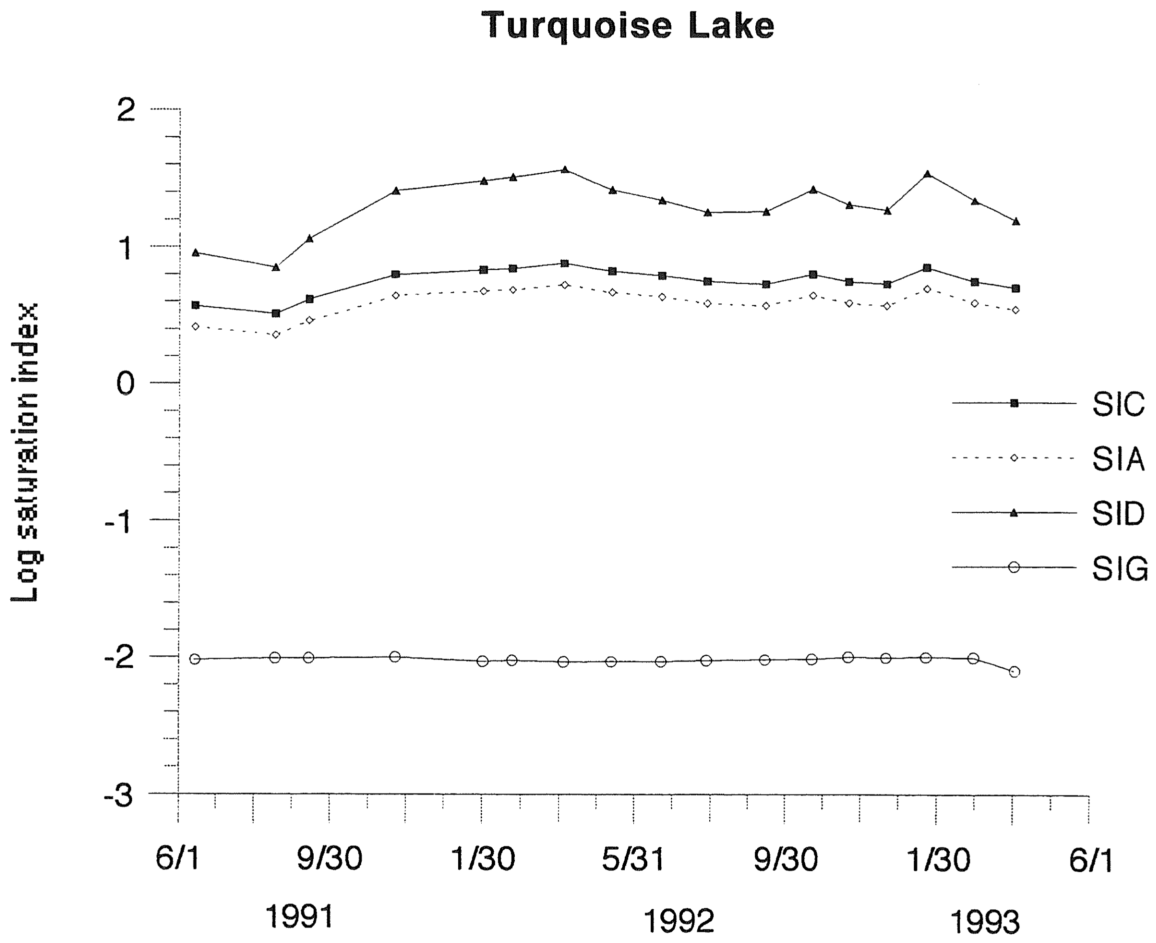


Figure 5.4. Saturation indices at Turquoise Lake, 1991-1993.

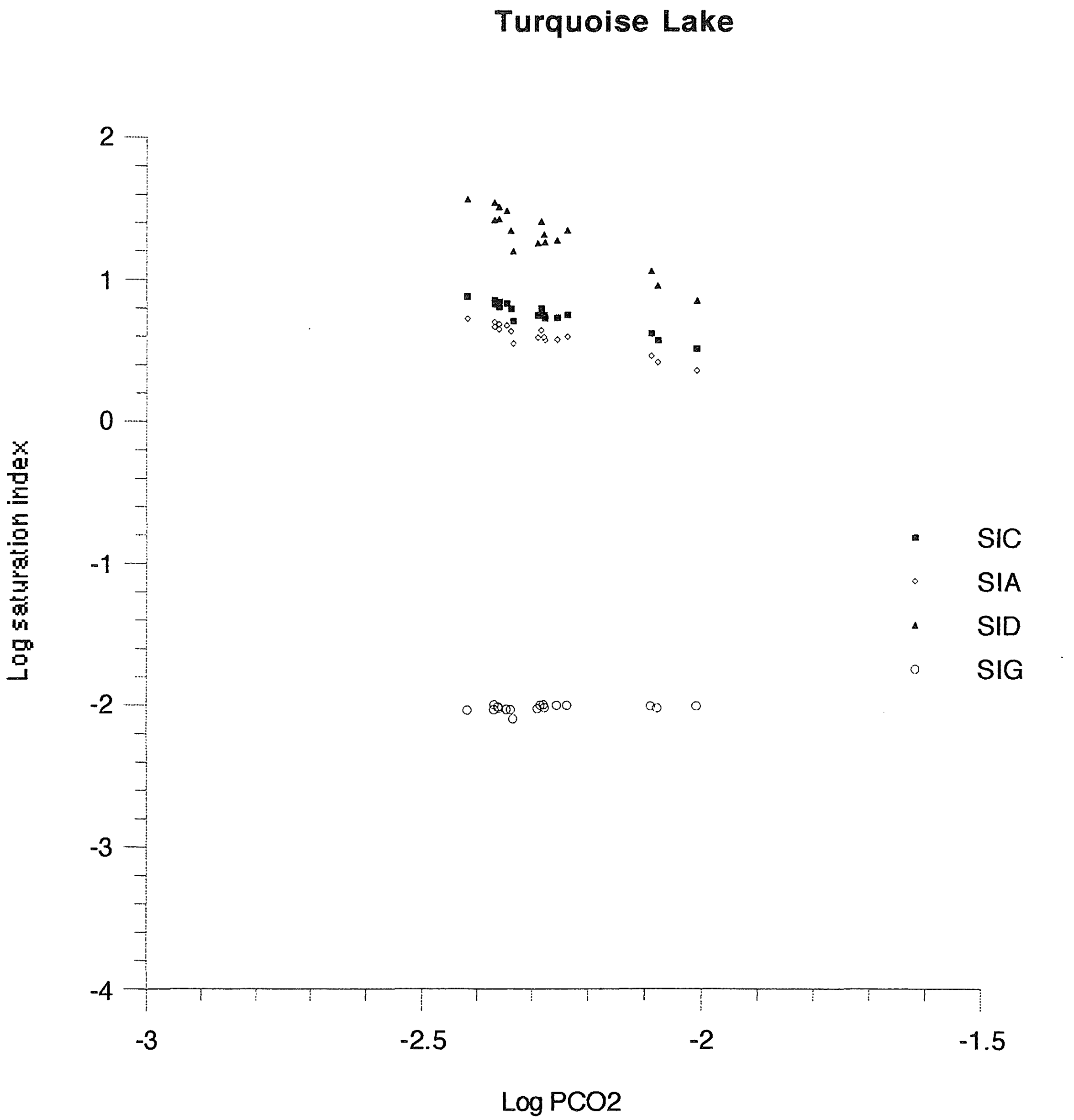


Figure 5.5. Log P_{CO_2} vs log saturation index for Turquoise Lake.

to the lack of recognizable discrete input points within its postulated recharge area. That recharge area is shown in Figure 3.4 and is discussed in Chapter 3.

In the past, Turquoise Lake was a natural pool, as shown by abundant subaqueous speleothems and folia. Folia at several levels on the walls extend past the dam toward the main passage. Folia are rare calcite speleothems that form along the water's surface at cave walls; they record extended periods of still stands of the water level. At the time speleothems were deposited, the water must have been at or above saturation for calcite. Such conditions continue to exist in the current Turquoise Lake. All 17 samples collected between June, 1991 and April, 1993 were supersaturated with respect to calcite, aragonite, and dolomite (Figure 5.4).

The water at Turquoise Lake is clear but has a distinct bluish cast---hence its name. The color is caused by Rayleigh scattering by calcite molecules ($CaCO_3{}^o$) and by complexes of up to a few thousand molecules in the water. Molecules and particles much smaller than the wavelength of light selectively scatter the blue wavelengths relative to the red wavelengths. When a light beam shines into the water the calcite molecules selectively scatter the blue light toward the observer. (This is the same process that causes the sky to appear blue, except in the sky nitrogen and oxygen molecules and very small aerosols produce the scattering. When you look directly at the light source, say a rising or setting sun, it appears reddish due to the removal by scattering of part of the blue light.) During this study, the water at Turquoise Lake became turbid only once. The silt and clay particles in the muddy water are much too large to cause Rayleigh scattering and this turbidity causes the water to appear gray or the color of the particles. The major flood on the Root River on March 30, 1993 back flooded Turquoise Lake with muddy water from the surface.

A discussion in Chapter 4 (see Estimation of Deep Cave Temperature) concluded that water temperature at Blue Lake was nearly constant at about 8.67 ± 0.06°C, except for the influence of the March flood. This rules out the Root River as a direct primary source for the water of Turquoise Lake. Water temperature in the Root River varies up to about 4°C on a daily basis in the summer, and ranges from near 1°C in the winter to over 25°C in the summer. The Root River is sufficiently close, that were it a primary source, we would have detected large seasonal temperature variations (such as were detected in the nearby Lower Level Stream, which does receive water from the Root River; see below), and probably would have detected smaller daily temperature variations as well.

The Root River introduced cold water (probably as cold as only a few degrees Celsius) from rain on snow and snow melt during the March 30, 1993 flood. Water temperature four days later on April 3, 1993 was colder than normal, at 8.25°C. Evidently, the flux of water at about 8.7°C into Turquoise Lake from its normal source (combined with heat transfer from bedrock at Turquoise Lake and the slightly warmer air above it) was nearly sufficient to return Turquoise Lake to its normal temperature over a four day period.

In all probability, the water in Turquoise Lake was completely flushed during the flood. We do not know whether any Root River floodwaters entered via the normal tributary. However, we do know that the water level from waters rising out of the lower-level fissures was sufficient to flow past the Turquoise Lake area in the main passage toward and past the Bomb Shelter. To flow past the Bomb Shelter, the water level at Turquoise Lake must have crested at least as high as a foot below the ceiling at Turquoise Lake. This is at least 2 ft above the height of the dam. At the time of the flood, a canoe and several planks were stored in the passage. The floodwaters transported the planks into Turquoise Lake, where they were observed floating on April 3, 1993.

During the flood, the water in Turquoise Lake was replaced with colder, more turbid, and more chemically dilute floodwaters derived from rain and snow melt. As the flood receded, the dam trapped floodwater (in addition to the planks and a considerable amount of silt). The trapped floodwater was then gradually replaced by influx from the Turquoise Lake feeder stream. Evidence for the initial floodwater replacement and the partial return to normal conditions can be seen in the sharp but limited decreases in conductivity, Ca, Mg, Na, HCO_3, SO_4, and Cl at the end of the time series plots (last data point on Figures 5.1-5.3 on April 3, 1993).

Throughout the study, concentrations of Cl and NO_3-N at Turquoise Lake were relatively high (29.2-40.5 ppm for Cl and 8.7-12.3 ppm for NO_3-N) compared to other cave waters. Chloride is probably derived largely from KCl-bearing fertilizers rather than from road salts or natural sources. Chloride has a spiky curve compared to the other anions. This response suggests intermittent mobilization of chloride, but a long lag time between recharge and the arrival at Turquoise Lake of a chemical signal can make this interpretation difficult to document. The signal is likely to be attenuated and spread out, because the water carrying it comes from a large, dispersed source area that takes a long time to drain.

As an example, we briefly consider the major recharge event of November 19-21, 1992, in which 2.18 in of rain fell at the Weather Station at Mystery I. (This event is explained in detail in Chapter 7, where the emphasis is on the long lag time of four days between the onset of precipitation and the arrival of water at Blue Lake.) Chloride was sampled at TL on 11/20/92, 12/21/92, 1/22/93, 3/1/93 and 4/3/93 (the last five data points on Figure 5.3). Chloride declined from 34.7 to 33.3 mg/l in the November to December samplings, then rose to 38.1 and 40.5 mg/l for the January and March, 1993 samplings. Much less precipitation fell in December and January (0.71 in and 0.80 in, respectively, at the Weather Station, but see Chapter 6) and much of that was in the form of ice and snow that probably did not lead to significant recharge. It is reasonable to interpret this part of the record as a long-term mobilization of chloride instigated primarily by the November recharge event. If this is true, then (for a storm of that magnitude and under the prevailing soil-moisture and other unknown boundary conditions) the lag time for water to arrive was at least as short as the period from November 20 to January 22, and at least as long as the period from November 20 to December 21.

Nitrate nitrogen has a more uniform curve with a slight but very consistent rise of more than 3 ppm during the study period. NO_3-N can be derived from a variety of anthropogenic and natural sources, including human and animal wastes, fertilizers, and nitrogen-fixing bacteria in the soil. Most sites in Mystery Cave show relatively uniform but lower levels of NO_3-N. Some sites show more variation, with peaks associated with recharge events. The remarkably constant but high NO_3-N suggests a relatively constant source of NO_3-N within the tributaries to Turquoise Lake. Both Cl and NO_3 are extremely mobile anions that should be readily flushed from surface stores during recharge events. If fertilizers were the direct primary source of both anions and they were applied simultaneously to fields recharging Turquoise Lake, then we might expect near-simultaneous peaks in their concentrations. This does not occur. Other processes (e.g., bacterially-mediated denitrification) or separate source areas must be involved.

THE FROZEN FALLS AREA: A POOL AND ITS TRIBUTARIES

Frozen Falls Pool is in the main passage of Mystery I (Figure 2.1), about 400 ft from the entrance. The pool is normally about 3 ft deep at its deepest point and measures about 5 by 10 ft. An irregular breakdown block fills perhaps a quarter of that area, making an estimate of the pool's volume difficult. The pool has a speleothem-lined bottom. Drainage is through a small hole in the wall on the north side of the passage.

The pool and surrounding area were extensively modified from their former states by the recommercialization project. Although some care was taken by DNR and Mystery Cave staff and construction personnel to protect Frozen Falls Pool and to limit the influx of foreign material, considerable silt and construction debris (washings from the concrete trail, etc.) accumulated in the pool. Consequently, the pool had to be pumped and cleaned with water piped in, apparently from the house well at Mystery I. To the best of our knowledge, the dates of pumping and cleaning were primarily in August of 1992. Although the flux of water into Frozen Falls Pool from natural sources is significant, resulting in a short residence time for the water, some cautions must be taken in interpreting the chemical data from the early part of the study---they are not to be taken at face value and should be interpreted cautiously.

The Frozen Falls area includes Frozen Falls Pool (FFP) and its four primary tributaries: (1) Frozen Falls Drips (FFD), (2) the Drips Across Bridge (DAB), (3) the Pipe Organ (PO), and (4) the drips Across from the Pipe Organ (APO). Below the Pipe Organ are several small flowstone pools with a volume of a few liters. Most of the water from the Pipe Organ passes through the largest of the pools, known as the Pipe Organ Pool (POP).

The water at FFP varies from clear to turbid, depending on weather conditions. Turbidity rapidly increases during storms as silty water flows from FFD, DAB, and the PO. No turbid water has been noted at the drips Across from the Pipe Organ. A rapid change from clear to turbid water during brief but intense thunderstorms has been observed several times at FFD, DAB, and the PO. Clearly, direct and open flow paths connect the surface above the Frozen Falls area to the cave. The surface above this part of Mystery I is a hillslope in a reentrant to the dissected plateau adjacent to the Root River. The hillslope has thin soils, a limited loess cover, and areas of exposed bedrock, allowing for direct sediment-laden recharge into open joints.

The primary tributary to Frozen Falls Pool is apparently **Frozen Falls Drips**, which issue from the ceiling above the pool but about 10 ft to the side. In the winter, during low-flow conditions, when the land surface is frozen, most of the drip points here and elsewhere in Mystery I are inactive or have very low discharge rates. At low flow, most of the FFD drips are from the ends of several large stalactites hanging out of a joint-guided cupola in the ceiling. Some of this water drips from the tips of the stalactites, but much of the water comes from ceiling joints and spreads out on the sides of the stalactites before falling. During periods of greater discharge, water cascades from additional sites in the ceiling as flows from joints.

The **Pipe Organ** is the second most important tributary to Frozen Falls Pool. Water issues mainly from joints and bed-joint intercepts on the wall and moves as sheet flow down the flowstone to drip points. After passing through small flowstone pools (including the Pipe Organ Pool) the water flows steeply down a flowstone slope into Frozen Falls Pool.

The final tributaries, Drips Across Bridge and the drips Across from the Pipe Organ, contribute only small amounts of water (less than a liter per minute at high flow from DAB and less than half a liter per hour from APO) to Frozen Falls Pool. **Drips Across Bridge** are less than 30 ft from Frozen Falls Drips, immediately adjacent to the opposite side of the bridge spanning Frozen Falls Pool. The drips issue from a distinctive cluster of incipient stalactites on the upper south wall. At times of high discharge, much of the water drips directly onto the bridge or splashes onto it from the wall.

The water at **Across from the Pipe Organ** issues from a small joint on the south wall of the passage about 8 ft above the floor. A small flowstone mound has built up at the opening of the joint. The water issuing from the joint is probably perennially supersaturated with respect to calcite and must be rapidly degassing as it enters the cave. The water spreads out as a thin film over the flowstone-covered wall, wetting an area about 4 ft across. Samples were taken from a small drip point on the flowstone about 4 inches above the floor, rather than from the joint, which is too high to reach. It is worth noting that the immediate area of flowstone on the wall is perennially wet. This keeps the flowstone in a stable, uncorroded condition as long as the water is not undersaturated and aggressive. Adjacent flowstone covering the wall a few feet farther into the cave (east) apparently is now perennially dry, and has deteriorated in its condition since its source was cut off. The adjacent, dry flowstone is noticeably corroded and flaky, a typical result of long-term drying of flowstone.

The major ion chemistry of Frozen Falls Pool is determined by the mixing of its tributary waters and by changes that occur in water chemistry within the pool after mixing. Such changes are most likely to be seen during the coldest period of the winter, in which influx is small. Then, most of the sources are partly cut off due to the freezing of the land surface. The water is supersaturated and precipitation of calcite, particularly of calcite rafts, may occur. Scattered rafts have been observed in Frozen Falls Pool during the winter several times during this project. Precipitation of calcite results in a decrease in the concentrations of calcium and bicarbonate, but such decreases are expected to be small compared to decreases resulting from dilution during recharge events. In any case, the frequency of periodic sampling (about once per month) is too low to be able to detect the changes in chemistry that would accompany precipitation. (Unless discharge were low from Frozen Falls Drips and the other tributaries, it might be very difficult to detect the changes or interpret them without monitoring of discharge and chemistry at each site, preferably at a high frequency using anion and cation sampling along with data loggers to monitor discharge, temperature, and conductivity.)

The chemistry of Frozen Falls Pool can best be described as highly variable (Figures 5.6-5.10). Time-series plots of chemical parameters are extremely spiky. Coefficients of variation (CV) are high (Ca, 13.4%; Mg, 24.7%; Na, 54%; K, 60.8%; HCO_3, 13.8%; NO_3, 64%; SO_4, 28.8%; Cl, 63.7%). Even sodium---which rarely shows significant variation in Mystery Cave waters, shows a spiky response (CV, 54.7%). In general, these results are not surprising, because several of the tributaries respond directly to recharge events, in which surface water rapidly flows into the cave, raising discharge above lower base-flow discharges. During recharge events, dilute waters

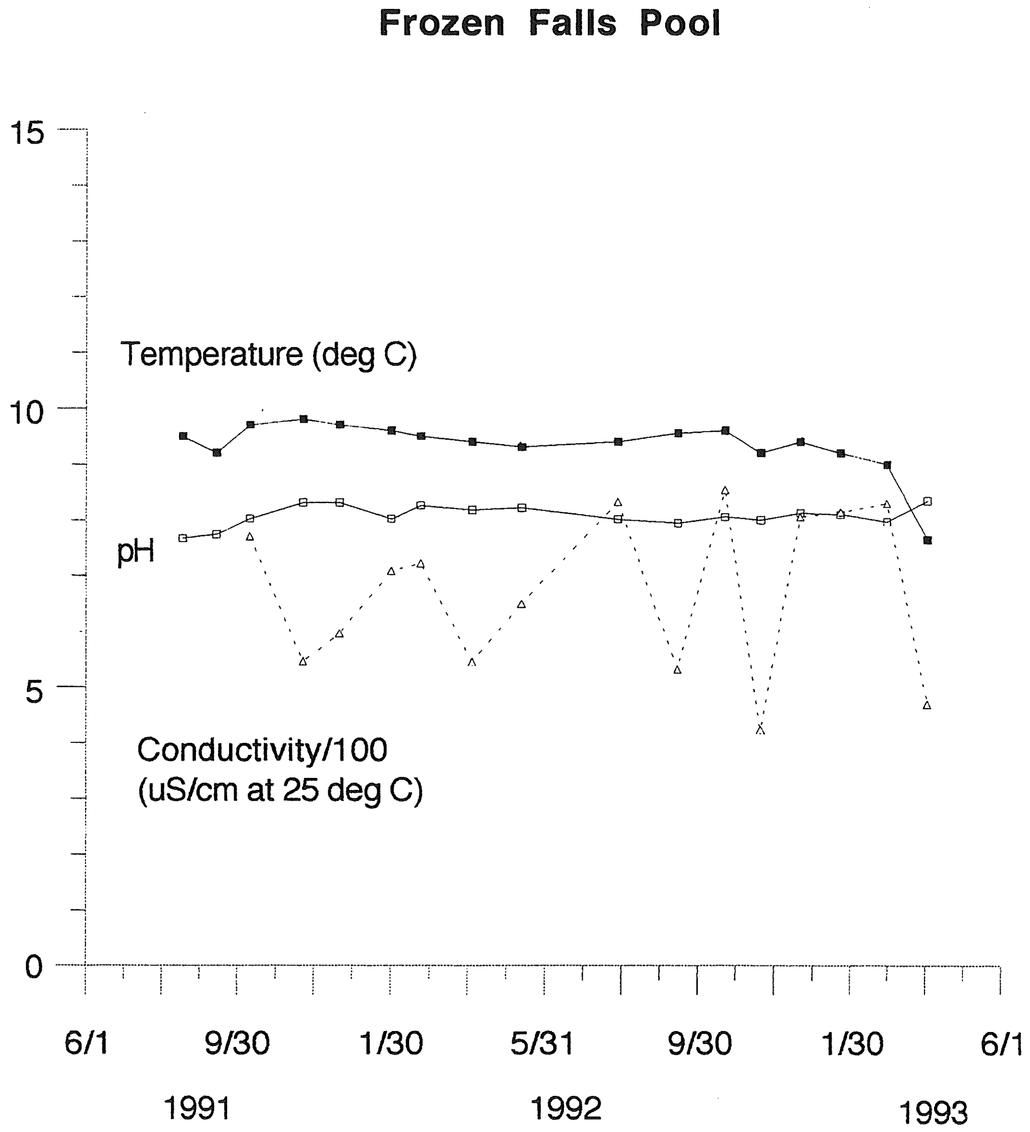


Figure 5.6. Field Parameters at Frozen Falls Pool, 1991-1993.

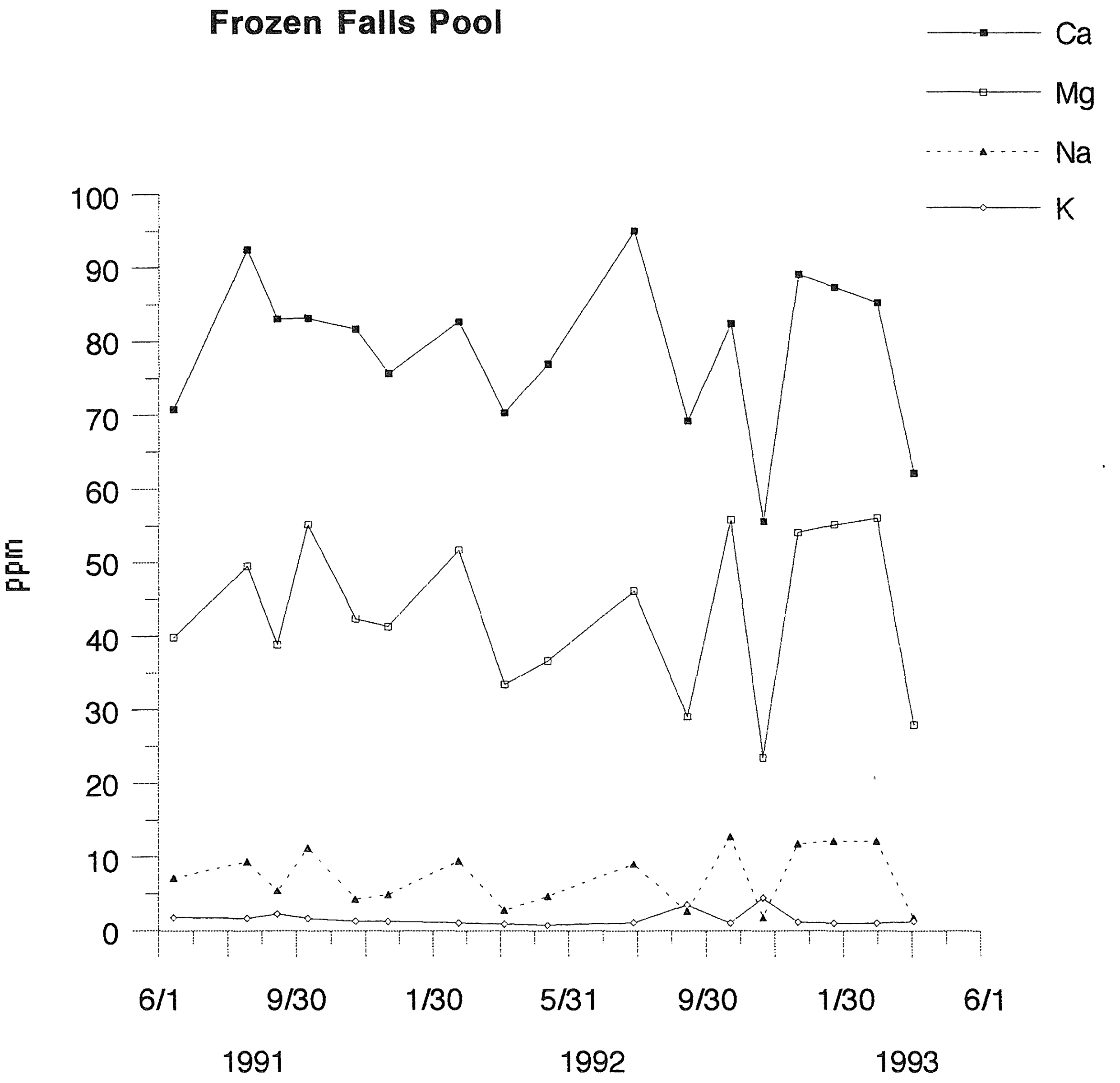


Figure 5.7 Cations at Frozen Falls Pool, 1991-1993.

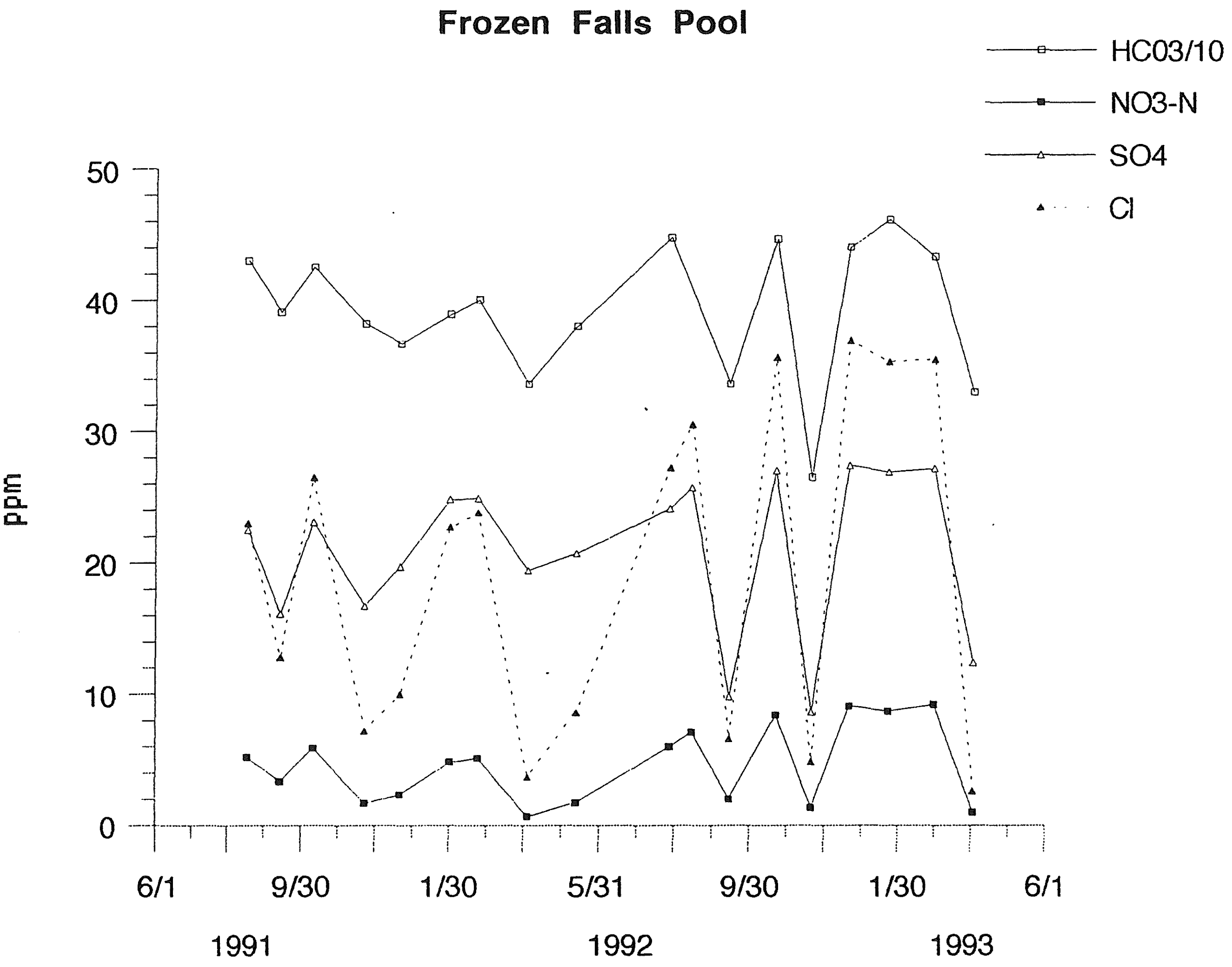


Figure 5.8. Anions at Frozen Falls Pool, 1991-1993.

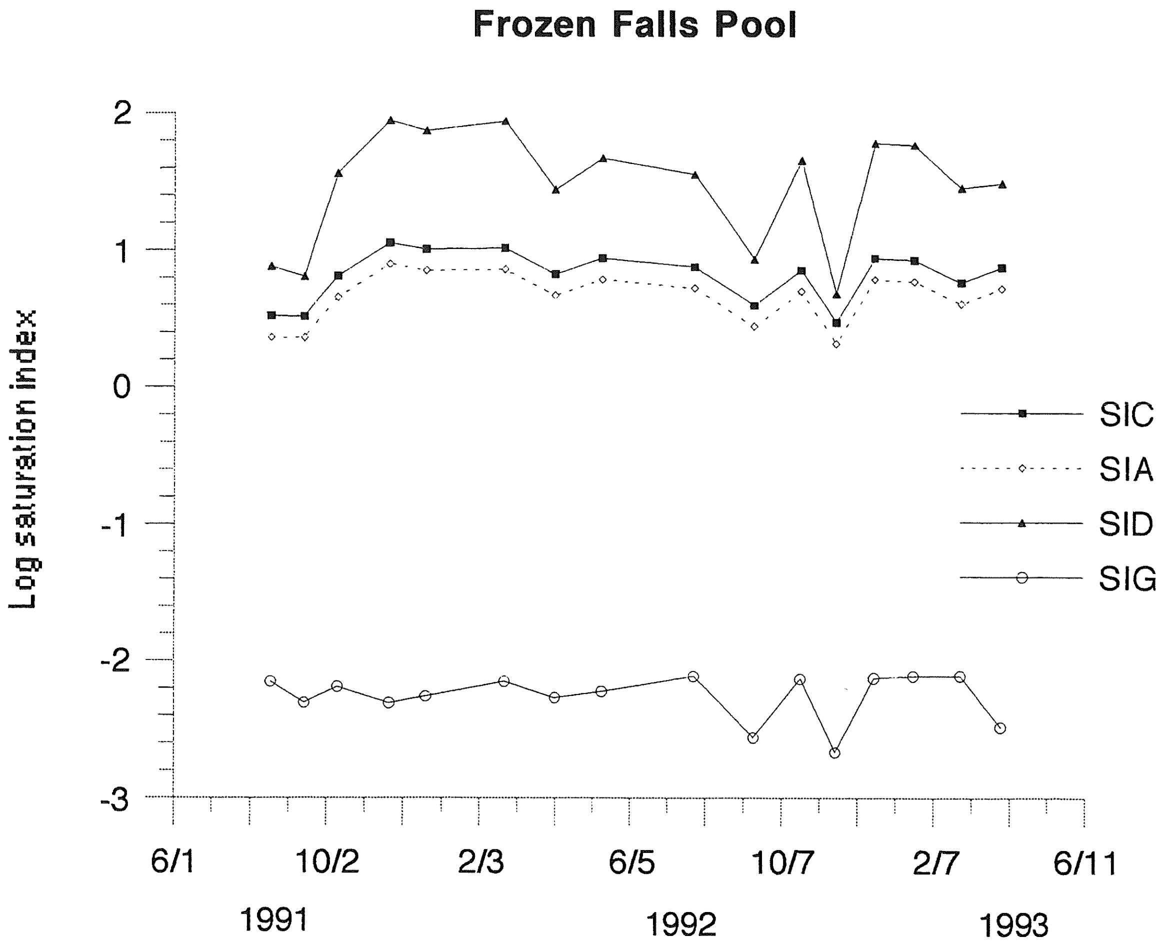


Figure 5.9. Saturation indices at Frozen Falls Pool, 1991-1993.

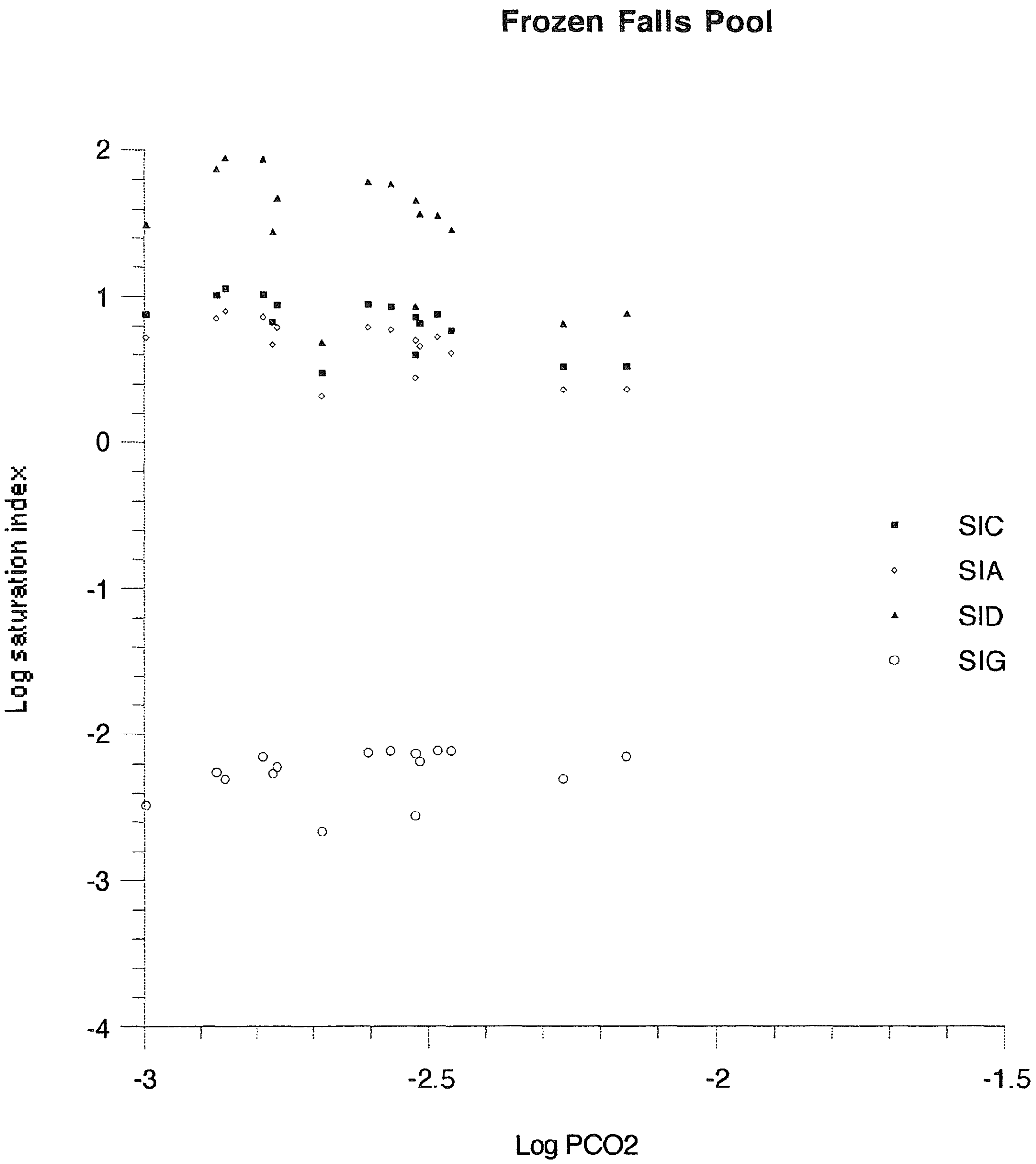


Figure 5.10. Log P_{CO_2} vs log saturation index for Frozen Falls Pool.

from the recharge mix with waters already present in the soil and fractured bedrock above the cave, thus lowering concentrations of ions.

Many of the chemical parameters behave similarly at Frozen Falls Drips (Figures 5.11-5.15), a fact consistent with the interpretation that the bulk of the recharge to Frozen Falls Pool is derived from Frozen Falls Drips. Additional support is provided by the observation that Na concentrations at FFD are consistently high (11.2 ± 2.2 mg/l for n = 19), and are very low (<2 mg/l) in the other tributaries. However, the behavior at FFD is much less spiky, and coefficients of variation are lower for all measured parameters. The remaining tributaries were sampled only a small number of times (4 for DAB and PO; 2 for POP; and 1 for APO), so detailed comparisons can usefully be made at most for the four dates on which FFD, FFP, DAB, and PO were sampled, or alternately, on the one date in which FFD, FFP, DAB, PO, and APO were all sampled.

As an example of the caution needed in interpretation of the time series plots, we point out the response of the five sites (just listed) to the November 19-21, 1992 recharge event. The sites were sampled on November 20 between 5:40 and 7:15. It had been raining steadily since the previous afternoon (see Figure 7.6). Discharge was highest by far at FFD, was smaller at PO, and was far less yet at DAB. The discharge at APO was higher than usual but the least of the five sites. Many other sites not usually wet were dripping. A site never sampled before---here named the Turnoff Cupola (TC) because of its location below the bridge at the turnoff to the Needle's Eye---was active as a turbid waterfall from a ceiling joint; its water temperature was 6.92°C and its conductivity was 289 µS/cm at 25°C. Another site---the Bridge Ceiling Joint (BCJ) located in the ceiling above the first galvanized bridge from the Mystery I entrance---was slightly turbid, and had a water temperature of 9.60°C and a conductivity of 300 µS/cm at 25°C. Frozen Falls Pool was turbid (9.20°C and 423 µS/cm at 25°C), as was the Pipe Organ (8.15°C, 365 uS/cm at 25°C). Frozen Falls Drips, suprisingly, was not turbid (9.10°C, 937 µS/cm at 25°C). Apparently rapid flow from precipitation had not yet reached the site, and high conductivity stored water was being displaced from the soil, loess, and fractures to drain out of the ceiling at FFD. In other words, the water from FFD was not diluted by recent recharge. Therefore, major ion concentrations and conductivity are generally much higher in the November 20 sample for FFD than they are in the samples from Frozen Falls Pool or the other sites (Table 5.1).

Returning to the time series plots of FFD and FFP, we can now suggest that the less spiky behavior of the Frozen Falls Drips plots is in part a function of the timing of the sampling events relative to the onset of recharge events. Note that there is no response discernible in the chemical plots for FFD, whereas there are distinct spikes in the responses of temperature, conductivity, and major ions for the Frozen Falls Pool sample (see the 5th point from the right on Figures 5.6-5.9 and 5.11-5.14).

Water temperature shows much less of a tendency to vary at FFD and FFP than the other parameters (CV 3.3% and 5.2%, respectively). The water temperatures of Frozen Falls Pool and its primary tributary, Frozen Falls Drips, are usually close, within 0.2°C, but are not well correlated. Linear regression of the 16 available pairs of temperatures (T) gives

$$T_{FFP} = 0.58\ T_{FFD} + 3.99 \quad \text{with a correlation coefficient } r = .76$$

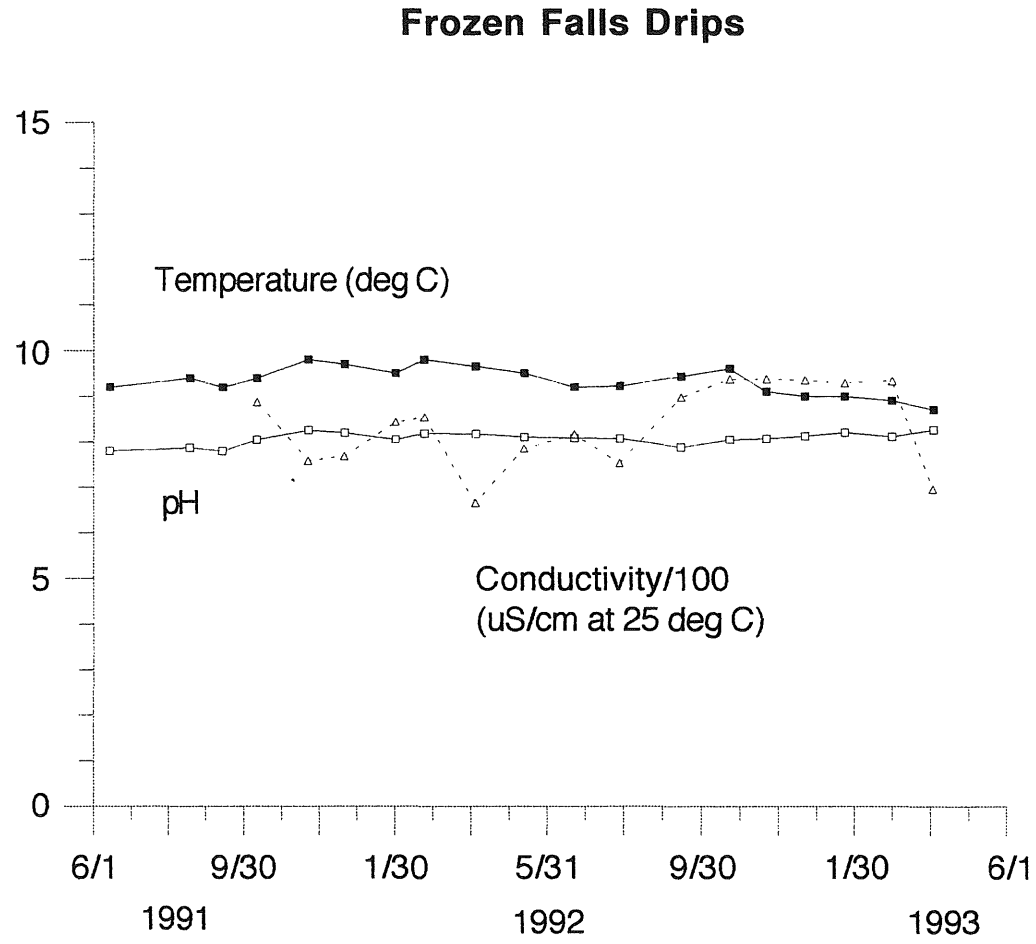


Figure 5.11. Field Parameters at Frozen Falls Drips, 1991-1993.

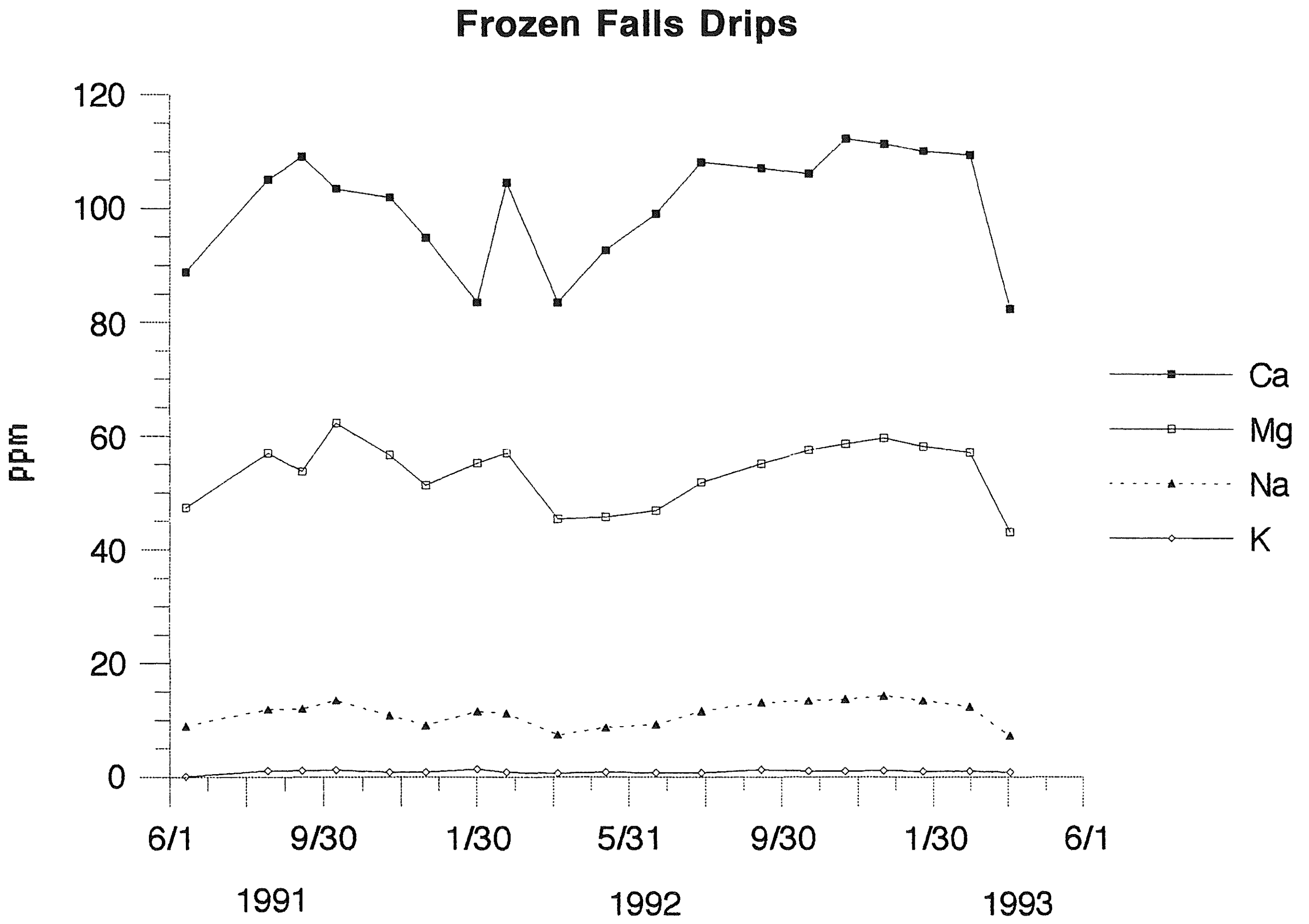


Figure 5.12 Cations at Frozen Falls Drips, 1991-1993.

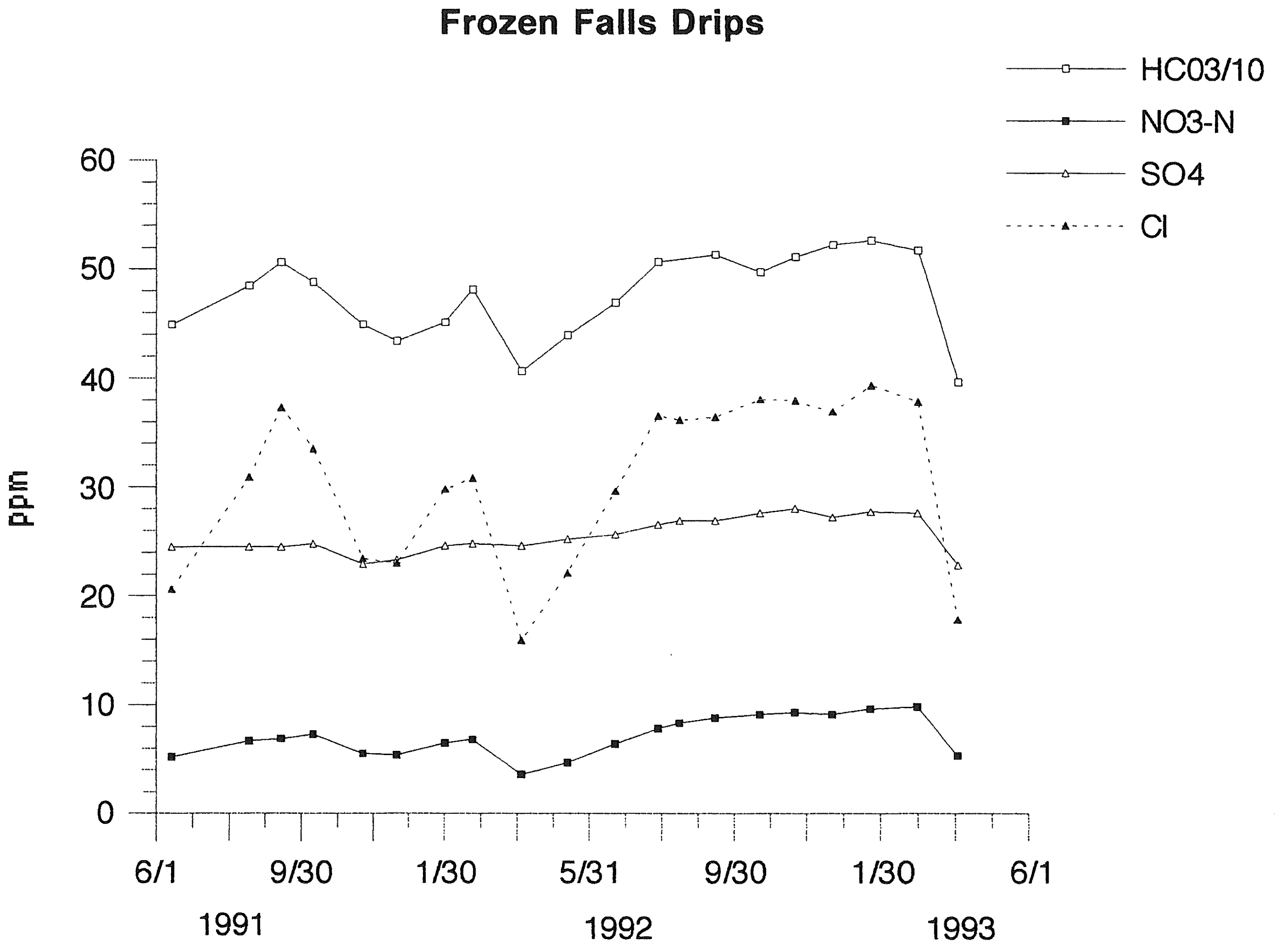


Figure 5.13. Anions at Frozen Falls Drips, 1991-1993.

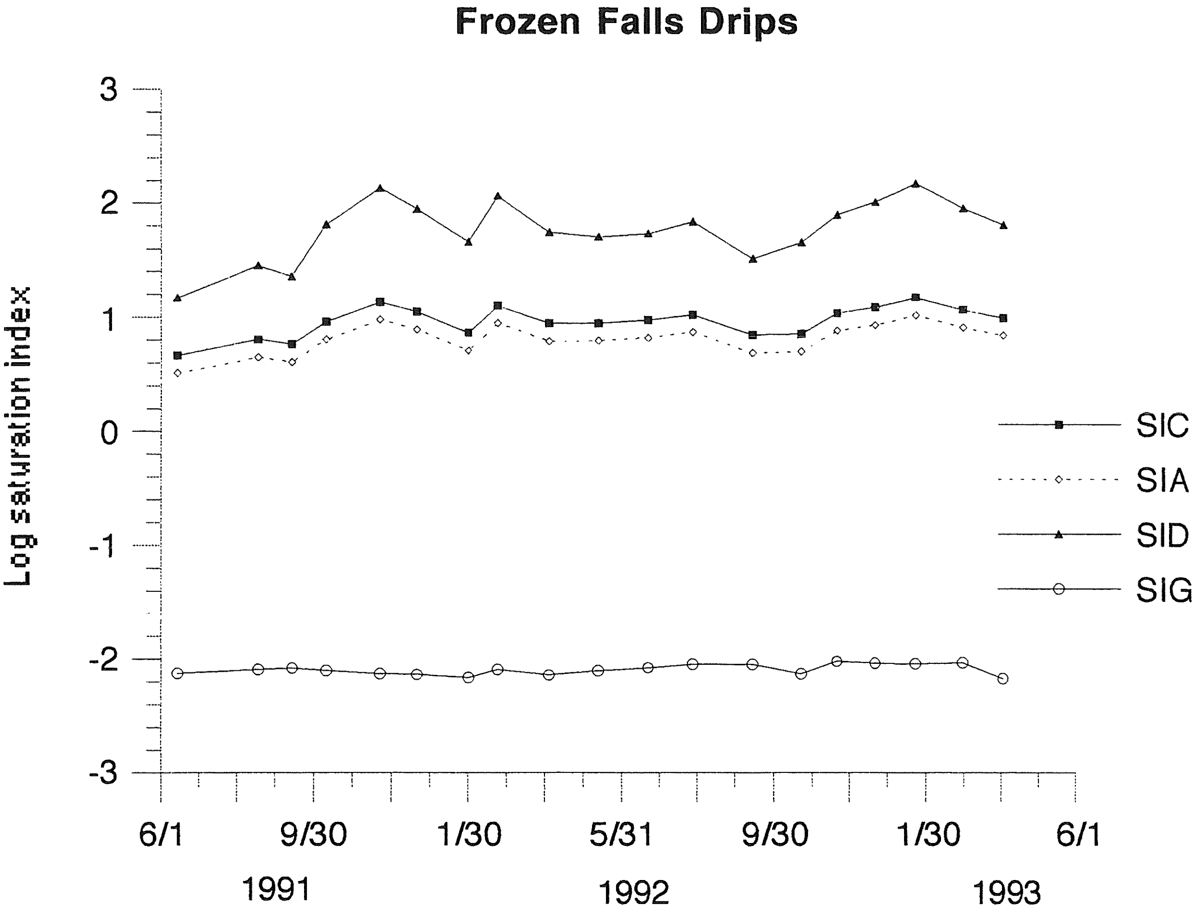


Figure 5.14. Saturation indices at Frozen Falls Drips, 1991-1993.

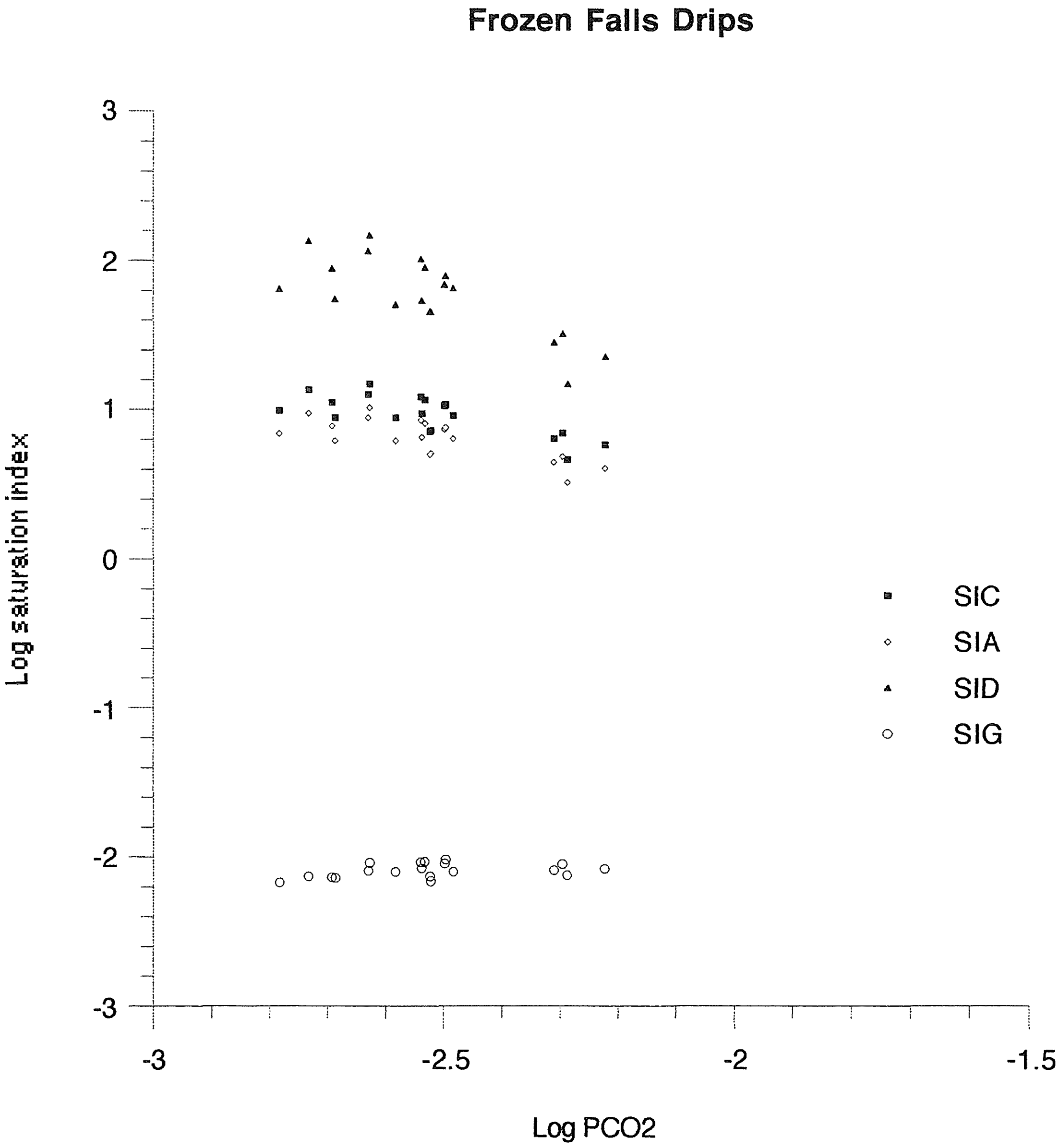


Figure 5.15. Log P_{CO_2} vs log saturation index for Frozen Falls Drips.

Table 5.1

Water Chemistry at Sites in Mystery I on November 20, 1992.

Parameter	Units	Frozen Falls Drips (FFD)	Frozen Falls Pool (FFP)	Pipe Organ (PO)	Drips Across Bridge (DAB)	Across from Pipe Organ (APO)
Ca	ppm	112.1	55.6	50.3	68.1	57.6
Mg	ppm	58.6	23.5	19.2	29.8	24
Na	ppm	13.7	1.85	0.49	0.66	1.17
K	ppm	1.04	4.5	5.28	2.81	3.86
HCO3	ppm	511	265	242	338	280
Cl	ppm	37.9	4.8	0.91	1.01	1.1
SO4	ppm	28	8.6	6.2	9.1	8.8
NO3	ppm	41.2	6	2.3	2.1	2
Temperature	degrees C	9.10	9.20	8.15	9.20	9.40
Conductivity	uS/cm at 25 deg C	937	423	365	501	424
pH	pH units	8.07	8.00	7.80	8.01	8.10

which suggests that other tributaries must on occasion contribute significantly to the chemistry of Frozen Falls Pool. As we saw for the November 20, 1992 sampling, that is indeed the case.

During the March 30-April 2, 1993 flood, water rose from lower level fissures in Mystery I and flooded much of the commercial trail. The flood completely inundated Frozen Falls Pool and changed its chemistry. The effects are not so easy to see as they were at Tùrquoise Lake, because the chemistry at Frozen Falls Pool is highly variable, while that of Turquoise Lake is not. Nonetheless, examination of the last sampling on the time-series plots of Figures 5.6-5.8 (a few days after the March 30-April 2 flood) shows distinct drops in water temperature, conductivity, calcium, magnesium, sodium, bicarbonate, nitrate-nitrogen, sulfate, and chloride. In contrast with circumstances at Turquoise Lake, however, water temperature was slower to return to the near-normal water temperature of about 9°C. The temperature was at 7.65°C when measured on April 3, 1993.

The Frozen Falls area has galvanized steel railings, or railings and bridges, near or immediately below drip points. Thus the water draining into Frozen Falls Pool has a significant drip and splash component that has come into contact with a source of zinc. These bridges were installed during the recommercialization project in Mystery I at various times during the winter, spring, and summer of 1992. As described in Chapter 4, we measured elevated zinc concentrations in Frozen Falls Pool, compared to waters feeding the pool and waters elsewhere in Mystery Cave. Zinc concentrations were in the parts per billion range and do not exceed regulatory concentration limits.

LOWER LEVEL STREAM

The Lower Level Stream (LLS) sampling site is within about 400 ft of the South Branch of the Root River (SB). It is in the lower level of Mystery I (Figure 2.1). The stream issues from a narrow fissure (0.5 ft wide) on the south side of a passage leading to the Disappearing River. The stream flows several hundred feet to the west before flowing into an inaccessible fissure on the north side of the passage. The sampling site is at a pool (2.5 ft by 0.5 ft by 0.8 ft deep) at the joint from which the water issues. Discharge was not measured but is on the order of 10-20 liters per minute. Discharge was relatively constant over the 10 sampling dates between January, 1992 and April, 1993. This conclusion is based on the negligible variation in stage of the pool at the sampling site. Flow velocities were on the order of ten-twenty ft per minute, as shown by the time it took induced pulses of muddy water to traverse the accessible part of the stream. Actual turbidity within the LLS from natural sources was never observed.

The Lower Level stream derives some of its discharge from the Root River. That part of the discharge probably arrives within a day. These conclusions are indicated, in part, by flow velocities. Also, water temperatures ranged from 5.60 to 11.60°C and show a seasonal rise and fall (Figure 5.16).

At the time of the initial sampling, on January 31, 1992, the water temperature was 7.8°C. The Root River was frozen over and its water temperature, though not measured, would have been only a few degrees Celsius at most and more likely was under 1°C, based on continuous measurements of water temperatures in the Root River under similar conditions made in the winter of 1994. (The air temperature was

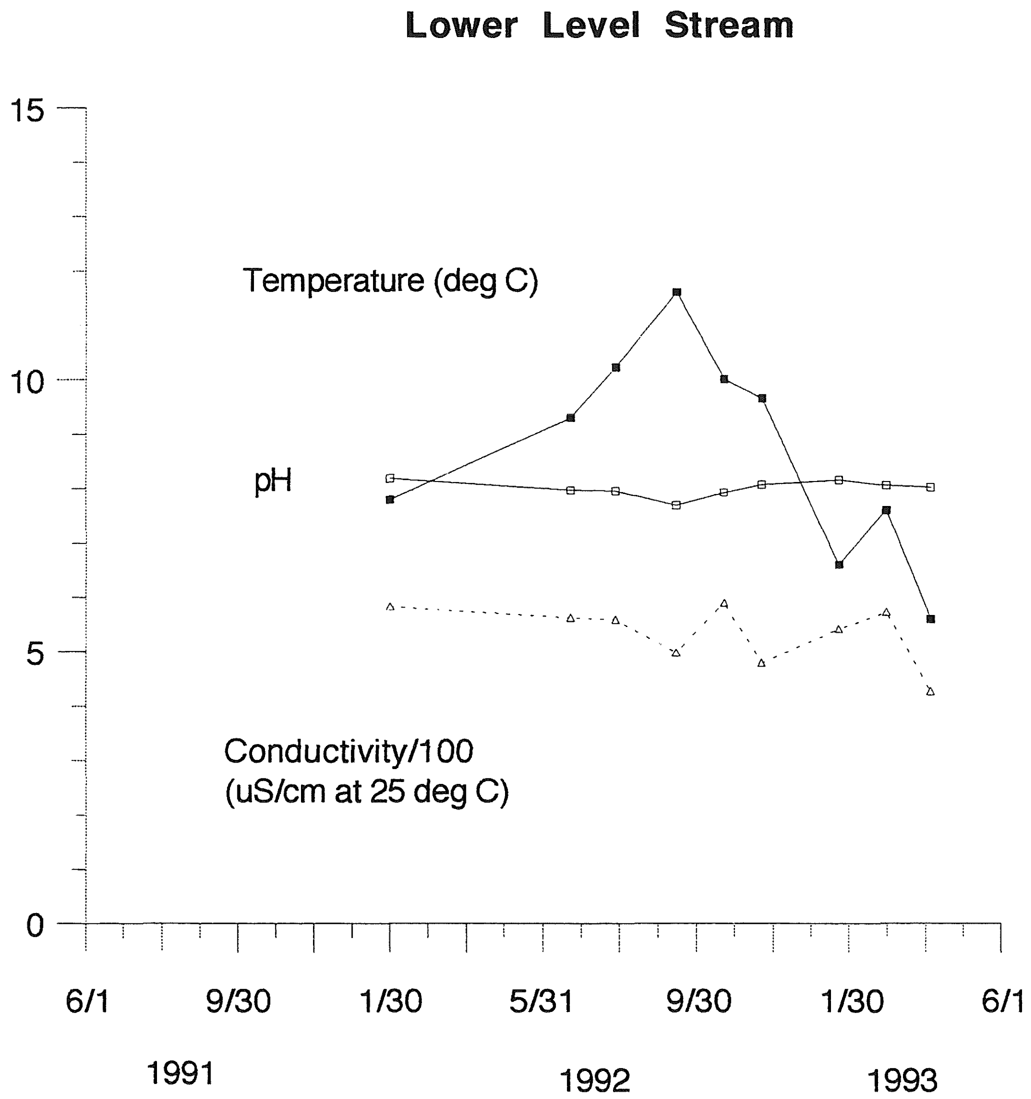


Figure 5.16. Field Parameters at the Lower Level Stream, 1991-1993.

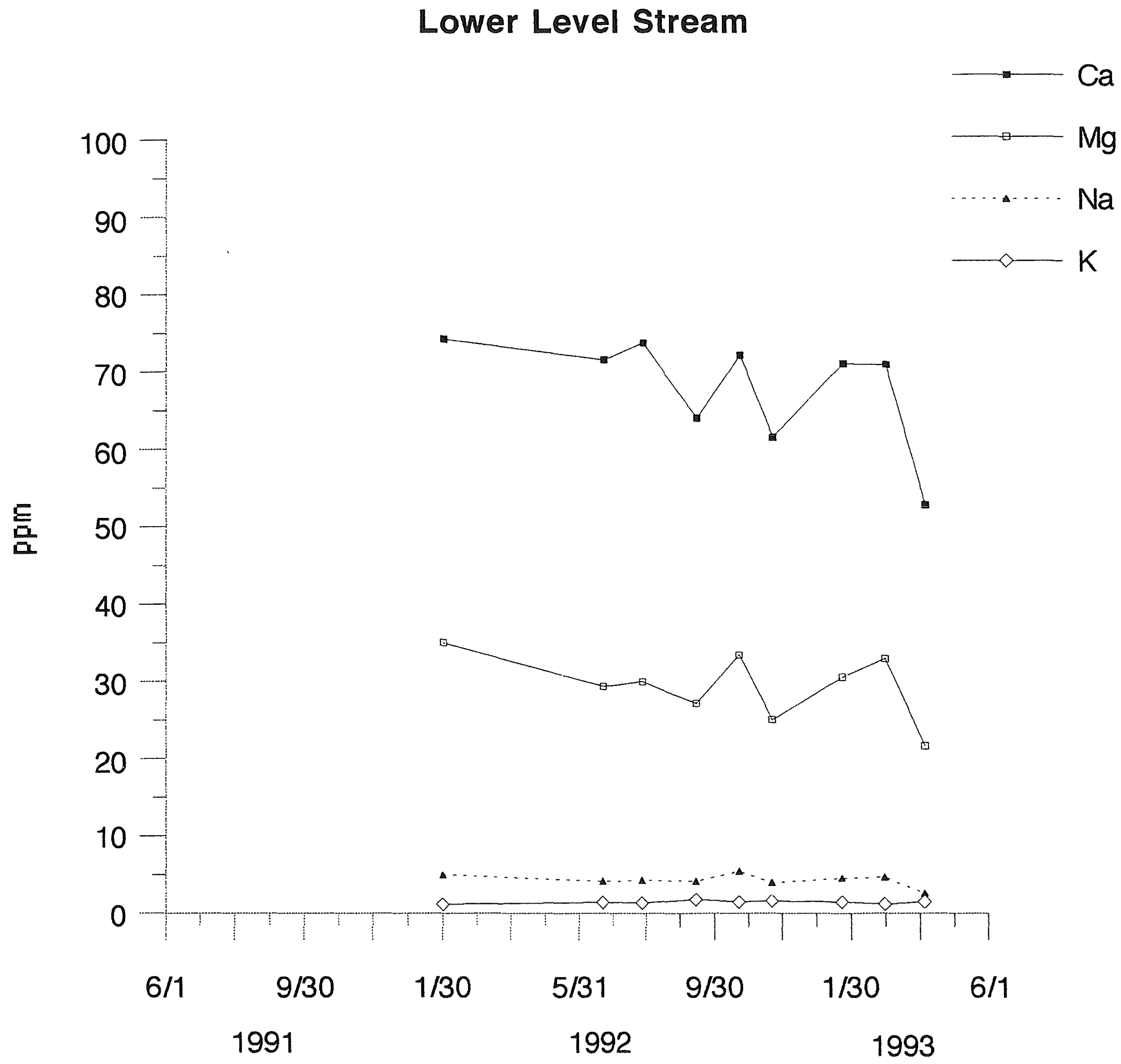


Figure 5.17. Cations at the Lower Level Stream, 1991-1993.

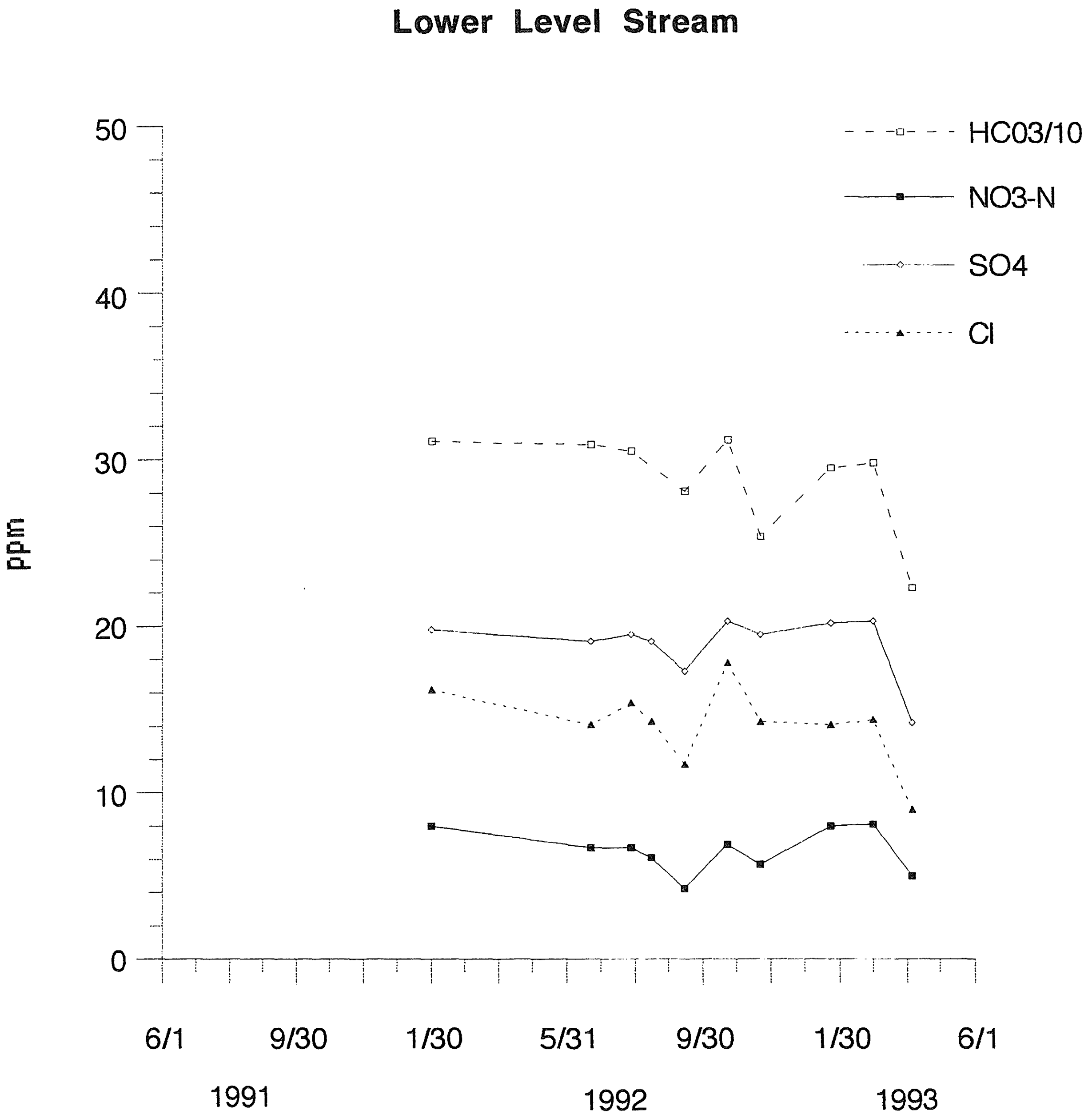


Figure 5.18. Anions at the Lower Level Stream, 1991-1993.

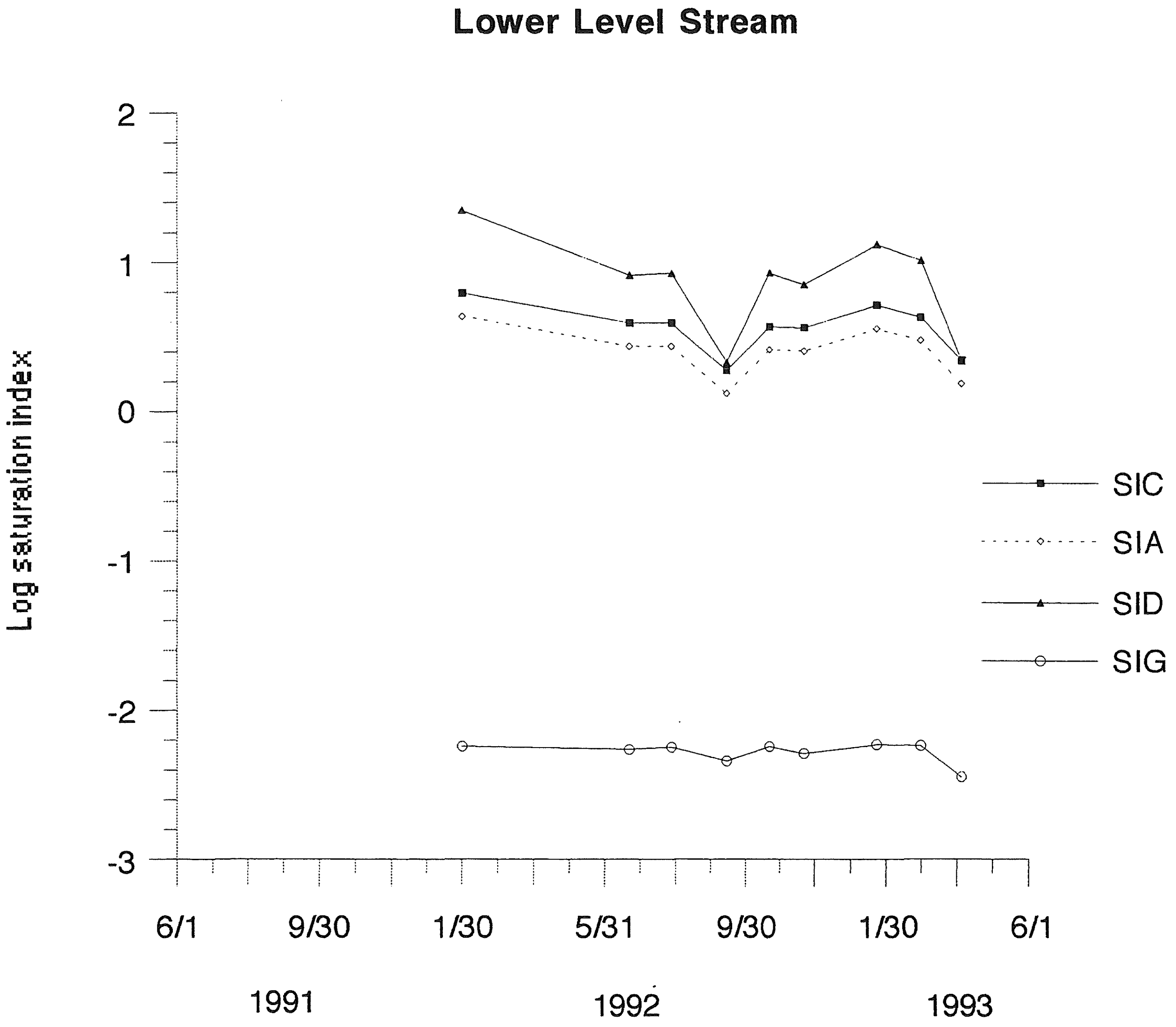


Figure 5.19. Saturation indices at the Lower Level Stream, 1991-1993.

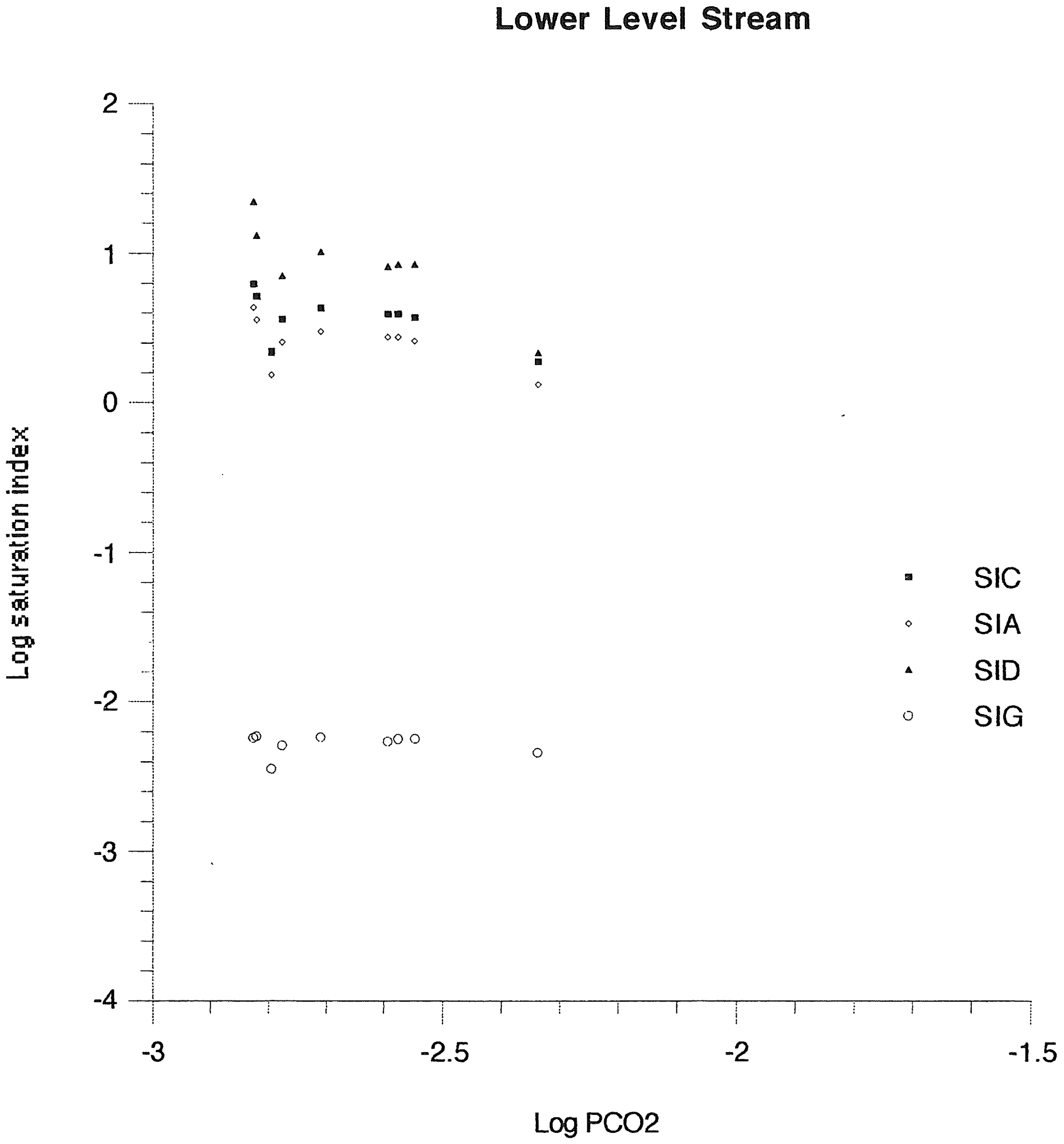


Figure 5.20. Log P_{CO_2} vs log saturation index for the Lower Level Stream.

below freezing and there had been no significant surface melting over previous days.) This line of reasoning suggests that the bulk of the discharge derives from sources that have been underground for a significant period of time---hence from sources other than rapid infiltration from the river. It is reasonable to assume that water close to 8.7°C mixed with a small amount of colder water from the Root River to produce a mixture at 7.8°C. The distance from the Root River is too short to allow significant warming by conduction from bedrock at the prevailing discharge. (By way of support, it should be noted that water at Flim Flam Creek is as warm as 22°C in the summer and as cold as 1.4°C in the winter. That water flows a minimum, straight-line distance of 2560 ft from its postulated source area on the Root River to the sampling site. See Chapter 8).

Water temperature and conductivity were measured twice on the same dates at both sites (Root River first, then the Lower Level Stream about 1-2 hours later):

Date	Location	Temperature (°C)	Conductivity (uS/cm at 25°C)
7/28/92	SB	21.10	556
	LLS	10.22	559
4/5/93	SB	6.30	351
	LLS	5.60	427

The data from the summer sampling support the reasoning of the previous paragraph. Water at about 21°C from the Root River apparently mixed with a significant quantity of cooler water to produce a water temperature of 10.22°C.

The data from the second sampling show the South Branch of the Root River as being warmer than the Lower Level Stream. However, they also show the LLS as being colder than deep cave temperature. These data have to be interpreted in context; they only appear to contradict the hypothesis suggested above.

The sampling was a few days after flood waters had receeded from the March 30-April 2 flood (see Chapter 10). During the flood, water from the Root River infiltrated its bed, flowed through the lower level passages, and was ponded downstream at constrictions. This resulted in backflooding. Water rose from the lower levels to the upper level in which the commercial trail lies. Water completely filled the lower level in this part of Mystery Cave. Every available fracture was filled with water, which then had to drain back out after water levels fell. Water levels remained high from the afternoon of March 30 through the morning of April 2nd at Flim Flam Creek, and probably receded only a few hours earlier at Mystery I. The floodwater was produced by rain on snow and was cold. By the time of its arrival at Flim Flam Creek, the water temperature ranged from 3 to 5°C. (See Figure 10.2.) Unfortunately, we did not have water temperature instrumented on the Root River, but that water should have been cooler---i.e., the cave warmed the infiltrate between the South Branch and Flim Flam Creek. Thus the water stored during the flood was much colder (by about 4°C at the end of the flood) than the deep cave temperature. Because the cool water filled the lower level passages for several days, and would have been even colder much of that time, there must have been a considerable cooling of bedrock in Mystery I.

With the preceeding in mind, it is now possible to offer two (speculative) hypotheses to resolve the apparent contradiction. In the first, the bulk of the water sampled at LLS on April 5th had drained from short-term storage induced by the flood. That storage would have been in available fractures and sediments and can be thought of as a kind of bank storage. The water was cooler than deep cave temperature because it was stored that way and had not yet had time to warm. Also, bedrock and sediments with which it came into contact as it slowly drained were cooled by the stored water. When the bulk of the water rapidly drained, it left cooler surfaces upon which the later, more slowly draining waters (sampled on April 5) had to flow.

In the second hypothesis, infiltration water from the normal sources (that form the bulk of the normal discharge at LLS) drained via normal processes. (This hypothesis assumes that sufficient time had elapsed to remove the bank storage.) However, the water probably was cooler than normal, and drained more quickly following this major recharge event. It might be displaced water from the soil and loess, and carry a seasonal cool temperature signal. Or it might be cool recharge derived from the precipitation and snowmelt recharge. In either case, it then mixed with a small amount of warmer water from the South Branch. Under this hypothesis, the sampled water would be cooler than deep cave temperature because it was derived mostly from cool recharge or cool displaced water and hadn't had time to warm up. Under this hypothesis, some cooling of the water could also occur as the water flowed over bedrock and sediments cooled during the flooding.

On April 5, the water conductivities were 351 μS/cm at 25°C on the Root River and 427 μS/cm at 25°C at the Lower Level Stream. For the Lower Level Stream, this represents a significant drop from conductivities characteristic of winter pre-melt conditions (Figure 5.16). All major ions except for potassium also showed sharp declines in concentration (Figures 5.17 and 5.18). These LLS data are probably compatible with either hypothesis; they mostly indicate that the sampled water contained a significant component of recently-recharged precipitation and snowmelt.

For the South Branch of the Root River, for which few data for 1991-1993 are available, we can only note the following. Data obtained during the winter of 1994 indicate that during the very cold part of the winter, when the river is frozen over and melt-water recharge is minimal, the Root River has a conductivity that is typically over 500 μS/cm at 25°C. (This suggests that most of the flow is derived from base-flow discharge from surrounding bedrock into the Root River.) When melting occurs, conductivity drops sharply (to as low as about 120 μS/cm at 25°C) for periods whose length depends on the magnitude and duration of snowmelt. (As an additional complication, pulses of meltwater from elsewhere in the basin can pass by, providing transient signals that can be very puzzling if one is not aware of the process.)

WISHING WELL DRIPS

Wishing Well Drips (WWD) is at the Smoking Chamber in Mystery II (Figure 2.1). Water falls from a joint in the ceiling and falls about 40 ft into the Wishing Well pool. The pool is artifical, consisting of an elliptical concrete-lined basin (8 by 5 by 2 ft deep in the center) with an overflow spout draining into breakdown. Fragments of flowstone and bedrock are set in the concrete, forming a rim. Coins (mostly pennies) were sometimes present in the pool during the summer tourist season. Our interest was more in the chemistry of Wishing Well Drips than in the effects of commercialization on the the pool chemistry. Thus, WWD waters were sampled in plastic bags spread over buckets supported by two pvc pipes temporarily set across the pool. Drip rates were not measured, but can be estimated to range from less than a half liter per hour in the winter to perhaps 10-15 liters per hour or more following recharge events.

Wishing Well Drips is below a narrow strip of grassland on the edge of cornfields (compare Figure 2.1 with Figure 3.4; WWD is about halfway between the boundaries of potential recharge areas for Blue Lake and Wishing Well Drips). The relatively constant chemistry for the major ions (CV's mostly between 2 and 9%, with the primary exception of Cl at 12.4%) suggests a diffuse source of recharge despite the 10-fold range in discharge. Plots for the field parameters, cations, anions, saturation indices, and P_{CO_2} vs saturation indices at Blue Lake appear in Figures 5.21-5.25.

The water temperature at WWD (8.84 ± 0.26°C; CV = 2.7%) is probably more stable than appears on Figure 5.21. The two data points for 9/13/91 and 2/22/92 of 9.40 and 9.50°C, respectively, probably reflect samples allowed to collect for too lengthy a time before the measurement of water temperature. The second point is not correlated with precipitation at Spring Valley (see Table 6. in Chapter 6), and in any case occurred in a cool period of February, a month of only a minor amount of precipitation in the form of ice and snow. The first data point followed 2.6 inches of precipitation on 9/11/91 at Spring Valley, so it may represent a period of precipitation above Mystery Cave. However, other chemical parameters at this and other sites cast doubt on this hypothesis. The data point probably reflects warming of the sample before temperature was measured.

The slight drop in water temperature from 8.90 to 8.70°C for the last two sampling periods (March 2 and April 5, 1993) is matched by declines in concentrations of major ions (Figures 5.21-5.23). It is probably real, and with the other data, indicates the presence of a rapid-flow component to Wishing Wells Drips resulting from the recharge that coincided with the March flood.

RIMSTONE CREEK

Rimstone Creek is north of 4th Avenue, in Mystery III (Figure 2.1). The sampling site is a very small pool, scarcely one foot square and 0.2 ft deep. The pool is at the intersection of the main Rimstone Creek stream and a tributary stream that issues from a joint on the north side of the east-west trending main pasage. (Flow is east to west at this point). Rimstone Creek has a discharge on the order of a few liters per minute to perhaps 15-20 liters per minute. The main stream receives part of its discharge from flows leaving the Lily Pad Lake area of Mystery III. The tributary stream has a discharge on the order of perhaps half a liter per minute. That discharge appeared to vary little during the study, which included 17 sampling dates between June, 1991 and April, 1993.

At times of high discharge, Rimstone Creek appeared to become slightly turbid. This was a very subtle increase in turbidity, and was difficult to distinguish in the poorly lit conditions. If true, it suggests a component of rapid flow from surface sources. The potential recharge area for Rimstone Creek is discussed in Chapter 3 and is shown on Figure 3.4. The area includes the ravines draining croplands (usually planted in corn; see Figure 3.4). It is reasonable to suggest that a minor amount of rapid flow occurs based on the chemical sampling (Figures 5.26-5.30),

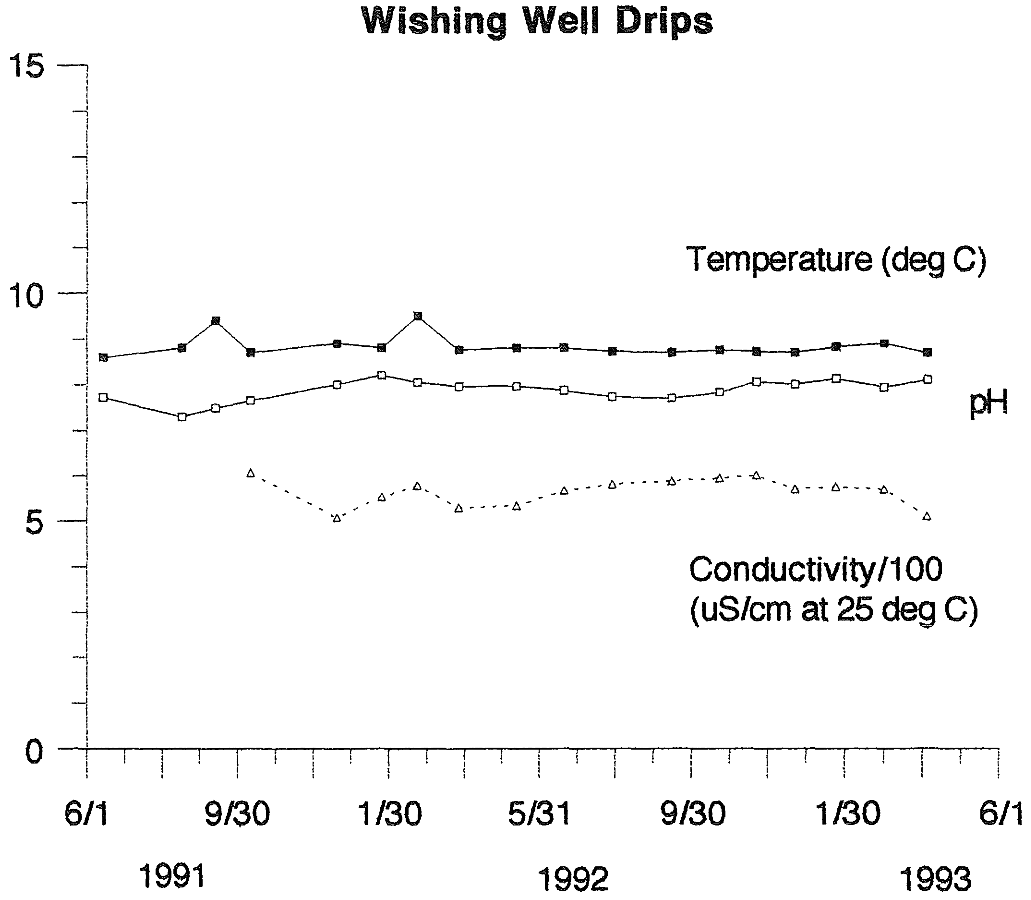


Figure 5.21. Field Parameters at Wishing Well Drips, 1991-1993.

