



# Arkansas Water Resources Center

## GROUNDWATER QUALITY AND MINERAL DEPOSITS RELATIONSHIPS IN THE OZARK MOUNTAINS

PREPARED BY:

Kenneth F. Steele  
Department of Geology  
University of Arkansas  
Fayetteville, Arkansas 72701

**PUB-109**

March 1981

ARKANSAS WATER RESOURCES CENTER  
UNIVERSITY OF ARKANSAS  
112 OZARK HALL  
FAYETTEVILLE, ARKANSAS 72701

GROUNDWATER QUALITY AND MINERAL  
DEPOSITS RELATIONSHIPS IN THE  
OZARK MOUNTAINS

Kenneth F. Steele  
Department of Geology  
University of Arkansas  
Fayetteville, AR 72701

Research Project Technical Completion Report  
Project G-829-03

The research on which this report is based was financed in part by the United States Department of the Interior as authorized by the Water Research and Development Act of 1978, (P. L. 95-467).

Arkansas Water Resources Research Center  
University of Arkansas  
223 Ozark Hall  
Fayetteville, Arkansas 72701

Publication No. 109

September, 1984

Contents of this publication do not necessarily reflect the views and policies of the U. S. Department of the Interior, nor does mention of trade names or commercial products constitute their endorsement or recommendation for use by the U. S. Government.

The University of Arkansas, in compliance with federal and state laws and regulations governing affirmative action and nondiscrimination, does not discriminate in the recruitment, admission and employment of students, faculty and staff in the operation of any of its educational programs and activities as defined by law. Accordingly, nothing in this publication should be viewed as directly or indirectly expressing any limitation, specification or discrimination as to race, religion, color or national origin; or to handicap, age, sex, or status as a disabled Vietnam-era veteran, except as provided by law. Inquiries concerning this policy may be directed to the Affirmative Action Officer.

## A B S T R A C T

### GROUNDWATER QUALITY AND MINERAL DEPOSITS RELATIONSHIPS IN THE OZARK MOUNTAINS

Ninety-nine groundwater sites were sampled in northern Arkansas in order to determine the effect of local manganese, phosphate, pyrite, lead-zinc and uranium mineralization on the groundwater chemistry. Most of this study (75 springs) was concentrated in the Batesville manganese district. Hydrogeochemical exploration for these types of manganese deposits appears possible with 44 percent of the springs within 2000 feet of mineralization having anomalous metal concentrations (especially manganese). Because only a few springs were sampled in the remaining areas, the results are not conclusive; however, only the pyrite and small lead-zinc deposit would appear worthy of additional investigation. None of the springs appeared to have geothermal water.

Eighteen of the springs exceed U.S. Public Health Service drinking water limits, but most only exceed manganese or iron limits. One spring exceeded the drinking water limits for lead. Thus, these carbonate spring waters are generally of good chemical quality.

Kenneth F. Steele

Completion Report to the U.S. Department of the Interior, Washington, D.C., September, 1984.

Keywords -- Groundwater, Water Quality, Mineralization, Trace Elements.

## TABLE OF CONTENTS

	Page
Abstract . . . . .	i
List of Figures . . . . .	iii
List of Tables . . . . .	iv
Acknowledgements . . . . .	v
Introduction . . . . .	1
A. Purpose and Objectives . . . . .	1
B. Related Research or Activities . . . . .	1
Methods and Procedures . . . . .	8
Principle Findings and Significance . . . . .	12
Batesville Area - . . . . .	12
General Geology . . . . .	12
Mineralization . . . . .	15
Water Quality . . . . .	18
Comparison of Water Chemistry . . . . .	27
Geochemical Exploration . . . . .	30
Four Mineralized Areas - . . . . .	40
General Geology . . . . .	40
Water Quality . . . . .	44
Summary of Chemistry . . . . .	47
Conclusions . . . . .	55
Literature Cited . . . . .	57

LIST OF FIGURES

	Page
Figure 1 . . . . .	2
Figure 2 . . . . .	13
Figure 3 . . . . .	17
Figure 4 . . . . .	31
Figure 5 . . . . .	33
Figure 5A . . . . .	34
Figure 6 . . . . .	39
Figure 7 . . . . .	41
Figure 8 . . . . .	43
Figure 9 . . . . .	45
Figure 10 . . . . .	46

LIST OF TABLES

	Page
Table 1 . . . . .	3
Table 2 . . . . .	7
Table 3 . . . . .	9
Table 4 . . . . .	10
Table 5 . . . . .	19
Table 5A . . . . .	23
Table 6 . . . . .	28
Table 6A . . . . .	29
Table 7 . . . . .	35
Table 8 . . . . .	36
Table 9 . . . . .	37
Table 10 . . . . .	48
Table 10A . . . . .	50
Table 11 . . . . .	52
Table 11A . . . . .	53

## ACKNOWLEDGEMENTS

I gratefully acknowledge the local citizens of the study area for allowing their springs to be sampled and helping to locate many of the springs. Much of the field and laboratory work was carried out by Myles Overton and Ali Sadeghi. Mr. Overton also assisted in data reduction and aided in writing the general geology of the Batesville area.

I acknowledge the assistance of Pauline Mueller for typing this report and Gloria Wood for preparation of the typed tables.

## INTRODUCTION

Ninety-nine springs were sampled in northern Arkansas in the vicinity of manganese, phosphate, pyrite, a small lead-zinc, and uranium deposits (Figure 1) in order to determine the effect of the mineralization on the groundwater chemistry. Springs were utilized in order to avoid metal contamination except for the use of a few wells in the phosphate area. Most of the springs have low discharge (less than 4 liters per minute) and issue from carbonate rock. Seventy-five of the springs are located in the manganese district because of the much larger extent of this deposit in comparison with the others. The spring locations are given in Tables 1 and 2 along with distance to nearest mineralization and the formation from which they issue.