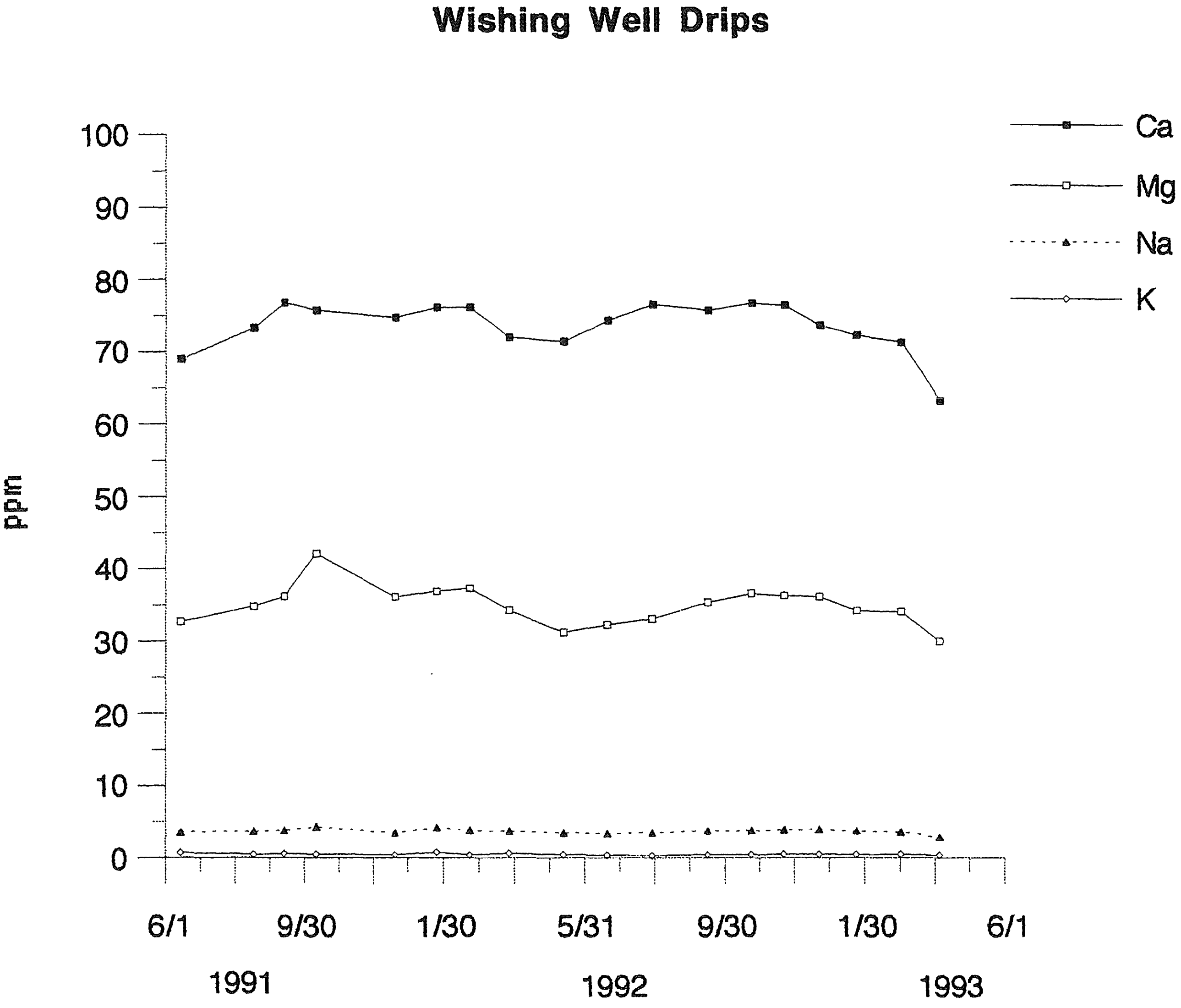


Figure 5.22. Cations at Wishing Well Drips, 1991-1993.

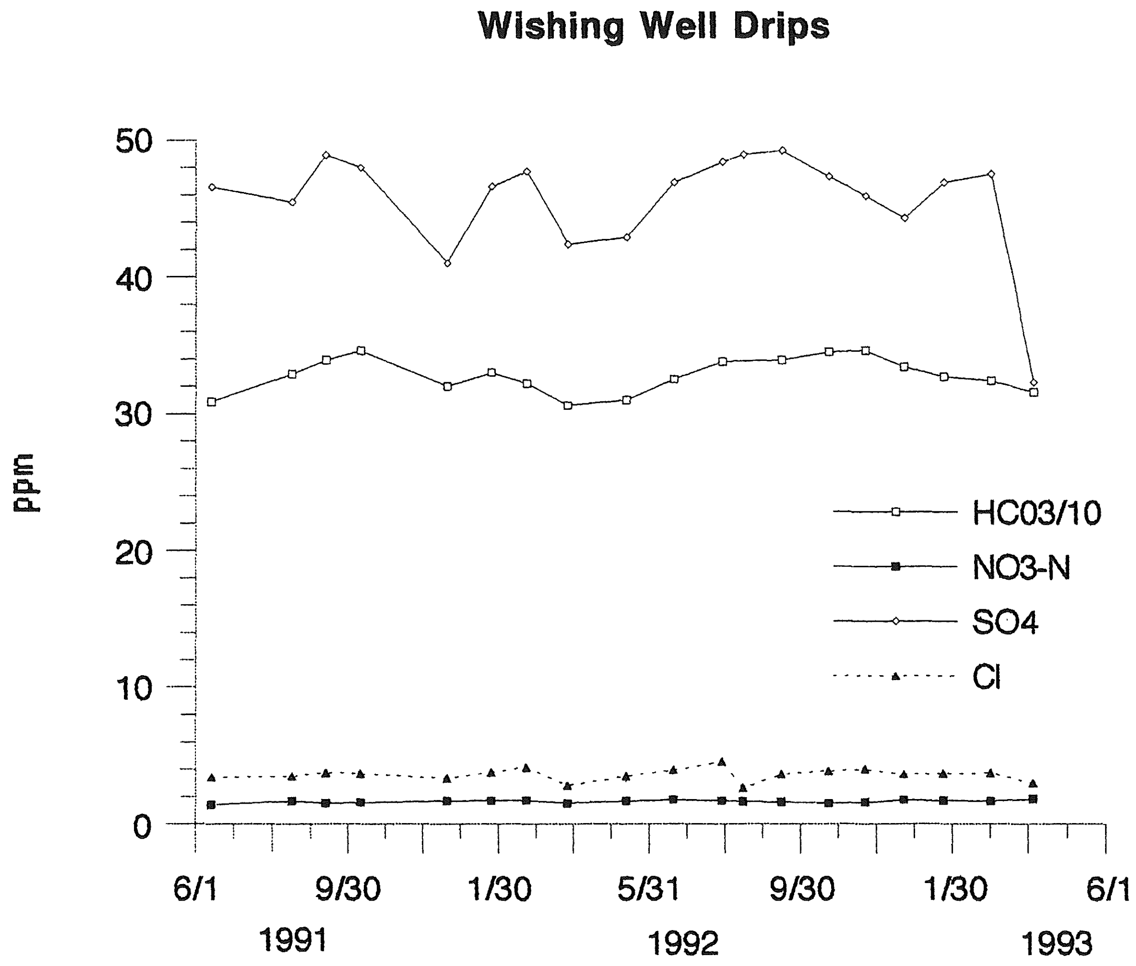


Figure 5.23. Anions at Wishing Well Drips, 1991-1993.

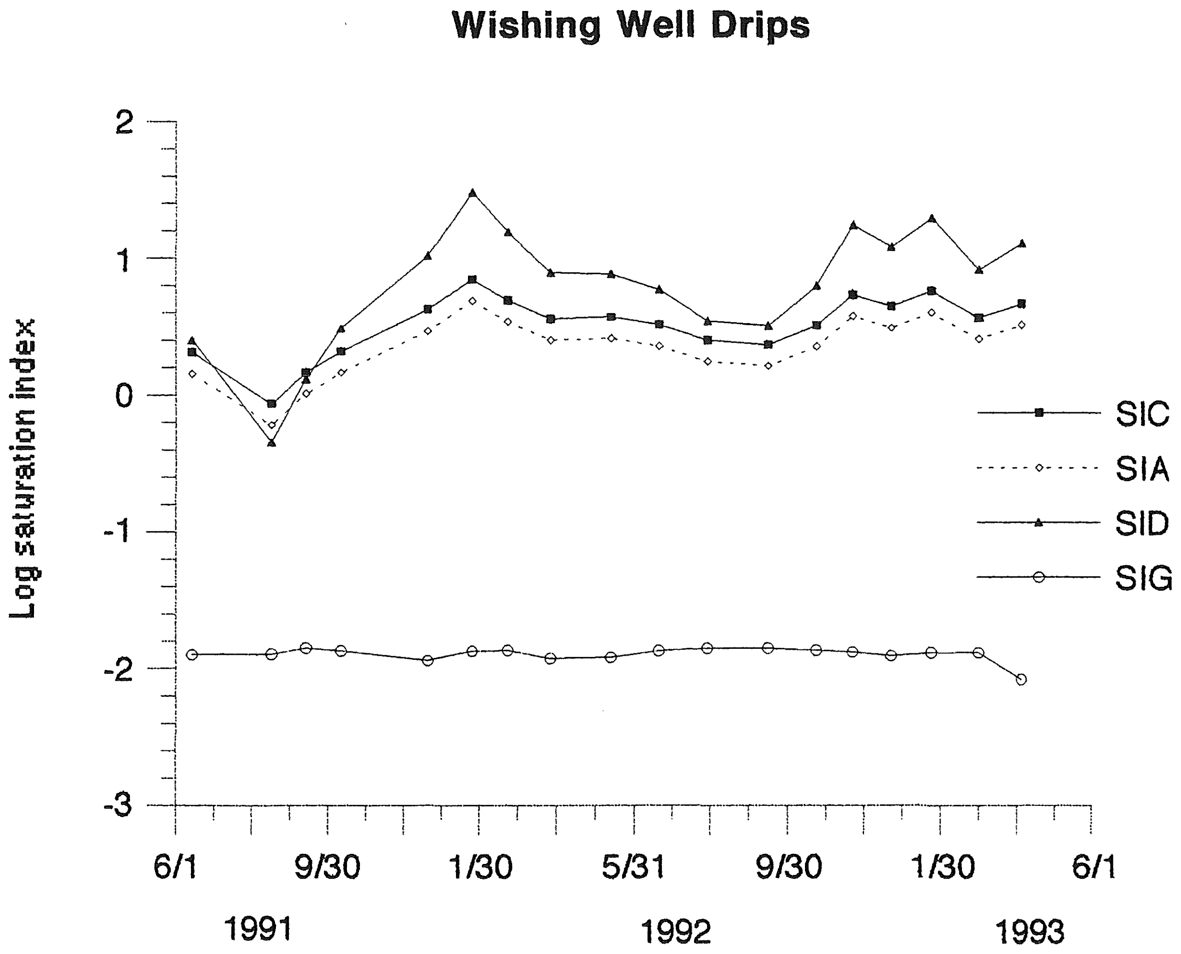


Figure 5.24. Saturation indices at Wishing Well Drips, 1991-1993.

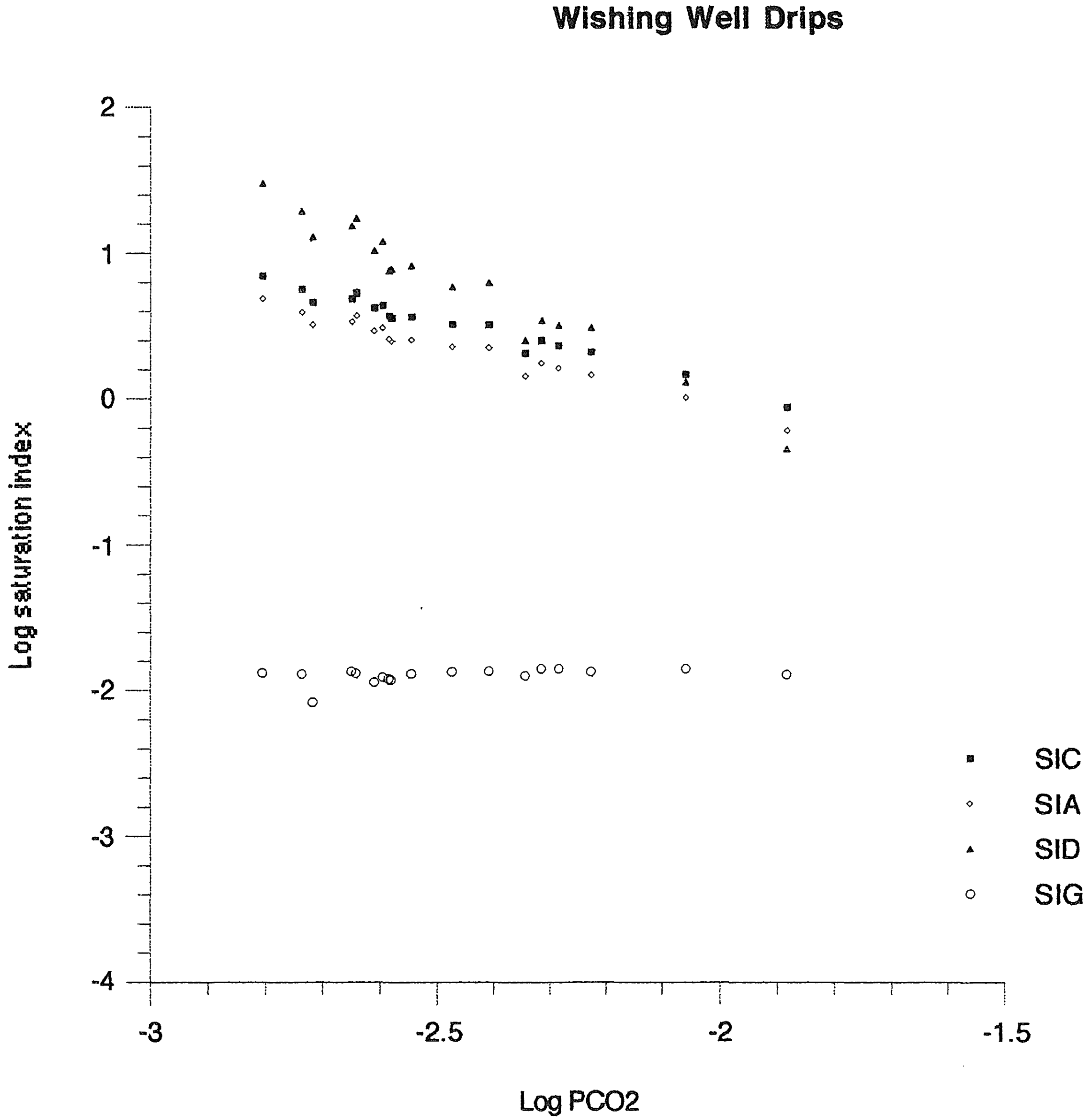


Figure 5.25. Log P_{CO_2} vs log saturation index for Wishing Well Drips.

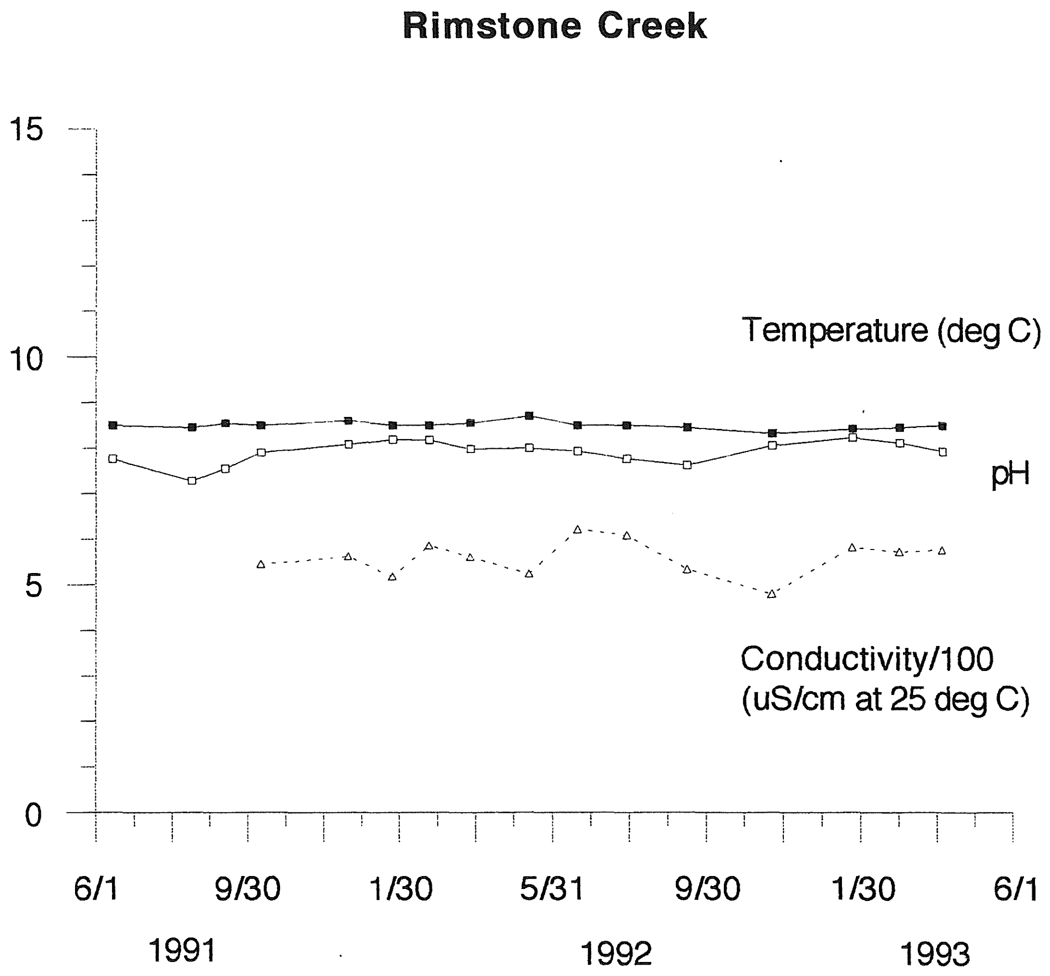


Figure 5.26. Field Parameters at Rimstone Creek, 1991-1993.

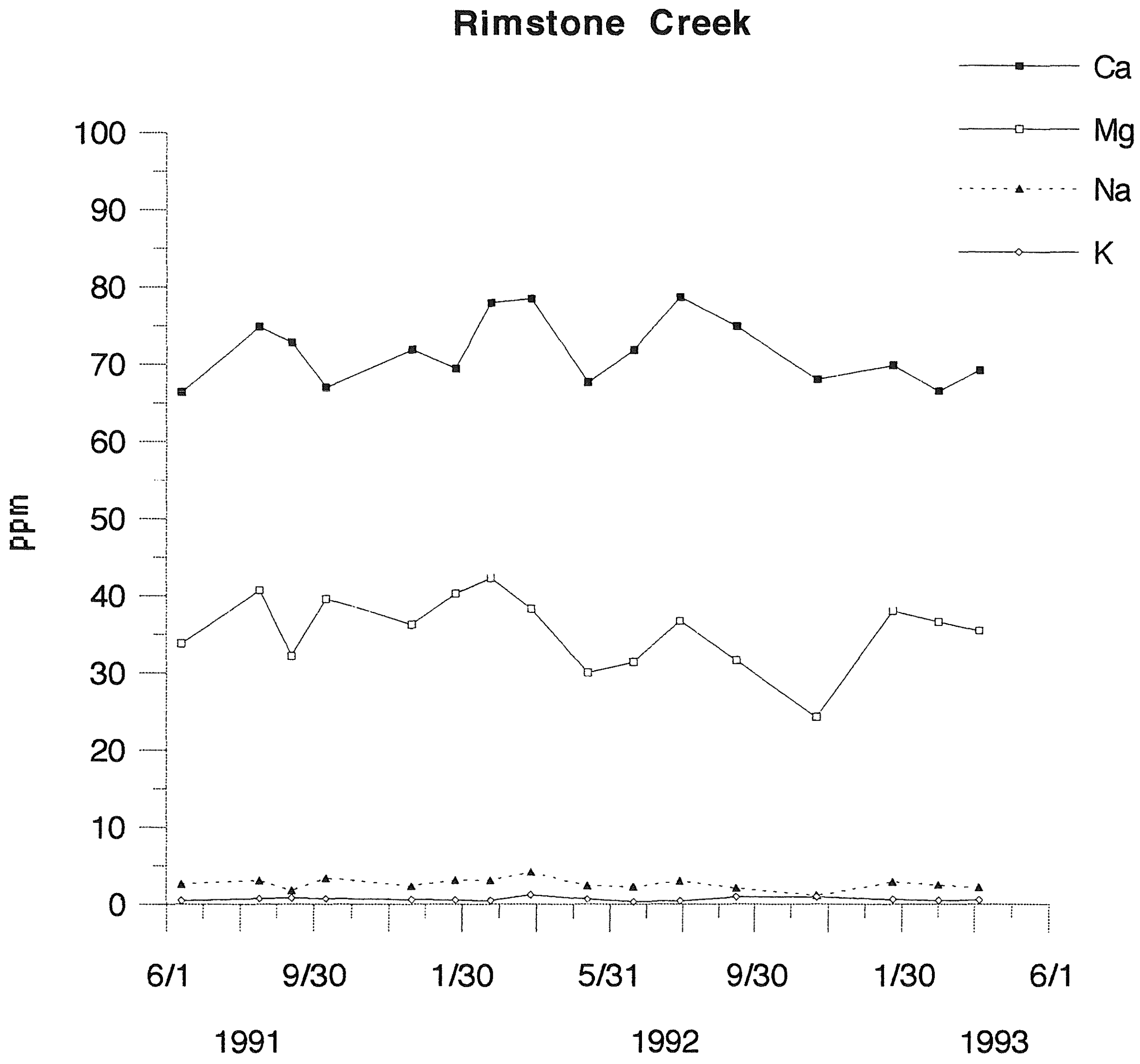


Figure 5.27. Cations at Rimstone Creek, 1991-1993.

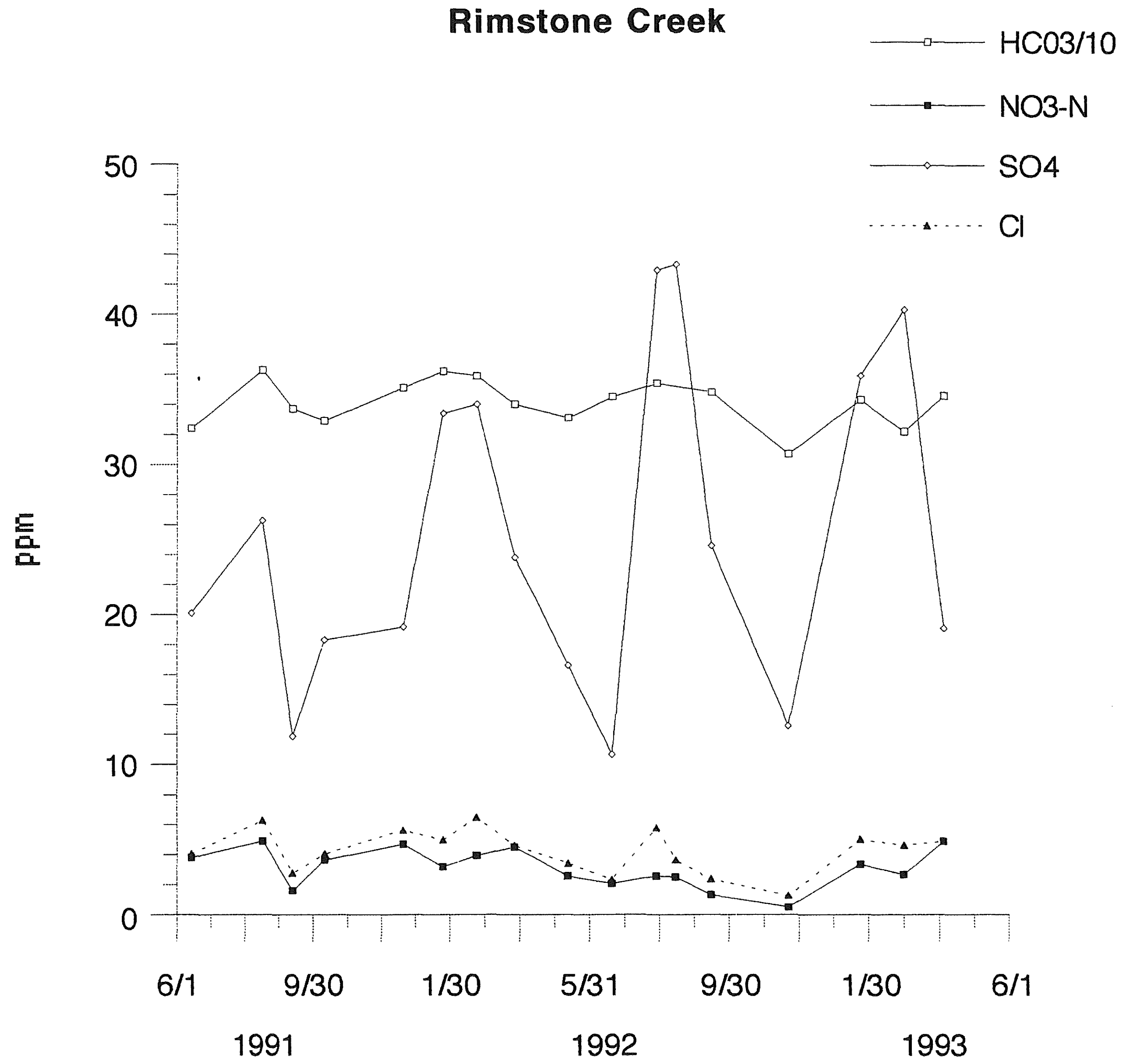


Figure 5.28. Anions at Rimstone Creek, 1991-1993.

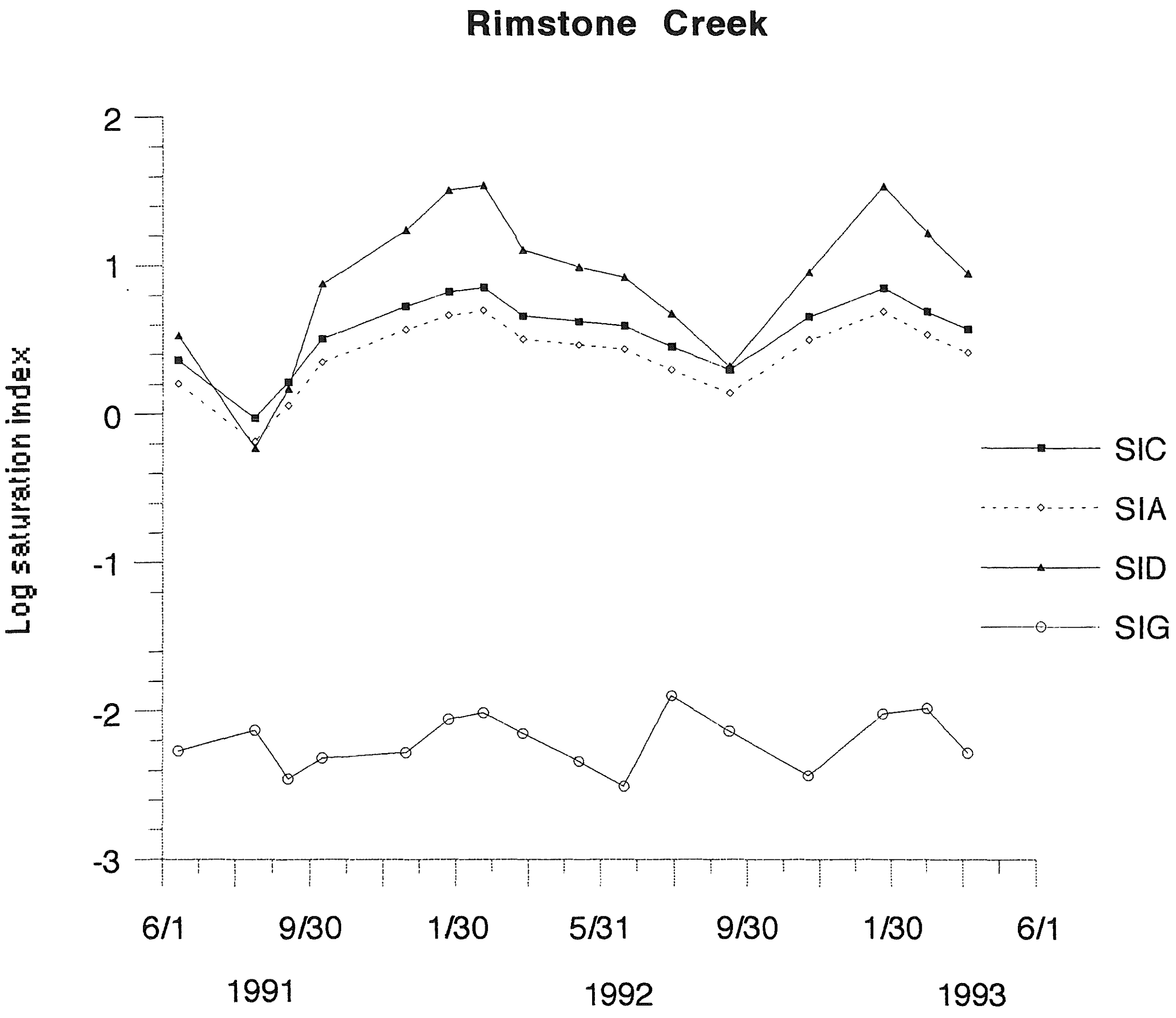


Figure 5.29. Saturation indices at Rimstone Creek, 1991-1993.

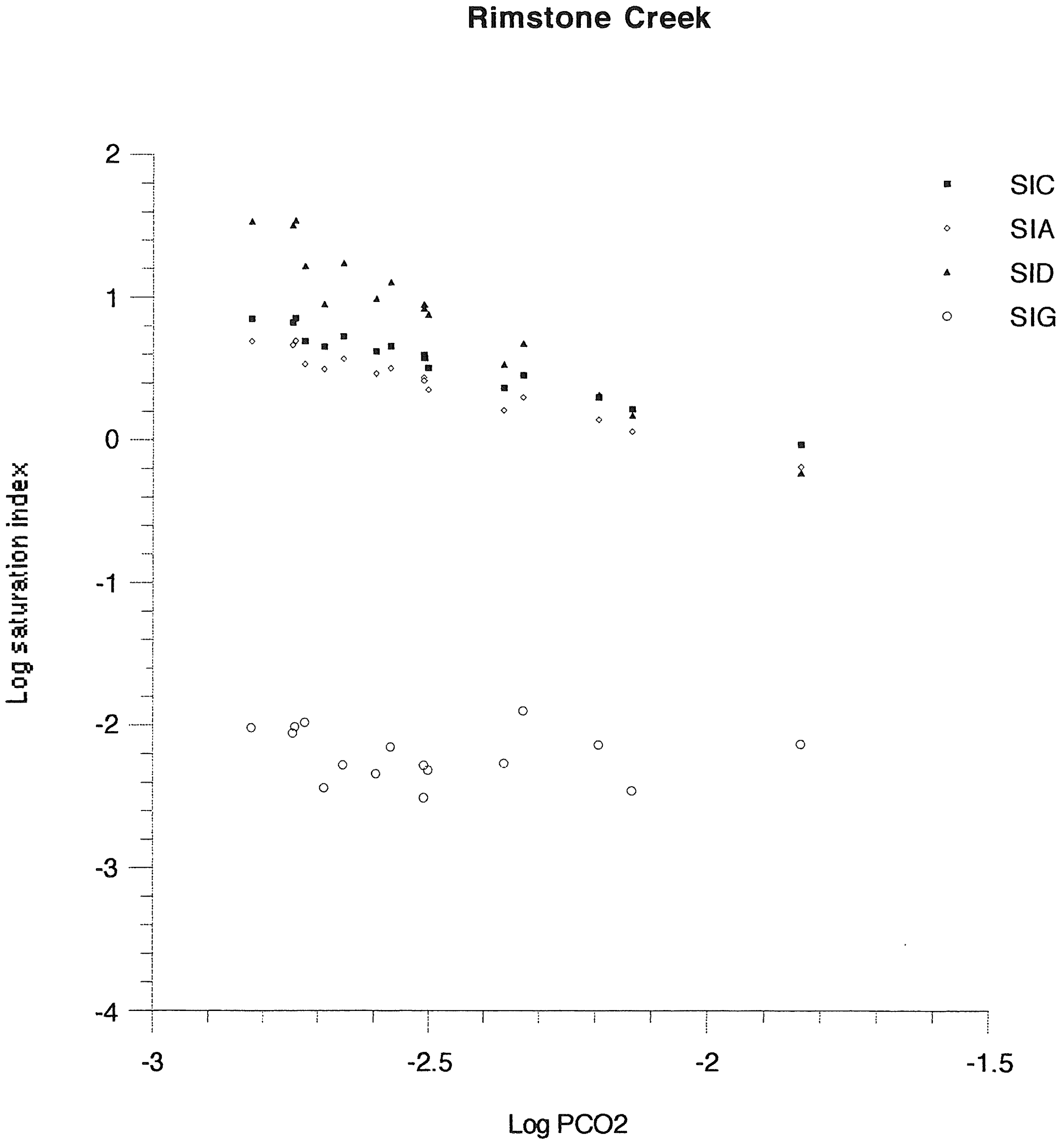


Figure 5.30. Log P_{CO_2} vs log saturation index for Rimstone Creek.

which shows considerable variation for major ions. However, there are some important subtleties to consider, the first being the anomalous water temperature.

The water temperature ranged 8.32 to 8.70°C with a mean of 8.49 ± 0.08°C and a low coefficient of variation of 1.0%. This is the lowest mean water temperature recorded at any cave site. It is tempting to suggest that the low coefficient of variation, combined with the low mean temperature, suggest that our previous estimate of 8.7°C for a deep cave temperature is too high.

This may be correct. If so, then the water temperature at Blue Lake and Turquoise Lake---however stable---may be high because of their location closer to the surface, which might place them within the thermal dampening depth for heat conduction within the bedrock, or within the relaxation distance for temperature fluctuations driven by advective heat transport from water and air combined with heat exchange resulting from phase changes (see Chapter 4).

However, there are at least two explanations to consider first before rejecting our current approximation of deep cave temperature. One possibility is that the measured temperatures are erroneous. This is rejected because the measurements were made carefully by total immersion of two calibrated ASTM Method 63C thermometers. These were randomly selected when it came time to perform measurements. We did not record which thermometer was used at each site, but the thermometers were cross-checked for consistency on a regular basis. (On most sampling trips, the thermometers were left outside their cases on the cave floor overnight between the first and second sampling days, and then read by flashlight before use.) A significant problem can arise if the temperature is measured with the thermometer only partly immersed---evaporative cooling can lower water temperature. This might not be a problem in the cave unless noticeable air currents were present. However, it was noticed that a wet thermometer tended to give colder temperatures than a dry one, during a period in which evaporation was occurring without noticeable air currents. This explanation is also rejected, because the thermometer was totally immersed in the sampling pool and read by flashlight.

The second possibility is that this section of the cave is anomalously cold. There could be a number of reasons. One speculative reasons is as follows. Water cascades over flowstone, losing an elevation of at least 20 ft over the 300 ft of passage preceeding the sampling site. Perhaps the water is cooled by evaporation. If this hypothesis is correct, it should be realitively easy to confirm it by measuring water temperature above and below the cascades.

SITES AT THE GARDEN OF THE GODS

Setting and Sampling Procedure

The Garden of the Gods is near the east end of Mystery II (Figure 2.1). It lies beneath the lower part of a hillside field (Figure 3.4) that is often planted in corn.

Four sites were sampled at the Garden of the Gods. Stalactite drips site GG1 and GG2 were sampled on a periodic basis. Flowstone drip sites GG3 and GG4 were sampled only once. An unnamed nearby stream in a passage beyond the Garden of the Gods was not sampled, in part because of time and accessibility constraints. This stream had a discharge of a few liters per minute the one time it was visited. It flows from east to west, traversing about 200 ft of a low, muddy passage. The stream sinks in sediments just east of, but about 10 ft below floor level of the main upper part of the Garden of the Gods. The stream apparently drains an area of agricultural grassland to the east of the gate at the driveway entrance to Mystery II (Figure 3.4). It is conceivable that this stream contains a component of infiltration from a cattle pond; the pond is about 400 ft from the gate, less than 200 ft from the east end of surveyed passage.

Stalactite drips site GG1 (hereafter, GG1) is a prominent stalactite above a flowstone ledge on the south side of the Garden of the Gods. Water drips from the stalactite into a low, broad stalagmite set on the edge of the east end of the flowstone.

Sampling was accomplished at GG1 by suspending a plastic bag across the flowstone. The bag was held in place by the stalagmite and a rock placed on one edge of the bag, away from the drip area. The bag was allowed to droop downward into a bucket to keep the bag from breaking as it filled. Most of the time, the drip rate was so low that it required several hours to obtain a liter sample and there was little danger of breakage. On many occasions, particularly during the winter, the drip rate was so low that the bag was placed in the evening and allowed to fill overnight to obtain one or two liters. The sampling method therefore has implications for the interpretation of (1) chemical parameters that are influenced by degassing of carbon dioxide and (2) water temperature. When the time came for actual sampling, the plastic bag was held upright from the top (which was twisted shut), perforated with a clean knife or scissors just above the water level, and by tilting the bag a fine stream was allowed to flow freely for a few seconds to ensure cleaning. The stream was then directed into the sampling bottles. An attempt was made to hold the bag so that as little contact with the hands occurred as possible, so as to minimize heat transfer (but we do not believe this was successful; see below). After the filling of sample bottles, the remainer in the bag was used for measurements of water temperature and conductivity. Water temperature was measured first. The thermometer (already equilibrated to air temperature of about 9.2°C) was inserted into the bag and the bag was gently swirled, then held sideways at an angle with the bulk of the bag resting on the floor. Rarely was there sufficient sample to ensure full immersion of the thermometer. A flashlight was finally used to read the temperature while attempting to keep the basal part of the thermometer (the part below about 15°C on a foot-long instrument reading to 40°C) submerged without allowing the water to spill. Conductivity was measured last with a probe that was completely submerged. A similar sampling procedure was employed for sites GG3 and GG4, which had even lower discharges and were sampled only once.

Stalactite drips site GG2 (hereafter, GG2) is a cluster of stalactites that have merged by growth, in part forming a curtain. The cluster hangs from the south wall of a major enlarged ceiling joint about 10 ft east of GG1. The water drips onto a large stalagmite (several feet high and one foot in diameter). Drip rate varies from perhaps a liter per day to tens of liters per hour. Sampling was accomplished by placing a plastic bag over a bucket and placing the bucket on top of the stalagmite. One end of the plastic bag was pulled beneath the bucket to protect the stalagmite. Much of the time, drip rates were sufficiently high to collect a few liters sample within half an hour. Site GG2 usually had sufficient water (4-5 liters) so that the thermometer could be fully immersed within the bag while in the bucket by tilting the bucket. Thus uncertainties about water temperature are less for GG2 than GG1.

Flowstone drips sites GG3 and GG4 are low-discharge drips from ceiling joints lined with flowstone. Site GG3 drips to a spot about a foot from the top of the stairs;

site GG4 drips onto the center of the floor grate at the constricted area below the stairs. The classification of the sites as flowstone drips is somewhat arbitrary---in each case the ceiling joint is abundantly lined with flowstone and the drips appear to come from the flowstone rather than from small stalactites set in the flowstone.

Geochemical Behavior

Time series plots of GG1 and GG2 are in Figures 5.31-5.34 and Figures 5.36-5.39. Plots of P_{CO_2} vs saturation indices of calcite, aragonite, dolomite, and gypsum are in Figures 5.35 and 5.40. A plot of NO_3-N and Cl for GG1 and GG2 is in Figure 5.41.

GG1 and GG2 are only 10 ft apart, but differ considerably in their chemical behavior. This behavior is not what one might expect on the basis of their discharge behavior alone. In general, we might expect low-discharge stalactite sites such as GG1 to have a less variable discharge and to have more stable water temperatures and chemistries than higher discharge stalactite drip sites. This is because we would also expect them to be fed by more diffuse or slow-flow sources. However, the GG2 site might actually be better classified as a flowstone-drip site rather than a stalactite site, because the water often seems to issue from the sides of the merged stalactites (and hence probably from unseen joints above) rather than from the stalactite tips. In contrast, at GG1 the water issues as a slow drip except at times of higher discharge, when some of the water may be coming down the sides of the stalactite.

The mean water temperature at GG2 was 9.34 ± 0.19°C (CV = 2.1%, n = 11). At GG1, the mean temperature was 9.66 ± 0.50°C (CV = 5.2%, n = 18). Part of the greater variability at GG1 might be interpreted as a function in the greater length in the time of sampling, during which the sample was equilibrating to ambient air temperature. We believe, however, that the sampling procedure resulted in transferral of heat from the hand through the bag into the water. The air temperature at the Garden of the Gods is usually about 9.20°C, which is lower than the recorded temperatures for GG1. Most of the variability of the water temperature shown on Figure 5.31 is therefore suspect and the temperature data must be considered to have error bars of at least 1°C.

Inspection of the time series plots for other variables shows that the chemistry at GG1 is generally more variable than that at GG2. Plots of GG1 chemistries tend to exhibit five spikes (see Figure 5.31 for Ca and Mg and 5.32 for HCO_3, Cl, and SO_4). The first two were during 1991, for which we have precipitation data only for Spring Valley. The 8/17/91 peak correlates with totals of 0.2, 0.0, 0.8, 0.4, 0.8 and 0.3 in of daily precipitation on 8/13 to 8/18, respectively, at Spring Valley (Table 6.4). The second event on 12/20/91 correlates with totals of 1.0, 0.1, 0.2, and 0.1 in of daily precipitation on 12/12, 12/13, 12/20 and 12/21, respectively, at Spring Valley (Table 6.4). The third peak was on 5/13/92, for which no data are available at Spring Valley. The fourth peak was on 11/21/92, at the time of the previously noted November storm in which 2.18 in fell from November 19-21. The 5th peak was on 4/4/93, following the rain on snow that produced the March flood.

From these observations, we conclude that the peaks on GG1 plots are associated with recharge events in which precipitation overcomes soil-moisture deficits to produce infiltration. Further, the infiltrate displaces stored water with higher solute concentrations. The peaks are not readily distinguishable on the plots for GG2,

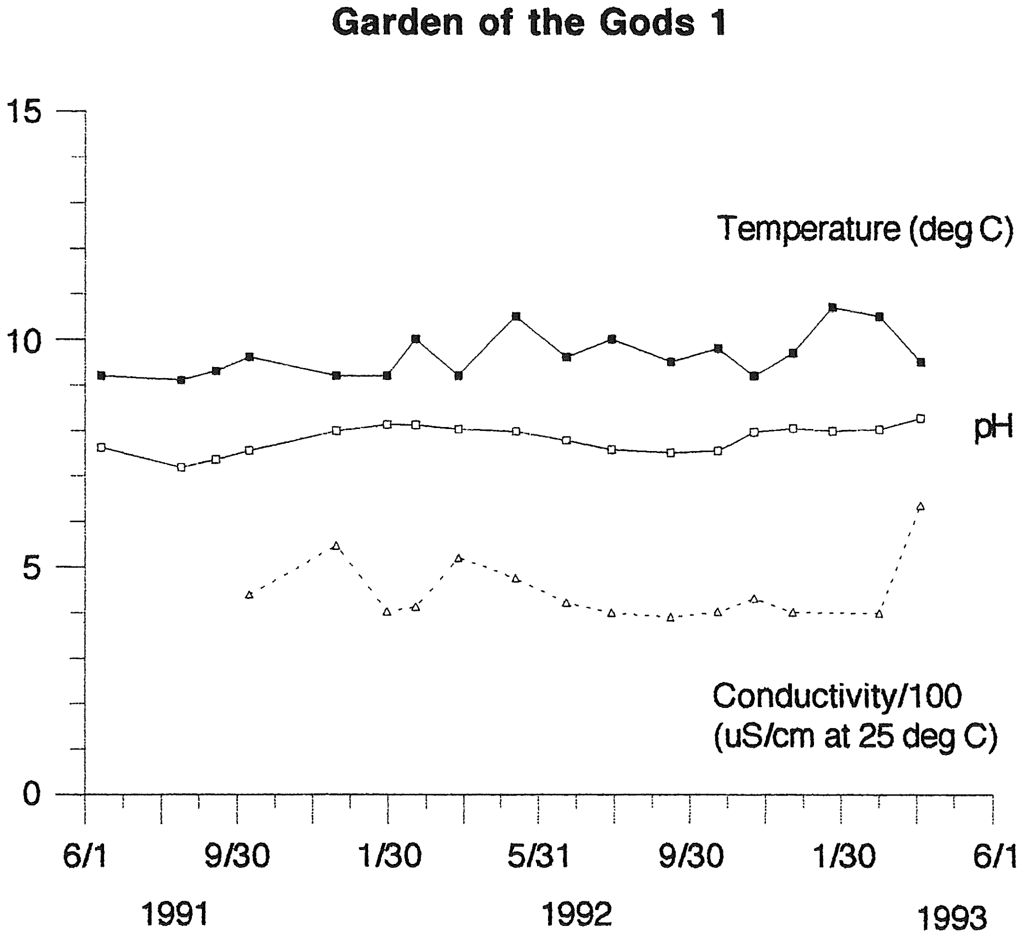


Figure 5.31. Field Parameters at GG1, 1991-1993.

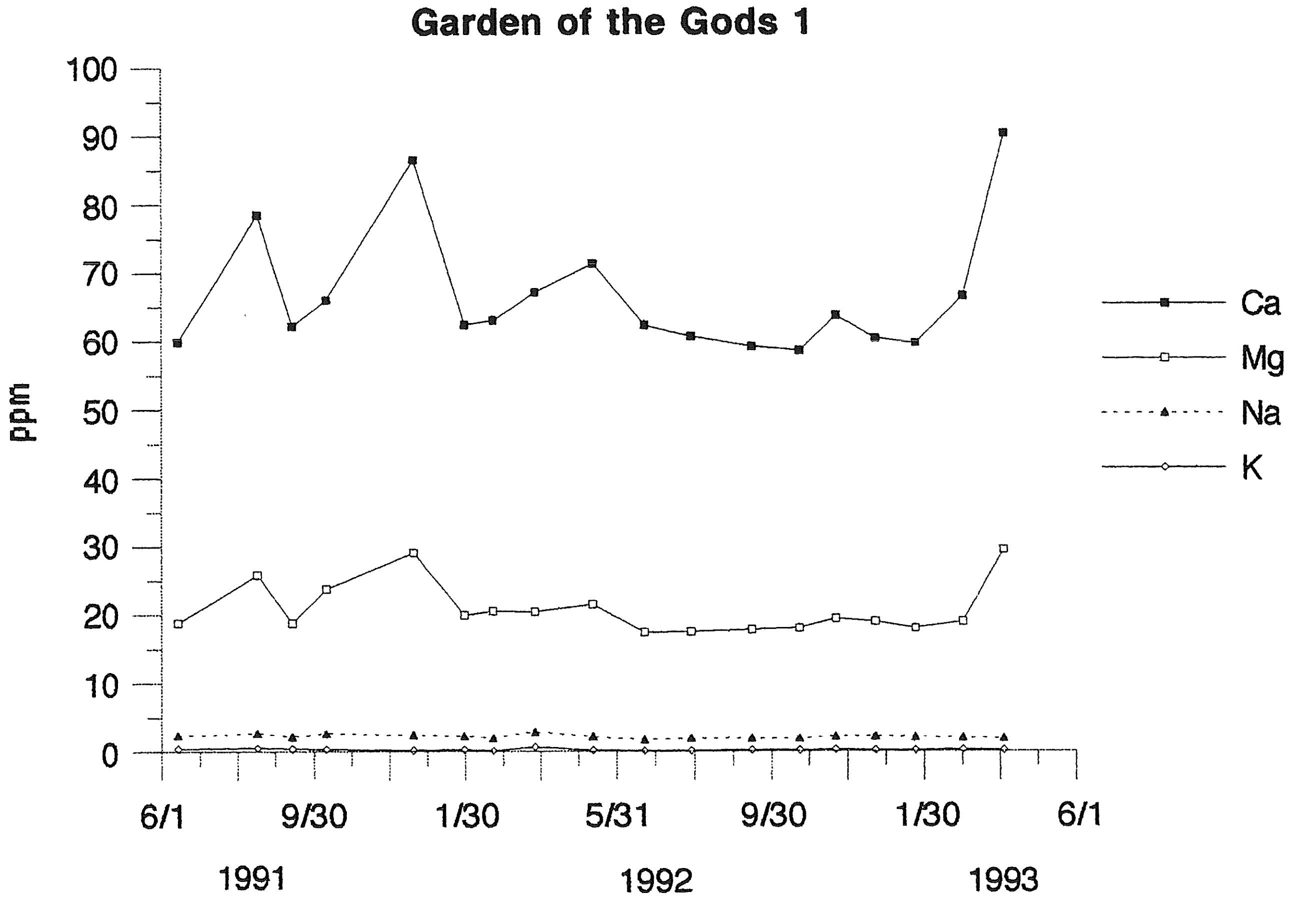


Figure 5.32. Cations at GG1, 1991-1993.

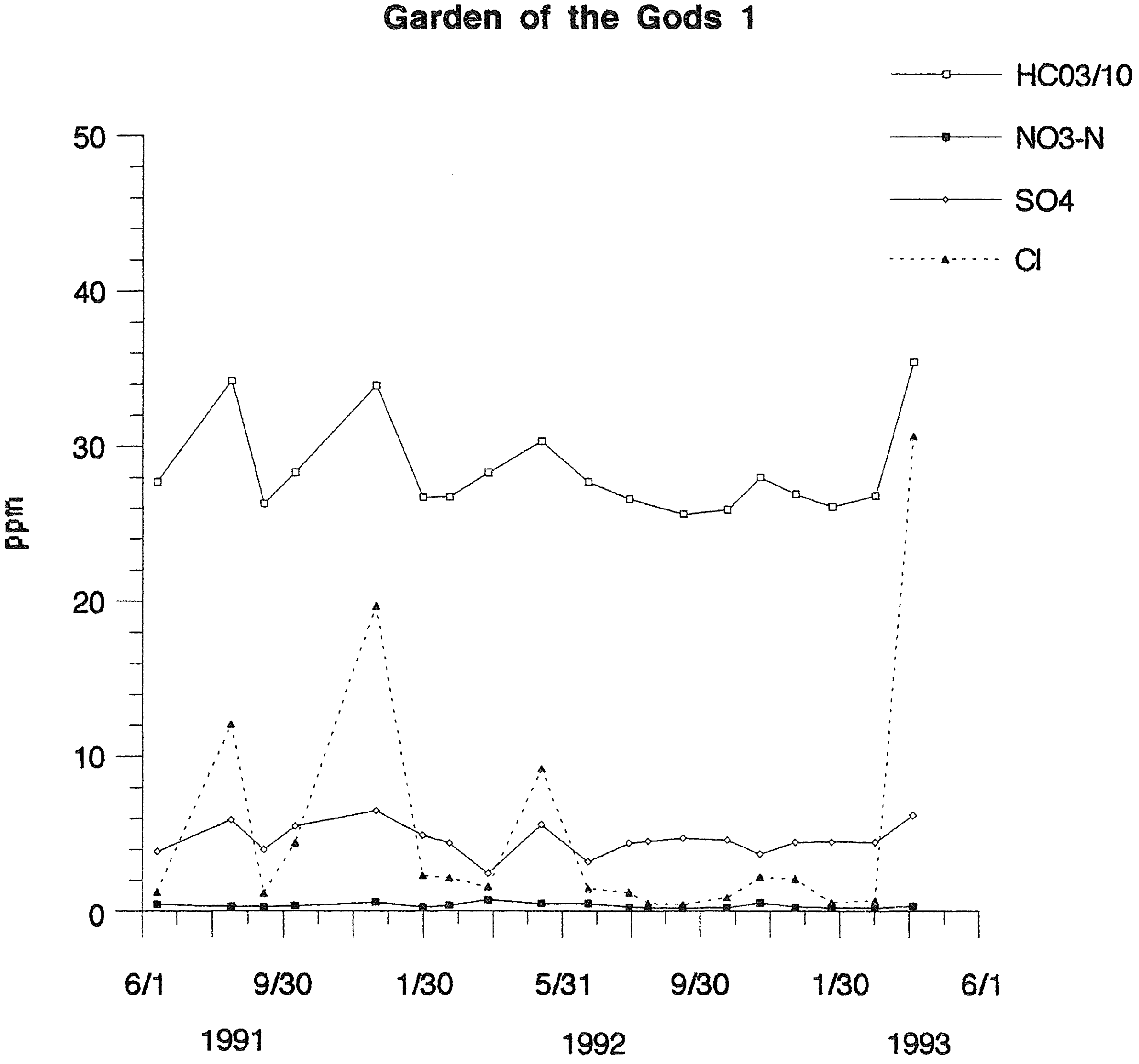


Figure 5.33. Anions at GG1, 1991-1993.

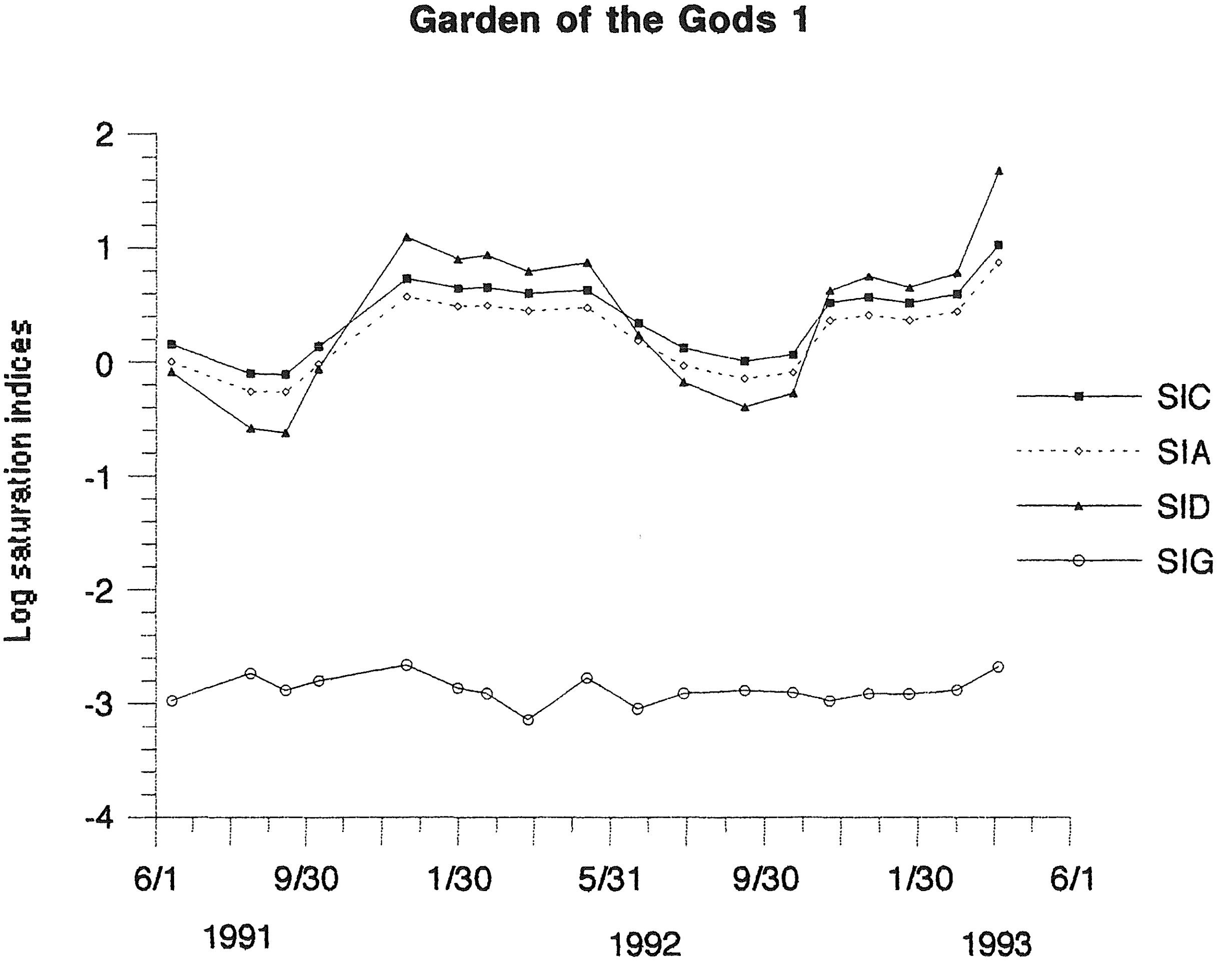


Figure 5.34. Saturation indices at GG1, 1991-1993.

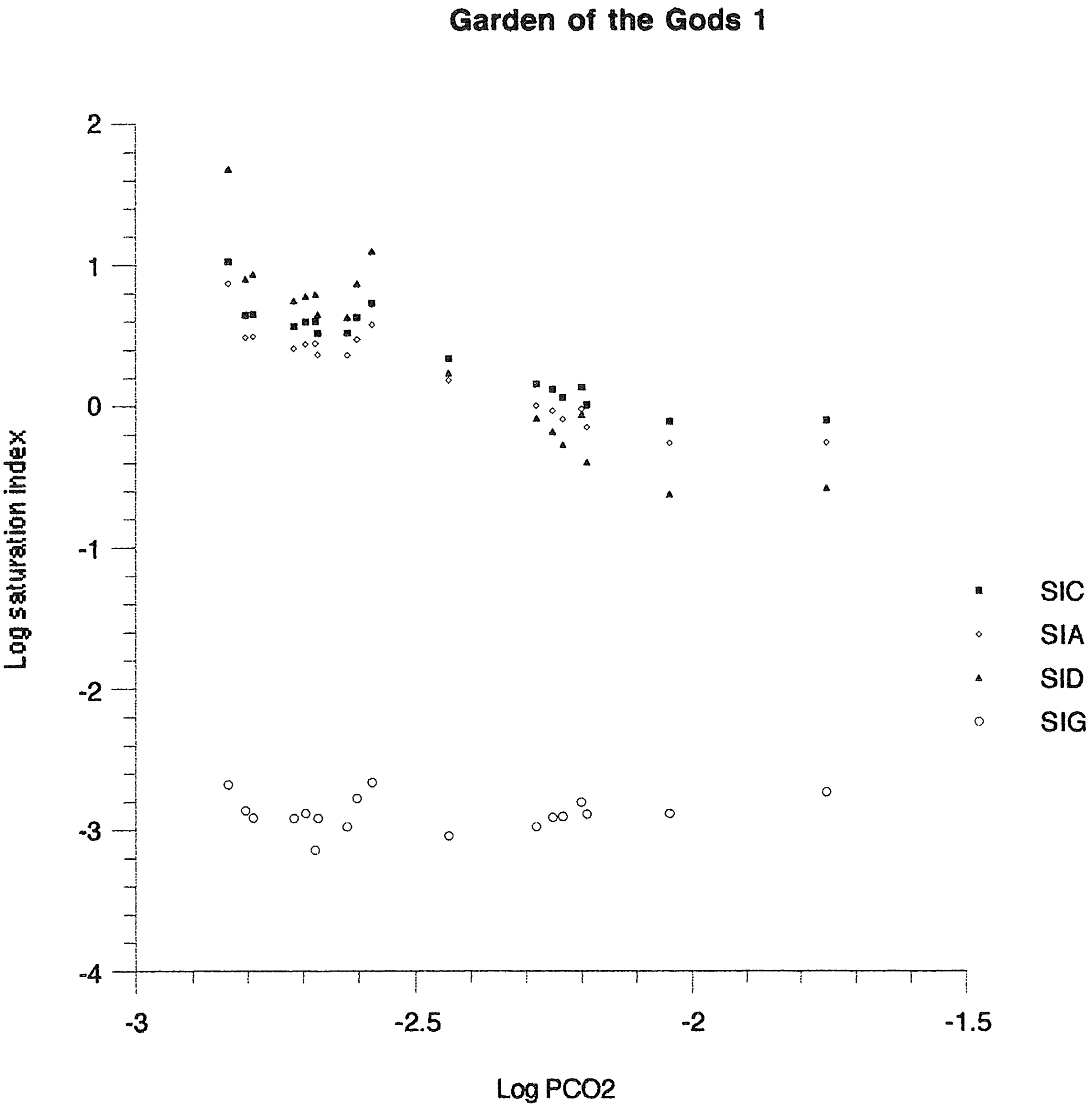


Figure 5.35. Log P_{CO_2} vs log saturation index for GG1.

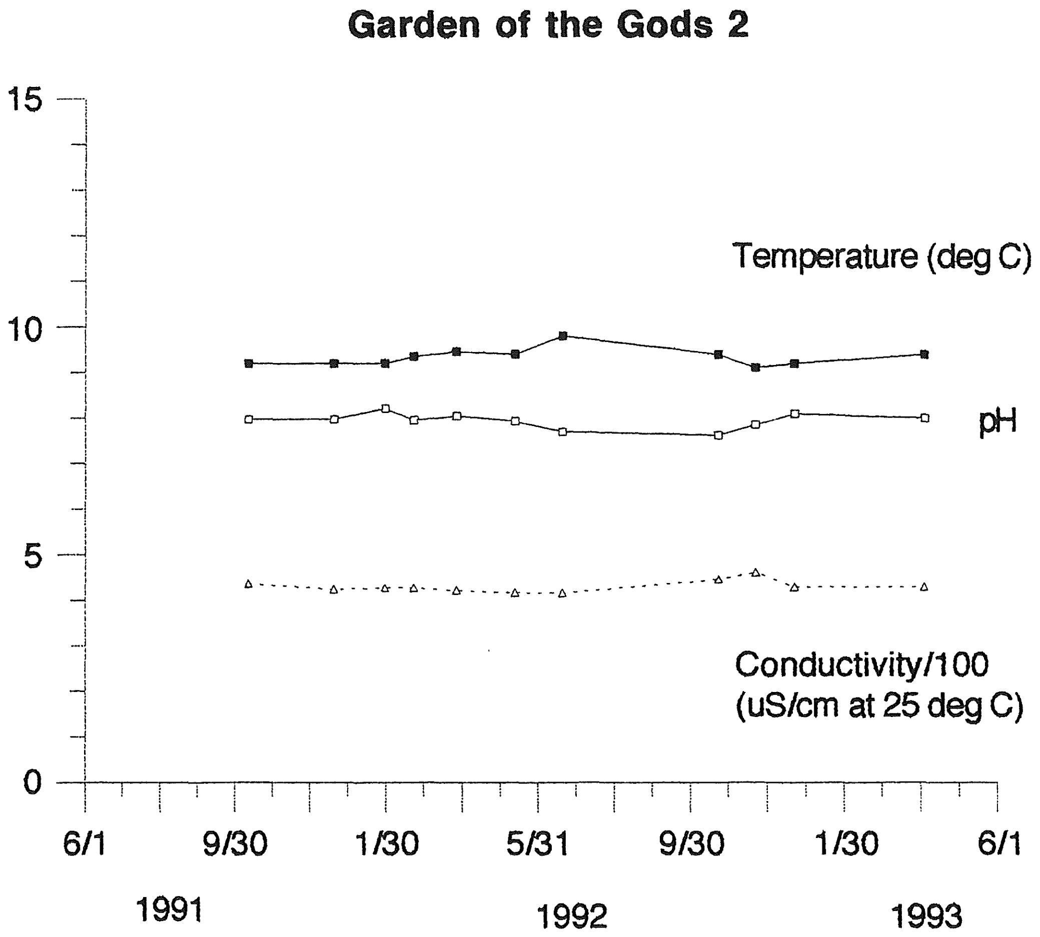


Figure 5.36. Field Parameters at GG2, 1991-1993.

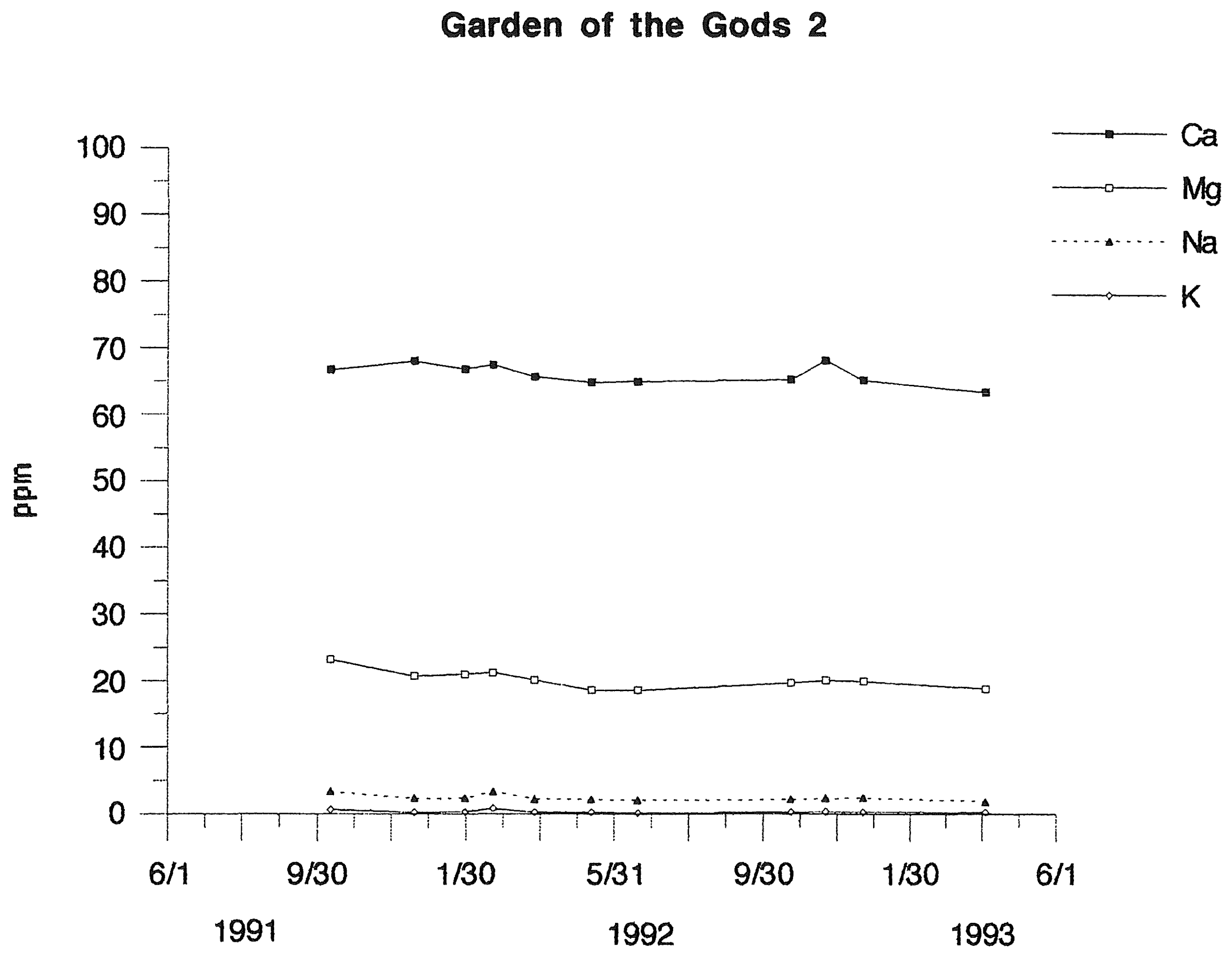


Figure 5.37. Cations at GG2, 1991-1993.

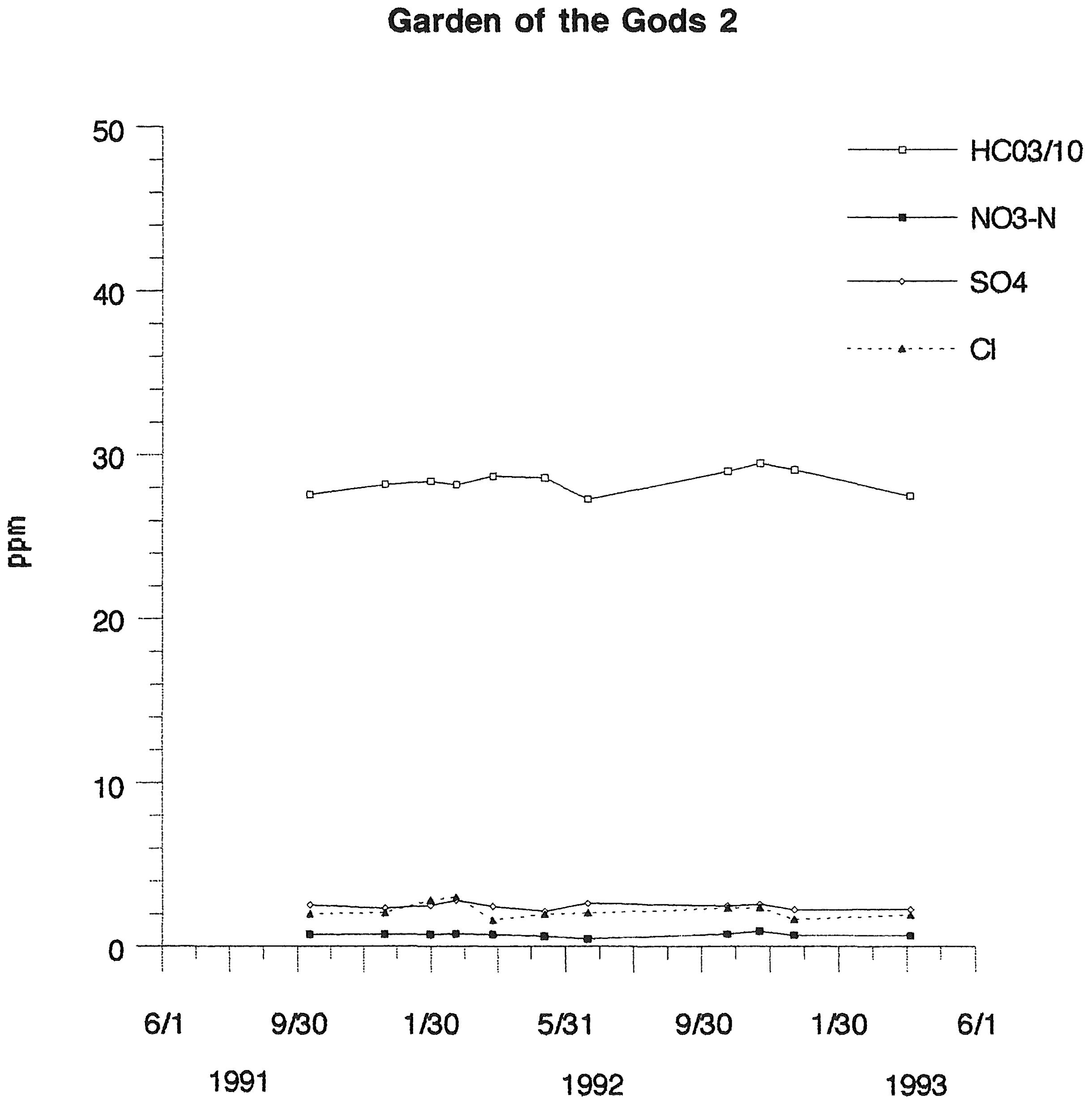


Figure 5.38. Anions at GG2, 1991-1993.

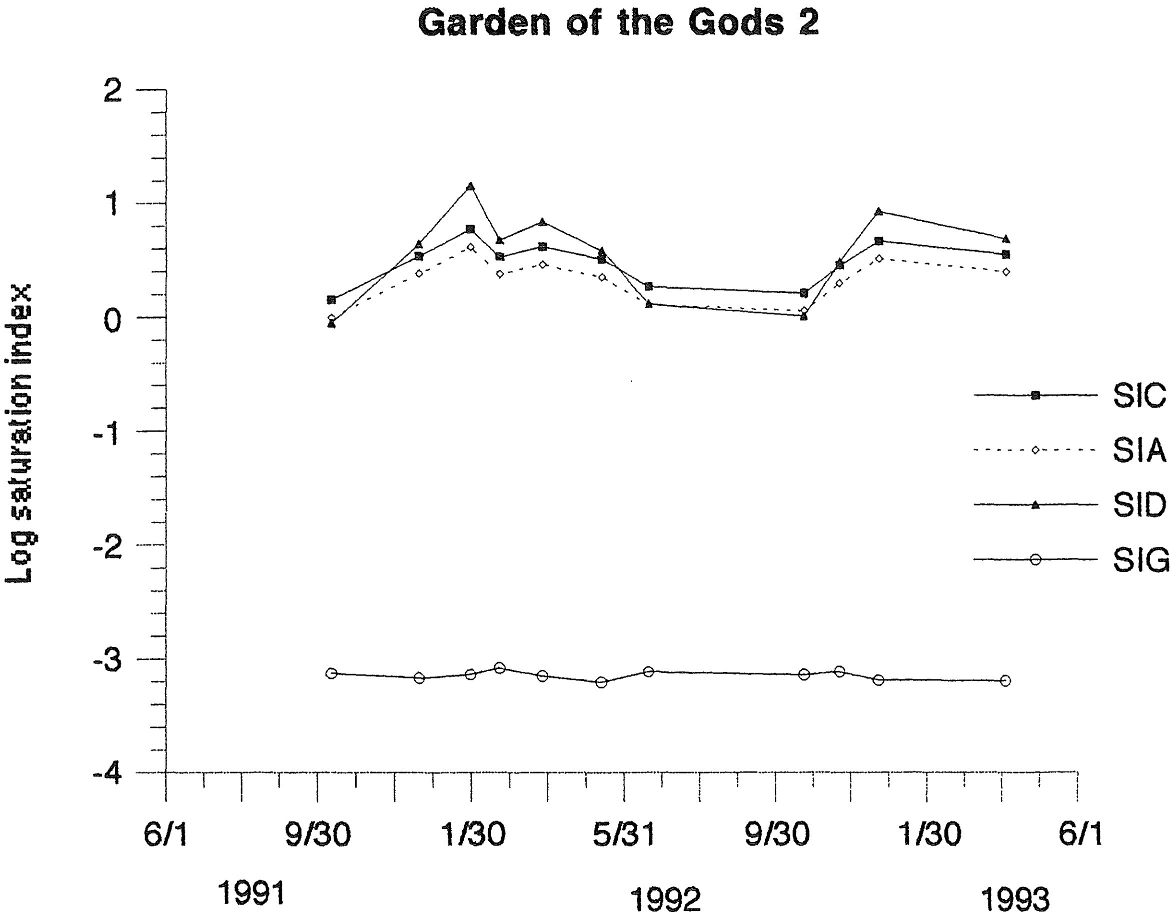


Figure 5.39. Saturation indices at GG2, 1991-1993.

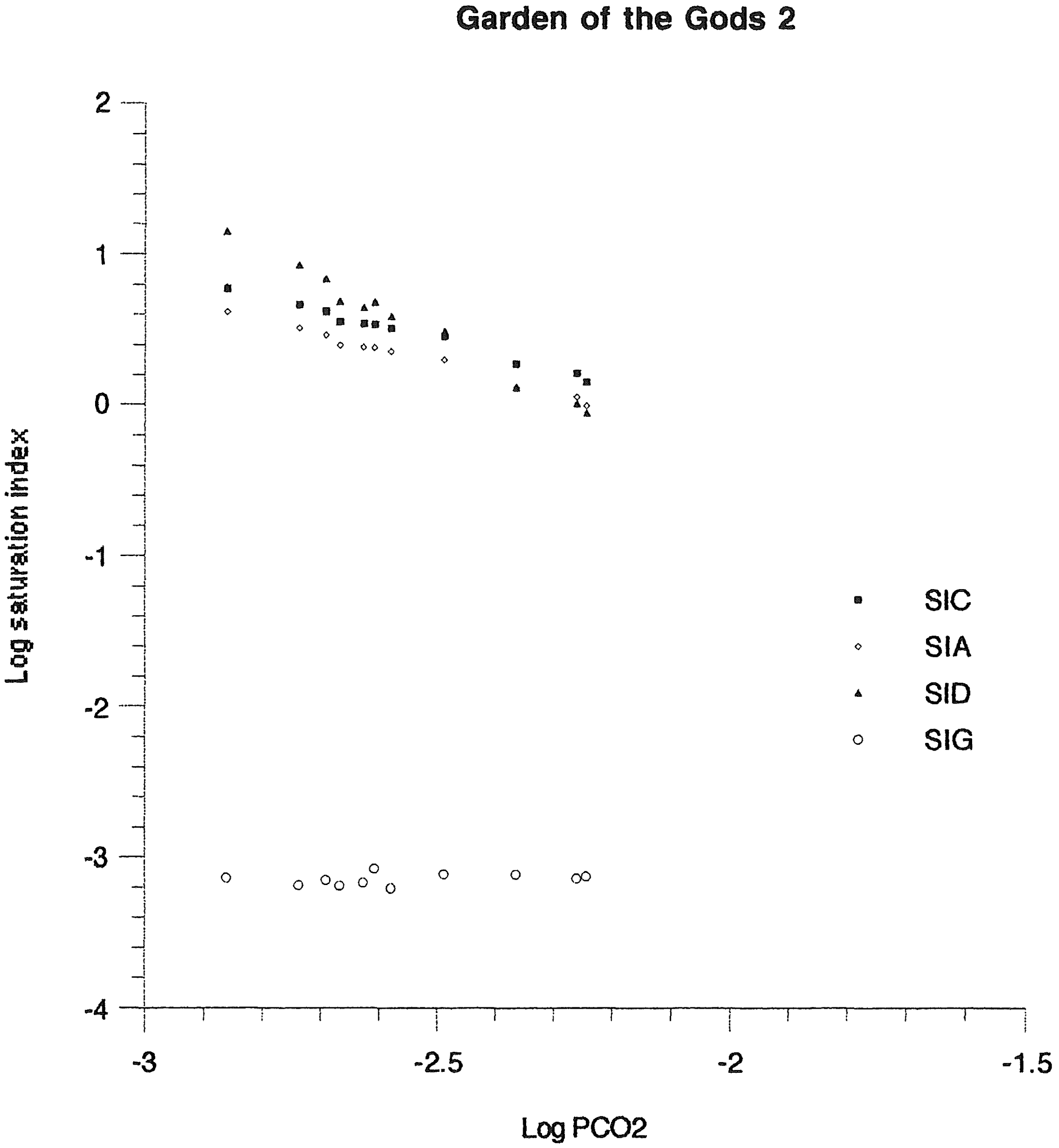


Figure 5.40 Log P_{CO_2} vs log saturation index for GG2.

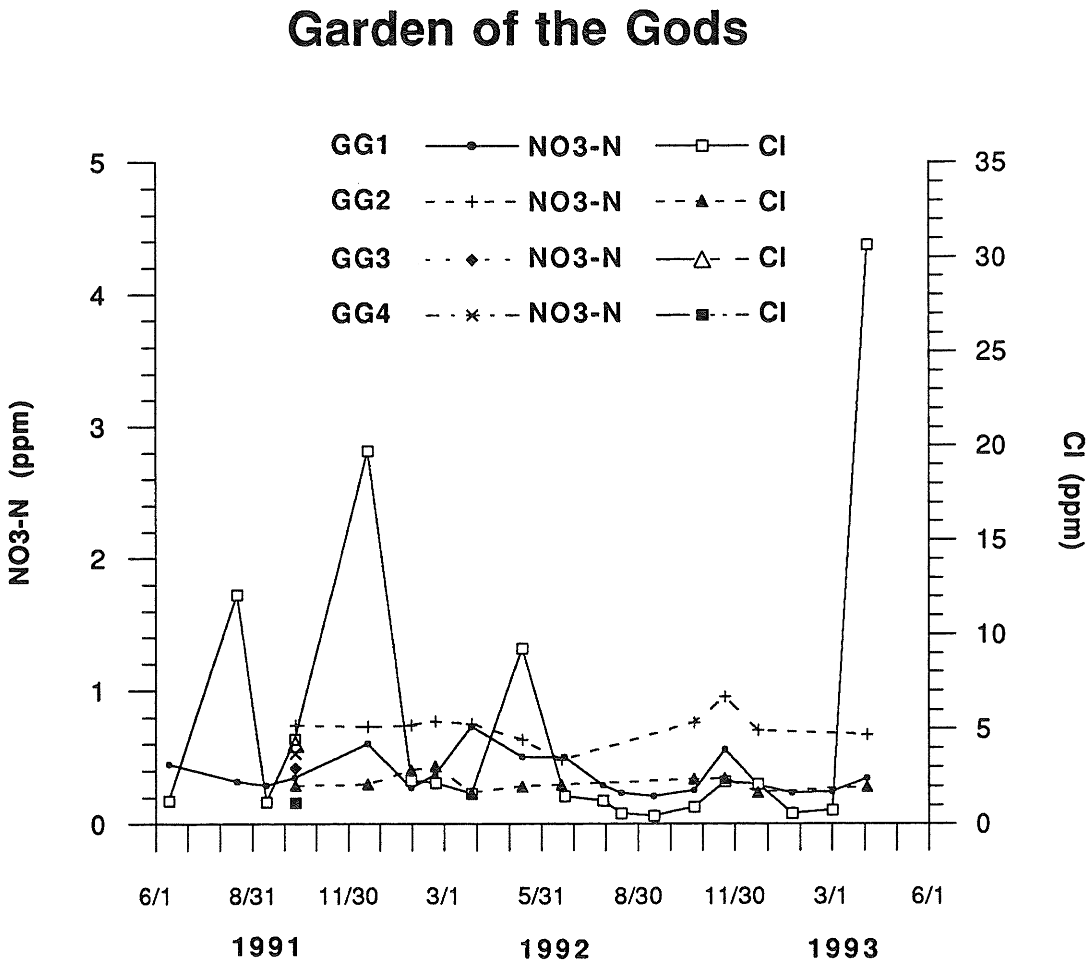


Figure 5.41. NO_3-N and Cl at GG1 and GG2.

except perhaps for the 11/21/92 sampling. On that date, there is a slight peak for Ca (Figure 5.36) and HCO_3 (Figure 5.37), and a barely distinguishable peak for NO_3-N (better seen in Figure 5.41).

The consistent rises in concentrations of Ca, Mg, and HCO_3 for GG1 following recharge events suggests that the water is primarily displaced water rather than event water. If this is true, then Cl, which shows very large rises in concentration (1.22 up to 12.06 mg/l for peak 1 and 0.7 up to 30.6 mg/l for peak 5, for example) must be stored in significant quantities in the deeper soil, loess, subcutaneous zone, or fractured bedrock above the cave. The mobilized chloride is unlikely to be chloride stored in the uppermost soil, because water transporting that chloride would be expected to be event water with lower concentrations of Ca, Mg, and HCO_3.

There is a further complication to be considered regarding the possible influence of ion exchange processes. If the source of chloride were from road salt (as NaCl) from the nearby gravel road, then we would expect a plot of Na meq/l vs Cl meq/l to plot as a 1:1 line in the absence of processes that would remove Na, such as ion exchange processes in soil or loess. Such plots (Chapter 4, Figure 4.23) show that many Mystery Cave waters plot above the line, with an excess of chloride. The plot for stalactite drips GG1 and GG2 (Figure 4.29) shows that Cl concentrations are essentially independent of Na. Either Na is being lost, or the Cl has a different source. KCl-based deicing salts are in use in some areas; we do not know what is being used locally or whether it varies from year to year, as happens in some areas of the country. KCl-based fertilizers (muriate of potash) are also used, but as a potassium source for crops. If the Cl is derived from KCl, then we would expect K concentrations to rise, unless K were being lost. (Plots of K meq/l vs Cl meq/l (not shown) depict very large scatter, with essentially no correlation between K and Cl; chloride varies a great amount and potassium very little.)

Potassium is relatively insoluble in natural waters and is readily exchanged in soils for calcium. This process would increase the amount of calcium in solution. It must be accompanied by increases in HCO_3 or othe anions to maintain electroneutrality. The process will tend to consume soil CO_2. We suspect that the overall process is unlikely to be fast enough to be the primary reason for the rises in concentration of Ca and HCO_3 associated with the five peaks, however.

Nitrate shows at best a minor response to the recharge events that produced the peaks in concentrations of Ca, Mg, HCO_3, Cl, and SO_4 (see Figure 5.41). Three of the five events have minimal associated peaks or rises in NO_3-N, and there is an additional minor peak in late March of 1992. It is reasonable to suggest that nitrate concentrations are higher within the tributaries to GG1 at points near the surface, because manure spreading and nitrate fertilization by farmers is ubiquituous. If this speculation is correct, the residence time for water in the upper part of the flow paths are sufficiently long for denitrification to reduces nitrate concentrations.

Figure 5.33 shows that SO_4 rose concurrent with 4 of the five peaks for GG1 (it fell for the November, 1992 peak). Sulfate is relatively low (2.44-6.5 mg/l, with a mean of 4.62 ± 1.0 mg/l, $n = 19$; $CV = 21.8\%$) at GG1 compared to other sites at Mystery Cave.

On the single day sampled, 10/12/91, the chemistries of GG3 and GG4 were very similar to those of GG1 and GG2. The primary difference is that Cl at GG3 was 4.21 mg/l, which is close to that of GG1 (4.43 mg/l) and higher that that for GG2 2.03 mg/l) and GG4 (1.11 mg/l).

Comparison of the chemistries of GG1 and GG2 (see tables in Appendix 3) shows that the two sites have similar overall chemistries (the means are not significantly different except for Cl, SO_4, and NO_3, which are all larger at GG1). The main difference---expressed differently than the statement that there is a distinct correlation of peaks in chemistry for GG1 with peaks in recharge---is that the chemistry of GG1 is much more variable.

Summary and Recommendations

It is possible to summarize these observations in a number of ways. Here we regard the two sites as independent black boxes. The only input data we have are the timings of precipitation, which we believe led to significant recharge for five events. For outputs we have relative discharges based on scattered, purely qualitative observations. We also have measurements of field parameters and chemistry. The temperature data are too coarse for GG1 (error bar of at least 1°C) to have interpretative value. From the inputs and outputs previously described, we offer the following tentative model.

GG1 at low flow is primarily a stalactite drip site. Following larger recharge events, GG1 augments its discharge with displaced water from sources that contain a significant component of Cl. These sources lie beneath the upper layer of soil, but within soil, loess, the subcutaneous zone, or fractured rock above the cave, where water is stored for a relatively long period of time. That time is sufficient to increase concentrations of Ca, Mg, HCO_3, and SO_4. It is also sufficient to allow denitrification if significant nitrate is being supplied to the fields in the form of manure or fertilizers.

GG2 at low flow is primarily a stalactite drip site or a flowstone drip site; we can't tell which because the drips originate too high within the enlarged ceiling joint. On the basis of hydrologic behavior, much of the time GG2 might be better characterized as a flowstone drips site or even a ceiling drips site. GG2 responds more rapidly to smaller recharge events than does GG1. It has a more variable and larger average discharge. The source area of GG2 probably lacks a major source of Cl (speculatively, it may be an uncultivated area of grass or grassy brush between the Garden of the Gods and Coon Lake Drips; see chapters 3 and 9). Were much Cl stored within that source area, it probably would have been flushed by one or more of the observed primary recharge events.

The model could be tested, in part, by installing continuous data acquisition systems to measure drip rates, water temperature, and conductivity, in conjunction with periodic sampling for major and minor ions. Samples of road salts and fertilizers from adjacent fields should be obtained. It also would be useful to sample the unnamed stream below the Garden of the Gods. Finally, we recommend a trace from the linear depressions in the roadway near the gate at the entrance to Mystery II. The latter project might best be done at a time in which the road could be excavated to (1) determine the extent of underlying soil and loess, and (2) assess the collapse potential of the road at these locations. Any such trace should be designed to minimize the potential effects on drip sites were the water to drain into Mystery Cave.

CHAPTER 6

THE SURFACE RECORD: PRECIPITATION AND AIR TEMPERATURE

INTRODUCTION

This chapter presents precipitation and air temperature data as recorded at the Weather Station on the South Branch of the Root River in parts of 1992 and 1993. Because the record is incomplete, the data are supplemented by available data from a cooperative observer station in Spring Valley, Minnesota. That station measured precipitation as daily or monthly totals. Spring Valley is approximately 6 miles north-northwest of the Mystery Cave Weather Station. At the time of preparation of the tables, data were available only through September, 1993 for Spring Valley and through December, 1993 for the Weather Station.

Elsewhere within this report, the data from Spring Valley are used sparingly, mostly as supporting evidence in the interpretation of time series plots for periods of missing data. In these instances, the primary questions were:

(1) Did precipitation occur before or concurrent with observed changes in monitored parameters (stage, discharge, chemical variables) at Mystery Cave?

(2) Was precipitation widespread---i.e., was it likely to have occurred also at Mystery Cave?

(3) Was precipitation of sufficient magnitude to have led to recharge?

We make no attempt to answer these questions for each event. We do, however, provide the data in tables to help readers interpret the time series plots, particularly for time periods not discussed. Our answers to the questions are evident in Chapters 5 and 7-10, for those events which we do discuss in detail (for example, the November 19-21, 1992 recharge event and the March 30-April 2, 1993 recharge event).

Measurements of air temperature from the Weather Station on the South Branch of the Root River are presented in summary form as yearly plots below. More detailed plots are used in interpretations of the temperature of recharge (for the November 19-21 event; see Chapter 7), and the timing and extent of insolation-driven snowmelt and subsequent recharge (for the period preceeding the March 30-31 event; see Chapter 9 on Coon Lake Drips). Those measurements are not tabulated here (because they consist of one data point per half hour), but are available in computer files which include all of the data from each monitored site.

PRECIPITATION AND AIR TEMPERATURE AT THE WEATHER STATION

The Weather Station was installed on June 24, 1992. Monthly precipitation is presented in Table 6.1 for available periods of 1992 and 1993. Daily precipitation is in Tables 6.2 (1992) and 6.3 (1993). Hourly precipitation (the sum of the previous hour's precipitation) is plotted for 1992 and 1993 in Figures 6.1 and 6.2. Air temperature (at half hour intervals) is plotted for 1992 and 1993 in Figures 6.3 and 6.4. Gaps in the record for air temperature show when precipitation and other data were lost. Data were lost when power was interrupted or the storage module failed to recover the data during the downloading procedure.

The primary observation to make is that 1993 was an unusually wet year in the midwest. This is readily apparent in the data for the Mystery Cave Weather Station. From January to mid March the weather was cold and there was little melting of the snow cover. In mid March significant melting occurred, but this primarily ripened the snowpack and produced little surface runoff. At the end of the month some runoff or internal melting beneath the snow cover occurred, resulting in cyclic recharge (daily melt and freeze cycles) to such sites as Coon Lake Drips (Chapter 9, Figure x). On March 30, 1993, a major storm dumped several inches of rain on the snowcover, producing rapid and extensive flooding throughout southeast Minnesota. The following months of the spring and summer were extremely wet. Major tributaries to the Mississippi and then the Mississippi itself flooded extensively. At Mystery Cave, the Root River was within a foot of its banks most of the summer and left its banks at least three times for short periods. Further details appear within the context of discussions of the hydrology of Flim Flam Creek, Blue Lake, and Coon Lake Drips (Chapters 8-10).

PRECIPITATION AT SPRING VALLEY

The record at Spring Valley is presented in Tables 6.4-6.6, which show daily and monthly totals for 1991, 1992, and 1993. These data are plotted as daily precipitation totals by year in Figures 6.5-6.7.

COMPARISON OF PRECIPITATION

Figure 6.8 plots daily precipitation at Spring Valley vs daily precipitation at the Root River Weather Station for 1992. Points are plotted only for days on which both stations had records. Figure 6.8 appears to show that if it rained at Spring Valley, there was a reasonably good chance that it also rained at the Weather Station at Mystery Cave. This is actually misleading; on 25 days out of 61 days of precipitation, one station recorded no rain and the other did. The relationship for days on which both stations recorded precipitation is approximately linear, with much scatter at higher precipitation totals. The relationship may be expressed as

$$P_{RR} = 0.82\,P_{SV} + .05$$

with a correlation coefficient r = 0.82, where P = precipitation, RR = Root River station, and SV = Spring Valley. The correlation is higher than one would expect if

Table 6.1. Monthly precipitation at the Root River Weather Station, 1992 and 1993.

Monthly Precipitation at the Root River Weather Station

Year	Month	Days not Covered	Monthly Precipitation (inches)
1992	June	1 to 24	0.00
	July		4.11
	August		2.77
	September		5.45
	October		1.11
	November	25 to 30	4.71
	December	1 to 3; 22 to 31	0.71
1993	January	1 to 6	0.80
	February		0.25
	March		2.71
	April		5.32
	May		7.89
	June		3.88

Table 6.2. Daily precipitation at the Root River Weather Station, 1992.

Julian day 1992	Daily Precipitation (inches)
184	0.04
185	0.01
189	0.04
190	0.79
191	0.25
193	0.07
194	0.5
195	0.72
197	0.03
201	0.43
204	1.15
205	0.02
207	0.02
211	0.04
215	0.34
219	0.15
220	1.15
224	0.19
225	0.02
230	0.33
231	0.01
238	0.48
246	0.71
249	0.7
251	0.29
253	0.58
257	0.12
258	2.27
260	0.68
281	0.07
282	0.56
283	0.03
289	0.04
290	0.02
291	0.04
293	0.02
294	0.15
305	0.13
306	1.41
307	0.9
308	0.01
310	0.01
313	0.03
315	0.02
317	0.02
324	0.83
325	1.31
326	0.07
345	0.02
349	0.23
350	0.46

Table 6.3. Daily precipitation at the Root River Weather Station, 1993.

Julian day 1993	Daily Precipitation (inches)	Julian day 1993	Daily Precipitation (inches)
21	0.15	128	0.04
22	0.19	129	0.21
23	0.1	130	2.33
26	0.37	134	0.06
40	0.1	137	0.71
41	0.05	139	0.01
43	0.01	143	0.93
44	0.01	144	0.03
52	0.01	146	0.1
59	0.07	147	0.02
60	0.12	148	0.02
74	0.16	149	0.49
78	0.11	150	0.72
81	0.16	152	0.17
82	0.2	153	0.3
89	0.62	158	1.54
90	1.09	159	0.2
91	0.16	163	0.05
97	0.39	164	0.35
98	0.4	167	0.38
100	0.13	168	1.11
101	0.15	169	0.89
103	0.3	170	0.33
104	0.26	171	0.01
105	0.45	174	0.29
106	0.16	175	0.1
108	0.55	179	0.13
109	1.32	180	1.04
110	0.48	183	0.01
116	0.02	184	0.38
117	0.55	186	0.07
121	0.56	187	0.02
122	0.13	188	0.01
123	0.73	189	0.31
124	0.65	190	0.27
126	0.13	191	0.41
127	0.01	192	0.29

Table 6.4. Daily and monthly precipitation at Spring Valley, 1991.