### A. Purpose and Objectives

The purpose of this study was to investigate the effect of manganese, phosphate, pyrite, lead-zinc, and uranium mineralization on groundwater chemistry in northern Arkansas. The objectives of this study were to:

1. Evaluate the potential value of hydrogeochemical exploration for these types of mineral deposits.
2. Determine the groundwater quality of these mineralized areas.
3. Investigate the geothermal potential of the areas using silica geothermometry.

### B. Related Research or Activities



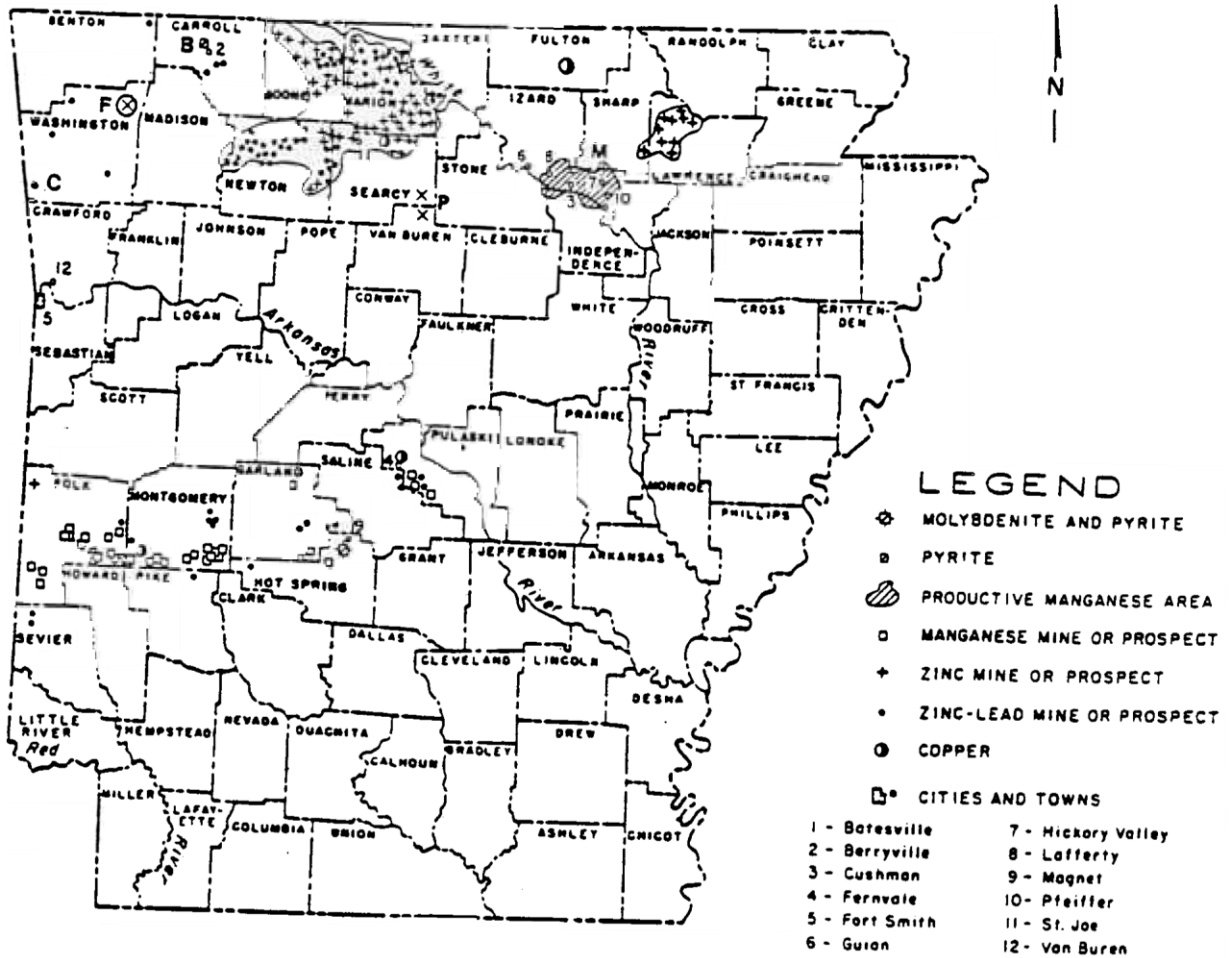


Figure 1. Manganese, lead-zinc, copper, molybdenum, phosphate, pyrite and uranium deposits in Arkansas. The specific study area sites are indicated by the letters M (Batesville Mn district), P (Peyton Creek phosphate area), B (Berryville pyrite area), C (Morrow lead-zinc deposit), and F (Friendship Creek U deposit). Map modified from Stroud et al. (1969).

TABLE 1. LOCATION OF SPRINGS, FORMATION FROM WHICH SPRINGS ISSUE AND DISTANCE OF SPRINGS TO NEAREST MINERALIZATION IN THE BATESVILLE AREA.

Sample	County*	Quad**	Location				Formation <sup>†</sup>	Distance to Mineralization (in feet)	
			Township	Range	Section	Quarter Section			
M 1	ID	ST	T14NR7W	Sec 3	NW $\frac{1}{4}$	NW $\frac{1}{4}$	NW $\frac{1}{4}$	Ocj	850
M 2	ID	ST	T14NR7W	Sec 3	SW $\frac{1}{4}$	NE $\frac{1}{4}$	NE $\frac{1}{4}$	Mbn/Ocj	300
M 3	ID	ST	T14NR7W	Sec 4	SE $\frac{1}{4}$	SE $\frac{1}{4}$		Ocj	300
M 4	ID	ST	T14NR7W	Sec 3	SE $\frac{1}{4}$	SW $\frac{1}{4}$		Ospe/Ocj	1000
M 5	ID	MP	T14NR7W	Sec 4	NW $\frac{1}{4}$	NE $\frac{1}{4}$		Ospe/Ocj	1000
M 6	ID	MP	T14NR7W	Sec 4	NW $\frac{1}{4}$	NW $\frac{1}{4}$	SE $\frac{1}{4}$	Ospe/Ocj	1600
M 7	ID	MP	T15NR7W	Sec 33	NW $\frac{1}{4}$	NE $\frac{1}{4}$	NE $\frac{1}{4}$	Ospe/Ocj	2000
M 8	ID	MP	T15NR7W	Sec 33	NW $\frac{1}{4}$	NE $\frac{1}{4}$		Ospe/Ocj	2000
M 9	ID	ST	T15NR7W	Sec 21	SW $\frac{1}{4}$	NE $\frac{1}{4}$		Ospe	1800
M10	ID	BV	T14NR7W	Sec 26	SW $\frac{1}{4}$	NW $\frac{1}{4}$	SE $\frac{1}{4}$	Mbn	9200
M11	ID	BV	T14NR7W	Sec 27	SE $\frac{1}{4}$	NE $\frac{1}{4}$	SW $\frac{1}{4}$	S/Sc/Mbn	9800
M12	ID	BV	T14NR7W	Sec 22	NE $\frac{1}{4}$	SE $\frac{1}{4}$	NW $\frac{1}{4}$	Mbn	3900
M13	ID	BV	T14NR7W	Sec 14	SE $\frac{1}{4}$	SE $\frac{1}{4}$	NW $\frac{1}{4}$	S/Sc/Ocj	1300
M14	ID	BV	T14NR7W	Sec 23	NE $\frac{1}{4}$	SE $\frac{1}{4}$	NE $\frac{1}{4}$	Ocj/Mbn	800
M15	ID	BV	T14NR7W	Sec 21	SE $\frac{1}{4}$	SE $\frac{1}{4}$	SW $\frac{1}{4}$	Ospe/Ocj	2100
M16	ID	BV	T14NR7W	Sec 21	SE $\frac{1}{4}$	SE $\frac{1}{4}$	SW $\frac{1}{4}$	Ospe/Ocj	1900
M17	ID	BN	T14NR6W	Sec 18	SW $\frac{1}{4}$	SE $\frac{1}{4}$	NW $\frac{1}{4}$	Ocj	1900
M18	ID	BV	T14NR6W	Sec 29	SW $\frac{1}{4}$	NW $\frac{1}{4}$		Ocj/S1sc	400
M19	ID	BV	T14NR6W	Sec 29	SW $\frac{1}{4}$	NW $\frac{1}{4}$		Ocj/S1sc	500
M20	ID	BV	T14NR7W	Sec 13	SW $\frac{1}{4}$	SW $\frac{1}{4}$	NE $\frac{1}{4}$	Ocj	2200
M21	ID	BV	T14NR7W	Sec 11	SE $\frac{1}{4}$	NW $\frac{1}{4}$	NW $\frac{1}{4}$	Ocj/Ospe	2300
M22	ID	ST	T14NR7W	Sec 11	SE $\frac{1}{4}$	NW $\frac{1}{4}$	NW $\frac{1}{4}$	Ocj/Ospe	2400
M23	ID	ST	T14NR7W	Sec 11	NW $\frac{1}{4}$	SE $\frac{1}{4}$	SE $\frac{1}{4}$	Ocj/Ospe	2700
M24	ID	BV	T14NR7W	Sec 11	SW $\frac{1}{4}$	NE $\frac{1}{4}$	SE $\frac{1}{4}$ SW $\frac{1}{4}$	Ospe/Ocj	1200

TABLE 1. LOCATION OF SPRINGS, FORMATION FROM WHICH SPRINGS ISSUE AND DISTANCE OF SPRINGS TO NEAREST MINERALIZATION IN THE BATESVILLE AREA. (continued)