Month	Day	Daily Precipitation	Monthly Precipitation
January	5	0.3	
	11	0.2	
	22	0.1	0.6
February	13	0.1	
	18	0.1	
	26	0.1	0.3
March	1	0.3	
	12	0.3	
	17	0.1	
	20	0.5	
	21	0.1	
	22	0.8	
	23	0.2	
	27	0.4	
	28	0.1	2.8
April	8	0.7	
	9	0.1	
	12	0.8	
	14	0.7	
	18	0.8	
	19	0.2	
	22	0.2	
	26	0.5	
	27	0.7	
	29	1.2	5.9
May	3	0.1	
	5	1.3	
	8	0.4	
	13	0.2	
	15	0.8	
	16	0.4	
	17	0.8	
	18	0.3	
	23	0.4	
	25	0.6	
	26	0.2	
	28	0.1	
	30	0.1	
	31	1.2	6.9
June	10	0.7	
	13	0.1	
	14	0.4	
	15	0.3	
	30	0.1	1.6
July	1	0.5	
	4	0.1	
	7	1.4	
	11	1.8	
	17	3.1	
	20	0.5	
	22	0.7	
	27	0.1	
	28	0.4	
	29	0.1	8.7
August	2	0.2	
	4	0.1	
	6	0.1	
	7	2.5	
	8	0.5	
	16	1.1	
	17	0.3	
	21	0.1	
	25	0.1	5
September	2	0.1	
	3	0.1	
	5	0.2	
	8	1.2	
	9	0.2	
	11	2.6	
	13	0.1	
	14	0.5	
	17	0.1	
	23	0.1	
	24	0.3	
	25	0.1	5.6
October	4	0.2	
	5	0.2	
	12	0.1	
	13	0.1	
	18	0.1	
	23	1.1	
	24	0.3	
	28	0.2	
	31	0.7	3
November	1	2.3	
	5	0.1	
	10	0.1	
	14	0.3	
	17	0.9	
	18	0.2	
	22	0.1	
	23	0.2	
	26	0.2	
	27	0.1	
	29	0.4	
	30	0.1	5
December	2	0.1	
	4	0.1	
	5	0.1	
	12	1	
	13	0.1	
	20	0.2	
	21	0.1	1.70 E

* Notes

1. Source: Hourly Precipitation Data, Minnesota, Vol. 41
2. Monthly totals as given by source; an E (E) indicates estimated value

Table 6.5. Daily and monthly precipitation at Spring Valley, 1992.

Month	Day	Daily Precipitation	Monthly Precipitation
January	8	0.1	
	12	0.4	
	14	0.1	
	22	0.4	1.12 E
February	29	0.4	
March	21	0.2	
	28	0.6	
	29	0.2	-
April	-	-	3.6
May	14	0.1	
	15	0.2	
	16	0.9	
	25	0.1	
	26	0.1	1.4
June	8	0.1	
	13	0.1	
	16	0.6	
	17	0.7	
	19	0.1	
	22	0.1	
	23	0.7	2.4
July	2	0.1	
	8	1.8	
	9	0.4	
	11	0.4	
	12	0.2	
	13	0.6	
	14	0.1	
	19	0.1	
	22	1.0	
	25	0.1	4.8
August	2	0.4	
	6	0.2	
	7	0.9	
	11	0.1	
	12	0.1	
	17	0.2	
	25	0.4	2.3
September	2	0.5	
	5	1.2	
	7	0.3	
	9	0.4	
	14	1.0	
	16	1.4	
	18	0.1	4.9
October	7	0.2	
	8	0.7	
	9	0.1	
	15	0.1	
	20	0.2	
	31	0.1	1.4
November	1	1.7	
	2	0.8	
	9	0.1	
	19	0.8	
	20	1.3	
	25	0.1	4.8
December	3	0.2	
	6	0.1	
	9	0.1	
	12	0.1	
	14	0.2	
	15	0.2	
	17	0.1	
	18	0.1	
	28	0.1	
	29	0.3	1.5

* Notes

1. Source: Hourly Precipitation Data, Minnesota, Vol. 42, Nos. 1-12.
2. A dash(-) indicates that daily or monthly totals are unavailable.
3. Monthly totals as given by source; an E (E) indicates estimated value.

Table 6.6. Daily and monthly precipitation at Spring Valley, 1993.

Month	Day	Daily Precipitation	Monthly Precipitation
January	2	0.1	
	11	0.1	
	12	0.5	
	13	0.2	
	20	0.1	
	21	0.1	1.1
February	10	0.1	
	11	0.1	
	20	0.1	
	21	0.4	
	22	0.1	
	24	0.1	0.9
March	9	0.2	
	19	0.1	
	21	0.2	
	22	0.2	
	30	0.6	
	31	1.3	2.6
April	3	0.1	
	7	0.4	
	8	0.6	
	10	0.1	
	11	0.1	
	13	0.2	
	14	0.2	
	15	0.3	
	16	0.1	
	18	0.3	
	19	1.8	
	20	0.1	
	27	0.5	
	30	0.1	4.9
May	1	0.6	
	2	0.1	
	3	0.3	
	4 to 31	4.3	5.3
June	1 to 30	6.8	7.72 E
July	1 to 31	-	6.1
August	6	0.1	
	8	0.8	
	9	0.7	
	13	0.1	
	14	0.2	
	15	2.2	
	18	0.7	
	22	0.1	
	30	1.6	8.20 E
September	1 to 30	-	1.8

* Notes

1. Source: Hourly Precipitation Data, Minnesota, Vol. 43, Nos. 1-9
2. A dash(-) indicates that daily or monthly totals are unavailable. For some months, only monthly totals are given.
3. Monthly totals as given by source; an E (E) indicates estimated value

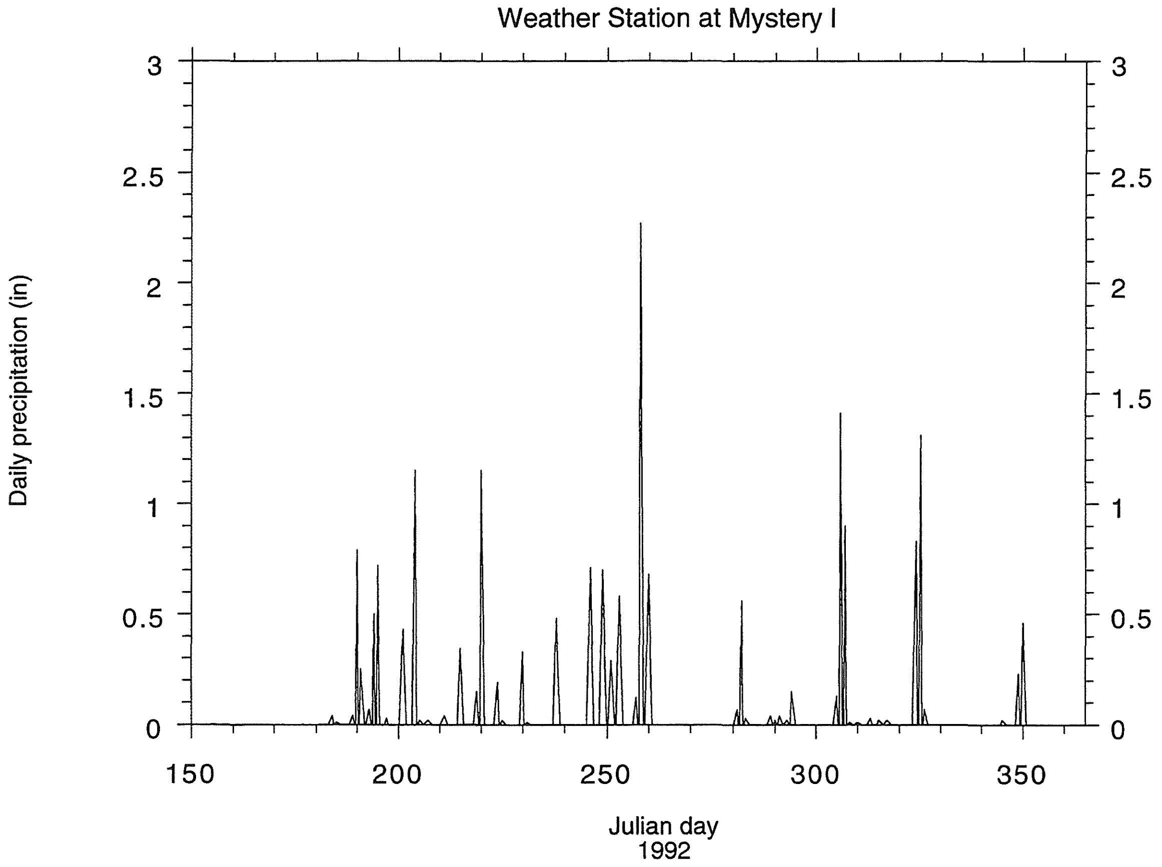


Figure 6.1. Precipitation at the Root River Weather Station, 1992.

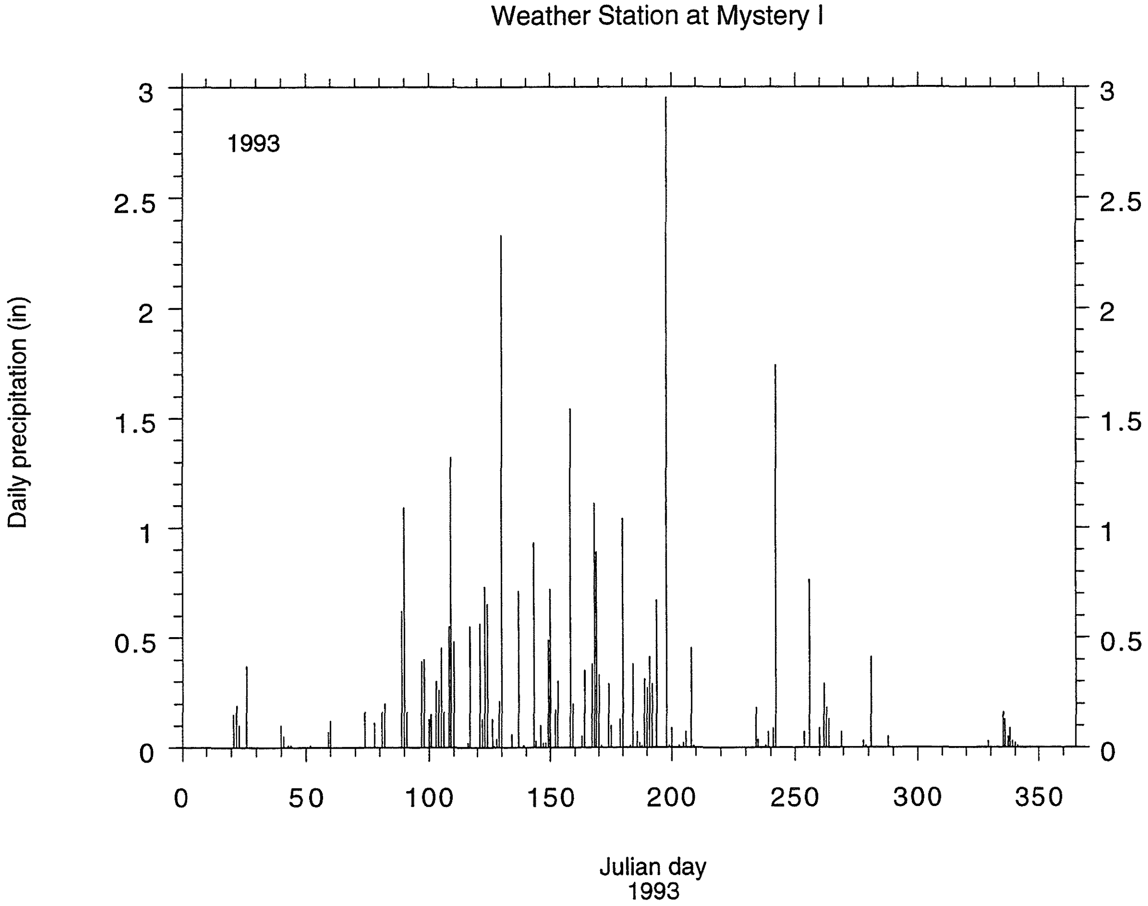


Figure 6.2. Precipitation at the Root River Weather Station, 1993.

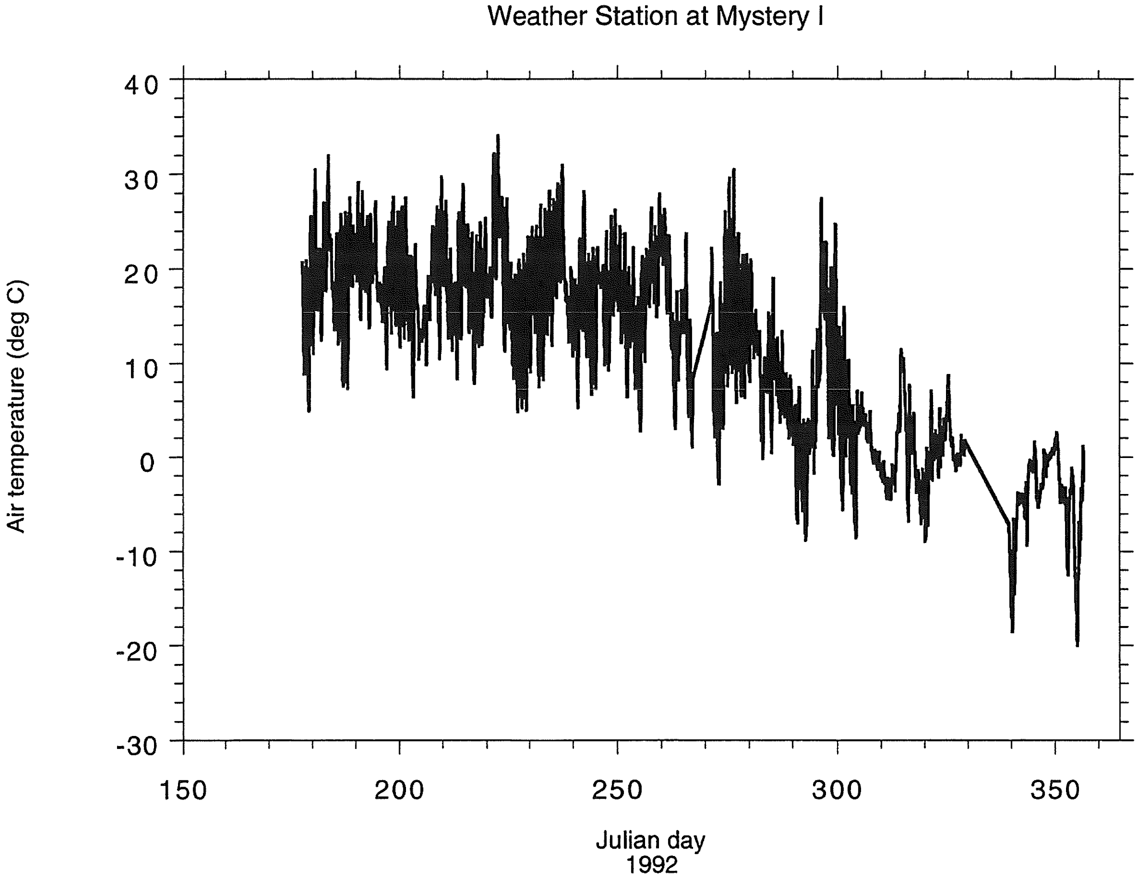


Figure 6.3. Air temperature at the Root River Weather Station, 1992.

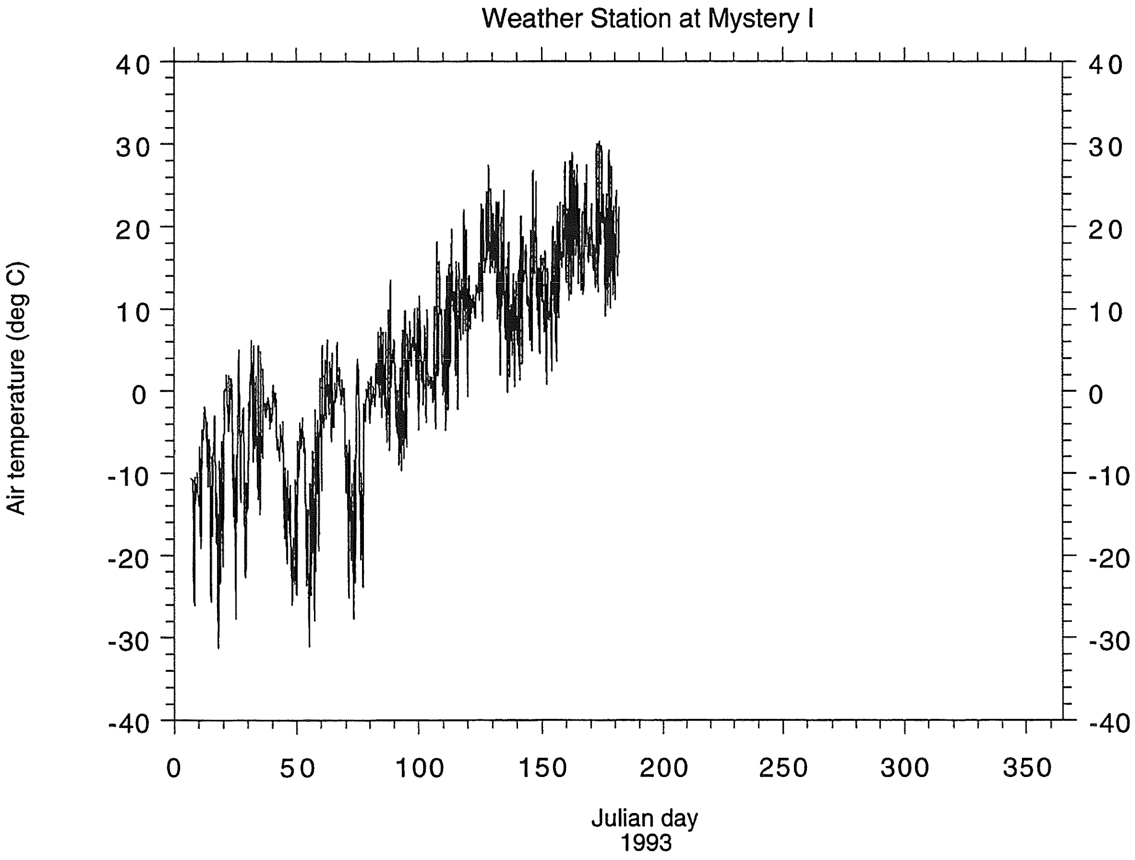


Figure 6.4. Air temperature at the Root River Weather Station, 1993.

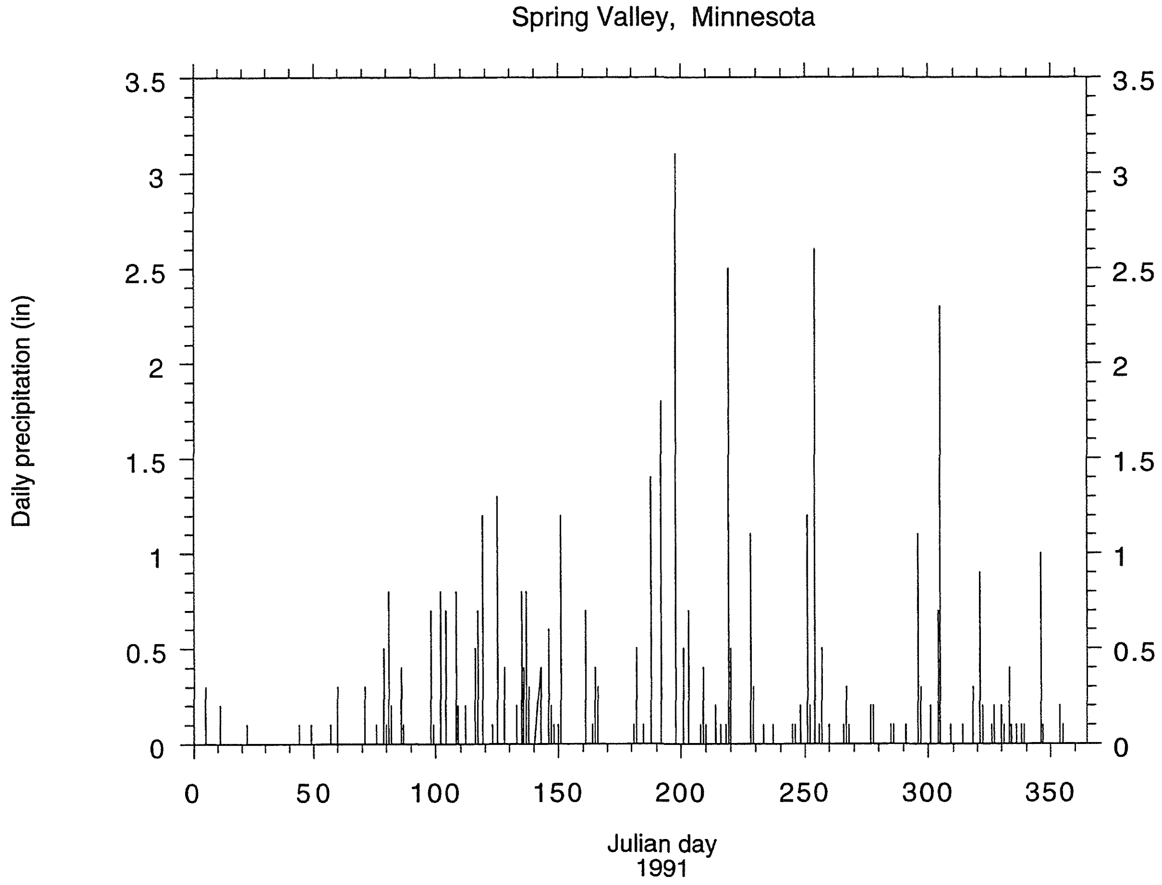


Figure 6.5. Daily precipitation at Spring Valley, 1991.

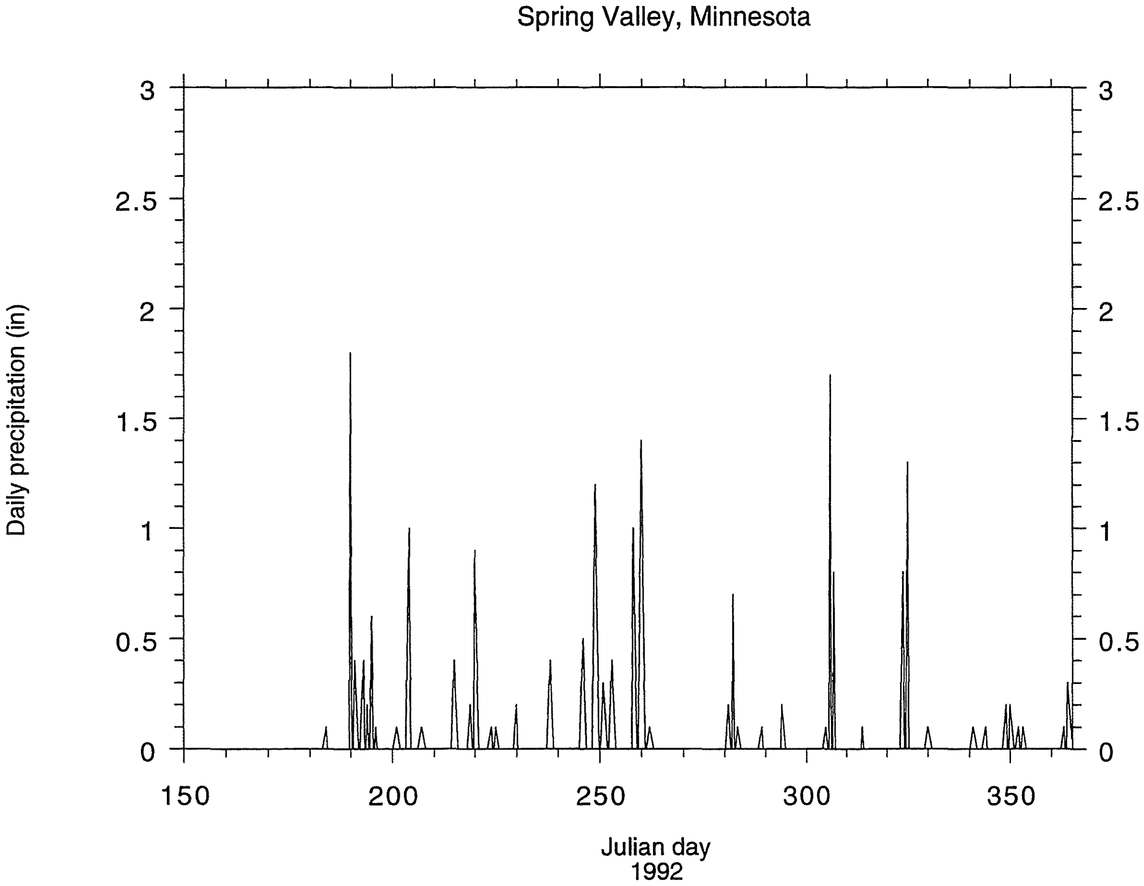


Figure 6.6. Daily precipitation at Spring Valley, 1992.

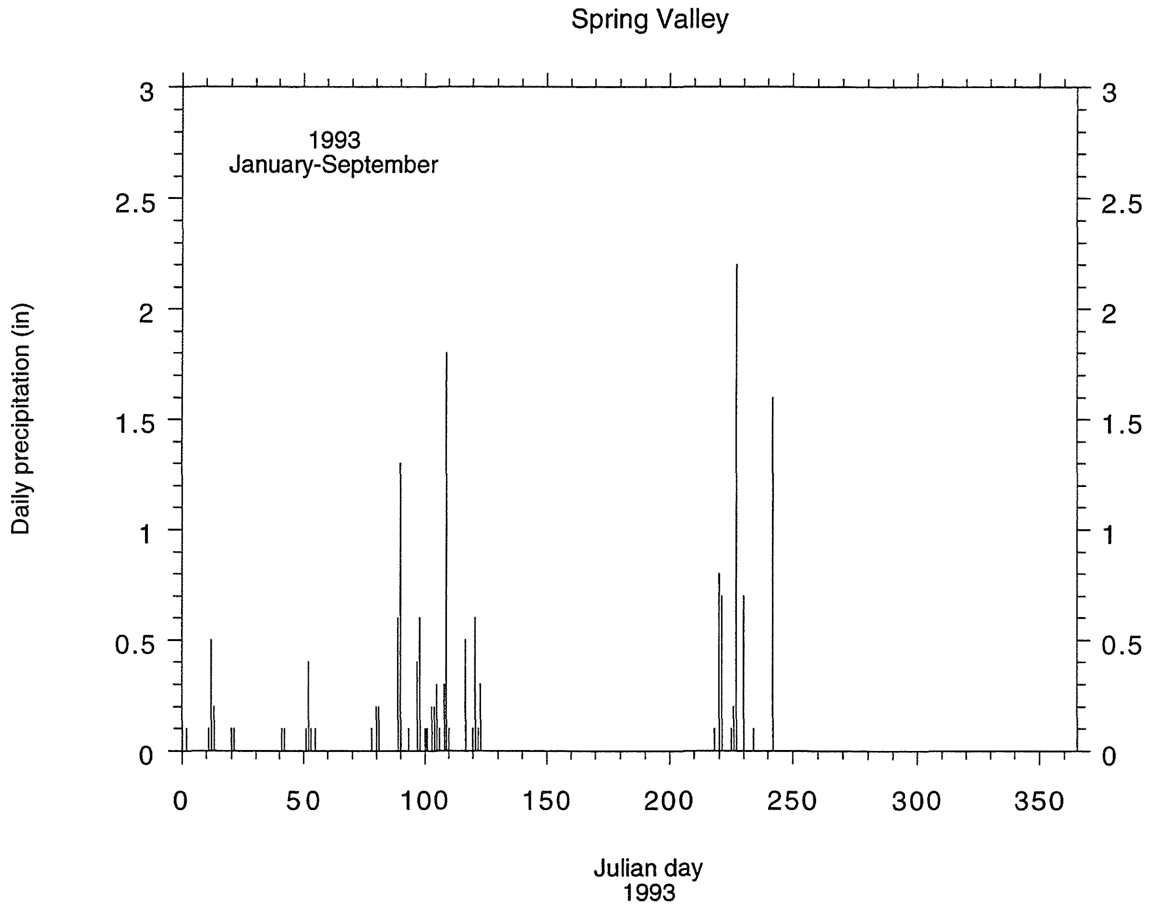


Figure 6.7. Daily precipitation at Spring Valley, 1993.

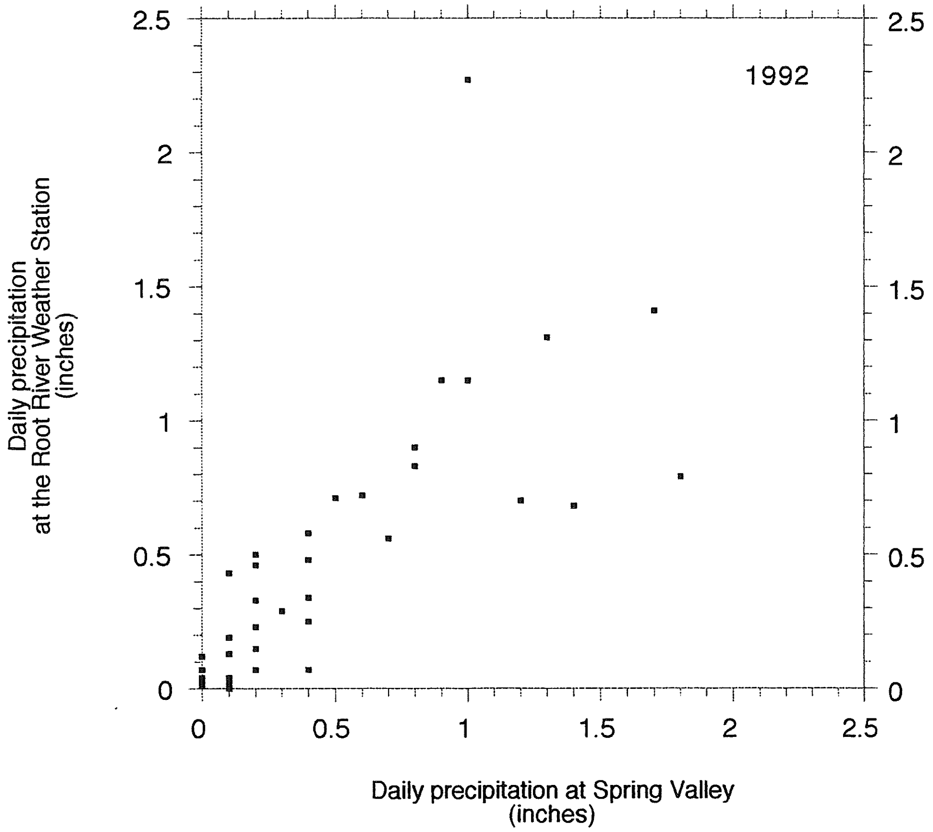


Figure 6.8. Correlation of daily precipitation for 1992.

precipitation were primarily a result of thunderstorms, which tend to be widely scattered and localized if they are of convective rather than frontal origin. The higher daily values of precipitation tend to be associated with summer storms. A plot for 1993 is similar, but is much less helpful in understanding the relationship between these stations. The primary difficulty is that daily values are missing for Spring Valley in nearly all of May, all of June and July, and much of August in a very wet year.

CHAPTER 7

BLUE LAKE AND ADJACENT SITES

SITE DESCRIPTIONS AND MONITORED PARAMETERS

Blue Lake is a major pool in 4th Avenue of Mystery II, between the Hills of Rome and Diamond Caverns. **Blue Lake Springs** are intermittent (in-cave) springs in the floor of the gravel trail, about 60 to 70 ft to the east of Blue Lake. The springs occupy a series of seeps and small holes spread out over a 5 to 10 ft long area, depending on discharge. Discharge varies with stage in Blue Lake, but flow only occurs when stage is very high. **Blue Lake Drips** are flowstone drips. The drip site is below a large flowstone mound immediately west of Blue Lake. It is beneath 4th Avenue in a passage much modified from its pre-commercial state. The drips apparently pass through the upper flowstone mound, and then fall from flowstone and rudimentary stalactites on the north wall and ceiling of the passage below 4th Avenue. The drip site---which is only one of a number of drip sites beneath the mound---is at the start of a widening in the passage, opposite the end of the south retaining wall.

Water temperature, conductivity, stage, and air temperature, respectively, were measured at Blue Lake with a thermistor wire, a Campbell conductivity probe, a Druck pressure transducer, and a thermistor wire. At the start of the 1993-1994 continuation of the LCMR project (July, 1993), a new Campbell 247 Conductivity/Temperature probe was installed; it provides better quality water temperature and conductivity data that provide additional support for conclusions reached below on the basis of the original data obtained from March, 1992 to June, 1993. Drip rates at Blue Lake Drips were first measured in the fall of 1992 with a siphon action rain gage, but the data were of such poor quality as to be unusable. A Texas Instruments rain gage was then used to measure drip rates from February through July of 1993, but it eventually malfunctioned and was not replaced. Throughout the project, data were recorded every 15 minutes with a Campbell CR10 data logger set on the north wall of the passage between the lake and the flowstone mound. The above instrumented parameters are supplemented by measurements of water temperature and conductivity at the times of chemical water sampling (21 dates for Blue Lake).

IMMEDIATE SOURCES AND SINKS OF FLOW AT BLUE LAKE

The water of Blue Lake comes primarily from a passage to the north of 4th Avenue. Some water may also enter from beneath the flowstone mound. More likely, water from the mound drains vertically downward through breakdown without entering Blue Lake. When stage is high in Blue Lake, the water level is above the elevation of the passage beneath the flowstone mound, and no leakage through the retaining wall into that passage has been observed. Ceiling drips above Blue Lake have been observed in all seasons and provide a negligible input.

Most of the water at Blue Lake leaks slowly through sediments (silt and breakdown) in the floor; these sediments undoubtedly cover vertical joints that transmit the water downward. Some loss may be through fractures in the walls of the passage, which is in the Dubuque Formation. A minor amount of the water evaporates. When the water level is high, some water drains out the retaining wall at the east end of the bridge, flows through floor sediments beneath the graveled tourist trail, and then reappears as seeps and springs at Blue Lake Springs. On April 17, 1993, the stage of Blue Lake was -5.80 ft below the level of the 3rd rail post (datum) at 1233.39 ft, and the 2nd highest seep at 1233.12 ft was active, giving a head difference of 0.27 ft over a horizontal distance of 59.8 ft (elevations by A. N and M. V Palmer; A. N. Palmer, written communication, 1993). At that time, the topmost seep (1233.28 ft) was not active. At high stage in Blue Lake, Blue Lake Springs discharges up to at least seven liters per minute. This estimate is based on eight repetitions of the time (1.1 seconds by stopwatch) it took to fill a 125 ml anion bottle at a spot about 30 ft downslope of the seeps on April 25, 1992, when the stage at Blue Lake was at -4.46 ft. The measurements were at a channel on the north side of the passage. An estimated 10-15% of the flow was not within this channel, so the estimate of seven liters per minute is conservative.

SIGNIFICANCE OF BLUE LAKE AND ADJACENT SITES

With the exception of a loss of volatile organic compounds from creosote-impregnated pilings (see Chapter 4), the hydrology and chemistry of Blue Lake and Blue Lake Springs are produced by processes that operate at sites throughout the cave. The changes in water level and in the chemistry of Blue Lake are a record of the movement of water from the surface into the soil and loess and then into the fractured bedrock before finally reaching the cave. Accordingly, these parameters provide information on water storage and transmission in the area upstream of Blue Lake as well as at Blue Lake. They also provide information relevant to our understanding of the raft cones at Blue Lake.

The following discussion uses observations of stage (water level), drip rates, water temperature, conductivity, and chemical analyses to explain the hydrology and chemistry of Blue Lake and its companion sites.

RAFT CONES AND THE CHEMISTRY OF BLUE LAKE

Raft cones are relatively rare conical speleothems built up of accumulations of calcite rafts. At times, Blue Lake water is sufficiently saturated with respect to calcite to precipitate rafts. Although calcite is denser than water, the rafts initially float on the surface of the water due to surface tension. Drips from individual points over the lake which fall on the rafts cause them to sink. As the rafts sink they move nearly straight down and accumulate as piles beneath the ceiling drip points. As the rafts accumulate, they are cemented together by additional precipitation of calcite, eventually building up into conical mounds.

Fluctuating water level can also play a role in the formation of raft cones. As the water levels fall during dry periods and drop below the tops of the cones, rafts floating on the water can drift into the cones and become attached. Raft cones are extremely delicate and fragile, in part because of their porous nature. Unlike stalactites and stalagmites, which tend to be firmly cemented to bedrock substrates, and which tend to be strong, raft cones are relatively weak accumulations of rafts and are less solidly cemented. The raft cones at Blue Lake appear brown because of mud and silt, but this fine material does not merely cover the cones, it is also incorporated within their structure. Raft cones tend to be only weakly attached to pool floors and run the risk of being dislodged if pressed sideways.

Blue Lake water was supersaturated or at saturation (within the limits of error of ± .1 saturation units) with respect to calcite, aragonite, and dolomite on all 21 of the sampling dates from 1991 to 1993. Blue Lake water probably is saturated with respect to calcite all of the time, assuming that water is always present. However, floating calcite rafts were noted on only a few occasions during the study. Although no systematic check was made for rafts, the chemistry of Blue Lake is compatible with their continued deposition. No matter when they may have begun growing, the raft cones, in all probability, are still actively being deposited.

STAGE AND THE VOLUME OF BLUE LAKE

Blue Lake may be perennial or it could dry out entirely over a period of extended drought. Water level fluctuated over 11 ft between 1991 and 1993. At low stage, the lake breaks up into a series of pools at 4th Avenue and in the tributary passage to the north. At the lowest levels observed, water depth was less than half a foot in the deeper of two isolated pools immediately below the center of the bridge over Blue Lake. At the highest level, water was about 11.6 ft deep and only 3.7 ft below the top of the third rail post from the west end of the bridge.

As a rough estimate, based on measurements of passage shape during low stage, the volume of water at Blue Lake fluctuates from less than 20 ft^3 (150 gal) to over 10,000 ft^3 (74,800 gal). Correlations of volume with stage can be only approximate, but as a rough estimate, the following will suffice. At low stage, when water is less than about 2 ft deep at the pressure transducer (-13.25 ft relative to datum) irregularities in floor shape and elevation, combined with the presence of breakdown and raft cones, make it problematic to correlate volume with stage. Between a water depth of about 2 ft and 9.65 ft (-5.7 ft relative to datum), volume (ft^3) is roughly 1000 times the depth of water in feet. The depth of water (next to the pressure transducer) is equal to 15.35 plus the reported stage height in feet (a negative number on plots).

For water depths greater than 9.65 ft, it is not at present useful to estimate volume. The problem is two-fold: first, the water is above ceiling height in much, but not all of the tributary passage. Second, there are far too many other irregularities in passage shape and elevation in the tributary. The problems here are not insurmountable, but would require a detailed survey of the passage at low stage, with precision elevations of the ceiling, floor, recessed wall pockets, and irregularities that include extensive flowstone pools in muddy crawlways. An attempt was made to approximate the relationship within this range of stage, but conditions within the tributary passage preclude an estimate without at least a detailed compass and tape survey. We would be surprised if our correlations of volume to stage were within 15%. It has not escaped our notice (to steal a phrase from Watson and Crick's famous DNA paper) that the rough correlation of volume with stage allows calculations of net discharge (input discharge minus output discharge) at Blue Lake, along with further mathematical modeling, but that approach shall be reserved for later reports to include a larger data base.

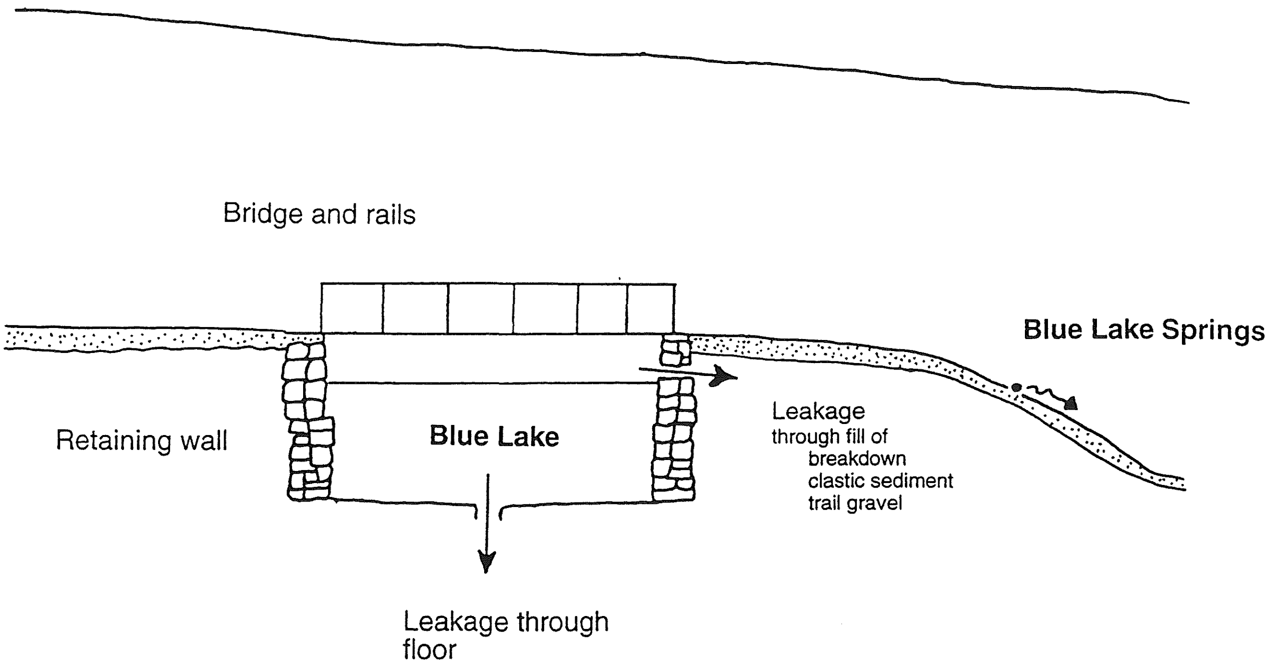
INTERPRETING THE HYDROLOGY AND CHEMISTRY: BLUE LAKE AS A LEAKY BATHTUB

Water flows into Blue Lake only *after* the larger recharge events each year, when soil-moisture deficits have first been satisfied and precipitation or snowmelt can infiltrate past the top few inches of soil. As we shall see, there is a significant lag time between the onset of the recharge event and the arrival of recharge water at Blue Lake. The water that initially arrives is stored water that has been displaced from the soil, loess, subcutaneous zone, fractured bedrock above the cave, and cave pools upflow of Blue Lake.

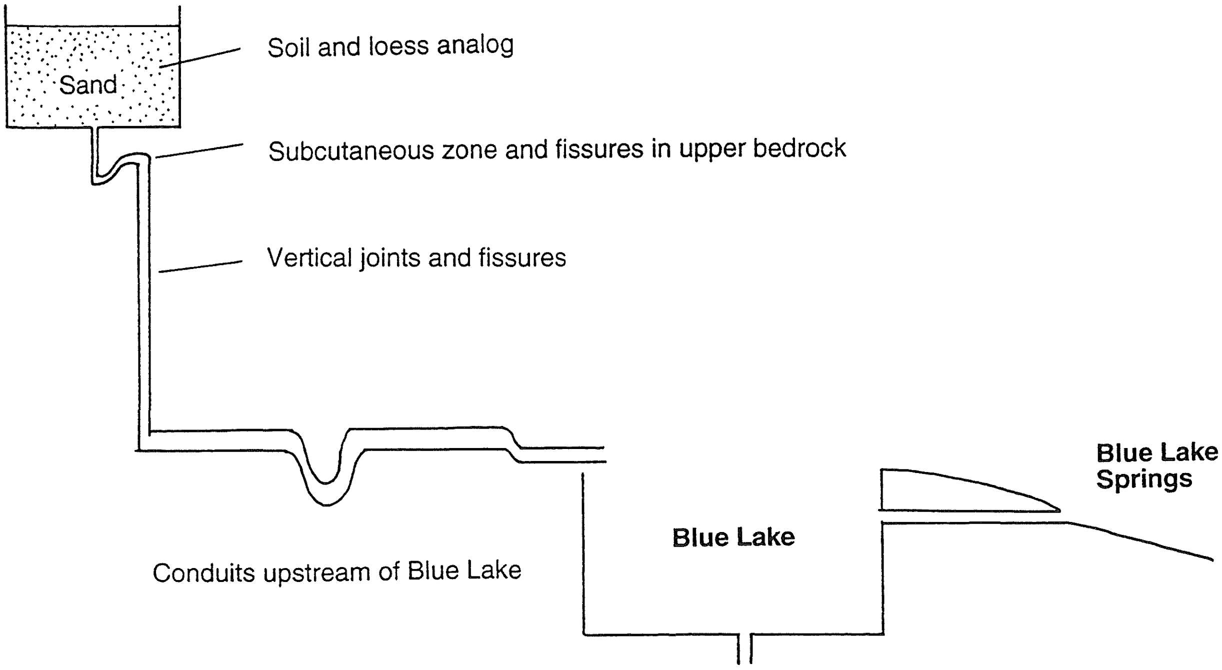
Blue Lake can be pictured as a huge but leaky bathtub (Figure 7.1). If flow into the lake exceeds the capacity of the drains to accept water, then the lake starts to fill. If the discharge is sufficiently high, Blue Lake fills rapidly, reaching a stage of about -5 to -3.6 ft following yearly spring melt off. While soil-moisture deficits remain satisfied, additional surface recharge (in the late winter and early spring) produces hydrologic pulses that result in continued flow into Blue Lake. Stage may then rise and fall through an observed range of about 1.5 ft. Eventually, periods without recharge at the surface lead to a decrease in flow into Blue Lake and the water level declines over a period of four or five months to -13 to -14.5 ft.

The water that flows into Blue Lake varies in its chemistry. We have no *direct physical access to the chemistry of the incoming water*, except at very low stage, and then only if we are present to sample that water upstream of its discharge point into Blue Lake. As water level rises, the tributary passage is flooded. We can only sample the mixture of incoming water and Blue Lake water. When we are not present, at very low stage, our instruments can readily detect the influence of the incoming water, *if* the temperature and conductivity vary from that of Blue Lake. The volume of incoming water is large compared to that of the water already present. Thus we can see the chemical and temperature signals of the incoming water.

However, as stage rises, the volume of incoming water becomes small compared to that of the water already present. Under these conditions, mixing may be slow, especially at the highest stages. Moreover, because the instruments are at a fixed location beneath the bridge near the deepest point, they can only detect temperature and conductivity at that point. If these parameters vary with location (vertical or horizontal) as water level varies, then we will not see these variations. The periodic sampling for field parameters was made on "accessible" water. Accessible water varied in its location depending on stage, but usually was collected at the west end of the lake, from the top foot of water. The easiest part of the record to interpret should be periods of very low stage and periods immediately following an influx of water when stage is low. It is these periods that we shall concentrate on here, for they provide the most readily interpretable signals---signals that contain information about the recharge to Blue Lake, and water storage upstream of Blue Lake.



A. Blue Lake and Blue Lake Springs



B. Hydrologic model for Blue Lake and Blue Lake Springs

Figure 7.1. The hydrologic setting of Blue Lake.

DRAIN AND FILL EVENTS AT BLUE LAKE: NOMENCLATURE

Between January, 1992 and June, 1993, Blue Lake underwent two and a half major cycles of fill and drain events. Figure 7.2 is a summary of stage for Blue Lake for this study; it shows the numbering system we have adopted. The record begins when the lake was full in the late winter of 1992. We see the end of a fill event that began before the Blue Lake instrumentation was installed. After this installation, Blue Lake underwent one complete drain event, a partial fill and drain event, and another major fill event. The instrumented events will be referred to as Drain event 1, Fill event 2, Drain event 2, and Fill event 3. Because the fill event before Drain event 1 was not instrumented except near its end, it will not be discussed. Nor will the later Drain event 3, which covers the late summer and fall of 1993, be discussed here.

DRAIN EVENT 1

Figure 7.3 shows the stage, water temperature, and conductivity (as 1/volts) for Blue Lake for 1992. At the start of the record (March 27, 1992), stage was high, about -5 ft. Stage fluctuated slightly over the following three weeks, rising to a height of nearly -4 ft. The stage then fell from May 1 onward in a smooth curve over most of 1992. By early October (day 275 = October 1) water level had fallen to a minimum at about -14.15 ft (point X on Figure 7.3). Stage remained nearly constant until the onset of Fill event 2 in late November. During this time of constant low stage, no visible inputs (either as streams or seeps) to Blue Lake were noted.

Figures 7.3, 7.4, and 7.5 compare the stage, water temperature, conductivity, and water chemistry for Blue Lake in 1992. During the first drain event, conductivity (here expressed as 1/volts; see Chapter 2) remained constant, rose, and then fell. The decline is shown on Figure 7.3b between points a and b. Field conductivity (Figure 7.4; independently measured at the times of water sampling) behaved similarly.

It is not possible to correlate chemical variations and stage in a detailed fashion throughout the drain event. Among other problems, we do not know exactly when input to the lake ceased, and there are problems in correlating precipitation recharge during a declining stage.

However, at the end of the first drain event, from day 255 (September 11, 1992) until the onset of the second fill event on day 330 (November 25), stage is very low and only slowly declining or is nearly constant. During this time (points a to b in Figure 7.3), conductivity (as 1/volts and field conductivity, Figure 7.3b) declined, as did concentrations of Ca^{+2}, Mg^{+2}, and HCO_3^- (Figure 7.5). Only SO_4^{-2} of the major ions increased.

One possible explanation of these observations begins as follows. As stage declined, the pressure head at the base of the pool declined, and so the infiltration rate of water into the basal sediments declined. Eventually, so little water was left that the driving force to produce infiltration was practically zero. The remaining water sat and evaporated very slowly.

During evaporation, solute concentrations generally increase incrementally unless precipitation or other reactions occur. Did sufficient evaporation occur to

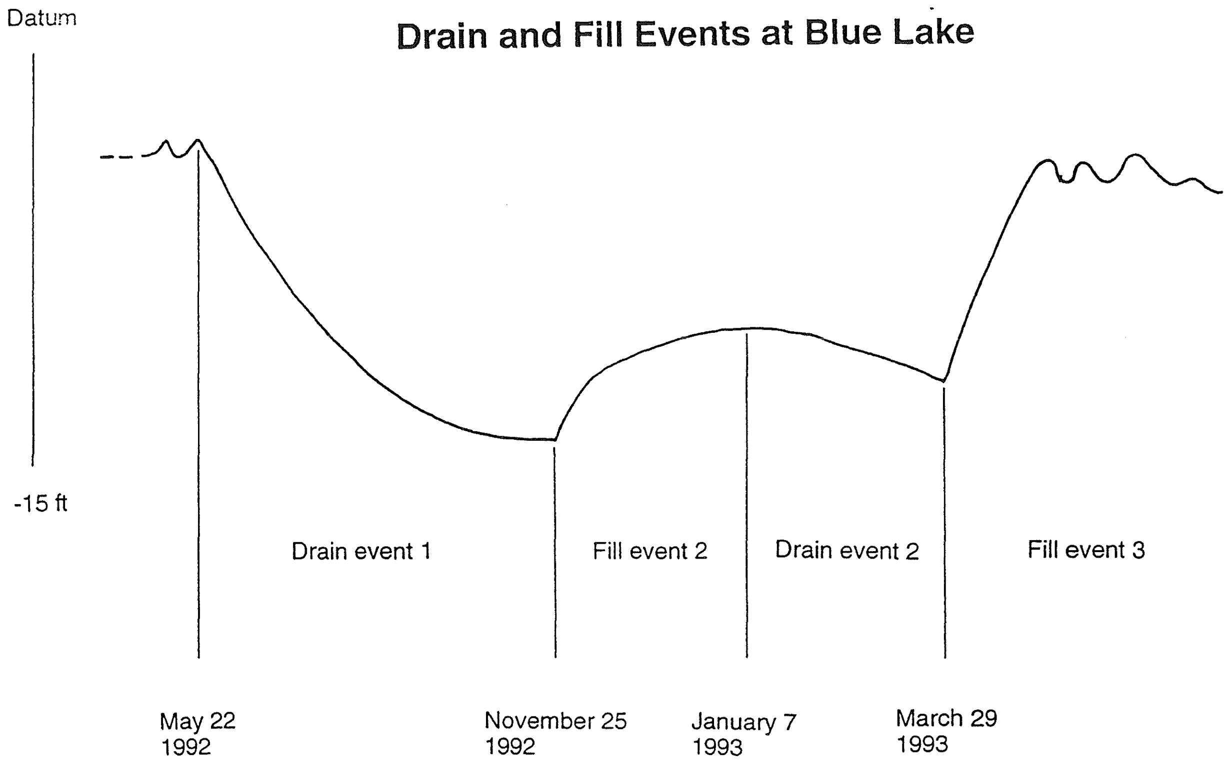


Figure 7.2. Nomenclature for instrumented events at Blue Lake.

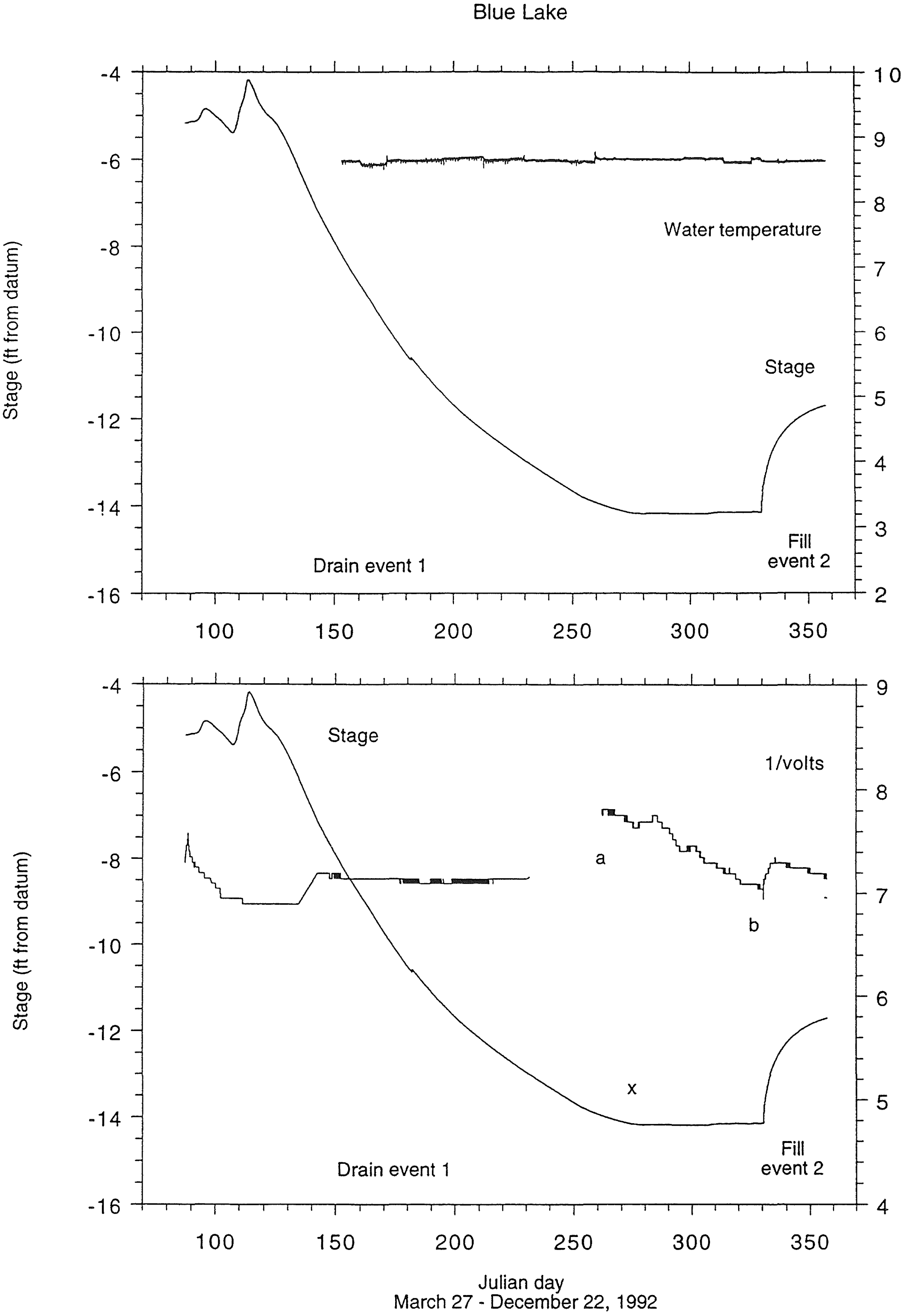


Figure 7.3. Stage, water temperature, and conductivity (1/volts) at Blue Lake in 1992.

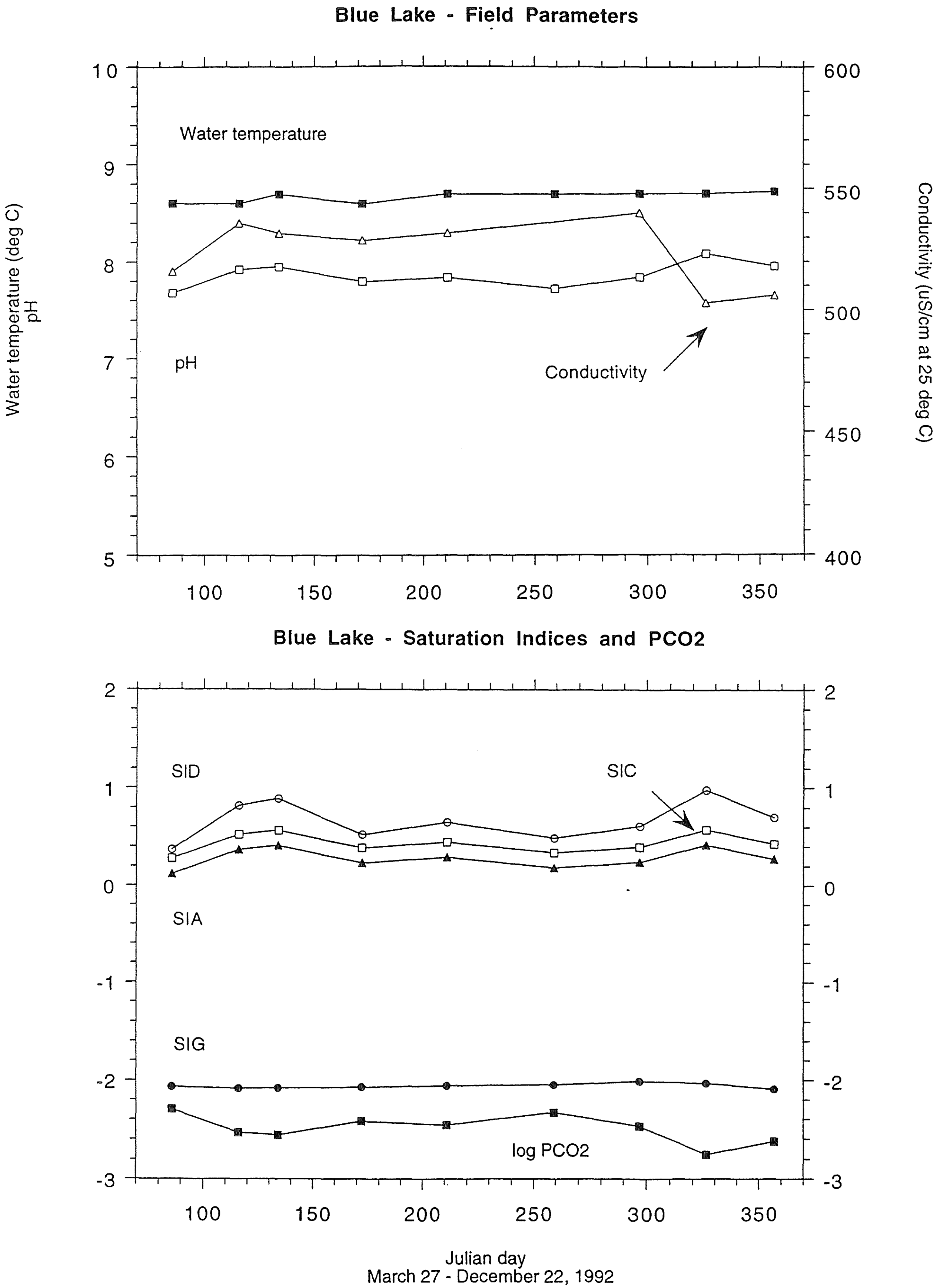


Figure 7.4. Field parameters, saturation indices, and P_{CO_2} at Blue Lake in 1992.

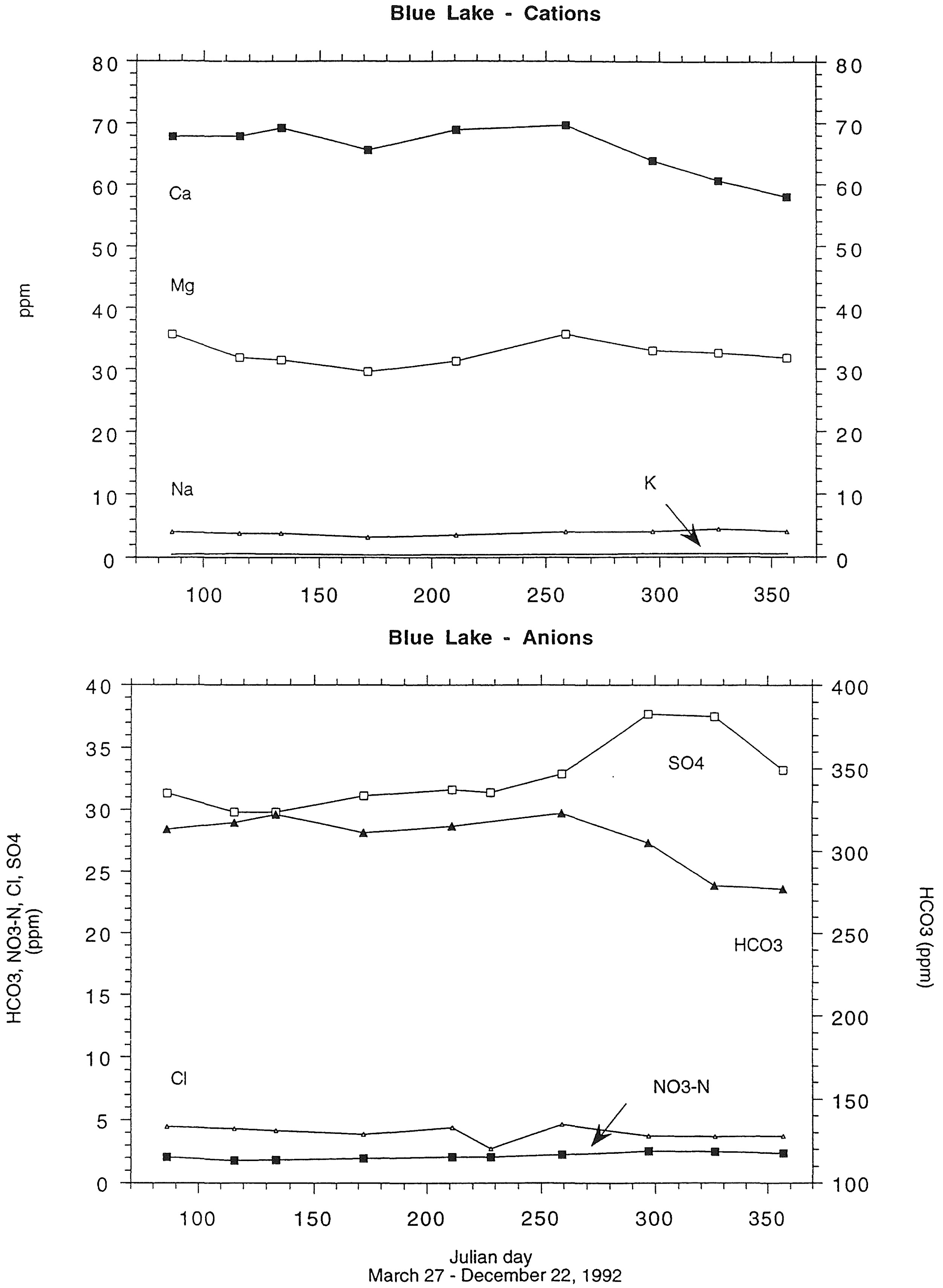


Figure 7.5. Cations and anions at Blue Lake in 1992.

precipitate calcite and remove Ca^{+2}, Mg^{+2}, and HCO_3^-? At plausible maximum evaporation rates (2 $g/m^2/day$; see Chapter 11) in the vicinity of Blue Lake, over the 55 day period in which stage was most stable and lowest, about 0.0004 ft of evaporation per square foot of exposed water surface would have occurred. Even if this estimate of evaporation were ten times too low, the evaporation rate would be far too low to significantly influence solute concentrations, or to drive calcite precipitation. It is necessary to consider other factors.

It will be recalled that Blue Lake waters were at or above saturation throughout the study. On a thermodynamic basis alone, one would expect supersaturated waters to always be precipitating calcite, but in actual fact there is an energy barrier to be overcome that may result in a need for "seeding" or even biological intervention (e.g., by the recently posited nanobacteria; Folk, 1994) to begin calcite deposition. In any case, calcite supersaturations of more than five times (Jacobson and Usdowski, 1975) or even ten times (Dandurand et al, 1982) the thermodynamic saturation value have been found in natural waters without precipitation of calcite in surface streams. In a study of one travertine-depositing surface stream, Herman (1989) found calcite saturations (SIC) of +0.8, or 6.3 times supersaturation, to be present before measurable amounts of calcite precipitation occurred. In her, and many other studies, CO_2 degassing (or outgassing) has been invoked as the primary mechanism driving calcite deposition.

The waters of Blue Lake probably are slowly degassing. They derive largely from displaced waters that can be presumed to have a large CO_2 concentration from the soil zone. The rate of degassing of these waters may largely control the timing of precipitation, in combination with an additional factor. That factor is the ratio of the surface area (for diffusion of CO_2 into the atmosphere) to the depth of water. If this ratio is very low, diffusion may not be fast enough to allow rapid degassing of the entire water body. (Even the rapid degassing of waters dripping from a stalactite are not sufficient to bring water P_{CO2} to equilibrium with cave atmospheric P_{CO2}; it takes time for degassing to occur.) A speculative interpretation---which needs to be mathematically modeled---is the following. The degassing rate is so slow for the large depth of Blue Lake water at high and medium stage, that sufficient supersaturation for deposition is not reached (except, perhaps, for a small amount at the surface). Eventually sufficient CO_2 degasses as water level declines (and discharge into the pool ceases), sufficient super-saturation is reached, and significant deposition of calcite occurs.

With the previous in mind, we might therefore hypothesize that (1) a threshold was reached by degassing under a declining stage, and that (2) calcite then precipitated. (More specifically, calcite rafts and other speleothems were precipitated.) This (3) removed Ca^{+2} and HCO_3^- from the water, producing the observed drop in conductivity (from a to b on Figure 7.3b).

FILL EVENT 2

Fill event 2 followed a storm that began on November 19 (day 324) at 2:30 PM and ended about 37.5 hours later at 4:00 AM on November 21, 1992 (Figure 7.6a). Total precipitation at the Weather Station at Mystery I was 2.18 in. The air and rain temperature varied in a complex fashion during the storm.

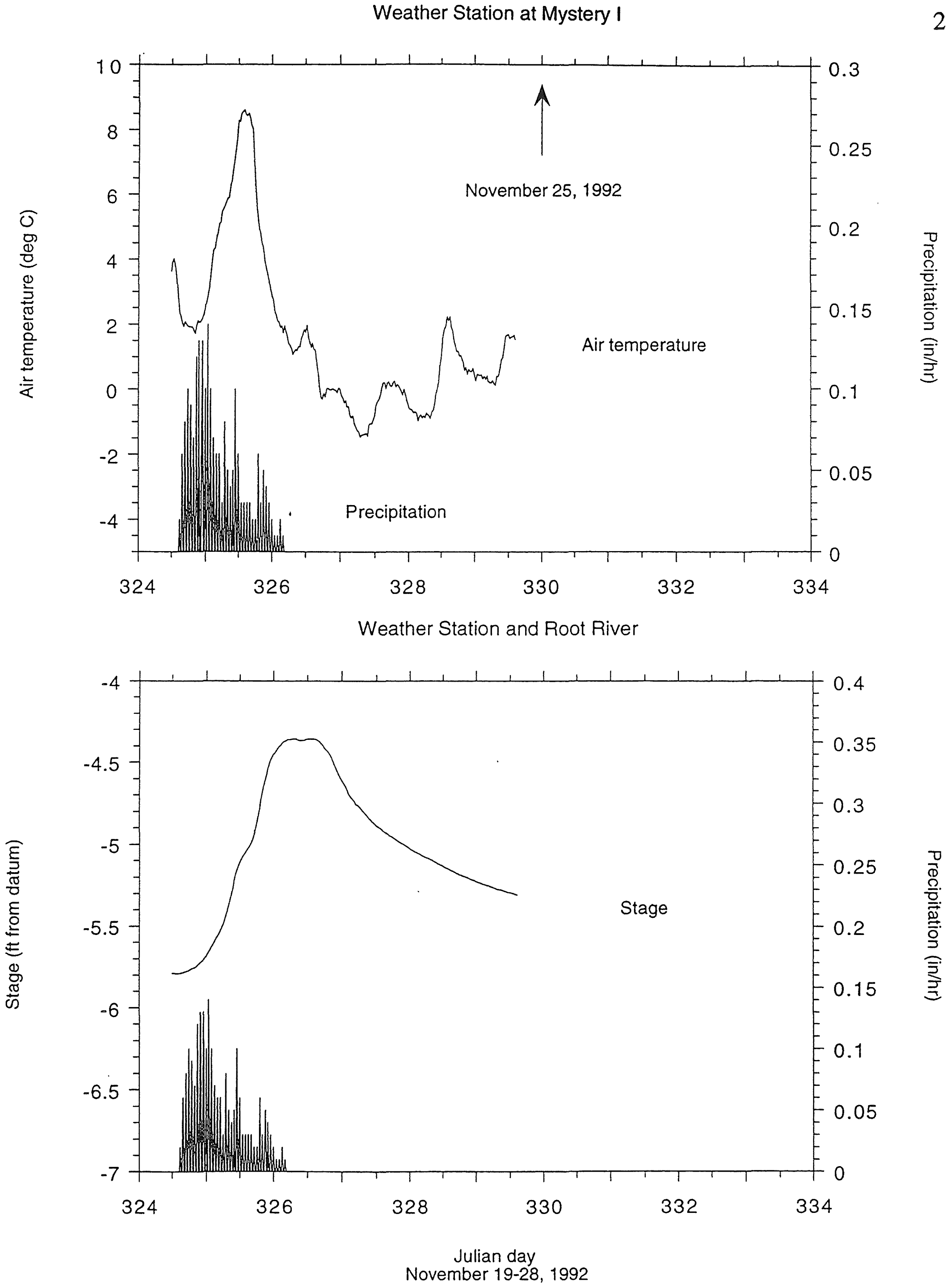


Figure 7.6. The November, 1992 storm and the response in stage on the Root River.

Air temperature was about 2°C at the start of the storm, rose later to nearly 9°C, but then fell to about 1°C by the end of the storm. About half of the rain fell by 2:00 am on November 20, before the air temperature had risen to 4°C. About half of the rain fell during the near-symmetrical rise and fall in the air temperature. We assume that the first half of the rain satisfied soil-moisture deficit conditions. We further assume that percolation recharge came primarily from the second half of the storm. Then (ignoring considerations of heat transfer between the soil and infiltrate) as an extremely rough guess, we could estimate the mean temperature of recharge water to the soil to have been about half of the difference between 2°C and 8.5°C, or about 5°C.

In actuality, the mean temperature of the recharge was probably colder than 5°C. At the time of the storm in late November, soil moisture was probably high, and infiltration likely began before half of the rain had fallen. The temperature of the upper soil should have been colder than 5°C, based upon air temperatures, which were below 2°C nearly all of the time from November 14 to the onset of the storm, as measured at the Root River weather station. In any case, the bulk of the precipitation recharging the soil zone was clearly colder than the mean cave temperature of 8.7°C. Any recharge rapidly reaching cave locations should therefore carry a temperature signal with a water temperature less than 8.7°C. More slowly recharging water, water that had a longer contact time with lower layers of soil, and with the underling loess and bedrock, would begin to warm toward the deep cave temperature of 8.7°C.

In response to the storm, the Root River rose about 1.5 ft to a flat crest lasting eight hours. The crest began near midnight at the end of November 21, about 4 hours before the end of the storm (Figure 7.6b).

No major response in stage was recorded at Blue Lake until November 25. The water level data in Figure 7.7 for Blue Lake shows that stage was nearly constant at -14.15 ft until November 25 (day 330).

(The details of the response at Blue Lake are instructive and deserve some scrutiny. It would be helpful if comparisons could be made with other sites. However, the record at Flim Flam Creek was lost for this time period when equipment failed, so no discussion can be made of the response there; similarly, equipment had not yet been installed at Coon Lake Drips. The fluctuations in water temperature and the offset from 8.6 to 8.7°C beginning about 12:00 on Julian day 326 are artifacts. The site was visited that day and the conductivity and water temperature probes were adjusted. It is possible that this visit is responsible for the slight offset in the stage on day 326. The pressure transducer may have been inadvertantly raised about .005 ft; this would have produced an apparent depth less than before adjustments. Such an apparent drop in stage is present in the record and is barely visible in Figure 7.7. The probe then may have slipped back to a position about .005 ft lower than before adjustments, producing a rise in pressure seen as an increase in depth and a rise in stage about 4:00 PM.)

Fill event 2 began almost 6 days (141 hours) after the onset of the storm (Figure 7.7), at about 11:15 AM on November 25, 1992 (Julian day 330). Water temperature initially declined at about 11:15, and fell by .04°C total over the next day. Conductivity, expressed as 1/volts (Figure 7.7), initially dropped at about 11:30, but then began to rise. Conductivity continued to rise until November 28, 1992 (day 333), remained at a peak until about December 7 (day 342), and then declined through late March of 1993 at the start of the Fill event 3 (Figures 7.8a , 7.9). The stage, in contrast,

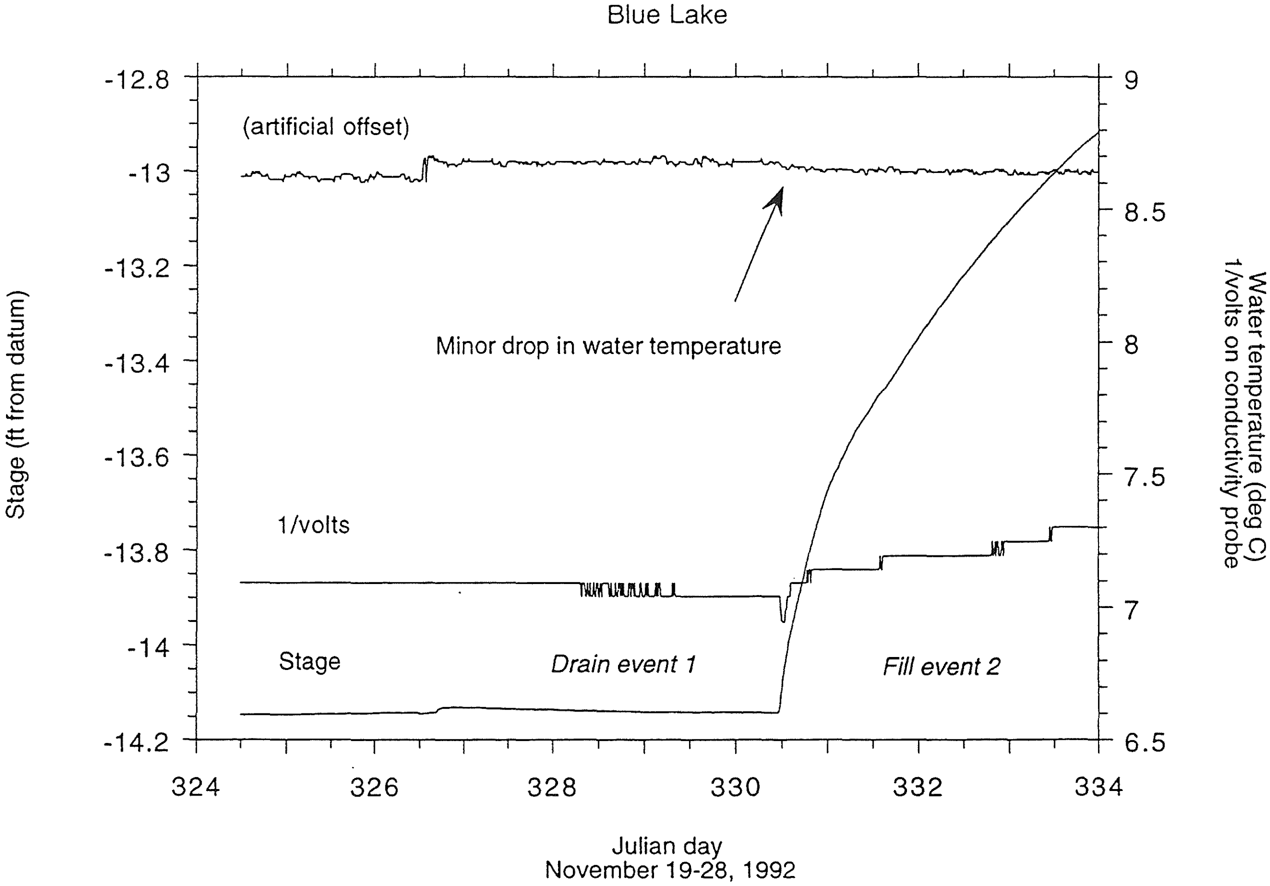


Figure 7.7. Stage, conductivity (as 1/volts), and water temperature at Blue Lake following the November, 1992 storm.

rose throughout December to a peak of about -11.58 ft from January 7-16, 1993. The stage then fell smoothly until the start of Fill event 3.

An interpretation of these observations needs to begin with a comment on response time. **Response time** can be defined as the time it takes for a signal to be transmitted from a specified site of origin to a specified observation site. Several types of response times can be distinguished depending on the signal being observed. Water that flows between two sites has an associated travel, or transit time. This is the time it takes for water molecules to physically move between the sites. This response time has been called the **flow through time** (Ford and Williams, 1989). There is also an hydraulic response time. This is the time it takes for a hydrologic response to travel between the sites; it has been called the **pulse through time**. The pulse flow through time can be much faster than the water flow-through-time. For example, imagine a stream flowing at 3 ft/second. If an explosion were set off in the stream, the water away from the explosion continues flowing at 3 ft/sec, but the sound created by the explosion travels through the water as a pressure pulse at the speed of sound in water (about 5000 ft/sec).

More directly relevant to the present discussion of Blue Lake is a second example. Imagine a plastic, clear-sided tank filled with very fine sand. (The sand is analogous to the soil and loess above the cave; see Figure 7.1b.) A narrow, clear plastic tube comes vertically out of the base of the tank, curves horizontally, and then has a U-shaped loop in it before turning vertical again. (The tube and U-loop are analogous to the fissures in the subcutaneous zone and fissures in the upper bedrock above the cave that can store water. The second vertical part of the tube represents vertical joints and fissures above the cave.) The narrow tube leads to a wider horizontal tube that has another U-loop before reaching a tank representing Blue Lake. (The lower horizontal tube and U-loop represent inaccessible voids that can store water, upstream of the point of interest in the cave.)

Now dye some water red. Pour the red water (analogous to recharge) into the top of the tank, evenly over the sand surface. The water will infiltrate. If enough is added, water will eventually seep through the sand in the tank, flow through the upper part of the tube, fill the U-loop, and then flow out the end. Even after the red water is no longer applied, there should be leakage as water drains under the influence of gravity, but eventually flow will stop. At this time, some red water will be left in the U-loop, and some will be left in the pore spaces between the sand grains; it is held in place by surface tension. This is stored water. Now add water dyed blue to the top. Again, it takes time for the water to seep in. Eventually, a small amount of red water comes out of the hole, followed by a larger quantity of blue water. We can say that the new recharge (blue water) has flushed out or *displaced* the stored water (red water stored in the U-loop and between the grains).

Now return to the distinction between pulse through time and flow through time. The pulse through time, as observed from the start of pouring of blue dye, is the time it takes until the small amount of red dye is displaced out the end of the tube. The flow through time is the longer time it takes before the blue dye first appears. Of course, there can be an added complication: the two dyes might mix somewhat, making it a little harder to distinguish the type of water reaching the observation point.

We can now return to our discussion of the observations at Blue Lake. The rise in conductivity at the onset of the second fill event suggests the following. Before the onset of the recharge event, subsurface waters were stored upstream of Blue Lake.

This stored water could have been in the soil, the loess, the subcutaneous zone, and/or in fractures and conduits upstream of Blue Lake. These waters had a higher solute load, and a higher conductivity than the pre-storm waters in Blue Lake. These stored waters were displaced by the recharge. It took about 141 hours from the onset of the storm for the displaced water to first show up at Blue Lake. That displaced water most likely was the major component of water entering Blue Lake for a several day period, until day 340 (December 5) when the conductivity began to drop. By then, old stored water probably had begun to mix with new recharge water; this would cause the conductivity to decrease because the new water should be more dilute. Also, as time progressed, newer recharge water began to make up a larger percentage of the total water flowing in, as well as the water stored in Blue Lake as water level rose.

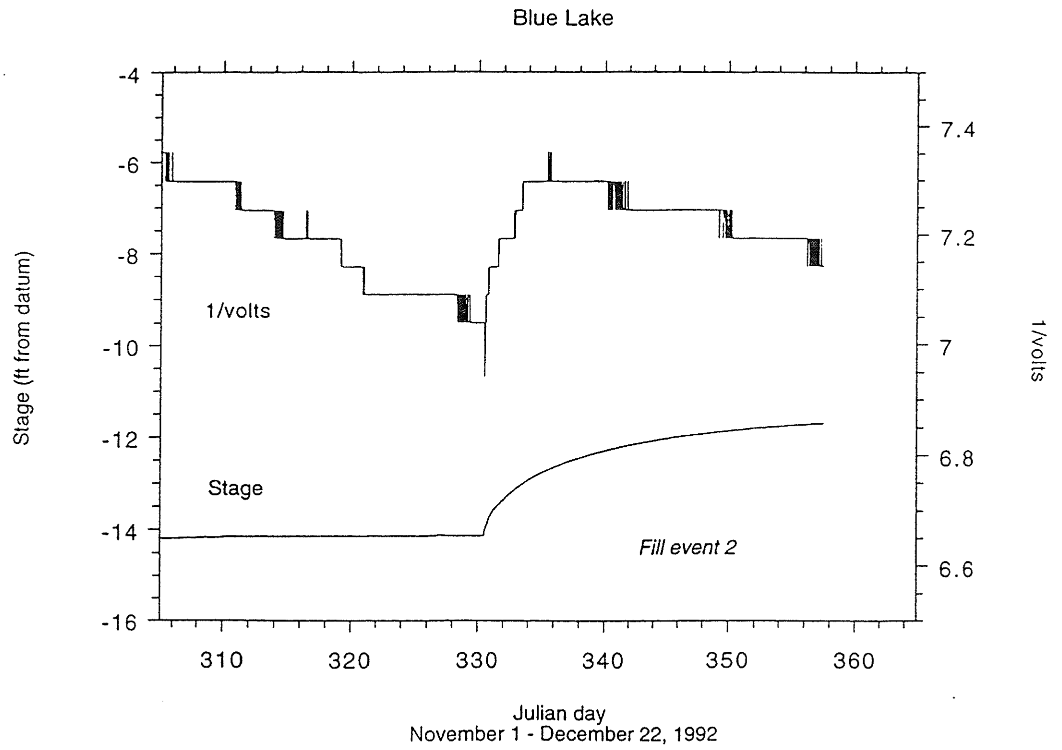
The water temperature curves (Figure 7.3a and 7.9a) suggest that water temperature is close to deep cave temperature of 8.7°C throughout the study. But there are minor, abrupt offsets, and some fine structure is present. The manipulation associated with periodic maintenance of the probes is responsible for the offsets. The fine structure, however, does not correlate with the maintenance visits. It is possible to discern a real temperature response at the start of the second fill event. It is subtle, but it can be seen at the scale of Figure 7.7. More usefully, it can be seen at the scale of Figure 7.8b, which plots stage and water temperature for November 24-29. There appears to be a drop in water temperature of 0.03°C when the stage begins to rise. This is a small drop, barely larger than the resolution of the thermistor wire (0.01°C), but the drop appears to be real. It is, moreover, persistent. Four similar drops have been seen with a better temperature probe (that produces less noisy data and lacks the abundant offsets) in later fill events at Blue Lake (through spring 1994). (Additional fine structure in the temperature record is apparently a function of cyclic electronic interferences; these diminished after modifications were made to the equipment, but disappeared only with installation of the Campbell 247 Conductivity/Temperature probe.)

(The slight initial drop in conductivity associated with the temperature drop in Figure 7.7 is possibly an artifact of the instrument response. As the water arrived, there may have been a faster response to the temperature drop than to the increase in the solute load. We have to remember that "small" changes in temperature produce a greater change in conductivity than do "small" changes in solute concentration.)

The drop begins with the onset of the fill event; it probably indicates only that the water displaced into Blue Lake was barely colder than the water at Blue Lake. More importantly, it supports the interpretation that the initial water to arrive was displaced water. Had it been rapid run-in water, it should have arrived sooner than 141 hours, and should have been colder (recall our estimate of the temperature of the recharge water was < 5°C).

Drain Event 2

Fill event 2 and the subsequent Drain event 2 were only partial. After the November storm, the surface above Mystery Cave froze, limiting recharge. We do not know if recharge to Blue Lake ceased totally during the winter, but many drip points and small vadose flows in Mystery do cease or go to very low discharge in the period from roughly December to March. The water level rose to about -11.5 ft, then fell through the winter. Conductivity also fell during this period, as did calcium,



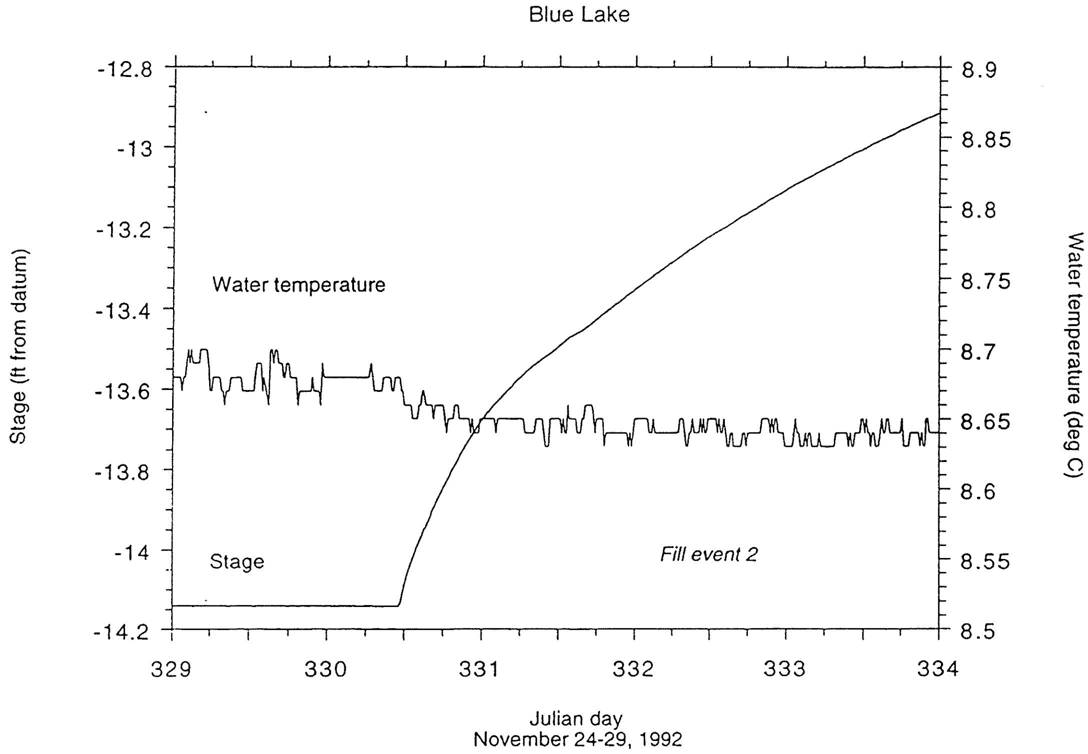


Figure 7.8. The record at Blue Lake from November and December, 1992. a. Stage and conductivity (1/volts). b. Detail of the water temperature drop, November 24-29,1992.

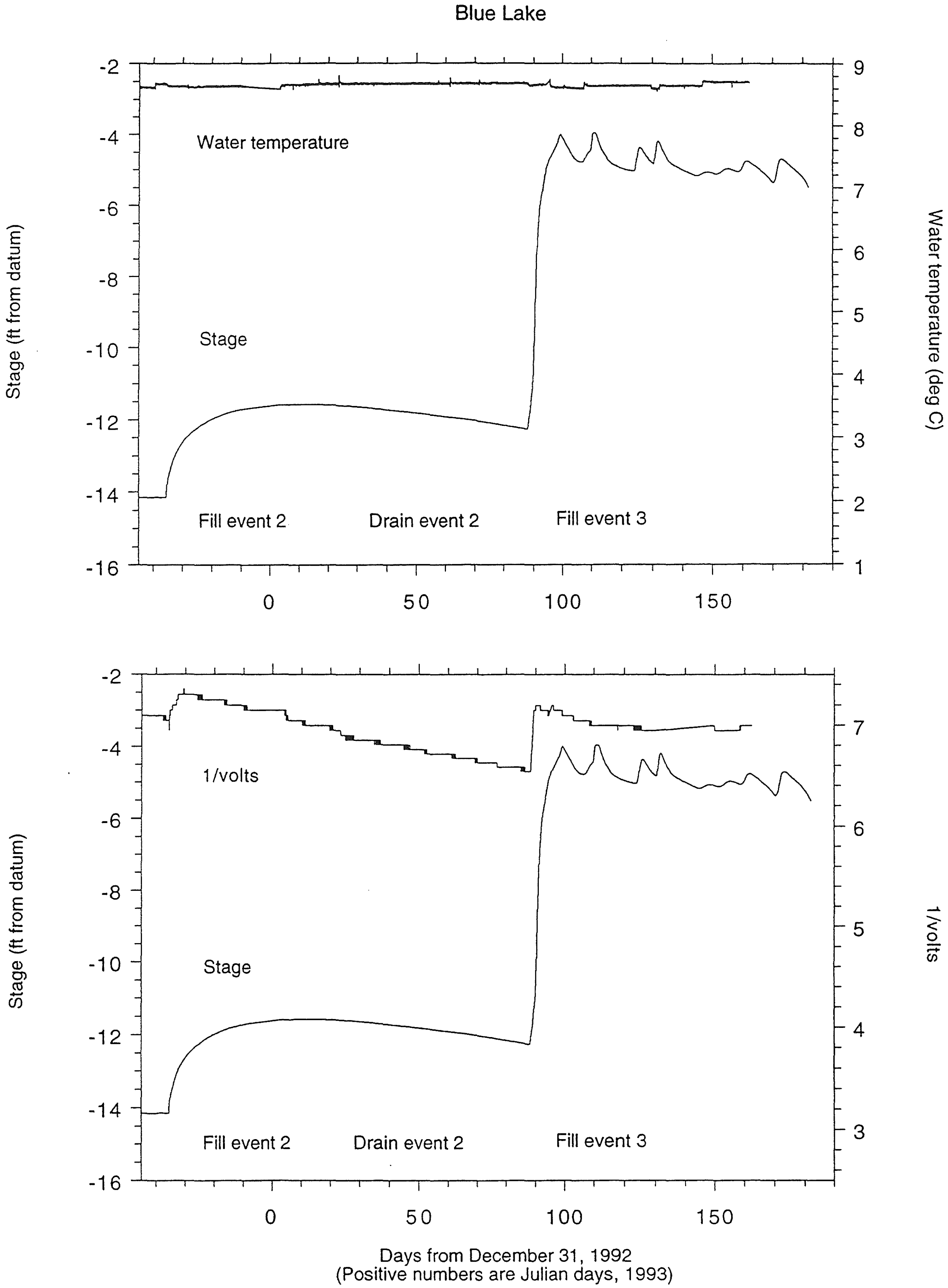
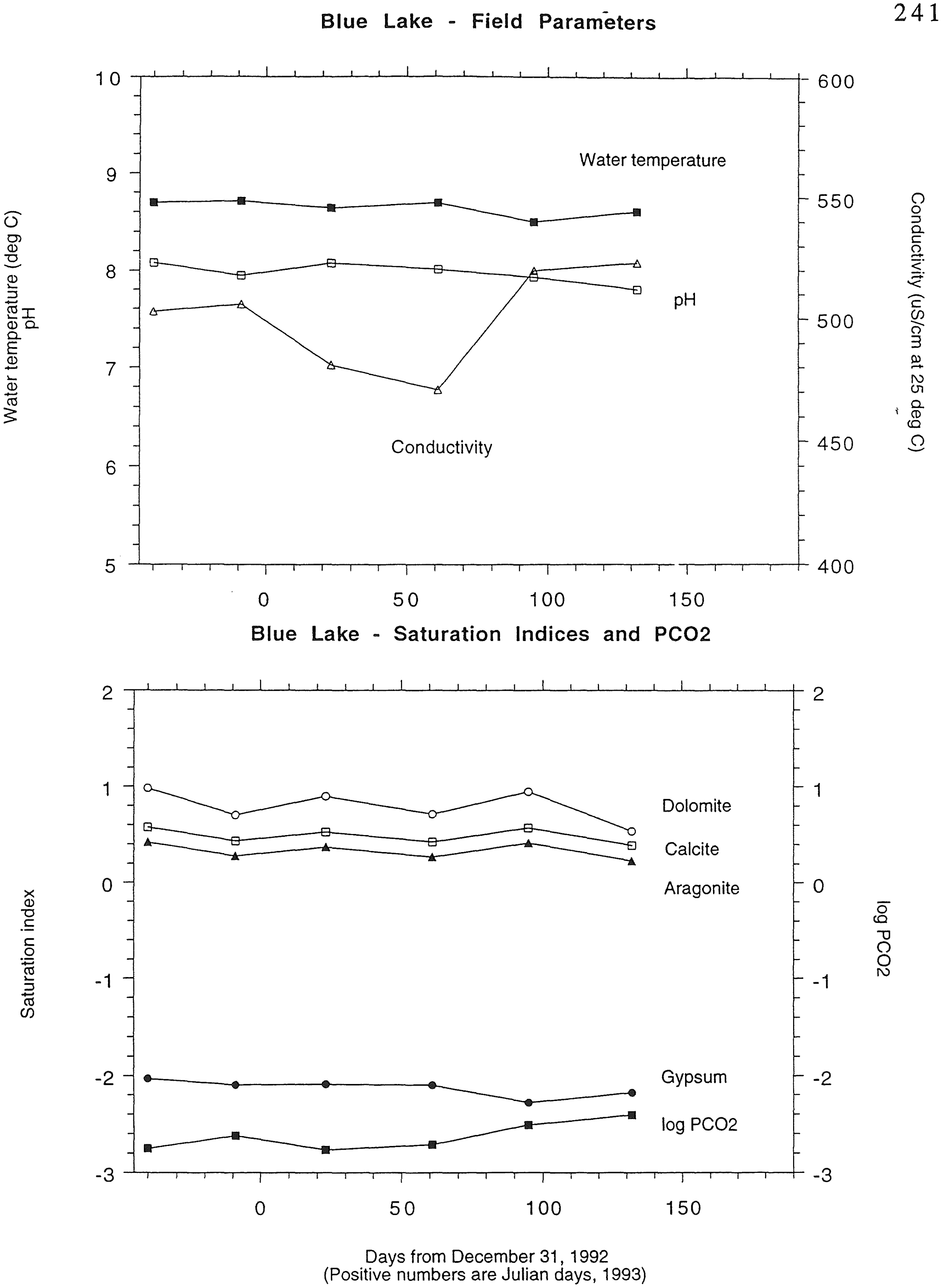


Figure 7.9. Stage, water temperature, and conductivity (1/volts) at Blue Lake in late 1992 and the first half of 1993. Day zero is December 31, 1992.