Sample	County*	Quad**	Location				Formation <sup>†</sup>	Distance to Mineralization (in feet)	
			Township	Range	Section	Quarter Section			
M25	ID	BV	T14NR7W	Sec 11	SW $\frac{1}{4}$	NE $\frac{1}{4}$	SW $\frac{1}{4}$	Ospe/Ocj	1200
M26	ID	BV	T14NR7W	Sec 11	SW $\frac{1}{4}$	NE $\frac{1}{4}$	SE $\frac{1}{4}$ SE $\frac{1}{4}$	Ospe/Ocj	1400
M27	ID	BV	T14NR7W	Sec 11	SW $\frac{1}{4}$	NE $\frac{1}{4}$	SW $\frac{1}{4}$	Ospc/Ocj	100
M28	ID	ST	T14NR7W	Sec 11	SW $\frac{1}{4}$	NW $\frac{1}{4}$	NW $\frac{1}{4}$	Ocj	1200
M29	ID	MP	T15NR7W	Sec 32	SE $\frac{1}{4}$	NW $\frac{1}{4}$	SW $\frac{1}{4}$	Ospe/Ocj	1200
M30	ID	MP	T15NR7W	Sec 31	NE $\frac{1}{4}$	SE $\frac{1}{4}$		Ospe/Ocj	2000
M31	ID	MP	T15NR7W	Sec 32	SW $\frac{1}{4}$	NW $\frac{1}{4}$		Ospe/Ocj	400
M32	ID	MP	T15NR7W	Sec 32	SW $\frac{1}{4}$	SE $\frac{1}{4}$	SW $\frac{1}{4}$	Ospe/Ocj	1200
M33	IZ	MP	T15NR8W	Sec 10	SW $\frac{1}{4}$	SE $\frac{1}{4}$		Ospe	9200
M34	IZ	MP	T15NR8W	Sec 14	NE $\frac{1}{4}$	NE $\frac{1}{4}$	SW $\frac{1}{4}$	Ospe/Ocj	3600
M35	IZ	MP	T15NR7W	Sec 7	SE $\frac{1}{4}$	SW $\frac{1}{4}$	NE $\frac{1}{4}$	Ospe/Ocj	1900
M36	IZ	ST	T15NR7W	Sec 10	SE $\frac{1}{4}$	NW $\frac{1}{4}$		Ospe	7100
M37	IZ	ST	T15NR7W	Sec 9	SE $\frac{1}{4}$	NE $\frac{1}{4}$	SE $\frac{1}{4}$	Ospe	6000
M38	IZ	ST	T16NR7W	Sec 34	SE $\frac{1}{4}$	SE $\frac{1}{4}$		Ospe	12600
M39	ID	SR	T14NR5W	Sec 19	NW $\frac{1}{4}$	NW $\frac{1}{4}$	NW $\frac{1}{4}$	Ssc/Mbn	6100
M40	ID	SR	T14NR5W	Sec 11	NE $\frac{1}{4}$	SE $\frac{1}{4}$		Of/Soc	600
M41	ID	SR	T14NR5W	Sec 11	SE $\frac{1}{4}$	SE $\frac{1}{4}$	SW $\frac{1}{4}$	Of	1400
M42	ID	BV	T14NR6W	Sec 21	SE $\frac{1}{4}$	NW $\frac{1}{4}$	SE $\frac{1}{4}$	Mbn/Ocj	500
M43	ID	SR	T14NR6W	Sec 22	NE $\frac{1}{4}$	SW $\frac{1}{4}$	NW $\frac{1}{4}$	Of/Mbn	800
M44	ID	BD	T14NR7W	Sec 18	NW $\frac{1}{4}$	NE $\frac{1}{4}$	NE $\frac{1}{4}$	Ocj/Mbn	800
M45	ID	BD	T14NR8W	Sec 14	NE $\frac{1}{4}$	NW $\frac{1}{4}$	SW $\frac{1}{4}$	Ocj/S	200
M46	ID	BD	T14NR7W	Sec 8	SW $\frac{1}{4}$	SW $\frac{1}{4}$	NE $\frac{1}{4}$	S/Ocj	2000
M47	ID	BD	T14NR7W	Sec 8	SW $\frac{1}{4}$	SW $\frac{1}{4}$	NE $\frac{1}{4}$	S/Ocj	2100
M48	ID	MP	T14NR7W	Sec 9	NW $\frac{1}{4}$	NW $\frac{1}{4}$	SW $\frac{1}{4}$	Mbn/Ocj	600



TABLE 1. LOCATION OF SPRINGS, FORMATION FROM WHICH SPRINGS ISSUE AND DISTANCE OF SPRINGS TO NEAREST MINERALIZATION IN THE BATESVILLE AREA. (continued)

Sample	County*	Quad**	Location				Formation <sup>†</sup>	Distance to Mineralization (in feet)
			Township	Range	Section	Quarter Section		
M49	IZ	MP	T15NR7W	Sec 18	NW $\frac{1}{4}$	NW $\frac{1}{4}$	Ospe/Ocj	2400
M50	IZ	MP	T15NR8W	Sec 34	SE $\frac{1}{4}$	SE $\frac{1}{4}$ NW $\frac{1}{4}$	Ospe/Ocj	800
M51	IZ	MP	T15NR8W	Sec 33	NW $\frac{1}{4}$	NW $\frac{1}{4}$	Mbn/Ocj	5300
M52	IZ	MP	T15NR8W	Sec 28	SW $\frac{1}{4}$	NE $\frac{1}{4}$	Mbn/Ocj	5800
M53	IZ	MP	T15NR8W	Sec 35	SW $\frac{1}{4}$	SW $\frac{1}{4}$ NW $\frac{1}{4}$	Ospe/Ocj	1400
M54	IZ	MP	T15NR8W	Sec 25	NE $\frac{1}{4}$	NW $\frac{1}{4}$ SW $\frac{1}{4}$	Ocj/Ospe	3200
M55	ID	ST	T15NR7W	Sec 34	SE $\frac{1}{4}$	NW $\frac{1}{4}$ SW $\frac{1}{4}$	Ocj	1600
M56	ID	ST	T15NR6W	Sec 31	NW $\frac{1}{4}$	SW $\frac{1}{4}$	Ospe	3300
M57	ID	ST	T15NR7W	Sec 26	NE $\frac{1}{4}$	NW $\frac{1}{4}$ SE $\frac{1}{4}$	Ospe	6500
M58	ID	ST	T14NR7W	Sec 2	NE $\frac{1}{4}$	SE $\frac{1}{4}$ SW $\frac{1}{4}$	Ospe/Ocj	2000
M59	ID	ST	T14NR7W	Sec 3	NE $\frac{1}{4}$	NE $\frac{1}{4}$ SW $\frac{1}{4}$	Ocj	2000
M60	ID	CC	T15NR5W	Sec 20	NW $\frac{1}{4}$	SE $\frac{1}{4}$	Mbn/Ospk	2200
M61	ID	CC	T15NR6W	Sec 26	NE $\frac{1}{4}$	SE $\frac{1}{4}$	Ospe	9900
M62	ID	CC	T15NR6W	Sec 26	SE $\frac{1}{4}$	SW $\frac{1}{4}$ SE $\frac{1}{4}$	Ospe	8800
M63	ID	CC	T15NR6W	Sec 26	NE $\frac{1}{4}$	SE $\frac{1}{4}$	Ospe	9300
M64	ID	CC	T15NR5W	Sec 30	NE $\frac{1}{4}$	SW $\frac{1}{4}$ SE $\frac{1}{4}$	Ospe	8400
M65	ID	BV	T14NR6W	Sec 9	SE $\frac{1}{4}$	NE $\frac{1}{4}$ NW $\frac{1}{4}$	Ocj	200
M66	ID	ST	T15NR6W	Sec 33	NE $\frac{1}{4}$	SW $\frac{1}{4}$ NE $\frac{1}{4}$	Ospe	3600
M67	ID	ST	T15NR6W	Sec 33	NE $\frac{1}{4}$	SW $\frac{1}{4}$ SW $\frac{1}{4}$	Ospe	3200
M68	ID	CC	T15NR6W	Sec 35	SW $\frac{1}{4}$	SE $\frac{1}{4}$	Mbn/Ojpk	2900
M69	SH	CC	T15NR6W	Sec 13	SW $\frac{1}{4}$	SE $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$	Ospe	1900
M70	SH	CC	T15NR6W	Sec 13	SW $\frac{1}{4}$	SE $\frac{1}{4}$ NE $\frac{1}{4}$ NE $\frac{1}{4}$	Ospe	1800
M71	SH	CC	T15NR6W	Sec 10	NW $\frac{1}{4}$	NE $\frac{1}{4}$ SE $\frac{1}{4}$	Ospe	14800
M72	SH	CC	T15NR5W	Sec 17	SW $\frac{1}{4}$	SE $\frac{1}{4}$	Ojpk	2500