Blue Lake - Field Parameters

Blue Lake - Saturation Indices and PCO2

Figure 7.10. Time series of field parameters, saturation indices, and log P_{CO_2} at Blue Lake in late 1992 and the first half of 1993.

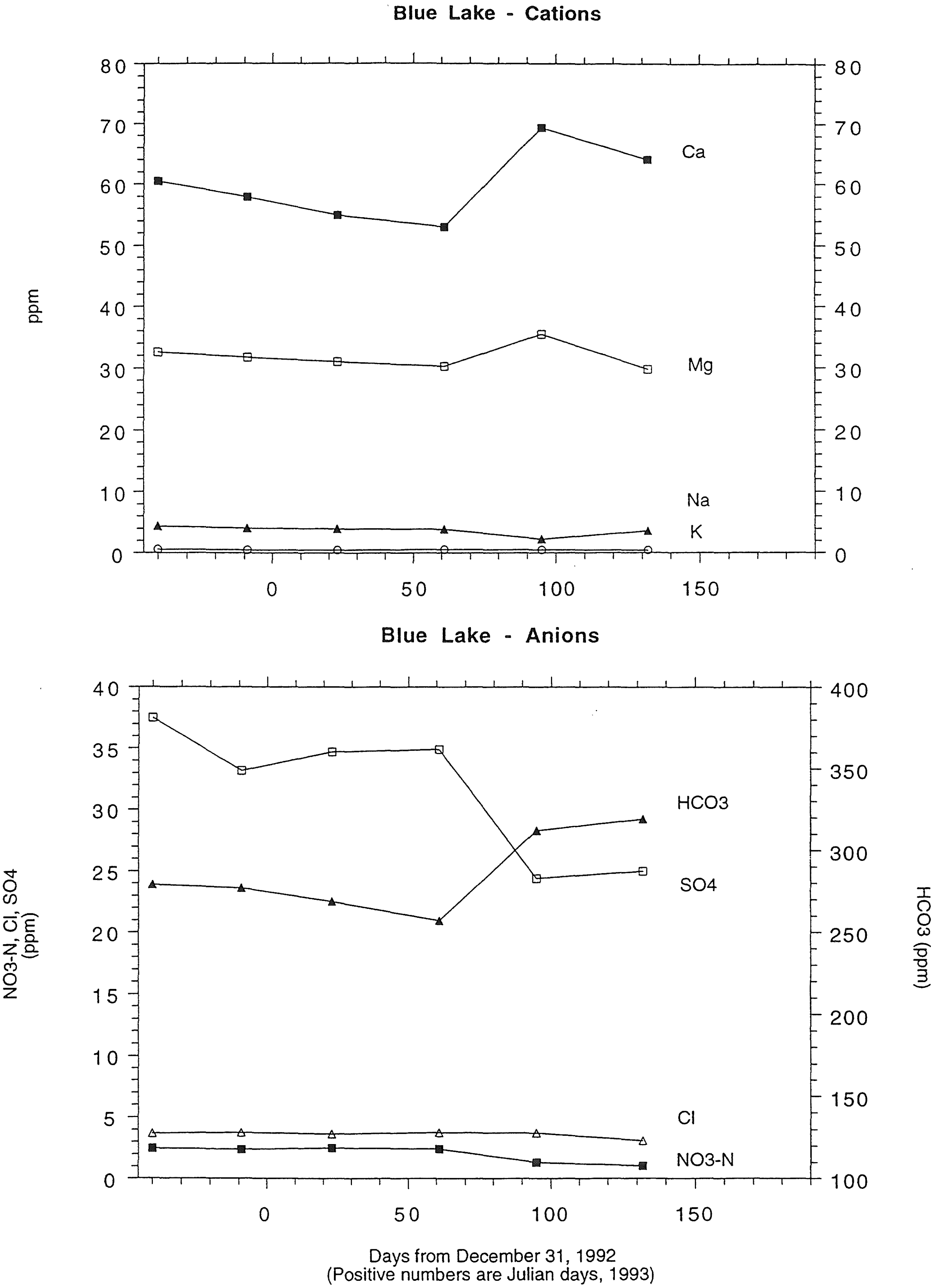


Figure 7.11. Time series of cations and anions at Blue Lake in late 1992 and the first half of 1993.

magnesium, and bicarbonate (the first three data points in Figures 7.11a and 7.11b). As in the previous drain event, sulfate rose. At the very end of Drain event 1, during near-constant low stage with no visible influx of water, similar trends were interpretes as indicating precipitation of calcite in the small, isolated pools that make up Blue Lake. Here we have a single pool, over 2 ft deep, extending upstream the full width of the tributary passage. Calcite rafts were not recorded in our field notes during that time period, but they could have been present. It is also possible that precipitation was taking place elsewhere than at the surface.

One interpretation is that precipitation again occurred, but that is not the only hypothesis to consider. Progressively more dilute water might have flowed into the lake most, if not all of the recession, producing a continually declining conductivity. However, there are difficulties with this alternative. As residence time of the incoming water increased, it should have become more concentrated, so there would be a tendency for conductivity to slow in its rate of decline. But the decline in conductivity is remarkably constant starting before the end of Fill event 2 and continuing throughout Drain event 2. (Compare the conductivity trend with that at the end of Drain event 1 between points a and b on Figure 7.3b).

FILL EVENT 3

Fill event 3 is a response to a major recharge event, at the end of March and the beginning of April, 1993, that culminated in extensive flooding on the surface in southeastern Minnesota, both on the Root River and other surface rivers. The response in the cave was dramatic at Blue Lake. It was spectacular at Flim Flam Creek, which flooded for several days. It was traumatic on the Root River, and in the Mystery I commercial passages. Many of those passages flooded, in places clear to the ceiling, causing damage to the lighting system, minor sediment slumping, and widespread deposition of a thin layer of silt. More extensive descriptions of the flooding are in a later chapter. To keep from being overly repetitive, and to preserve the continuity of explication of the in-cave responses to that flood, we shall not discuss the third fill event here. We note only that stage rose rapidly from about -12.3 ft to -4 ft, and that stage remained very high throughout the rest of the spring. Further, the third fill event displaced higher conductivity water into Blue Lake. Finally, a very small temperature drop, of similar magnitude to the one just discussed, was also observed (but is not readily seen in Figure 7.9a).

VARIATION OF CONDUCTIVITY WITH DEPTH AT BLUE LAKE

Background

Stratification of water temperature and chemical parameters is ubiquitous in lakes on the surface, particularly in temperate climates with distinct seasons and large temperature ranges. Stratification in stagnant cave waters is also possible, but little studied. Kempe (1972) describes the formation of what he calls facets (Fazetten) in German gypsum caves formed by slow moving waters. Sub water-table dissolution produces relatively high-density films that slide down walls as a density flow, initiating a chemically-driven convection current. Kempe (personal communication to Jameson, 1981, believes this process also operates in limestone caves, and cited morphologic evidence in Bone Cave (West Virginia) to support the hypothesis. Bone Cave is a phreatic cave for which extremely large-wavelength scallops, a variety of other geomorphic features, and the hydrologic setting, all testify to its enlargement by slow-moving waters near a former base level.

Temperature stratification in cave waters---if such exists---can be expected to be subdued and short-lived compared to that of surface lakes, and would require different mechanisms for initiation. Advecting air, if much warmer than local bedrock and water cave temperature (and if sufficiently persistent and strong), might warm the surface layer of stagnant pools sufficiently to produce thermal stratification. Advecting water probably would have a more difficult time producing a stable stratification, because the introduction of warmer or cooler water will likely be turbulent and promote significant mixing, which would tend to produce a water of an intermediate temperature. Nonetheless, there are plausible mechanisms to introduce pulses of warm or cool waters into caves and produce transient thermal stratification of water bodies.

For example, at Blue Lake, relatively cool water could flow into the bottom of the lake once water was sufficiently deep and these waters might resist significant mixing. In support of this hypothesis, we first note that thermal stratification requires very little temperature difference. If a pulse of slightly cooler water, on the order of the 0.3°C seen above, were to flow into Blue Lake during relatively high stage, it might well move as a density current along the base of a descending flowstone mound about 60 ft from the water temperature probe, and flow along the floor to reach that probe with very little turbulent mixing. If this kind of temperature stratification occurs, it is liable to be of a small magnitude and will be difficult to document without the installation of a vertical network of highly accurate temperature sensors.

Chemical stratification is also conceivable at Blue Lake, at least for periods of stage when input has ceased and water level is declining (i.e., during the drain events). Since the water is supersaturated with respect to calcite, chemical differences may develop within the pool profile if precipitation is preferentially distributed. Calcite rafts on the surface of the water may form in response to degassing of CO_2 at the air/water interface and precipitate at a faster rate than other deposits precipitate elsewhere within the water column or along pool walls. Precipitation, of course, removes Ca^{+2} and HCO_3^- to deposit $CaCO_3$. This process could remove a sufficient quantity of ions to result in water with a lower density and with a lower conductivity at the surface than at depth. Once again, if this type of chemical stratification occus, it is liable to be of a small magnitude and will be difficult to document without the installation of a vertical network of highly accurate conductivity sensors. (For conductivity sensors, this would require considerable and sophisticated design, because of problems associated with ground looping between instruments.)

Measurements at Blue Lake

To check for thermal and chemical stratification, water temperature and conductivity were measured at varying depths at several locations in Blue Lake in April, May, and June of 1993 (Table 7.1). Measurements were made by lowering the probe to the water's surface and then measuring temperature and conductivity at

Table 7.1

Variation of Conductivity and Temperature with Depth at Blue Lake

Depth (ft) from top rail	At 3rd post 17-Apr-93 uS/cm at 25 deg C	At 3rd post 17-Apr-93 Temperature deg C	At east end BL 17-Apr-93 uS/cm at 25 deg C	At east end BL 17-Apr-93 Temperature deg C	At 3rd post 12-May-93 uS/cm at 8.6 deg C	At 3rd post 12-May-93 uS/cm at 25 deg C	At 3rd post 12-May-93 Temperature deg C	At 3rd post 11-Jun-93 uS/cm at 8.6 deg C	At 3rd post 11-Jun-93 uS/cm at 25 deg C	At 3rd post 11-Jun-93 Temperature deg C
6	-	-	-	-	360	534	8.6	-	-	-
7	562	8.6	-	-	361	536	8.6	360	535	8.6
8	562	8.6	567	8.7	361	537	8.6	361	536	8.6
9	562	8.6	565	8.6	362	538	8.6	360	535	8.6
10	566	8.6	566	8.6	365	542	8.6	360	535	8.6
10.5	-	8.6	567	8.6	-	-	-	360	535	8.6
11	567	8.6	568	8.6	365	543	8.6	365	542	8.6
12	567	8.6	-	-	366	544	8.6	365	542	8.6
13	568	8.6	-	-	367	545	8.6	365	542	8.6
14	569	8.6	-	-	-	-	-	365	542	8.6
14.5	572	8.6	-	-	-	-	-	366	543	8.7
15	573	8.6	-	-	-	-	-	-	-	-

half-foot to one-foot intervals going down and then again coming back up. Care was taken to move the probe slowly to minimize disturbance of the water column. The conductivity was measured on a scale that had a resolution of 1 µS/cm. The water temperature was measured on a scale that has a resolution of 0.1°C. The top measurement in each case was made within 6 inches of the water's surface.

No thermal stratification was observed. This result does not preclude thermal stratification or a systematic but minor decrease in water temperature with depth. Any such temperature variation would be expected to lie within the temperature range of 0.01 to 0.05°C, based on variations seen with the temperature thermistor attached to the data logger in 1992-1993 and more recently with better equipment.

Conductivity, however, varied with depth. On April 17, about three weeks after the onset of Fill event 2, there appeared to be three layers of water with conductivities that increased with depth within the two lower layers (Figure 7.12). Conductivity rose from 562 to 573 µS/cm over a distance of 7.5 ft. On that date, conductivity was measured only on the instrument setting which automatically transforms conductivity at ambient temperature to conductivity at 25°C. On May 12 and June 11, conductivity was measured on both settings. On these dates there appeared to be two layers (Figures 7.13 and 7.14). Conductivities were lower, following a lengthy wet spring in which water levels remained unusually high at Blue Lake and elsewhere on the surface and in the cave. On May 12, conductivity rose 534 to 545 µS/cm at 25°C over a distance of 7 ft. On June 11, conductivity rose from 535 to 543 µS/cm at 25°C over a distance of 8 ft.

The significance of these observations is not clear. The observed differences in conductivity are consistent, but without further documentation are merely suggestive. One possibility that needs to be checked is that the measured response is real---that it is not simply a function of some poorly understood aspect of the response of the YSI conductivity/water temperature probe. It is reassuring that the conductivity readings on both scales (ambient temperature conductivity and conductivity corrected to 25°C) *increase* with depth. If the meter were responding to a decreasing temperature gradient (colder water at the bottom), then it would produce decreasing ambient conductivities. It is possible that the meter responds to conductivity (as a result of minor temperature changes) at a level finer than it reads on the temperature scale. If the internal algorithm for translating ambient conductivity to conductivity at 25°C operates properly, based on a continuous measurement of water temperature on a finer scale of resolution than that displayed, then those conductivities at 25°C will also rise with depth, as was found. If they did not, then we might suspect we were at the limits of the instrument response.

COMPARISON OF CHEMISTRY AT BLUE LAKE, BLUE LAKE SPRINGS, AND BLUE LAKE DRIPS

The chemistry of Blue Lake and Blue Lake Springs are very similar (Table 7.2), as is expected from the setting and their hydrologic behavior. Blue Lake Springs is near Blue Lake and flows only when stage at Blue Lake is higher than the level of the springs. The lack of significant differences in field parameters (Figures 7.15 and 7.17) and ions (Figures 7.16 and 7.18) suggests that Blue Lake Springs water is derived directly from Blue Lake. The water changes little in chemistry while flowing approximately 60 ft through trail gravel and breakdown. It is unlikely that the water of Blue Lake Springs is augmented by water from other flow paths, but that

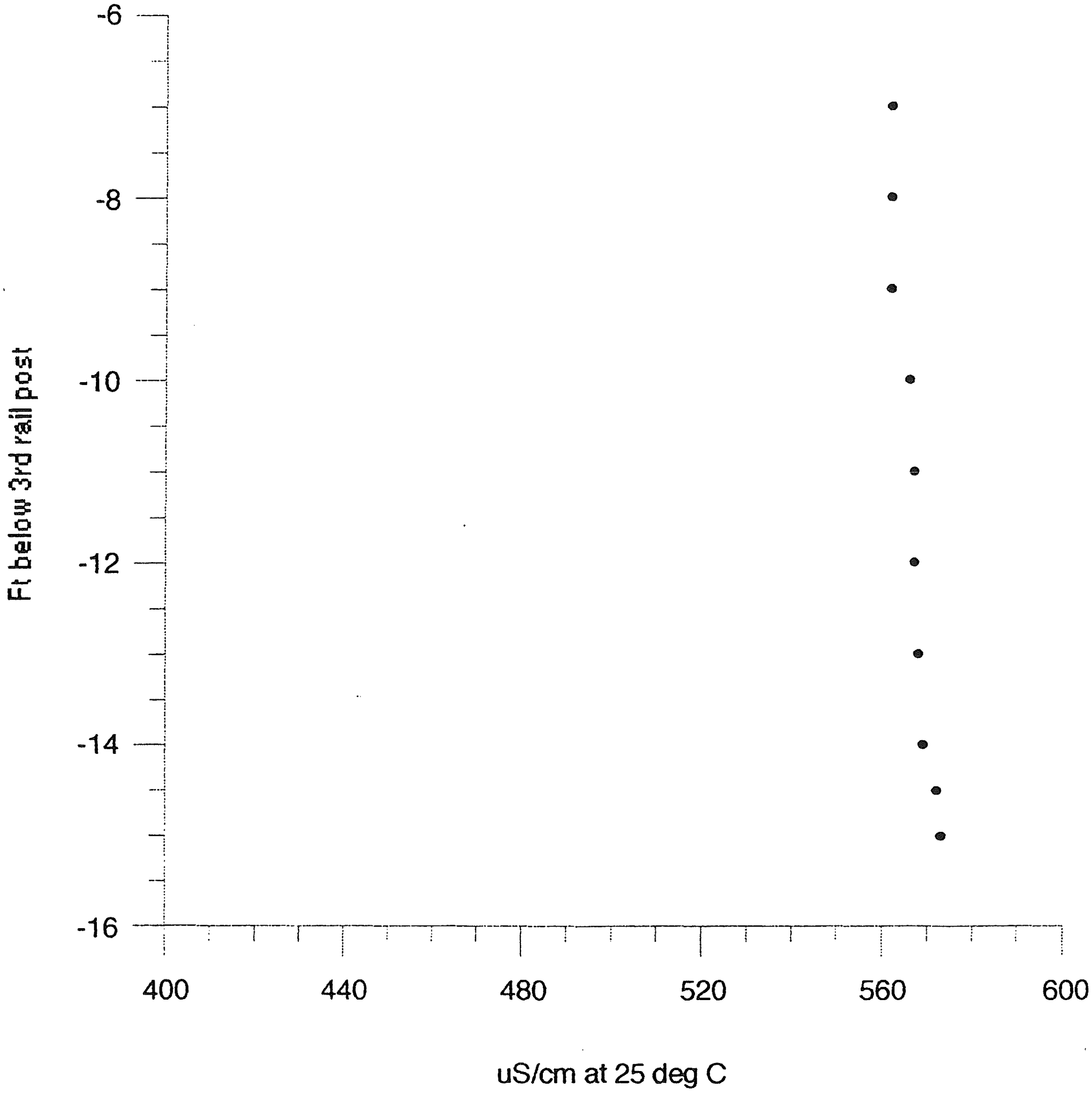


Figure 7.12. Variation of conductivity with depth at Blue Lake, April 17, 1993.

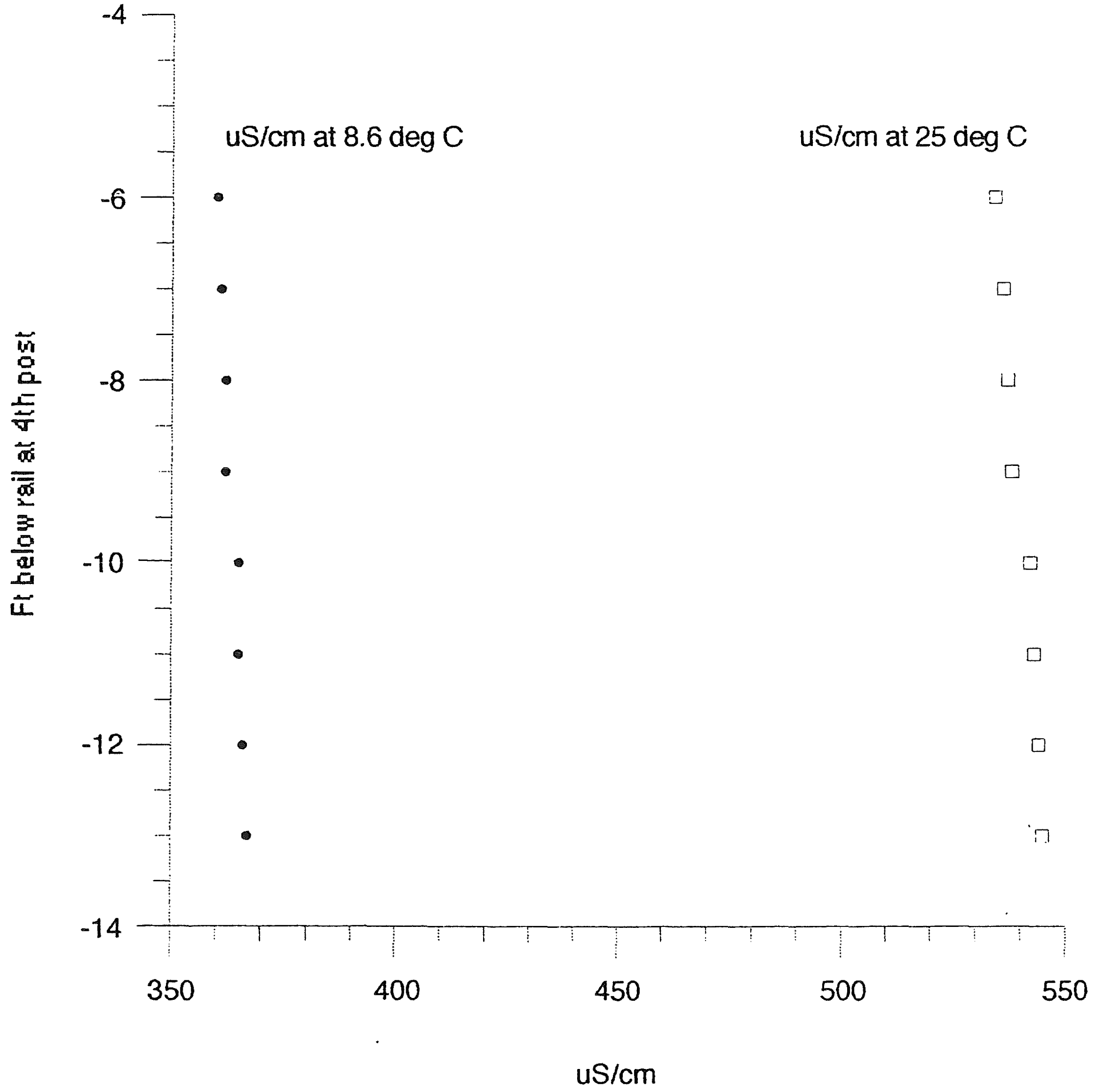


Figure 7.13. Variation of conductivity with depth at Blue Lake, May 12, 1993.

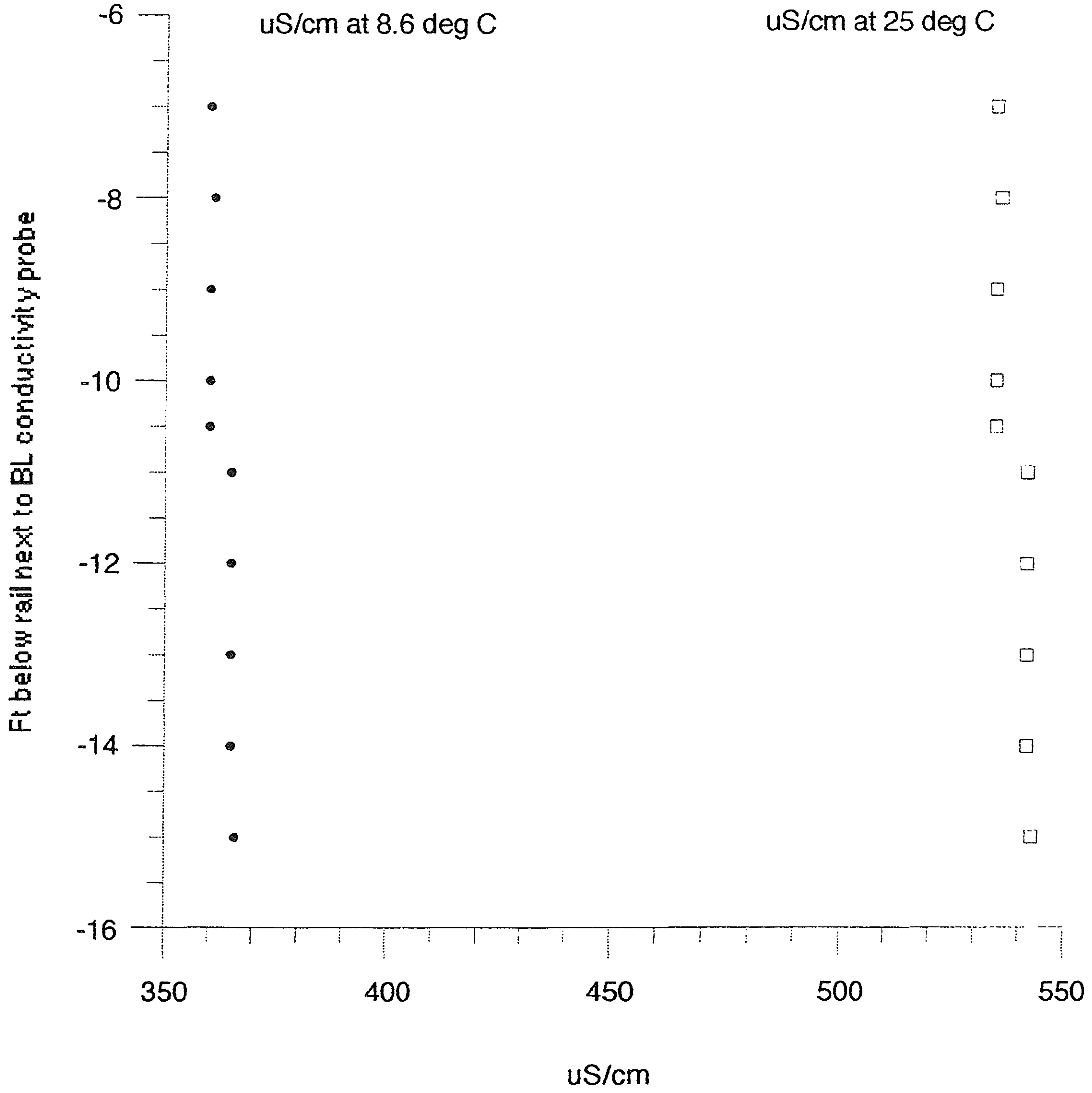


Figure 7.14. Variation of conductivity with depth at Blue Lake, June 11, 1993.

Table 7.2

Comparisons of Water Chemistry at Blue Lake, Blue Lake Springs, and Blue Lake Drips							
	Blue Lake	Blue Lake Springs	Blue Lake Drips		Blue Lake	Blue Lake Springs	Blue Lake Drips
Date	4/25/92	4/25/92	4/25/92		4/4/93	4/4/93	4/4/93
Temperature	8.6	8.7	8.8		8.63	8.65	8.7
pH	7.92	7.94	8.1		8.09	8.03	8.36
Conductivity	536	532	534		520	502	523
log PCO2	-2.53	-2.54	-2.7		-2.71	-2.68	-2.98
log SIC	0.52	0.566	0.72		0.662	0.57	0.93
log SIA	0.364	0.41	0.564		0.505	0.413	0.774
log SID	0.811	0.885	1.215		1.094	0.904	1.66
log SIG	-2.088	-2.076	-2.143		-2.188	-2.107	-2.23
TDS	485	477	503		468	450	483
Ca/Mg	1.28	1.34	1.279		1.28	1.3	1.21
IS	0.009	0.0091	0.0091		0.008548	0.00836	0.00869
Ca	67.9	69.9	68.9		64.5	63.5	64.4
Mg	31.9	31.4	32.4		30.3	29.4	32
Na	3.83	3.7	4		3.64	3.5	3.94
K	0.62	0.57	0.51		0.49	0.49	0.48
Sr	0.0887	0.0847	0.0861		0.086	0.083	0.088
Ba	0.0552	0.0508	0.0797		0.057	0.048	0.077
Alk	260	268.5	271		256	240	264
HCO3	317	327	330		312	292	322
NO3-N	1.78	1.6	2.65		1.31	1.35	1.89
NO3	7.9	7.1	11.7		5.8	6	8.4
SO4	29.8	30	26.2		24.4	29.6	22.6
Cl	4.31	4.54	4.9		3.7	3.58	3.76
SiO2	21.4	21.8	24.1		22.7	21.5	24.7

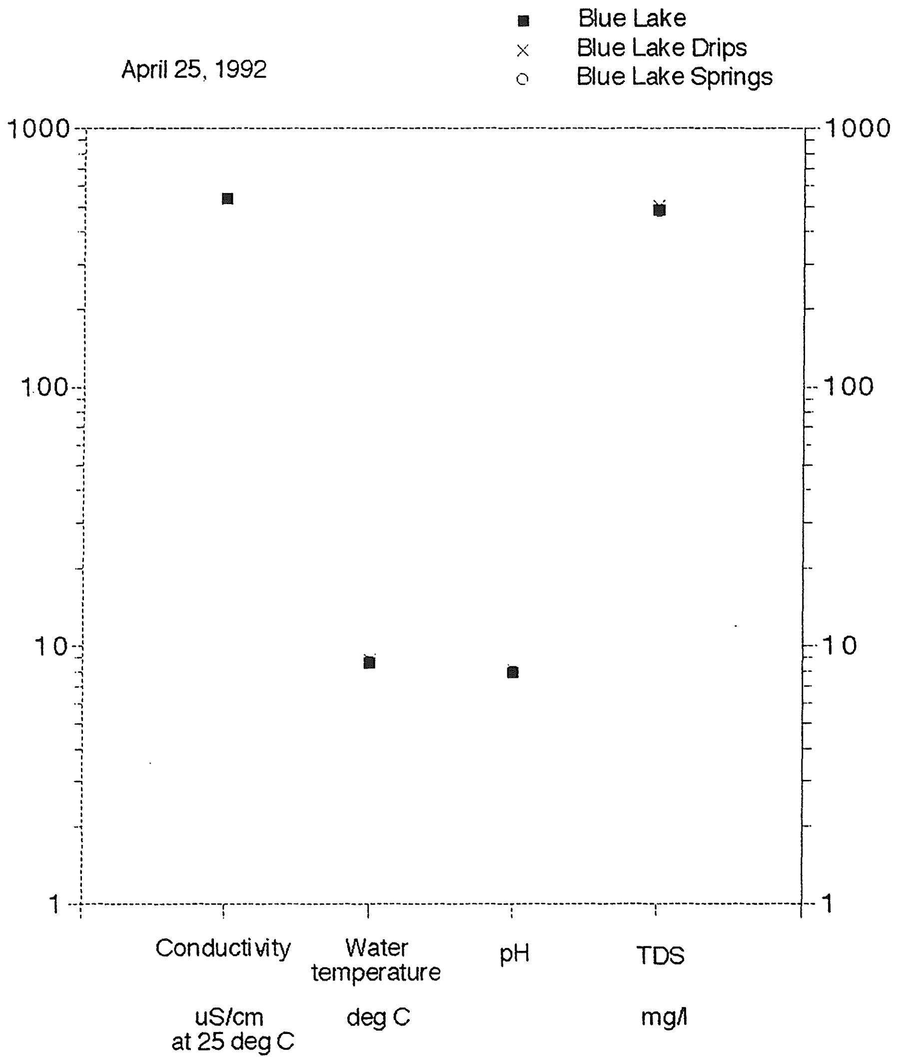


Figure 7.15. Field parameters and total dissolved solids (TDS) for Blue Lake, Blue Lake Springs, and Blue Lake Drips on April 25, 1992.

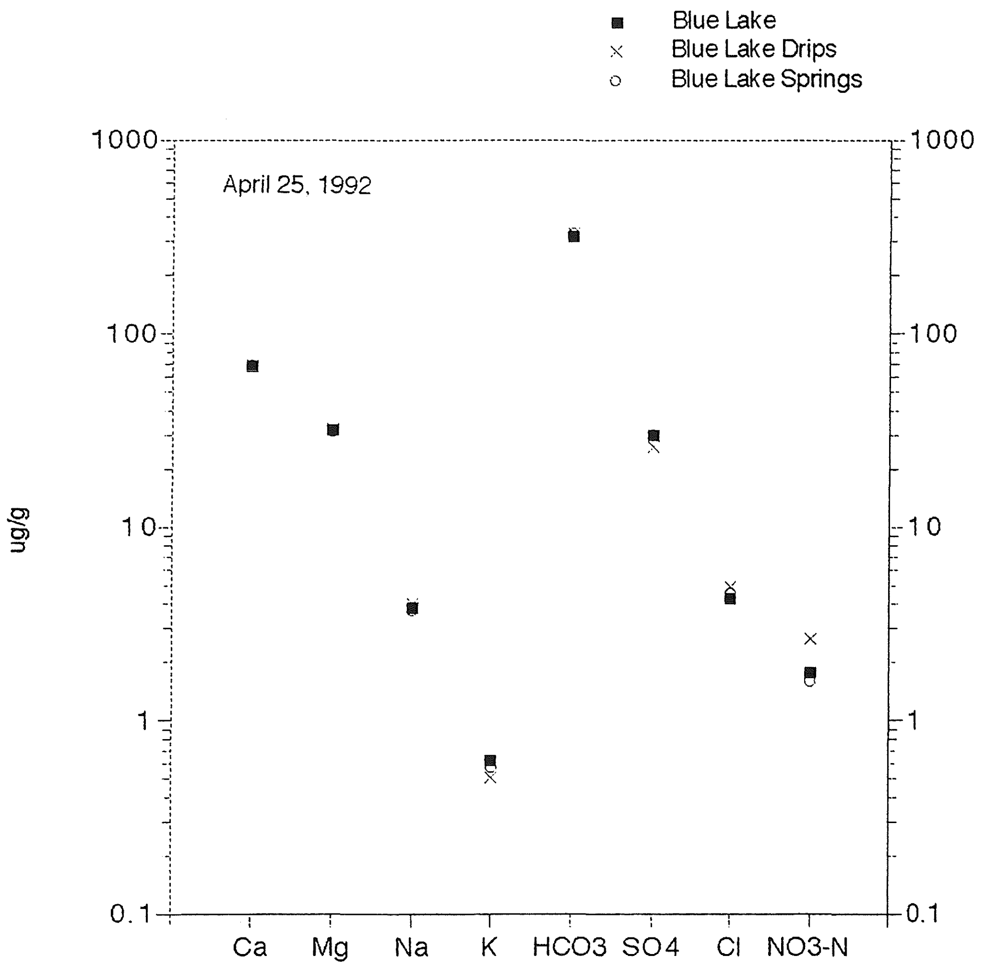


Figure 7.16. Ions at Blue Lake, Blue Lake Springs, and Blue Lake Drips on April 25, 1992.

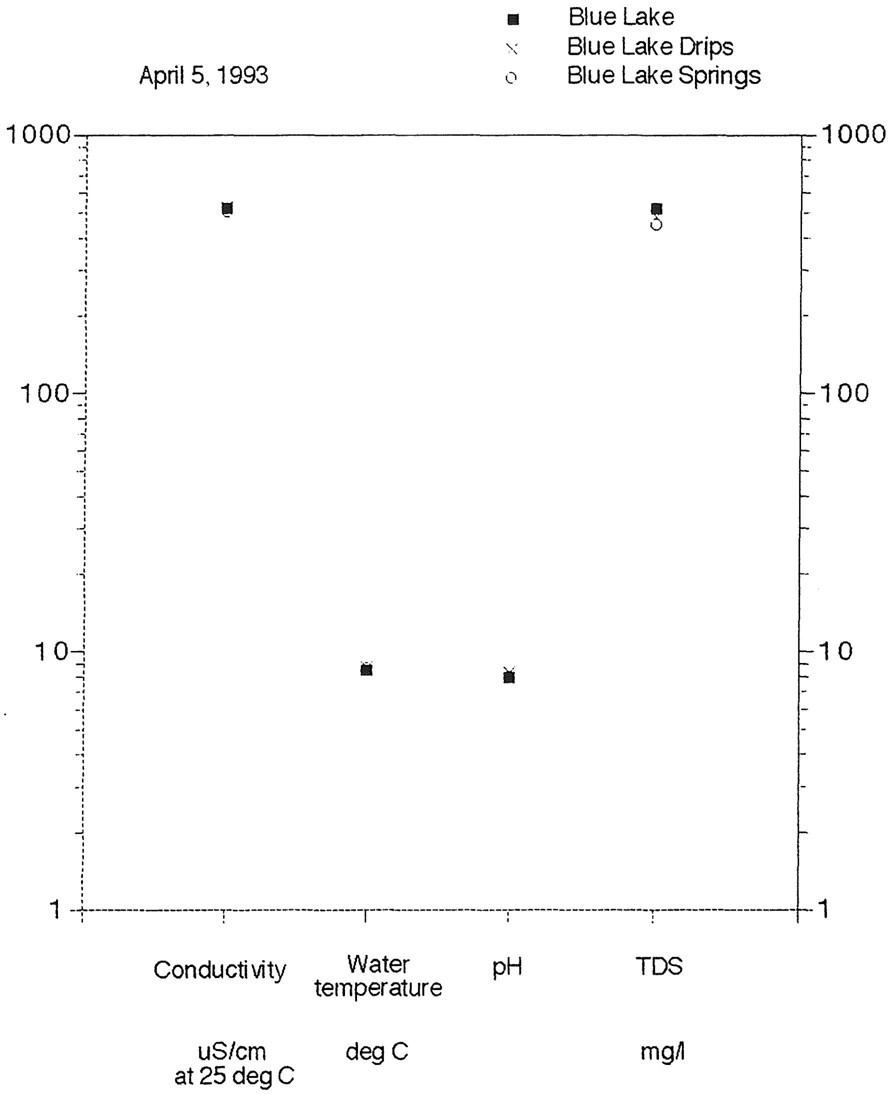


Figure 7.17. Field parameters and total dissolved solids (TDS) for Blue Lake, Blue Lake Springs, and Blue Lake Drips on April 5, 1993.

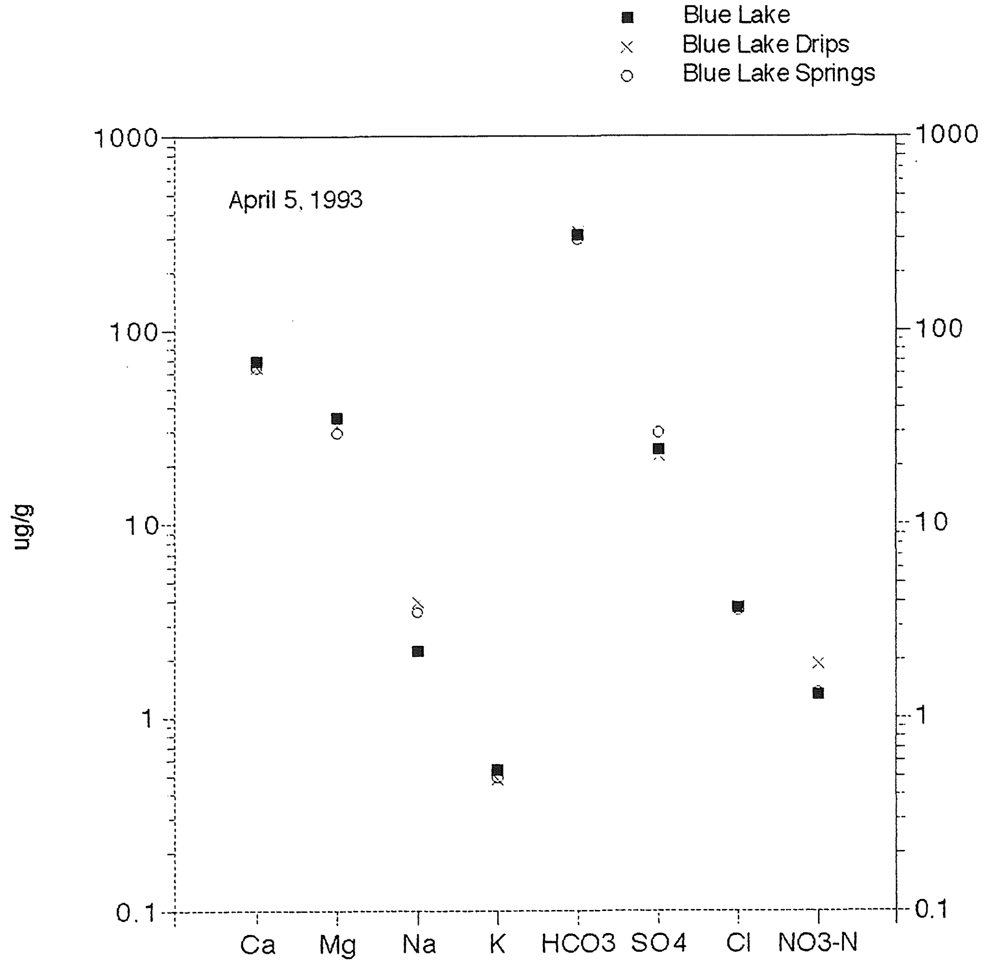


Figure 7.18. Ions at Blue Lake, Blue Lake Springs, and Blue Lake Drips on April 5, 1993.

possibility cannot be ruled out entirely on the basis of chemistry. Blue Lake Drips, the only other nearby water, also has a chemistry nearly indistinguishable from that of Blue Lake, at least on the two dates on which all three sites were sampled (Table 7.2, Figures 7.15-7.18). Only nitrate shows any difference. Blue Lake Drips has slightly higher nitrate levels. Both the drips and lake seem to respond to similar recharge sources. We do not mean to imply, however, that Blue Lake Drips could be tributary to Blue Lake Springs, for Blue Lake Springs is slightly higher and lies on the opposite side of Blue Lake.

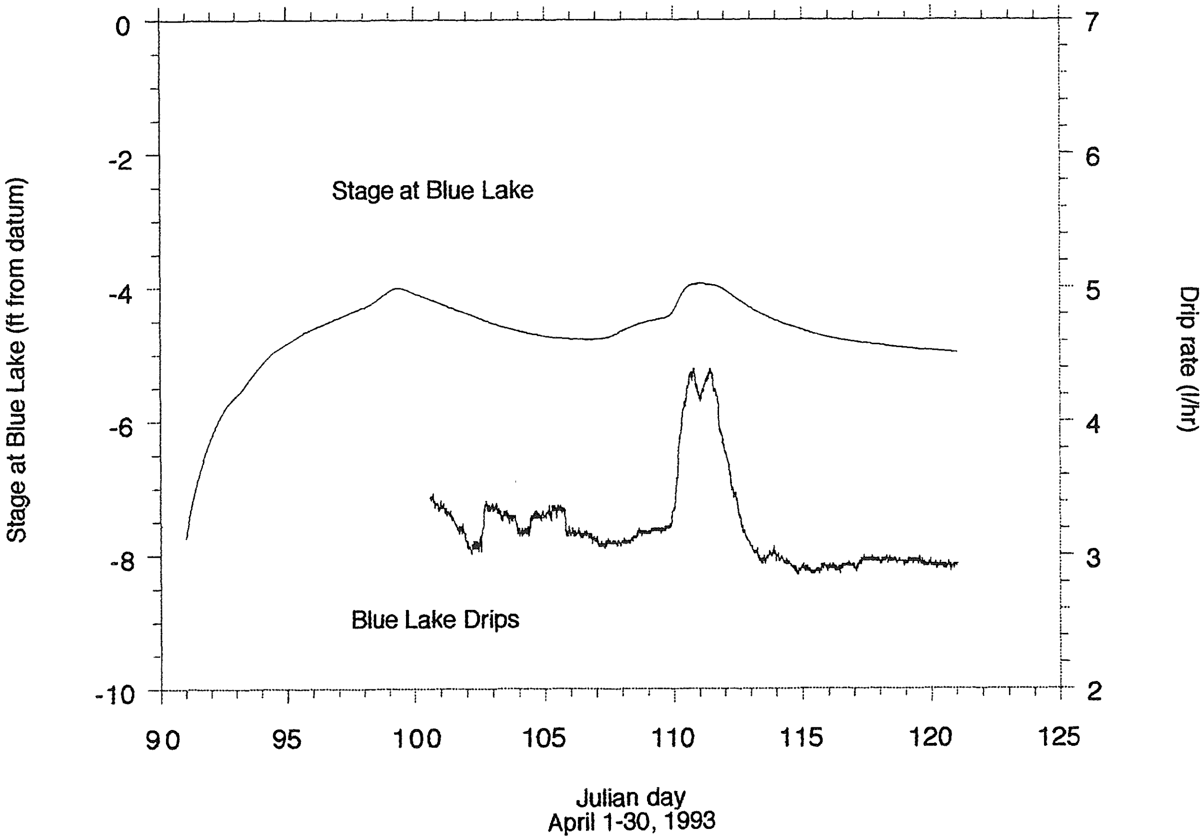
COMPARISON OF THE HYDROLOGY OF BLUE LAKE AND BLUE LAKE DRIPS

Blue Lake fills rapidly and remains at a high stage during much of the spring. It then drains with long periods in which little or no water enters and during which chemical changes can occur in a static water body. The water that initiates fill events is believed to be displaced water. Actual recharge event water is then so slow in arriving that it has already reacted chemically with the materials in which it has come into contact, making a clear distinction between displaced water and recent event water impossible without additional natural or artificial tracers. During the period of high stage, Blue Lake responds somewhat more rapidly to precipitation, apparently because soil moisture deficits are smaller on the surface and subsurface stores are full or nearly so. At high stage, Blue Lake may begin to rise within a day or less, reach a peak of 1 to 1.5 ft above pre-event stage, and take as long as ten days to return to that stage.

Blue Lake Drips, in contrast, is perennial and is fed by low-discharge seeps and drips. During the period drip rates were monitored, Blue Lake Drips had drip rates varying between about 2.8 and 4.5 l/hr. It responded rapidly to storms with sharp rises in discharge in which discharge rose 1 to 1.5 l/hr over a day and took 2-5 days to fall back to pre-event levels (Figures 7.19-7.21).

A comparison of the responses of Blue Lake and Blue Lake Drips to precipitation can usefully be made for four events in the spring of 1993. A generalized hydrograph that illustrates definitions of relevant lag times appears in Figure 7.22, and data for the lags are in Table 7.3. L_L is the lag time between the onset of a major rise in precipitation and the onset of a sharp rise in stage at Blue Lake. L_D is is the lag time between the onset of a major rise in precipitation and the onset of a sharp rise in drip rates at Blue Lake Drips. ΔL is the lag time between the rise in stage at Blue Lake and the rise in drip rates at Blue Lake Drips. L_P is the lag time between the peak of drip rate at Blue Lake Drips and the peak in stage at Blue Lake.

The first event (Figure 7.19) had a double peak in precipitation; this is reflected in the hydrologic record for Blue Lake Drips but not Blue Lake. The remaining events have single peaks in drip rate and stage. The records and lag times can be summarized briefly. Blue Lake responds faster to precipitation recharge than does Blue Lake Drips, but the drip rate rises very fast and the peak is reached sooner. The peak is narrower than the broad peaks in stage for Blue Lake. Although we are comparing a discharge with a stage (which would be misleading if Blue Lake were a stream rather than a basin with a restricted drain), the geometry and hydrologic behavior of Blue Lake are such that the comparison is reasonable. Moreover, we can interpret the data in a coherent---if preliminary---fashion. (The interpretation is



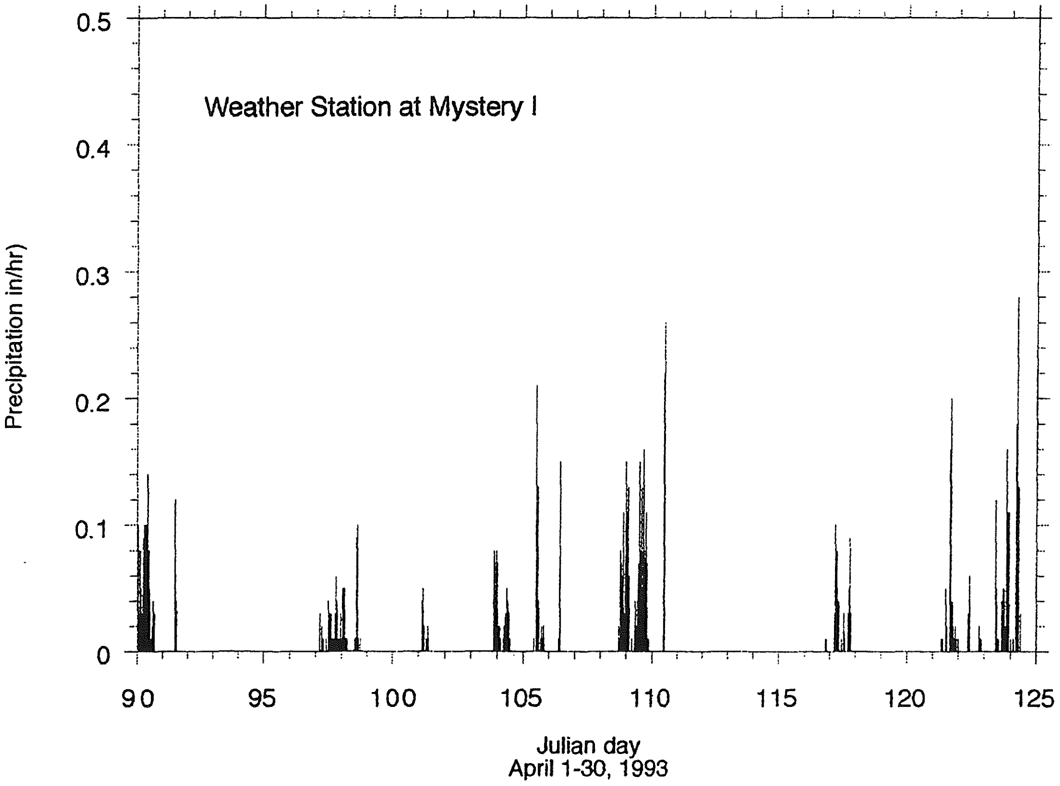


Figure 7.19. Time series for Blue Lake and Blue Lake Drips, compared with precipitation in April, 1993.

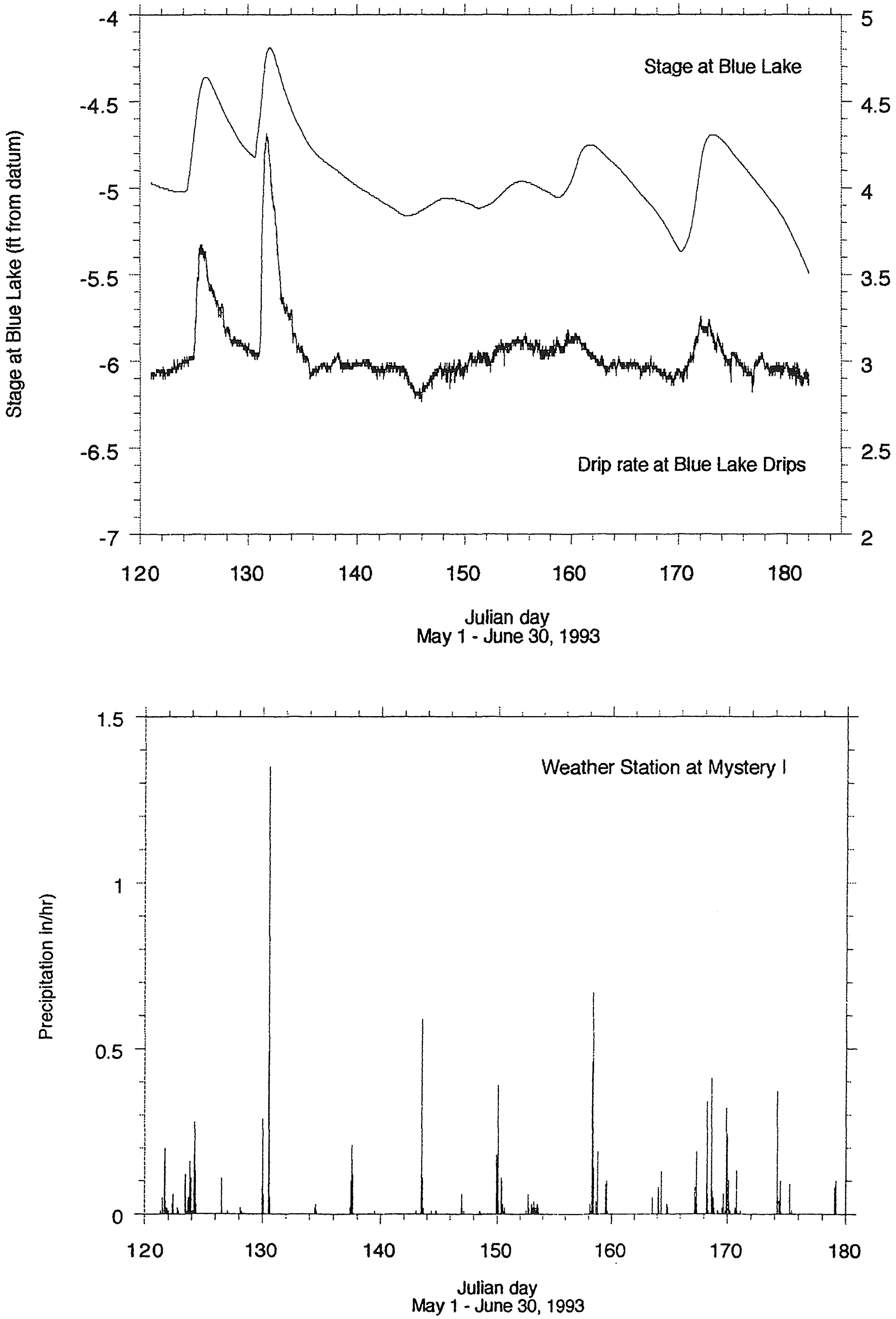
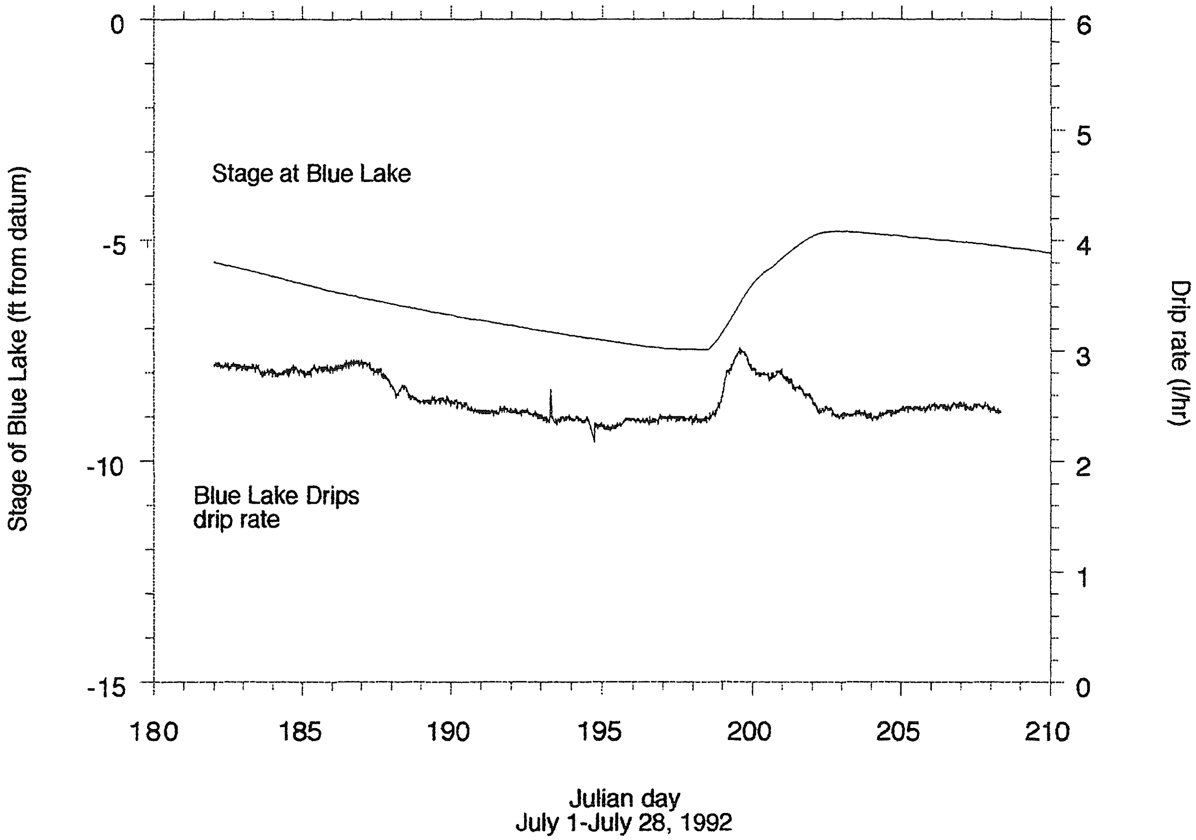


Figure 7.20. Time series for Blue Lake and Blue Lake Drips, compared with precipitation, for May 1 to June 30, 1993.



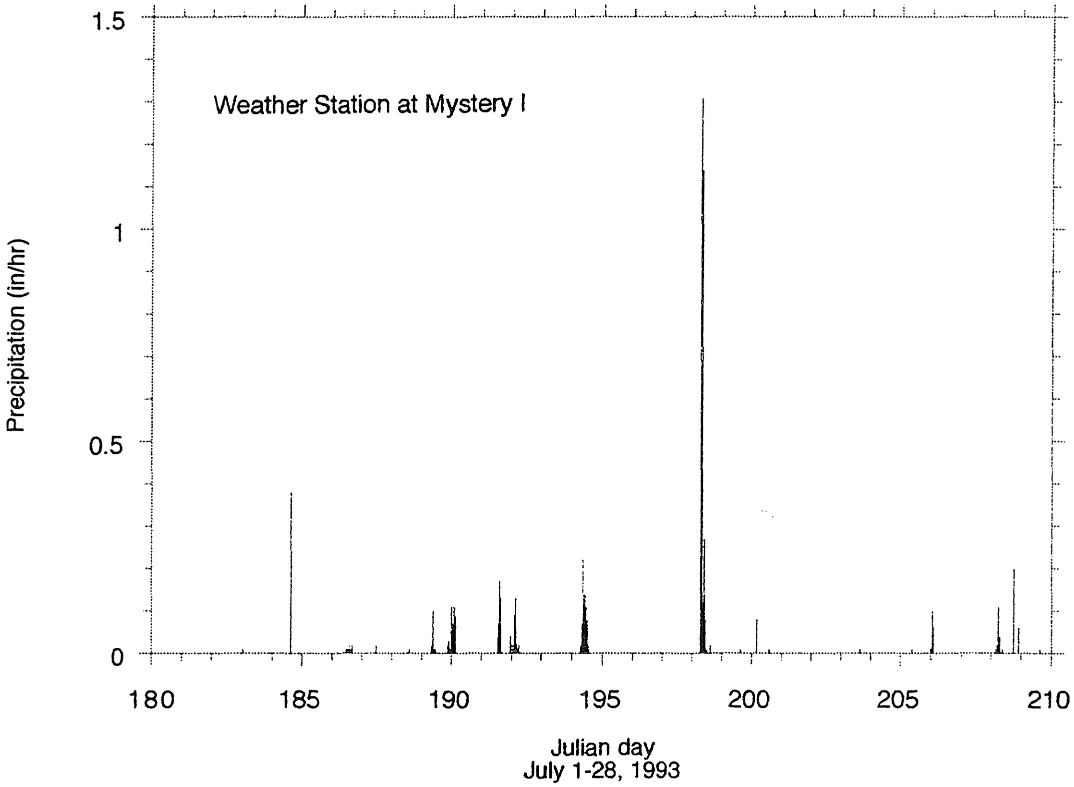


Figure 7.21. Time series for Blue Lake and Blue Lake Drips, compared with precipitation in July, 1993.

Table 7.3
Lag Times at Blue Lake and Blue Lake Drips

Event	Approximate Time Frame (Julian days)	L_L (hrs)	L_D (hrs)	ΔL (hrs)	L_p (hrs)
1a	108-111	22	43.5	21.5	7.5
1b	109-113	---	46	---	-8*
2	120-124	2	14.5	12.5	9
3	130-136	4	11.5	7.5	7.5
4	198-210	4.5	7.5	3	149

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* The second peak at Blue Lake Drips precedes the peak at Blue Lake.

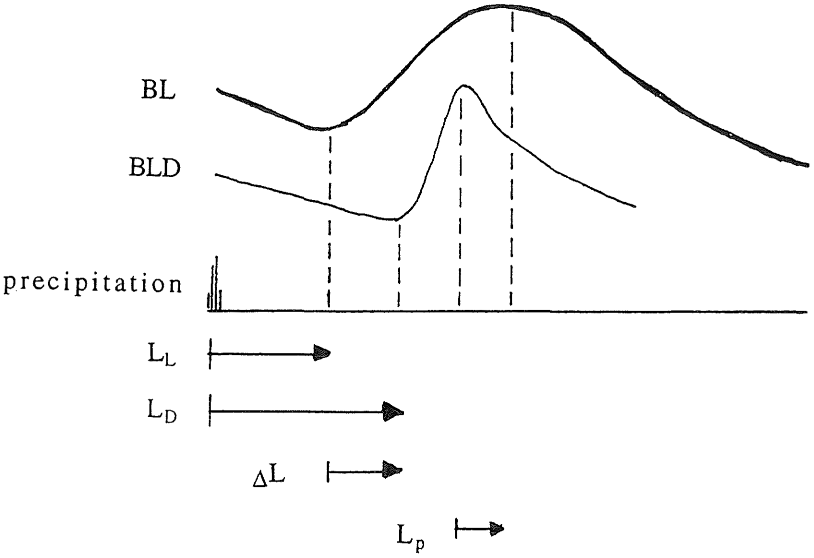


Figure 7.22. Schematic of precipitation, stage at Blue Lake, and drip rates at Blue Lake Drips, to illustrate lag times.

preliminary because it is, we think, amenable to a more protracted mathematical analysis, which may modify some conclusions.)

Blue Lake must have a larger surface basin feeding it than does Blue Lake Drips. Probably there are a large number of inputs feeding into the tributary passage immediately upstream of Blue Lake. The paths from soil, loess, subcutaneous zone, and the zone of fractured bedrock immediately above the cave are of variable lengths so water arrives at different times. Different paths may also have different proportions of storage deficits to fill before water can be displaced. Finally, in a tributary network, it takes only one constriction to result in backflooding during higher flows, and ponding slows down the water upflow of Blue Lake (though not as much as flow is slowed by Blue Lake itself). The net result is a broad peak and a relatively high discharge rate compared to that of Blue Lake Drips. [Although this can only be a very rough estimate at present, the maximum discharge rate at Blue Lake during fill events is on the order of 1000 l/hr (1000 times the maximum rate of change of depth of Blue Lake, in ft above -15.35 ft, for stage between -13.35 and -9.66 ft). This is more than 200 times the discharge of Blue Lake Drips at its maximum of 4.5 l/hr.]

Blue Lake Drips has a smaller drainage basin, and is fed by only a few tributary fractures from the overlying loess and soil. The smaller volume of stored water upflow requires a shorter time to be displaced, so its peak is narrower and leads the Blue Lake peak.

CHAPTER 8

FLIM FLAM CREEK

Flim Flam Creek (FFC) is a perennial stream in the lower level of Mystery Cave. It is in a narrow fissure in the Stewartville Formation, about 45 ft below the Straddle Gallery. The fissure is on a cross joint, about 100 ft southwest of The Bar, near the Angel Loop of Mystery II. The Straddle Gallery consists of keyhole-shaped passages. They generally have a tubular top and deep fissures in the floor. One or both sides of each fissure has ledges that can be crawled or walked upon where the fissure is too wide to straddle.

HYDROLOGIC SETTING OF FLIM FLAM CREEK

Although not proven by dye tracing, most of the discharge of Flim Flam Creek must derive from sediment-filled fissures in the bed or banks of the Root River. Mohring (1983) dye traced Formation Route Creek in Mystery III to Flim Flam Creek and then to Seven Springs. This result demonstrates that Formation Route Creek is a major (and perhaps the major) connection route between the South Branch and Flim Flam Creek. A diagrammatic sketch of these flow paths is shown in Figure 8.1. The sketch uses the straight-line horizontal distance from the Root River at the bend closest to the west end of Mystery III (just downstream of the bridge over the Root River at the start of the Mystery I driveway) to the 1st Triangle Room. The distance is about 820 ft. The straight-line distance from the 1st Triangle Room to Flim Flam Creek is about 1740 ft. The straight-line distance from Flim Flam Creek to Seven Springs is about 3740 ft. These distances are short enough to expect relatively fast flow-through and pulse-through times.

Water from the South Branch is the predominant source of water in Flim Flam Creek. There is always, however, a component of infiltration water present in the stream. Under extreme conditions this infiltration component may temporarily become a major component of flow.

Figure 8.1 shows the types of flow expected along these paths. Near the Root River, flow is in occluded fractures, and then in fractures that may be partially filled or full, depending on their size, geometry, and the discharge. The water then follows a course in which flow is usually in partially filled passages as vadose streams alternating with full (sumped) passages. Some of these flooded passages probably remain sumped even at low water levels while other stretches may alternate between sumped and partially filled conditions. At Flim Flam Creek, the water emerges from a sump, flows only 50 ft as a free-surface stream, and then sumps again. Several major open joints cross what is presumed to be the downstream extension of Flim Flam Creek east of the Straddle Galleries. Flim Flam Creek is probably one of the major tributaries of the Disappearing River, as shown in Figures 3.7 and 3.8.

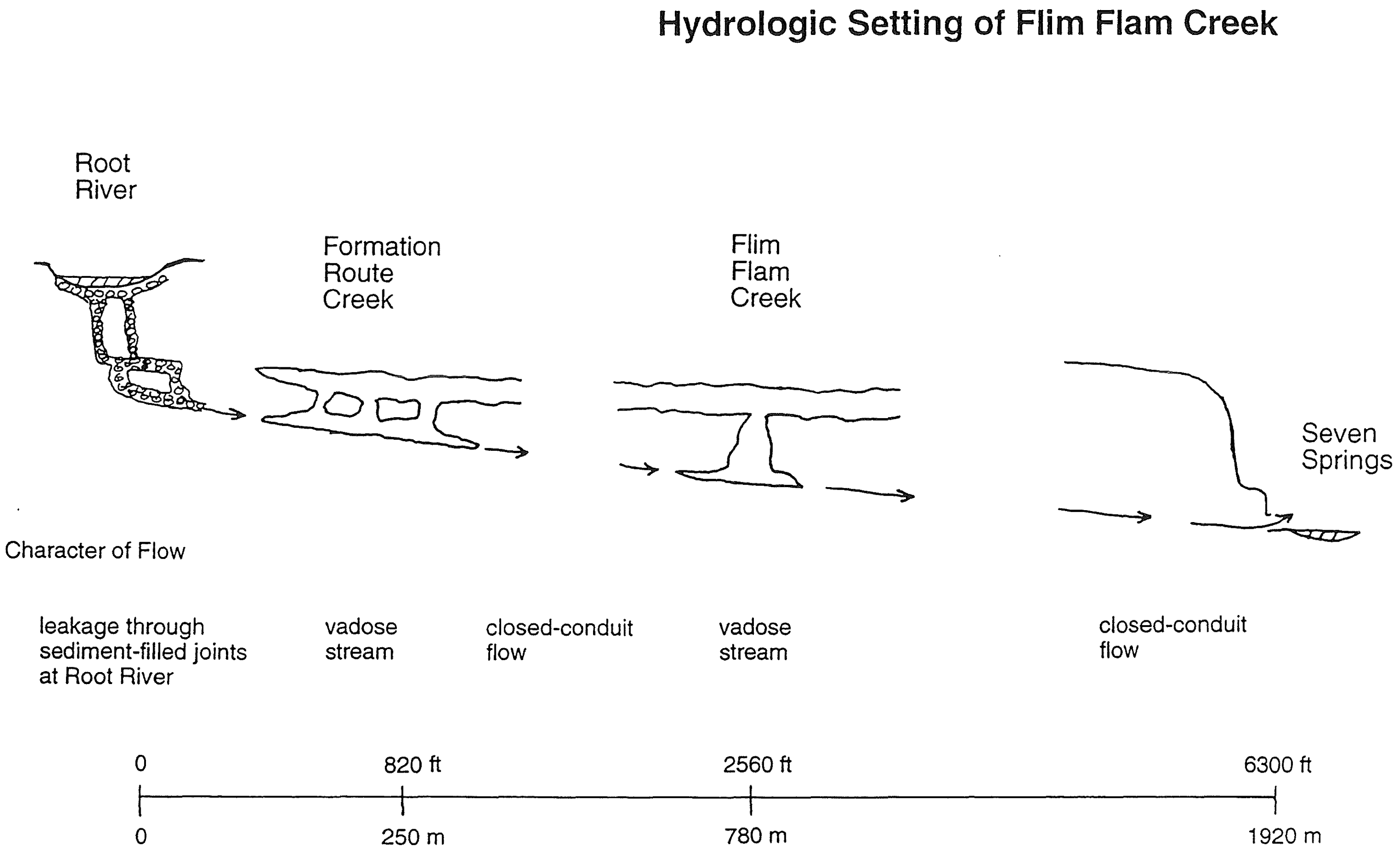


Figure 8.1. Hydrologic setting of Formation Route Creek and Flim Flam Creek.

SUMMARY PLOTS FOR MONITORED PARAMETERS

Water level, water temperature, and conductivity were measured continuously at Flim Flam Creek beginning in late March, 1992 and continuing to early May, 1993. Summary plots for these parameters are in Figures 8.2 and 8.3. Figure 8.2 shows the data from 1992. Figure 8.5 shows the data for the first half of 1993. These figures are plotted for the same time periods as the summary plots for Blue Lake (Chapter 7) to facilitate comparisons. Additional plots of the field parameters, anions and cations, and saturation indices are in Figures 8.3, 8.4, 8.6, and 8.7.

Data obtained since July, 1993 are used to confirm some of the observed trends and clarify obscurities in the original conductivity data. These data appear as plots in the quarterly report (Jameson and Alexander, 1994) for the 1993-1994 continuation of the present study, and were generated with higher quality conductivity/temperature probes.

SCALES OF RESPONSE AT FLIM FLAM CREEK

Flim Flam Creek responds to changes in the stage or in the chemical and physical properties of the South Branch of the Root River. Consequently, signals are observed at Flim Flam Creek on several time scales. The various time scales can be divided into: (1) seasons, (2) mesoscale periods lasting a several days to a week or more, (3) individual storms lasting a couple of days, (4) daily cycles, and (5) events that last less than a day. The wealth of information in these complex signals can quickly become overwhelming.

SCOPE OF DISCUSSION

To keep the discussion manageable, in this chapter we emphasize the major conclusions and provide typical examples. An account of the effects of the March 30-April 3, 1993 flood at Flim Flam Creek is in a later chapter.

A few cautionary words are in order. We are interpreting only the first year and a half of information from the digital data loggers. We almost certainly have not observed all of the phenomena Mother Nature has up her sleeves. Specifically, 1992 and 1993 were unusually wet. We have no data or observations from a significant dry period. We have seen some interesting phenomena only once. Murphy is alive and well. Everything that could go wrong, did---usually at the worst possible times. Nonetheless, we have been lucky enough to observe a number of fascinating phenomena that tell us fundamental things about the hydrogeology of Mystery Cave.

The following discussion is greatly simplified and at several points we cautiously extrapolate. Some trends will be discussed as if we were interpreting a longer time span. This approach allows us to emphasize the major conclusions, but at several points the discussion will show particularly interesting shorter time-scale events. Many of these interesting events and phenomena need to be examined at shorter time scales than can be seen in the summary Figures 8.2 through 8.7. At the risk of overwhelming the reader, we zoom in on these events with expanded scale figures below.

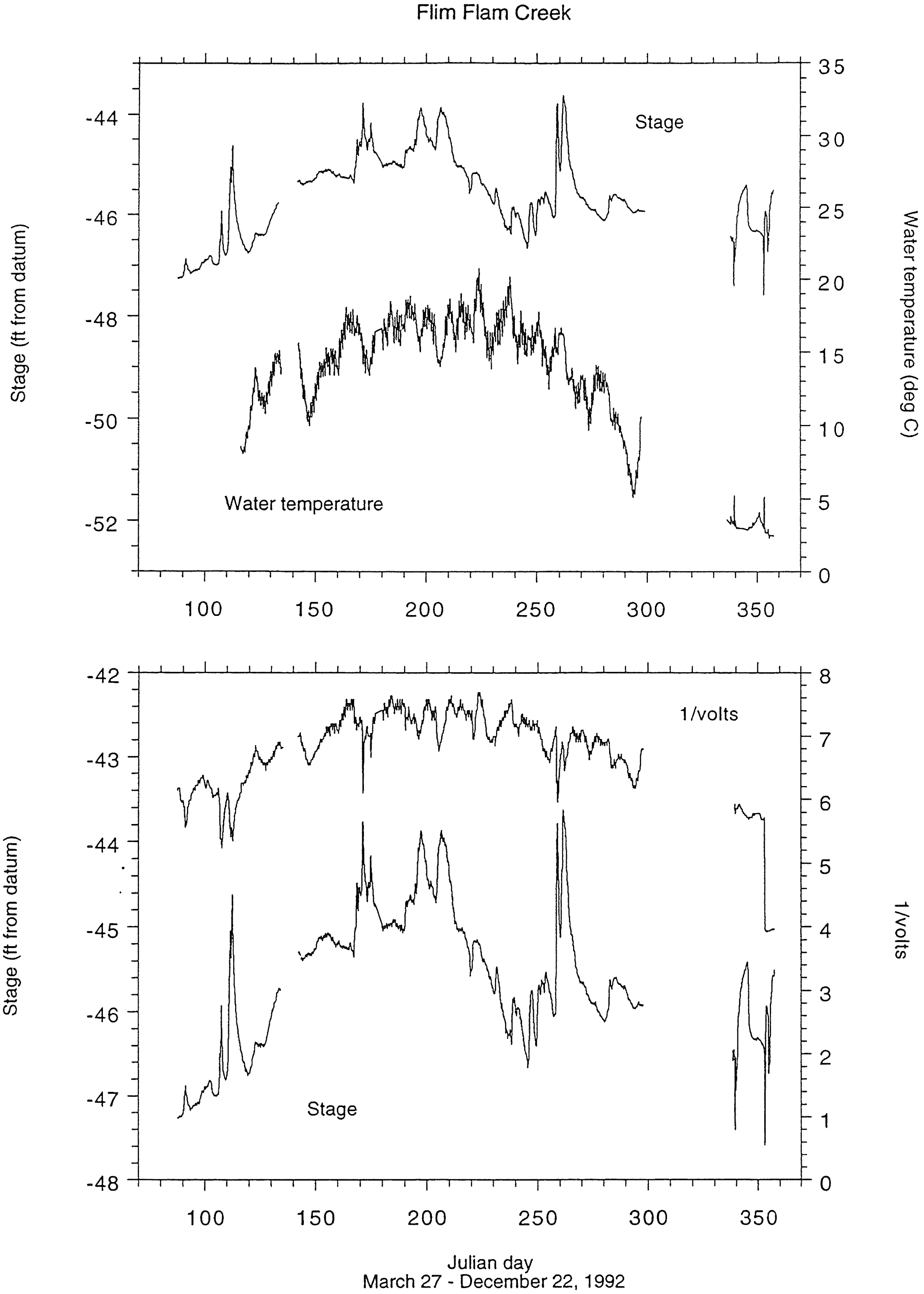


Figure 8.2. Stage, water temperature, and 1/volts, Flim Flam Creek, 1992.

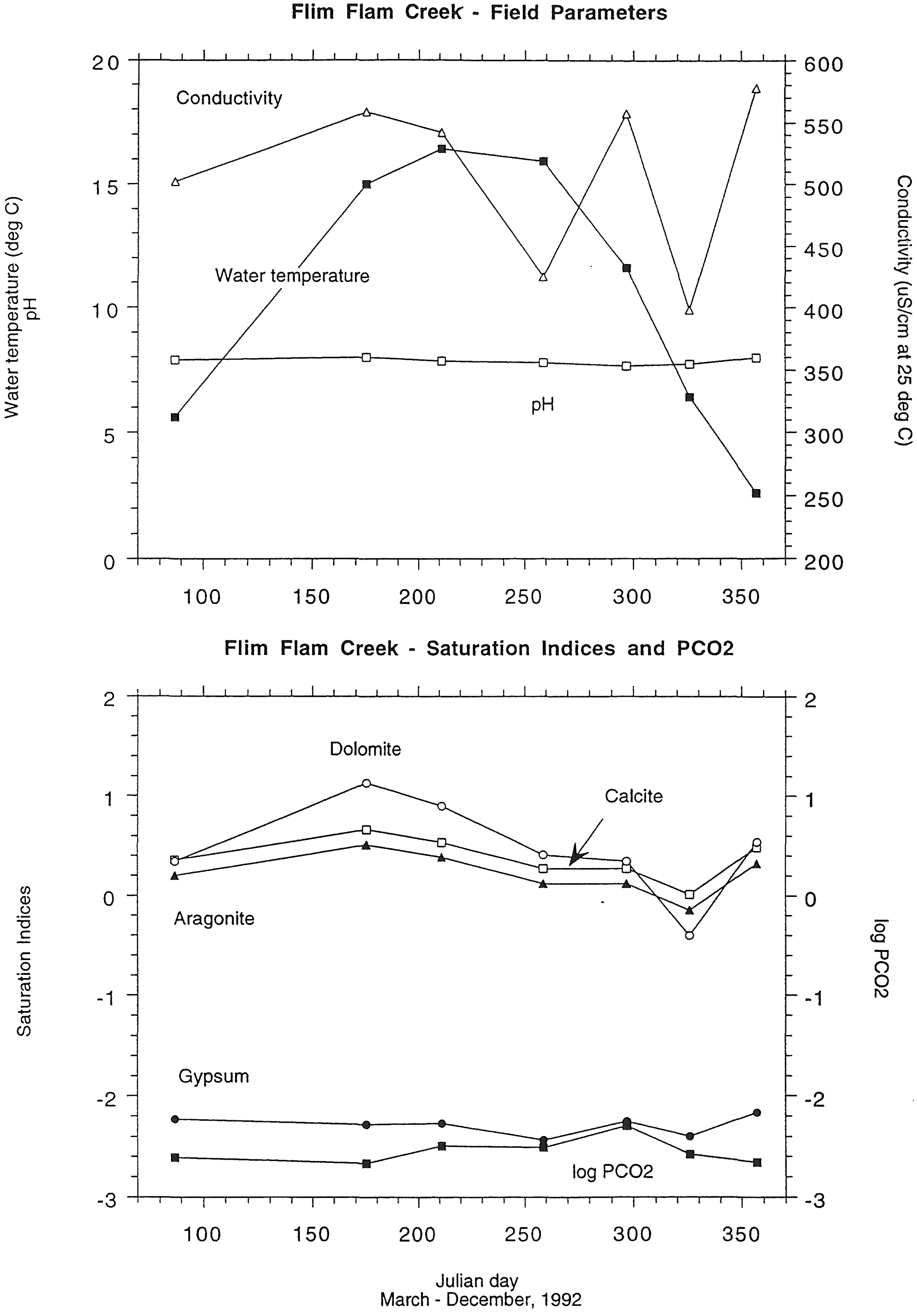
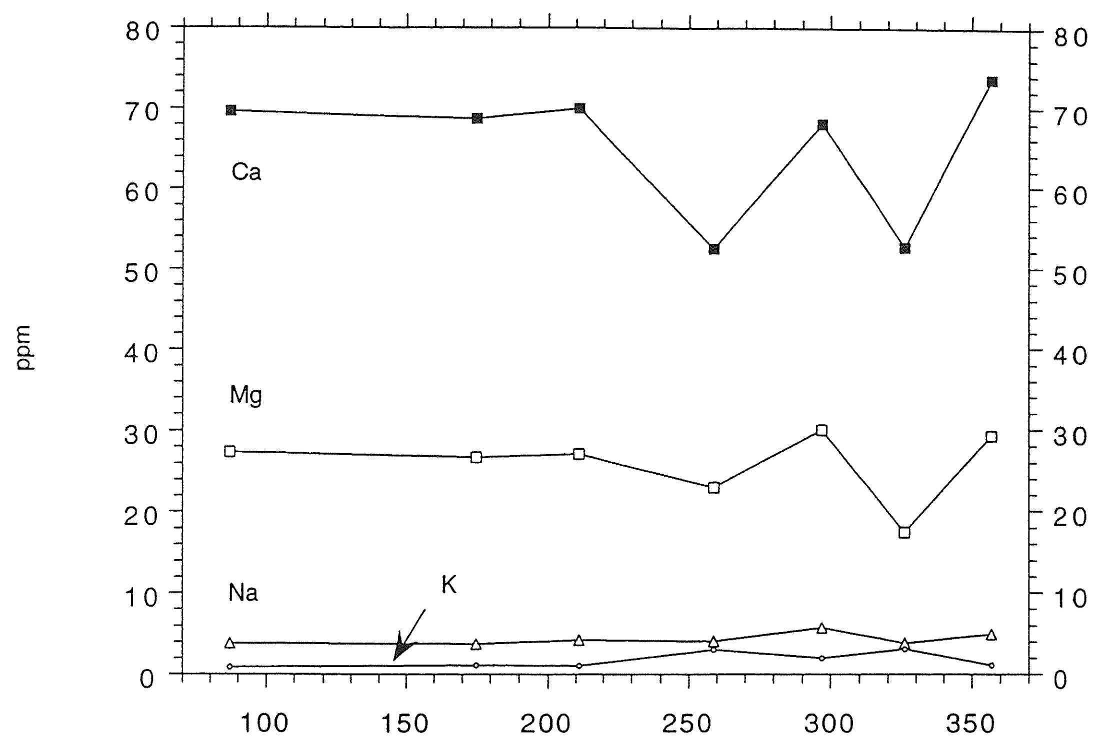


Figure 8.3. Field parameters and saturation indices, Flim Flam Creek, 1992.

Flim Flam Creek - Cations



Flim Flam Creek - Anions

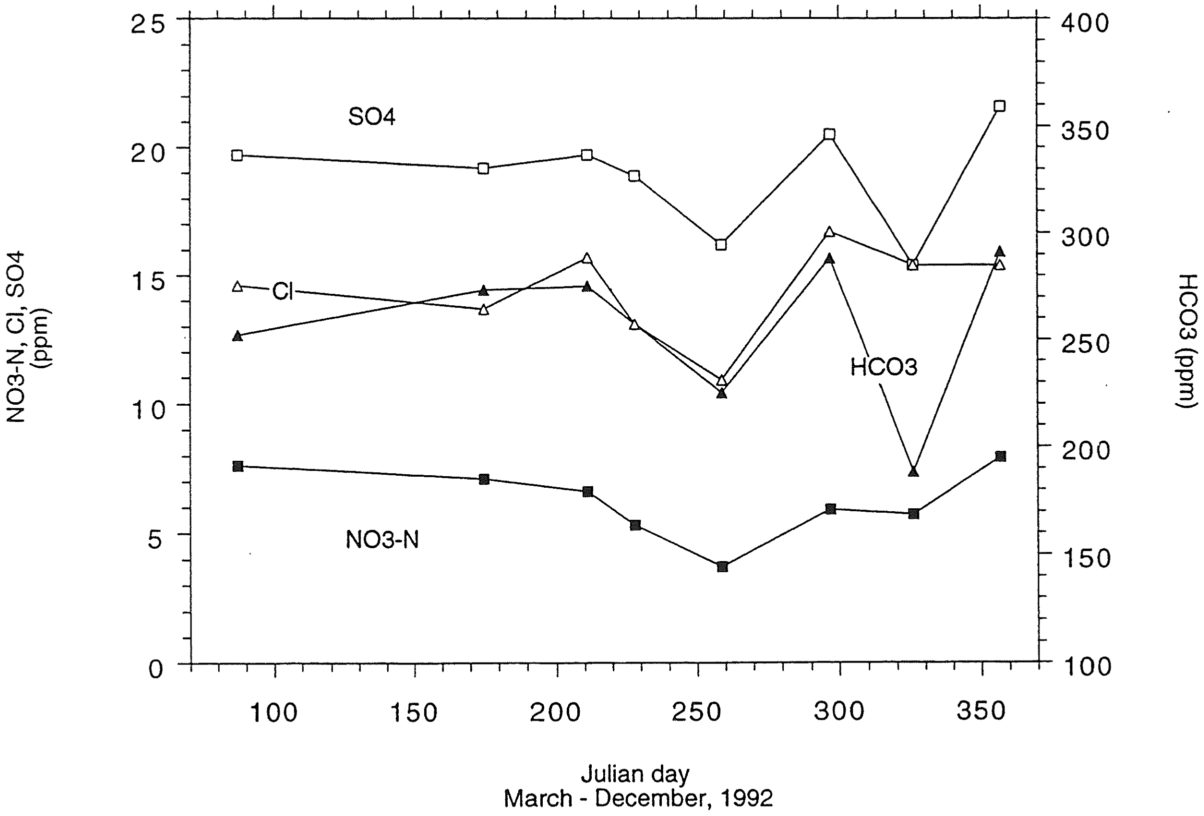


Figure 8.4. Cations and anions, Flim Flam Creek, 1992.

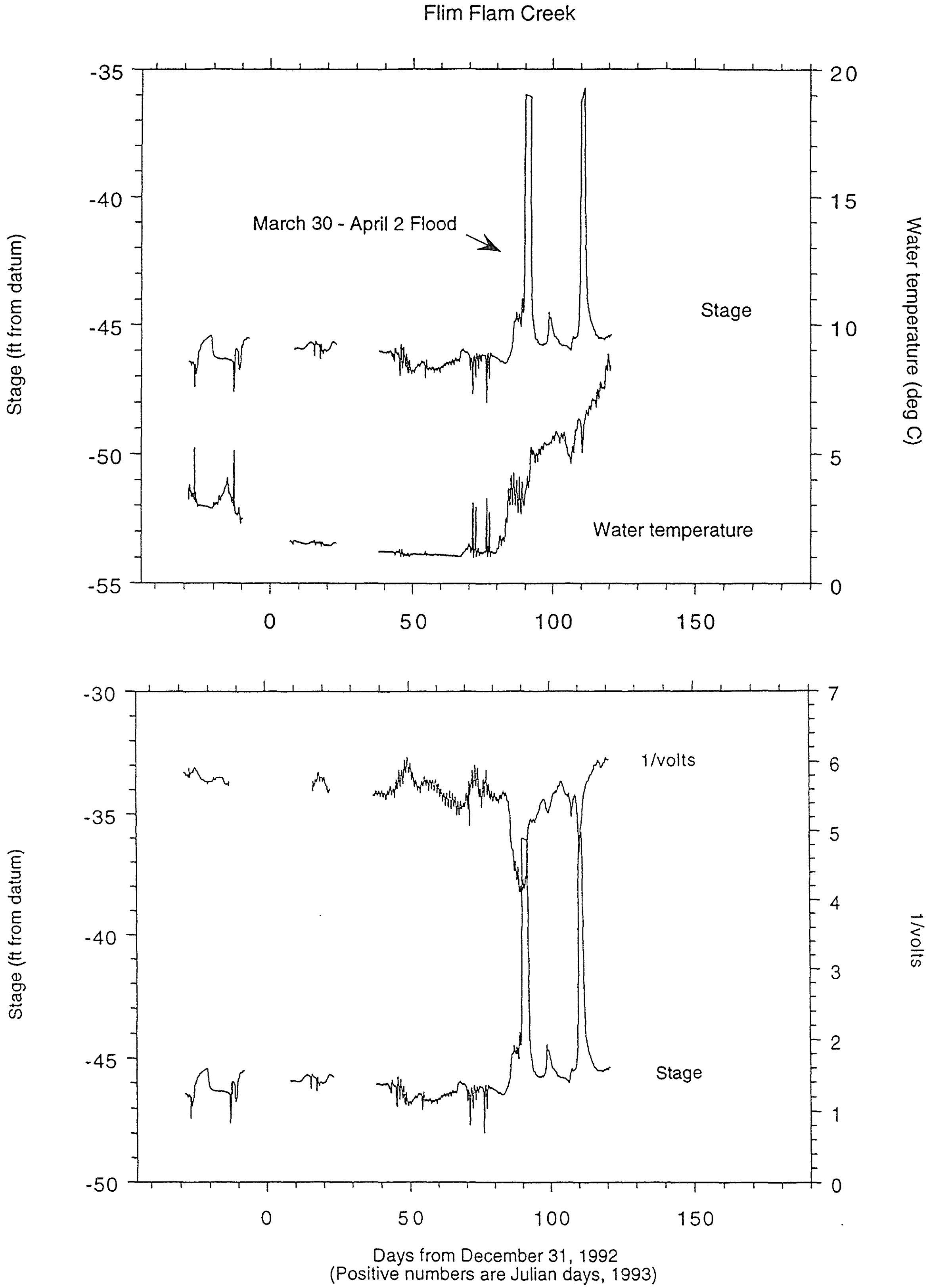


Figure 8.5. Stage, water temperature, and conductivity (1/volts) at Flim Flam Creek.

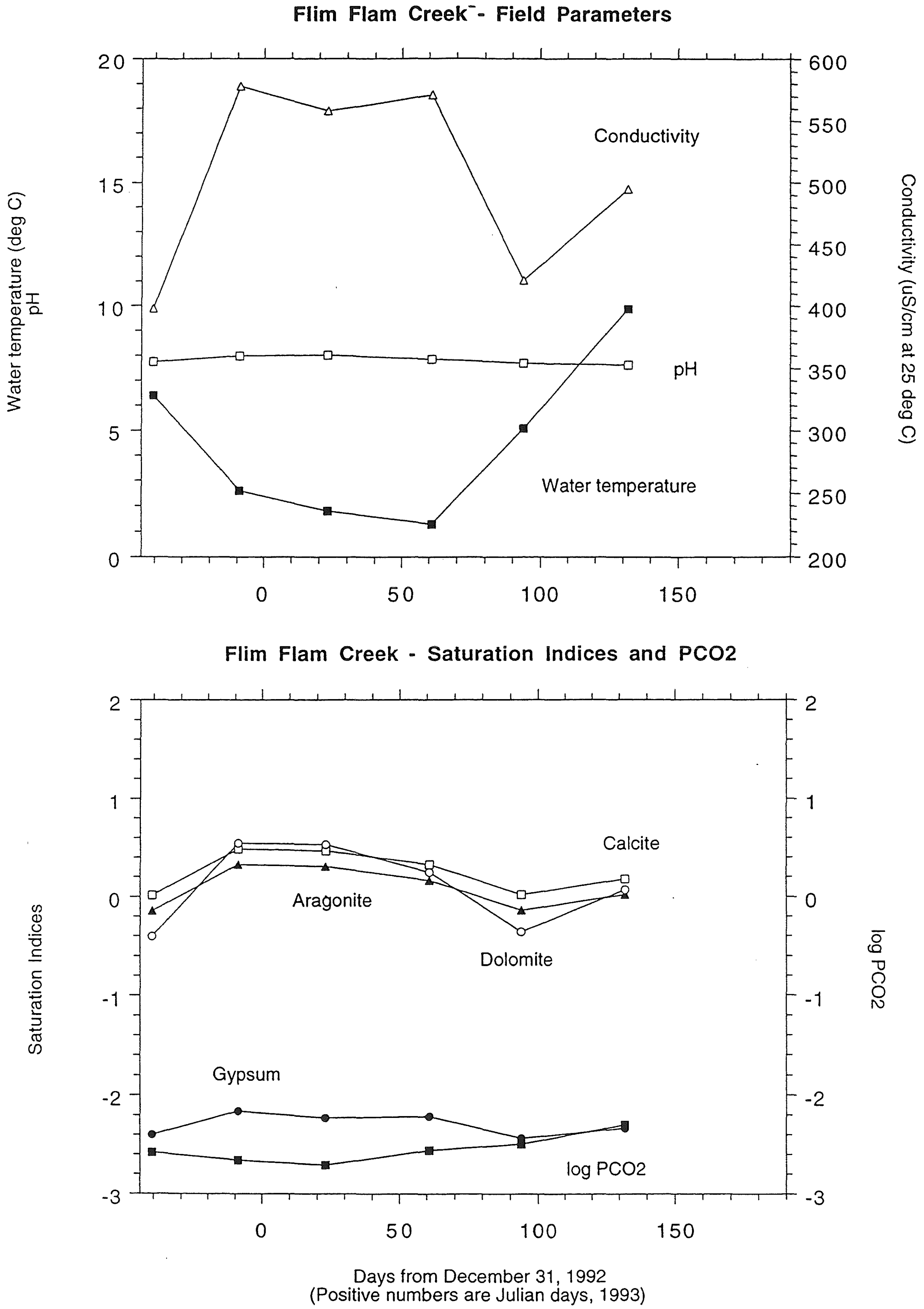


Figure 8.6. Field parameters, saturation indices, and PCO_2 at Flim Flam Creek.

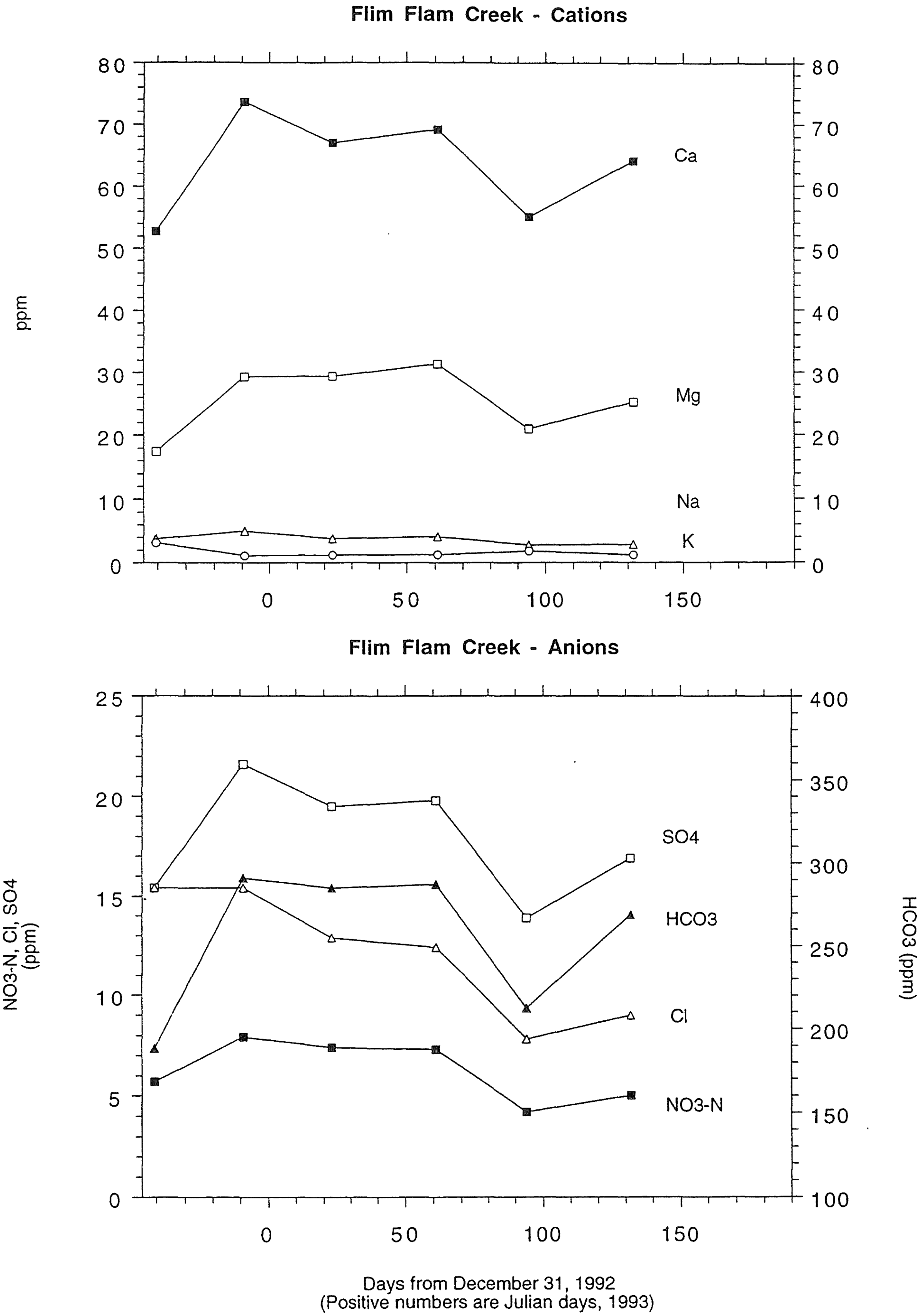


Figure 8.7. Cations and anions, Flim Flam Creek.

TRENDS IN WATER TEMPERATURE

Water temperatures at Flim Flam Creek range about 1 to 20°C through the annual seasonal cycle (Figures 8.2 and 8.5). Over mesoscale periods (corresponding to 5-10 or 15 day weather trends), water temperature varies as much as 7°C during the summer and as much as 2°C in the winter (Figure 8.8). Within stable mesoscale periods, water temperature varies 1-3°C depending on surface weather conditions (air temperature, amount of sunshine, etc.). Over transitional periods, (about 1-5 days; Figure 8.8) water temperatures may rise or fall as much as 5°C. Storms produce waters warmer or colder than those already present, depending on the season and on variations in air temperature during the storms.

Much of the year, but especially in the summer, there is a daily temperature variation of 1 to 3°C (Figure 8.9). The daily temperature cycle disappears during the winter when the Root River is iced over and air temperatures are below freezing (Figure 8.9). The daily temperature cycle is driven primarily by solar radiation heating of the river. Bright cloudless days, even if the air temperature is cool, produce larger daily cycles than to do warm but cloudy days. The biggest effects are observed on hot, sunshiny days.

The primary source of water to Flim Flam Creek is the Root River, but some contributions come from cave waters that have longer residence times. Such waters have temperatures close to 8.7°C. Therefore, we see a dampening of the temperature signal from the Root River that depends on the relative contribution of Root River water and the other cave waters. Additional dampening of the temperature signal arises from heat exchange with cave air, bedrock, and sediments. The water temperature at Flim Flam never gets as hot in the summer or as cold in the winter at does water in the South Branch. The temperature response of Flim Flam to changes in the South Branch is a **muted** version of the surface temperature changes.

We were surprised to observe short time-scale events occurring in the middle of winter. During extremely cold periods in the late fall and winter, the already low stage in Flim Flam Creek sometimes abruptly falls but the water temperature rises (Figure 8.10). Although a complete quantitative interpretation for these events is not yet available (there are additional complications), the outlines of an explanation is possible. When the river is frozen over, the water flowing beneath the ice and sinking is close to 0°C. If a sudden cold snap freezes the river to the bed, either at the sink points or at some shallow point upstream, the input of cold surface water can be temporarily halted. The water level in Flim Flam drops. As the water level drops the fraction of groundwater infiltration left in the stream increases. The temperature in the creek, therefore, increases toward 8.7°C. When the pressure of the water flowing beneath the ice reopens the sinkpoints, very cold water again flows into Flim Flam, the flow increases and the temperature drops. The additional complications involve the heat exchange between the rock walls of the creek and the very cold water.

One of the more important aspects of the temperature variation is the amount of time water temperatures are significantly above or below mean cave temperature. The water flowing in the lower streams either cools or warms the cave depending on the season. During the winter, cave passages adjacent to the underground streams tend to dry out. During the summer, these passages tend to become more moist, in part because of condensation effects. This time is important because of the effects the lower level streams may have on cave meteorology. Lively (1993) has found that Mystery Cave seems to have two air circulation patterns, a summer pattern and a

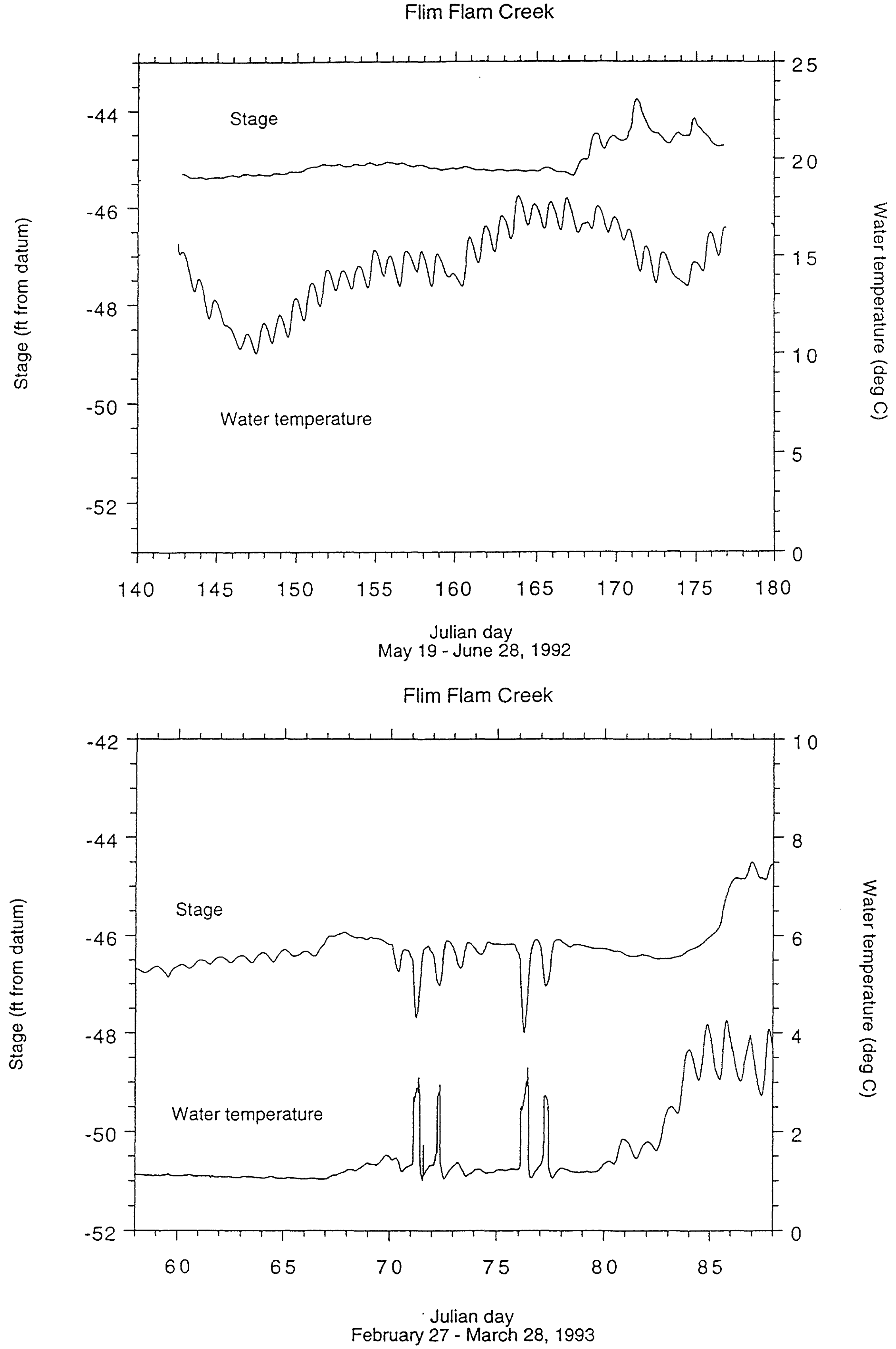
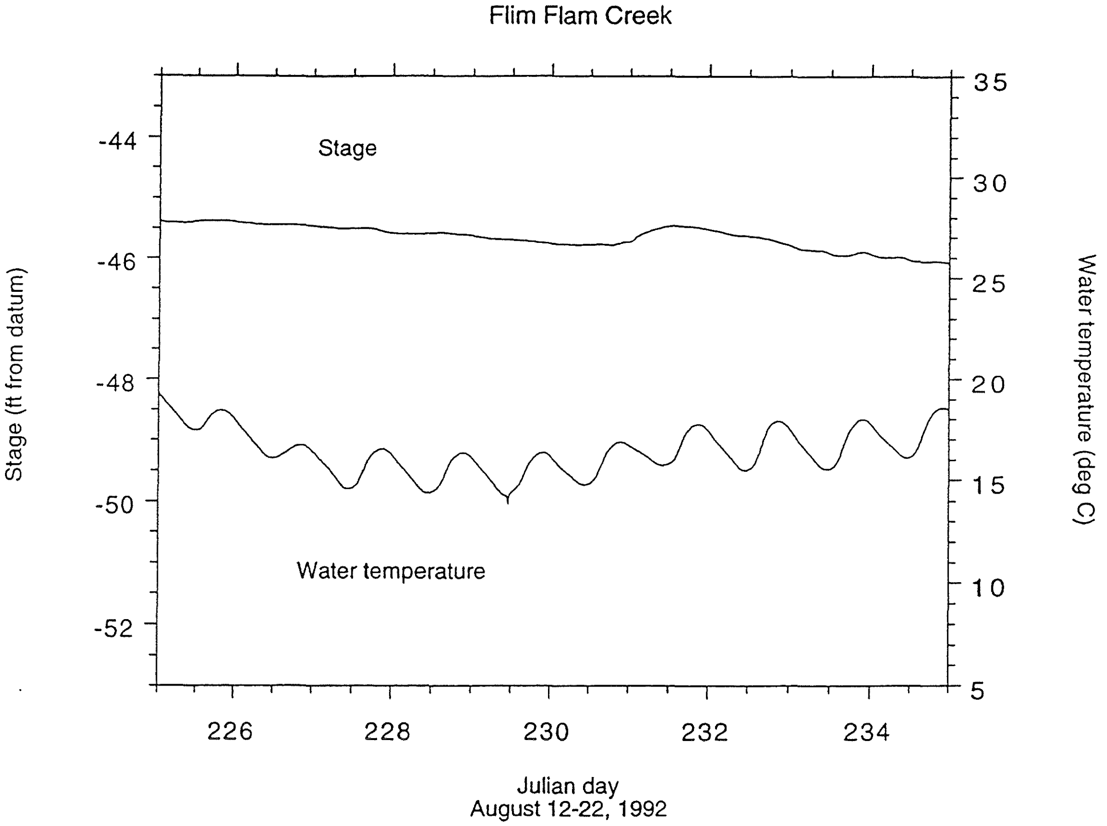


Figure 8.8. Mesoscale variations in temperature and transitional periods.



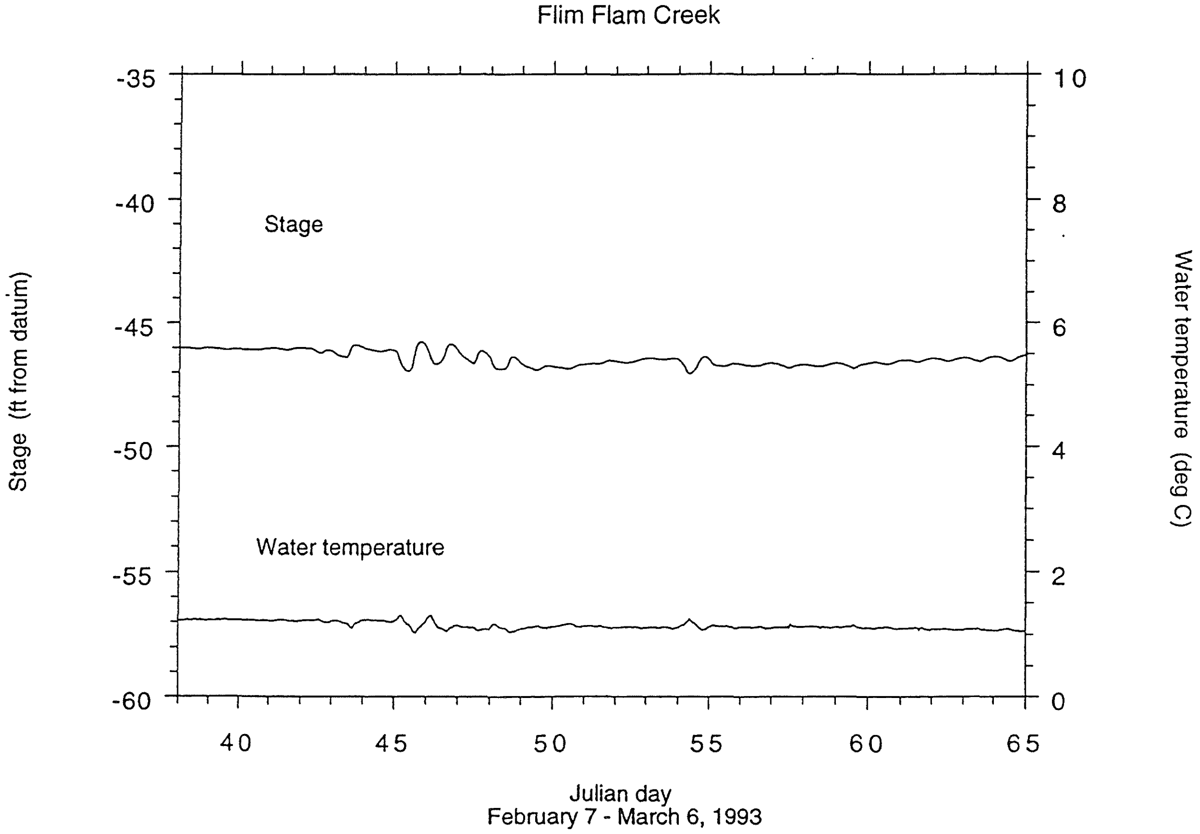


Figure 8.9. Daily cycles in temperatures.

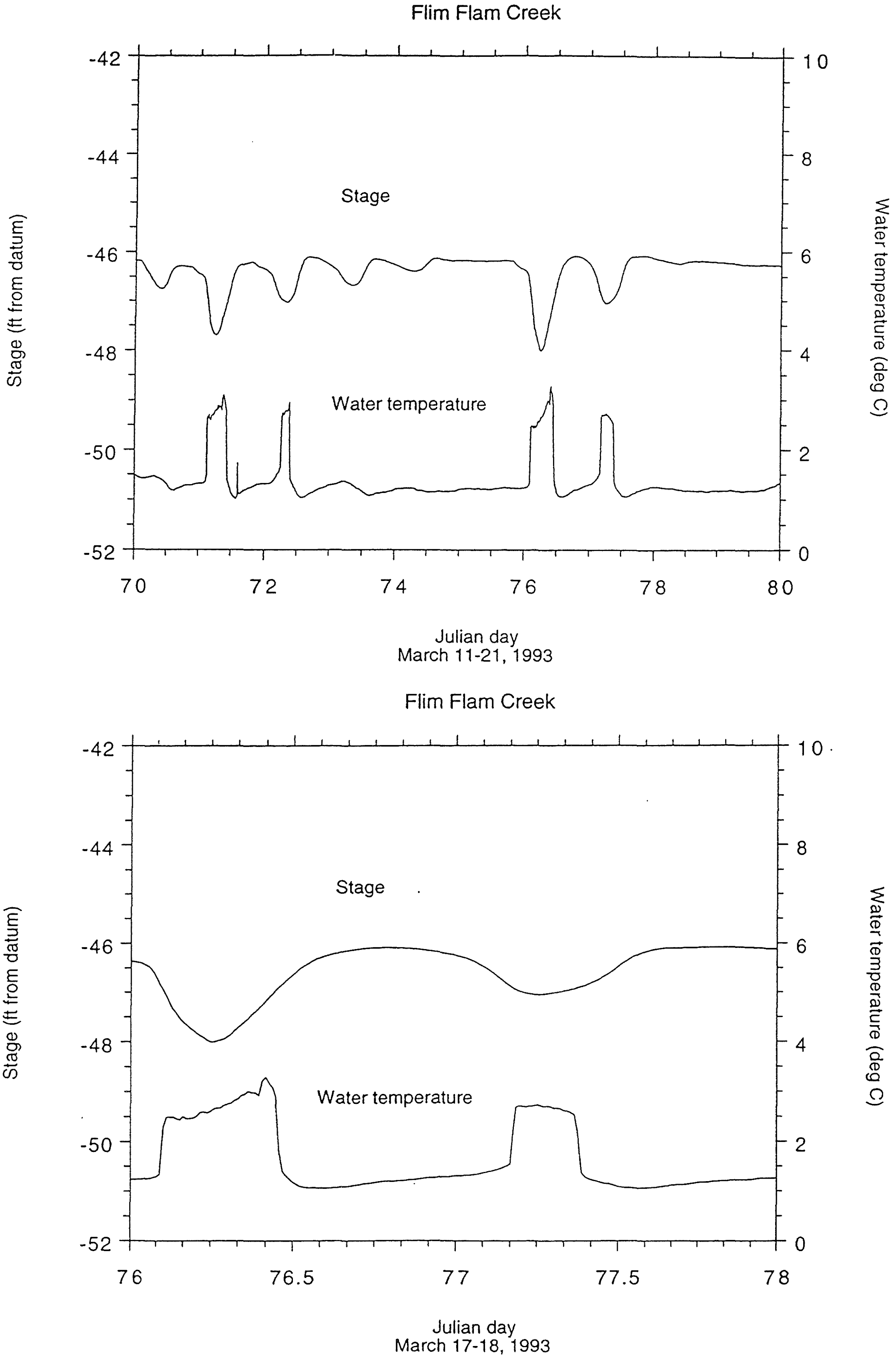


Figure 8.10. Short-term variations in stage and water temperature in the winter.

winter pattern. During the summer pattern, the radon levels in the cave air are higher on average than during the winter pattern. During 1992, the transition from winter to summer patterns occurred during March and April (Lively, 1993, Fig. F15 and F16). The transition from summer to winter conditions occurred October 9 to 12 (Lively, 1993, Fig. F18 and F23). For comparison, water temperatures during 1992 were above mean cave temperature (8.7°C) from about April 24 (day 115) through October 16 (day 290).

When water temperatures are higher than mean cave temperature, fogging can occur. Water vaporizes from Formation Route Creek and Flim Flam Creek, increasing local humidity. Water condenses on colder cave walls, releasing latent heat. The water itself is warm, so several factors combine to produce a rise in local air temperature. Air circulation patterns may change. All of these effects are noticeable during the summer in the vicinity of the Bar and in part of the Angel Loop along the commercial trail.

STAGE OR WATER LEVEL

Hydrologists prefer to work with the flow volume rather than simply with stage or water level. Stage is what is normally monitored and then it is converted to flow volume through an empirically determined relationship, a rating curve. Rating curves are determined by measuring the flow of a stream under a variety of flow conditions. Unfortunately, Flim Flam Creek is relatively inaccessible at the base of a 45-ft deep narrow fissure. The enterable passage is low and wet, ends in sumps both upstream and downstream , and is cold much of the year. The geometry at low flow is not conducive to stream gauging. Storms typically induce a one to two foot rise in stage from a low-flow water depth of about a foot. The largest storms (three in 1993) produce rises of over 20 ft in stage. During the early summer of 1993, water level rose high enough so that water was visible at the Bar, according to tour guides. The conditions during high flow make flow measurements impossible. In the absence of a rating curve for Flim Flam Creek, the following discussion of flow is in terms of stage.

At Flim Flam Creek, stage is lowest during the winter, rises somewhat during wet springs, and shows sharp responses to rises on the Root River. Such responses are clearly visible in Figures 8.2 and 8.5. The stage in Flim Flam is a **multiplied** version of the surface stage changes. A rise of a couple of feet in the South Branch can cause a 20 foot rise in the stage in Flim Flam if stage in the South Branch is already high. The importance of this observation can not be overemphasized. The multiplier effect produces a major, life-threatening danger to exploration of the lower levels whenever there is any possibility that the surface water level may increase. At times when the stage in the South Branch hiccups, Flim Flam Creek belches.

There are some additional responses---for example, abrupt, sharp drops in stage---that deserve mention. Stage is generally low during the coldest part of the winter. Water in the Root River is in contact with ice. For two or three months there is an ice cover on the river. If there are recharge points on the bank margins, they may be iced over, lowering the surface recharge to Flim Flam Creek. At such times, water temperature in the underground river may rise (Figure 8.10), as discussed above. However, the response is not universal. Sometimes as stage falls there is a fall in water temperature that lags behind the fall in stage. These events are very cryptic.

RESPONSE TIMES

The *flow through time* from the Root River to Flim Flam Creek is rapid. The flow through time clearly varies with stage in both the Root River and at Flim Flam Creek, but is difficult to precisely quantify with the available data. Flow through times can in principle be measured directly by dye traces but the appropriate sink points in the South Branch have not been identified and it will be difficult to sample Flim Flam every few minutes for several hours to pin down the transit times.

Part of the difficulty in making precise estimates arises because the Root River weather station is about 3800 ft upstream of the postulated sinkpoints. The signal measured at the Root River at the weather station has to pass downstream before transmission into the subsurface and we have only stage data for the Root River. Only one data logger was available for both weather parameters and measurements on the Root River during this study. It was not possible with available channels to monitor conductivity or water temperature.

Nonetheless, correlations can be made between surface air temperatures and cave water temperatures. Comparisons can be made for time periods in which air temperatures fall rapidly several degrees, because the water temperature then responds most quickly (Figure 8.11).

Comparisons can be made for daily cycles in air temperature (Figure 8.12). Correlations can also be made for periods of intense precipitation, if air temperature during precipitation is significantly different from that of the Root River (Figure 8.13). Such correlations give flow through times on the order of a couple of hours to 5 or 6 hours. The shorter flow through time estimates are more consistent with Mohring's (1983) dye trace measurement of 6 hours flow through time from the 1st Triangle Room in Mystery III to Seven Springs.

The *pulse through time* is at least partly a function of pre-existing stage. It can be extremely rapid if stage is already high. At high flow a nearly completely connected network of submerged conduits transmits the pressure pulse. Under these conditions, an increase in leakage at the sinkpoints (from rapid flooding, for example) produces a rapid rise in stage at the upstream end of the flooded conduits, and stage can rise rapidly at Flim Flam Creek, long before the water can flow from the Root river to Flim Flam Creek. If stage is low, then some water must flow through parts of the network to raise water levels to a point at which there is a complete hydrologic connection of flooded conduits, before a pressure pulse can transmitted.

CONDUCTIVITY AND WATER CHEMISTRY

It was not technically or economically feasible to monitor the chemistry of the waters in Flim Flam Creek on a continuous basis. Conductivity was monitored instead as a crude proxy of the total dissolved load in the stream. Conductivity is shown on Figures 8.2 and 8.5 as 1/volts. The conductivity records shown in Figures 8.2 and 8.5 have lots of structure. Conductivity, however, is a function of water temperature as

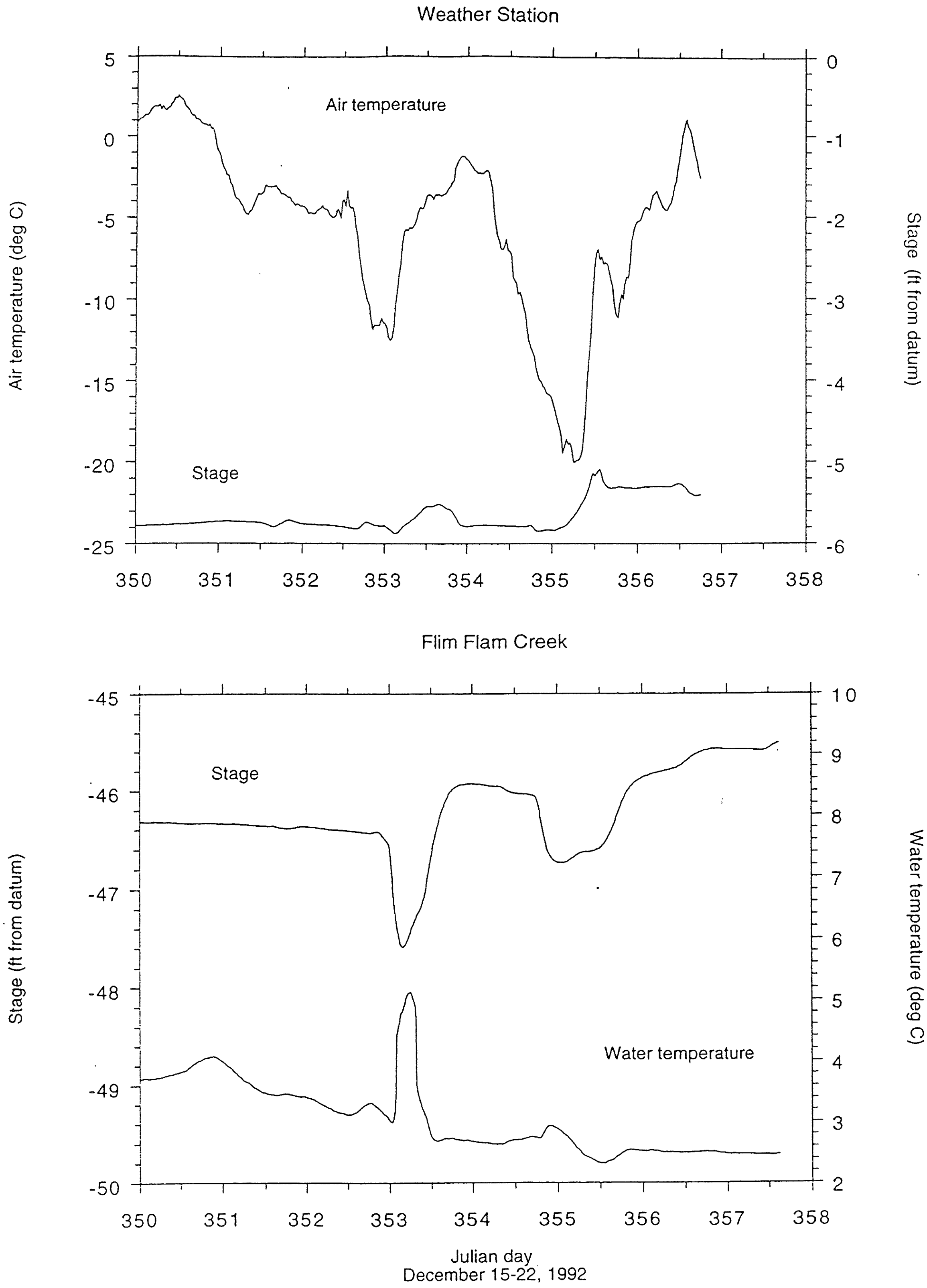


Figure 8.11. Correlation between surface air temperature and cave water temperature at Flim Flam Creek when air temperature falls abruptly.

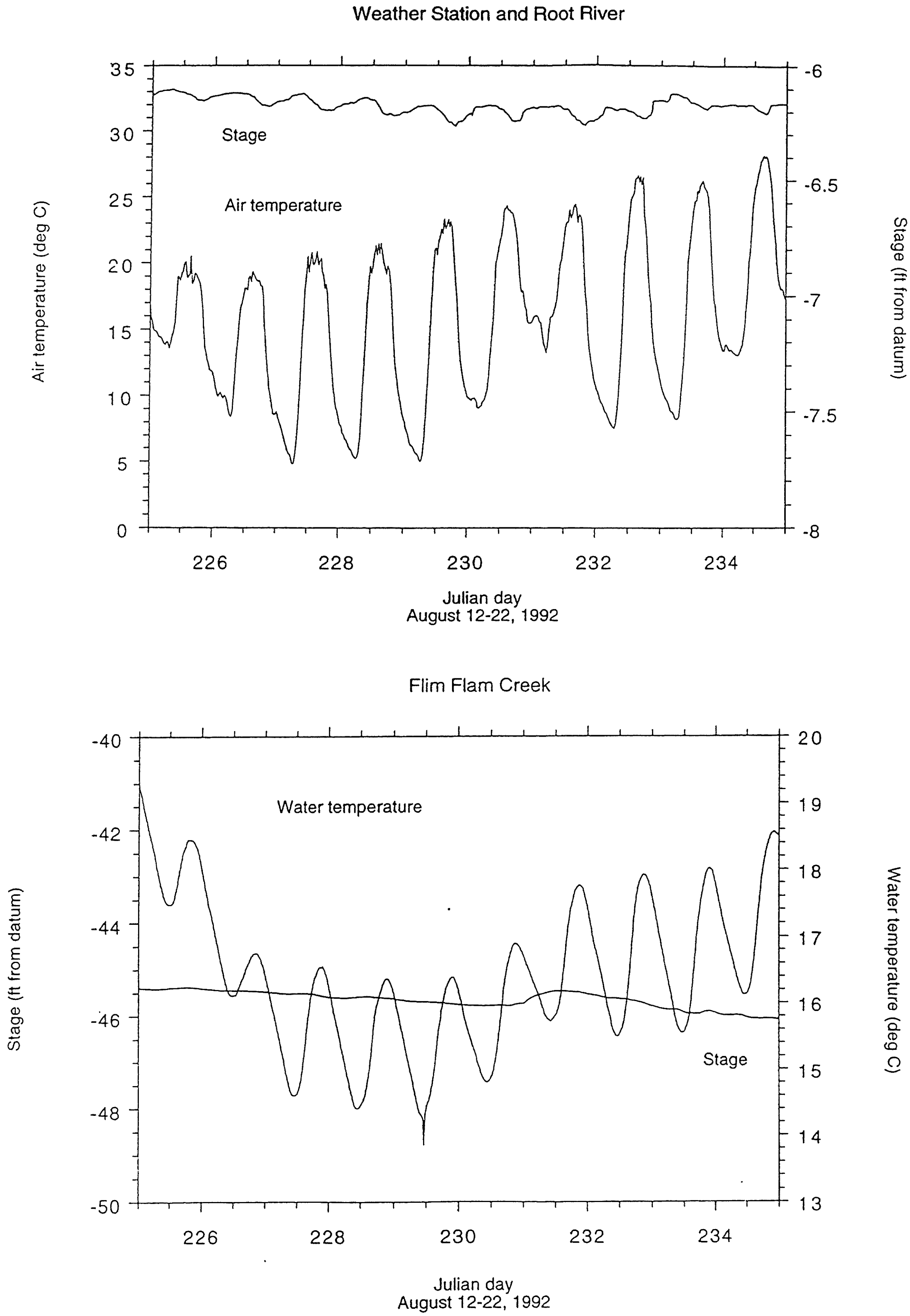
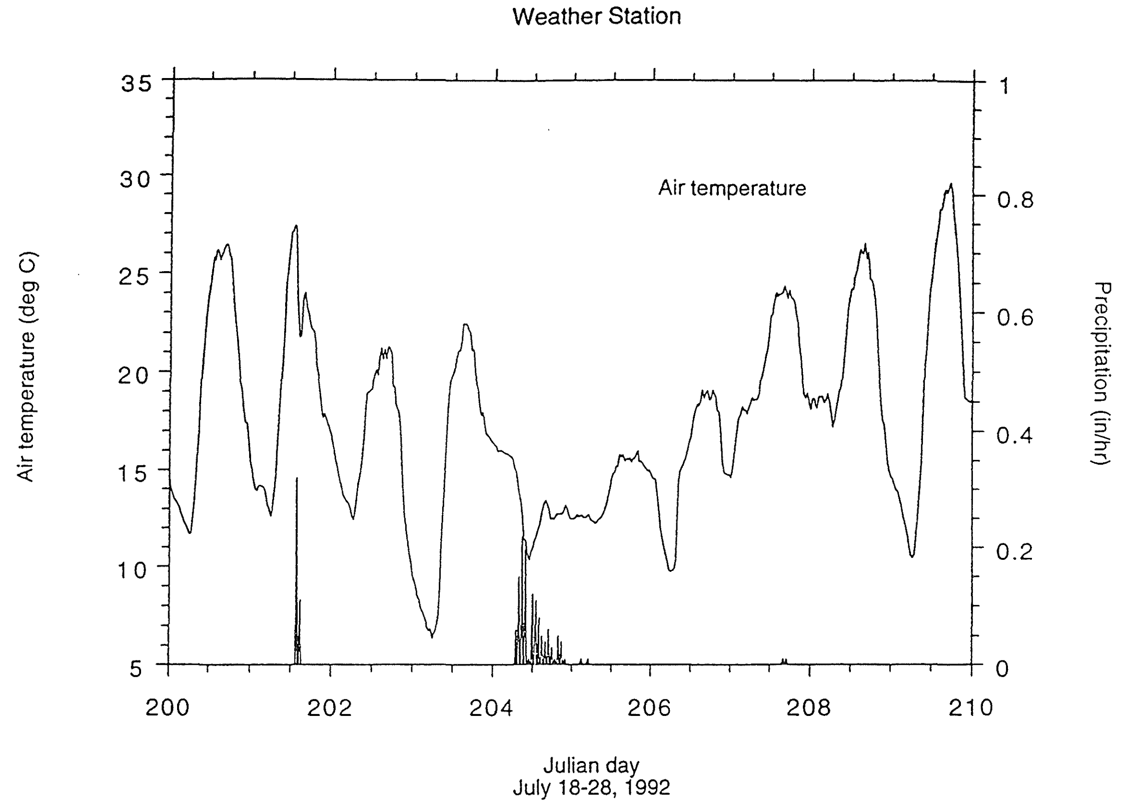


Figure 8.12. Comparison of surface air temperature and cave water temperature at Flim Flam Creek during times of maximum daily variations in air temperature.



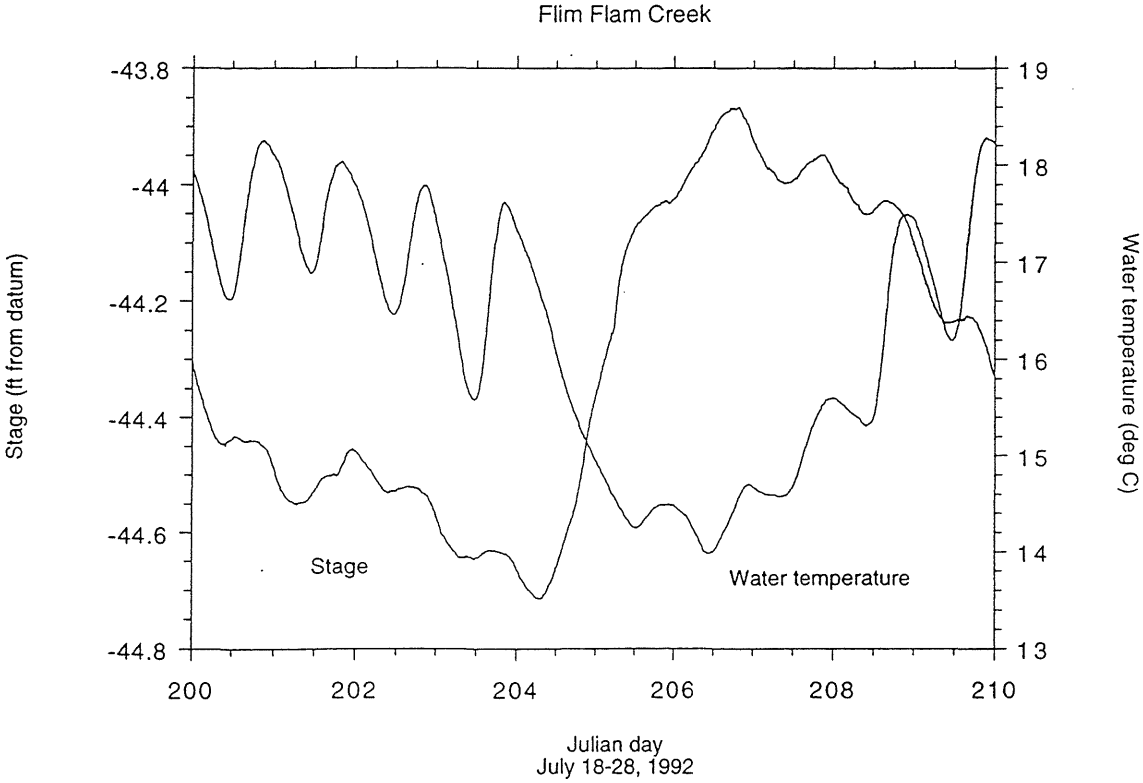


Figure 8.13. Correlation between cave water temperature and air temperature during periods of intense precipitation.

well as solute load. In Flim Flam Creek this voltage was measured at water temperatures ranging from 1 to 20°C. The size of the temperature effect can be as large or larger than the variations caused by changes in the solute load. Normally, conductivity is corrected to a standard temperature (usually 25°C) before comparisons are made. This temperature correction may not be possible for this data set and interpretation of conductivity at Flim Flam Creek as 1/volts must proceed with caution. Data obtained with better quality conductivity probes between July, 1993 and June, 1994 which could be corrected for effects of temperature, allow reasonable interpretations of the earlier data to be made---at least with respect to major trends. (We were able to use 1/volts more extensively in the discussion of Blue Lake, because Blue Lake water temperature was nearly constant and the temperature effect was not significant.)

The arched overall trend of 1/volts on Figure 8.2 is primarily due to the temperature effect. The field measurements of conductivity (Figures 8.3a and 8.6a), where the appropriate temperature corrections were made, do not unambiguously support a seasonal trend in the conductivity. Neither do the measured concentrations of the major ions calcium, magnesium and bicarbonate (Figures 8.4 and 8.7). A seasonal effect should be present in the system, however, and was confirmed in the 1993-1994 data.

Most of the abrupt rises and falls in 1/volts in Figure 8.2b are primarily due to changing water temperature. Some reflect changes in solute load correlated with peaks in stage. During these times, precipitation dilutes river water, causing drops in conductivity. However, because water temperature usually falls during these events, some of the drop in the values of 1/volts can be attributed to the change in water temperature. In Figure 8.5b, the values of 1/volts decline at times of the introduction of snowmelt.

The results of the cation and anion analyses of Flim Flam Creek waters are shown in Figures 8.4 and 8.7. The saturation indices calculated from these data are shown as part of Figures 8.3 and 8.6. Most of these waters are close to saturation for calcite, aragonite and dolomite. The ion concentrations in Figures 8.4 and 8.7 are spiky, much more so than those of Blue Lake or most other cave waters. The levels of cations and anions respond to events on the Root River.

The plots of the anions (Figures 8.4 and 8.7) are revealing. Note that the levels of nitrate and chloride in Flim Flam are significantly higher than the levels of these two ions in Blue Lake (Figures 7.5b and 7.11b). Nitrates and chlorides are indicators of human impact. Conversely, the level of sulfate in Flim Flam is about half that found in Blue Lake. Sulfate is produced naturally by oxidation of sulfides in the bedrock, and possibly also derives from the loess; it shows the influence of infiltration waters. This distinction is also backed up by the coliform bacteria and pesticide analyses. Flim Flam Creek typically contained coliform bacteria and pesticides. Blue Lake did not.

The overall picture is very consistent. The water in Blue Lake is dominated by recharge from infiltration sources that have only low levels of human induced pollutants. Blue Lake can fill rapidly, but most of the time it is a stable bath tub for days, weeks or months. Flim Flam Creek, in stark contrast, is dominated by direct recharge from the South Branch. The water in Flim Flam shows all of the human pollutants that affect the South Branch. The water quality and level in Flim Flam Creek changes dramatically on time-scales that can be as short as minutes.

CHAPTER 9

COON LAKE DRIPS AND COON LAKE

SITE DESCRIPTION

Coon Lake Drips (CLD) is in 5th Avenue of Mystery II. The site is on the north side of the passage (Figure 9.1), 10 ft across from Coon Lake, several hundred feet west of the Garden of the Gods. The water drips from flowstone covering the north wall. Some of the water drains from fissures in the ceiling and spreads out on the flowstone. Some issues from small stalactites set in the flowstone. The water drips onto a flowstone- and silt-covered floor. Coon Lake Drips were sampled periodically throughout the project for chemical parameters. Drip rates were monitored continuously with a rain gage during the late winter and spring of 1993.

Coon Lake Drips feeds **Coon Lake**, a shallow pool (usually about 4 by 10 by less than 1 ft deep) whose size varies with the discharge rate at Coon Lake Drips. Water from Coon Lake slowly seeps into floor sediments or evaporates. During the winter the pool nearly dries up as the discharge declines at Coon Lake Drips.

TOPOGRAPHIC SETTING

Coon Lake Drips lie beneath a grass-covered hillslope, just south of the driveway to the Mystery II entrance (Figure 3.3). The precise position of CLD beneath the hill has not been located by surveying. Superposition of the cave map on a topographic sheet suggests that the elevation of the surface directly above CLD is about 1300 ft. The elevation at Coon Lake is approximately 1205 ft (Palmer and Palmer, 1993a). The ceiling at CLD is at about 1220 ft, so the spot where water enters to feed Coon Lake Drips is approximately 80 ft below the surface.

Immediately west of CLD the surface is a forested hillslope leading into a re-entrant valley. A few tens of feet east of a point directly above CLD, the grassy hillslope flattens into a gently rolling plateau. Most of the immediate plateau is a pasture, but to the south of the pasture is a field planted in corn in recent years. Seismic work by Palmer and Palmer (1993a) nearby above the Garden of the Gods gave a depth to bedrock of 22 ft. This indicates a 22 ft thickness of soil, loess, and possibly additional glacial material. The grassy hillslope above the driveway has been carefully checked for open drains, sinkholes, or other indicators of concentrated recharge. The only features found were mounds (several feet in diameter) of sandy material with adjacent holes apparently dug by gophers. In all probability, there are additional macropores on the hill. Along the driveway itself, near the east end close to the Garden of the Gods, a few linear depressions extend across the roadbed. Below the driveway, to the north, are a few sinkholes (Figure 3.4).

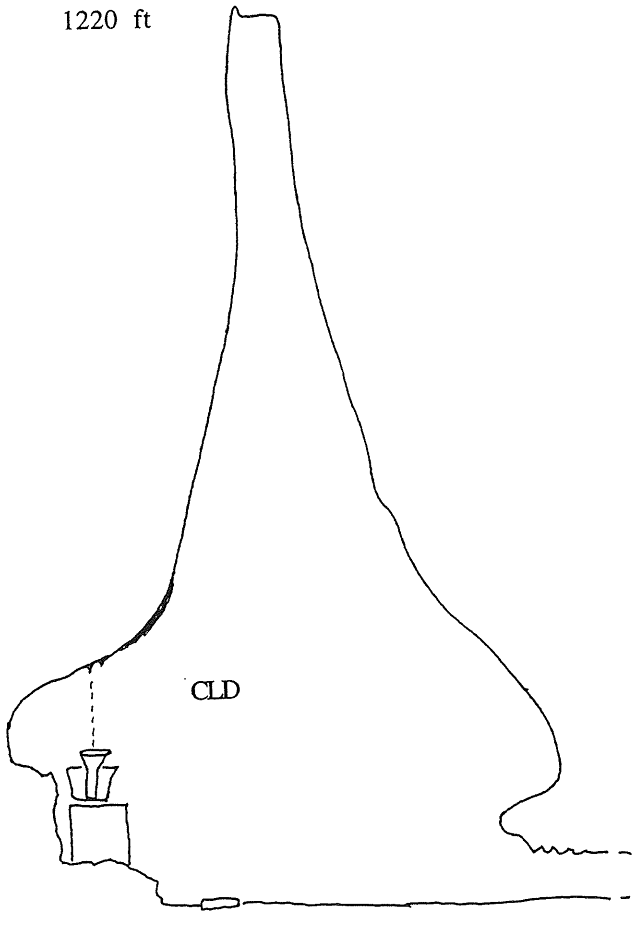


Figure 9.1. Setting of Coon Lake Drips.

DRIP RATES DURING PERIODS OF SNOWMELT

Coon Lake Drips appear to be perennial. A data logger and drip rate recorder (rain gage) were installed on February 26, 1993, to measure drip rates. The low flow in the winter, when the surface was frozen and covered with snow, was about 0.2 l/hr (Figure 9.2). The drip rate was constant until late March and can be considered a type of baseflow.

On March 18 (Julian day 77) a warming trend began following a few days with lows below -20°C (Figure 9.3). From noon March 18 through noon March 23 (day 82) the air temperatures remained near zero. These temperatures warmed the top of the snowpack, preparing it for the melting soon to come. From noon March 23 through the start of March 27 (day 86), air temperatures were mostly above freezing, with a daytime high of 6°C and temperature ranges of about 6°C (Figure 9.4). Over the following days, daytime high temperatures rose progressively, reaching about 14°C on March 29.

The snowpack must have begun to melt and induce recharge by March 25 (day 84), because late that day the drip rate began rising at Coon Lake Drips (Figure 9.4). Over the next several days, as daily air temperature rose and fell, sufficient snow melted to produce daily cycles in drip rates. The first cycle, marked by a peak late on March 26 (day 85) is poorly developed, but the three following ones are clear. Just as high air temperatures progressively increased, so did the drip rates. Late on March 29 (day 88), the drip rate reached about 4 l/hr.

RESPONSE TIME FROM SNOWMELT

The daily temperature cycles and corresponding drip-rate cycles allowed the calculation of response times. The response times were calculated both from the peaks of the air temperature to the peaks of the drip rates and from the minima of the air temperatures to the minima of the drip rates, as shown in Table 9.1. These data show a rapid response time for Coon Lake Drips. Similar or more rapid responses have been obtained for recharge events driven by precipitation. During these events, no temperature responses have been recorded, even during times in which recharge water was significantly colder than mean cave temperature. The temperature data (Figure 9.4) and the chemical analyses (Figures 9.5 and 9.6) suggest that these responses do not represent flow through times. Coon Lake Drips are similar to Blue Lake, but with a much faster time scale. Recharge moves rapidly through the surface materials and displaces pre-existing groundwater from the loess, the subcutaneous zone (insofar as one is present above the site), and fissures that lead to the cave. Drip rates respond rapidly to storms, reaching a maximum observed discharge of about 14 l/hr.

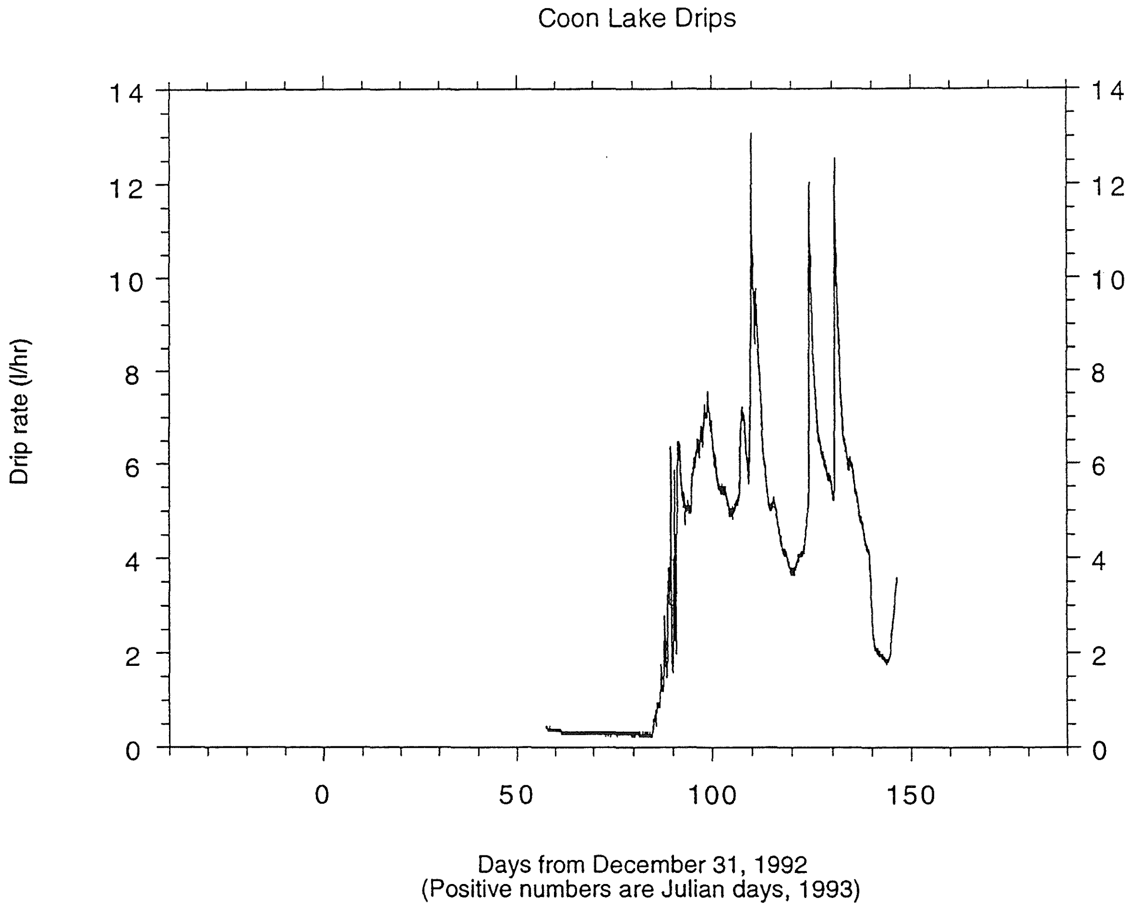


Figure 9.2. Drip rate at Coon Lake Drips from February 26 to May 23, 1993.

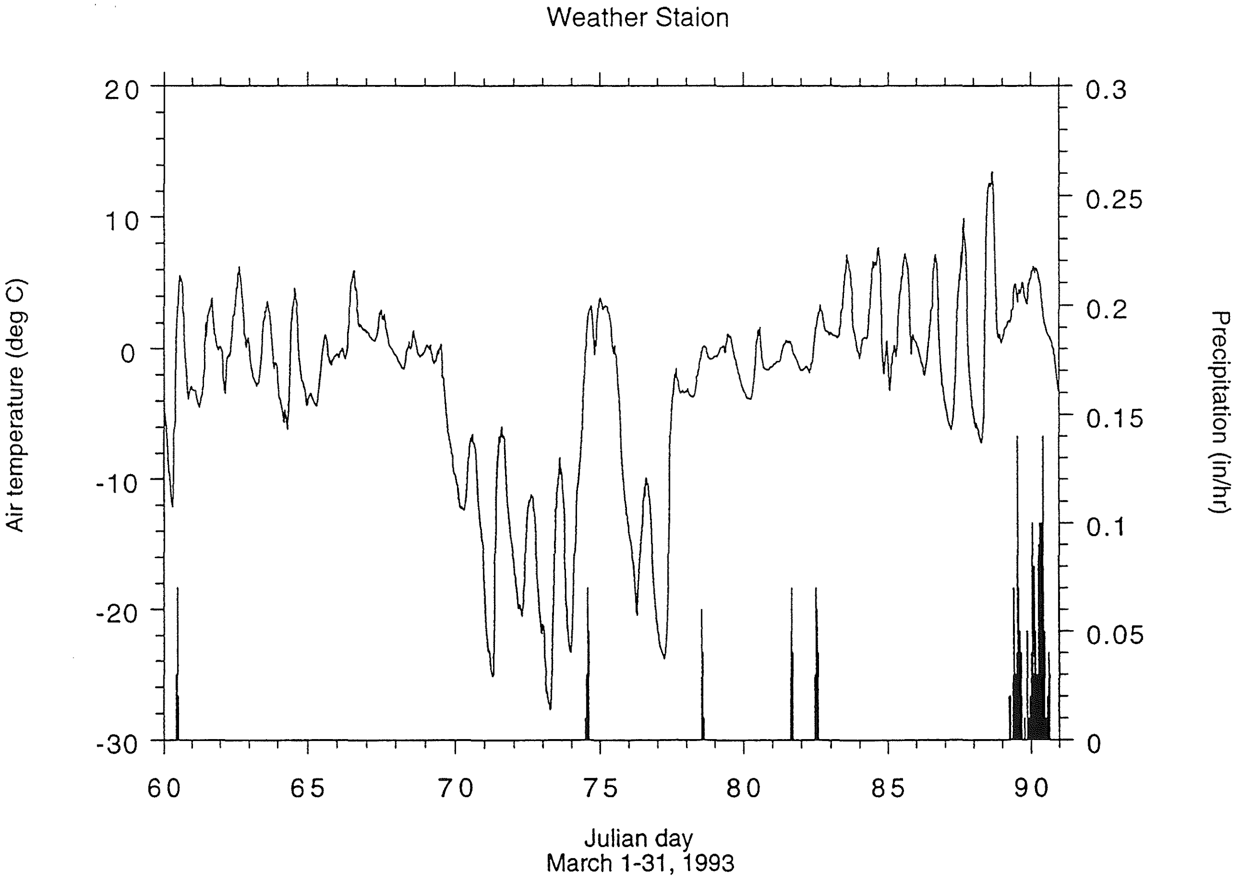


Figure 9.3. Air temperature and precipitation at the Mystery I weather station, March, 1993.

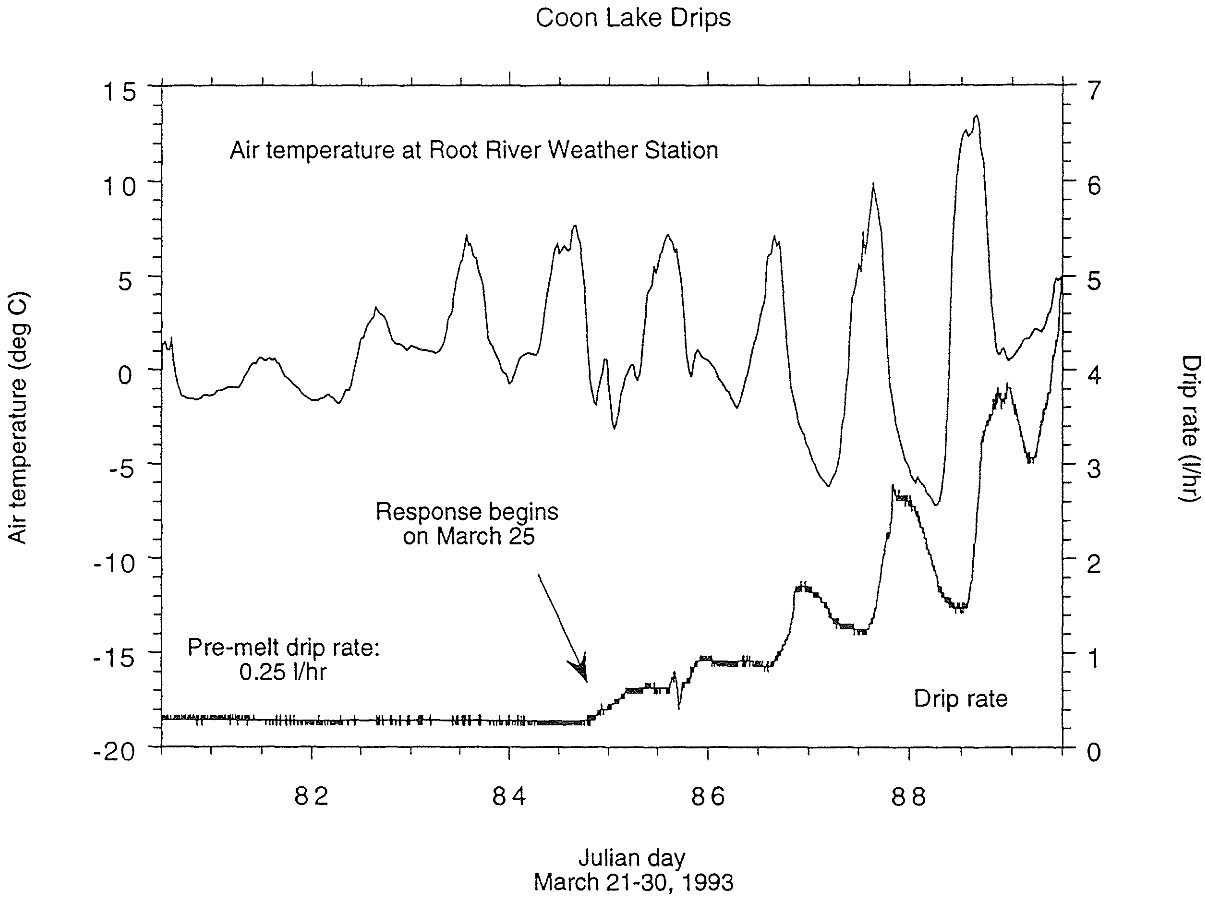


Figure 9.4. Drip rate at Coon Lake Drips and air temperature at the weather station for March 21-30, 1993.

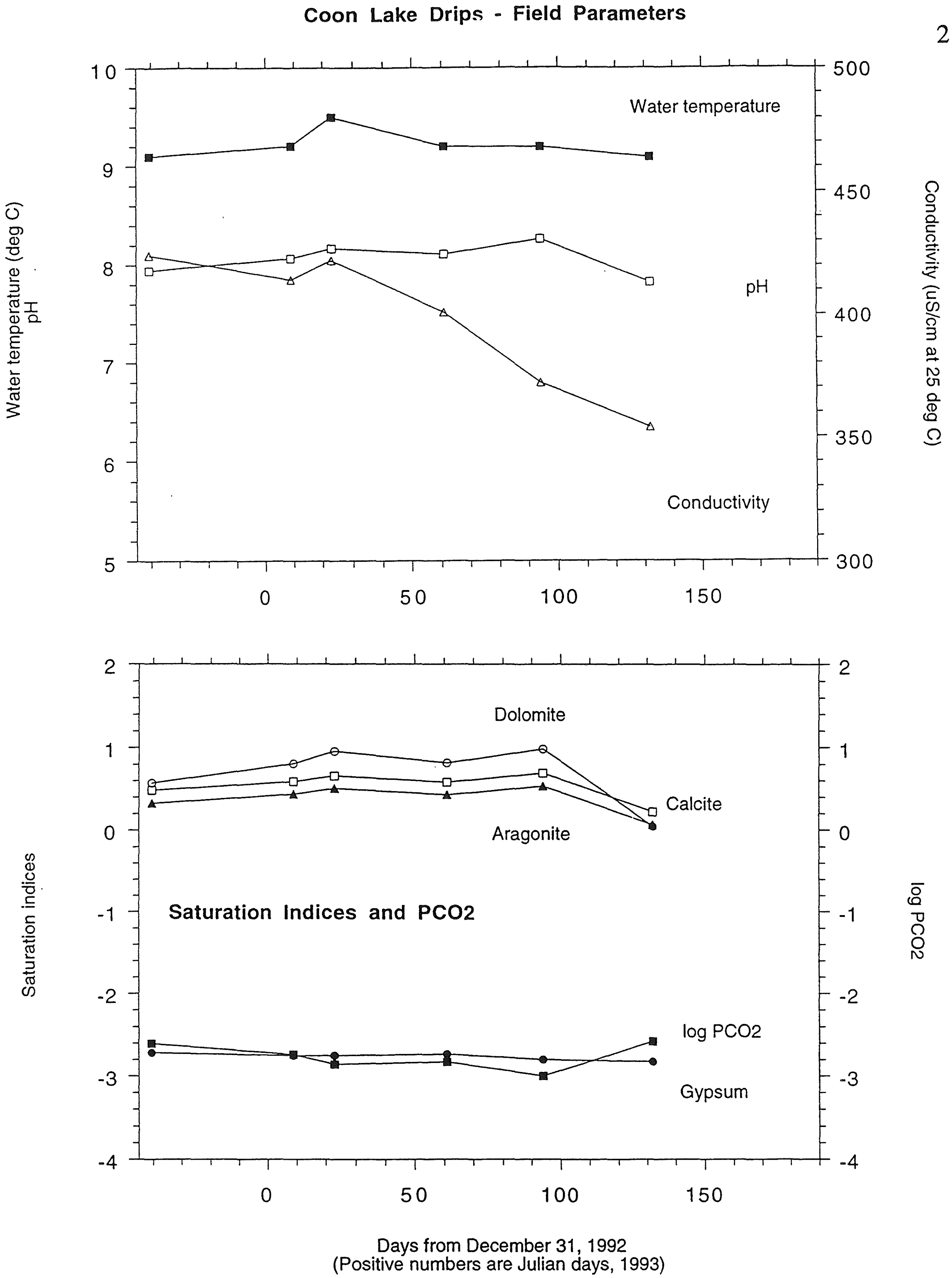


Figure 9.5. Field parameters and saturation indices at Coon Lake Drips.

Table 9.1 Response Times from Snowmelt at Coon Lake Drips

Julian day 1992	Time between peaks (hours)	Time between minima (hours)
86	7	----
87	4.5	9.5
88	7.5	7
89	----	6.5

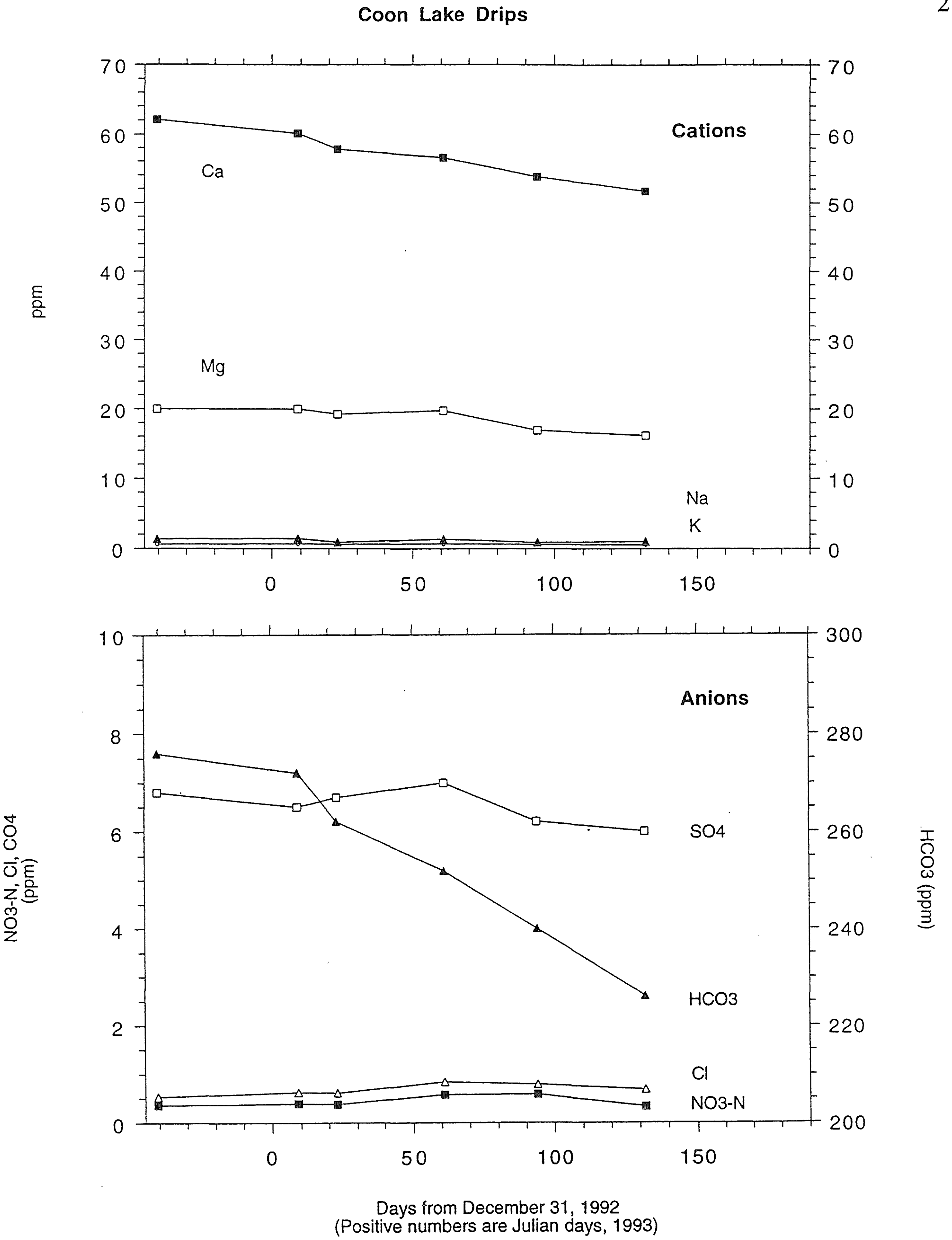


Figure 9.6. Cations and anions at Coon Lake Drips in 1993.

CHAPTER 10

FLOODING AT MYSTERY CAVE: THE MARCH 30-APRIL 2, 1993 FLOOD

SCOPE OF THE DISCUSSION

The spring and summer of 1993 were unusually wet in the midwestern U.S., resulting in a series of flood events throughout the region. In southeastern Minnesota, the flooding began on March 30, as a cold front dumped several inches of rain on an extensive snow cover. Flooding began rapidly on the Root River. At Mystery I, water crested the banks by late on the 30th or early on the 31st. Water was above the banks most of the time until the end of the 31st. Commercial passages in Mystery I were inundated on the 31st and possibly on the first of April. At Flim Flam Creek, water rose over 20 ft and apparently stayed at least 10 ft above normal for over 48 hours beginning about midnight on March 31. Although the effects of the flooding lasted longer, it is convenient to refer to the flood as the March 30-April 2 flood.

Three other major but less intense flood events occurred at Mystery Cave in 1993. One was in May and one was in July. In August, the Root River briefly left its banks (for about one hour, according to Mystery Cave staff) but this did not result in flooding of commercial passages. For brevity, these floods can be termed the first, second, third, and fourth floods. Only the first flood will be discussed here.

We have organized our discussion around four interrelated questions: (1) What conditions led to the flood? (2) What happened on the Root River? (3) How high did waters get in Mystery I, and what were the flow patterns? (4) How did the waters at instrumented cave sites respond to the flood?

Summary diagrams for the flood are in Figures 10.1 through 10.4. Figure 10.1 shows data from the Root River weather station and the Root River. Figure 10.2 shows data from Flim Flam Creek. Figure 10.3 is for Blue Lake, and Figure 10.4 shows data from Coon Lake Drips. A plot of precipitation and cumulative precipitation is in Figure 10.5.

PRE-FLOOD CONDITIONS: SURFACE

Before a snowpack contributes to runoff, it must undergo a process called *ripening*. During ripening, the snowpack warms to 0°C and changes to a state in which it cannot hold any more water (Brooks and others, 1991). Warm air temperatures, solar heat (insolation), conduction of heat upward from the ground, and rainfall can add heat to the snowpack. Some of the snow melts, infiltrates under the influence of gravity, and fills open spaces between the snow crystals. When all

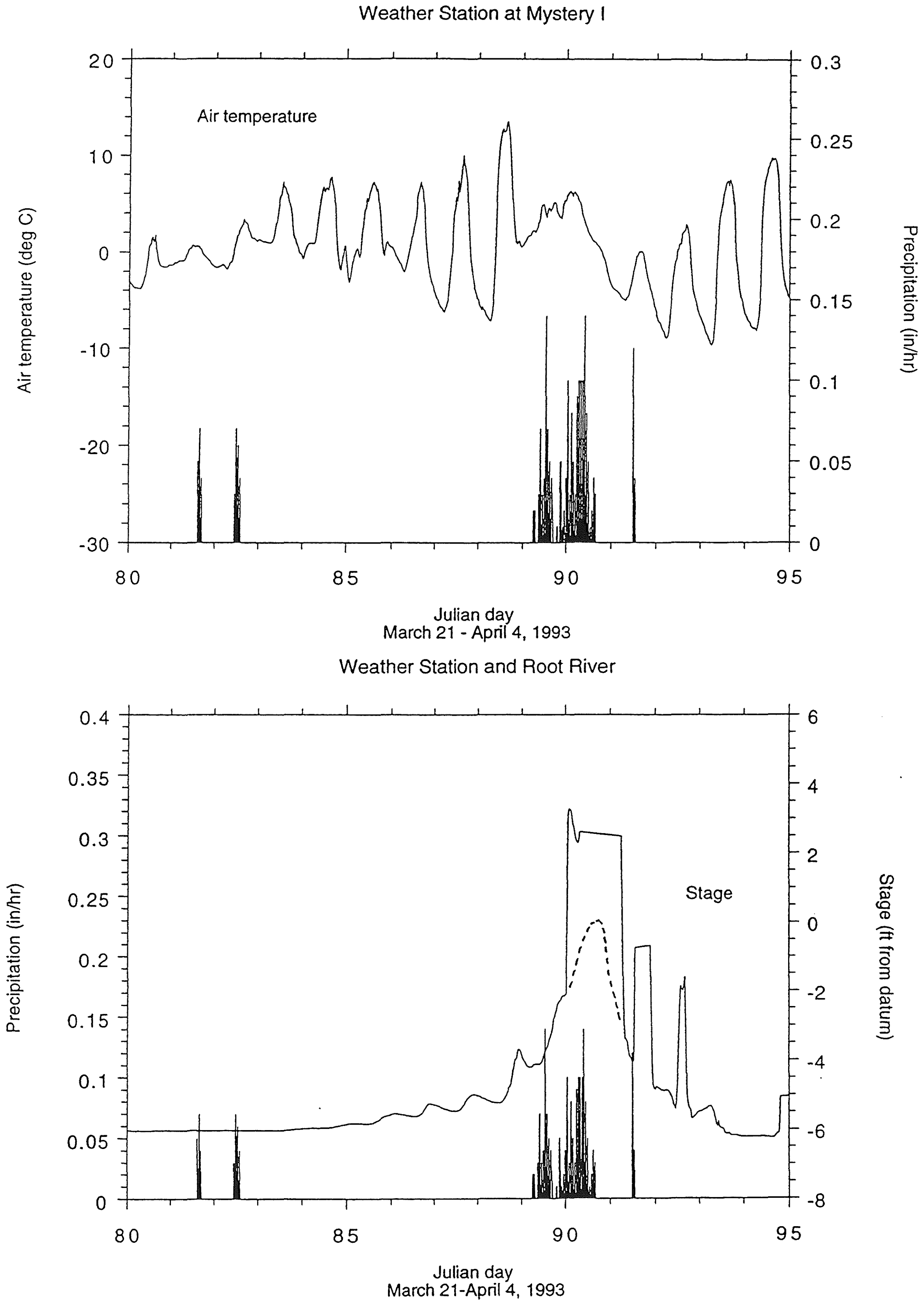
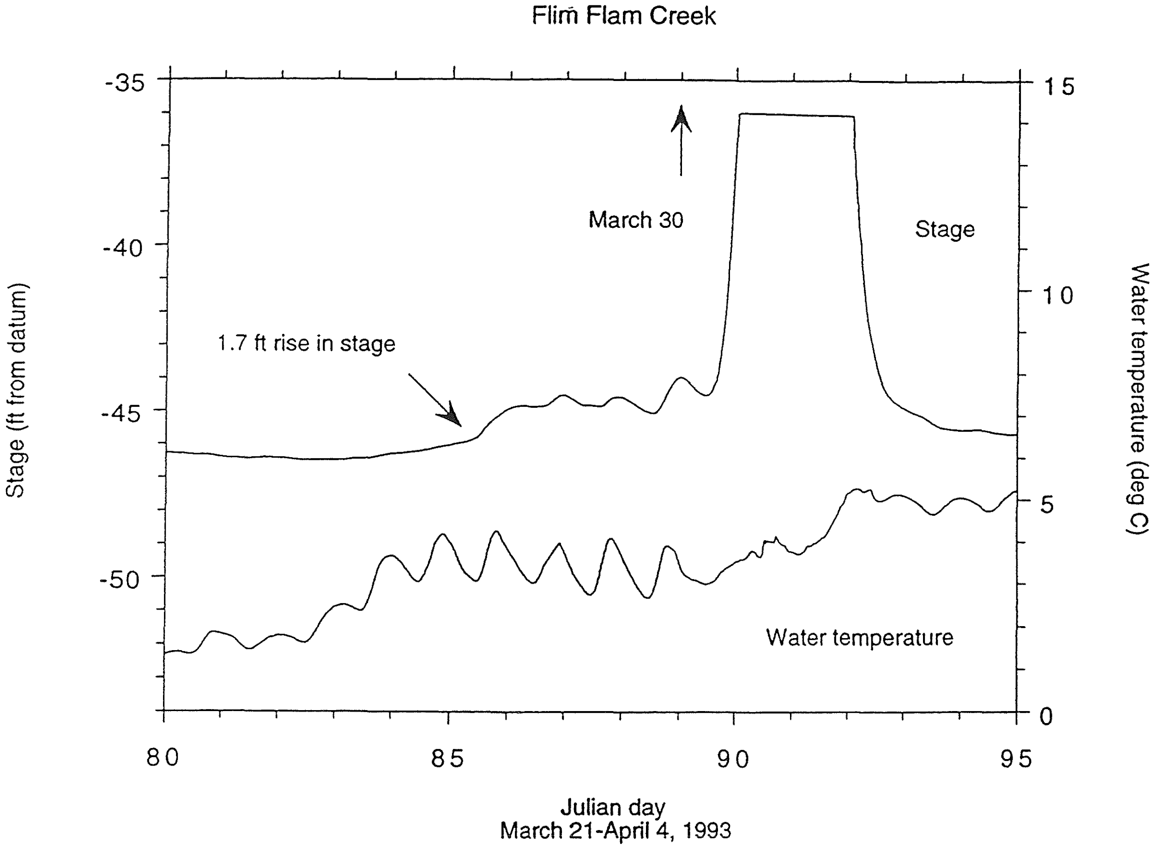


Figure 10.1. The weather station and Root River records at the time of the March flood.



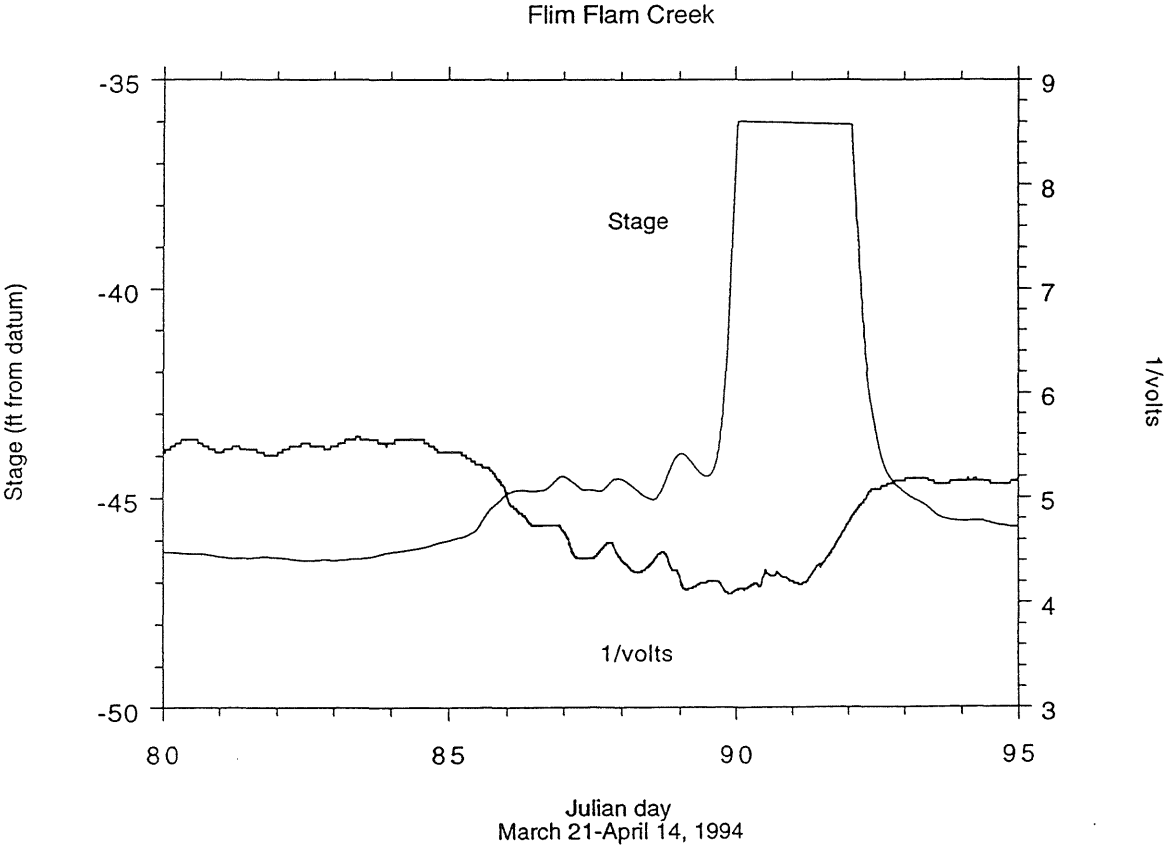


Figure 10.2. The record at Flim Flam Creek of the March flood.

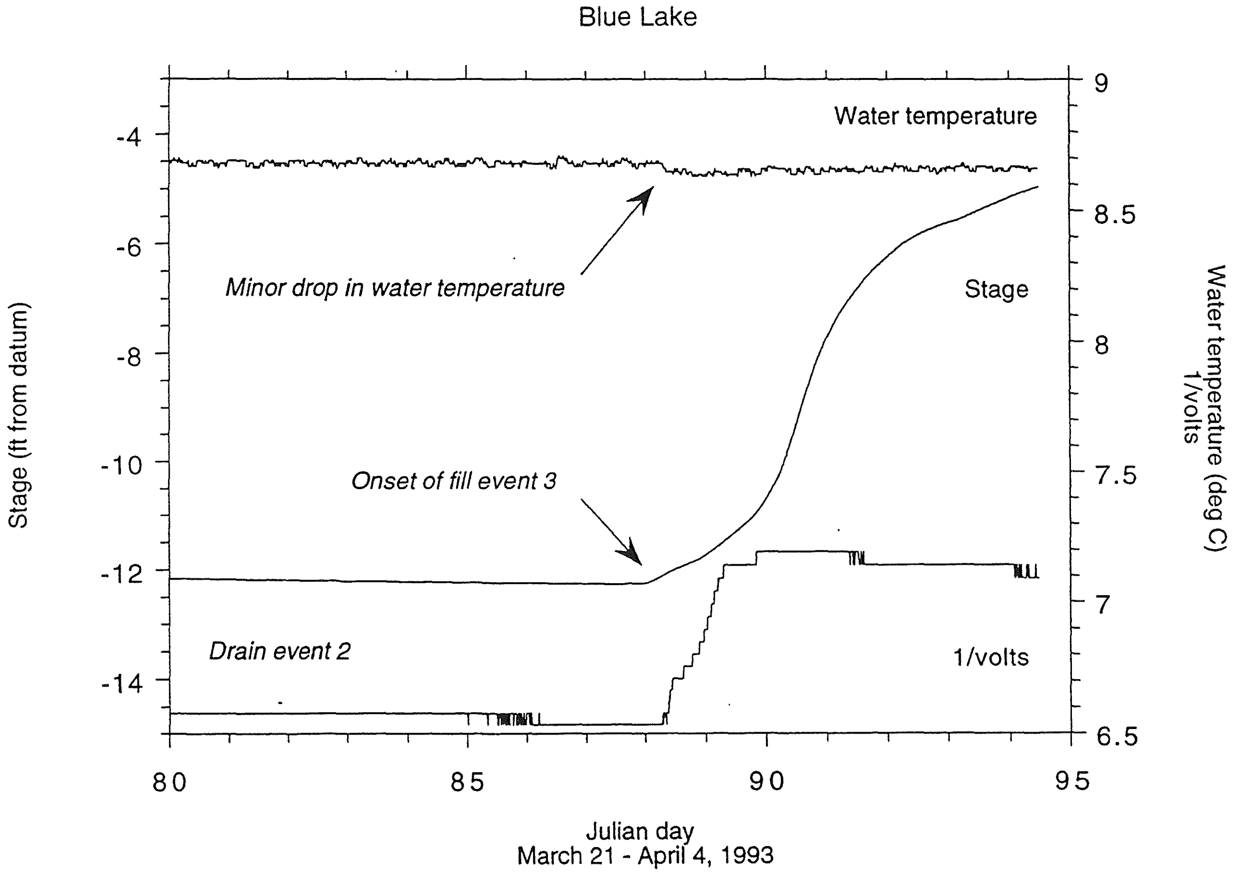


Figure 10.3. The record at Blue Lake of the March flood.

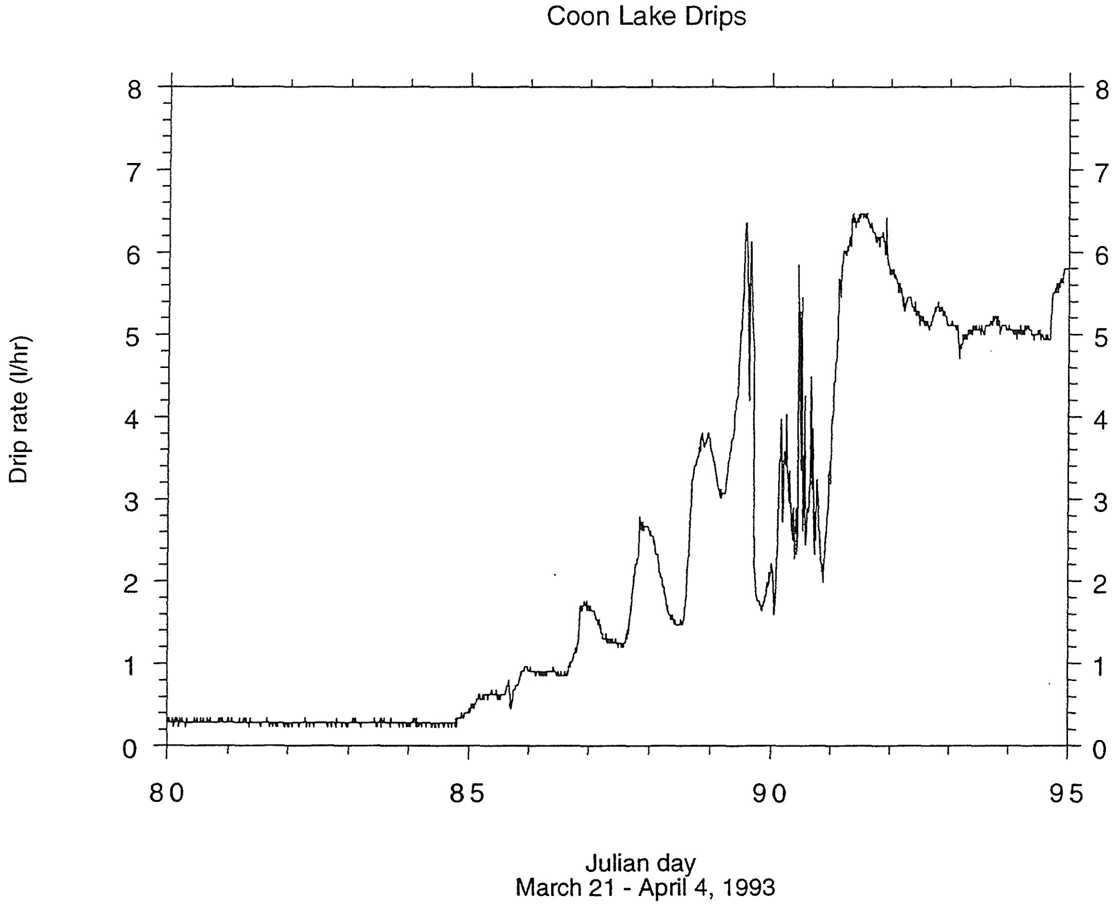


Figure 10.4. The Coon Lake Drips record of the March flood.

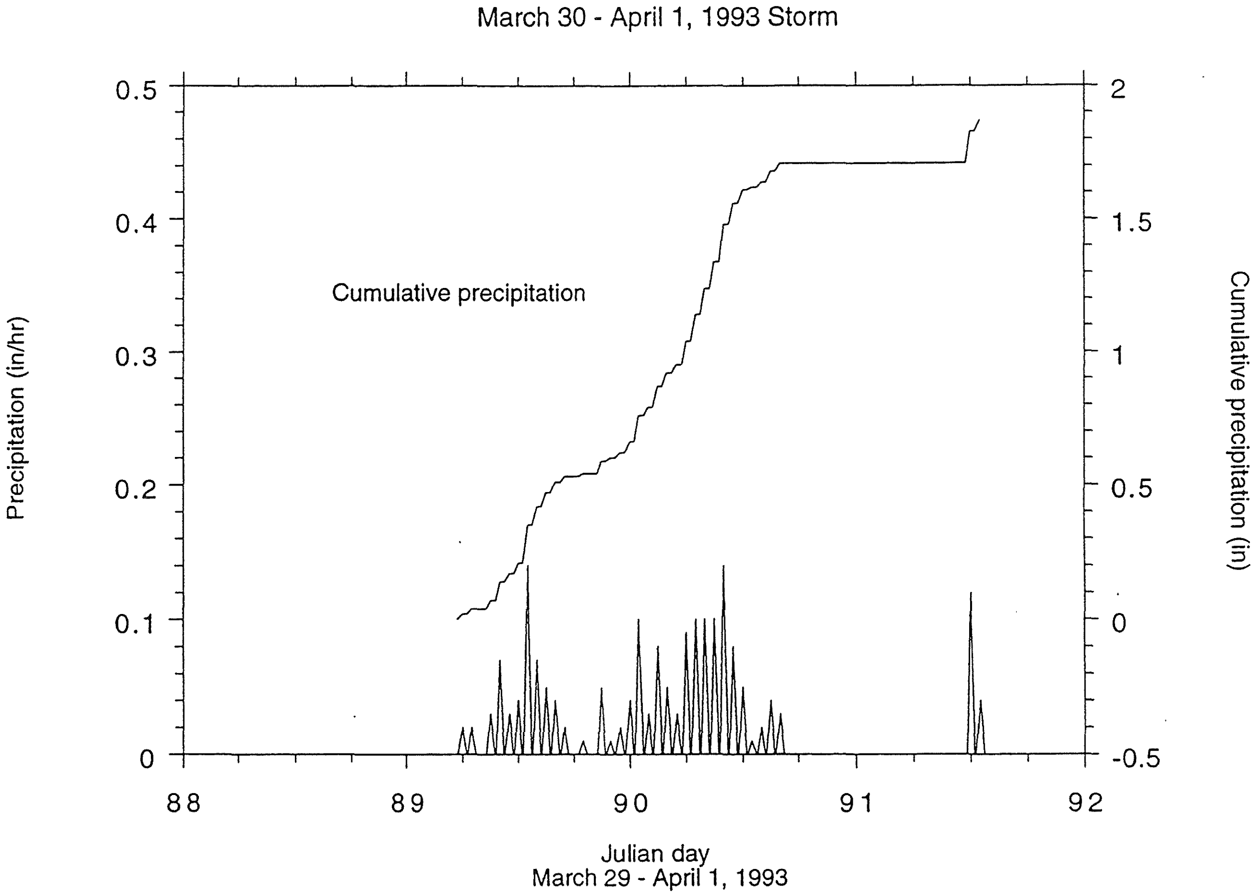


Figure 10.5. Precipitation and cumulative precipitation for the March 30-April 1, 1993, storm.

of the spaces are filled, and the snow is at 0°C, it is ripe. Any further melting will produce runoff.

Of course, some water may infiltrate from the base of the snowpack before the pack is fully ripe, if it can get past ice lenses and frozen soil. The infiltration that led to an abrupt rise in drip rates at Coon Lake Drips on March 25, 1993, probably occurred before the snowpack above Mystery II was fully ripe. Over the next few days, the pack must have fully ripened for short periods over much of the surface basin of the South Branch of the Root River. We can infer this directly from cyclic rises and falls of about 0.3-0.5 ft in stage on the Root River, and an overall rise in stage of about 2 ft from March 25 to March 30, before the onset of precipitation (Figure 10.1).

The eleven days leading up to the flood, beginning on March 18, directly contributed to the intensity of flooding. It did this by bringing the snowpack close to a state of ripeness, primed for runoff during the warmer parts of the day, or for runoff once rain began. Minor rains earlier in the month (Figure 9.3) produced no noticeable response in stage on the Root River; the rain simply infiltrated the snow, adding to its water content.

PRE-FLOOD CONDITIONS: BLUE LAKE AND FLIM FLAM CREEK

The pre-flood melting produced a response at Coon Lake Drips (Figure 9.3), as discussed above. At Blue Lake (Figure 10.3) there also was a pre-flood response. This response begins Fill event 3.

Stage started rising at about midnight at the start of March 29 (day 88). Conductivity (as 1/volts) started to rise at about 6:45 am. Water temperature began a 0.02°C drop from 8.68°C at about 7:15 am; the drop was reasonably complete by about 8:30 am. Conductivity, in contrast, fluctuated until 9:15 am, then began a steady rise that lasted over 24 hours (until 7:15 am, March 30) before flattening out. During this period, stage rose from about -12.23 ft to -11.50 ft.

These observations can be interpreted as follows, recalling our model for fill events at Blue Lake. Infiltration, induced by pre-flood snowmelt, displaced higher conductivity water stored upflow from Blue Lake, which slowly started to fill the pool. At the start of Fill event 3, Blue Lake was already about 2 ft deep, as a result of Fill event 2 and Drain event 2. The displaced water was slightly colder than the water at Blue Lake, so water temperature fell slightly. The incoming water was *not* rapidly infiltrating snowmelt; such waters would have started near 0°C, been very dilute (thus had a low conductivity), and should not have been able to thermally or chemically equilibrate rapidly enough to produce the observed responses at Blue Lake.

For Fill event 2, it was possible to calculate a response time of 141 hours (almost 6 days) from the onset of a 2.18 inch November, 1992, storm to the arrival of displaced water at Blue Lake. It is harder to calculate a response time for displaced water for Fill event 3, because it is not clear which surface event(s) (air temperature, Root River daily melt cycles, or Coon Lake Drips drip rate cycles) to use.

Air temperatures consistently rose above 0°C beginning on March 23 (day 82; see Figure 9.3). At Coon Lake Drips, a displaced water response of about 5-10 hours was inferred, but this assumes some melting had already occurred to open flow paths and establish a more-or less continuous hydrologic connection. As a rough approximation, we can consider the onset of cyclic response in stage on the Root River (Figure 10.1) and the onset of the rise in drip rate at Coon Lake Drips (Figure 9.4). Both of these can be placed on March 25 (day 84). We also can consider the rise in water temperatures at Flim Flam Creek on March 23 (day 82; see Figure 10.2). On that day, water temperature, which already showed a cyclic response, rose from about 2 to 3°C. From March 25 to the onset of the flood on March 30, the water temperature shows a daily cycle fluctuating about 3.5°C. Whichever events we use for correlation, we get a response time on the order of at least four days for the displaced water at Blue Lake. There, stage rose on March 28 (day 88).

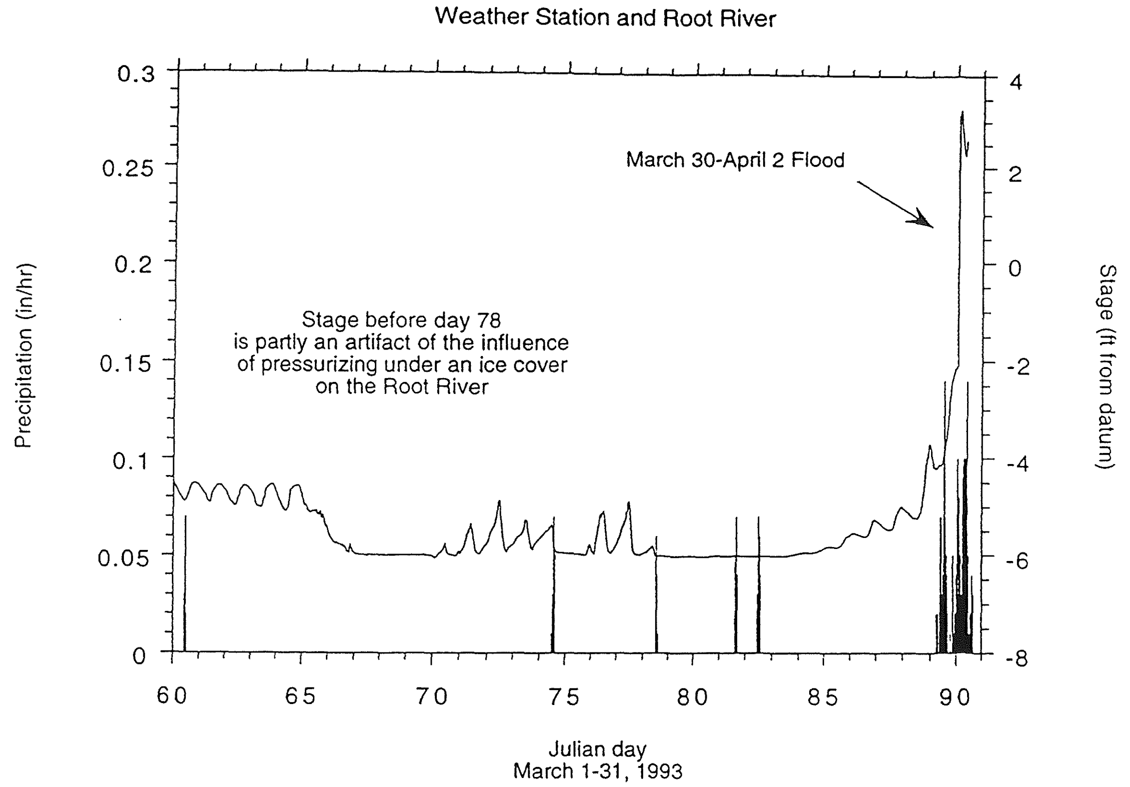
CHARACTERISTICS OF THE MARCH 30-APRIL 1, 1993 STORM

Figure 10.5 shows the precipitation record for the storm, as precipitation over one-hour periods. It also shows cumulative precipitation. The storm left 1.71 inches in two waves on March 30 and 31. An additional 0.16 in fell about midday on April 1, 1993, for a storm total of 1.87 inches.

RESPONSE ON THE ROOT RIVER

The stage record must be interpreted cautiously because the capacity of the pressure transducer was exceeded during the storm. If stage exceeds a threshold value, the pressure transducer ceases to record physically meaningful values and may be permanently damaged or broken. After removing data that clearly are due to over pressuring, we obtain the plots of Figures 10.1 and 10.6. The higher parts of these plots -- those parts with positive elevations above datum -- are also problematic, because stage is recorded as rising to 3.28 ft above the top of the stilling well that contains the pressure transducer. This is impossible. Had water risen that high, it would have inundated the weather station and overturned it. The top of the stilling well is only one foot below the bottom of the weather station. During the flood, the water level rose to less than six inches of the base of the box, according to Mystery Cave and DNR staff who were on the scene. Valiant efforts by these people saved the weather station from being turned over and destroyed. Had they not done so, we would have had no stage record, because the data logger would have become wet and would have short circuited. (One data logger in the Bomb Shelter of Mystery I, used by Richard Lively for recording radon and meteorological measurements, did flood and short circuited. The data logger was damaged and all of the data on it lost.)