TABLE 1. LOCATION OF SPRINGS, FORMATION FROM WHICH SPRINGS ISSUE AND DISTANCE OF SPRINGS TO NEAREST MINERALIZATION IN THE BATESVILLE AREA. (continued)

Sample	County*	Quad**	Location			Formation <sup>/</sup>	Distance to Mineralization (in feet)
			Township	Range	Section Quarter Section		
M73	SH	CC	T15NR5W	Sec 18	NE $\frac{1}{4}$ SE $\frac{1}{4}$ NW $\frac{1}{4}$	Ospe	2100
M74	ID	ST	T15NR6W	Sec 33	SE $\frac{1}{4}$ NW $\frac{1}{4}$ SE $\frac{1}{4}$	Ospe	2700
M75	ID	ST	T15NR6W	Sec 33	SE $\frac{1}{4}$ NW $\frac{1}{4}$ NW $\frac{1}{4}$	Ospe	2000

\* ID = Independence IZ = Izard SH = Sharp  
 \*\* BD = Bethesda BV = Batesville CC = Cave City  
 MP = Mt. Pleasant ST = Sandtown SR = Sulfur Rock

<sup>/</sup> Ospe = St. Peter Sandstone and Everton Limestone  
 Oj = Joachim Limestone  
 Op = Plattin Limestone Ojpk  
 Ok = Kimmswick Limestone  
 Of = Fernvale Limestone Ojc  
 Oc = Cason Shale  
 Ssc = St. Clair Limestone  
 Slsc = Lafferty Limestone and St. Clair Limestone  
 S = Silurian  
 Mbn = Boone Chert  
 / = contact

9



TABLE 2. LOCATION OF SPRINGS, FORMATION FROM WHICH SPRINGS ISSUE AND DISTANCE OF SPRINGS TO NEAREST MINERALIZATION IN PEYTON CREEK (P) PHOSPHATE AREA, BERRYVILLE (B) PYRITE AREA, MORROW (C) LEAD-ZINC AREA AND FRIENDSHIP CREEK (F) URANIUM AREA.

Sample	County*	Quad**	Location			Formation <sup>†</sup>	Distance
P76	SY	LE	T13NR14W	Sec 6	SW $\frac{1}{4}$ SW $\frac{1}{4}$	Pch/Mp	4600
P77	SY	LE	T13NR14W	Sec 6	SW $\frac{1}{4}$ SE $\frac{1}{4}$	Pch/Mp	4700
P78	VB	LE	T13NR15W	Sec 13	NE $\frac{1}{4}$ NE $\frac{1}{4}$	Pch/Pmm	5800
P79	VB	LE	T13NR15W	Sec 11	NE $\frac{1}{4}$ SE $\frac{1}{4}$	Pch	2200
P80	VB	LE	T13NR15W	Sec 11	NE $\frac{1}{4}$ SE $\frac{1}{4}$	Pch	2000
P81	SY	LE	T13NR15W	Sec 12	NW $\frac{1}{4}$ NW $\frac{1}{4}$	Mp/Pch	1000
P82	SY	LE	T14NR15W	Sec 26	SW $\frac{1}{4}$ NE $\frac{1}{4}$	Mfb	1200
P83	SY	LE	T14NR15W	Sec 17	SE $\frac{1}{4}$ NW $\frac{1}{4}$	Mfb/Mp	17900
B84	CL	GV	T20NR25W	Sec 1	NW $\frac{1}{4}$ SE $\frac{1}{4}$	Oc	3300
B85	CL	GV	T20NR25W	Sec 1	NE $\frac{1}{4}$ SW $\frac{1}{4}$	Oc	3500
B86	CL	GV	T20NR25W	Sec 12	NE $\frac{1}{4}$ NW $\frac{1}{4}$	Oc	0
B87	CL	GV	T20NR24W	Sec 7	SW $\frac{1}{4}$ SW $\frac{1}{4}$ NW $\frac{1}{4}$	Oc	3300
B88	CL	GV	T20NR25W	Sec 13	SE $\frac{1}{4}$ NW $\frac{1}{4}$	Oc	8000
B89	CL	GV	T20NR24W	Sec 5	SE $\frac{1}{4}$ SW $\frac{1}{4}$	Oc	4500
B90	CL	GV	T21NR24W	Sec 26	NW $\frac{1}{4}$ SW $\frac{1}{4}$	Oc	25700
B91	EA	CL	T20NR26W	Sec 15	NW $\frac{1}{4}$ NE $\frac{1}{4}$	Oc	40000
C92	WN	EV	T14NR32W	Sec 31	SW $\frac{1}{4}$ NW $\frac{1}{4}$	Pch/Phb	5200
C93	WN	EV	T13NR32W	Sec 6	NW $\frac{1}{4}$ SE $\frac{1}{4}$	Pch/Phb	8200
C94	WN	EV	T13NR32W	Sec 5	NW $\frac{1}{4}$ SW $\frac{1}{4}$	Pch/Mpfb	9600
C95	WN	LN	T14NR32W	Sec 4	NW $\frac{1}{4}$ SE $\frac{1}{4}$	Pbh/Mpfb	28500
F96	WN	SA	T18NR23W	Sec 35	SE $\frac{1}{4}$ SE $\frac{1}{4}$ NE $\frac{1}{4}$	MDC/Mbn	5800
F97	WN	SA	T18NR29W	Sec 36	SE $\frac{1}{4}$ SE $\frac{1}{4}$ NE $\frac{1}{4}$	MDC/Mbn	2500
F98	WN	SA	T17NR29W	Sec 3	SE $\frac{1}{4}$ SE $\frac{1}{4}$ NE $\frac{1}{4}$	Mbv/Mbn	12700
F99	WN	SA	T17NR29W	Sec 4	SW $\frac{1}{4}$ NW $\frac{1}{4}$	Mbn	21000