In addition, the pressure transducer cable has a tube that extends alongside the wires that lead to the data logger. The transducer uses atmospheric pressure as a reference. The tube must remain open to the atmosphere for the pressure transducer to yield accurate values. If the tube is blocked or no longer open to the atmosphere, then the readings become suspect. The pressure transducer used at the stilling well had sufficient cable for the tube to extend only to near the top of the stilling well. The end of the tube was covered with a plastic bag along with a desiccant package, but to maintain contact with the atmosphere, the bag was taped so that an opening was present at the top. The bag hung about 1 ft below the top of the stilling well, above and to the side of a light bulb hung even lower in the well. The light bulb was used as a heat source to keep the water from freezing during the



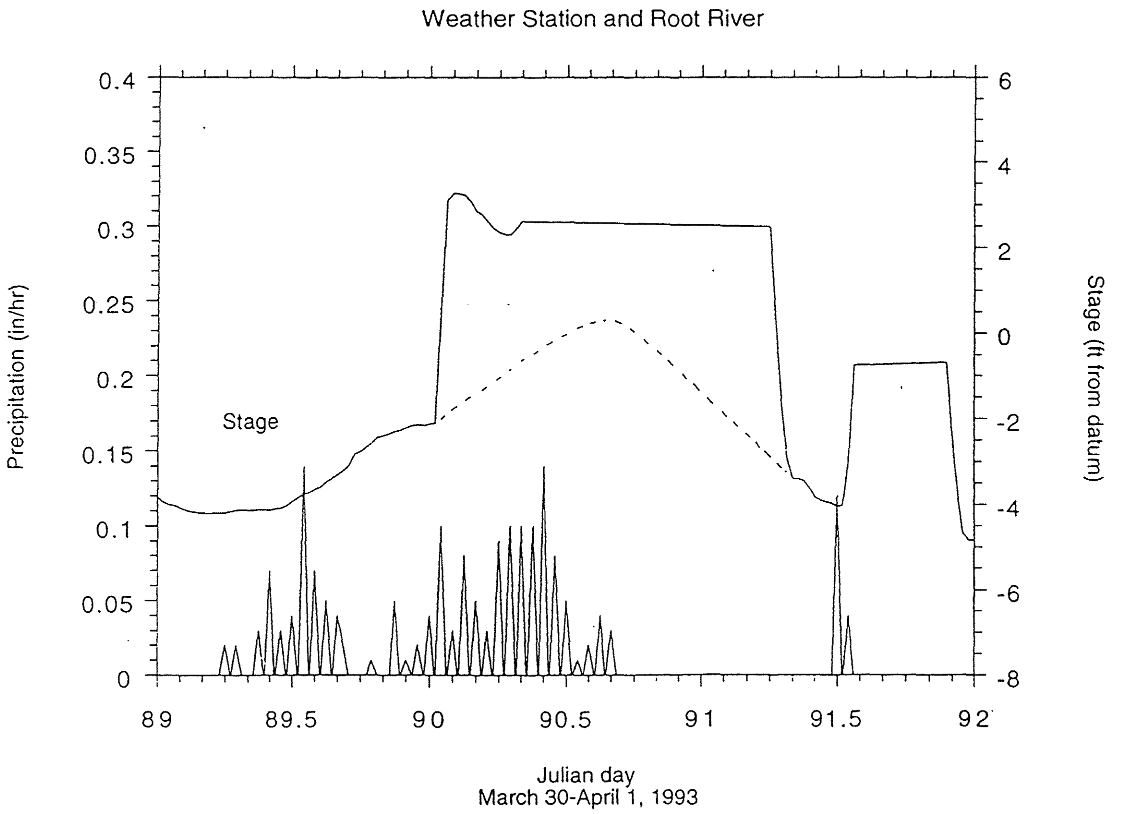


Figure 10.6. Stage and precipitation on the Root River for March, 1993.

winter; an inverted bucket was used to cover the stilling well. When examined on April 3, after the flood, the plastic bag was partially filled with water.

With these cautions in mind, we note the following. The initial response at 6:30 AM on March 30 began shortly after the onset of rain. The initial stage was at -4.2 ft, which is within thebanks but high. Stage rose 0.1 ft between 6:30 and 10:00 AM on March 30 (rate of rise = 0.03 ft/hr). Between 10:00 AM and about 30 minutes after midnight on March 30 (00:30 on March 31) the river rose 2.1 feet to a stage of -2.1 feet. That corresponds to an average rate of rise of 0.14 ft/hr. This part of the record is plausible.

The stage plot in Figure 43 next shows an abrupt rise of 5.38 ft from -2.1 ft to +3.28 ft from 00:30 AM to 2:00 AM on March 31. That corresponds to an average rate of rise of 3.6 ft per hour. A rise that fast is difficult to believe, however, given the abuse the pressure transducer suffered and the physical implausibility of the highest numbers.

The elevation at the top of the stilling well (0 datum) is 1230.86 ft (Palmer and Palmer, 1993a). On the Mystery I entrance door, the highest debris line indicated a high water level of about 1231 ft. The Mystery I entrance is about 100 yards downstream of the stilling well. Although we do not know what the gradient was during flooding, it was not reversed -- the water must have reached higher than the top of the stilling well. It could not have gone much higher, certainly not 3.28 ft higher, because the weather station is only one foot higher than the top of the stilling well.

A plausible interpretation is that the bag floated and partly protected the tube from becoming filled with water, but water eventually covered the bag, at which point stage readings became unreliable. We do not know at what stage the unreliable data began. Based on our estimate that the plastic bag was 1 foot below the top of the stilling well, all data above -1 ft stage must be considered suspect. We do not think the pressure transducer was permanently damaged, however, because the system gave reasonable responses to stage variations in the days and month following the flood. The wet bag was replaced on April 3, and at that time the plastic tube appeared to be free of trapped water. Later calibrations of stage made by filling the stilling well with water and recording falling water level in the well gave consistent results that differed little from earlier lab calibration of the pressure transducer before installation.

Reasonable stage readings resumed, perhaps, at about 8:00 AM on April 1, when stage was at about -3.5 ft. The dashed lines in Figures 10.1 and 10.6 show one estimate of the stage during the flood. This interpretation derives some credence from the rapid response of stage to precipitation recorded on April 1 shortly after 12 noon. (Other more complex scenarios are also possible, however.) Stage is seen in Figure 10.1 to rise to about -0.7 ft before the reading again went off scale. Readings remained off scale until about 9:30 PM on April 1, when they fell to about -0.7 ft.

A third sharp peak in stage was recorded during the afternoon of April 2 (Figure 9.6). Assuming this was real (it had no overpressure component), it can be interpreted as the passage of a runoff pulse from some upstream tributary to the South Branch of the Root River---from either the March 30-31 rain or the April 1 rain.

RESPONSE IN MYSTERY I

Water did not enter the cave through the Mystery I entrance, but the flooding was high enough to have done so were the entrance not gated. As previously noted, the water level at the Mystery I entrance crested at about 1230.4 ft. This level is about 2.3 ft above the cement floor at the entrance floodgate. The floodgate in fact prevented water from entering the entrance and running into the cave.

However, inside the cave water rose up out of lower level fissures and flowed east through the cave away from the Root River. DNR and Mystery Cave staff entered the cave before and after the flood crest, and observed flow along the main tour route. Water rose from fissures near the entrance, flowed past the Pipe Organ, the Frozen Falls area, and Turquoise Lake en route to the Bomb Shelter and the rest of the Door-to Door route.

A polyethylene beaker used for water sampling left at a drip point across from the Pipe Organ (a few days before the flood) was found on a ledge 50 ft past Turquoise Lake after the flood on April 3. A canoe and large wooden planks used at Turquoise Lake and left by DNR staff on the walkway at the lake were moved. The planks were left in Turquoise Lake and the canoe was moved up on a ledge. Considerable sediment was eroded from several banks. Many of the light bulb holders floated up out of their moorings but remained attached by connecting wires. Some cracked and filled with water. Other light bulb holders were wet but appeared little the worse for wear. The lighting system sustained considerable damage although the computer-driven control system at the entrance was not flooded and functioned normally after the water receded.

Monitoring equipment used by Richard Lively at the Bomb Shelter was washed farther into the cave. Before the flood, some of the equipment was on a table about 1.5 ft high; after the flood, the equipment was stretched out down the passage, still attached by electrical cords. An evaporation pan and basket cover was installed a few days before the flood at the Bomb Shelter. After the flood the pan was 30 ft farther in, submerged in a new pool left by the floodwaters.

The rising water was turbulent and turbid. Existing sediments along the trails were rearranged by erosion and redeposition. A fine silt covering was ubiquitous on railings. Cement walkways were covered by mud, silt, sand, and in a few locations, small breakdown fragments eroded from overhanging walls in the relatively weak beds of the Dubuque Formation. However, in comparison with floods in other eastern U.S. caves that receive direct surface flood waters from sinking streams, this flood did surprisingly little re-arrangement of sediments---at least along the trails. Much of the surface debris and large sediment was filtered by the occluded joints through which the food waters entered the cave. Only the finest sediments could be lifted by the flood water up to the commercial level to be deposited as thin coatings on rails and on cement floors. The thicker accumulations on the trails were sediments with local sources within the upper level.

The heights reached by floodwaters can be estimated by observing locations of such features as (1) sediment deposited on passage walls, on railings, and on floors; (2) sediments deposited in pools or small indentations; (3) areas of erosion or collapse of bedrock; (4) disturbed light fixtures; or (5) disturbance of equipment or materials left in the cave.

At the Formation Room in Mystery I, water rose barely to the level of the cement pad above the steps leading into the room. A sandbank next to the steps was severely eroded. The cement pad, which is nearly, but not quite level, had a thin coating of silt on its lower section near the steps. A radon detector a few inches away on the pad barely escaped inundation.

Confirmed heights reached by floodwaters at locations near leveling stations listed by Palmer and Palmer (1993a) are as follows:

Entrance Floodgate to Mystery I	1230.4 ft
Turquoise Lake	>1220 ft
Bomb Shelter	>1220 ft
Formation Room pad	1218 ft

A rise in stage on the Root River increases the pressure head on the sediments of the streambed thereby increasing infiltration rates. Water is injected into every available opening. Some of those openings probably do not transmit significant amounts of water until threshold pressures are reached. Other fractures are probably above low-flow stage on banks or along the cliff near the Mystery I entrance. Such fractures cannot transmit water from the river until stage is high. The net effect is that a given increase in stage injects a greater amount of water per unit time as the flood stage increases.

The capacity of the lower levels of Mystery Cave to accept this water is not infinite. Some sections of passage are of smaller diameter than others. There are constrictions. As the flood waters pour into the lower levels the capacities of these constrictions are exceeded. The result is backflooding. The water level rises. If the flood is of sufficient magnitude and duration, water rises completely out of the lower levels and enters the commercial trails of Mystery I.

It is important to note that most of Mystery I is below the level of the bed of the Root River, but adjacent to it (Sheets 1 through 4, Palmer and Palmer, 1993a). Passages in Mystery I trend east away from the Root River (Figure 1). Therefore, water from the flood had a strong component of flow to the east, into the cave.

RESPONSE AT BLUE LAKE

The pre-flood response at Blue Lake (Figure 10.3) raised stage from -12.23 at the end of Fill event 2 to about -11.50 ft, increasing water depth from about 2 ft to about 2.7 ft at the time conductivity leveled out on March 30, 1993 (day 89).

What happened next? Stage continued to rise, but when did Blue Lake respond to the March 30 flood? And what was the nature of that response? Is it unequivocally present as a distinct point in the plots of stage, water temperature, or conductivity?

We believe that the March 30-April 1 storm induced infiltration which induced another pressure pulse. The pulse displaced additional stored water (rather than directly transmitting a rapidly arriving batch of recent snowmelt and rain) into Blue Lake. This is suggested by the unchanging water temperature and conductivity that continued long after the storm. The 0.02°C drop in water temperature at the start of Fill event 3 was interpreted above to reflect minimally colder displaced water. A similar temperature drop followed the March 30-April 1 storm as shown in Figure 10.3.

Eventually, of course, water that infiltrated during the storm should have arrived at Blue Lake. The question is, when did it arrive, and did it carry a signal that clearly marks its arrival? The longer the flow-through transit time, the more time the cold, dilute infiltrate would have had to thermally and chemically equilibrate, or so mix with other waters that they would be difficult to discern as different from water present in Blue Lake.

The arrival time *of the start of the response (however expressed) at Blue Lake to the March 30-April 1 storm* is, in fact, not clear. The difficulty could arise in part because of the nature of the surface conditions that led to the pre-flood response. We saw previously that it is difficult to correlate the onset of Fill event 3 with a specific surface event. However, signals at several surface and cave sites (air temperature at the Root River weather station; rise in stage on the Root River; water temperature rise at Flim Flam Creek; and the time of the change from winter base flow at Coon Lake Drips to higher drip rates) suggested a response time on the order of at least four days.

There is also the difficulty of deciphering the structure of the system of flow path(s) that feed into Blue Lake. If there are several major tributaries that combine upflow of Blue Lake, then arrival times from the same surface signal could vary. Arrival times would depend on travel times of through-flow and pulse-through components along the separate tributaries. Total response time would be the sum of through-flow and pulse-through times. Further, even if average response velocity was identical for each component, then total response time could be different, if flow path lengths (tributary lengths) were different.

A final difficulty arises because of the structure of Blue Lake itself. It is, we said, a leaky bathtub with at least two sets of drains. The lowest are into the sediment in the floor. The highest drains consist of the routes that feed Blue Lake Springs. These drains have to be higher than Blue Lake Springs (but not by much) to induce flow out the springs. The highest of the seeps and holes that constitute the springs are at an elevation of 1233.28 ft (Palmer, personal communication, 1993). The next lower are at 1233.12 ft. The water level in Blue Lake must rise higher than -5.62 ft relative to datum to create a head difference and induce flow out Blue Lake Springs. The water level reached this elevation after the storm early on April 3 (day 93). At that time, were discharge into the lake approximately constant, then the addition of an extra drain should have slowed the rate of rise in stage. Instead, the rate of rise of stage increased shortly after the critical elevation was reached. The stage continued to increase until April 9 (day 99). In all probability, discharge into Blue Lake increased throughout this time period.

RESPONSE AT FLIM FLAM CREEK

At Flim Flam Creek (Figure 10.2), stage rose about 1.7 ft during the pre-flood interval from a low at about -46.5 ft on March 23 (day 82) to about -44.8 ft on March 26 (day 85). Between March 21 (day 80) and this rise in stage, the water level showed no daily cyclicity that could be attributed to daily snowmelt cycles. After the rise, daily melt cycles are reflected in stage cycles at Flim Flam Creek.

In contrast, daily *temperature* cycles were evident at FFC before the 1.7 ft rise in stage (Figure 10.2a), but were subdued, with amplitudes of about 0.5°C. After the rise in stage, the temperature cycles intensified, with amplitudes of 1°C or greater. The conductivity (expressed as 1/volts) was nearly stable as long as stage was stable (with minor daily cyclicity due to variations in temperature), but dropped sharply with the 1.7 ft rise in stage. Because water temperature rose correlative with the stage rise but temperature declined, the rise in stage reflects a significant increase in the dilute snowmelt flow component derived from rapid run in from the Root River.

The flood response began on March 30, within about 11 hours of the onset of precipitation at 5:30 am. A minimum in stage of -44.5 appears at about 11:30 am. A gradual rise to -44 ft was completed at 4:00 PM. Thereafter, stage rose rapidly. By 1:00 AM on March 31, stage had risen to -36 ft, an 8.5 ft rise. At this point, the capacity of the pressure transducer was exceeded. From the height of silt and sand deposited on chockstones in the FFC fissure, and silt deposited on wall indentations even higher, we know that stage rose to at least -19 ft (Palmer, written communication, 1993). This represents a rise of 27.5 ft. Stage readings began again about 49 hours later, at about -36 ft, the same elevation recorded just before readings were first lost. By 4:30 PM on April 2 (day 92), stage fell back to the pre-flood minimum stage recorded on March 30. Thus the primary flood response at Flim Flam Creek can be estimated at three days and five hours. The duration of the response is longer, by more than a day, than the duration of the initial peak on the Root River (which ended by about 7:00 AM on April 1). A second peak in stage on the Root River, from roughly noon to about 10:00 PM on April 1, no doubt is partly responsible for the long duration of the primary response in stage at Flim Flam Creek. Other factors involved may include the time it takes for waters to drain past constrictions downstream of FFC. For the subsurface upstream of FFC, there would be a variation in arrival times for incoming water from various sources, so the response at Flim Flam Creek can be expected to be spread out longer than flooding on the Root River under most circumstances.

The cyclic variation in water temperature that immediately preceded the flood was lost during it, but re-established rapidly starting April 2, after water returned to about -43 ft, well above the pre-flood minimum of -45.5 ft. (Two minor fine-structure rises and falls with short periods less than a day during the flood probably represent periods during which water from a particular tributary became dominant, or at least modified the temperature of a larger volume of floodwaters with which it had mixed.) During the flood response, water temperature rose from a 3.5°C mean temperature (within daily cycles) to about 5°C. The conductivity (as usual, expressed as 1/volts without temperature corrections) initially exhibited fine structure at a low level, through the middle of April 1, but then rose as soon as water temperature increased.

RESPONSE AT COON LAKE DRIPS

The drip rate, which was recorded over five minute intervals, shows considerable fine structure (Figure 10.4, 10.7 and 10.8). In the pre-flood period of March 25-30 (days 84-89) daily drip rate cycles became established; they are associated with daily snowmelt cycles. The minima in drip rates were broad (at least 4 hours) on March 28 and 29 and occurred about noon each day. On both days, the rise from the minimum was abrupt, beginning about 2:00 PM.

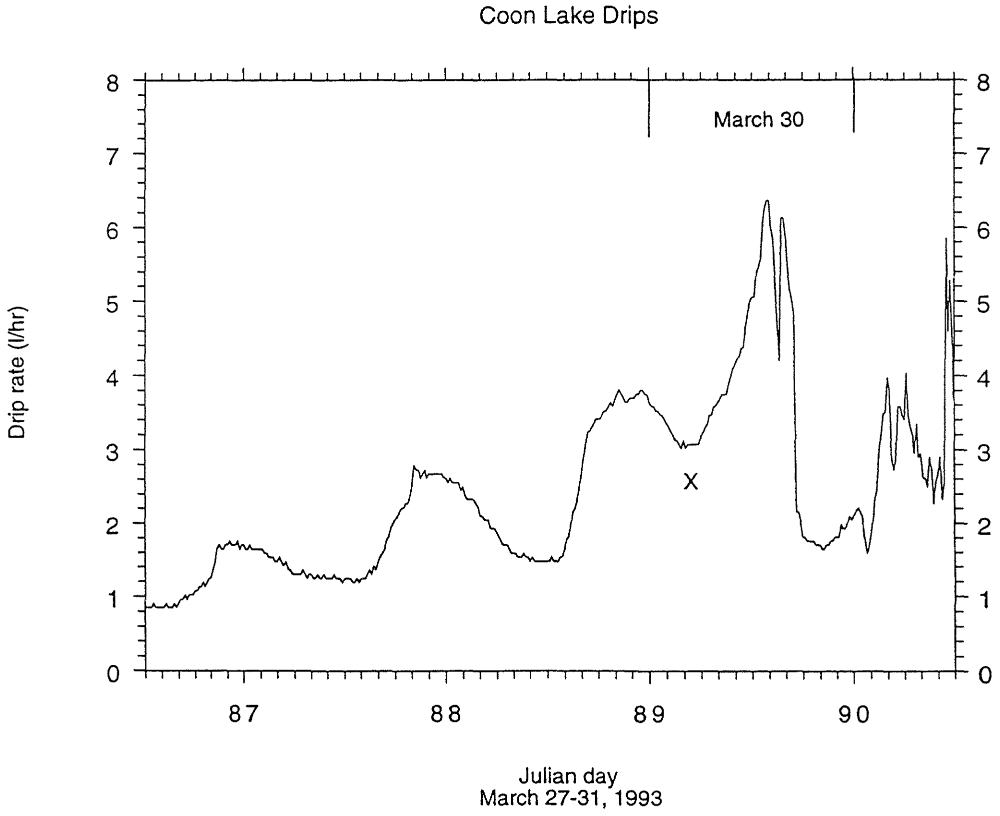
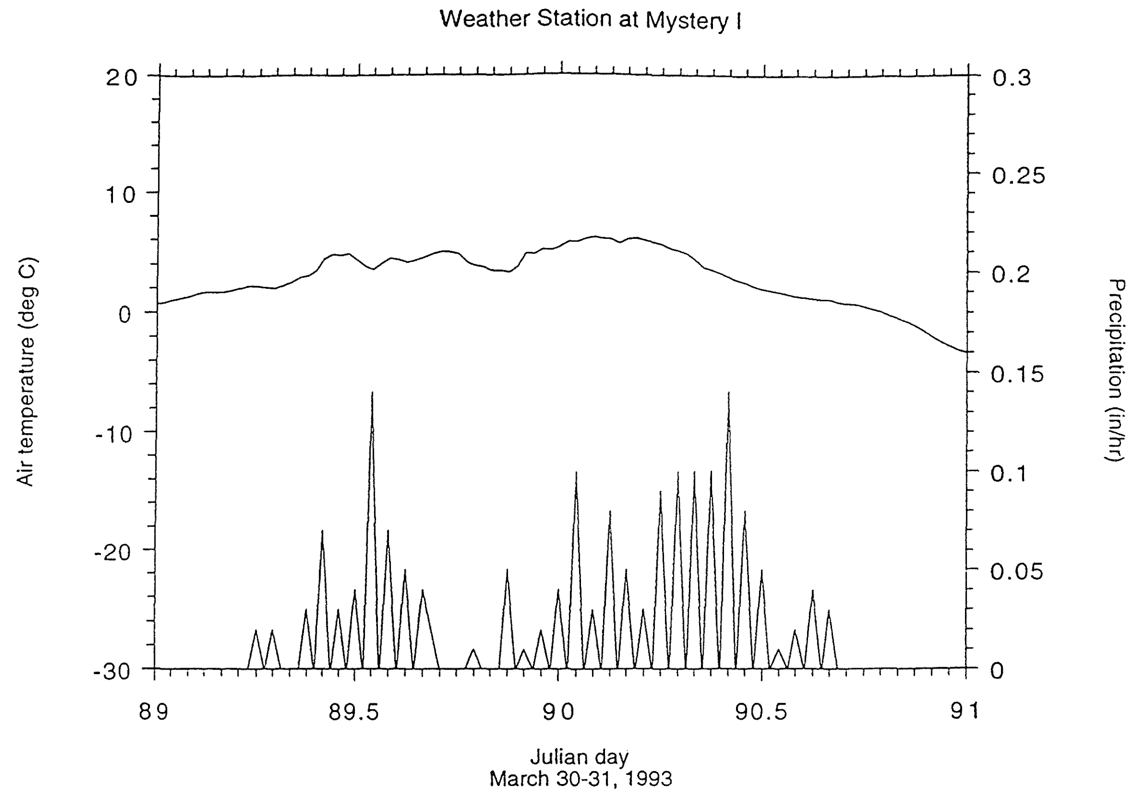


Figure 10.7. Drip rate at Coon Lake Drips from March 27 to March 31, 1993.

We do not believe that the data imply rapid transmission of meltwater to Coon Lake Drips. Instead, pulses of stored water were being displaced, in response to surface infiltration of snowmelt, into the cave passage. Both through-flow time and pulse-through time were involved.

The storm began at 6:00 AM on March 30. Had no storm occurred, there would probably have been a minimum in drip rate on March 30 in the early afternoon. That minimum would have been higher than the minimum observed on March 29, but lower than the actual minimum observed on March 30 (point X, Figure 10.7). The actual minimum came about 5:00 AM, when the drip rate was 3.l/hr. The rise in drip rate began about 5:45 at the onset of the storm. This suggests a nearly complete hydraulic link from the base of the snowpack to Coon Lake Drips. The snow pack would have been ripe, even at night (air temperatures were above freezing (Figure 41) the night of March 29-30). As soon as rain fell, infiltration increased beneath the snowpack. Water was immediately displaced to fall at Coon Lake Drips and begin a rise in drip rates. Such a model for the response is tempting, especially for the onset of the storm. However, the response at Coon Lake is too variable (and too complex) to fit this explanation throughout the storm.

Drip rates rose to a maximum of about 6.4 l/hr at 2:00 PM on March 30, fell to about 4.2 l/hr at 3:30 PM, then rose rapidly again by about 3:50 PM to 6.4 l/hr (Figure 10.8a). Next, drip rates rapidly declined to just over 2 l/hr by 6:00 PM, declined slowly to 1.7 l/hr, and rose to 2.2 l/hr until about 1:30 AM on March 31. A consistent rise to about 3.5 l/hr at 4:00 AM is followed by chaotic behavior. For the next 14 hours, drip rates fluctuate wildly from 2.2 to 6.1 l/hr. It is tempting to try a correlation of these drip rates with rainfall (Figure 10.8b) using mathematical techniques from time-series analysis, but that analysis shall not be pursued here.



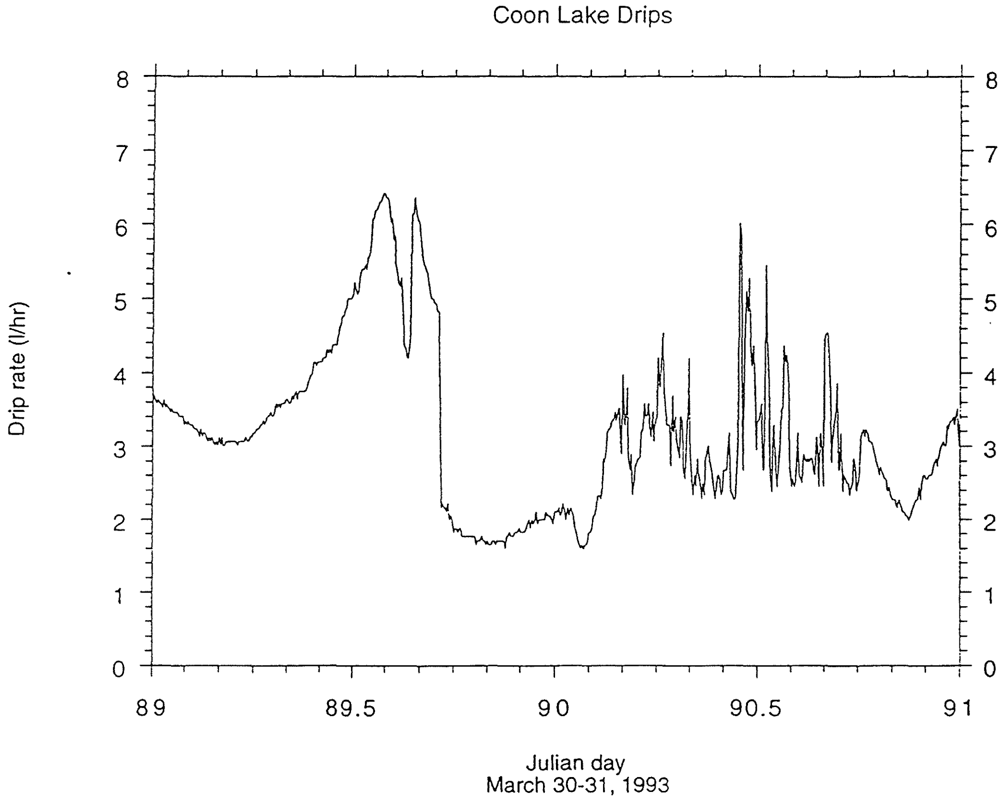


Figure 10.8. Fine-structure of drip rates at Coon Lake Drips, and precipitation and air temperature at the weather station, March 30-31, 1993.

CHAPTER 11

EVAPORATION AND CONDENSATION

The atmospheric moisture of caves is an important variable affecting speleothem deposition and stability. Low relative humidities can contribute to the deposition of speleothems as moisture moves from bedrock into the cave and evaporates. But low humidities can also contribute to the drying of flowstone deposits and to their degradation if seeping or flowing waters are not available to keep surfaces moist.

The lower the atmospheric moisture content, the greater the evaporative flux from a free-standing water body. In caves, moisture evaporates from seeping, dripping, splashing, flowing, or free-standing water bodies. Moisture evaporates at bedrock surfaces as water seeps through pores under a moisture gradient. Flowing water wets sediments during floods and water evaporates from those sediments after water levels recede. In dry passages, water moves from the bedrock into clastic sediments and evaporates from their surfaces.

In temperate climates, caves have relative humidities near 100%. Atmospheric moisture contents near saturation are difficult and expensive to measure with accuracy. Sling psychrometers or other inexpensive instruments used to measure wet and dry bulb temperatures do not provide sufficient resolution to accurately calcultate humidities that vary a few percent or less near saturation vapour pressures. To investigate spatial and temporal variations in atmospheric moisture in caves and to relate them to cave features, it is helpful to employ alternate techniques---techniques that measure proxy variables such as evaporation and condensation.

PURPOSE AND SCOPE

This chapter describes results of a study of evaporation and condensation in Mystery Cave. Its purpose was fourfold. First, we wanted to see if evaporation and condensation rates were sufficiently large to be measurable at sites where these processes were predominant---so predominant as to be readily notable by even casual visitors. It was clear that condensation occurred near entrances and cave streams fed by the Root River. It was also clear that relatively wet areas of the cave dried out at times, particularly during the winter. But it was not apparent that condensation or evaporation rates were quantifiable at any sites, let alone at sites where rates were low.

Second, early in the study we noted a distinctive distribution of aragonite crusts and needles within parts of 5th Avenue in Mystery II. Aragonite crusts are confined to the lower parts of walls, in areas that seemed to always be dry. Higher parts of walls and ceilings seemed to be moist much of the year and lacked aragonite. Reaches of passage as long as 60 ft have distinct, near-horizontal boundaries between regions with and without aragonite. We therefore wanted to see if evaporation rates were in fact high in areas with aragonite, and low (or if there was condensation) in areas without aragonite.

Third, we wanted to survey evaporation and condensation rates and see if they related to cave features in any other ways. We would expect, as noted above, condensation near entrances and lower-level streams during the summer. We also would expect evaporation rates to be relatively low near persistent water bodies. But it also seemed worthwhile to see if relatively dry and wet locations elsewhere within the cave had corresponding rates of evaporation and condensation.

Finally, evaporation and condensation are a part of the hydrology of caves that deserve more attention than they are usually given. Evaporation and condensation are only minor components of the water budget of most caves, but they can be important processes. They contribute to chemical alteration of the outer few inches of bedrock. They are instrumental in the formation of bedrock weathering rinds. The waters involved transport ions that precipitate to form speleothems. Where condensation rates are high, the waters can alter the surface by dissolving such features as drop dents and condensation trails (Jameson, 1986; Jameson and Alexander, 1990).

EQUIPMENT AND PROCEDURE

Initial Installation at the Garden of the Gods

To test the feasibility of an evaporation study, three evaporation pans were installed at the Breakdown Stack (Figure 11.1) near the Garden of the Gods in Mystery II on July 30, 1992. One pan was placed on the floor; a second was directly above on a breakdown block about 7 ft above the floor; and a third was set on another block less than 3 ft to the side, about 9.5 ft up. In each case, 200 ml (about 200 g) of distilled water were pipetted into the pan. The pan was then covered with an overturned plastic basket with a solid base and slotted sides. The slotted sides allow air circulation. The solid base functions as a cover to prevent drips from the ceiling from falling into the pan. The pans are rectangular, constructed of plastic, and have an inside surface area of about 305 cm^2.

The site at the Breakdown Stack was chosen because it is relatively dry at the floor and moist near the ceiling, so that evaporation and condensation rates might be high enough to measure. Aragonite crusts appear on the lower wall, but not higher up Figure 11.1). Finally, the Breakdown Stack allowed placement of three pans at varied heights at one location and allowed ready access to them. Few sites in Mystery Cave provide relatively accessible flat surfaces for pans at varying heights at one location.

Forty-seven days after installation, on September 15, 1992, the pipette was used to remove the remaining water into pre-weighed bottles stored in plastic bags. A re-weighing at the lab suggested that 3.59 g (floor pan), 3.19 g (middle pan), and 4.73 g (top pan) of water had evaporated, but some water was inadvertently spilled from the top pan during the transfer. Another difficulty encountered was the awkwardness of safely handling and transporting the glass pipette, which eventually would be dropped and broken. Nonetheless, the results suggested that evaporation rates were

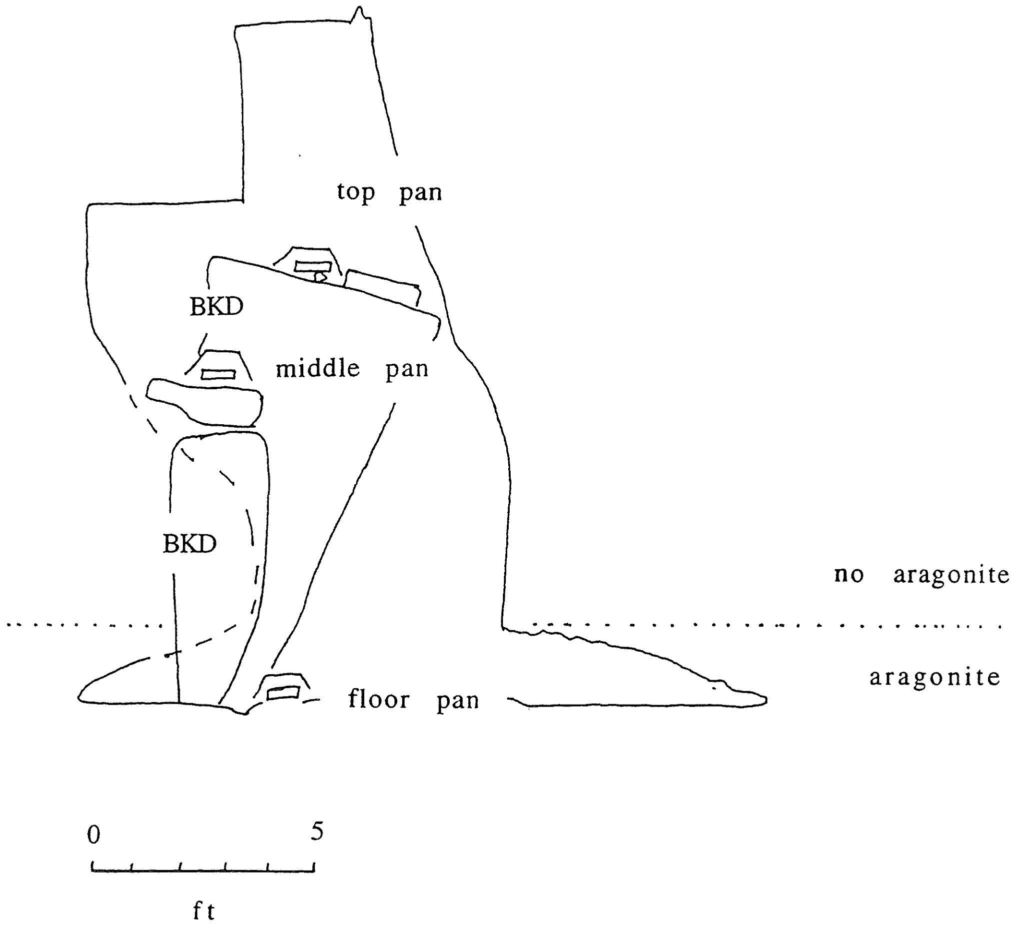


Figure 11.1 Location of evaporation pans at the Breakdown Stack near the Garden of the Gods in Mystery II. The cross section is drawn facing east toward the Garden of the Gods. Bkd = breakdown.

sufficient to be measurable (about 2.5 and 2.2 grams/square meter/day for the floor and middle pans) and that a more extensive study might be warranted.

Additional Installations and Modifications to the Procedure

On September 23, 1992, seven additional evaporation pans were installed in Mystery II. Other pans were added at later times, giving the distribution of study sites shown in Figure 11.2.

A few pans were used only briefly. For example, the pan at the Bomb Shelter in Mystery I was washed away by the March 30-April 2 flood only three days after initial placement and had to be replaced. It was discontinued after a few months due to fear of loss by additional flooding. In a few instances, pans were moved a few feet from their original locations to more suitable nearby sites less subject to potential interference from dripping or splashing water.

In July, 1993, pans were installed in 5th Avenue of Mystery II, about 60 ft east of the junction with the entrance passage. This site had five pans at varying heights within the passage (Figure 11.3). One pan was 3.1 ft from the ceiling. A second was 2.7 ft lower, about three ft above the line separating wall without aragonite crusts from wall with aragonite crusts. A third pan was about a foot below the top of the crusts. These upper pans rested on three platforms attached to a wooden stand wedged against the wall and ceiling and buried in the floor. Two final pans were on the floor to the side of the stand. The five pans in 5th Avenue were installed to further test the hypothesis of variations in evaporation with height within a passage, as was being done at the Breakdown Stack near the Garden of the Gods. The two pans on the floor were placed adjacent to one another, under a single large basket, in an unsuccessful attempt (see below) to check the reproducibility of the estimates of evaporation.

Two evaporation pans were placed at sites relatively near water bodies; these were initially expected to have low evaporation rates (Blue Lake and Wishing Well Drips). Three evaporation pans were placed at sites relatively far from major water sources; these were initially expected to have relatively high evaporation rates (17 Layer Rock, base of Hills of Rome, the Angel Loop). The pan at the Bomb Shelter was installed because Richard Lively had a radon and meteorological station (with air temperature and wind speed) nearby, but his equipment was destroyed during the same flood that removed the original pan.

After the initial sampling period at the Breakdown Stack, the measurement technique was changed to one based upon mass. Pre-weighed bottles of water were used to fill pans at the start of a period. At the end, pre-weighed dry bottles with paper towels were used to collect the water from the pans. Recloseable plastic bags were used to keep the bottles dry and prevent contamination by dirt or water. At each site, the dry bottle was removed from its bag and placed on it. The paper towels were removed and placed on a clean dry notebook or plastic bag. The contents of the evaporation pan were carefully poured into the bottle. The paper towels were then used to dry the pan and soak up any spilled water from the sides of the bottle or the plastic bag. The paper towels were inserted in the wet bottle with the contents of the pan, reclosed and replaced in the plastic bag. After a little practice, it was possible to limit spillage to an average of only a few drops at only one site out of ten to twelve sites per sampling period. Reweighings of emptied bottles and filled bottles (from

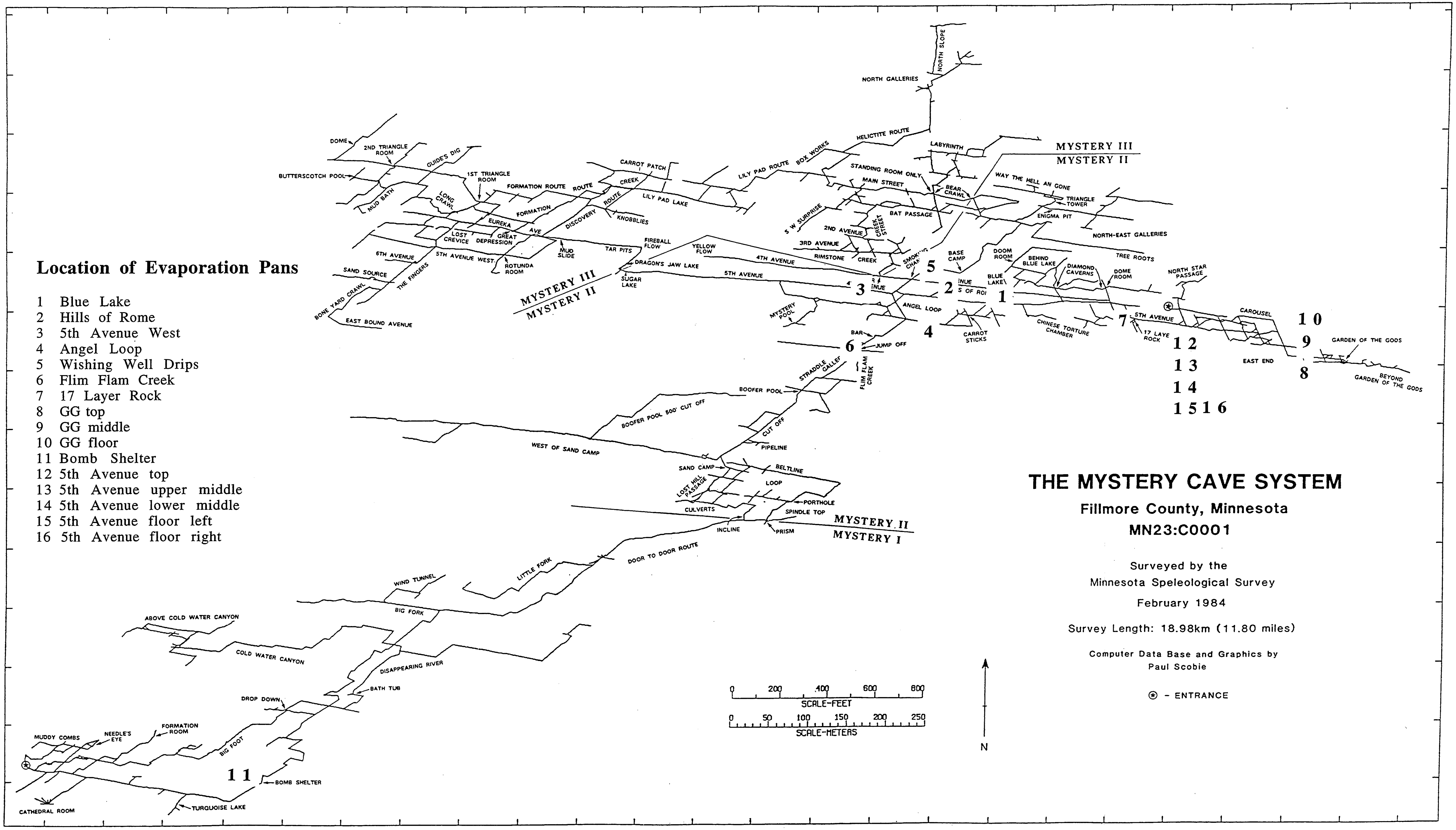


Figure 11.2. Location of evaporation pan sites in Mystery Cave.

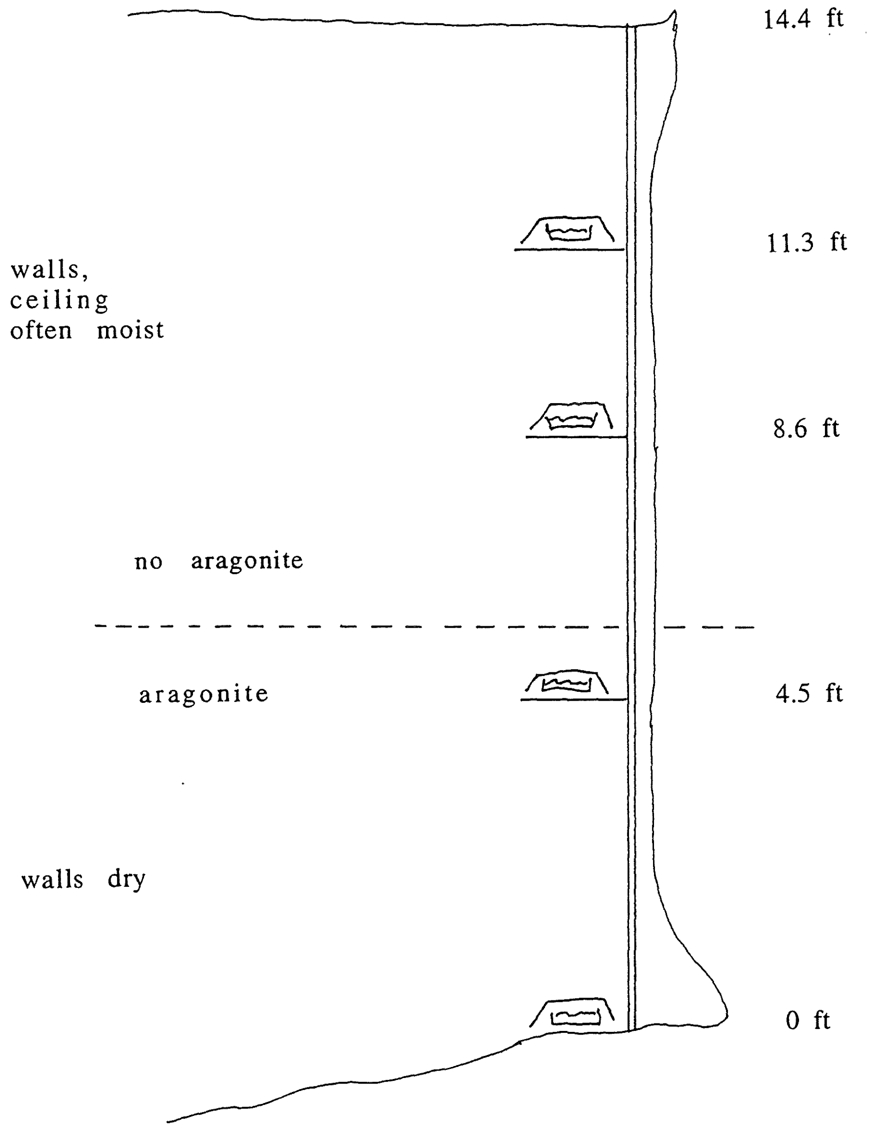


Figure 11.3. Evaporation pans in 5th Avenue near the Mystery II entrance.

separate trips) allowed calculation of mass differences between sampling times. Sampling times and dates were recorded, so that evaporation or condensation rates could be calculated.

RESULTS AND DISCUSSION

Table 11.1 shows the data, which are plotted in Figures 11.4-11.8. Positive numbers indicate evaporation, and negative numbers condensation. On Figures 11.4-11.8, the data points represent values obtained for the time periods immediately preceeding the points. Time periods were usually about one month in duration. The data represent net evaporation or condensation for the entire time periods. Because weather conditions on the surface (and to a certain extent the cave) vary on several time scales (daily cycles, frontal cycles, seasonal cycles) it is possible for evaporation and condensation rates to combine at individual sites so that extremely misleading average results are obtained. Monthly sampling intervals were chosen primarily because water sampling trips were about once a month. It would have been helpful to have shorter intervals, such as a week, so that evaporation could better be related to surface weather conditions. However, this was not feasible and would undoubtedly have surpassed the ability of the technique to measure small amounts of evaporation in pans of the size used.

Some sites, such as Flim Flam Creek (Figure 11.4), exhibited evaporation most of the time and condensation only during the warmer part of the year. Other sites, such as the one in the Angel Loop (Figure 11.8), always showed evaporation. No sites exhibited condensation all of the time.

Evaporation rates varied from near zero to almost 3.5 $g/m^2/day$ at sites that might approach conditions representative of a free-standing water body (see next paragraph). Our data are potentially representative of only a small subset of evaporative environments. Water is liable to evaporate at different rates under the same temperature and wind conditions depending on the characteristics of the water surface and it's mode of flow. Evaporation rates may be fundamentally different from a stationary water body than from a waterfall, or from water that is evaporating from clastic sediments or depositing speleothems. More troubling, water evaporating from an artificial site---an evaporation pan, may be different yet and may vary significantly according to details of its construction and placement.

By "sites that might approach conditions representative of a free-standing water body", we mean sites in which the water being evaporated is is confined within a pan whose bottom closely touches sediment, breakdown, or bedrock. The water within these pans should approach thermal equilibrium with underlying solid materials and the overlying air. At most sites, the underlying solid materials should be within a degree of 8.7°C and should vary little in temperature annually, except near cave entrances. Evaporation rates should therefore mostly reflect the characteristics of the overlying air. The relevant characteristics should be air temperature, the saturation deficit (amount of water required to reach saturation vapour pressure for water vapour in undersaturated air), and wind speed, *if water is evaporating.* If conditions favor condensation, whereby water vapour is condensed to form fogs in the air and liquid on the surfaces of solids, then latent heat is released and conditions are further modified.

Table 11.1
Evaporation Pan Data

Date	Blue Lake*	Hills of Rome**	5th Avenue West	Angel Loop	Wishing Well Drips	Flim Flam 17 Creek	Layer Rock	GG top	GG middle	GG floor	Bomb Shelter	5th Avenue top	5th Avenue upper middle	5th Avenue lower middle	5th Avenue Floor left	5th Avenue Floor right
10/23/92	0.3	0.33	0.01	1.71	0.65	-2.08	-0.04	0.01	-	0.51	-	-	-	-	-	-
11/20/92	1.68	0.76	1.47	3.43	0.47	-	0.71	-	0.09	1.25	-	-	-	-	-	-
12/22/92	1.11	1.04	0.87	2.08	0.87	0.85	1.1	0.6	0.57	1.21	-	-	-	-	-	-
1/23/93	0.7	0.82	0.36	1.04	1.06	-	0.86	0.16	0.21	1.34	-	-	-	-	-	-
3/2/93	0.46	0.49	-0.15	1.05	0.91	1.02	0.66	-0.18	0.06	1.34	-	-	-	-	-	-
3/27/93	0.88	0.79	0.21	1.74	0.37	1	0.7	0.28	0.55	2.19	-	-	-	-	-	-
4/17/93	0.53	0.6	0.05	2.3	0.52	1.06	-	-0.3	0.02	1.56	-	-	-	-	-	-
5/26/93	0.43	0.5	0.05	2.5	0.52	1.32	2.74	0.01	0.19	1.31	0.71	-	-	-	-	-
7/13/93	0.53	0.63	0.26	3.06	1.2	0.16	1.8	0.46	0.69	2.04	-	-	-	-	-	-
7/21/93	-	-	-	-	-	-	-	-	-	-	0.57	-	-	-	-	-
8/21/93	0.88	0.71	-	2.99	-	-7.78	-0.01	0.28	0.19	1.32	-	7.04	7.1	9.29	3.64	-
10/1/93	-	-	-	2.39	-	-4.32	-0.52	0.36	0.09	0.41	-	2.74	3.03	4.26	2.12	2.58
11/7/93	0.6	0.62	-	2.21	-	-0.36	0.8	1.39	0.97	2.09	-	2.01	2.13	3.18	2.24	2.75
12/11/93	0.59	0.76	-	1.85	-	0.41	-0.15	0.4	0.22	1.01	-	0.94	1.01	2.27	3.56	5.15
2/22/94	0.32	0.26	-	1.26	-	0.85	-1.81	-0.01	-0.03	0.26	-	0.36	0.38	1.61	5.13	6.53
4/21/94	0.52	0.49	-	1.99	-	0.78	1.14	0.14	0.23	0.4	-	0.23	0.37	3.45	5.82	7.72
5/28/94	0.28	0.53	-	2.64	-	-	-	0.64	0.56	1.41	-	0.2	0.36	4.7	6.37	8.39

Notes:

* all values in g/square meter/day

** Positive numbers denote net evaporation; negative denote net condensation

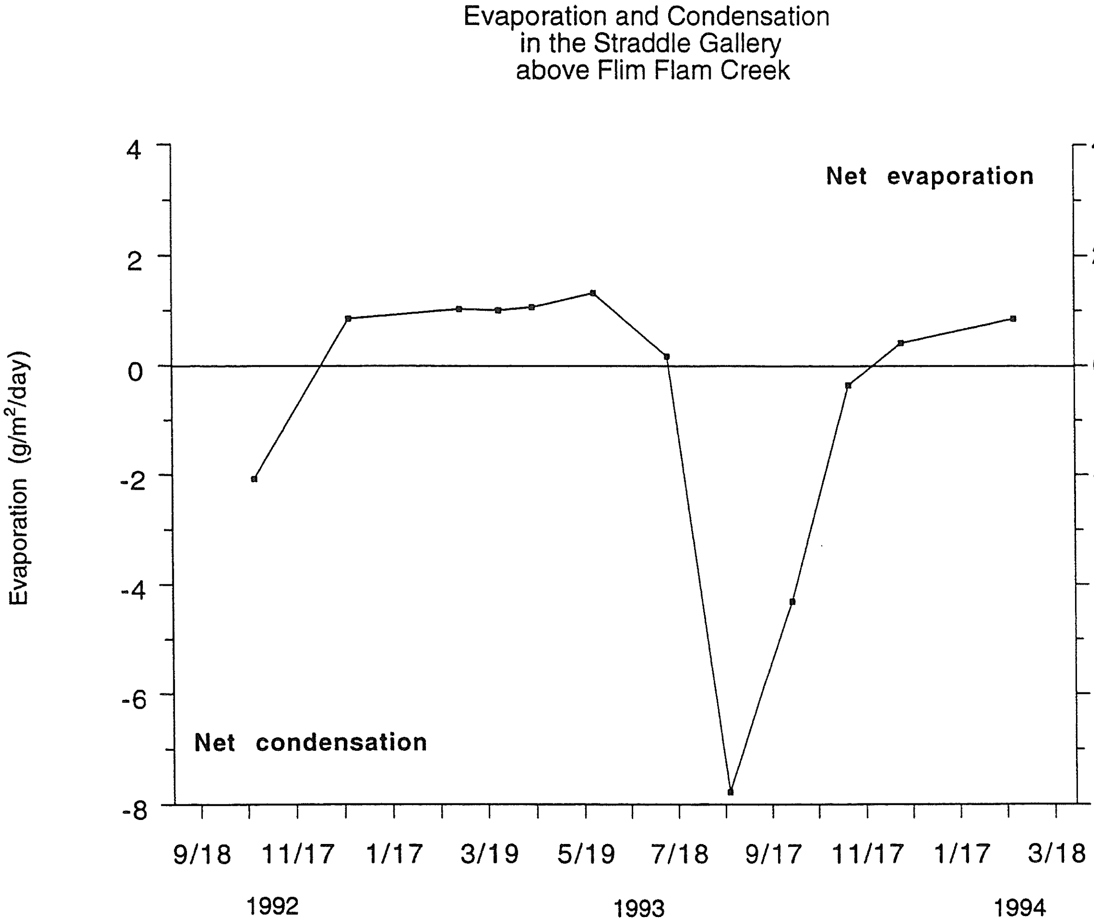


Figure 11.4. Evaporation and condensation in the Straddle Gallery above Flim Flam Creek in Mystery II.

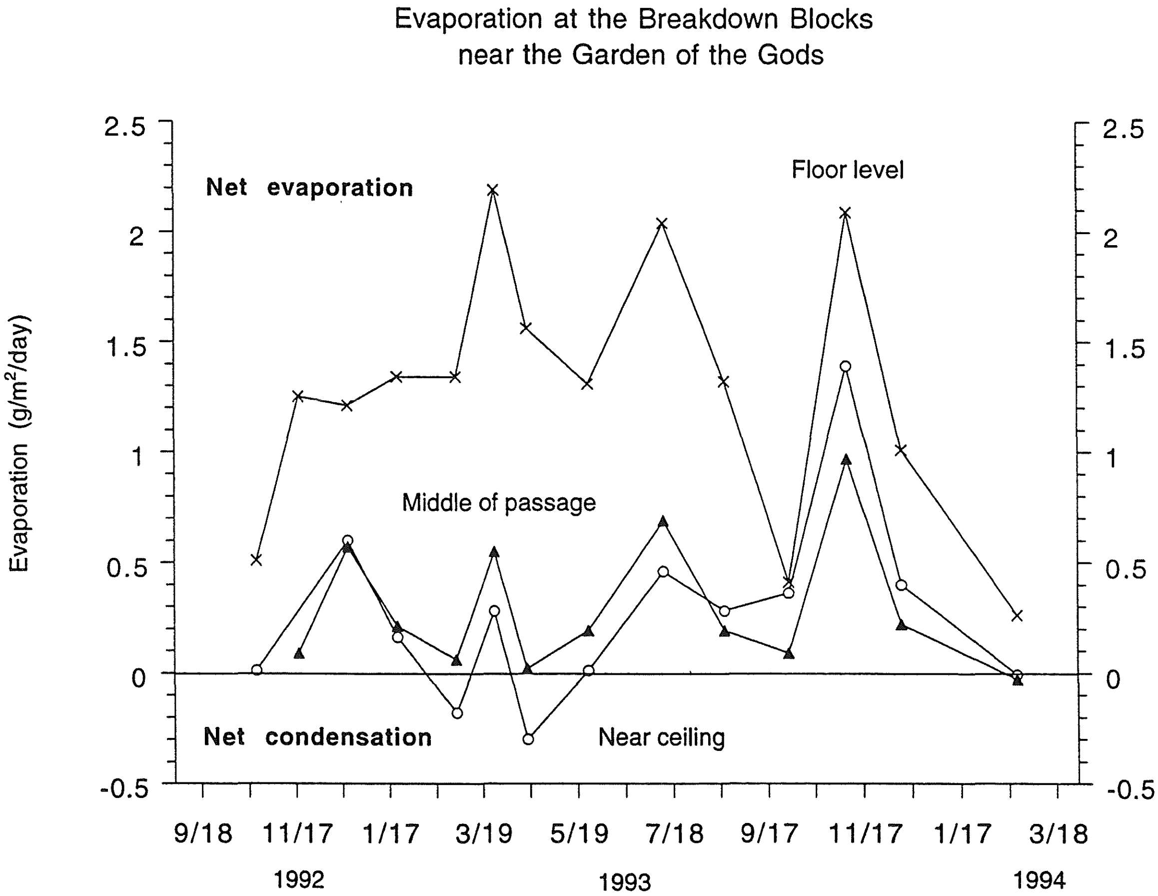


Figure 11.5. Evaporation at the Breakdown Stack near the Garden of the Gods in Mystery I.

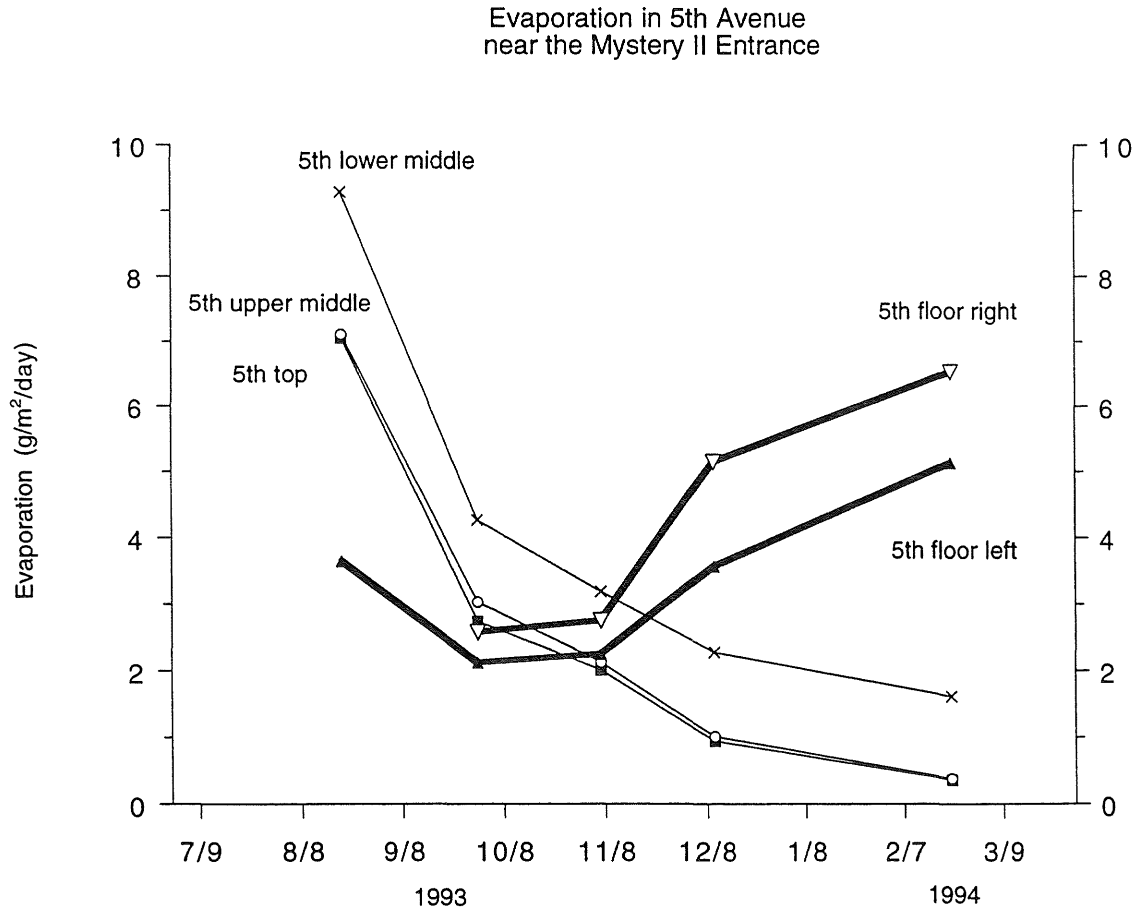


Figure 11.6. Evaporation in 5th Avenue near the Mystery II entrance.

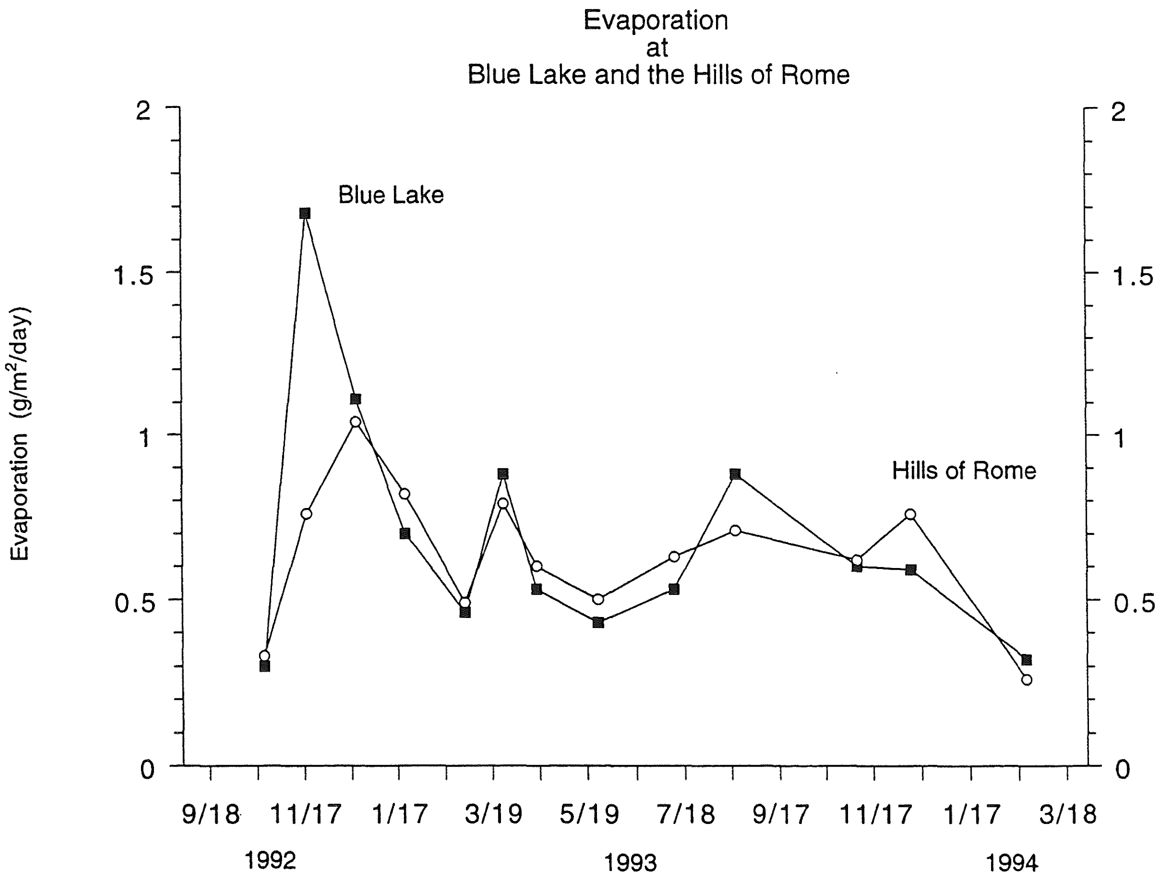


Figure 11.7. Evaporation at Blue Lake and the Hills of Rome in Mystery II.

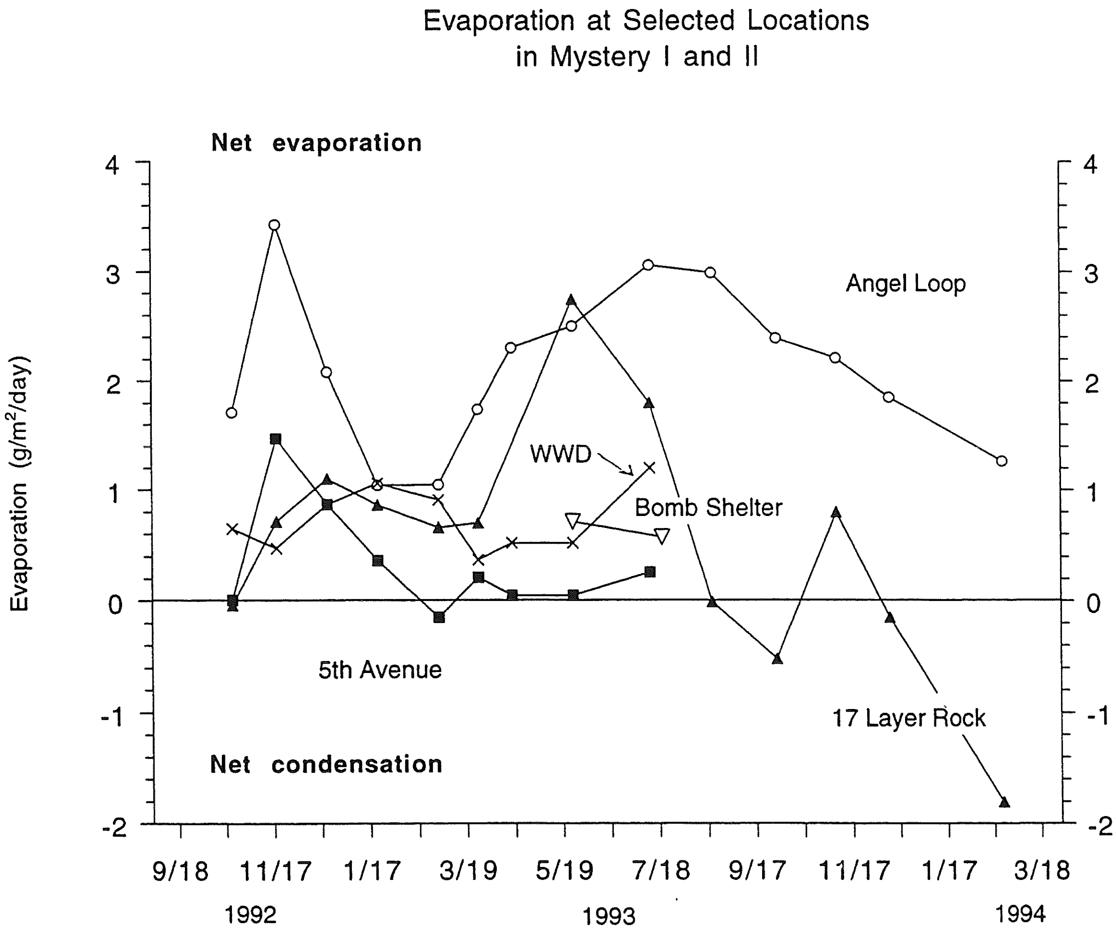


Figure 11.8. Evaporation at selected locations in Mystery I and II.

The site at 5th Avenue near the Mystery II entrance had three pans suspended on thin plywood sheets in the air and two on gravel on the floor. The top three pans may behave very differently from the others because air currents can flow beneath them and add or remove heat. Thermal equilibrium, if it occurs, will be with air alone rather than with solid cave surfaces and air. The interpretation of these sites must proceed with caution. It may not be reasonable to compare these sites with the other types of sites. However, data from these sites may yield useful information when internally compared (see below).

Considering all sites, condensation rates ranged from near zero to almost 8 $g/m^2/day$, as shown in Figures 11.4, 11.5, and 11.7.

Evaporation and Condensation near a Lower-Level Stream

Figure 11.4 shows evaporation and condensation in the Straddle Gallery above Flim Flam Creek. Net evaporation predominates during the late fall through early summer. During the fall, winter, and early spring, cave air is relatively cool near entrances and near lower-level cave streams such as Flim Flam Creek. Lower-level cave streams are cold (as low as 1.4°C at Flim Flam Creek). At many locations, including the Straddle Gallery, the cave is visibly drier in winter than it is in the late spring or in summer in terms of observable water fluxes (flowing or dripping water) and in terms of stationary thin films or drops of moisture visible on passage walls and ceilings.

Net condensation occurs in the summer to late fall. During the summer, warm waters from the Root River flow through the lower levels. At Flim Flam Creek and other locations (e.g., the Triangle Room at Formation Route Creek) some of the warm water (to over 20°C) vaporizes, contributing to increased air moisture. Passages near the streams become foggy and have elevated air temperatures. Condensation occurs onto relatively cold bedrock walls and ceilings or onto clastic sediments and speleothems. At Flim Flam Creek, condensation occured directly onto the inverted basket and the sides of the evaporation pan, as shown by thousands of tiny drops. At no time were the drops on the inside of the basket observed to coalesce to form larger drops, although coalescence occasionally was observed on the top of the basket. It is unlikely but possible that condensation rates were artificially elevated by drippage from the inside of the basket. The water on the top and outsides of the basket never appeared to come from dripping or seeping water. The top of the basket was less than 6 inches below the ceiling. Drops or dripping water were never seen on the bedrock above.

Zonation in Air Movement, Evaporation, and Condensation

Mystery Cave has a significant air circulation. Much of that circulation is driven by the passage of pressure fronts. The entrances lie at different elevations, so chimney effects also influence air movement. In the winter, warm cave air (relative to surface air) flows out the upper entrance and cooler air flows into the lower entrance. In the winter the flow is reversed. This simple picture is complicated further by the fact that air flow may be in reverse directions within the profile of a passage at entrances. For example, in winter, warmer air can be observed to flow out both entrances near the ceiling while cool air flows in near the floor.

Superposed on these flow patterns are others. Cave streams and waterfalls alter meteorological conditions and induce local patterns of air circulation. At some locations far from entrances, relatively warm air moves along ceilings and cooler air moves along floors, sometimes in opposite directions. At some sites this pattern of air flow may be persistent, altering only with the passage of major fronts.

The Breakdown Stack. At the Breakdown Stack near the Garden of the Gods, evaporation and condensation data suggest a distinct floor to ceiling zonation in meteorological conditions. In the zone of aragonite crusts at the floor, evaporation rates have been consistently higher (by about 0.5 to 1 g/m^2/day; see Figure 11.5) than those in the middle of the passage or nearer the ceiling, where condensation has occasionally been measured.

These results could reflect a zonation in the moisture content of the air combined with a zonation in wind speed from floor to ceiling. (The upper part of the passage is somewhat isolated, almost a dead end at the Breakdown Stack.) The meteorological conditions probably are the primary control on the moisture present at the surface of the bedrock. No evidence has been found for the influx of seeping water from the bedrock ceiling or upper walls at the times of monthly changing of the pans. Moisture appeared as drops and films that were widely distributed and not concentrated along fractures. However, water moving toward the cave passage from within the bedrock undoubtedly has a greater flux out of the ceiling and upper walls than from lower walls and from the floor.

5th Avenue Site. The picture at the site in 5th Avenue (Figure 11.6) is somewhat more complicated. The site is on the side of 5th Avenue, at the mouth of a major side joint developed as a keyhole passage. The lower fissure of the keyhole passage is filled with silt, which should limit air circulation into it. The upper tubular hole is open, and the passage continues, so air can flow into it. All five pans are in positions that allow free air circulation through the basket sides; none are up against a real dead-end position that would prevent air circulation. During the winter, this area is noticeably cooler than areas farther from the Mystery II entrance. Cool air moves from the entrance down the entrance passage and spreads out in 5th Avenue in the lower part of the passage. Air temperature in the upper part of the passage usually felt slightly warmer than at the floor, though this was not confirmed by measurements of temperature.

There is a distinct zonation in moisture on bedrock at this site in the late spring and summer. Condensation forms in the upper part of the passage and has been observed to extend down to within a foot of the top of the aragonite zone. When an aluminum ladder is left in place adjacent to the wood stand, condensation drops form on the top of the ladder. The lowest visible drops on the ladder are above the aragonite line.

Even in the winter, the driest part of the year in the cave, there is abundant but scattered moisture on the ceiling at the 5th Avenue site. That moisture is not condensation moisture: it is not uniformly distributed, and extends as seepage from joints, spreading outward on the flat, beddding-determined ceiling. In the winter, the lower parts of the passage (both walls and floor) are very dry.

The evaporation rates at the 5th Avenue site (Figure 11.6) were anomalously high for most of the pans for most of the time. For the period ending in late August, 1993, evaporation rates ranged 3.5 to 9.2 g/m^2/day. By late September, evaporation rates had fallen to more modest levels (2-4 g/m^2/day). They continued to fall during the winter for pans suspended in the air (to < 2g/m^2/day), but rose significantly through the winter for pans on the floor (to > 6 g/m^2/day).

Pans that were suspended in air had evaporation rates much higher than those on the floor during the period ending in mid August of 1993. This is a period in which condensation might normally be expected near the ceiling, but the summer of 1993 was wet and relatively cool. Condensation was not noted for this time period on the pans, but condensation was noted on nails set in the wood support structure.

For the pans suspended in the air, evaporation was lowest in the higher pans. Very little difference in evaporation was measured between the higher pans. The lower of the pans, which is within the zone of observed condensation and above the aragonite line, had the highest evaporation rate at the August and at later samplings. This result makes sense within the context of the observed moisture and the postulated air flow patterns, even if the relatively high evaporation rates (compared to other sites in Mystery Cave) remain unexplained. Perhaps air flow along the ceiling and upper walls was anomalously rapid during the period from June through September. It is also possible that air flow into or out of the side passage is high in the summer and is progressively lower in the fall and winter, leading to the observed drop in evaporation rates.

More problematic yet is the record for the two pans on the floor. These pans are adjacent to one another but are beneath a single large inverted basket. At all other sites, pans are beneath smaller inverted baskets. These pans were placed beneath a single basket in an attempt to check the replicability of the mass-based sampling technique. It was reasoned that adjacent pans would have evaporation rates that were identical, and that differences would reflect errors in the sampling technique. For all four time periods in which data can be compared, there was a significant difference in the evaporation rate between the left (east) and the right (west) pans. The difference is greater than can be explained by errors in pouring water into and out of the pans, or in the use of paper towels to dry the pans. It is notable that the right pan always had a greater evaporation rate than the left pan. This observation suggests that air flow was from right (west) to left, and that moisture removed from the right pan was sufficient to partly satisfy the moisture deficit of the air before it arrived at the left pan. If this interpretation is correct, then there must be a consistent air flow in that direction at the floor level.

Evaporation near Blue Lake and the Hills of Rome

Figure 11.7 shows evaporation at the Blue Lake site and the base of the Hills of Rome. The pan near Blue Lake is actually in the 4th Avenue passage, about 50 ft from Blue Lake toward the Hills of Rome. It is on a ledge on the south side of the passage, just past the west end of the flowstone mound above Blue Lake Drips. It is not near Blue Lake. Most of the time, the air circulation is from the Hills of Rome toward Blue Lake and on to Diamond Caverns, so Blue Lake should exert minimal influence on evaporation at the pan. We did not know this when the pan was installed; we originally expected evaporation rates to be lower at this site than at the Hills of Rome site.

The other pan is near the base of the Hills of Rome, two feet from the north wall. The pan was placed near the north wall because that was a convenient location away from the commercial trail. The south wall is dry and has gypsum crusts, so we expected relatively high evaporation rates. That expectation was not realized. It turned out that the north wall is consistently moist. It has descending films that drip and evaporate only a few feet from the pan.

Evaporation rates at Blue Lake and the Hills of Rome turned out to be remarkably similar, ranging from 0.5 to 1.7 $g/m^2/day$.

Evaporation at Other Sites

Figure 11.8 shows the remainder of the evaporation rates. The Angel Loop, a very dry section of cave, consistently had high rates of net evaporation. The site at 5th Avenue west showed low net evaporation rates most of the time. The Wishing Well Drips site always exhibited net evaporation. From the name, that site might be expected to have even lower rates of evaporation, being near falling water. However, the site is actually over 150 farther along the passage toward Enigma Pit, because there was no level site near Wishing Well Drips that was isolated from dripping water that could splash through the sides of the inverted basket and invalidate results.

CHAPTER 12

SUMMARY AND CONCLUSIONS

INTRODUCTION

This chapter is a summary of the hydrogeology and hydrochemistry of Mystery Cave. Recommendations for further research, mostly of an applied nature, are included. Additional recommendations of an applied nature are in a separate Management Report. A separate Interpretative Report summarizes major findings in a non-technical fashion. The Interpretative Report also answers questions submitted by tour guides and other Department of Natural Resources staff, based in part on questions posed by the public.

STATUS OF MYSTERY CAVE

Mystery Cave is in Fillmore County of southeast Minnesota. The cave is owned by the State of Minnesota. It is operated commercially by the Minnesota Department of Natural Resources, roughly from late May to early September in recent years. The cave is about 14 miles long and has two entrances known as the Mystery I and Mystery II entrances. Tours are operated from both entrances in cave sections known as Mystery I and II. This terminology is based on a long history of discovery, exploration, and mapping by members of the Minesota Speleological Survey. An additional section of cave, Mystery III, is accessed from within Mystery II.

SIGNIFICANCE

Mystery Cave is a world-class network maze. A network maze consists of an angular network of passages in a maze-like configuration (Palmer, 1991). Maze caves form by roughly simultaneous growth of a large number of fractures (usually vertical joints) to dimensions large enough to admit exploration by humans.

Mystery Cave contains a significant geomorphic, hydrologic, and sedimentologic record that deserves continued scientific investigation. Briefly, the record contains information about (1) cave development, (2) past climates, and (3) the hydrogeological and glacial histories of Minnesota (Milske et al, 1983; Lively, 1983; Palmer and Palmer, 1993a). Much of the geomorphic and hydrologic record is contained within the details of passage morphology and elevation. Much of the climatic and glacial record is preserved in clastic sediments (silts and gravels) and speleothems (flowstone and stalagmites).

SCOPE OF STUDY

This study had five primary objectives. We attempted to:

(1) Inventory water chemistry and water quality throughout the cave,
(2) Identify the sources and sinks of selected cave waters,
(3) Measure the response of cave waters to recharge and other events,
(4) Measure the response of cave waters to human activities, and to
(5) Identify seasonal hydrologic and chemical trends.

To accomplish these objectives, we:

(1) Surveyed water chemistry and water quality (field parameters, major cations and anions, zinc, fecal coliform bacteria, atrazine, and volatile organic compounds) at 48 sites, including cave, well, spring, and surface waters;
(2) Sampled 11 cave water sites (pools, streams, waterfalls, flowstone flows, stalactite drips) on a periodic basis for selected water quality parameters;
(3) Measured precipitation and air temperature at a weather station on the South Branch of the Root River, for comparison with stage of a cave pool (Blue Lake) and a stream (Flim Flam Creek), and for comparison with drip rates at Blue Lake Drips and Coon Lake Drips;
(4) Measured stage of the Root River near the weather station;
(5) Measured stage, water and air temperature, and conductivity at Flim Flam Creek and Blue Lake on a continuous basis for varying periods from March, 1992, through May, 1993; and
(6) Measured evaporation and condensation rates at selected sites.

CONTEXT OF THE RESULTS

This study provides a broader conceptual framework for the interpretation of the hydrology of Mystery Cave than was previously available. Insofar as they discussed the hydrology, Milske et al. (1983) and Mohring and Alexander (1986) were concerned primarily with flow in the lower levels of Mystery Cave as revealed by dye tracing. We summmarize that and more recent unpublished work and expand upon it to include inferences about the hydrology of the porous-media aquifer present in loess over much of the cave. That aquifer regulates recharge to many areas of Mystery Cave. We also discuss other aspects of flow within the cave's upper levels.

Previous hydrochemical work by Grow (1986) was primarily on nearby surface streams and springs. An initial sampling of a few cave waters in Mystery I and II was made by Sethi (unpublished data, 1990) as part of an Undergraduate Research Opportunities project at the University of Minnesota. We therefore provide the first integrated account of the chemistry of Mystery Cave. That account includes an initial analysis of the environmental chemistry and the carbonate chemistry. The data set consists of analyses on over 400 samples (combined) of such parameters as water temperature, pH, conductivity, major and minor ions, zinc, triazine pesticides, alachlor, fecal coliform bacteria, and selected volatile organic compounds. The data set is rich and will occupy us for years to come, in addition to supplying a base line against which to compare future changes in the chemistry. We expect---or at least hope for---changes in that chemistry for the better as ongoing water-quality improvement programs take effect and new ones are instituted.

HYDROGEOLOGIC SETTING

Mystery Cave is in a mantled fluviokarst. Karst is a terrane whose surface and subsurface geomorphology and hydrology are a product of dissolutional processes that dissolve soluble rock (limestone and dolomite) and create such features as sinkholes, caves, sinking streams, and springs. A fluviokarst is a terrane produced by a combination of karstic and fluvial processes. A mantled karst has an extensive covering of unconsolidated deposits. At Mystery Cave, the mantle is primarily the Peoria loess, an aeolian deposit derived from late Wisconsinian glacial deposits of the Des Moines Lobe (Mason et al., 1984). The Peoria loess has a significant component of calcareous material, mostly dolomite. The loess varies in thickness and apparently has a scattered distribution. On the upland above the cave, its thickness may be as great as 25 ft. On hillslopes it may thin to less than three feet or be absent.

Nearly all of Mystery Cave is developed in the Dubuque Formation and the underlying Stewartville Formation. The Dubuque consists of interbedded limestone and shale in thin beds. The Stewartville consists of massively bedded dolomite. A few upper level passages extend above the Dubuque into the Maquoketa Formation (mostly limesone and dolostone). All three units are of Ordovician age.

Mystery Cave lies beneath an upland adjacent to the South Branch of the Root River. The upland is gently rolling. Land use is principally agricultural, consisting of row crops in corn and soybean rotations. A smaller amount of the land is planted in alfalfa or used as pasture land. Hillslopes leading down to the Root River are mostly forested.

The cave functions as a subterranean meander cutoff for the Root River. Water sinks within the streambed over a several mile reach of the river and reappears at one or more of three spring clusters: Seven Springs, Saxifrage Springs, and Crayfish Springs. The upstream sinkpoints are near the Mystery I entrance. At times of high flow, the river exceeds the capacity of the riverbed to accept water and flow is continuous to the springs. At some unknown lower discharge, there is a downstream terminal sinkpoint. As discharge falls below this threshold value (which may vary) the terminal sinkpoint migrates upstream and much of the riverbed is left dry. During especially dry periods, the terminal sinkpoint is a few hundred feet downstream of the new bridge over the Root River (the access bridge to the parking lot at Mystery I).

Mystery Cave can be thought of as a natural underground laboratory beneath the upland. It allows direct access for the sampling of waters that pass through soil, loess, a subcutaneous zone, and the fractured bedrock above the cave. The subcutaneous zone is a zone of irregularly dissolved bedrock at the soil/bedrock contact; its extent and character are largely unknown due to lack of surface exposures.

Infiltration water tends to move vertically downward under the influence of gravity through the soil and loess (except on hillslopes and sides of sinkholes, where some lateral interflow may occur). In the soil and upper loess, the water moves as a classical porous-media flow, except where flow follows dessication cracks, gopher burrows, or other macropores. The water apparently collects in small basins at the top of the subcutaneous zone. In the absence of large open fractures and conduits in the upper bedrock, water is thus ponded in the subcutaneous zone and lower loess, forming a perched aquifer. Major recharge events raise the head within this aquifer, providing a driving force sufficient to eject stored water within it and in fractured bedrock beneath it but above the cave. That ejected water moves into the upper levels of Mystery Cave, appearing as seeps, drips, waterfalls, or vadose flows out of joints, bed partings, or fissures enlarged from joints. The ejected water tends to have a high solute concentration, because it has been stored for periods ranging from weeks to months and has had time to approach equilibrium with respect to calcite, aragonite, and dolomite.

On hillslopes near the Root River, particularly near the Mystery I and II entrances where soils and loess are thin or absent, some waters rapidly infiltrate and move into the cave on a time scale of minutes to hours. These waters tend to have lower solute concentrations. They may carry a temperature signal derived from the temperature of the recharge water. Often, the water is turbid when it arrives in the cave. Rapidly-infiltrating waters may mix with stored waters, producing mixtures with intermediate chemical compositions that may lack a clearly distinguishable temperature signal.

Waters that infiltrate into the bed of the Root River rapidly pass through sediment-filled fractures and appear as streams in the lower levels of the cave. The water carries strong temperature and chemical signals from the surface. As discharge rises on the Root River, water level in the lower-level streams can rise rapidly at an even faster rate than the river rises, because water sinks through many fractures that converge in a downflow direction within the cave. In the absence of an increase in passage size in a downstream direction, the inevitable result is flooding of the lower levels when some unknown threshold stage is reached on the Root River. The flooding can be extensive, even high enough to reach the upper level passages in commercial sections of Mystery I, as occurred several times in 1993.

WATER TYPES

The waters of Mystery Cave appear as streams, pools within streams, isolated pools, artificial pools, stalactite drips, flowstone flows and seeps, and waterfalls and ceiling drips. Thin films and drops of condensed water are also present, especially during the summer near lower-level streams.

Most isolated pools are small and fed by low-discharge sources such as stalactite drips and flowstone flows. Isolated pools are not fed by, nor are they drained by normal cave streams. Their water generally seeps into clastic sediments or evaporates.

A few pools, such as the pool below Wishing Wells Drips, are entirely artificial. Two major pools, Turquoise Lake and Blue Lake, are artificial in their present configuration, but exhibit speleothems indicative of long-term ponding. These pools have long been active, but their form has been modified for the sake of accessibility for tours. One pool, Frozen Falls Pool, was buried during an earlier phase of commercialization.

CARBONATE CHEMISTRY AND ITS INFLUENCE ON CAVE FEATURES

The waters of Mystery Cave are predominantly calcium-magnesium-bicarbonate waters, with varying amounts of nitrate, chloride, and sulphate. The carbonate chemistry is typical of karst regions with mixed dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) bedrock. For waters in contact with dolomite and calcite at saturation, the expected molar ratio of Mg to Ca is about 0.8. This ratio was observed for the waters of Mystery Cave. However, absolute concentrations of calcium, magnesium, and bicarbonate are relatively high. They are higher than would be expected from dissolution of bedrock alone under atmospheric concentrations of carbon dioxide. Much of the carbonate chemistry is determined above the bedrock, in the soil zone and the loess. The amount of carbon dioxide in the soil and upper loess apparently increases during the summer growing season, tapers off during the fall, and should be lower in the winter (unless microbial activity beneath the frozen surface continues and carbon dioxide is trapped beneath that surface). Water that passes through the soil and loess picks up carbon dioxide en route to the subcutaneous zone. The water often has a relatively long residence time in the loess and subcutaneous zone---weeks to months---so there is ample time for the water to dissolve calcite and dolomite before the bulk of the carbonate bedrock is encountered.

Most of the waters sampled in Mystery Cave were saturated or supersaturated with respect to calcite, aragonite, and dolomite. Such waters are incapable of dissolving bedrock without undergoing additional processes that renew their capacity for dissolution. Mystery Cave has probably had a preponderance of saturated waters in its upper levels for a very long time. This is evident from the lack of vertical dissolutional features (such as vertical shafts and flutes) that are so characteristic of caves with vertically descending undersaturated waters.

The supersaturated waters are responsible for the ongoing deposition of speleothems in many areas of the cave. An indication of the rapidity with which supersaturated waters can deposit speleothems is visible along the left (north) side of the commercial trail of Mystery I, near the flowstone ledges with calcite rafts, before Turquoise Lake. At floor level, white deposits of calcite (up to 1/2 in thick) already cover part of the cement walkway installed during 1992.

Seasonal signals in the calcium and magnesium concentrations were noted for a number of waters periodically sampled for ions in Mystery Cave. These signals are readily detected by measurements of conductivity. So are signals resulting from dilution events, in which ion concentrations decline. So also are flushing events, in which stored waters with high solute concentrations (or stored contaminants) are expelled from the soil or loess. Conductivity is therefore a useful parameter with which to monitor the bulk chemistry of the water and can be combined with digital measurements of drip rates, discharge, stage, and water temperature.

Continuous monitoring of conductivity at Blue Lake, Coon Lake Drips, and Flim Flam Creek has been instrumental in deciphering the above and other details of the hydrology and chemistry of Mystery Cave. We have learned much from these sites, and expect to learn more in the future.

ENVIRONMENTAL CHEMISTRY

The waters of Mystery Cave have a variable anthropogenic component. This component includes NO_3-N and Cl, pesticides, and fecal coliform bacteria. Some of this comes from local agricultural uses on lands immediately adjacent to or directly over the cave. Much of the anthropogenic component comes primarily from more regional sources and is transmitted into Mystery Cave via the Root River.

NO_3-N and Cl

Sources of NO_3-N include fertilizers, animal and human wastes (abandoned outhouses, septic systems, feedlots, manure spreading), nitrogen fixation by plants, and atmospheric deposition. Sources of Cl include fertilizers (e.g. fertilizer with KCl components), road salt, septic systems, and atmospheric deposition.

Much of the NO_3-N observed in Mystery Cave undoubtedly derives from anthropogenic sources. It is difficult to distinguish between anthropogenic and natural sources of NO_3-N, although promising efforts have been made in recent years through the study of nitrogen isotopes. We did not perform any nitrogen isotope analyses in this study, but any future study should consider doing so.

Data collected during this study suggest that three populations of NO_3- N concentrations are present in Mystery Cave waters. One group (79 of 261 analyses) consisted of waters with NO_3-N less than 1 mg/l. A second group (80 analyses) consisted of waters with NO_3-N between 1 and 3 mg/l; 42 of those analyses were between 1 and 2 mg/l, and 38 were between 2 and 3 mg/l. The third group (102 analyses) consisted of waters with NO3-N between 3 and 13 mg/l.

Most of the waters with higher NO3-N are stream waters. The lower level streams in particular had high NO_3-N concentrations, as would be expected for cave waters derived from the South Branch of the Root River. Sites with concentrations that approached or exceeded the EPA drinking water limit of 10 mg/l NO_3-N include Turquoise Lake, Frozen Falls Drips, and Frozen Falls Pool in Mystery I; Flim Flam Creek in Mystery II; and Formation Route Creek in Mystery III.

Turquoise Lake showed a consistent, slowly rising trend in NO_3-N from 8.7 to about 12 mg/l during the 1991-1993 study. At a sampling in May, 1994, NO_3-N measured 10.9 mg/l. We suspect that Turquoise Lake derives a significant component of its recharge from agricultural lands, because its Cl concentration is also high, typically greater than 30 mg/l.

Data collected during this study suggest that two populations of Cl are present in Mystery Cave waters. One group (156 of 261 analyses) consisted of waters with Cl less than 5 mg/l. The other group (105 analyses) consisted of waters with Cl between 5 and about 43 mg/l.

Many of the waters with high Cl concentrations were from lower level streams. However, some sites that one might expect to have low Cl concentrations occasionally had high Cl concentrations. The most significant example is provided by the stalactite drips known as Garden of the Gods 1 (GG1) in Mystery II. This site is beneath a hillslope with brush, grass, and a field planted in corn. Following major recharge events, the Cl and Ca concentrations were observed to rise sharply at GG1. We believe that KCl-bearing fertilizer is responsible for the observed changes in water chemistry. Recharge transports KCl into the soil and loess, where K is exchanged for Ca and Mg. Ca and Mg are then transported along with the highly mobile conservative species Cl, which has little affinity for soil or loess. It is worth noting that this ion exchange process introduces a further complication into the carbonate chemistry previously discussed: not all of the observed calcium in the waters of Mystery Cave presently is directly derived from the natural processes of carbonate dissolution chemistry.

The observed changes in water chemistry at GG1 provide the best documented evidence for direct contamination of Mystery Cave waters by practices on adjacent agricultural lands. We recommend that this and adjacent drip sites at the Garden of the Gods be further studied to confirm our findings, and to check for additional degradations of water quality, such as might be expected from the application of pesticides. Such studies might monitor conductivity, water temperature, and drip rates, and also include periodic sampling for anions, cations, pesticides, and fecal coliform bacteria.

Pesticides

Atrazine is widely used as a selective herbicide for weed control in corn. The maximum contaminant level (MCL) set by the EPA for drinking water is 3 ppb. Atrazine was below the MCL for all samplings, which included 45 samples collected in the winter, summer, and spring seasons. Atrazine values ranged from below the 0.1 ppb detection limit (17 samples) to 0.8 ppb. The highest concentrations (0.5-0.8 ppb) were in the lower-level streams (Flim Flam Creek, Formation Route Creek, the Lower Level Stream) and in the South Branch of the Root River. Turquoise Lake had relatively high concentrations (0.4-0.5 ppb) all three times it was sampled, supporting a source area on agricultural lands.

Fecal Coliform Bacteria

Potential sources of fecal coliform bacteria include abandoned outhouses, septic systems, feed lots, and manure spreading. Recommended limits of fecal coliform bacteria in drinking water are zero colonies per 100 ml. Results are reported as present, not present, too numerous to count, or inconclusive. For some samples, serial dilutions were performed and so results reported as present were further quantified.

Fecal coliform bacteria were sampled in winter and summer at 19 sites, including the South Branch of the Root River. Bacteria were not present in 16 of 28 samples, were present in seven samples and were too numerous to count in four samples. One test in the winter was inconclusive.

The highest bacterial counts were in the Root River. In the cave, high counts were obtained for Flim Flam Creek and Formation Route Creek. As previously noted, both of these cave streams are fed by the Root River, so high bacterial concentrations are expected. The high counts at Formation Route Creek were obtained during the winter, the only time it was sampled. The high winter counts suggest the possibility that fall and winter spreading of manure in fields contributes significantly to bacterial concentrations in surface runoff, which then reaches the cave. Further work is recommended on this topic.

Turquoise Lake was sampled twice; results indicated fecal coliform bacteria were present (1 colony) during the winter sampling, and not present during the summer sampling. Garden of the Gods 1 was sampled twice, in both winter and summer, and bacteria were not present. We recommend additional sampling for fecal coliform bacteria at these sites.

Zinc from Galvanized Steel Bridges

Low but elevated concentrations of zinc in Frozen Falls Pool, which is directly below a major bridge, are up to eight times the background values measured in Frozen Falls Drips and other sources feeding the pool. Some leaching of zinc from the galvanized steel bridges and railings is indicated. We recommend that zinc be monitored on an infrequent but periodic basis at any sites where zinc concentrations might build up and significantly impact water quality. Such sites might include isolated pools below or adjacent to bridges and railings. Because some isolated pools occasionally harbor springtails, zinc concentrations may be of biological significance. We also recommend that periodic inspections be made of the bridges and railings to check the integrity of the zinc coatings.

No sediment samples or biological materials were checked for zinc during this study. Zinc can be adsorbed on sediment, accumulate, and then be released at later times. Zinc can also build up to detrimental concentrations in organisms. We recommend that the zinc sampling be extended to include sediments and biological materials.

Volatile Organic Compounds

A single sampling in May, 1993 at five sites failed to detect volatile or semi-volatile organic compounds (VOC's) from the MNDH Method 465C list. The sites were Turquoise Lake, Blue Lake, Flim Flam Creek, the South Branch of the Root River at Mystery I, and Coon Lake Drips.

Although no VOC's were detected at Blue Lake, a strong creosote-like odor emanating from Blue Lake suggests that semi-volatile and volatile organic compounds are being leached from two creosote-impregnated wood poles at times of high water level. The poles are supports for a bridge across Blue Lake. The odor is objectionable to some people and can be considered a degradation of the cave experience. The odor is not confined to the immediate area of Blue Lake, because (1) air flow caries the odor east at least as far as Diamond Caverns, and possibly as far as the ramp at 5th Avenue. Also (2), at very high water levels in Blue Lake, water from Blue Lake seeps through the breakdown retaining wall at the east end of the lake and re-appears 60 ft farther east as Blue Lake springs. The springs are in the graveled trail. The water flows downslope along the trail into a ditch on the north side of the passage, losing over 3 ft of elevation in more than 50 ft of horizontal distance. The stream, which can have a discharge as high as 7 liters/min, is in a turbulent flow regime, allowing rapid degassing of volatile organic compounds.

We recommend that the impregnated wood pilings be replaced. This will require significant reconfiguration of the bridge, but may entail little modification to the support systems at the ends of the bridge. If possible, the replacement bridge should not use pilings. If such a bridge is not feasible for engineering, economic, or management reasons, we recommend that replacement pilings should be chosen that are compatible with the hydrogeochemistry of Blue Lake and that do not produce potentially objectionable odors.

HYDROGEOLOGY OF SELECTED SITES

Blue Lake

Blue Lake is in Mystery II. In its present configuration, it is an artificial lake. However, Blue Lake has a long history as a natural lake, as shown by speleothem wall linings in its tributary passage and the large raft cones within the lake. Raft cones are conical accumulations of calcite rafts. Rafts are thin, cornflake-like deposits that form at the surface of pools, usually as supersaturated water degasses carbon dioxide. The rafts float on the water's surface under surface tension but can sink and accumulate in a single location below drip points. Also, fluctuating water levels can allow floating rafts to accumulate and attach on the sides of raft cones.

Blue Lake periodically fills with water as a result of major recharge events. Water level can rise from about 14 ft below the top of the bridge railing (datum) to about -3.7 ft in a period of a few weeks or less. Such events can be expected to occur mostly at the time of the spring melt off. The water that first arrives is water displaced from pools upstream of Blue Lake, combined with water flushed from the overlying fractured bedrock, the subcutaneous zone, and the loess and soil. The water carries a minor temperature signal, in which water temperature drops about 0.2-0.5°C from an initial water temperature of about 8.65°C. The water also carries a conductivity signal, in which conductivity rises, indicating the flushing of stored waters with solute concentations higher than those already present at Blue Lake. As the stage rises, conductivity rises to a peak, then falls only slightly with minor fluctuations as stage fluctuates from about -5 to -3.5 ft. The water temperature remains nearly constant, however. The behaviour of conductivity and water temperature during high stages suggest that the water feeding Blue Lake is a mixture of a small amount of event water and much more stored water displaced from the soil, loess, and fractured bedrock. We have yet to see temperature, conductivity, or solute signals indicating a predominant rapid recharge component to Blue Lake. However, we have data for only a few years that include a partial fill event in November, 1992, a full fill event in late March and April of 1993, and a sequence of 4 partial fill events that totally filled Blue lake in February and March of 1994.

Although we have only four years of personal observations, and three years of continuous data, we have seen enough to suspect that in a typical year, water level probably remains high at Blue Lake through at least a month of the late winter or early spring, then falls as its intermittent tributary dries up. Water level probably falls as a smooth exponential curve through a normal or dry summer, declining to about -14 to -14.5 ft by November. As the water level falls below about -12 to -13 ft, Blue Lake begins to break up into isolated pools. At the lowest stage, there may be five or more irregularly-shaped pools in the region where there was only one pool at high stage. During the decline in stage during this study, calcite rafts were occasionally noted floating in pools. Some evidence exists for the idea that calcite rafts can form rapidly at very low stage, because we have seen consistent drops in conductivity concurrent with measured drops in concentrations of calcium, magnesium, and bicarbonate at those times. In any case, those consistent drops in conductivity and concentrations argue for deposition of speleothems.

Coon Lake Drips

Coon Lake Drips (CLD) are in Mystery II, between the entrance and the Garden of the Gods. Water issues from a joint in the ceiling and flows down a flowstone-covered wall to a drip site about 4 ft above the floor. Some of the water drips out of a few small stalactites set in the flowstone. Drip rates range from about 0.25 to almost 14 l/hr.

The CLD drip point is about 60 ft below the surface. The soil and loess cover may be as thick as 20-30 ft above CLD. Water infiltrates through the soil and loess, and probably also runs directly through gopher holes and macropores on the hillside. Water is stored within the overburden, perhaps in sufficient quantity at the loess/bedrock contact to maintain a perennial perched water table. This water would mostly be in the loess, but if the loess/bedrock interface is irregular beneath the hillslope, as is possible, some of the water might also be in adjacent fractured bedrock. There probably is a lateral component of flow within this perched water body to a central drain that feeds fractures that lead to the CLD drip site.

Major precipitation events produce a rapid response at CLD if antecedent soil moisture is sufficiently high. The drip rate may begin to rise within 15 minutes of the onset of heavy rain. The water probably moves rapidly down macropores and gopher burrows to the perched water table and induces a pressure pulse that rapidly ejects stored water from the bedrock fracture system.

In the winter, daily melt cycles can induce a cyclical response in drip rates at CLD. Lag times between peak air temperatures measured at the Root River Weather Station and peak drip rates at CLD were 7, 4.5, and 7.5 hours for 3 days in late March, 1993. Lag times between minimum air temperatures and minimum drip rates for the same events were 9.5, 7, and 6.5 hours.

The total flow path (through soil, loess, fractured bedrock) to the drip site is insufficiently open to allow rapid transmission of the water under the prevailing range of hydraulic gradients. (Imagine a glass tank of sand with a small drain at the bottom leading to a vertical plastic tube with a small internal diameter. You pour water in it and you see a rising water table in the tank because the water can't drain out fast enough.) The path has not been traced with dyes, so we do not have a direct measure of the flow through time for water molecules. Instead, we have to rely on recognizable natural tracers or signals to estimate flow through times. One such possible signal is the water temperature. However, the water temperature at CLD does not vary significantly (9.02-9.04°C in 1994) and does not correlate with the temperature of recharge water (snowmelt in winter, warm rain in summer, etc.). The conductivity also does not correlate well with recharge events, but exhibited in the summer and early fall of 1993 a broad peak that may reflect solute concentrations peaking in response to the growing season.

Flim Flam Creek

Flim Flam Creek is in Mystery II. It is about 100 ft past The Bar (near the Angel Loop), but is about 47 ft lower in a lower-level fissure in the Stewartville Formation. Flim Flam Creek obtains its primary flow from infiltration from the bed of the South Branch of the Rooot River. The straight-line distance from the postulated sinkpoints to Flim Flam Creek is about 2560 ft. From Flim Flam Creek, the water flows to Seven Springs, another 3740 ft in a straight line.

Water temperature and conductivity vary rapidly in response to changes in the temperature and composition of the river. Water temperature in the Root River varies at the time scale of seasons (about 1°C in January to 25°C in the summer), at the time scale of the passage of weather systems (<1°C to perhaps 5°C), and at the time scale of a day (diurnal cycles of <1°C to about 3°C, highest in the summer). Similar trends are seen at Flim Flam Creek, but heat is lost or gained along the flow path depending on the season. Thus there is a slight dampening (0.5-1.5°C) of the temperature signal. Conductivity also varies at the scale of seasons, the scale of weather systems, and at the scale of a day. In the summer, a weak diurnal conductivity signal (5-20 µS/cm at 25°C) tied to biologic activity can be seen on the Root River; it survives for distances at least as far as Flim Flam Creek in cave streams. Recharge events (either rainfall or snow melt) introduce signals (drops of conductivity as much as 300 µS/cm at 25°C) indicative of dilution of existing waters; the signals can last from hours to days on the river and at Flim Flam Creek. At the scale of seasons, conductivity on the Root River ranges from less than 150 µS/cm at 25°C to about 600 µS/cm at 25°C, and similar values are seen at Flim Flam Creek.

The chemistry of Flim Flam Creek is fundamentally the same as the chemistry of the South Branch of the Root River. It is strongly impacted by agricultural runoff. It contains a significant but highly variable loading of nitrate, chloride, sulfate, fecal coliform bacteria, and pesticides such as atrazine and alachlor. Other cave streams in the lower levels of Mystery that obtain their primary discharge from the Root River should exhibit similar chemistries, water temperatures, and conductivities. However, the precise values of the parameters will depend on the distance from the sinkpoints and the proportions of admixed tributary waters that come from the overlying passages in the Dubuque Formation, and above that, the soil, loess, and fractured-bedrock aquifer.

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APPENDIX 1

DESCRIPTION OF A TYPICAL SAMPLING TRIP

Field time was limited to two-day trips, unless equipment was being installed or calibrated. Preparation time for trips usually took about 5-6 hours. This included organizing equipment and sampling bottles, preparing field standards (e.g., pH buffers or KCl conductivity standards), and preparing bottles for the evaporation pan study.

Loading equipment and driving to the cave took 3.5-5.5 hours, depending on the amount of equipment and weather conditions.

On a typical trip, the first day allowed sufficient time at the cave to download data at the weather station, perform necessary equipment maintenance, and change batteries. Four water samples in Mystery I were collected at Turquoise Lake, Frozen Falls Drips, Frozen Falls Pool, and the Lower Level Stream. The evaporation pan bottles were also placed in 5th Avenue of Mystery II for overnight equilibration to cave temperature.

On the second day, data were downloaded at the three cave sites (Coon Lake Drips, Blue Lake, and Flim Flam Creek). Equipment was briefly checked to ensure plausible readings, and batteries were exchanged at the Coon Lake Drips site. Water samples were collected and field parameters (water temperature, conductivity, pH) were measured at 6-8 periodic sampling sites. The sites included Garden of the Gods 1, Coon Lake Drips, Blue Lake, Wishing Well Drips, Rimstone Creek, Flim Flam Creek, and Enigma Pit.

The evaporation pans were changed at 10-13 sites, as listed in Chapter 11. This process would have taken about 2 hours if performed separately from water sampling, but usually took less. To save time, evaporation pans were changed while waiting for other tasks to be completed. For example, the Blue Lake and Hills of Rome pans were changed while waiting for the pH reading to stabilize for the Blue Lake water sample.

By the time equipment was returned to the vehicle and unloading was completed back at the lab at the University of Minnesota, it was usually close to midnight of the second day. The next day, about four hours were spent performing alkalinity titrations, weighing evaporation pan bottles, and preparing samples for submission to the geochemical lab for analysis of anions and cations. On three-day trips, alkalinity was measured in the field on the second or third day.

APPENDIX 2

GROUNDWATER FIELD AND LABORATORY FIELD METHODS

Department of Geology and Geophysics
University of Minnesota

The following pages describe standard groundwater field and laboratory methods used in our lab at the Department of Geology and Geophysics at the University of Minnesota. As techniques improve or equipment changes, these methods and protocols are also modified. The version below was current as of September 17, 1992, a time near the middle of field work for the Groundwater portion of the LCMR Resource Evaluation. As noted in Chapter 2, modifications to standard field methods were made to accomodate the conditions underground in Mystery Cave. As written, the field methods below are intended for use in sampling Minnesota well waters.

Table of Parameters and Methods

Parameter	Method	Reference	Precision	Accuracy	Measurement Range
Temperature	mercury thermometer	ASTM 63C	0.1°C	±0.1°C	-8 to 32°C
pH	Ag/AgCl electrode		0.01 unit	0.01 unit	4 to 10
Conductance			10μmhos	±5%	10 to 10,000μmhos
Redox	Pt electrode		10 mV	±50 mV	-250 to 250 mV
Dissolved Oxygen	Winkler titration		0.01ppm	±2%	0.01 to 25.0ppm
Ca	ICP/MS	pending	0.01ppm	±2%	0.01 to 1,000ppm
Mg	ICP/MS	pending	0.01ppm	±2%	0.01 to 1,000ppm
Na	ICP/MS	pending	0.01ppm	±2%	0.01 to 1,000ppm
K	ICP/MS	pending	0.01ppm	±2%	0.01 to 1,000ppm
Al	ICP/MS	pending	0.001ppm	±2%	0.01 to 50ppm
Fe	ICP/MS	pending	0.01ppm	±2%	0.01 to 50ppm
Mn	ICP/MS	pending	0.001ppm	±2%	0.001 to 50ppm
Sr	ICP/MS	pending	0.001ppm	±2%	0.001 to 50ppm
Ba	ICP/MS	pending	0.001ppm	±2%	0.001 to 50ppm
Si	ICP/MS	pending	0.01ppm	±2%	0.01 to 50ppm
P	ICP/MS	pending	0.005ppm	±2%	0.005 to 10ppm
Alkalinity as $CaCO_3$	titration		0.5ppm	±2%	0.5 to 1,000ppm
Cl	IC	EPA 300.0	0.02ppm	±2%	0.02 to 2,000ppm
Br	IC	EPA 300.0	0.02ppm	±2%	0.02 to 100ppm
NO_2-N*	IC	EPA 300.0	0.02ppm	±2%	0.02 to 100ppm
NO_3-N	IC	EPA 300.0	0.01ppm	±2%	0.005 to 100ppm
PO4-P	IC	EPA 300.0	0.03ppm	±2%	0.03 to 50 ppm
SO_4	IC	EPA 300.0	0.02ppm	±2%	0.02 to 2,000ppm
F*	IC	EPA 300.0	0.05ppm	±2%	0.05 to 1ppm

Precision is reported as the limit of quantification defined as $LOQ = 10\sigma \pm 3\sigma$.
Accuracy is the larger of the percent error estimate and the LOQ.
The ICP/MS is under review by the EPA, approval pending.
* Nitrite and fluoride are subject to possible interfences.

Assuring quality is an ongoing process that requires constant updating. Quality implies that the reported data are both precise and accurate. Precision is assured and quantified by a process of replication. Repeated measurements allow calculation of an averages along with an estimate of the measurement errors. Replication only quantifies the reproducibility or precision of a measurement. Accuracy is a more difficult parameter to quantify since it assumes knowledge of a true or actual value. The primary accuracy quantification steps include 1) the careful preparation and maintenance of high quality calibration standards, 2) internal consistency checks and 3) participation in inter-laboratory round-robins and split sampling.

A fairly complete inorganic water chemistry is necessary to characterize waters that, at present, have been minimally impacted by pollution. Calcium, magnesium and bicarbonate alkalinity will dominate most of the waters found in Minnesota. As the major dissolved species they contain important information about the waters path through the soil zone and into the aquifer. The minor ions, while most are not considered contaminants, are often indicators of human activity. Chloride and nitrate are often indicators of septic system contamination. Nitrate and phosphorous can indicate leaching of fertilizers. Iron and manganese are good indicators of Eh potential which is an important control on the mobility of many heavy metals. The inexpensive inorganic chemistry can then be used as a guide for the much more expensive contaminant testing.

Controls on quality are primarily based on a principal of redundancy. The idea is to check reported values against one another in as many ways as is physically and financially possible. Commonly employed controls include duplicate samples, blanks, spiked samples, control standards and split samples between independent laboratories and techniques. Checks on the internal consistency of the data are also an essential control.

Duplicate and blank samples will be used as controls. About one in ten samples will be collected in duplicate. The measured values should fall within the 3σ error estimates of each other. Problems with duplicates that do not agree with one another will be tracked down via the following procedure. First the remaining sample will be re-run to help isolate any analytical problems. The preparation of new standards may be required. If a discrepancy remains the sample should be recollected and tested as soon as possible. Remaining problems should be resolved through inter-laboratory testing. Duplicates samples are defined as two identical samples. To ensure that the samples are identical they should be poured from a single, larger container. Samples collected in sequence are **not** duplicates. By splitting a larger sample you help ensure that any observed differences are due to laboratory procedures and are not sampling variations. Split sampling for trace metals and pesticides requires much stricter protocols than major cation and anion sampling.

True blanks are often difficult to prepare. Selection of appropriate blanks is important. While deionized water works well for the major chemistry, it will not work for pesticide and isotope samples. Distilled water blanks should be avoided. The New Brighton #11 municipal well will be used as a pesticide blank. This water has been age dated as about 10,000 years old and should not contain any pesticides. Stable isotopic samples measure the ratios of hydrogen to deuterium and oxygen-16 to oxygen-18; blanks do not have any meaning in this context.

Spiked samples are prepared by adding carefully prepared amounts of specific analytes. As with any control standard it is assumed that control is properly prepared; an often dangerous assumption. It is important that the controls have a similar matrix to the samples. A solution of deionized water spiked with NaCl has a very different matrix than a carbonate dominated ground water. The purity and uniformity of the spiking reagents should be carefully tested and verified. Spiked samples can be created and analyzed as needed.

Inter-laboratory splits are a very important check of accuracy and reproducibility. Currently the Department of the Geology and Geophysics is participating in the USGS Standard Reference Sample Program. The Geology lab has consistently ranked in the top third of the nearly 200 labs participating nation-wide. Periodic splits samples are also run between the Geology lab and the Minnesota Department of Health Lab and/or the Research Analytical Lab in the Soil Science Department.

For chemical data the primary check of internal consistency is the charge balance. Simply, the sum of the cations should equal the sum of the anions. The charge balance is primarily controlled the dominant cations and anions. Errors in minor ions are difficult to detect in the charge balance. Imbalances can be the result of typos, measurement errors, mis-identified samples or an incomplete chemical analysis. Charge balance is calculated as the difference of the cations and anions divided by the sum of the cations and anions in units of milli-equivalents per kilogram. Charge balances of less than 2% are consider excellent. Balances of 2 to 5% will be considered acceptable. Imbalances of 5% or more will be rechecked for data entry and analytical errors.

Secondary consistency checks compare measured and calculated parameters. Comparisons of the iron and manganese concentrations with dissolved oxygen will be made. Iron and manganese levels should increase, in a non-systematic way, with decreasing oxygen levels. The level of pCO_2 dissolved in the sampled waters will be calculated. Surface waters should have a pCO_2 consistent with atmospheric levels of carbon dioxide. Ground waters will range from the low levels found in surface waters to levels two the three orders of magnitude higher. Additional checks will be used as the need arises.

Quality assurance and control (QA/QC) is not a fixed recipe that guarantees perfect results. Contrary to the idea that perfect planning will completely eliminate errors, one should assume that errors will occur. QA/QC should therefore work to reduce, identify and correct, but not completely eliminate errors while providing the most accurate and precise data possible. The goals of QA/QC are to: 1) reduce the absolute number of errors, 2) identify and correct, in a timely fashion, as many of the errors as possible, 3) improve the accuracy and precision of the data and 4) quantify the accuracy and precision of the reported data.

While prompt analysis of the samples is critical, the most important quality process begins once the results of controls are received. Control results must be examined and reduced in a timely fashion. The earlier any inconsistencies or discrepancies are identified, the fewer questionable data are generated. Likewise if problems are identified early there is a greater chance that usable data may still be recoverable. QA/QC programs all to often degenerate into a process of identifying and discarding poor data long after the fact. The generation of data that is later rejected consumes large amounts of resources and time. QA/QC should ensure the collection of the best possible data while watching for and correcting the inevitable problems in a timely fashion. Remember that if you catch and correct a problem before reporting a value it is not an error.

Sampling Etiquette

Sample collection occurs on both public and private property. When working with people's water supplies and resources it is vital that you remember that water is a very important resource that requires considerate handling. Always carefully identify yourself. An ID and business cards are essential.

Be polite and courteous, dress neatly but appropriately for field work. A clean appearance and organized sampling system leads to good public relations. Many people will want to chat while you are sampling. Answer questions with a friendly tone trying not to preach. If working in a pair one person can answer questions while the other samples. Remember that even if you have heard the question a thousand times the questioner has not. Try not to stop sampling while chatting.

Avoid running pumps for overly long periods of time. It costs electricity to pump and creates an appearance of wastage. Work quickly and efficiently. Label bottles while the well is stabilizing, start equilibrating pH buffers and electrodes immediately and start filling out the field notes. Try to run water on to a grassy area unless requested otherwise. Avoid muddying up driveways and sidewalks or, in January, icing them over. Never allow water to run towards a building foundation. Shut off the faucet as soon as possible returning all hoses, connections and valves to their original positions.

The individual collecting the water samples must be properly trained and have an understanding of the procedures involved. Summer interns should not collect samples unsupervised. The samplers will be involved in the analysis and reporting of data. An understanding of how and where the data will be used is an important part of water sampling. One group of people will collect, reduce and analyze the data to reduce uncertainty in whether or not the samples were collected with appropriate methods and care.

Safety

Safety is a paramount concern. Work in pairs at all times. Drive with care since driving to and from a site is by far the most dangerous part of water sampling. Avoid thunderstorms and extreme heat or cold. The samplers will use their own judgement in postponing sample collection. The sample can always be collected tomorrow; replacing people is a little more difficult. If the weather is compromising the careful measurement and collection of samples you should not be collecting data. If it is not possible to postpone sampling, notes of the difficulties encountered should be made.

Equipment Maintenance and Calibration

All field equipment will be maintained in a clean, ready to use state. Verification that all equipment is working properly shall be conducted each day before sampling. More frequent calibration of equipment is required as specified below. Immediately upon return from sampling all equipment should be cleaned and laid out to dry. All reagents and materials used should be restocked.

Temperature will be measured with an ASTM 63C mercury thermometer. The thermometers are factory calibrated by NBS procedures using NBS certified masters. The thermometers are designed for total immersion and have 0.1°C divisions. The thermometers will transported in 1" diameter PVC pipe lined with a closed cell foam. Daily inspection shall include visual checks that the thermometer is not broken and that the mercury has not separated.

Conductivity will be measured with a YSI 3000 Temperature-Level-Conductivity meter A conductivity standard should be checked daily. The meters have automatic temperature correction (ATC). Samplers should remember that this temperature correction is not precise which leads to uncertainties the measured value. Conductivity values should be considered to have at least 5 to 10 percent uncertainties.

The measurement of pH is perhaps the most important field parameter in carbonate dominated waters. It is essential that the samplers take great care to accurately measure the pH. Calibration of the pH meter will done at each sampling site by a two buffer calibration. Fresh buffers will be prepared daily. The pH will be measured with an Orion SA210 pH meter and Orion 91-06 pH electrode.

Dissolved oxygen levels will be measured by a modified Winkler Titration at the sampling site. Since low dissolved oxygen ground waters are easily contaminated by oxygen from the air great care must be taken in sample collection. Titration and sampling technique can be verified against waters with high iron and/or a hydrogen sulfide odor which indicates very low dissolved oxygen levels.

Field Measurements and Sample Collection

The following page is a copy of the field data sheet that will be used. The primary site data includes a site name, date and time of sampling, a Minnesota unique well number, depth and aquifer being sampled, the name of the samplers and a location that will include the township, range, section and quarter sections of the sample site. The field measurements will be recorded at the site. The meters and equipment used are listed on the data sheet. Any variations from the standard equipment will be noted. It will sometimes be impossible to collect all samples and make all the field measurements. Careful notes as to problems encountered as well as the improvised solutions will be kept in the notes section of the data sheet.

Ground water samples from private wells are usually collected at an outside tap that is not water softened and preferably not chlorinated. Water wells should be run for a period of time before sampling to flush out the water system; commonly used guides are a stable temperature and conductivity. Most well systems will stabilize within 10 to 15 minutes or less depending on prior usage. Well stabilization will be defined as a stable temperature and conductivity measurement for a period of five minutes. Temperature and conductivity will be monitored throughout the sampling to spot any changes indicating that the well has not stabilized. In the event of an unstablized well the samples will be recollected. Samplers should remember that water traversing a length of hose can warm up several degrees on a sunny day.

Most municipal wells have a sampling port prior to chlorination and fluoridation. The geometry of this port varies considerably so a variety of tubing and connectors should be included in the sampling gear. An air tight connection is very important for D.O. and redox measurements. The samplers should work quickly and efficiently at to municipal sites to avoid overflowing the water system. Well stabilization occurs very rapidly with high volume pumps and if the well is running when you arrive it should be assumed as stable. Arrive ready to sample and notify the attendant turn off the pump as soon as you have adequate water to complete sampling.

At surface sites, samples are collected directly. Sites should be selected for ease of access and should be reproducibly located. Samples should be collected far enough out to minimize any shore effects.

The pH measurement is temperature dependent. To compensate for this the sample, buffers and electrode should all be at the same temperature. The buffers and electrode should be put in a bath of sample water as soon as possible. Buffers will be selected to bracket the pH of the sample, in most cases we use pH 7 and 10 buffers. Starting with the pH 7 buffer the pH meter should be calibrated. Take care that the proper temperature is set. A stable reading is required before calibration and measurement. This is defined as either a stable reading for 30 seconds or a fluctuation up and down between two numbers. If the reading is steadily rising or falling the meter has not stabilized. Then the pH 10 buffer will be checked. If the reading is within 1 or 2 hundredths of a pH unit of the expected value the meter will be deemed as properly operating. If not, the meter will be re-calibrated and both buffers will be rechecked. If the pH buffers are not agreeing properly one of the buffers is likely contaminated. Calibration will restart with fresh buffers.

Other potential causes, in order of decreasing probability, of disagreement between the buffers are a cold pH meter, a low battery or a bad electrode in order of decreasing probability. While the pH electrodes themselves have a wide operation range, the pH meter does not tolerate cold. A cold meter and used electrodes also tend to slow down the calibration and measurement process. If the meter is still not calibrating properly a pH measurement will be made on the remainder of the alkalinity sample back at the lab.

Dissolved oxygen will be measured by a modified Winkler titration using a Hach digital titrator. Since the sample is easily contaminated in an oxygen atmosphere the sample collection, particularly in low D.O. waters, is the most important step. To minimize interactions with air one end of a piece of tubing is pushed up a hose or a hose fitting while the other end runs to the bottom of a BOD bottle. With the water running at a moderate flow the BOD bottle is slowly filled from the bottom up and then allowed to flush for a minute or more. The bottle is then capped until the titration is started.

A unique identifier, site name and date will be written on all labels as the samples are collected. A typical sample ID follows the form of a two letter abbreviation for the sampling project, four digits for the month and year, two letters for the sample site and one digit for the type of sample. Pre-labelled bottles will not be used as they are easily switched in the field.

Site:	Date:
Unique #:	Time:
Depth/Aquifer:	Samplers:
Location:	

Temp: °C	pH:	Cond: µmho/cm	Redox: mV
ASTM 63C	Orion SA210 7 & 10 buffer	YSI 3000	Orion SA210 Pt electrode

Sample #	Yes		No
________	___	1. ^{14}C and $\delta^{13}C$	___
	___	2.	___
	___	3. δD and $\delta^{18}O$	___
	___	4. Cation (60 ml) + 3dr. 6N HCl	___
	___	5. Anion (60 ml)	___
	___	6. Alkalinity (500 ml)	___
	___	7. Tritium (1ℓ HDPE)	___
	___	8.	___
	___	9.	___
	___	0. Immuno-Assay (30 ml)	___

Alkalinity Titration BG-MR color end point ______N titrant

Aliquot	Mass (g)	raw Alkalinity	corrected alkalinity		
1					
2					
3				x =	±
4					

Dissolved Oxygen Winkler titration ______N titrant

1
2

Notes:

Samples are usually collected in a separate bottle for each type of analysis. Once the well has stabilized all sample bottles should be filled quickly. Ideally all of the samples are poured from a single, larger container. A five gallon plastic pail is usually used. A white pail helps minimize any warming and helps identify any sediments settling out of the water. In some sampling environments several small bottles can be replaced with one larger bottle. In this case no preservatives are added and the bottle is kept on ice. As soon as possible the sub-samples are split out and the appropriate preservatives are added.

All container lids should be double-checked for a tight seal. Sample containers should always be kept clean and properly stored. Coolers containing ice should be periodically drained so that sample are not sitting under water. Sample should be systematically tracked from collection to analysis to final reporting preventing loss and/or tampering. You should know where you samples and data are at all times.

Alkalinity

Usually 500 ml plastic bottle. Bottles should be filled with no air bubble to prevent degassing. Dependent on the size and bicarbonate content of the water source and/or transportation considerations, samples as small as 30 ml may be collected. Washed with 2N HCl, triple rinsed with distilled water and oven dried at 80°C. Sample bottles are rinsed three times with sample water before the final sample is collected and then cooled to ice water temperature and transported. Sample should be analyzed with 24 hours of collection.

Cation

Usually 60 ml HDPE bottle. Washed with 2N HCl, triple rinsed with distilled water and oven dried at 80°C. Sample bottles are rinsed three times with sample water before the final sample is collected. Sample is acidified with 2 drops of 6N reagent grade HCl. The addition of HCl as a preservative is noted on the sample bottle. Cool to ice water temperature for transport and storage. Samples are usually analyzed within 2 to 3 weeks of collection but should have considerably longer storage life.

Anion

Usually 60 ml HDPE bottle. Soaked in distilled water for one week then triple rinsed with distilled water and oven dried at 80°C. Sample bottles are rinsed three times with sample water before the final sample is collected. Cool to ice water temperature for transport and storage. Sample are usually analyzed within 2 to 3 weeks of collection but should have a longer storage life.

Transition Metals and Heavy Metals

Samples are collected in 30 ml teflon bottles. Bottles are prepared by acid washing in 2N HCl acid followed by a 24 hour soaking in 18.3 NW deionized water. Bottles are then rinsed and oven dried at 80°C for 24 hours. Bottles are pre-weighed to account for sample dilution due to acidification. Sample bottles should be rinsed three times with sample water before final sample collection. Samples are then acidified to 0.8N with concentrated, trace-metal grade HM_3 acid immediately after sample collection. Extreme care must be taken when dealing with concentrated acids. Safety glasses and gloves are required. Systematically avoid sudden interruptions and talking while handling the acid. For a 30 ml sample 1.5 ml of concentrated, trace-metal grade HM_3 acid should be added to reach 0.8N. Sample dilution is accounted for by dividing the mass of the sample into the mass of the acid aliquot plus the sample mass to define a dilution factor. Cool to ice water temperature for transport and storage. Samples are usually analyzed within 2 to 3 weeks of collection but should have a considerably longer storage life.

The largest source of uncertainties are contamination by and loss of metals to the sample bottle. Extreme care in preparation, handling and sampling are critical. Improper acidification can be a source of trace metals or lead to the loss of metals to the walls of the sample bottles. Duplicate samples in combination with blanks are necessary to increase the levels of confidence in the reported values.

δD and $\delta^{18}O$

Sample is collected in a new 30 ml glass vial with a teflon lid liner. Usually collected in duplicate in case one bottle breaks during transport. Sample bottles are rinsed three times with sample water before the final sample is collected. The bottle lid is then sealed in a clockwise direction with electrical tape. No refrigeration or preservative necessary. Glass vials are used instead of plastic to prevent diffusion of water through the plastic over long periods of storage. Plastic bottles may be used for short term sample storage.

Tritium

Collected in a one liter HDPE bottle. Washed with 2N HCl, triple rinsed with distilled water and oven dried overnight at 80°C. The person collecting the tritium sample should avoid watches with "glow-in-dark-dials". Sample bottle should **not** be rinsed before sample collection. Fill the bottle slowly to minimize bubbling. No refrigeration or preservative necessary.

^{14}C and $\delta^{13}C$

The procedure used to extract the dissolved carbonate species is designed to avoid contamination from atmospheric CO_2 which contains relatively large amounts ^{14}C. The ^{14}C analysis requires 2 to 3 grams of carbon. Samples of 120 to 200 liters are collected in large plastic bags supported in 30 or 55 gallons drums. While the water is pumped into the bag 500 ml of concentrated NH_4OH in added to raise the pH to about 10. The high pH converts the dissolved bicarbonate ions to carbonate. The NH_4OH is pretreated with $BALK_2{\cdot}2H_2O$ to precipitate all the carbon including any ^{14}C and filtered immediately before use. About 200 g of $BALK_2{\cdot}2H_2O$ is added as the bag fills. The barium reacts with the carbonate ions to precipitate $PACE_3$. Sample waters with relatively high conductivities should be tested for sulfate. Since sulfate is difficult to test in the field, a titration to determine the chloride content is performed instead. For samples with low chloride and high conductivities additional $BALK_2{\cdot}2H_2O$ must be added to precipitate the suspected sulfate in addition to the carbonate. The drums of water are allowed to sit overnight while the precipitate settles. All but one or two liters are then siphoned off and the remaining slurry is transferred to plastic bottles for storage and shipping. No refrigeration or preservatives are necessary. $\delta^{13}C$ is determined from the ^{14}C sample.

Pesticides

Collected in 30 ml glass vials with teflon lined caps. Samples cooled to ice water temperature and analyzed within 2 weeks. Samples that will not be analyzed within 2 weeks can be frozen at -20°C for later analysis. If samples are to be frozen the vials should not be more than about half full to prevent breakage.

Alkalinity Titrations

Alkalinity samples can be analyzed in the field, at an off-site location or in the lab within 24 hours of sample collection. Titrations are performed in triplicate with a Hach digital titrator using a 1.6N H_2SO_4 titrant to a bromcresol green-methyl red color end-point. For low alkalinity waters, less than about 100 ppm, a 0.16N H_2SO_4 titrant is used. Color reference standards of pH 4.5 and 4.8 are used as a guide for the correct endpoint. Remember that the endpoint varies with the concentration. Titrations are typically done in 250 ml or 100 ml erlenmeyer flasks. In the lab glass flasks are usually used. In the field use PMP plastic flasks. PMP plastic flasks are cleaned by triple rinsing with distilled water and are shaken to remove most of the cleaning water; do not scrub or use brushes on PMP flasks or they will scratch.

Samples can be measured out in the field one of two ways. One method is to measure out 100 ml aliquots with a volumetric flask. The preferred method is to weigh out about 100 g of sample with a portable scale. The scale should have a minimum accuracy of 0.1 g. The advantages of weighing samples are 1) for triplicate samples a slightly different mass is used for each titration and then corrected to 100 g thus preventing biasing the second and third values towards the first and 2) no particular mass is required allowing each aliquot to be easily prepared by weighing out a mass near 100 g. Aliquots in the lab and at off-site locations are almost always measured by mass. Aliquot mass typically ranges anywhere between 90 and 110 g. For samples with a high alkalinity, greater than about 400 ppm, the aliquot mass can be reduced to 50 g or lower. In cases where there is only a small amount of sample water available titrations can be performed on samples as small as 10 g. The dilute titrant is then used to retain a high level of precision.

All titrations are replicated at least three times. The reported error estimate is the larger of: 1) the 0.5 ug/g detection limit, 2) 2% of the average value or 3) the measured standard deviation. For samples with standard deviations of 2% or larger additional titrations are carried out to isolate the problem. If a sample has unresolved problems or has anomalous colors a Gramm plot titration is done using an Orion SA 210 pH meter.

Cations
Inductively Coupled Plasma - Mass Spectrometry

Perkin-Elmer/Sciex Elan 5000 ICP-MS
EPA Method: under EPA review, approval pending

Detection Limits: all values reported as µg/g. 1 µg/g = 1 ppm (≅ 1 mg/l in dilute solutions)

Ca = 0.01	Mg = 0.01	Na = 0.01	K = 0.01
Al = 0.003	Fe = 0.01	Mn = 0.001	Sr = 0.001
Ba = 0.001	Si = 0.01	P = 0.005	

Reported Precision: each sample is replicated five times. The reported error estimate is the measured standard deviation from the five replicates.

The linear range for each element is determined during initial setup for that element by running a range of known concentrations. Concentrated standard solutions are purchased as Specpure ICP/DCP 1000 ppm standards from Johnson Matthey/Aesar Chemicals. These standards are NBS traceable. Mixed elements working standards are prepared gravimetrically from the stock standard solutions. Each set of new standards are cross-calibrated to the old standards and have been checked against the available EPA standards and NIST certified standards.

In addition, rhodium and scandium are used as internal standards. Constant monitoring of internal standards insures that the machine is stable and has reproducible peak heights. Scandium is used as a reference for Sr and Ba while rhodium is used for Ca, Mg, Na, K, Al, Fe, Mn and Si.

The specific run sequence is as follows: blank, standard, four samples, blank, standard. The standard is run as a sample at the end of each run to check recovery. Dwell times on each peak are 40 milliseconds, slightly longer for the Fe peak. At 25 sweeps of 40 milliseconds each the internal standards are checked about once per second.

Al and Si values in unfiltered samples may be anomalously high due to suspended sediment. Fe and Mn may show significant variations between splits in improperly acidified samples and unfiltered samples. P in unfiltered samples, particularly samples with settleable particles, has a shorter storage time and should be analyzed within 2 to 3 days for the greatest accuracy.

Anions
Ion Chromatography

Dionex Series 4000I
EPA method 300.0, "The Determination of Inorganic Anions in Water by Ion Chromatography."

Detection limits: all values reported as µg/g. 1 µg/g = 1 ppm (≅ 1 mg/l, dilute solutions)

Major anions	Cl = 0.03	NO_3-N = 0.01	SO_4 = 0.01	
Other anions	F = 0.05	Br = 0.02	PO_4-P = 0.03	NO_2-N = 0.02

Samples with ion concentrations above the highest standards are diluted and re-run. The detection limits are then increased by the dilution factor in these concentrated samples. All detection limits are increased by the dilution factor in concentrated solutions where the minor ions peak was swamped by a neighboring peak. F is subject to possible interferences. NO_2-N is easily masked by large Cl concentrations. PO_4-P and NO_2-N values may change in improperly stored samples and/or samples that have been stored for longer periods of time.

Reported precision: each sample is analyzed in duplicate. The reported error estimate is the larger of: 1) 2% of the reported value, 2) the measured deviation of the replicates or 3) the detection limit.

Concentrated standard solutions are prepared from reagent grade chemicals for each of the elements analyzed. Mixed elements working standards are prepared gravimetrically from stock standards solutions. These standards are cross compared to standards provided by the manufacturer and are checked against available EPA standards and NIST certified standards.

The specific daily run sequence on the IC is: blank, six IC standards, samples. The six IC standards are mixed anion standards that cover the working range for each of the anions. These six standards are used to establish a daily calibration curve for each of the anions. Replicate anion analyses include replication of the standards. The IC is stable for long periods of time and a daily calibration curve that differs significantly from the previous curve is immediately investigated to see if the instrument or standards have changed.

Transition Metals and Heavy Metals
Inductively Coupled Plasma - Mass Spectrometry.

EPA Method: under EPA review, approval pending
Perkin-Elmer/Sciex Elan 5000 ICP-MS

Reported detection limits will vary with each run and are estimated as three times the measured standard deviation. Expected detection limits are approximated as follows:

All values reported as ng/g. 1 ng/g = 1 ppb (≅ 1 µg/l, dilute solutions)

Transition Elements

V = 0.5 Cr = 5 Mn = 0.5 Fe = 5
Co = 0.05 Ni = 0.05 Cu = 0.05 Zn = 0.5

Heavy Metals

As = 0.5
Se = 2
Ag = 0.05
Cd = 0.05
Ba = 0.05
Hg = 10
Pb = 0.02

The standard run sequence is blank, standard, sample, blank, standard. The standard is also run as a sample to check recovery. Analytical precision and accuracy of Hg concentration can be improved greatly by increasing the rinsing time between standards and samples. Pb and particularly Hg are easily contaminated and/or lost to container walls. Reported values may reflect the sample composition at the time of testing rather than the time of sampling.

Sample Custody

Careful tracking of samples from collection to analysis to final data reporting is an important part of quality assurance. While tampering is not a large concern for most research projects, the loss or improper handling of a sample could require re-sampling. Sample custody starts with a carefully labelled bottle that includes a sample ID number, site name, date, time and the sample collectors' initials.

An important step in the sample handling process begins upon return from sampling. It is very important to verify that all sample bottles have been properly filled and labelled. Any labelling errors should be promptly resolved. If samples have ambiguous labels, are not labelled or are empty the samples should be recollected as soon as possible. At this time the field note books should be photocopied and the copies filed. If a field notebook is lost you want to have copies backing up the records on at least a daily basis.

Sample tracking forms will then follow the progress of the samples, in batches, from collection to final analysis with check points at the following steps to ensure proper handling and guard against loss. A final step involves comparing the QA/QC checks and controls in a timely fashion after the data is reported. The earlier problems are discovered the more likely it is that lab reporting errors and/or analytical problems can identified and corrected. If problems lie undetected for months it may not be possible to recover any usable data.

Batch	Date Collected	Storage	Shipped via	Date Shipped	Date Received	Date Analyzed	Date Reported	QA/QC checks

Data Handling
Quality Control Checks

It is extremely important that the quality controls are employed in a timely fashion. Discovery of inconsistencies months or years after the fact almost always results in the loss of all data involved which is a very expensive waste. The QA/QC checks are designed to prevent and identify problems as they occur creating the opportunity to correct and isolate problems before quantities of data have to be thrown away.

The primary checks, as discussed above, are the collection and comparison of duplicate and blank samples in conjunction with inter-laboratory comparisons. Measured values for duplicate samples should fall within the 3σ error estimate for the analyses. Blank samples, that have been properly prepared should contain undetectable or trace levels of the constituents. Chloride is a very common contaminant in blanks.

Data Reduction and Verification

Data reduction utilizes secondary checks of the internal consistency checks to verify the data. The major check is the charge balance. The charge balance compares the sum of the cations and the sum of the anions. After converting the reported values of each ion into units of milli-equivalents per kilogram the charge balance is defined as the sum of the cations minus the sum of the anions divided by the of the sum of the cations plus the sum of the anions. Note that the anions are negatively charged and imbalances to the anion side should be reported as negative values. Charge balances within 2% of zero are considered excellent. Imbalances of 2 to 5% are acceptable but a check for typographical errors is warranted. Imbalances of 5% or more will be rechecked for typographical errors, mis-labelled samples or switched samples, and/or analytical problems.

APPENDIX 3

CHEMICAL ANALYSES IN MYSTERY CAVE

The following pages list chemical analyses of samples obtained during this project in Mystery Cave, Old Mystery Cave, at the House Well at Mystery I, and at surface sites including the South Branch of the Root River and the three spring clusters, Crayfish springs, Seven springs, and Saxifrage springs.

Turquoise Lake																					
					CP 1	CP 2	Corr CP	YSI 9	YSI 10	Corr YSI											
Sample ID	Loc	Date	Temp	pH	Cond	Cond	Cond	Cond	Cond	Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC010691	TL	6/14/91	8.60	7.64							10.31	10.04	1.24	-2.078	0.57	0.414	0.955	-2.019	784	1.16	0.0146
MC010891	TL	8/18/91	8.70	7.57							10.77	10.15	2.83	-2.009	0.512	0.356	0.848	-2.004	797	1.14	0.0151
MC010991	TL	9/14/91	8.70	7.66							11.00	10.43	2.56	-2.089	0.616	0.46	1.06	-2.004	817	1.14	0.0154
MC011191	TL	11/22/91	8.70	7.84	898		868				11.21	10.18	4.61	-2.285	0.797	0.641	1.408	-1.997	810	1.17	0.0155
MC010192	TL	1/31/92	8.70	7.90	890		896				10.62	10.18	1.99	-2.347	0.83	0.674	1.482	-2.028	795	1.15	0.0149
MC010292	TL	2/23/92	8.70	7.91	890		896				10.85	10.18	3.03	-2.361	0.841	0.685	1.51	-2.02	797	1.13	0.0151
MC010492a	TL	4/4/92	8.65	7.96	850		838	895		909	10.41	9.90	2.37	-2.418	0.878	0.722	1.565	-2.033	766	1.18	0.0146
MC010592	TL	5/13/92	8.80	7.91	879		867				9.73	9.79	0.29	-2.369	0.823	0.667	1.417	-2.031	766	1.30	0.0139
MC010692	TL	6/22/92	8.60	7.88	858		846				9.64	9.87	-1.12	-2.339	0.79	0.634	1.341	-2.03	768	1.32	0.0139
MC010792	TL	7/28/92	8.60	7.83				917			9.86	9.91	-0.28	-2.29	0.746	0.589	1.253	-2.021	773	1.31	0.0141
MC010892	TL	8/15/92																			
MC010992	TL	9/14/92	8.65	7.82	877		865				10.12	10.03	0.44	-2.277	0.729	0.572	1.26	-2.016	782	1.19	0.0144
MC011092	TL	10/22/92	8.70	7.90	892		880				10.21	10.02	0.92	-2.361	0.804	0.648	1.422	-2.009	785	1.17	0.0145
MC011192	TL	11/20/92	8.60	7.83	917		904				10.41	10.32	0.41	-2.279	0.748	0.592	1.313	-1.994	804	1.16	0.0148
MC011292	TL	12/21/92	8.62	7.81					939	905	10.31	10.30	0.04	-2.256	0.73	0.574	1.274	-2.000	801	1.16	0.0147
MC010193	TL	1/22/93	8.70	7.93	934		918				10.50	10.68	-0.79	-2.368	0.854	0.698	1.541	-1.996	823	1.12	0.015
MC010393	TL	3/1/93	8.70	7.81	955		954				10.82	10.89	-0.29	-2.237	0.751	0.595	1.345	-1.998	839	1.09	0.0154
MC010493	TL	4/3/93	8.25	7.85	833		833	879		842	9.36	9.42	0.27	-2.334	0.706	0.549	1.199	-2.095	736	1.22	0.0134

Turquoise Lake																				
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC010691	TL	105.7	0.9	55.2	0.3	10.47	0.08	0.9	0.1	<.06		<.014		0.096	0.001	0.134	0.005	0.08	0.02
MC010891	TL	109.1	0.5	57.9	0.3	11.9	0.06	1.3	0.2	0.19	0.06	0.016	0.008	0.106	0.001	0.149	0.008	0.19	0.02
MC010991	TL	110.7	0.6	59.1	0.3	12.17	0.07	2.4	0.2	0.12	0.07	0.02	0.01	0.11	0.01	0.15	0.01	0.015	0.05
MC011191	TL	115.4	0.7	59.6	0.6	11.68	0.03	1.02	0.02	0.28	0.04	<.0001		0.097	0.001	0.143	0.002	<.001	
MC010192	TL	108.4	0.6	57.1	0.2	10.72	0.08	1.09	0.01	0.29	0.01	0.0002	0.0001	0.0953	0.0007	0.141	0.001	0.007	0.001
MC010292	TL	109.9	0.3	58.7	0.2	11.24	0.08	1.04	0.04	0.41	0.01	0.00136	0.0001	0.0971	0.0007	0.1437	0.0008	<.001	
MC010492a	TL	108.0	0.5	55.4	0.2	9.42	0.07	0.83	0.02	0.28	0.02	0.0056	0.0005	0.076	0.001	0.054	0.0006	0.15	0.01
MC010592	TL	105.5	0.8	49.1	0.5	9.18	0.08	1.03	0.01	<.01		0.0014	0.0001	0.0934	0.0008	0.139	0.002	<.001	
MC010692	TL	105.2	0.6	48.3	0.4	8.9	0.1	0.85	0.01	<.01		<.001		0.098	0.001	0.144	0.001	0.01	0.003
MC010792	TL	107	1	49.4	0.6	9.8	0.1	0.84	0.03	<.01		0.005	0.001	0.098	0.001	0.1438	0.001	0.004	0.003
MC010892	TL																		
MC010992	TL	105.0	0.8	53.2	0.6	10.86	0.08	0.95	0.01	<.01		<.001		0.099	0.001	0.142	0.001	<.003	
MC011092	TL	104.8	0.3	54.2	0.6	11.3	0.2	1.03	0.01	<.01		<.001		0.102	0.001	0.143	0.001	3	
MC011192	TL	106.0	0.7	55.5	0.3	11.9	0.09	1.07	0.03	0.01	0.01	<.001		0.102	0.001	0.147	0.001	0.003	0.003
MC011292	TL	105.5	0.5	54.8	0.3	11.6	0.1	1.08	0.03	0.03	0.01	<.001		0.0997	0.001	0.144	0.001	0.004	0.003
MC010193	TL	105.3	0.7	56.8	0.7	12.4	0.3	1.1	0.05	<.01		<.001		0.100	0.001	0.146	0.001	0.006	0.003
MC010393	TL	107	1	59.2	0.8	13.2	0.2	1.12	0.02	0.02	0.01	<.001		0.101	0.001	0.148	0.001	0.009	0.003
MC010493	TL	97	1	48.7	0.2	9.6	0.1	1.62	0.02	0.02	0.01	0.001	0.001	0.093	0.001	0.135	0.001	0.017	0.003

Turquoise Lake

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC010691	TL	400	2	488	8.7	0.2	38.4	28.4	0.6	29.2	0.6	0.03	0.02	<.05			MC010691	TL	12.8	0.3	27.4
MC010891	TL	399	1	487	8.9	0.2	39.3	28.9	0.6	33.5	0.7	0.036	0.02	<.05			MC010891	TL	13.1	0.1	28.0
MC010991	TL	410.7	5	501	8.9	0.2	39.5	28.8	0.6	35.0	0.7	0.05	0.02	0.44	0.05		MC010991	TL	13.22	0.09	28.3
MC011191	TL	399	2	486	9.9	0.2	43.8	28.3	0.6	31.8	0.6	0.03	0.02	0.379	0.05		MC011191	TL	14.7	0.1	31.4
MC010192	TL	396	2	483	10.5	0.2	46.5	27.5	0.5	33.5	0.7	0.04	0.02	<.05			MC010192	TL	12.58	0.06	26.9
MC010292	TL	393	1	480	10.5	0.2	46.3	27.8	0.6	34.8	0.7	0.03	0.02	0.25	0.05		MC010292	TL	12.6	0.07	27.0
MC010492a	TL	387	2	472	10.5	0.2	46.3	27.0	0.5	29.7	0.6	0.03	0.02	0.23	0.05		MC010492a	TL	7.62	0.09	16.3
MC010592	TL	383	3	467	10.2	0.2	45.0	27.1	0.5	29.9	0.6	<.02		0.11	0.05		MC010592	TL	14.7	0.4	31.4
MC010692	TL	383	8	467	11.0	0.2	48.7	27.1	0.5	30.4	0.6	0.04	0.02	0.12	0.05		MC010692	TL	14.5	0.1	31.0
MC010792	TL	382	8	465	11.3	0.2	50.0	27.4	0.5	32.2	0.6	0.04	0.02	0.15	0.05		MC010792	TL	14.5	0.2	31.0
MC010892	TL				11.5	0.2	51.0	27.6	0.6	30.7	0.6	0.039	0.02	0.07	0.05		MC010892	TL			
MC010992	TL	385	8	469	11.7	0.2	51.9	28.5	0.6	32.2	0.6	<.03		<.05			MC010992	TL	14.1	0.1	30.2
MC011092	TL	382	8	466	11.6	0.2	51.4	29.2	0.6	33.4	0.7	<.03		<.05			MC011092	TL	15.4	0.1	32.9
MC011192	TL	393	8	479	11.9	0.2	52.7	30.1	0.6	34.7	0.7	0.03	0.02	0.21	0.05		MC011192	TL	15.00	0.08	32.1
MC011292	TL	395	8	482	11.8	0.2	52.2	29.7	0.6	33.4	0.7	0.03	0.02	<.05			MC011292	TL	14.2	0.1	30.4
MC010193	TL	404	8	493	12.3	0.2	54.3	30.5	0.6	38.1	0.8	0.02	0.02	0.19	0.05		MC010193	TL	14.43	0.05	30.9
MC010393	TL	413	8	504	11.9	0.2	52.7	30.2	0.6	40.5	0.8	0.03	0.02	0.07	0.05		MC010393	TL	14.3	0.2	30.6
MC010493	TL	361	7	440	12	0.2	53.1	24.4	0.5	29.6	0.6	0.03	0.02	0.11	0.05		MC010493	TL	14.2	0.2	30.4

Frozen Falls Pool

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC020691	FFP	6/14/91																			
MC020891	FFP	8/18/91	9.50	7.67							9.18	8.54	3.42	-2.155	0.518	0.362	0.88	-2.151	677	1.13	0.0128
MC020991	FFP	9/14/91	9.20	7.74							7.66	7.35	1.96	-2.264	0.514	0.358	0.807	-2.306	585	1.29	0.0109
MC021091	FFP	10/11/91	9.70	8.02		762	770				9.24	8.61	3.34	-2.516	0.81	0.654	1.561	-2.187	679	0.91	0.0128
MC021191	FFP	11/22/91	9.80	8.31	569		546				6.94	7.80	5.44	-2.856	1.053	0.898	1.946	-2.307	565	1.16	0.0107
MC021291	FFP	12/21/91	9.70	8.31	620		596				7.45	6.88	3.69	-2.872	1.005	0.85	1.871	-2.259	550	1.10	0.0104
MC020192	FFP	1/31/92	9.60	8.02	704		708														
MC020292	FFP	2/23/92	9.50	8.26	718		722				8.84	8.12	4.01	-2.789	1.012	0.856	1.938	-2.151	641	0.96	0.0122
MC020492a	FFP	4/4/92	9.40	8.18				542		542	6.44	6.08	2.69	-2.772	0.823	0.668	1.439	-2.269	487	1.26	0.0091
MC020592	FFP	5/13/92	9.30	8.22				643		649	7.09	7.03	0.37	-2.764	0.939	0.783	1.669	-2.223	558	1.26	0.0101
MC020792	FFP	7/28/92	9.40	8.01				820		832	9.97	9.03	-0.3	-2.484	0.874	0.719	1.55	-2.112	703	1.24	0.0128
MC020892	FFP	8/15/92																			
MC020992	FFP	9/14/92	9.55	7.94	538		532				6.06	6.04	0.14	-2.524	0.595	0.44	0.93	-2.559	482	1.44	0.0087
MC021092	FFP	10/22/92	9.60	8.05	865		853				9.29	9.53	-1.19	-2.523	0.852	0.696	1.653	-2.13	732	0.89	0.0133
MC021192	FFP	11/20/92	9.20	8.00	427		423				4.91	4.76	1.47	-2.685	0.473	0.317	0.68	-2.667	384	1.43	0.007
MC021292	FFP	12/21/92	9.40	8.12					840	805	9.45	9.14	1.56	-2.605	0.941	0.786	1.781	-2.126	713	0.99	0.0133
MC020193	FFP	1/22/93	9.20	8.10	829		814				9.46	9.74	-1.37	-2.566	0.928	0.772	1.767	-2.11	746	0.95	0.0136
MC020393	FFP	3/1/93	9.00	7.97	830		830				9.43	9.32	0.56	-2.46	0.765	0.609	1.455	-2.11	719	0.92	0.0134
MC020493	FFP	4/3/93	7.65	8.35	468		470	506		485	5.54	5.38	1.34	-2.997	0.877	0.72	1.49	-2.482	434	1.34	0.0079

Frozen Falls Pool

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC020691	FFP	70.8	0.4	39.9	0.2	7.17	0.06	1.8	0.1	0.08	0.04	<.015		0.082	0.009	0.084	0.009	0.13	0.07
MC020891	FFP	92.5	0.4	49.6	0.2	9.4	0.05	1.7	0.2	0.19	0.06	0.037	0.009	0.093	0.006	0.115	0.008	0.19	0.04
MC020991	FFP	83.1	0.4	38.9	0.2	5.44	0.07	2.3	0.2	0.08	0.05	<.015		0.086	0.006	0.8	0.006	0.14	0.04
MC021091	FFP	83.2	0.8	55.2	1	11.3	0.1	1.7	0.07	0.27	0.04	0.0015	0.0002	0.091	0.001	0.107	0.001	0.006	0.01
MC021191	FFP	81.7	0.7	42.4	0.5	4.3	0.07	1.29	0.03	0.2	0.05	0.003	0.0002	0.0748	0.0003	0.066	0.001	0.03	0.02
MC021291	FFP	75.7	0.5	41.4	0.2	4.97	0.05	1.3	0.03	0.23	0.01	0.0061	0.0006	0.076	0.001	0.069	0.001	0.042	0.001
MC020192	FFP																		
MC020292	FFP	82.7	0.3	51.7	0.3	9.5	0.1	1.12	0.02	0.35	0.01	0.0018	0.0002	0.0765	0.0008	0.0947	0.0004	0.02	0.01
MC020492a	FFP	70.3	0.3	33.5	0.3	2.78	0.04	0.95	0.01	0.29	0.02	0.0056	0.0005	0.076	0.001	0.0542	0.0006	0.16	0.01
MC020592	FFP	76.9	0.4	36.7	0.3	4.7	0.02	0.75	0.02	0.02	0.01	0.0031	0.0002	0.0742	0.0005	0.0675	0.0005	0.04	0.01
MC020792	FFP	95	1	46.2	0.6	9.1	0.1	1.16	0.03	0.01	0.01	0.003	0.001	0.088	0.001	0.107	0.001	0.02	0.003
MC020892	FFP																		
MC020992	FFP	69.2	0.7	29.1	0.2	2.66	0.03	3.55	0.05	<.01		<.001		0.088	0.001	0.07	0.001	0.018	0.003
MC021092	FFP	82.4	0.8	55.8	0.6	12.8	0.06	1.04	0.02	<.01		<.001		0.09	0.001	0.118	0.001	<.003	
MC021192	FFP	55.6	0.3	23.5	0.1	1.85	0.03	4.5	0.05	0.06	0.01	<.001		0.07	0.001	0.054	0.001	0.057	0.003
MC021292	FFP	89.1	0.4	54.1	0.2	11.8	0.1	1.18	0.03	0.03	0.01	0.001	0.001	0.087	0.001	0.111	0.001	0.029	0.003
MC020193	FFP	87.4	0.9	55.2	0.6	12.2	0.3	1.05	0.04	<.01		0.001	0.001	0.088	0.001	0.117	0.001	0.004	0.003
MC020393	FFP	85.3	0.4	56.1	0.5	12.2	0.2	1.02	0.02	<.01		<.001		0.089	0.001	0.117	0.001	0.005	0.003
MC020493	FFP	62.2	0.6	28.0	0.3	1.76	0.05	1.29	0.02	0.07	0.01	0.004	0.001	0.067	0.001	0.047	0.001	0.125	0.003

Frozen Falls Pool

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC020691	FFP	70.8	0.4	39.9	0.2	7.17	0.06	1.8	0.1	0.08	0.04	<.015		0.082	0.009	0.084	0.009	0.13	0.07
MC020891	FFP	92.5	0.4	49.6	0.2	9.4	0.05	1.7	0.2	0.19	0.06	0.037	0.009	0.093	0.006	0.115	0.008	0.19	0.04
MC020991	FFP	83.1	0.4	38.9	0.2	5.44	0.07	2.3	0.2	0.08	0.05	<.015		0.086	0.006	0.8	0.006	0.14	0.04
MC021091	FFP	83.2	0.8	55.2	1	11.3	0.1	1.7	0.07	0.27	0.04	0.0015	0.0002	0.091	0.001	0.107	0.001	0.006	0.01
MC021191	FFP	81.7	0.7	42.4	0.5	4.3	0.07	1.29	0.03	0.2	0.05	0.003	0.0002	0.0748	0.0003	0.066	0.001	0.03	0.02
MC021291	FFP	75.7	0.5	41.4	0.2	4.97	0.05	1.3	0.03	0.23	0.01	0.0061	0.0006	0.076	0.001	0.069	0.001	0.042	0.001
MC020192	FFP																		
MC020292	FFP	82.7	0.3	51.7	0.3	9.5	0.1	1.12	0.02	0.35	0.01	0.0018	0.0002	0.0765	0.0008	0.0947	0.0004	0.02	0.01
MC020492a	FFP	70.3	0.3	33.5	0.3	2.78	0.04	0.95	0.01	0.29	0.02	0.0056	0.0005	0.076	0.001	0.0542	0.0006	0.16	0.01
MC020592	FFP	76.9	0.4	36.7	0.3	4.7	0.02	0.75	0.02	0.02	0.01	0.0031	0.0002	0.0742	0.0005	0.0675	0.0005	0.04	0.01
MC020792	FFP	95	1	46.2	0.6	9.1	0.1	1.16	0.03	0.01	0.01	0.003	0.001	0.088	0.001	0.107	0.001	0.02	0.003
MC020892	FFP																		
MC020992	FFP	69.2	0.7	29.1	0.2	2.66	0.03	3.55	0.05	<.01		<.001		0.088	0.001	0.07	0.001	0.018	0.003
MC021092	FFP	82.4	0.8	55.8	0.6	12.8	0.06	1.04	0.02	<.01		<.001		0.09	0.001	0.118	0.001	<.003	
MC021192	FFP	55.6	0.3	23.5	0.1	1.85	0.03	4.5	0.05	0.06	0.01	<.001		0.07	0.001	0.054	0.001	0.057	0.003
MC021292	FFP	89.1	0.4	54.1	0.2	11.8	0.1	1.18	0.03	0.03	0.01	0.001	0.001	0.087	0.001	0.111	0.001	0.029	0.003
MC020193	FFP	87.4	0.9	55.2	0.6	12.2	0.3	1.05	0.04	<.01		0.001	0.001	0.088	0.001	0.117	0.001	0.004	0.003
MC020393	FFP	85.3	0.4	56.1	0.5	12.2	0.2	1.02	0.02	<.01		<.001		0.089	0.001	0.117	0.001	0.005	0.003
MC020493	FFP	62.2	0.6	28.0	0.3	1.76	0.05	1.29	0.02	0.07	0.01	0.004	0.001	0.067	0.001	0.047	0.001	0.125	0.003

Frozen Falls Drips

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC030691	FFD	6/14/91	9.20	7.80							8.75	8.54	1.16	-2.288	0.665	0.509	1.17	-2.125	669	1.13	0.0124
MC030891	FFD	8/18/91	9.40	7.87							10.51	9.81	3.24	-2.311	0.802	0.647	1.45	-2.09	773	1.11	0.0146
MC030991	FFD	9/14/91	9.20	7.80							10.72	10.34	1.72	-2.223	0.762	0.606	1.354	-2.079	805	1.15	0.0151
MC031091	FFD	10/11/91	9.40	8.04		880	887				10.91	9.98	4.26	-2.483	0.958	0.803	1.811	-2.099	789	1.00	0.015
MC031191	FFD	11/22/91	9.80	8.25	785		758				10.25	8.90	6.67	-2.733	1.131	0.976	2.131	-2.129	718	1.08	0.0138
MC031291	FFD	12/21/91	9.70	8.19	760		768				9.38	8.64	3.89	-2.693	1.045	0.889	1.945	-2.136	683	1.11	0.013
MC030192	FFD	1/31/92	9.50	8.05	838		843				9.26	9.21	0.26	-2.522	0.859	0.704	1.656	-2.162	711	0.91	0.0131
MC030292	FFD	2/23/92	9.80	8.18	848		854				10.43	9.77	3.11	-2.63	1.1	0.945	2.061	-2.091	767	1.10	0.0144
MC030492a	FFD	4/4/92	9.65	8.17	674		666	695			8.24	7.87	2.16	-2.687	0.943	0.788	1.741	-2.141	621	1.11	0.0116
MC030592	FFD	5/13/92	9.50	8.10				775		785	8.78	8.69	0.53	-2.583	0.946	0.79	1.702	-2.1	680	1.22	0.0124
MC030692	FFD	6/22/92	9.20	8.08	827		816				9.21	9.52	-1.54	-2.537	0.972	0.816	1.73	-2.076	737	1.27	0.0133
MC030792	FFD	7/28/92	9.22	8.07	763		753				10.18	10.44	-1.2	-2.497	1.021	0.866	1.835	-2.044	805	1.26	0.0145
MC030892	FFD	8/15/92																			
MC030992	FFD	9/14/92	9.43	7.88	910		897				10.48	10.62	-0.64	-2.297	0.841	0.685	1.507	-2.046	822	1.17	0.0149
MC031092	FFD	10/22/92	9.60	8.05	951		937				9.29	9.53	-1.19	-2.523	0.852	0.696	1.653	-2.13	732	0.89	0.0133
MC031192	FFD	11/20/92	9.10	8.07	951		937				11.04	10.70	1.49	-2.496	1.033	0.877	1.894	-2.018	835	1.15	0.0154
MC031292	FFD	12/21/92	9.00	8.12					975	935	11.11	10.81	1.29	-2.539	1.084	0.928	2.005	-2.035	843	1.12	0.0155
MC030193	FFD	1/22/93	9.00	8.21	946		929				10.90	10.99	-0.42	-2.628	1.169	1.013	2.169	-2.039	849	1.14	0.0154
MC030393	FFD	3/1/93	8.90	8.11	935		934				10.72	10.82	-0.44	-2.532	1.064	0.908	1.952	-2.031	835	1.15	0.0152
MC030493	FFD	4/3/93	8.70	8.25	695		696	737		706	7.99	7.85	0.85	-2.783	0.993	0.837	1.807	-2.172	619	1.15	0.0113

Frozen Falls Drips

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC030691	FFD	88.8	0.4	47.4	0.3	8.96	0.05	0.08	0.1	<.07		<.015		0.077	0.099	0.09	0.01	0.07	0.07
MC030891	FFD	105	0.5	57.0	0.3	11.9	0.1	1.1	0.2	0.16	0.08	0.024	0.009	0.1	0.01	0.13	0.01	0.18	0.05
MC030991	FFD	109.1	0.6	53.7	0.3	12.0	0.1	1.1	0.2	0.07	0.03	<.015		0.09	0.01	0.12	0.02	0.09	0.06
MC031091	FFD	103.4	2	62.2	1	13.5	0.3	1.2	0.06	0.29	0.05	<.0001		0.095	0.002	0.127	0.004	<.001	
MC031191	FFD	101.9	0.3	56.6	0.4	10.8	0.1	0.86	0.03	0.27	0.04	<.001		0.077	0.001	0.104	0.001	0.008	0.001
MC031291	FFD	94.8	0.7	51.3	0.3	9.1	0.1	0.84	0.02	0.25	0.01	0.0001	0.0001	0.077	0.001	0.099	0.002	0.01	0.003
MC030192	FFD	83.5	0.2	55.2	0.4	11.6	0.1	1.40	0.01	0.2	0.001	0.0005	0.0002	0.0794	0.0006	0.104	0.001	0.0134	0.001
MC030292	FFD	104.5	0.9	57.0	0.4	11.21	0.06	0.85	0.02	0.4	0.01	<.0001		0.0842	0.0005	0.1162	0.0006	<.001	
MC030492a	FFD	83.4	0.4	45.3	0.6	7.4	0.1	0.67	0.02	0.24	0.02	0.0003	0.0001	0.0683	0.0009	0.0813	0.0006	0.0075	0.0007
MC030592	FFD	92.6	0.8	45.7	0.4	8.7	0.05	0.86	0.01	<.01		<.0001		0.0761	0.0005	0.095	0.001	0.005	0.001
MC030692	FFD	99.0	0.7	46.8	0.2	9.19	0.07	0.76	0.01	<.01		<.001		0.085	0.001	0.113	0.001	<.003	
MC030792	FFD	108.0	0.3	51.8	0.7	11.6	0.1	0.79	0.03	<.01		<.001		0.09	0.001	0.125	0.001	<.003	
MC030892	FFD																		
MC030992	FFD	107	1	55.1	0.5	13.16	0.08	1.30	0.02	<.01		<.001		0.093	0.001	0.133	0.001	<.003	
MC031092	FFD	106	1	57.5	0.8	13.4	0.3	1.01	0.02	<.01		<.001		0.095	0.001	0.134	0.001	<.003	
MC031192	FFD	112.1	0.9	58.6	0.4	13.7	0.1	1.04	0.02	<.01		<.001		0.095	0.001	0.135	0.001	<.003	
MC031292	FFD	111.2	0.5	59.6	0.5	14.3	0.2	1.09	0.02	0.04	0.01	<.001		0.092	0.001	0.134	0.001	0.004	0.003
MC030193	FFD	110	1	58.1	0.8	13.5	0.2	1.03	0.03	<.01		<.001		0.092	0.001	0.133	0.001	<.003	
MC030393	FFD	109.3	0.7	57.1	0.2	12.4	0.1	0.99	0.01	<.01		<.001		0.094	0.001	0.132	0.001	0.004	0.003
MC030493	FFD	82.3	0.7	43.1	0.5	7.24	0.06	0.84	0.02	0.02	0.01	<.001		0.074	0.001	0.088	0.001	0.014	0.003

Frozen Falls Drips

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC030691	FFD	368	2	449	5.2	0.1	22.8	24.5	0.5	20.6	0.4	0.02	0.02	0.35	0.05		MC030691	FFD	11.2	0.1	24.0
MC030891	FFD	398	2	485	6.7	0.1	29.7	24.5	0.05	30.9	0.6	0.022	0.02	<.05			MC030891	FFD	12.45	0.08	26.6
MC030991	FFD	415	5	506	6.9	0.1	30.3	24.5	0.5	37.3	0.7	0.03	0.02	0.43	0.05		MC030991	FFD	12.5	0.1	26.8
MC031091	FFD	400	4	488	7.3	0.1	32.4	24.8	0.5	33.5	0.7	0.024	0.02	<.02			MC031091	FFD	14.0	0.2	30.0
MC031191	FFD	368	4	449	5.5	0.1	24.3	22.9	0.5	23.4	0.5	<.02		0.29	0.05		MC031191	FFD	12.83	0.09	27.4
MC031291	FFD	356	5	434	5.4	0.1	24	23.3	0.5	23	0.5	<.02		0.15	0.05		MC031291	FFD	10.38	0.06	22.2
MC030192	FFD	369.5	5	451	6.5	0.1	28.8	24.6	0.5	29.8	0.6	0.024	0.02	<.05			MC030192	FFD	11.7	0.08	25.0
MC030292	FFD	394.8	1	481	6.8	0.6	30.2	24.8	0.5	30.8	0.6	0.02	0.02	0.19	0.05		MC030292	FFD	11.83	0.09	25.3
MC030492a	FFD	333	1	406	3.59	0.07	15.9	24.6	0.5	15.9	0.3	<.02		0.12	0.05		MC030492a	FFD	10.0	0.1	21.4
MC030592	FFD	360	2	439	4.7	0.1	21.1	25.2	0.5	22.1	0.4	<.02		0.1	0.05		MC030592	FFD	11.6	0.3	24.8
MC030692	FFD	384	8	469	6.4	0.1	28.3	25.6	0.5	29.6	0.6	<.04		0.11	0.05		MC030692	FFD	13.4	0.1	28.7
MC030792	FFD	415	8	506	7.8	0.2	34.5	26.5	0.5	36.5	0.7	0.03	0.02	0.16	0.05		MC030792	FFD	13.6	0.1	29.1
MC030892	FFD				8.3	0.2	36.7	26.9	0.5	36.1	0.7	<.02		0.07	0.05		MC030892	FFD			
MC030992	FFD	421	8	513	8.8	0.2	39	26.9	0.5	36.4	0.7	<.03		<.05			MC030992	FFD	13.9	0.1	29.7
MC031092	FFD	408	8	497	9.1	0.2	40.3	27.6	0.6	38	0.8	0.03	0.02	<.05			MC031092	FFD	15.02	0.07	32.1
MC031192	FFD	419	8	511	9.3	0.2	41.2	28	0.6	37.9	0.8	0.03	0.02	0.2	0.05		MC031192	FFD	14.7	0.1	31.4
MC031292	FFD	428	9	522	9.1	0.2	40.3	27.2	0.5	36.9	0.7	<.03		<.05			MC031292	FFD	14.1	0.2	30.2
MC030193	FFD	431	9	526	9.6	0.2	42.7	27.7	0.6	39.3	0.8	<.03		0.17	0.05		MC030193	FFD	14.1	0.1	30.2
MC030393	FFD	424	8	517	9.8	0.2	43.5	27.6	0.6	37.8	0.8	0.03	0.02	0.07	0.05		MC030393	FFD	13.4	0.2	28.7
MC030493	FFD	325	7	396	5.3	0.1	23.5	22.8	0.5	17.8	0.4	<.02		0.11	0.05		MC030493	FFD	11.65	0.09	24.9

Enigma Pit																					
					CP 1	CP 2	Corr CP	YSI 9	YSI 10	Corr YSI											
Sample ID	Loc	Date	Temp	pH	Cond	Cond	Cond	Cond	Cond	Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC040691	EP	6/14/91	8.70	7.61							5.25	5.24	0.04	-2.271	0.136	-0.02	-0.02	-2.159	415	1.49	0.0077
MC040891	EP	8/17/91	9.10	7.20							5.89	5.77	0.97	-1.821	-0.193	0.349	-0.66	-2.103	459	1.45	0.0086
MC040991	EP	9/13/91	9.20	7.40							6.45	6.18	1.95	-1.997	0.077	-0.078	-0.145	-2.025	493	1.55	0.0093
MC041091	EP	10/11/91	9.95	7.60	551	515	528			523	6.43	6.47	-0.35	-2.229	0.203	0.048	0.227	-2.065	494	1.21	0.0095
MC041291	EP	12/20/91	8.75	8.01	440		420				5.50	5.29	1.77	-2.656	0.59	0.433	0.848	-2.258	424	1.64	0.008
MC040192	EP	1/25/92	8.80	8.21	455		457				5.58	5.27	2.55	-2.878	0.75	0.594	1.21	-2.148	423	1.49	0.008
MC040392	EP	3/27/92	8.80	8.06	455		451				5.58	5.27	2.65	-2.707	0.486	0.642	0.955	-2.269	421	1.63	0.008
MC040592	EP	5/13/92	8.90	8.06	459		455				5.40	5.30	0.88	-2.723	0.612	0.456	0.893	-2.116	421	1.64	0.0079
MC040692	EP	6/20/92	9.20	7.74	477		472				5.45	5.40	0.45	-2.397	0.308	0.152	0.279	-2.047	431	1.68	0.008
MC040892	EP	8/15/92																			

Enigma Pit																			
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC040691	EP	61.6	0.4	25.0	0.2	2.19	0.02	0.6	0.1	<.06		<.013		0.091	0.007	0.053	0.009	0.03	0.07
MC040891	EP	68.0	0.3	28.3	0.1	2.65	0.02	0.8	0.2	0.17	0.05	0.02	0.02	0.106	0.007	0.074	0.008	0.16	0.02
MC040991	EP	76.8	0.6	30.0	0.1	2.63	0.06	0.9	0.2	<.07		<.015		0.11	0.02	0.06	0.02	0.06	0.05
MC041091	EP	68.6	0.8	34.2	0.5	3.4	0.1	1.00	0.04	0.25	0.03	0.0013	0.0003	0.103	0.002	0.057	0.001	0.026	0.002
MC041291	EP	69.3	0.4	26.1	0.2	1.6	0.1	0.76	0.03	0.18	0.02	0.002	0.0001	0.107	0.001	0.038	0.002	0.013	0.006
MC040192	EP	65.6	0.4	26.5	0.2	2.11	0.03	0.78	0.01	0.18	0.01	0.0004	0.0002	0.0965	0.0007	0.0396	0.0006	0.015	0.004
MC040392	EP	68.2	0.4	25.3	0.1	1.43	0.03	0.79	0.01	0.192	0.009	0.0009	0.0001	0.104	0.0005	0.0357	0.0005	0.016	0.003
MC040592	EP	66.1	0.5	24.2	0.3	2.1	0.01	0.69	0.02	0.01	0.01	0.0022	0.0002	0.1006	0.0004	0.0415	0.0006	0.02	0.01
MC040692	EP	67.0	0.3	24.0	0.2	2.52	0.03	0.79	0.01	<.01		0.002	0.001	0.099	0.001	0.048	0.001	0.01	0.003
MC040892	EP																		

Enigma Pit																					
Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC040691	EP	229	4	280	0.87	0.02	3.8	26.0	0.5	1.97	0.04	<.02		0.24	0.05		MC040691	EP	6.61	0.06	14.1
MC040891	EP	251	5	306	1.41	0.03	6.2	28.1	0.6	2.67	0.05	<.02		<.05			MC040891	EP	7.26	0.06	15.5
MC040991	EP	267	2	325	1.55	0.03	6.9	31.1	0.6	3.55	0.07	<.02		0.2	0.04		MC040991	EP	7.69	0.07	16.5
MC041091	EP	247	2	301	2.00	0.04	2	31.9	0.6	26.3	0.5	<.02		<.05			MC041091	EP	8.7	0.1	18.6
MC041291	EP	241	2	294	0.37	0.01	1.6	19.3	0.4	1.68	0.03	<.02		0.12	0.05		MC041291	EP	5.63	0.06	12.0
MC040192	EP	231.2	1	282	0.75	0.01	3.3	25.8	0.5	2.20	0.04	<.02		<.05			MC040192	EP	6.52	0.04	13.9
MC040392	EP	240.8	3	294	0.26	0.01	1.2	18.7	0.4	1.46	0.03	<.02		0.06	0.05		MC040392	EP	4.65	0.06	9.9
MC040592	EP	231	2	282	0.59	0.01	2.6	27.3	0.5	2.12	0.04	<.02		0.08	0.05		MC040592	EP	6.2	0.3	13.3
MC040692	EP	231	5	282	0.78	0.02	3.4	31.8	0.6	1.98	0.04	<.04		0.08	0.05		MC040692	EP	8.26	0.06	17.7
MC040892	EP				1.02	0.02	4.5	35.4	0.7	1.28	0.03	0.027	0.02	<.05			MC040892	EP			

Rimstone Creek

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC050691	RC	6/14/91	8.50	7.76							6.25	6.12	0.95	-2.364	0.364	0.207	0.529	-2.266	488	1.19	0.0091
MC050891	RC	8/17/91	8.45	7.28							7.27	7.02	1.63	-1.835	-0.028	-0.185	-0.229	-2.127	556	1.12	0.0105
MC050991	RC	9/13/91	8.55	7.55							6.43	5.96	3.45	-2.135	0.216	0.059	0.172	-2.455	484	1.37	0.0091
MC051091	RC	10/11/91	8.50	7.90		537	545				6.78	6.16	4.46	-2.501	0.505	0.349	0.878	-2.315	500	1.02	0.0095
MC051291	RC	12/20/91	8.60	8.08	585		562				6.39	6.66	1.97	-2.655	0.726	0.57	1.238	-2.277	521	1.24	0.0094
MC050192	RC	1/25/92	8.50	8.18	540		518				6.96	7.00	-0.25	-2.747	0.821	0.665	1.505	-2.055	549	1.03	0.0101
MC050292	RC	2/23/92	8.50	8.17	610		586				7.53	7.07	2.97	-2.742	0.853	0.697	1.54	-2.01	562	1.11	0.0107
MC050392	RC	3/27/92	8.55	7.98	567		561				7.29	6.52	5.19	-2.57	0.659	0.503	1.106	-2.149	525	1.24	0.0102
MC050592	RC	5/13/92	8.70	8.00	530		524				5.97	6.06	0.67	-2.596	0.622	0.465	0.99	-2.337	483	1.36	0.0087
MC050692	RC	6/20/92	8.50	7.93		618	621				6.28	6.10	1.36	-2.509	0.593	0.436	0.92	-2.507	496	1.39	0.009
MC050792	RC	7/29/92	8.50	7.76	615		608				7.13	7.05	0.51	-2.329	0.454	0.298	0.675	-1.896	558	1.29	0.0104
MC050892	RC	8/15/92																			
MC050992	RC	9/15/92	8.45	7.62	540		534				6.57	6.38	1.4	-2.195	0.3	0.143	0.318	-2.135	516	1.44	0.0094
MC051192	RC	11/21/92	8.32	8.06	485		480				5.47	5.37	0.82	-2.689	0.655	0.498	0.954	-2.437	432	1.69	0.0079
MC050193	RC	1/23/93	8.42	8.23	593		582				6.75	6.76	-0.05	-2.821	0.85	0.693	1.533	-2.016	531	1.10	0.0098
MC050393	RC	3/2/93	8.45	8.11	570		572				6.46	6.45	0.06	-2.724	0.691	0.534	1.219	-1.978	505	1.09	0.0095
MC050493	RC	4/5/93	8.50	7.93	574		576				6.49	6.56	-0.5	-2.509	0.572	0.415	0.948	-2.28	520	1.18	0.0095

Rimstone Creek

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC050691	RC	66.4	0.4	33.8	0.2	2.61	0.02	0.5	0.1	0.14	0.03	0.022	0.007	0.079	0.005	0.076	0.006	0.16	0.03
MC050891	RC	74.9	0.4	40.7	0.2	3.07	0.03	0.7	0.2	0.13	0.08	0.02	0.01	0.084	0.009	0.08	0.01	0.18	0.05
MC050991	RC	72.8	0.5	32.2	0.2	1.81	0.07	0.8	0.2	0.24	0.06	0.03	0.02	0.1	0.02	0.07	0.02	0.03	0.07
MC051091	RC	67	1	39.6	0.5	3.40	0.08	0.71	0.04	0.17	0.03	0.0084	0.0006	0.078	0.002	0.067	0.002	0.039	0.003
MC051291	RC	71.9	0.7	36.3	0.2	2.39	0.07	0.6	0.06	0.38	0.02	0.01	0.002	0.073	0.002	0.059	0.002	0.21	0.02
MC050192	RC	69.4	0.1	40.3	0.2	3.15	0.02	0.54	0.02	0.30	0.02	0.003	0.001	0.0819	0.0005	0.0648	0.0007	0.167	0.008
MC050292	RC	77.9	0.3	42.3	0.2	3.11	0.03	0.47	0.02	0.31	0.01	<.0001		0.0826	0.0005	0.0685	0.0004	0.01	0.01
MC050392	RC	78.4	0.8	38.3	0.3	4.18	0.07	1.23	0.01	0.27	0.01	0.0018	0.0001	0.0896	0.0007	0.0617	0.0005	0.016	0.002
MC050592	RC	67.6	0.7	30.0	0.3	2.40	0.02	0.66	0.02	0.08	0.01	0.0115	0.0003	0.0719	0.0008	0.0524	0.0005	0.1	0.02
MC050692	RC	71.8	0.2	31.4	0.1	2.25	0.03	0.31	0.01	<.01		0.003	0.001	0.083	0.001	0.066	0.001	0.042	0.003
MC050792	RC	78.6	0.7	36.7	0.3	3.00	0.06	0.45	0.03	0.25	0.03	0.018	0.001	0.092	0.001	0.076	0.001	0.29	0.01
MC050892	RC																		
MC050992	RC	74.9	0.5	31.6	0.5	2.08	0.05	0.96	0.09	0.71	0.04	0.047	0.001	0.119	0.002	0.072	0.001	0.83	0.04
MC051192	RC	68.0	0.6	24.3	0.2	1.14	0.03	0.93	0.02	<.01		<.001		0.134	0.001	0.043	0.001	0.007	0.003
MC050193	RC	69.8	0.7	38.0	0.3	2.90	0.3	0.58	0.04	<.01		0.001	0.001	0.077	0.001	0.063	0.001	0.006	0.003
MC050393	RC	66.5	0.8	36.6	0.3	2.50	0.1	0.51	0.01	<.01		<.001		0.080	0.001	0.062	0.001	0.015	0.003
MC050493	RC	69.3	0.5	35.5	0.2	2.20	0.05	0.54	0.01	<.01		0.001	0.001	0.079	0.001	0.061	0.001	0.016	0.003

Rimstone Creek

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC050691	RC	266	2	324	3.82	0.08	16.9	20.1	0.4	4.07	0.08	<.02		0.24	0.05		MC050691	RC	8.7	0.1	18.7
MC050891	RC	298	2	363	4.9	0.1	21.8	26.3	0.5	6.3	0.1	<.02		<.05			MC050891	RC	8.84	0.07	18.9
MC050991	RC	276	3	337	1.60	0.03	7.1	11.9	0.2	2.77	0.06	<.02		0.23	0.05		MC050991	RC	8.09	0.08	17.3
MC051091	RC	269.7	2	329	3.64	0.07	16.1	18.3	0.4	4.08	0.08	<.02		0.2	0.05		MC051091	RC	10.2	0.1	21.8
MC051291	RC	288	4	351	4.72	0.09	20.9	19.2	0.4	5.64	0.1	<.02		0.28	0.05		MC051291	RC	8.16	0.09	17.5
MC050192	RC	297	5	362	3.20	0.06	14.2	33.4	0.7	5	0.1	0.025	0.02	<.05			MC050192	RC	9.5	0.06	20.3
MC050292	RC	295	2	359	3.94	0.08	17.5	34	0.7	6.5	0.1	0.02	0.02	0.15	0.05		MC050292	RC	9.37	0.04	20.0
MC050392	RC	279	1	340	4.54	0.09	20.1	23.8	0.5	4.63	0.09	<.02		0.05	0.05		MC050392	RC	6.6	0.06	14.1
MC050592	RC	271	0.5	330.8	2.60	0.05	11.5	16.6	0.3	3.44	0.07	<.02		0.1	0.05		MC050592	RC	9.1	0.1	19.5
MC050692	RC	283	6	345	2.07	0.04	9.2	10.7	0.2	2.34	0.05	<.04		0.11	0.05		MC050692	RC	10.4	0.07	22.2
MC050792	RC	290	6	354	2.60	0.05	11.5	42.9	0.9	5.8	0.1	0.03	0.02	0.13	0.05		MC050792	RC	11.1	0.2	23.7
MC050892	RC				2.54	0.05	11.2	43.3	0.9	3.67	0.07	<.02		0.07	0.05		MC050892	RC			
MC050992	RC	285	6	348	1.33	0.03	5.9	24.6	0.5	2.39	0.05	<.03		0.11	0.05		MC050992	RC	11.0	0.2	23.5
MC051192	RC	252	5	307	0.51	0.01	2.3	12.6	0.3	1.28	0.03	<.03		0.1	0.05		MC051192	RC	6.58	0.08	14.1
MC050193	RC	281	6	343	3.36	0.07	14.9	35.9	0.7	5.04	0.1	<.03		0.17	0.05		MC050193	RC	9.6	0.1	20.5
MC050393	RC	264	5	322	2.68	0.05	11.9	40.3	0.8	4.66	0.09	0.03		0.15	0.05		MC050393	RC	9.2	0.2	19.7
MC050493	RC	283	6	346	4.90	0.1	21.7	19.1	0.4	4.9	0.1	<.02		0.12	0.05		MC050493	RC	9.4	0.1	20.1

Wishing Well Drips

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC060691	WWD	6/14/91	8.60	7.72							6.32	6.23	0.66	-2.344	0.312	0.156	0.4	-1.894	493	1.27	0.0093
MC060891	WWD	8/17/91	8.80	7.29							6.71	6.56	1.05	-1.884	-0.061	-0.217	-0.344	-1.89	521	1.27	0.0098
MC060991	WWD	9/13/91	9.40	7.48							7.00	6.79	1.43	-2.06	0.165	0.009	0.117	-1.849	538	1.28	0.0102
MC061091	WWD	10/11/91	8.70	7.65	630		606				7.46	6.91	3.58	-2.227	0.32	0.164	0.487	-1.87	555	1.08	0.0107
MC061291	WWD	12/20/91	8.90	8.00	530		508				6.44	6.34	0.76	-2.61	0.623	0.467	1.017	-1.94	502	1.30	0.0094
MC060192	WWD	1/25/92	8.80	8.20	550		553				7.05	6.61	3.01	-2.806	0.844	0.688	1.479	-1.875	528	1.23	0.01
MC060292	WWD	2/22/92	9.50	8.04	575		578				7.06	6.52	3.72	-2.65	0.69	0.534	1.189	-1.866	521	1.22	0.0101
MC060392	WWD	3/27/92	8.75	7.95	535		529				6.61	6.09	3.76	-2.581	0.555	0.399	0.892	-1.923	487	1.26	0.0094
MC060592	WWD	5/13/92	8.80	7.96	540		534				6.30	6.20	0.73	-2.585	0.568	0.412	0.881	-1.917	495	1.37	0.0092
MC060692	WWD	6/20/92	8.80	7.87	574		567				6.53	6.55	-0.14	-2.474	0.513	0.357	0.768	-1.869	519	1.38	0.0096
MC060792	WWD	7/29/92	8.72	7.73	588		581				6.71	6.80	-0.66	-2.316	0.4	0.244	0.538	-1.848	536	1.39	0.0099
MC060892	WWD	8/15/92																			
MC060992	WWD	9/15/92	8.70	7.70	595		588				6.87	6.80	0.48	-2.285	0.366	0.21	0.503	-1.848	541	1.29	0.0101
MC061092	WWD	10/23/92	8.75	7.83	602		595				7.02	6.87	1.04	-2.409	0.507	0.351	0.796	-1.864	548	1.26	0.0102
MC061192	WWD	11/21/92	8.72	8.06	608		601				6.98	6.87	0.79	-2.642	0.729	0.573	1.238	-1.879	547	1.26	0.0102
MC061292	WWD	12/22/92	8.70	8.00					595	570	6.84	6.64	1.43	-2.596	0.643	0.487	1.08	-1.904	530	1.22	0.0099
MC060193	WWD	1/23/93	8.82	8.13	585		575				6.60	6.57	0.19	-2.737	0.755	0.599	1.29	-1.884	521	1.27	0.0097
MC060393	WWD	3/2/93	8.90	7.94	568		570				6.54	6.53	0.04	-2.546	0.563	0.407	0.913	-1.882	516	1.26	0.0096
MC060493	WWD	4/5/93	8.70	8.10	509		511	546		523	5.76	6.08	-2.44	-2.718	0.667	0.511	1.112	-2.077	480	1.27	0.0086

Wishing Well Drips																			
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC060691	WWD	69.0	0.4	32.7	0.2	3.55	0.03	0.7	0.1	<.07		0.015	0.007	0.107	0.005	0.086	0.007	0.09	0.04
MC060891	WWD	73.3	0.4	34.8	0.2	3.72	0.05	0.5	0.2	<.09		<.015		0.112	0.008	0.09	0.009	0.11	0.06
MC060991	WWD	76.8	0.4	36.2	0.2	3.84	0.03	<.6		0.14	0.05	<.02		0.13	0.01	0.11	0.01	0.13	0.02
MC061091	WWD	75.7	0.6	42.1	0.5	4.30	0.05	0.55	0.04	0.16	0.02	0.001	0.0003	0.118	0.002	0.09	0.003	0.038	0.002
MC061291	WWD	74.7	0.7	36.1	0.4	3.5	0.1	0.42	0.04	0.19	0.02	0.001	0.001	0.106	0.002	0.081	0.003	0.013	0.006
MC060192	WWD	76.1	0.6	36.9	0.2	4.20	0.05	0.79	0.01	0.21	0.01	0.0004	0.0005	0.1036	0.0003	0.081	0.0003	0.008	0.001
MC060292	WWD	76.1	0.6	37.3	0.3	3.8	0.1	0.40	0.09	0.31	0.04	0.003	0.004	0.105	0.002	0.083	0.002	0.015	0.007
MC060392	WWD	72.0	0.2	34.3	0.2	3.74	0.03	0.64	0.02	0.22	0.01	0.00056	0.00007	0.0961	0.0005	0.0736	0.0005	0.026	0.002
MC060592	WWD	71.4	0.6	31.2	0.2	3.5	0.04	0.45	0.01	<.01		0.0012	0.0002	0.099	0.001	0.0745	0.0006	<.001	
MC060692	WWD	74.3	0.5	32.3	0.1	3.41	0.05	0.37	0.01	<.01		<.001		0.109	0.001	0.083	0.001	0.004	0.003
MC060792	WWD	76.5	0.6	33.1	0.2	3.5	0.06	0.32	0.03	<.01		0.001	0.001	0.109	0.001	0.085	0.001	0.019	0.003
MC060892	WWD																		
MC060992	WWD	75.7	0.9	35.4	0.2	3.76	0.05	0.43	0.01	<.01		<.001		0.111	0.001	0.084	0.001	<.003	
MC061092	WWD	76.7	0.9	36.6	0.3	3.8	0.1	0.47	0.02	<.01		<.011		0.111	0.001	0.085	0.001	<.003	
MC061192	WWD	76.4	0.3	36.3	0.2	3.86	0.09	0.52	0.02	0.01	0.01	0.002	0.001	0.111	0.001	0.086	0.001	0.006	0.003
MC061292	WWD	73.6	0.5	36.2	0.1	3.95	0.08	0.50	0.02	0.06	0.01	<.001		0.105	0.001	0.083	0.001	0.016	0.003
MC060193	WWD	72.3	0.7	34.2	0.3	3.7	0.3	0.49	0.03	<.01		0.002	0.001	0.102	0.001	0.079	0.001	0.009	0.003
MC060393	WWD	71.3	0.7	34.1	0.5	3.6	0.1	0.51	0.01	<.01		<.001		0.101	0.001	0.078	0.001	0.005	0.003
MC060493	WWD	63.2	0.4	30.0	0.3	2.91	0.06	0.38	0.01	<.01		<.001		0.094	0.001	0.066	0.001	0.01	0.003

Wishing Well Drips

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±
MC060691	WWD	253	4	309	1.39	0.03	6.2	46.6	0.9	3.41	0.07	0.03	0.02	0.29	0.05		MC060691	WWD	10.3	0.1
MC060891	WWD	270	3	329	1.69	0.03	7.5	45.5	0.9	3.49	0.07	0.024	0.02	<.05			MC060891	WWD	10.76	0.07
MC060991	WWD	278	2	339	1.52	0.03	6.7	48.9	1	3.74	0.07	0.03	0.03	0.35	0.05		MC060991	WWD	10.63	0.08
MC061091	WWD	284	2	346	1.57	0.03	7	48	0.1	3.70	0.07	0.026	0.02	0.25	0.05		MC061091	WWD	12.53	0.03
MC061291	WWD	263	4	320	1.69	0.03	7.5	41	0.8	3.35	0.07	<.02		0.17	0.05		MC061291	WWD	9.77	0.08
MC060192	WWD	270.9	3	330	1.70	0.03	7.5	46.6	0.9	3.78	0.08	0.06	0.02	<.05			MC060192	WWD	10.26	0.06
MC060292	WWD	263.9	4	322	1.74	0.03	7.7	47.7	1	4.14	0.08	0.03	0.02	0.15	0.05		MC060292	WWD	10.09	0.06
MC060392	WWD	251	1	306	1.50	0.63	6.7	42.4	0.8	2.80	0.06	0.022	0.02	0.08	0.05		MC060392	WWD	8.30	0.06
MC060592	WWD	254.3	0.3	310	1.68	0.03	7.4	42.9	0.9	3.51	0.07	<.02		0.12	0.05		MC060592	WWD	11.4	0.2
MC060692	WWD	267	5	325	1.77	0.04	7.8	46.9	0.9	3.92	0.08	<.04		0.13	0.05		MC060692	WWD	11.5	0.1
MC060792	WWD	277	5	338	1.70	0.03	7.5	48.4	1	4.54	0.09	0.04	0.02	0.12	0.05		MC060792	WWD	11.2	0.1
MC060892	WWD				1.65	0.03	7.3	48.9	1	2.65	0.05	0.042	0.02	0.09	0.05		MC060892	WWD		
MC060992	WWD	278	6	339	1.60	0.03	7.1	49.2	1	3.65	0.07	<.03		0.17	0.05		MC060992	WWD	12.2	0.1
MC061092	WWD	283	6	345	1.50	0.03	6.6	47.3	0.9	3.86	0.08	0.03	0.02	0.2	0.05		MC061092	WWD	12.73	0.09
MC061192	WWD	284	6	346	1.58	0.03	7	45.9	0.9	4.00	0.08	0.32	0.02	0.19	0.05		MC061192	WWD	12.21	0.06
MC061292	WWD	274	5	334	1.77	0.04	7.8	44.3	0.9	3.63	0.07	0.03	0.02	0.2	0.05		MC061292	WWD	11.85	0.08
MC060193	WWD	268	5	327	1.72	0.03	7.6	46.9	0.9	3.71	0.07	<.03		0.19	0.05		MC060193	WWD	11.6	0.1
MC060393	WWD	266	5	324	1.66	0.03	7.3	47.5	0.9	3.72	0.07	<.03		0.17	0.05		MC060393	WWD	11.2	0.2
MC060493	WWD	259	5	316	1.84	0.04	8.1	32.3	0.6	2.99	0.06	0.038	0.02	0.17	0.05		MC060493	WWD	11.2	0.07