\* CL = Carroll SY = Searcy VB = Van Buren WN = Washington

\*\* EA = Eureka Springs EV = Evansville GV = Grandview LE = Leslie LN = Lincoln SA = Sonora  
<sup>†</sup> Mbn = Boone Limestone Mbv = Batesville Sandstone MDC = Chattanooga Shale Mfb = Fayetteville Shale and Boone Limestone Pmm = Middle Morrow Group Mp = Pitkin Limestone Oc = Cotter Chert  
Pbh = Brentwood Limestone and Hale Formation Pch = Cane Hill Formation.



There are not many published studies concerning the use of groundwater chemistry in mineral exploration, the main thrust of this study. A few papers have been published concerning hydrogeochemical exploration for lead-zinc deposits (Steele, 1984 & 1983; Deering, 1982; Vales and Jurak, 1969 and Ginzburg, 1960) and many papers have been concerned with hydrogeochemical exploration for uranium (e.g., Langmuir and Chatham, 1980). Therefore, much of this present study is frontier-type investigation

#### METHODS AND PROCEDURES

Temperature, pH, conductivity and total alkalinity as mg/L  $\text{CaCO}_3$  were determined in the field on raw water samples. The temperature measurements were not made in the springs but were made while conductivity was determined. Thus, the temperatures do not always reflect aquifer temperatures. A one liter sample and a 500 milliliter sample were filtered through a 0.4 micron pore-size membrane using a freon-pressurized unit. The one liter sample was acidified with three milliliters of 1:1 nitric acid for cation analyses in the laboratory. The 500 milliliter sample was refrigerated for anion, silica and ammonia analyses also at the laboratory.

U.S. Environmental Protection Agency (EPA, 1982) Hach Chemical Company (1976) and Standard Methods (APHA, 1975) methods were used for analyses. See Table 3 for summary of the analytical methods used. Table 4 gives the precision and detection limits for the analyses.

Springs were located from U.S. Geological Survey topographic

TABLE 3. SUMMARY OF ANALYTICAL METHODS. THE METHOD USED IS INDICATED IN ( ) IF NO ( ), THEN THE METHOD IS THE SAME AS OR SLIGHTLY MODIFIED EPA (1982) METHOD.

Parameter	Method
Temperature	thermometer
pH	pH meter
Specific Conductivity	conductivity meter
Total alkalinity	titration to methyl red end point with 0.02N sulfuric acid (APHA, 1975).
NO <sub>3</sub>	colorimetry cadmium reduction (Hach, 1976)
NH <sub>4</sub>	colorimetry phenate (APHA, 1975)
PO <sub>4</sub> (ortho, dissolved)	colorimetry ascorbic acid (Hach, 1976)
SO <sub>4</sub>	colorimeter turbidimetric (Hach, 1976)
Cl	colorimetry Mercuric nitrate (Hach, 1976)
SiO <sub>2</sub>	colorimetry silicomolybdate (Hach, 1976)
Ca, Mg	AAS* C <sub>2</sub> H <sub>2</sub> -N <sub>2</sub> O flame, CsCl added
Sr	AAS* or flame emission C <sub>2</sub> H <sub>2</sub> -N <sub>2</sub> O flame, CsCl added
Na, K, Li	flame emission H <sub>2</sub> -air flame, CsCl added
Zn, Pb, Cd, Fe, Cu, Ni, Co, Mn	C <sub>2</sub> H <sub>2</sub> -air flame chelation - extraction method of Nix and Goodwin, 1974.

\*AAS atomic absorption spectrometry.



TABLE 4. VARIABLE, PRECISION, DETECTION LIMITS AND RECOMMENDED LIMITS (for drinking water) FOR WATER CHEMISTRY PARAMETERS.

	<u>Variable</u>	<u>Precision</u>	<u>Detection Limits</u>	<u>Limits</u>
Temperature	°C	± 0.5	0.50	
Specific Conductance	µmhos/cm at 25°C	± 5	2.00	
Alkalinity	ppm CaCO <sub>3</sub>	± 5	5	
pH		± 0.1	.01	5 - 9 <sup>1</sup>
PO <sub>4</sub> <sup>-3</sup>	as P ppm	± 0.02	.01	
Cl <sup>-</sup>	ppm	± 0.30	.30	250 <sup>2</sup>
NH <sub>4</sub> <sup>+</sup>	as N ppm	± 0.02	.01	0.5 <sup>2</sup>
SiO <sub>2</sub>	ppm	± 2.00	0.20	
SO <sub>4</sub> <sup>-2</sup>	ppm	± 5.0	2.0	250 <sup>2</sup>
NO <sub>3</sub> <sup>-</sup>	as N ppm	± 0.5	.02	10 <sup>1</sup>
Cd	ppb	± 10%	1	
Zn	ppb	± 10%	2	5000 <sup>1</sup>
Pb	ppb	± 10%	5	50 <sup>1</sup>
Fe	ppb	± 10%	10	300 <sup>1</sup>

TABLE 4. VARIABLE, PRECISION, DETECTION LIMITS AND RECOMMENDED LIMITS (for drinking water) FOR WATER CHEMISTRY PARAMETERS. (continued)

	<u>Variable</u>	<u>Precision</u>	<u>Detection Limits</u>	<u>Limits</u>
	Cu	± 10%	1	
	Ni	± 10%	4	
	Co	± 10%	5	
	Mn	± 10%	2	50 <sup>1</sup>
	Na	± 10%	0.1	
	K	± 10%	0.1	
	Sr	± 10%	0.002	
	Ca	± 10%	1	200 <sup>3</sup>
	Mg	± 10%	0.05	150 <sup>3</sup>

<sup>1</sup>EPA (1976)

<sup>2</sup>Public Health Service (1962)

<sup>3</sup>World Health Organization (1971)



maps and field excursions. Manganese deposits and prospects were obtained from Kline and Ryan (1956). The locations of phosphate, pyrite and lead-zinc deposits were obtained from Stroud (1964). The uranium deposit location was previously known to the author. Geologic worksheets were obtained from the Arkansas Geological Commission in order to determine/confirm the formations from which the springs issue.

## PRINCIPLE FINDINGS AND SIGNIFICANCE

### Batesville Area

General Geology. Rock types associated with the Batesville manganese

The rock types associated with the Batesville manganese district include limestone, chert, shale and sandstone ranging in age from Ordovician to Mississippian. The strata are essentially horizontal with a dip of less than 0.2° to the south and strike generally eastward (McGowen, 1981 and Gordon, 1944).

A generalized stratigraphic column from northern Arkansas is shown in Figure 2; however, not all of these rocks are exposed in the Batesville manganese district. Most of the springs issue from the Cotter, Everton, St. Peter, Silurian and Boone Formations; and manganese mineralization is located predominantly in the Fernvale Limestone, with some mineralization in the Cason Shale and St. Joe Formations. Therefore, only these formations will receive brief descriptions below.

The Cotter Dolomite consists largely of dolostone and nodular

The Cotter Dolomite consists largely of dolostone and nodular

The



System	Formation	Member	
PENNSYLVANIAN	Hartshorne ss. Atoka fm.		
	Morrow Group	Bloyd sh. (undiff.)	Kessler ls. Brentwood ls.
		Hale fm. (undiff.)	Prairie Grove Cane Hill
MISSISSIPPIAN	Pitkin ls. Fayetteville sh. Batesville ss. } Ruddell sh. } Moorefield fm. } Boone fm. Chattanooga sh.	Wedington ss. Hindsville ls.  Sylamore ss.	
DEVONIAN	Penters chert		
SILURIAN	Lafferty ls. } St. Clair ls. } Brassfield ls. }		
ORDOVICIAN	Cason sh.		
	Fernvale ls.		
	Kimmswick ls.		
	Plattin ls.		
	Joachim dol.		
	Everton fm.		
	Powell dol.		
	Cotter dol.		
	Jefferson City dol.		
	Roubidoux fm.		
	Gasconade-Van Buren fm. (undiff.)	Gunter	
CAMBRIAN	Eminence-Potosi fm. (undiff.)		
	Pre-Potosi (undiff)		
PRE-CAMBRIAN			

Figure 2. Generalized stratigraphic column for northern Arkansas. From Caplan (1957).

===== ~

chert and is of Ordovician age. A rather thick section of Eventon Limestone (>210 feet) is present in the study area. The Eventon Formation consists of limestone and some dolomite and sandstone. The Stratton Formation, a middle Ordovician unit, is a quartzite 120-200 feet thick and is 20-200 feet thick in the northern areas of the Batesville district (McGowen, 1981 and Miser, 1940). The Ferryville Formation is an upper Ordovician unit that is primarily a moderately sorted bryozoan and crinoid calcitic biosparite (Coffey, 1981). This formation is massive bedded and ranges in color from dark gray to dark pink to mottled pink and white. The upper 40 to 50 feet of the formation (maximum thickness 125 feet) weathers to a very dark gray, brown or black, reflecting the occurrence of iron and manganese oxides and carbonates (Miser, 1940). Unmanganiferous limestone weathers light gray to white in the lower beds. Accessory minerals include manganese minerals, pyrite, chert fragments and phosphate minerals (McGowen, 1981).