Blue Lake																					
					CP 1	CP 2	Corr CP	YSI 9	YSI 10	Corr YSI											
Sample ID	Loc	Date	Temp	pH	Cond	Cond	Cond	Cond	Cond	Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC080691	BL	6/14/91	8.60	7.76							6.15	5.98	1.29	-2.387	0.341	0.184	0.459	-2.041	475	1.26	0.0089
MC080891	BL	8/17/91	8.65	7.41							0.61	0.61	-0.06	-2.023	-0.003	-0.159	-0.215	-2.039	484	1.23	0.009
MC080991	BL	9/14/91	8.70	7.56							6.54	6.27	1.98	-2.165	0.193	0.037	0.156	-1.989	500	1.29	0.0095
MC081091	BL	10/12/91	8.70	8.32	539		517				6.95	6.26	4.86	-2.95	0.899	0.743	1.665	-2.005	505	1.03	0.0098
MC081291	BL	12/20/91	8.70	7.98	578		555				6.80	6.24	3.99	-2.593	0.602	0.446	1.009	-2.027	500	1.19	0.0096
MC080192	BL	1/30/92	8.70	8.15	513		516				6.36	5.93	3.18	-2.79	0.702	0.546	1.245	-2.055	475	1.09	0.0091
MC080292	BL	2/26/92	8.65	8.11	506		509				6.21	5.73	3.72	-2.772	0.625	0.469	1.104	-2.052	458	1.06	0.0089
MC080392	BL	3/26/92	8.60	7.68	522		516				6.52	6.06	3.4	-2.298	0.275	0.119	0.369	-2.072	483	1.15	0.0093
MC080492	BL	4/25/92	8.60	7.92	542		536				6.20	6.08	0.93	-2.534	0.52	0.364	0.811	-2.088	485	1.28	0.009
MC080592	BL	5/13/92	8.70	7.95	538		532				6.23	6.14	0.61	-2.559	0.564	0.408	0.887	-2.082	491	1.32	0.0091
MC080692	BL	6/20/92	8.60	7.80	535		529	559		563	5.87	6.00	-1	-2.42	0.383	0.226	0.519	-2.076	475	1.33	0.0087
MC080792	BL	7/29/92	8.70	7.84	538		532				6.19	6.10	0.67	-2.456	0.446	0.289	0.651	-2.058	486	1.32	0.009
MC080892	BL	8/15/92																			
MC080992	BL	9/15/92	8.70	7.72	565		554				6.60	6.27	2.39	-2.325	0.338	0.182	0.487	-2.044	504	1.18	0.0095
MC081092	BL	10/23/92	8.70	7.84	546		540				6.09	6.08	0.11	-2.469	0.398	0.242	0.612	-2.012	483	1.16	0.009
MC081192	BL	11/21/92	8.70	8.08	508		503				5.91	5.64	2.14	-2.751	0.575	0.419	0.984	-2.03	453	1.11	0.0085
MC081292	BL	12/22/92	8.72	7.95					528	506	5.71	5.52	1.59	-2.621	0.432	0.276	0.704	-2.093	442	1.10	0.0083
MC080193	BL	1/23/93	8.65	8.08	490		481				5.50	5.42	0.65	-2.768	0.524	0.368	0.9	-2.091	432	1.06	0.0081
MC080393	BL	3/2/93	8.70	8.01	469		471				5.35	5.23	1.1	-2.713	0.424	0.268	0.711	-2.1	416	1.04	0.0078
MC080493	BL	4/4/93	8.63	8.09	518		520				5.89	5.83	0.49	-2.714	0.662	0.505	1.094	-2.188	468	1.28	0.0085
MC080593	BL	5/12/93	8.60	7.80				546		523	5.82	5.92	-0.8	-2.409	0.386	0.229	0.537	-2.178	468	1.30	0.0086

Blue Lake																				
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC080691	BL	66.7	0.3	31.9	0.2	3.70	0.02	0.6	0.1	0.1	0.03	<.014		0.088	0.003	0.076	0.004	0.09	0.02
MC080891	BL	65.4	0.3	32.2	0.2	3.78	0.05	0.7	0.2	0.11	0.05	<.015		0.092	0.009	0.07	0.01	0.11	0.04
MC080991	BL	72.0	0.4	33.7	0.2	3.61	0.07	0.5	0.2	<.07		<.015		0.09	0.02	0.07	0.02	0.06	0.08
MC081091	BL	68.9	0.9	39.9	0.8	4.5	0.1	0.65	0.05	0.16	0.03	0.0016	0.0005	0.0954	0.0008	0.07	0.003	0.031	0.003
MC081291	BL	72.1	0.5	36.4	0.3	4.0	0.1	0.61	0.04	0.24	0.03	0.004	0.002	0.092	0.002	0.063	0.002	0.023	0.004
MC080192	BL	64.9	0.2	35.6	0.2	3.80	0.02	0.53	0.01	0.17	0.01	0.0002	0.0001	0.0851	0.0004	0.0623	0.0005	0.012	0.006
MC080292	BL	62.4	0.6	35.4	0.4	3.80	0.09	0.49	0.08	0.21	0.01	0.0005	0.0001	0.082	0.001	0.06	0.001	0.002	0.001
MC080392	BL	67.8	0.6	35.7	0.2	4.01	0.05	0.49	0.02	0.18	0.01	0.0009	0.0001	0.0846	0.0005	0.0595	0.0003	0.006	0.001
MC080492	BL	67.9	0.7	31.9	0.2	3.83	0.04	0.62	0.02	<.01		<.0001		0.0887	0.0002	0.0552	0.0002	0.007	0.002
MC080592	BL	69.2	0.5	31.5	0.2	3.77	0.04	0.55	0.01	0.01	0.01	<.0001		0.0834	0.0007	0.0605	0.0007	0.005	0.001
MC080692	BL	65.6	0.8	29.7	0.2	3.15	0.05	0.37	0.01	0.01	0.01	0.003	0.002	0.087	0.001	0.063	0.001	0.009	0.003
MC080792	BL	68.8	0.5	31.4	0.2	3.53	0.05	0.46	0.02	<.01		<.001		0.086	0.001	0.061	0.001	0.007	0.003
MC080892	BL																		
MC080992	BL	69.6	0.6	35.7	0.3	4.00	0.06	0.49	0.02	<.01		<.001		0.098	0.001	0.073	0.001	<.003	
MC081092	BL	63.8	0.5	33.0	0.2	4.04	0.06	0.54	0.01	<.01		<.001		0.093	0.001	0.069	0.001	<.003	
MC081192	BL	60.5	0.5	32.6	0.2	4.37	0.08	0.57	0.02	0.01	0.01	0.013	0.001	0.085	0.001	0.077	0.001	0.014	0.004
MC081292	BL	58.0	0.4	31.8	0.4	4.04	0.05	0.55	0.02	0.09	0.01	0.003	0.001	0.082	0.001	0.059	0.001	0.034	0.003
MC080193	BL	55.1	0.5	31.1	0.2	4	0.3	0.53	0.03	<.01		0.001	0.001	0.08	0.001	0.058	0.001	0.008	0.003
MC080393	BL	53.0	0.5	30.3	0.3	3.9	0.1	0.57	0.01	0.03	0.01	0.004	0.001	0.078	0.001	0.056	0.001	0.02	0.004
MC080493	BL	64.5	0.8	30.3	0.3	3.64	0.05	0.49	0.01	0.02	0.01	0.004	0.001	0.086	0.001	0.057	0.001	0.027	0.003
MC080593	BL	64.0	0.2	29.8	0.2	3.6	0.1	0.43	0.01	<.01		0.001	0.001	0.079	0.001	0.061	0.001	0.004	0.003

BLue Lake																					
Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC080691	BL	251	4	306	2.09	0.04	9.3	33.6	0.6	4.06	0.08	<.02		0.29	0.05		MC080691	BL	8.86	0.06	19.0
MC080891	BL	258	5	315	1.92	0.04	8.5	34.4	0.7	3.88	0.08	0.02	0.02	<.05			MC080891	BL	0.916	0.07	19.6
MC080991	BL	264	1	322	2.00	0.04	8.8	36.1	0.7	3.80	0.08	<.02		0.23	0.05		MC080991	BL	9.28	0.08	19.9
MC081091	BL	259	2	316	2.37	0.05	10.5	37.5	0.7	4.20	0.08	0.02	0.02	0.2	0.05		MC081091	BL	10.68	0.06	22.8
MC081291	BL	263	4	320	2.21	0.04	9.8	33.5	0.7	4.58	0.09	<.02		0.13	0.05		MC081291	BL	8.64	0.07	18.5
MC080192	BL	247.8	4	302	2.25	0.05	10	34.0	0.7	4.04	0.08	<.02		<.05			MC080192	BL	8.97	0.02	19.2
MC080292	BL	235	4	287	2.36	0.05	10.5	35.1	0.7	4.31	0.09	0.03	0.02	0.15	0.05		MC080292	BL	8.78	0.07	18.8
MC080392	BL	257	3	313	2.04	0.04	9	31.3	0.6	4.44	0.09	<.02		0.09	0.05		MC080392	BL	7.84	0.06	16.8
MC080492	BL	260.2	1.7	317	1.78	0.04	7.9	29.8	0.6	4.31	0.09	<.02		0.1	0.05		MC080492	BL	10.0	0.1	21.4
MC080592	BL	263.8	1.8	322	1.82	0.04	8.1	29.8	0.6	4.15	0.08	<.02		0.1	0.05		MC080592	BL	10.2	0.1	21.8
MC080692	BL	255	5	311	1.95	0.04	8.6	31.1	0.6	3.84	0.08	<.04		0.1	0.05		MC080692	BL	9.79	0.05	20.9
MC080792	BL	258	5	315	2.05	0.04	9.1	31.6	0.6	4.38	0.09	<.02		0.1	0.05		MC080792	BL	10.0	0.2	21.4
MC080892	BL				2.04	0.04	9	31.4	0.6	2.69	0.05	<.02		0.06	0.05		MC080892	BL			
MC080992	BL	265	5	323	2.24	0.04	9.9	32.9	0.7	4.63	0.09	<.03		0.13	0.05		MC080992	BL	11.0	0.07	23.6
MC081092	BL	250	5	305	2.50	0.05	11.1	37.7	0.8	3.71	0.08	<.03		0.17	0.05		MC081092	BL	11.1	0.08	23.8
MC081192		229	5	279	2.47	0.05	10.9	37.5	0.7	3.68	0.07	<.03		0.17	0.05		MC081192	BL	11.0	0.2	23.5
MC081292	BL	227	5	277	2.37	0.05	10.5	33.2	0.7	3.73	0.07	<.03		0.19	0.05		MC081292	BL	10.6	0.07	22.6
MC080193	BL	221	5	269	2.50	0.05	11.1	34.7	0.7	3.64	0.07	<.03		0.16	0.05		MC080193	BL	10.4	0.07	22.3
MC080393	BL	211	4	257	2.42	0.05	10.7	34.9	0.7	3.73	0.07	<.03		0.16	0.05		MC080393	BL	9.7	0.2	20.8
MC080493	BL	256	5	312	1.31	0.03	5.8	24.4	0.5	3.7	0.07	<.02		0.13	0.05		MC080493	BL	10.6	0.1	22.7
MC080593	BL	262	5	319	1.05	0.02	4.6	25	0.5	3.07	0.06	<.03		0.15	0.05		MC080593	BL	8.6	0.2	18.4

Garden of the Gods 1

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC090691	GG1	6/14/91	9.20	7.62							4.68	4.68	-0.06	-2.281	0.155	0.000	-0.087	-2.976	385	1.94	0.0068
MC090891	GG1	8/17/91	9.10	7.18							6.21	6.09	0.94	-1.754	-0.101	-0.257	-0.58	-2.732	494	1.85	0.009
MC090991	GG1	9/14/91	9.30	7.36							4.77	4.46	3.07	-2.041	-0.107	-0.262	-0.623	-2.884	376	2.00	0.0068
MC091091	GG1	10/11/91	9.60	7.55	460		439				5.38	4.91	0.414	-2.201	0.133	-0.023	-0.063	-2.803	413	1.68	0.0076
MC091291	GG1	12/20/91	9.20	7.99	570		547				6.83	6.30	3.78	-2.577	0.73	0.574	1.094	-2.661	509	1.80	0.0096
MC090192	GG1	1/30/92	9.20	8.12	400		402				4.87	4.56	2.94	-2.804	0.644	0.489	0.901	-2.862	382	1.90	0.0069
MC090292	GG1	2/22/92	10.00	8.11	410		412				4.93	4.56	3.51	-2.791	0.65	0.495	0.936	-2.912	382	1.86	0.007
MC090392	GG1	3/27/92	9.20	8.02	526		520				5.19	4.79	3.58	-2.678	0.6	0.445	0.791	-3.142	395	1.99	0.0073
MC090592	GG1	5/13/92	10.50	7.98	480		475				5.43	5.38	0.4	-2.603	0.628	0.473	0.868	-2.774	441	2.01	0.0079
MC090692	GG1	6/23/92	9.60	7.78	425		421				4.62	4.69	-0.67	-2.44	0.337	0.182	0.234	-3.042	385	2.17	0.0068
MC090792	GG1	7/29/92	10.00	7.58	403		400				4.56	4.51	0.45	-2.253	0.119	-0.036	-0.181	-2.912	377	2.11	0.0066
MC090892	GG1	8/15/92																			
MC090992	GG1	9/15/92	9.50	7.50	393		390				4.51	4.33	1.84	-2.191	0.007	-0.149	-0.397	-2.886	366	2.02	0.0065
MC091092	GG1	10/23/92	9.80	7.55	405		402				4.50	4.39	1.05	-2.235	0.061	-0.094	-0.273	-2.905	370	1.98	0.0065
MC091192	GG1	11/21/92	9.20	7.96	435		431				4.88	4.78	0.92	-2.62	0.518	0.362	0.626	-2.976	396	1.99	0.007
MC091292	GG1	12/22/92	9.70	8.04					419	401	4.69	4.59	1.01	-2.716	0.566	0.41	0.746	-2.913	383	1.92	0.0068
MC090193	GG1	1/23/93	10.70	7.99							4.56	4.41	1.52	-2.673	0.517	0.363	0.649	-2.915	372	2.01	0.0066
MC090393	GG1	3/2/93	10.50	8.02	395		398				5.02	4.53	4.65	-2.696	0.595	0.44	0.778	-2.882	387	2.12	0.007
MC090493	GG1	4/4/93	9.50	8.26	634		635				7.03	6.82	1.36	-2.836	1.024	0.869	1.679	-2.676	541	1.84	0.01

Garden of the Gods 1

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC090691	GG1	59.9	0.3	18.8	0.09	2.38	0.02	0.4	0.1	0.11	0.07	0.023	0.007	0.133	0.006	0.086	0.007	0.15	0.05
MC090891	GG1	78.5	0.4	25.9	0.1	2.69	0.08	0.5	0.2	0.26	0.06	0.03	0.01	0.185	0.006	0.12	0.01	0.19	0.04
MC090991	GG1	62.2	0.5	18.8	0.1	2.19	0.04	<.4		0.08	0.05	0.02	0.02	0.14	0.01	0.08	0.01	0.1	0.05
MC091091	GG1	66	1	23.8	0.5	2.60	0.09	0.33	0.04	0.27	0.03	0.0015	0.0002	0.151	0.001	0.083	0.002	0.05	0.002
MC091291	GG1	86.5	0.8	29.1	0.3	2.40	0.06	0.16	0.02	0.233	0.008	0.0005	0.0005	0.164	0.001	0.0968	0.0005	0.008	0.002
MC090192	GG1	62.4	0.5	19.9	0.2	2.24	0.04	0.25	0.01	0.18	0.01	0.0003	0.0002	0.1312	0.0008	0.0736	0.0005	0.02	0.001
MC090292	GG1	63.0	0.5	20.5	0.2	1.98	0.07	0.04	0.01	0.22	0.01	<.0001		0.1303	0.0008	0.0747	0.0007	0.003	0.002
MC090392	GG1	67.1	0.6	20.4	0.2	2.83	0.06	0.64	0.02	0.21	0.01	0.0197	0.0003	0.1196	0.0006	0.0506	0.0005	0.076	0.007
MC090592	GG1	71.3	0.6	21.5	0.1	2.16	0.03	0.17	0.01	<.01		<.0001		0.139	0.001	0.078	0.001	<.001	
MC090692	GG1	62.3	0.3	17.4	0.09	1.71	0.04	0.05	0.01	<.01		<.001		0.124	0.001	0.065	0.001	<.003	
MC090792	GG1	60.7	0.5	17.5	0.3	1.89	0.06	0.08	0.02	<.01		<.001		0.129	0.001	0.067	0.001	<.01	
MC090892	GG1																		
MC090992	GG1	59.2	0.7	17.8	0.2	1.90	0.06	0.16	0.01	<.01		<.001		0.133	0.001	0.07	0.001	<.003	
MC091092	GG1	58.6	0.6	18.0	0.2	1.90	0.05	0.16	0.01	<.01		<.001		0.134	0.001	0.067	0.001	<.003	
MC091192	GG1	63.7	0.9	19.4	0.3	2.18	0.05	0.25	0.01	<.01		<.001		0.13	0.001	0.065	0.001	<.003	
MC091292	GG1	60.4	0.2	19.0	0.07	2.17	0.02	0.18	0.01	0.08	0.01	0.001	0.001	0.133	0.001	0.07	0.001	0.01	0.003
MC090193	GG1	59.7	0.7	18.0	0.2	2.1	0.3	0.17	0.03	0.01	0.01	0.003	0.001	0.132	0.001	0.068	0.001	0.026	0.003
MC090393	GG1	66.6	0.5	19.0	0.3	2.0	0.1	0.26	0.01	0.25	0.02	0.047	0.001	0.14	0.002	0.075	0.002	0.24	0.02
MC090493	GG1	90.3	0.9	29.5	0.2	1.9	0.09	0.15	0.01	<.01		0.001	0.001	0.182	0.002	0.103	0.002	0.007	0.003

Garden of the Gods 1

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC090691	GG1	227	1	277	0.45	0.01	2	3.85	0.08	1.22	0.02	<.02		<.05			MC090691	GG1	9.02	0.07	19.3
MC090891	GG1	280	3	342	0.32	0.02	1.42	5.9	0.1	12.06	0.02	<.02		<.05			MC090891	GG1	11.25	0.08	24.1
MC090991	GG1	216	1	263	0.29	0.01	1.3	4. 63	0.09	1.17	0.02	<.02		0.27	0.05		MC090991	GG1	10.2	0.1	21.8
MC091091	GG1	232	4	283	0.347	0.007	1.54	5.5	0.1	4.43	0.08	<.02		0.17	0.05		MC091091	GG1	11.76	0.5	25.2
MC091291	GG1	278	2	339	0.60	0.01	2.7	6.5	0.1	19.7	0.4	<.02		0.16	0.05		MC091291	GG1	10.5	0.1	22.5
MC090192	GG1	218.9	1	267	0.27	0.01	1.2	4.9	0.1	2.31	0.04	<.02		<.05			MC090192	GG1	10.2	0.05	21.8
MC090292	GG1	219	4	267	0.37	0.01	1.6	4.38	0.09	2.15	0.04	<.02		0.15	0.05		MC090292	GG1	9.49	0.05	20.3
MC090392	GG1	232	5	283	0.73	0.01	3.3	2.44	0.05	1.59	0.03	<.02		<.05			MC090392	GG1	5.99	0.07	12.8
MC090592	GG1	248.4	1	303	0.50	0.01	2.2	5.6	0.1	9.2	0.2	<.02		0.11	0.05		MC090592	GG1	12.1	0.1	25.9
MC090692	GG1	227	5	277	0.50	0.01	2.2	3.2	0.06	1.46	0.03	<.04		0.1	0.05		MC090692	GG1	8.94	0.05	19.1
MC090792	GG1	218	4	266	0.29	0.01	1.28	4.4	0.1	1.21	0.03	<.02		0.1	0.05		MC090792	GG1	11.1	0.2	23.7
MC090892	GG1				0.23	0.01	1	4.53	0.09	0.54	0.01	<.02		0.08	0.05		MC090892	GG1			
MC090992	GG1	210	4	256	0.21	0.01	0.93	4.73	0.09	0.43	0.03	<.03		0.13	0.05		MC090992	GG1	11.5	0.2	24.6
MC091092	GG1	213	4	259	0.25	0.02	1.1	4.59	0.09	0.89	0.03	<.03		0.16	0.05		MC091092	GG1	11.68	0.08	25
MC091192	GG1	230	5	280	0.56	0.01	2.5	3.7	0.1	2.22	0.04	<.03		0.24	0.05		MC091192	GG1	9.84	0.08	21.1
MC091292	GG1	220	4	269	0.29	0.01	1.3	4.46	0.09	2.1	0.04	<.03		0.17	0.05		MC091292	GG1	11.3	0.1	24.2
MC090193	GG1	215	4	261	0.23	0.01	1	4.48	0.09	0.57	0.01	0.03		0.16	0.05		MC090193	GG1	11.51	0.08	24.6
MC090393	GG1	212	4	268	0.24	0.01	1.1	4.47	0.09	0.7	0.03	<.03		0.15	0.05		MC090393	GG1	11.4	0.1	24.4
MC090493	GG1	290	6	354	0.34	0.01	1.5	6.2	0.1	30.6	0.6	<.02		0.11	0.05		MC090493	GG1	12.4	0.1	26.5

Blue Lake Drips

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC100891	BLD	8/17/91	8.90	7.42							6.63	6.60	0.2	-2.004	0.071	-0.085	-0.067	-1.995	523	1.24	0.0097
MC100991	BLD	9/14/91	8.80	7.56							7.17	6.74	2.92	-2.14	0.253	0.096	0.272	-1.927	541	1.31	0.0103
MC101291	BLD	12/20/91	8.70	7.95	560		537				6.24	6.25	-0.07	-2.561	0.532	0.376	0.892	-2.097	493	1.13	0.0091
MC100192	BLD	1/30/92	8.70	8.07	520		523				6.45	5.98	3.5	-2.715	0.613	0.457	1.085	-2.04	479	1.05	0.0092
MC100292	BLD	2/26/92	8.70	8.14	530		533				6.51	5.99	3.84	-2.786	0.687	0.531	1.233	-2.024	480	1.05	0.0093
MC100392	BLD	3/26/92	8.70	7.86	540		534				6.59	6.07	3.8	-2.472	0.462	0.306	0.753	-2.069	486	1.13	0.0094
MC100492	BLD	4/25/92	8.80	8.10	540		534				6.29	6.29	0.04	-2.7	0.72	0.564	1.215	-2.143	503	1.28	0.0091
MC100692	BLD	6/23/92	8.75	7.84	577		570				6.25	6.57	-2.34	-2.429	0.485	0.329	0.705	-1.999	518	1.40	0.0093
MC100792	BLD	7/29/92	8.90	7.75	592		581				6.87	6.76	0.71	-2.328	0.44	0.284	0.623	-1.944	539	1.38	0.01
MC100892	BLD	8/15/92																			
MC100992	BLD	9/15/92	9.90	7.74	585		578				6.90	6.90	0.01	-2.301	0.451	0.296	0.681	-1.952	548	1.33	0.0101
MC101092	BLD	10/23/92	8.80	7.74	568		562				6.56	6.46	0.72	-2.337	0.372	0.216	0.536	-1.985	516	1.23	0.0096
MC101192	BLD	11/21/92	9.10	7.97	555		549				6.25	6.09	1.16	-2.596	0.538	0.383	0.915	-2.03	487	1.12	0.0091
MC101292	BLD	12/22/92	8.80	7.99					542	519	6.11	5.91	1.52	-2.627	0.526	0.369	0.906	-2.089	473	1.07	0.0088
MC100193	BLD	1/23/93	8.75	8.06	525		516				5.89	5.83	0.51	-2.709	0.568	0.412	0.994	-2.069	464	1.06	0.0086
MC100393	BLD	3/2/93	8.75	7.96	510		512				5.76	5.69	0.55	-2.622	0.45	0.294	0.753	-2.055	451	1.07	0.0084
MC100493	BLD	4/4/93	8.70	8.36	521		523				6.03	6.00	0.29	-2.979	0.93	0.774	1.66	-2.23	483	1.21	0.0087

Blue Lake Drips

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC100891	BLD	277	2	337	2.84	0.06	12.6	36.3	0.7	4.24	0.08	0.03	0.02	<.05			MC100891	BLD	10.25	0.07	21.9
MC100991	BLD	281	2	342	2.71	0.05	12	39.5	0.8	4.13	0.08	<.02		0.26	0.05		MC100991	BLD	10.58	0.08	22.6
MC101291	BLD	262	3	320	3.00	0.06	13.3	30.8	0.6	5.03	0.1	<.02		0.12	0.05		MC101291	BLD	9.67	0.05	20.7
MC100192	BLD	244.5	3	298	2.97	0.06	13.1	35.7	0.7	4.85	0.097	0.03	0.02	<.05			MC100192	BLD	9.72	0.07	20.8
MC100292	BLD	245	2	299	2.87	0.06	12.7	36.6	0.7	4.34	0.09	0.03	0.02	0.12	0.05		MC100292	BLD	9.6	0.06	20.5
MC100392	BLD	262	5	319	0.0205	0.02	2.83	31.7	0.6	4.68	0.09	<.02		0.08	0.05		MC100392	BLD	8.4	0.1	18
MC100492	BLD	270.7	0.5	330	2.65	0.05	11.7	26.2	0.5	4.9	0.1	<.02		0.11	0.05		MC100492	BLD	11.27	0.06	24.1
MC100692	BLD	275	6	335	3.17	0.06	14	35.5	0.7	3.93	0.08	<.04		0.11	0.05		MC100692	BLD	10.72	0.09	22.9
MC100792	BLD	282	6	344	2.82	0.06	12.5	38.2	0.8	4.35	0.09	0.03	0.02	0.09	0.05		MC100792	BLD	11.1	0.2	23.7
MC100892	BLD				2.70	0.05	11.95	38	0.8	2.74	0.05	0.027	0.02	0.08	0.05		MC100892	BLD			
MC100992	BLD	290	6	354	2.60	0.05	11.5	38.5	0.8	3.54	0.07	<.03		0.14	0.05		MC100992	BLD	11.1	0.1	23.7
MC101092	BLD	270	5	329	2.49	0.05	11	37.4	0.7	3.63	0.07	0.03	0.02	0.17	0.05		MC101092	BLD	11.8	0.1	25.2
MC101192	BLD	253	5	308	2.51	0.05	11.1	36.3	0.7	3.61	0.07	<.03		0.17	0.05		MC101192	BLD	11.2	0.1	24
MC101292	BLD	247	5	301	2.57	0.05	11.4	32.7	0.7	3.67	0.07	<.03		0.18	0.05		MC101292	BLD	10.92	0.06	23.4
MC100193	BLD	240	5	293	2.53	0.05	11.2	35.2	0.7	3.68	0.07	<.03		0.15	0.05		MC100193	BLD	10.85	0.05	23.2
MC100393	BLD	232	5	283	2.53	0.05	11.2	36.6	0.7	3.58	0.07	<.03		0.15	0.05		MC100393	BLD	10	0.1	21.4
MC100493	BLD	264	5	322	1.89	0.04	8.4	22.6	0.5	3.76	0.08	<.02		0.14	0.05		MC100493	BLD	11.55	0.07	24.7

Blue Lake Drips																					
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC100891	BLD	71.4	0.3	34.7	0.2	4.10	0.05	0.5	0.2	0.11	0.06	0.017	0.099	0.099	0.006	0.084	0.009	0.1	0.03
MC100991	BLD	79.1	0.4	36.5	0.2	4.31	0.04	0.6	0.2	0.08	0.08	0.019	0.01	0.11	0.01	0.1	0.01	0.11	0.04
MC101291	BLD	67.8	0.4	38.0	0.3	4.40	0.05	0.55	0.02	0.19	0.02	0.0019	0.0009	0.093	0.001	0.0863	0.0009	0.018	0.002
MC100192	BLD	64.2	0.2	36.7	0.3	4.49	0.07	0.68	0.01	0.18	0.01	0.0007	0.0001	0.0864	0.0004	0.0802	0.0004	0.013	0.007
MC100292	BLD	65.3	0.6	37.2	0.3	3.85	0.07	0.34	0.08	0.21	0.01	<.0001		0.0865	0.0006	0.0779	0.0007	<.001	
MC100392	BLD	68.0	0.3	36.4	0.4	4.12	0.07	0.48	0.02	0.17	0.01	<.0001		0.0865	0.0008	0.0805	0.0005	<.001	
MC100492	BLD	68.9	0.4	32.4	0.4	4.00	0.04	0.51	0.01	<.01		0.0011	0.0001	0.0861	0.0004	0.0797	0.0007	0.0015	0.0009
MC100692	BLD	71.3	0.6	30.6	0.3	3.61	0.03	0.48	0.01	<.01		<.001		0.092	0.001	0.084	0.001	0.012	0.003
MC100792	BLD	77.8	0.6	33.9	0.2	4.10	0.08	0.52	0.02	<.01		<.001		0.095	0.001	0.086	0.001	<.01	
MC100892	BLD																		
MC100992	BLD	76.9	0.4	34.8	0.3	4.13	0.03	0.52	0.01	<.01		0.003	0.001	0.097	0.001	0.086	0.001	0.007	0.003
MC101092	BLD	70.6	0.5	34.6	0.3	4.02	0.05	0.53	0.01	<.01		<.001		0.097	0.001	0.082	0.001	<.003	
MC101192	BLD	64.4	0.3	34.5	0.2	4.09	0.04	0.57	0.01	<.01		<.001		0.092	0.001	0.078	0.001	0.004	0.003
MC101292	BLD	61.3	0.4	34.6	0.2	4.17	0.05	0.55	0.01	0.07	0.01	0.003	0.001	0.089	0.001	0.077	0.001	0.026	0.003
MC100193	BLD	59.1	0.4	33.6	0.5	3.7	0.2	0.53	0.03	0.01	0.01	0.001	0.001	0.087	0.001	0.075	0.001	0.011	0.003
MC100393	BLD	58	0.3	32.6	0.3	3.78	0.05	0.53	0.01	<.01		<.001		0.086	0.001	0.072	0.001	0.005	0.003
MC100493	BLD	64.4	0.7	32.0	0.3	3.94	0.09	0.48	0.01	0.01	0.01	0.001	0.001	0.088	0.001	0.077	0.001	0.007	0.003

Coon Lake Drips

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC151091	CLD	10/12/91	9.10	7.64		462	470				5.64	5.21	3.6	-2.264	0.255	0.099	0.192	-2.698	425	1.61	0.008
MC151291	CLD	12/20/91	9.10	8.01	398		379				4.46	4.43	0.24	-2.706	0.459	0.34	0.595	-2.732	356	1.92	0.0065
MC150192	CLD	1/30/92	9.10	8.09	400		402				4.84	4.57	2.59	-2.78	0.599	0.443	0.832	-2.715	372	1.80	0.0069
MC150292	CLD	2/22/92	9.15	8.00	402		404				4.90	4.58	3.07	-2.692	0.51	0.354	0.661	-2.689	372	1.77	0.007
MC150392	CLD	3/27/92	9.10	8.09	379		376				4.48	4.27	2.12	-2.803	0.547	0.392	0.727	-2.754	346	1.80	0.0064
MC150592	CLD	5/13/92	9.10	7.92	380		377				4.38	4.32	0.66	-2.627	0.39	0.234	0.376	-2.753	350	1.96	0.0064
MC150692	CLD	6/20/92	9.60	7.65	410		406				4.47	4.56	-0.86	-2.333	0.162	0.006	-0.093	-2.726	366	2.06	0.0066
MC150792	CLD	7/29/92	9.40	7.59	426		422				4.86	4.78	0.79	-2.256	0.151	-0.004	-0.114	-2.682	386	2.04	0.0071
MC150892	CLD	8/15/92																			
MC150992	CLD	9/15/92	9.10	7.53	425		421				4.95	4.66	2.71	-2.202	0.079	-0.076	-0.235	-2.655	381	1.91	0.0071
MC151092	CLD	10/23/92	9.20	7.70	428		424				4.89	4.85	0.41	-2.351	0.264	0.108	0.139	-2.729	393	1.90	0.0071
MC151192	CLD	11/21/92	9.10	7.94	428		424				4.82	4.71	1.07	-2.607	0.479	0.323	0.572	-2.721	383	1.88	0.007
MC151292	CLD	12/22/92	9.20	8.07			404		422		4.73	4.64	0.82	-2.744	0.588	0.433	0.807	-2.753	376	1.82	0.0068
MC150193	CLD	1/23/93	9.50	8.17	430		422				4.52	4.46	0.60	-2.861	0.66	0.504	0.956	-2.752	361	1.82	0.0066
MC150393	CLD	3/2/93	9.20	8.12	398		401				4.53	4.34	1.91	-2.827	0.583	0.427	0.817	-2.738	354	1.73	0.0065
MC150493	CLD	4/4/93	9.20	8.27	369		372				4.13	4.13	0.00	-3.001	0.691	0.535	0.987	-2.801	334	1.92	0.006
MC150593	CLD	5/12/93	9.10	7.83			354	369			3.97	3.88	1.1	-2.577	0.224	0.068	0.048	-2.821	314	1.94	0.0058

Coon Lake Drips																				
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC151091	CLD	68.2	0.9	25.8	0.5	1.80	0.04	0.76	0.04	0.22	0.03	0.0015	0.0002	0.156	0.003	0.03	0.002	0.031	0.001
MC151291	CLD	61.7	0.4	20.1	0.2	1.31	0.07	0.57	0.02	0.18	0.01	0.001	0.001	0.1147	0.0009	0.025	0.001	0.028	0.005
MC150192	CLD	61.2	0.5	20.6	0.1	1.50	0.04	0.71	0.02	0.2	0.01	0.0003	0.0001	0.1126	0.0007	0.0243	0.0002	0.008	0.001
MC150292	CLD	61.6	0.5	21.1	0.2	1.39	0.04	0.61	0.02	0.22	0.01	<.0001		0.109	0.0009	0.0249	0.0004	0.015	0.001
MC150392	CLD	56.6	0.3	19.0	0.1	1.40	0.03	0.65	0.01	0.14	0.02	<.0001		0.1036	0.0006	0.0223	0.0003	0.0559	0.0006
MC150592	CLD	57.2	0.4	17.7	0.09	1.25	0.03	0.57	0.01	<.01		<.0001		0.1036	0.0008	0.0221	0.0003	<.001	
MC150692	CLD	59.0	0.5	17.4	0.1	1.56	0.04	0.8	0.01	0.03	0.01	0.002	0.001	0.117	0.001	0.026	0.001	0.011	0.003
MC150792	CLD	64.6	0.6	19.2	0.1	1.03	0.03	0.48	0.02	<.01		<.001		0.12	0.001	0.025	0.001	0.005	0.003
MC150892	CLD																		
MC150992	CLD	64.2	0.4	20.4	0.3	1.16	0.04	0.6	0.01	<.01		<.001		0.122	0.001	0.027	0.001	<.003	
MC151092	CLD	63.3	0.3	20.2	0.1	1.23	0.03	0.63	0.02	<.01		<.001		0.131	0.002	0.027	0.001	<.003	
MC151192	CLD	62.1	0.3	20.0	0.2	1.36	0.04	0.63	0.01	<.01		<.001		0.121	0.001	0.025	0.001	0.006	0.003
MC151292	CLD	60.1	0.4	20.0	0.2	1.4	0.03	0.66	0.01	0.07	0.01	<.001		0.121	0.001	0.026	0.001	0.004	0.003
MC150193	CLD	57.8	0.3	19.2	0.2	0.9	0.2	0.61	0.03	<.01		0.001	0.001	0.12	0.001	0.024	0.001	0.003	0.003
MC150393	CLD	56.6	0.5	19.8	0.1	1.35	0.09	0.68	0.02	<.01		0.001	0.001	0.119	0.001	0.024	0.001	0.005	0.003
MC150493	CLD	53.8	0.1	16.9	0.05	0.84	0.06	0.6	0.01	0.02	0.01	0.005	0.01	0.111	0.001	0.024	0.001	0.016	0.003
MC150593	CLD	51.7	0.3	16.2	0.1	1	0.1	0.56	0.01	<.01		0.004	0.001	0.102	0.001	0.026	0.001	0.008	0.003

Coon Lake Drips

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC151091	CLD	250	2	305	0.38	0.01	1.7	6.9	0.1	1.45	0.03	<.02		0.19	0.05		MC151091	CLD	6.61	0.05	13.2
MC151291	CLD	211	2	258	0.45	0.01	2	6.9	0.1	1.05	0.02	<.02		0.13	0.05		MC151291	CLD	5.02	0.05	10.7
MC150192	CLD	215.9	5	263	0.94	0.02	4.2	7.0	0.1	1.62	0.03	<.02		<.05			MC150192	CLD	5.37	0.03	11.5
MC150292	CLD	214	4	261	1.25	0.02	5.5	7.4	0.1	1.94	0.04	<.02		0.09	0.05		MC150292	CLD	5.22	0.07	11.2
MC150392	CLD	204	2	248	0.48	0.01	2.14	6.7	0.1	0.78	0.02	<.02		0.06	0.05		MC150392	CLD	4.32	0.02	9.3
MC150592	CLD	205.1	2	250	0.60	0.01	2.7	6.6	0.1	1.24	0.02	<.02		0.07	0.05		MC150592	CLD	5.94	0.09	12.7
MC150692	CLD	214	4	261	1.18	0.02	5.2	6.9	0.1	1.65	0.03	<.04		0.07	<.05		MC150692	CLD	5.74	0.06	12.3
MC150792	CLD	224	5	273	1.03	0.02	4.56	7.2	0.1	2.74	0.05	<.02		0.1	<.05		MC150792	CLD	5.8	0.1	12.4
MC150892	CLD				0.73	0.01	3.2	7.1	0.1	0.56	0.03	<.02		<.05			MC150892	CLD			
MC150992	CLD	222	4	270	0.69	0.01	3.1	7.7	0.2	0.87	0.02	<.03		0.07	0.05		MC150992	CLD	6.11	0.07	13.1
MC151092	CLD	233	5	284	0.48	0.01	2.1	6.6	0.1	0.68	0.01	<.03		0.09	0.05		MC151092	CLD	6.60	0.06	14.1
MC151192	CLD	227	5	276	0.36	0.01	1.6	6.8	0.1	0.53	0.01	<.03		0.1			MC151192	CLD	6.28	0.08	13.4
MC151292	CLD	223	4	272	0.39	0.01	1.7	6.5	0.1	0.62	0.03	<.03		0.09	0.05		MC151292	CLD	6.02	0.08	12.9
MC150193	CLD	215	4	262	0.38	0.01	1.7	6.7	0.1	0.61	0.01	<.03		0.1	0.05		MC150193	CLD	6.00	0.05	12.8
MC150393	CLD	207	4	252	0.57	0.01	2.5	7.0	0.1	0.83	0.03	<.03		0.09	0.05		MC150393	CLD	5.96	0.08	12.8
MC150493	CLD	197	4	240	0.58	0.01	2.6	6.2	0.1	0.79	0.03	<.02		0.09	0.05		MC150493	CLD	5.70	0.1	12.2
MC150593	CLD	186	4	226	0.33	0.01	1.5	6	0.1	0.68	0.03	<.03		0.09	0.05		MC150593	CLD	4.50	0.1	9.6

Garden of the Gods 2																					
					CP 1	CP 2	Corr CP	YSI 9	YSI 10	Corr YSI											
Sample ID	Loc	Date	Temp	pH	Cond	Cond	Cond	Cond	Cond	Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC161091	GG2	10/12/91	9.20	7.97		428	436				5.42	4.70	6.45	-2.244	0.152	-0.004	-0.051	-3.127	397	1.75	0.0075
MC161291	GG2	12/20/91	9.20	7.97	443		424				4.78	4.87	0.82	-2.628	0.538	0.382	0.645	-3.167	394	2.09	0.007
MC160192	GG2	1/30/92	9.20	8.20	425		427				5.18	4.84	3.08	-2.861	0.772	0.617	1.15	-3.135	399	1.93	0.0073
MC160292	GG2	2/22/92	9.35	7.95	425		427				5.29	4.83	4.18	-2.608	0.534	0.378	0.678	-3.077	400	1.92	0.0074
MC160392	GG2	3/27/92	9.45	8.04	426		422				5.05	4.85	1.83	-2.691	0.619	0.463	0.838	-3.149	395	1.97	0.0072
MC160592	GG2	5/13/92	9.40	7.93	420		416				4.87	4.84	0.31	-2.58	0.508	0.352	0.585	-3.203	397	2.11	0.0071
MC160692	GG2	6/20/92	9.80	7.70	420		416				4.87	4.62	2.33	-2.365	0.271	0.115	0.116	-3.112	383	2.12	0.007
MC161092	GG2	10/23/92	9.40	7.62	450		446				4.98	4.93	0.45	-2.261	0.21	0.055	0.01	-3.141	405	2.01	0.0072
MC161192	GG2	11/21/92	9.10	7.85	465		460				5.17	5.03	1.22	-2.488	0.455	0.299	0.485	-3.111	412	2.06	0.0074
MC161292	GG2	12/22/92	9.20	8.09					448	429	5.00	4.92	0.77	-2.737	0.667	0.512	0.928	-3.186	403	1.98	0.0072
MC160493	GG2	4/4/93	9.40	8.00	426		429				4.80	4.66	1.3	-2.668	0.551	0.396	0.686	-3.189	384	2.04	0.0069
Garden of the Gods 3																					
MC171091	GG3	10/12/91	9.20	7.61		440	448				5.55	4.84	6.25	-2.269	0.183	0.027	0.041	-2.869	410	1.64	0.0077
Garden of the Gods 4																					
MC181091	GG4	10/12/91	9.20	7.65		395	403				4.93	4.40	5.22	-2.339	0.152	-0.004	-0.04	-3.083	372	1.71	0.0069

Garden of the Gods 2																			
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC161091	GG2	66.7	0.6	23.2	0.2	3.36	0.07	0.66	0.04	0.21	0.03	0.0007	0.0002	0.141	0.002	0.06	0.003	0.03	0.004
MC161291	GG2	68.0	0.4	20.7	0.2	2.39	0.03	0.24	0.01	0.19	0.01	0.0011	0.0006	0.126	0.001	0.0505	0.0007	0.013	0.003
MC160192	GG2	66.8	0.5	21.0	0.07	2.40	0.04	0.28	0.01	0.18	0.01	0.0002	0.0001	0.124	0.0002	0.053	0.0002	0.015	0.001
MC160292	GG2	67.4	0.4	21.3	0.3	3.3	0.1	0.79	0.03	0.25	0.04	<.002		0.124	0.002	0.054	0.002	0.018	0.007
MC160392	GG2	65.6	0.3	20.2	0.2	2.25	0.02	0.26	0.01	0.16	0.01	0.00037	0.00007	0.1186	0.0009	0.0461	0.0003	0.012	0.001
MC160592	GG2	64.8	0.2	18.6	0.2	2.22	0.02	0.25	0.01	<.01		<.0001		0.12	0.001	0.0494	0.0003	<.001	
MC160692	GG2	64.9	0.6	18.6	0.2	2.08	0.05	0.15	0.02	<.01		<.001		0.123	0.001	0.054	0.001	<.003	
MC161092	GG2	65.2	0.6	19.7	0.4	2.21	0.05	0.25	0.01	<.01		<.001		0.128	0.001	0.052	0.001	<.003	
MC161192	GG2	68.1	0.4	20.1	0.2	2.34	0.04	0.31	0.01	<.01		<.001		0.135	0.001	0.049	0.001	0.004	0.003
MC161292	GG2	65.1	0.7	19.9	0.3	2.44	0.06	0.3	0.01	<.01		<.001		0.129	0.001	0.053	0.001	0.004	0.003
MC160493	GG2	63.3	0.3	18.8	0.1	1.88	0.08	0.25	0.01	0.02	0.01	<.001		0.124	0.001	0.045	0.001	0.005	0.003
Garden of the Gods 3																			
MC171091	GG3	66.3	0.9	24.6	0.5	4.10	0.08	0.94	0.06	0.2	0.02	0.0015	0.0002	0.147	0.002	0.076	0.003	0.033	0.001
Garden of the Gods 4																			
MC181091	GG4	59.1	0.6	21.0	0.5	4.7	0.1	1.25	0.04	0.16	0.02	0.0016	0.0002	0.118	0.001	0.06	0.001	0.105	0.009

Garden of the Gods 2																					
Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC161091	GG2	227	2	276	0.74	0.01	3.3	2.55	0.05	2.03	0.04	<.02		0.12	0.05		MC161091	GG2	8.70	0.06	18.6
MC161291	GG2	231	2	282	0.73	0.01	3.2	2.35	0.05	2.08	0.04	<.02		0.09	0.05		MC161292	GG2	7.03	0.09	15
MC160192	GG2	233	5	284	0.74	0.01	3.3	2.51	0.05	2.83	0.06	<.02		<.05			MC160192	GG2	7.4	0.06	15.8
MC160292	GG2	231	3	282	0.77	0.02	3.42	2.84	0.06	3.05	0.06	<.02		0.14	0.05		MC160292	GG2	7.2	0.05	15.4
MC160392	GG2	235	2	287	0.75	0.01	3.3	2.45	0.05	1.64	0.03	<.02		<.05			MC160392	GG2	5.87	0.03	12.6
MC160592	GG2	234.6	3	286	0.63	0.01	2.8	2.16	0.04	1.98	0.04	<.02		0.08	0.05		MC160592	GG2	8.3	0.1	17.8
MC160692	GG2	224	4	273	0.48	0.01	2.12	2.65	0.05	2.07	0.04	<.04		0.11	0.05		MC160692	GG2	7.9	0.1	16.9
MC161092	GG2	238	5	290	0.76	0.02	3.37	2.49	0.05	2.36	0.05	<.03		0.1	0.05		MC161092	GG2	8.7	0.1	18.6
MC161192	GG2	242	5	295	0.95	0.02	4.2	2.59	0.06	2.39	0.05	<.03		0.1	0.05		MC161192	GG2	7.84	0.08	16.8
MC161292	GG2	239	5	291	0.70	0.01	3.1	2.26	0.05	1.67	0.03	<.03		0.11	0.05		MC161292	GG2	7.7	0.1	16.5
MC160493	GG2	225	5	275	0.67	0.01	3	2.27	0.05	1.95	0.04	<.02		0.09	0.05		MC160493	GG2	8.05	0.07	17.2
Garden of the Gods 3																					
MC171091	GG3	229	2	280	0.418	0.008	1.85	4.70	0.09	4.21	0.08	<0.2		0.18	0.05		MC171091	GG3	11.0	0.2	23.5
Garden of the Gods 4																					
MC181091	GG4	213	3	260	0.53	0.01	2.3	3.06	0.06	1.11	0.02	<.02		0.13	5		MC181091	GG4	9.03	0.05	19.3

Flim Flam Creek

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC230192	FFC	1/25/92	4.10	7.94					525	503	6.41	6.10	2.31	-2.625	0.454	0.294	0.538	-2.198	476	1.44	0.0092
MC230392	FFC	3/27/92	5.60	7.88	507		502				5.93	5.50	3.41	-2.605	0.357	0.199	0.345	-2.228	430	1.54	0.0085
MC230692	FFC	6/23/92	15.00	8.02				555		558	5.84	5.77	0.5	-2.669	0.662	0.511	1.127	-2.285	451	1.55	0.0084
MC230792	FFC	7/29/92	16.40	7.86	547		541				5.96	5.85	0.86	-2.496	0.537	0.386	0.896	-2.272	456	1.56	0.0086
MC230892	FFC	8/15/92																			
MC230992	FFC	9/15/92	15.90	7.79			425	443			4.78	4.61	1.7	-2.509	0.273	0.123	0.414	-2.434	364	1.38	0.0069
MC231092	FFC	10/23/92	11.60	7.66				579		557	6.16	6.05	0.85	-2.298	0.275	0.121	0.347	-2.255	470	1.37	0.0089
MC231192	FFC	11/21/92	6.40	7.74				415		398	4.32	4.26	0.64	-2.581	0.013	-0.145	-0.402	-2.403	333	1.83	0.0063
MC231292	FFC	12/22/92	2.60	7.98					603	578	6.35	6.23	0.85	-2.659	0.484	0.323	0.541	-2.164	484	1.52	0.0092
MC230193	FFC	1/23/93	1.80	8.02				580		558	5.97	5.98	-0.06	-2.71	0.466	0.304	0.529	-2.234	464	1.38	0.0087
MC230393	FFC	3/2/93	1.30	7.87				596		571	6.27	6.00	2.04	-2.558	0.324	0.161	0.246	-2.216	470	1.34	0.00902
MC230493	FFC	4/4/93	5.10	7.70				439		421	4.67	4.29	3.83	-2.496	0.018	-0.141	-0.357	-2.434	347	1.59	0.0067
MC230593	FFC	5/12/93	9.90	7.63				516		495	5.44	5.38	0.5	-2.303	0.175	0.02	0.067	-2.336	423	1.54	0.0079

Flim Flam Creek

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC230192	FFC	73.0	0.4	30.8	0.2	4.30	0.06	1.22	0.01	0.24	0.01	0.0013	0.0002	0.072	0.0002	0.0663	0.0002	0.018	0.004
MC230392	FFC	69.6	0.4	27.3	0.3	3.86	0.05	0.92	0.02	0.24	0.01	0.01	0.0003	0.08	0.01	0.0724	0.0005	0.045	0.002
MC230692	FFC	68.7	0.5	26.7	0.4	3.80	0.04	1.14	0.03	0.14	0.01	0.044	0.001	0.075	0.001	0.083	0.001	0.096	0.005
MC230792	FFC	70.0	0.5	27.1	0.1	4.20	0.05	1.1	0.02	0.2	0.02	0.058	0.004	0.08	0.001	0.08	0.001	0.106	0.003
MC230892	FFC																		
MC230992	FFC	52.5	0.4	23.0	0.2	4.08	0.06	3.07	0.03	0.1	0.01	0.004	0.001	0.062	0.001	0.095	0.001	0.069	0.003
MC231092	FFC	68.0	0.3	30.0	0.6	5.70	0.03	2	0.02	<.01		<.001		0.079	0.001	0.079	0.001	<.003	
MC231192	FFC	52.7	0.4	17.4	0.1	3.84	0.04	3.13	0.04	0.05	0.01	0.003	0.001	0.075	0.001	0.072	0.001	0.042	0.003
MC231292	FFC	73.7	0.8	29.3	0.2	4.96	0.05	1.15	0.02	0.12	0.01	0.024	0.001	0.085	0.001	0.079	0.001	0.05	0.003
MC230193	FFC	67.1	0.7	29.4	0.3	3.80	0.2	1.2	0.02	0.05	0.01	0.018	0.001	0.063	0.001	0.065	0.001	0.035	0.003
MC230393	FFC	69.1	0.3	31.3	0.6	4.10	0.1	1.31	0.02	0.37	0.01	0.088	0.001	0.061	0.001	0.071	0.001	0.116	0.003
MC230493	FFC	55.0	0.5	21.0	0.3	2.76	0.09	1.79	0.03	0.25	0.01	0.046	0.001	0.065	0.001	0.057	0.001	0.193	0.003
MC230593	FFC	64.0	0.4	25.2	0.2	2.86	0.09	1.17	0.01	0.12	0.01	0.044	0.001	0.081	0.001	0.075	0.001	0.099	0.003

Flim Flam Creek

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC230192	FFC	232	6	283	8.8	0.2	39	20.5	0.4	14.3	0.3	<.02		<.05			MC230192	FFC	4.5	0.03	9.6
MC230392	FFC	207	2	252	7.6	0.2	33.5	19.7	0.4	14.6	0.3	<.02		0.11	0.05		MC230392	FFC	3.76	0.05	8
MC230692	FFC	224	5	273	7.1	0.1	31.4	19.2	0.4	13.7	0.3	<.04		0.14	0.05		MC230692	FFC	6.17	0.05	13.2
MC230792	FFC	252	5	275	6.6	0.1	29.2	19.7	0.4	15.7	0.3	0.03	0.02	0.3	0.05		MC230792	FFC	6.2	0.1	13.3
MC230892	FFC				5.3	0.1	23.5	18.9	0.4	13.1	0.3	<.02		0.17	0.05		MC230892	FFC			
MC230992	FFC	186	4	225	3.7	0.07	16.4	16.2	0.3	10.9	0.2	<.03		0.16	0.05		MC230992	FFC	5.88	0.07	12.6
MC231092	FFC	237	5	288	5.9	0.1	26	20.5	0.4	16.7	0.3	0.06	0.02	0.25	0.05		MC231092	FFC	5.67	0.06	12.1
MC231192	FFC	154	3	188	5.7	0.1	25.2	15.4	0.3	15.4	0.3	<.03		0.27	0.05		MC231192	FFC	5.49	0.04	11.7
MC231292	FFC	239	5	291	7.9	0.2	35	21.6	0.4	15.4	0.3	<.03		0.25	0.05		MC231292	FFC	5.27	0.07	11.3
MC230193	FFC	234	5	285	7.4	0.1	32.8	19.5	0.4	12.9	0.3	<.03		0.19	0.05		MC230193	FFC	5.76	0.06	12.3
MC230393	FFC	236	5	287	7.3	0.1	32.3	19.8	0.4	12.4	0.2	<.03		0.17	0.05		MC230393	FFC	5.4	0.1	11.6
MC230493	FFC	174	3	212	4.19	0.08	18.5	13.9	0.3	7.8	0.2	<.03		0.17	0.05		MC230493	FFC	6.13	0.08	13.1
MC230593	FFC	221	4	269	5	0.1	22.1	16.9	0.3	9.0	0.2	<.03		0.21	0.05		MC230593	FFC	5.76	0.09	12.3

Lower Level Stream																					
					CP 1	CP 2	Corr CP	YSI 9	YSI 10	Corr YSI											
Sample ID	Loc	Date	Temp	pH	Cond	Cond	Cond	Cond	Cond	Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC200192	LLS	1/31/92	7.80	8.19	580		583				6.86	6.54	2.23	-2.825	0.794	0.638	1.347	-2.239	511	1.28	0.0097
MC200692	LLS	6/22/92	9.30	7.97	569		563				6.22	6.35	-0.96	-2.594	0.594	0.438	0.912	-2.261	495	1.47	0.0091
MC200792	LLS	7/28/92	10.22	7.95	565		559				6.38	6.33	0.37	-2.575	0.594	0.439	0.925	-2.246	495	1.49	0.0092
MC200892	LLS	8/15/92																			
MC200992	LLS	9/14/92	11.60	7.69	503		498				5.68	5.61	0.57	-2.337	0.276	0.122	0.332	-2.339	442	1.43	0.0082
MC201092	LLS	10/22/92	10.00	7.93	597		590				6.64	6.54	0.7	-2.547	0.568	0.413	0.927	-2.243	510	1.30	0.0096
MC201192	LLS	11/21/92	9.65	8.07	485		480				5.38	5.39	-0.08	-2.776	0.561	0.405	0.848	-2.289	420	1.48	0.0078
MC200193	LLS	1/22/93	6.60	8.16	551		542				6.31	6.23	0.55	-2.82	0.713	0.555	1.119	-2.229	485	1.40	0.0091
MC200393	LLS	3/1/93	7.60	8.06	571		573				6.50	6.30	1.43	-2.71	0.633	0.476	1.012	-2.236	493	1.30	0.0093
MC200493	LLS	4/5/93	5.60	8.02	424		427				4.59	4.57	0.18	-2.795	0.345	0.186	0.339	-2.446	361	1.48	0.0067

Lower Level Stream

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC200192	LLS	74.3	0.4	35.1	0.3	5.03	0.07	1.2	0.01	0.213	0.006	<.0001		0.0727	0.0007	0.063	0.0005	0.0096	0.001
MC200692	LLS	71.6	0.4	29.4	0.2	4.20	0.07	1.46	0.02	<.01		<.001		0.079	0.001	0.073	0.001	0.009	0.007
MC200792	LLS	73.8	0.4	30.0	0.3	4.30	0.07	1.4	0.03	<.01		<.001		0.080	0.001	0.072	0.001	0.005	0.003
MC200892	LLS																		
MC200992	LLS	64.1	0.8	27.2	0.2	4.21	0.08	1.8	0.04	0.01	0.01	0.077	0.007	0.077	0.001	0.077	0.001	0.076	0.003
MC201092	LLS	72.2	0.8	33.5	0.2	5.50	0.08	1.5	0.03	<.01		<.001		0.081	0.001	0.075	0.001	<.003	
MC201192	LLS	61.6	0.4	25.1	0.2	4.00	0.05	1.65	0.01	0.13	0.01	0.014	0.001	0.072	0.001	0.063	0.001	0.16	0.003
MC200193	LLS	71.1	0.3	30.6	0.3	4.60	0.3	1.5	0.04	<.01		0.006	0.001	0.076	0.001	0.061	0.001	0.017	0.003
MC200393	LLS	71	0.6	33.0	0.3	4.70	0.1	1.23	0.02	0.01	0.01	0.001	0.001	0.073	0.001	0.062	0.001	0.013	0.003
MC200493	LLS	52.9	0.6	21.7	0.3	2.62	0.09	1.56	0.03	0.03	0.01	0.002	0.001	0.06	0.001	0.049	0.001	0.044	0.003

Lower Level Stream

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC200192	LLS	255	3	311	8	0.2	35.4	19.8	0.4	16.2	0.3	0.04	0.02	<.05			MC200192	LLS	6.05	0.04	12.9
MC200692	LLS	254	5	309	6.7	0.1	29.7	19.1	0.4	14.1	0.3	0.04	0.02	0.13	0.05		MC200692	LLS	7.65	0.06	16.4
MC200792	LLS	250	5	305	6.7	0.1	29.7	19.5	0.4	15.4	0.3	0.02	0.02	0.16	0.05		MC200792	LLS	7.50	0.09	16.0
MC200892	LLS				6.1	0.1	27	19.1	0.4	14.3	0.3	<.02		0.1	0.05		MC200892	LLS			
MC200992	LLS	230	5	281	4.23	0.08	18.7	17.3	0.3	11.7	0.2	<.03		0.19	0.05		MC200992	LLS	7.13	0.06	15.3
MC201092	LLS	256	5	312	6.9	0.1	30.4	20.3	0.4	17.8	0.4	0.03	0.02	0.22	0.05		MC201092	LLS	7.70	0.05	16.5
MC201192	LLS	208	4	254	5.7	0.1	25.2	19.5	0.4	14.3	0.3	<.03		0.22	0.05		MC201192	LLS	6.3	0.05	13.5
MC200193	LLS	242	5	295	8	0.2	35.4	20.2	0.4	14.1	0.3	<.03		0.2	0.05		MC200193	LLS	5.81	0.07	12.4
MC200393	LLS	244	5	298	8.1	0.2	35.9	20.3	0.4	14.4	0.3	<.03		0.17	0.05		MC200393	LLS	6.4	0.1	13.7
MC200493	LLS	183	4	223	5	0.1	22.1	14.2	0.3	9	0.2	<.03		0.16	0.05		MC200493	LLS	6.17	0.08	13.2

Formation Route Creek																					
					CP 1	CP 2	Corr CP	YSI 9	YSI 10	Corr YSI											
Sample ID	Loc	Date	Temp	pH	Cond	Cond	Cond	Cond	Cond	Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC220292	FRC	2/23/92	4.10	7.99	501		504				6.05	5.52	4.22	-2.723	0.429	0.269	0.504	-2.246	430	1.38	0.0086
MC220892	FRC	8/15/92																			
Blue Lake Spring																					
MC240492	BLS	4/25/92	8.70	7.94	538		532				6.25	6.24	0.09	-2.541	0.566	0.41	0.885	-2.076	477	1.34	0.0091
MC240493	BLS	4/4/93	8.65	8.03	500		502				5.76	5.61	1.25	-2.68	0.57	0.413	0.904	-2.107	450	1.30	0.0084
Pipe Organ																					
MC250692	PO	6/23/92	9.20	8.21	555		549				6.29	6.50	-1.57	-2.76	0.928	0.772	1.542	-2.315	519	1.60	0.0092
MC250792	PO	7/29/92	9.60	7.97	558		552				6.49	6.47	0.08	-2.516	0.708	0.552	1.117	-2.287	520	1.57	0.0094
MC251192	PO	11/20/92	8.15	7.80	368		365				4.27	4.16	1.11	-2.524	0.19	0.034	0.048	-2.823	339	1.59	0.0062
MC250493	PO	4/3/93	7.10	8.02	454		457	495		475	5.29	5.31	0.16	-2.655	0.565	0.407	0.796	-2.517	427	1.52	0.0077
Drips Across Bridge																					
MC260692	DAB	6/23/92	9.55	8.16	519		513				5.78	6.02	-1.86	-2.741	0.817	0.662	1.34	-2.399	478	1.55	0.0085
MC261192	DAB	11/20/92	9.20	8.01	506		501				5.96	5.80	1.21	-2.595	0.655	0.499	1.059	-2.594	466	1.38	0.0086
MC261292	DAB	12/21/92	9.40	8.29					540	517	6.30	6.05	1.85	-2.869	0.953	0.797	1.673	-2.431	485	1.34	0.009
MC260493	DAB	4/3/93	8.50	7.99	448		451	488		468	5.28	5.13	1.28	-2.629	0.526	0.37	0.803	-2.629	411	1.34	0.0076
Bedrock Drops 1																					
MC270992	BD1	9/14/92																			
Bedrock Drops 2																					
MC280992	BD2	9/14/92	10.00	7.46							13.11	13.49	-1.38	-2.374	0.029	-0.126	-0.267	-0.701	917	1.71	0.0203

Formation Route Creek																			
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC220292	FRC	67.7	0.3	29.6	0.2	4.17	0.02	1.48	0.02	0.27	0.04	0.0065	0.0008	0.0652	0.0007	0.0634	0.0004	0.027	0.003
MC220892	FRC																		
Blue Lake Spring																			
MC240492	BLS	69.9	0.6	31.4	0.2	3.70	0.04	0.57	0.01	0.01	0.01	0.0028	0.0001	0.0847	0.0008	0.0508	0.0005	<.001	
MC240493	BLS	63.5	0.5	29.4	0.2	3.50	0.1	0.49	0.02	0.04	0.01	0.007	0.001	0.083	0.001	0.048	0.001	0.042	0.003
Pipe Organ																			
MC250692	PO	76.5	0.3	28.8	0.3	1.83	0.04	0.67	0.01	<.01		0.001	0.001	0.084	0.001	0.061	0.001	<.003	
MC250792	PO	78.3	0.3	30.1	0.5	1.90	0.05	0.6	0.02	<.01		<.001		0.082	0.001	0.06	0.001	0.014	0.003
MC251192	PO	50.3	0.5	19.2	0.2	0.49	0.04	5.28	0.07	0.01	0.01	0.006	0.001	0.07	0.001	0.044	0.001	0.15	0.003
MC250493	PO	62.8	0.7	25.0	0.3	1.31	0.08	1.35	0.03	0.01	0.01	0.001	0.001	0.073	0.001	0.047	0.001	0.016	0.003
Drips Across Bridge																			
MC260692	DAB	69.4	0.8	26.9	0.4	1.11	0.08	1.91	0.03	0.01	0.01	0.006	0.001	0.082	0.001	0.059	0.001	0.026	0.009
MC261192	DAB	68.1	0.4	29.8	0.2	0.66	0.04	2.81	0.03	0.02	0.01	0.001	0.001	0.081	0.001	0.051	0.001	0.015	0.003
MC261292	DAB	71.4	0.4	32.1	0.3	1.08	0.04	1.81	0.02	0.02	0.01	0.002	0.001	0.082	0.001	0.047	0.001	0.008	0.003
MC260493	DAB	59.8	0.2	27.1	0.2	0.33	0.04	1.68	0.02	0.04	0.01	0.003	0.001	0.067	0.001	0.041	0.001	0.023	0.003
Bedrock Drops 1																			
MC270992	BD1	70.9	0.4	18.2	0.07	0.86	0.03	0.75	0.02	<.01		0.001	0.001	0.107	0.001	0.024	0.001	<.003	
Bedrock Drops 2																			
MC280992	BD2	168.8	0.8	55.8	0.6	0.72	0.05	2.26	0.02	<.01		<.001		0.294	0.001	0.038	0.001	<.003	

Formation Route Creek																					
Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC220292	FRC	207	1	253	7.8	0.2	34.6	19.2	0.4	14.6	0.3	0.02	0.02	0.16	0.05		MC220292	FRC	2.69	0.05	5.8
MC220892	FRC				5.4	0.1	23.9	18.6	0.4	13.3	0.3	0.033	0.02	0.13	0.05		MC220892	FRC			
Blue Lake Spring																					
MC240492	BLS	268.5	5	327	1.6	0.03	7.1	30	0.6	4.54	0.09	<.02		0.1	0.15		MC240492	BLS	10.2	0.1	218
MC240493	BLS	240	5	292	1.35	0.03	6	29.6	0.6	3.58	0.07	<.03		0.13	0.05		MC240493	BLS	10.06	0.07	21.5
Pipe Organ																					
MC250692	PO	305	6	372	0.33	0.01	1.46	16.1	0.3	1.48	0.1	<.04		0.11	0.05		MC250692	PO	9.17	0.05	19.6
MC250792	PO	302	6	369	0.33	0.01	1.46	16.9	0.4	1.65	0.03	<.02		0.09	0.05		MC250792	PO	9.4	0.1	20.1
MC251192	PO	198	4	242	0.52	0.01	2.3	6.2	0.1	0.91	0.02	<.03		0.04			MC251192	PO	5.55	0.04	11.9
MC250493	PO	251	5	306	0.45	0.01	2	11	0.2	0.81	0.03	<.02		0.11	0.05		MC250493	PO	7.7	0.08	16.5
Drips Across Bridge																					
MC260692	DAB	281	6	342	1.12	0.02	5	14.1	0.3	1.2	0.1	<.04		0.08	0.05		MC260692	DAB	7.46	0.04	16
MC261192	DAB	277	6	338	0.48	0.01	2.1	9.1	0.2	1.01	0.02	<.03		0.19	0.05		MC261192	DAB	6.37	0.06	13.6
MC261292	DAB	287	6	349	0.42	0.01	1.9	13.1	0.3	0.89	0.03	<.03		0.1	0.05		MC261292	DAB	6.32	0.08	13.5
MC260493	DAB	244	5	298	0.51	0.01	2.3	9	0.2	0.69	0.03	<.02		0.06	0.05		MC260493	DAB	5.44	0.06	11.6
Bedrock Drops 1																					
MC270992	BD1				4.8	0.1	21.2	7	1	0.84	0.02	<.03		<.05			MC270992	BD1	1.98	0.07	4.2
Bedrock Drops 2																					
MC280992	BD2	134	3	163	1.90	0.04	8.4	512	10	0.84	0.02	<.03		<.05			MC280992	BD2	2.16	0.03	4.6

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
Boofer Pool																					
MC070691	BP	6/14/91	9.20	7.80							6.86	7.01	-1.01	-2.36	0.439	0.283	0.795	-2.308	541	0.94	0.01
Coon Lake																					
MC110891	CL	8/17/91	9.15	7.18							5.36	5.11	2.12	-1.806	-0.199		-0.79		416	1.91	0.0077
MC110792	CL	7/29/92	9.10	7.70	408		405				4.68	4.56	1.11	-2.384	0.224	0.068	0.031	-2.717	370	2.02	0.0068
MC110892	CL	8/15/92																			
Dragon's Jaw Lake																					
MC120292	DJL	2/23/92	9.00	8.18	470		472				5.71	5.22	4.05	-2.898	0.489	0.333	1.073	-2.311	408	0.62	0.0081
Tar Pits																					
MC130991	TP	9/14/91	9.30	7.67							5.64	5.27	3.12	-2.299	0.163	0.007	0.261	-2.461	420	0.91	0.0081
MC130291	TP	2/23/92	9.10	8.09	412		414				5.09	4.70	3.65	-2.778	0.423	0.267	0.887	-2.545	373	0.70	0.0072
MC130892	TP	8/15/92																			
MC130593	TP	5/12/93	9.10	7.92							4.80	4.62	1.73	-2.612	0.232	0.076	0.498	-2.576	364	0.71	0.007
Lily Pad Lake																					
MC140991	LPL	9/13/91	9.42	7.63							7.19	6.93	1.73	-2.201	0.296	0.141	0.483	-2.331	547	1.01	0.0103
MC140292	LPL	2/23/92	9.50	8.03	565		568				6.97	6.33	4.48	-2.658	0.594	0.439	1.148	-2.413	503	0.86	0.0098
MC140892	LPL	8/15/92																			
Needles Eye Drips																					
MC191291	NE	12/21/91	10.70	8.29		540	548				6.61	6.13	3.52	-2.862	1.006	0.851	1.768	-2.391	500	1.45	0.0092
Sand Source Drips																					
MC210292	SSD	2/23/92	9.00	8.07	487		489				6.10	5.60	3.93	-2.697	0.585	0.429	1.115	-2.311	442	0.87	0.0087
MC210892	SSD	8/15/92																			

Boofer Pool																			
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC070691	BP	65.3	0.6	42.0	0.2	2.42	0.02	1	0.1	0.1	0.04	<.015		0.076	0.004	0.05	0.005	0.1	0.03
Coon Lake																			
MC110891	CL	68.9	0.04	22.0	0.1	1.61	0.04	0.7	0.2	0.11	0.07	<.017		0.14	0.01	0.05	0.01	0.12	0.05
MC110792	CL	61.8	0.6	18.6	0.2	1.00	0.04	0.46	0.02	0.02	0.01	0.003	0.001	0.12	0.001	0.027	0.001	0.027	0.003
MC110892	CL																		
Dragon's Jaw Lake																			
MC120292	DJL	42.9	0.4	41.6	0.3	2.59	0.08	0.82	0.03	0.15	0.02	0.002	0.002	0.055	0.022	0.037	0.002	0.029	0.008
Tar Pits																			
MC130991	TP	52.3	0.3	35.0	0.2	2.32	0.04	1.1	0.2	0.14	0.07	0.02	0.01	0.09	0.01	0.06	0.01	0.13	0.05
MC130292	TP	41.2	0.3	35.5	0.2	2.20	0.05	1.12	0.01	0.14	0.02	<.0001		0.064	0.001	0.033	0.001	0.011	0.002
MC130892	TP																		
MC130593	TP	39.1	0.2	33.2	0.2	1.90	0.1	1.23	0.02	<.01		0.004	0.001	0.071	0.001	0.036	0.001	0.017	0.003
Lily Pad Lake																			
MC140991	LPL	70.9	0.6	42.6	0.2	2.88	0.05	<.4		0.1	0.06	0.02	0.01	0.058	0.008	0.06	0.01	0.12	0.05
MC140292	LPL	63.4	0.3	44.3	0.4	3.04	0.04	0.47	0.01	0.27	0.02	0.0044	0.0005	0.0459	0.0007	0.0424	0.0006	0.038	0.002
MC140892	LPL																		
Needles Eye Drips																			
MC191291	NE	77.3	0.6	32.0	0.1	2.26	0.02	0.36	0.02	0.23	0.04	0.0017	0.0004	0.0897	0.0006	0.0448	0.0003	0.020	0.001
Sand Source Drips																			
MC210292	SSD	56.3	0.6	38.9	0.3	1.35	0.07	0.72	0.02	0.19	0.04	<.0001		0.034	0.002	0.031	0.002	0.011	0.002
MC210892	SSD																		

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
Boofer Pool																					
MC070691	BP	294	2	359	7.0	0.1	31	19.5	0.4	8.2	0.2	<.02		0.36	0.05		MC070691	BP	6.01	0.07	12.9
Coon Lake																					
MC110891	CL	247	2	302	0.57	0.01	2.5	7.1	0.1	0.97	0.02	<.02		<.05			MC110891	CL	5.49	0.06	11.7
MC110792	CL	215	4	263	0.85	0.02	3.76	6.8	0.1	1.62	0.03	<.02		0.08	0.05		MC110792	CL	5.97	0.07	12.8
MC110892	CL				0.91	0.02	4	6.8	0.1	0.61	0.03	<.02		<.05			MC110892	CL			
Dragon's Jaw Lake																					
MC120292	DJL	206	2	251	4.9	0.1	21.7	26.9	0.5	7.0	0.1	<.02		0.14	0.05		MC120292	DJ	6.34	0.06	13.6
Tar Pits																					
MC130991	TP	246	1	300	0.08	0.02	0.35	15.5	0.3	0.70	0.01	<.02		0.29	0.05		MC130991	TP	5.53	0.06	11.8
MC130292	TP	217	1	265	0.06	0.01	0.27	15.5	0.3	0.86	0.03	<.02		0.17	0.05		MC130292	TP	5.09	0.07	11.5
MC130892	TP				0.07	0.01	0.31	15.1	0.3	0.40	0.03	<.02		0.07	0.05		MC130892	TP			
MC130593	TP	214	4	260	0.04	0.01	0.2	15.2	0.3	1.03	0.03	<.03		0.20	0.05		MC130593	TP	5.5	0.2	11.8
Lily Pad Lake																					
MC140991	LPL	286	3	348	8.3	0.2	36.7	17.3	0.3	9.4	0.2	<.02		0.29	0.05		MC140991	LPL	8.36	0.09	17.9
MC140292	LPL	253	7	308	9.15	0.2	40.5	15.7	0.3	10.2	0.2	<.02		0.12	0.05		MC140292	LPL	7.87	0.06	16.8
MC140892	LPL				8.6	0.2	38.1	16.0	0.3	9.2	0.2	<.02		0.08	0.05		MC140892	LPL			
Needles Eye Drips																					
MC191291	NE	288	1	352	0.26	0.01	1.2	13.7	0.3	1.66	0.03	<.02		0.13	0.05		MC191291	NE	8.74	0.08	18.7
Sand Source Drips																					
MC210292	SSD	253	5	309	0.53	0.01	2.36	21.2	0.4	1.86	0.04	<.02		0.11	0.05		MC210292	SSD	4.79	0.07	10.2
MC210892	SSD				2.42	0.05	10.7	21.2	0.4	1.7	0.03	<.02		0.06	0.05		MC210892	SSD			

Sample ID	Loc	Date	Temp	pH	CP 1 Cond	CP 2 Cond	Corr CP Cond	YSI 9 Cond	YSI 10 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
Sugar Lake																					
MC290892	SL	8/15/92																			
MC290992	SL	9/15/92	9.00	7.70	522		516				6.31	6.13	1.32	-2.267	0.325	0.169	0.514	-2.346	485	1.05	0.0091
MC290593	SL	5/12/93	8.90	7.85							5.82	5.64	1.45	-2.459	0.382	0.226	0.67	-2.384	443	0.95	0.0084
Across from Pipe Organ																					
MC301192	APO	11/20/92	9.40	8.10	428		424				5.01	4.85	1.48	-2.763	0.609	0.454	0.95	-2.649	395	1.45	0.0072
Beyond Sand Source																					
MC320892	BSS	8/15/92																			
Iron Drips																					
MC330892	ID	8/15/92																			
Dragon's Jaw First Lake																					
MC340892	DJ1	8/15/92																			
Pipe Organ Pool																					
MC351292	POP	12/21/92	9.60	8.40					535	513	6.38	6.14	1.75	-2.978	1.075	0.919	1.9	-2.418	496	1.41	0.009
MC350393	POP	3/1/93	9.00	8.26	457		460				5.46	5.61	-1.25	-2.906	0.761	0.606	1.361	-2.377	438	1.12	0.008
Bridge Ceiling Joint																					
MC360493	BCJ	4/3/93	8.70	8.16	299		303	322		309	3.36	3.17	2.58	-3.013	0.382	0.226	0.353	-2.651	261	1.95	0.0049
Ramp Stream																					
MC370593	RS	5/12/93	8.50	7.83				424		407	4.58	4.28	3.09	-2.554	0.282	0.125	0.176	-2.539	348	1.83	0.0066
Turquoise Lake Source																					
MC380593	TLS	5/12/93	9.30	7.81				847		811	9.38	9.42	-0.19	-2.268	0.71	0.554	1.222	-2.063	736	1.23	0.0135

Sugar Lake																			
Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC290892	SL																		
MC290992	SL	63.5	0.3	36.5	0.3	2.26	0.05	1.24	0.01	0.01	0.01	0.003	0.001	0.073	0.001	0.036	0.001	0.015	0.003
MC290593	SL	55.8	0.2	35.5	0.2	1.92	0.09	1.02	0.01	0.01	0.01	0.003	0.001	0.069	0.001	0.038	0.001	0.019	0.003
Across from Pipe Organ																			
MC301192	APO	57.6	0.3	24.0	0.3	1.17	0.03	3.86	0.03	0.04	0.01	0.004	0.001	0.071	0.001	0.045	0.001	0.035	0.003
Beyond Sand Source																			
MC320892	BSS																		
Iron Drips																			
MC330892	ID																		
Dragon's Jaw First Lake																			
MC340892	DJ1																		
Pipe Organ Pool																			
MC351292	POP	73.5	0.2	31.3	0.1	2.08	0.04	1.15	0.02	0.09	0.01	0.014	0.001	0.085	0.001	0.052	0.001	0.097	0.003
MC350393	POP	56.7	0.5	30.5	0.3	2.20	0.1	0.82	0.02	0.03	0.01	0.007	0.001	0.074	0.001	0.048	0.001	0.035	0.004
Bridge Ceiling Joint																			
MC360493	BCJ	44.0	0.5	13.6	0.2	0.53	0.07	0.65	0.03	<.01		<.001		0.106	0.001	0.023	0.001	0.06	0.003
Ramp Stream																			
MC370593	RS	58.1	0.4	19.2	0.2	1.2	0.1	0.95	0.03	0.10	0.01	0.05	0.001	0.105	0.001	0.053	0.001	0.176	0.003
Turquoise Lake Source																			
MC380593	TLS	100	1	49.1	0.4	7.5	0.1	0.87	0.01	0.03	0.01	<.001		0.097	0.001	0.13	0.001	0.014	0.003

Sugar Lake																					
Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±		Sample ID	Loc	Si	±	SiO2
MC290892	SL				0.08	0.01	0.36	17	0.4	0.57	0.01	<.02		0.09	0.05		MC290892	SL			
MC290992	SL	287	6	350	0.02	0.01	0.09	17.6	0.4	0.51	0.01	<.03		0.19	0.05		MC290992	SL	5.90	0.07	12.6
MC290593	SL	261	5	318	0.25	0.01	1.1	17.7	0.4	1.1	0.03	0.03	0.02	0.18	0.05		MC290593	SL	4.80	0.1	10.3
Across from Pipe Organ																					
MC301192	APO	230	5	280	0.45	0.01	2	8.8	0.2	1.1	0.02	<.03		0.19	0.05		MC301192	APO	7.5	0.1	16
Beyond Sand Source																					
MC320892	BSS				3.59	0.07	15.9	12.1	0.2	1.23	0.02	<.02		0.1	0.05		MC320892	BSS			
Iron Drips																					
MC330892	ID				5.4	0.1	23.9	25.4	0.5	4.11	0.03	<.02		0.06	0.05		MC330892	ID			
Dragon's Jaw First Lake																					
MC340892	DJ1				3.21	0.06	14.2	23.7	0.5	3.14	0.06	<.02		0.05	0.05		MC340892	DJ1			
Pipe Organ Pool																					
MC351292	POP	291	6	354	0.35	0.01	1.5	13.3	0.3	1.11	0.03	<.03		0.16	0.05		MC3521292	POP	8.18	0.08	17.5
MC350393	POP	244	5	297	0.39	0.01	1.7	17.5	0.4	12.3	0.2	<.03		0.15	0.05		MC350393	POP	8.6	0.1	18.4
Bridge Ceiling Joint																					
MC360493	BCJ	146	3	179	0.16	0.01	0.7	9.8	0.2	0.58	0.03	<.02		0.07	0.05		MC360493	BCJ	5.31	0.05	11.4
Ramp Stream																					
MC370593	RS	199	4	242	0.45	0.01	2.0	10.7	0.2	1.9	0.03	<.03		0.07	0.05		MC370593	RS	5.5	0.2	11.8
Turquoise Lake Source																					
MC380593	TLS	379	8	462	8.9	0.2	39.4	26.2	0.5	23.4	0.5	0.03	0.02	0.16	0.05		MC380593	TLS	12.6	0.2	27

House Well at Mystery I

Sample ID	Loc	Date	Temp	pH	CP1 Cond	Corr CP Cond	YSI 9 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
HW010691	HW	6/14/91	11.0	7.59					4.53	4.60	-0.70	-2.307	0.028	-0.126	-0.206	-2.171	356	1.53	0.0067

South Branch of the Root River at Mystery I

Sample ID	Loc	Date	Temp	pH	CP1 Cond	Corr CP Cond	YSI 9 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
SB010991	SB	9/14/91	19.3	8.04					5.43	5.37	0.47	-2.728	0.676	0.528	1.147	-2.322	421	1.83	0.0078
SB010492	SB	5/13/92	14.8	8.49			524	526	5.673	5.679	-0.05	-3.172	1.059	0.907	1.963	-2.345	435	1.39	0.0081
SB010792	SB	7/28/92	21.1	8.39			553	556	5.922	5.84	0.64	-3.024	1.103	0.956	2.087	-2.297	455	1.59	0.0084
SB010493	SB	4/5/93	6.3	8.27			366	351	4.01	3.874	1.52	-3.146	0.474	0.316	0.524	-2.487	307	1.81	0.0058
SB010593	SB	5/12/93	16.9	7.9			485	464	5.096	4.864	2.12	-2.570	0.392	0.242	0.561	-2.373	381	1.76	0.0073

Surface Stream at Mystery II

Sample ID	Loc	Date	Temp	pH	CP1 Cond	Corr CP Cond	YSI 9 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
SS20493	SS2	4/5/93	6	8.09			511	490	5.343	5.099	2.14	-2.7632	0.585	0.427	0.824	-2.603	410.4	1.49	0.0077

Old Mystery Cave

Sample ID	Loc	Date	Temp	pH	CP1 Cond	Corr CP Cond	YSI 9 Cond	Corr YSI Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
OM010792	WOM	7/28/92	8.4	7.75	767	757			8.295	8.376	-0.46	-2.254	0.564	0.407	0.892	-2.196	658	1.29	0.012

House Well at Mystery I

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
HW010691	HW	52.9	0.3	20.8	0.1	2.47	0.02	1.6	0.1	0.28	0.03	0.014	0.007	0.103	0.003	0.047	0.005	0.11	0.020

South Branch of the Root River at Mystery I

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
SB010991	SB	66.7	0.3	21.9	0.1	4.69	0.05	2.1	0.2	0.20	0.08	0.04	0.01	0.11	0.01	0.11	0.01	0.24	0.050
SB010492	SB	63.8	0.3	27.3	0.3	4.63	0.06	1.33	0.02	0.08	0.008	0.0149	0.0005	0.069	0.001	0.073	0.001	0.032	0.001
SB010792	SB	70.7	0.5	26.4	0.2	4.30	0.06	0.99	0.02	0.06	0.01	0.016	0.001	0.084	0.001	0.084	0.001	0.035	0.004
SB010493	SB	48.6	0.3	16.2	0.1	3.57	0.06	2.02	0.03	0.18	0.01	0.015	0.001	0.068	0.001	0.088	0.001	0.318	0.003
SB010593	SB	62.3	0.6	21.4	0.2	4.11	0.09	1.26	0.02	0.09	0.01	0.026	0.001	0.075	0.003	0.093	0.001	0.075	0.003

Surface Stream at Mystery II

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
SS20493	SS2	62.8	0.5	25.5	0.3	1.62	0.05	1.09	0.02	0.05	0.01	0.008	0.001	0.102	0.001	0.05	0.001	0.073	0.003

Old Mystery Cave

Sample ID	Loc	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
OM010792	WOM	90.6	0.7	42.6	0.3	5.6	0.1	0.9	0.02	<.01		<.001		0.08	0.001	0.107	0.001	<.003	

House Well at Mystery I

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±	Si	±	SiO2
HW010691	HW	195	4	238	<.01		<.044	28.3	0.6	3.20	0.06	<.02		0.30	0.05	3.89	0.04	8.3

South Branch of the Root River at Mystery I

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±	Si	±	SiO2
SB010991	SB	194	1	236.5	8.8	0.2	38.8	18.0	0.4	16.7	0.3	0.024	0.020	0.45	0.05	6.65	0.06	14.2
SB010492	SB	217	1	265	7.3	0.1	32.4	18.0	0.4	15.3	0.3	<.02		0.14	0.05	3.0	0.1	6.4
SB010792	SB	224	5	273	7.1	0.1	31.4	19.3	0.4	15.9	0.3	0.02	0.02	0.18	0.05	5.9	0.13	12.6
SB010493	SB	145	3	177	5.3	0.1	23.5	13.4	0.3	10.8	0.2	<.02		0.21	0.05	5.19	0.05	11.1
SB010593	SB	179	4	218	7.5	0.2	33.2	16.3	0.3	14.3	0.3	<.03		0.25	0.05	4.5	0.2	9.6

Surface Stream at Mystery II

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±	Si	±	SiO2
SS20493	SS2	233	5	284	2.24	0.04	9.9	8.9	0.2	3.35	0.07	<.02		0.09	0.05	6.05	0.08	12.9

Old Mystery Cave

Sample ID	Loc	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	Br	±	F	±	Si	±	SiO2
OM010792	WOM	340	7	415	8.7	0.2	38.5	19.8	0.4	19.0	0.4	<.02		0.11	0.05	12.1	0.1	25.9

APPENDIX 4

CHEMICAL ANALYSES BY TARUN SETHI IN MYSTERY CAVE

The following pages list chemical analyses of samples obtained by Tarun Sethi in Mystery I and II as a part of an Undergraduate Research Opportunity Project at the University of Minnesota.

Sethi	Mystery	Mystery																
Sample ID	Sample ID	Location ID	Date	Type	Temp	pH	Cond	Cations	Anions	Balance	PCO2	SIC	SIA	SID	SIG	TDS	Ca/Mg	IS
MC1	MC090990	GG1	9/14/90	Stalactite drips	10.5	7.22	443	4.734	4.967	-2.18	-1.84	-0.18	-0.34	-0.75	-2.86	406	1.99	0.007
MC2	MC110990	CL	9/14/90	Small pool	9.1	7.24	530	5.612	5.765	-1.23	-1.81	-0.06	-0.22	-0.54	-2.7	461	2.06	0.0083
MC3	MC060990	WWD	9/14/90	Waterfall	9.3	7.52	613	6.469	6.787	-2.23	-2.09	0.182	0.026	0.142	-1.87	529	1.30	0.0097
MC4	MC080990	BL	9/14/90	Large pool	8.55	7.51	574	6.135	6.386	-1.85	-2.10	0.129	-0.03	0.023	-1.99	498	1.30	0.0092
MCII-8	MC081290	BL	12/14/90	Large Pool	9.85	7.76	490	5.572	5.776	-1.66	-2.42	0.274	0.118	0.378	-1.97	4580	1.18	0.0084
MC5	MC120990	DJL	9/14/90	Large pool	8.9	7.56	615	6.596	6.761	-1.15	-2.13	0.18	0.024	0.25	-2.07	521	0.99	0.0098
MC6	MC290990	SL	9/14/90	Small pool	9.0	7.56	454	6.285	6.512	-1.64	-2.10	0.231	0.075	0.287	-2.36	507	1.15	0.0093
MCI-1	MC011290	TL	12/13/90	Large pool	8.72	7.93	860	10.63	10.59	0.21	-2.36	0.858	0.701	1.568	-2.01	813.4	1.07	0.0151
MCI-2	MC391290	BSD	12/13/90	Stalactite drips	9.9	7.56	885	9.986	9.93	-0.27	-1.98	0.504	0.349	0.856	-2.05	767.7	1.14	0.0143
MCI-3	MC401290	MFD	12/13/90	Flowstone flows	10.5	8.23	725	9.836	9.655	0.88	-2.66	1.148	0.994	2.173	-2.08	754.9	1.09	0.0138
MCI-4	MC411290	CSD	12/13/90	Stalactite drips	10.7	8.20	360	10.51	10.42	0.42	-2.62	1.165	1.011	2.191	-2.06	805.8	1.14	0.0148
MCII-7	MC041290	EP	12/14/90	Waterfall	10.7		422											
MCII-9	MC101290	BLD2	12/14/90	Flowstone flows	10.2	8.10	550	6.329	6.468	-1.01	-2.71	0.725	0.57	1.254	-1.92	509	1.27	0.0093

Sethi																			
Sample ID	Location ID	Ca	±	Mg	±	Na	±	K	±	Fe	±	Mn	±	Sr	±	Ba	±	Al	±
MC1	GG1	61.7	0.4	18.9	0.1	2.08	0.02	0.2	0.02	0.06	0.04	<.01		0.139	0.003	0.075	0.003	<.02	
MC2	CL	74.3	0.5	22.0	0.1	1.59	0.02	0.7	0.1	0.07	0.03	<.01		0.154	0.003	0.038	0.002	<.02	
MC3	WWD	71.7	0.5	33.2	0.2	3.22	0.04	0.6	0.1	0.05	0.03	<.01		0.109	0.003	0.078	0.003	<.02	
MC4	BL	67.9	0.4	31.5	0.2	3.17	0.03	0.58	0.1	<.05		<.01		0.09	0.003	0.062	0.002	<.02	
MCII-8	BL	58.8	0.5	29.9	0.2	3.55	0.04	0.64	0.08	0.12	0.04	<.01		0.089	0.002	0.06	0.002	0.06	0.02
MC5	DJL	64.5	0.4	39.5	0.3	2.26	0.02	0.9	0.1	0.11	0.03	<.01		0.07	0.002	0.048	0.002	0.05	0.02
MC6	SL	66.0	0.4	34.8	0.2	2.18	0.02	1.1	0.1	0.1	0.03	<.01		0.077	0.002	0.038	0.002	0.06	0.02
MCI-1	TL	104.2	0.7	58.9	0.3	12.63	0.08	1.3	0.1	0.05	0.06	<.01		0.102	0.002	0.131	0.002	<.02	
MCI-2	BSD	101.7	0.6	54.0	0.3	10.1	0.1	1.1	0.1	0.05	0.04	<.01		0.093	0.005	0.094	0.005	<.02	
MCI-3	MFD	98.5	0.5	54.0	0.3	10.16	0.05	1.14	0.06	0.06	0.03	<.01		0.091	0.004	0.096	0.004	<.02	
MCI-4	CSD	107.1	0.5	56.4	0.3	11.25	0.07	1.19	0.06	0.05	0.03	<.01		0.094	0.002	0.116	0.002	<.02	
MCII-7	EP	61.0	0.3	25.7	0.1	2.2	0.02	0.9	0.1	<.04		<.01		0.097	0.003	0.039	0.004	<.02	
MCII-9	BLD2	69.2	0.5	32.5	0.2	3.74	0.05	0.95	0.08	0.34	0.03	<.01		0.104	0.003	0.086	0.003	0.59	0.02

Sethi																
Sample ID	Location ID	Alk	±	HCO3	NO3-N	±	NO3	SO4	±	Cl	±	F	±	Si	±	SiO2
MC1	GG1	242.0	4	296.0	0.22	0.01	0.97	5	0.1	0.63	0.03	0.11	0.05	10.3	0.1	22
MC2	CL	279.0	1	340.0	0.42	0.01	1.9	6.4	0.1	0.77	0.03	0.08	0.05	5.84	0.05	12.5
MC3	WWD	281.0	4	343.0	1.06	0.02	4.7	48	1	2.89	0.06	0.21	0.05	10	0.1	21.4
MC4	BL	270.0	3	329.0	1.48	0.03	6.6	37.8	0.8	3.26	0.07	0.11	0.05	8.49	0.09	18.2
MCII-8	BL	231.0	1	282.0	2.04	0.04	9	44	0.9	3.37	0.07	0.05	0.05	8.8	0.1	18.8
MC5	DJL	286.0	2	349.0	2.83	0.06	12.5	33	0.7	5	0.1	0.18	0.05	6.34	0.07	13.6
MC6	SL	307.0	2	374.0	0.09	0.01	0.4	16.5	0.3	0.63	0.03	0.18	0.05	4.92	0.04	10.5
MCI-1	TL	413.0	6	504.0	8.1	0.2	35.9	30.3	0.6	39.4	0.8	0.31	0.05	12.5	0.1	26.7
MCI-2	BSD	407.0	2	496.0	5.5	0.1	24.4	27	0.5	29.2	0.6	0.14	0.05	10.8	0.1	23.1
MCI-3	MFD	407.0	2	496.0	5.6	0.1	24.8	26.8	0.5	29.5	0.6	0.19	0.05	10.74	0.09	23
MCI-4	CSD	422.0	2	515.0	6.7	0.1	29.7	26.9	0.5	33	0.7	0.26	0.05	11.7	0.1	25
MCII-7	EP	229.0	3	279.0	1.26	0.03	5.6	33.1	0.7	4.09	0.08	<.05	<.05	6.51	0.05	13.9
MCII-9	BLD2	264.0	1	322.0	2.05	0.04	9.1	44.9	0.9	3.83	0.08	0.07	0.05	10.6	0.2	22.7

APPENDIX 5

VOLATILE ORGANIC COMPOUNDS IN MYSTERY CAVE

The following page lists the volatile organic chemicals on the Minnesota Department of Health Method 465C List. All five samples at the South Branch of the Root River, Turquoise Lake Source, Blue Lake, Flim Flam Creek, and Coon Lake Drips tested below detection limits for all volatile compounds on the list.

Volatile Organic Compounds
MNDH Method 465C

Acetone
Allyl Chloride
Benzene
Bromodichloromethane
Bromoform
Bromomethane
Carbon tetrachloride
Chlorobenzene
Chloroethane
Chloroform
Chloromethane
Dibromochloromethane
1,2-Dibromoethane
Dibromoethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichlorothene
trans-1,2,Dichlorothene
Dichlorofluoromethane
1,2-Dichloropropane
1,3-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethyl Ether
Ethylbenzene
Isopropylbenzene
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methylene chloride
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Tetrahydrofuran
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlofluromethane
1,2,3-Trichloropropane
Trichlorotrifluoroethane
Vinyl chloride
o-Xylene
m-p-Xylenes