Manganese and ferruginous manganese ores are widely distributed in the Cason Shale. The manganese oxides, mainly psilomelane and braunite, occur as irregular masses in thin horizontal seams and beds, and in replaced alga fossils (Miser, 1940). Although the maximum thickness of the formation is only 12 feet, it varies from shale to limestone to diphasite in the Batesville area. The shale is platy, calcareous, and clayey to silty in texture. The sandstone unit consists of quartz and phosphatic material in the form of shell fragments (Miser, 1922) 14

The dominant Silurian formations in the Batesville district are the St. Clair and Lafferty Formations. The upper and lower most parts of the St. Clair are composed of thin-bedded calcilutite consisting mostly of well-cemented, fine-grained calcite; whereas, the middle unit is a calcirudite which contains accessory minerals which include manganese minerals, pyrite, fluorite, and glauconite (McGowen 1981) The Lafferty is composed of thin-bedded, compact, fine-grained, earthy limestone. The contact between the St. Clair and Lafferty is gradational (Miser, 1940).

The Boone Formation in Figure 2 includes the St. Joe Formation. The St. Joe is a thinly bedded, coarse-grained calcarenite. Minor manganese minerals are present in the St. Joe in the Batesville district. The Boone Formation, Mississippian in age, is composed mainly of chert in the Batesville area, but also contains limestone with a little sandstone and shale (McMahon, 1957)

Although structural features are subtle in the district, anticlines, synclines, basins, arches, and faults are present (Miser, 1940). However, as a whole this district has undergone little deformation, having been warped slightly by minor folds and broken by a few normal faults (Gordon, 1944). The more prominent faults are in the southwestern part of the district and generally trend east-northeast (McGowen, 1981).

#### Mineralization

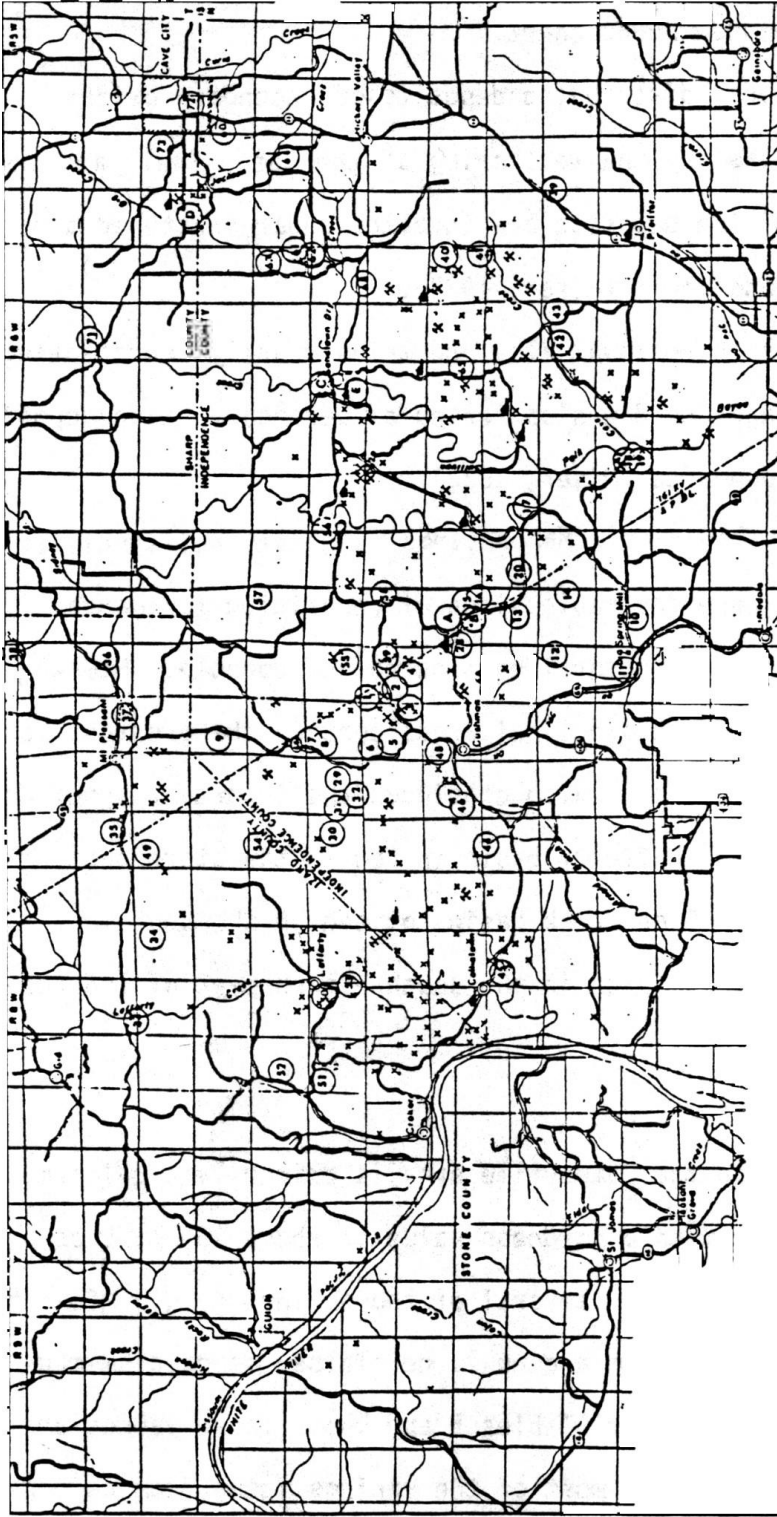
Manganese ore was first produced from the Batesville district in 1849 and continued until 1953, although mining was not continuous

during that period. All mining operation ended with cessation of the government stockpiling program of the 1950's. During that period about 196,000 long tons of ore of at least 35 percent manganese and 236,000 tons of 10-35 percent ferruginous manganese ore were mined at 189 mines and prospects (Kline and Ryan, 1956). Prospects, mines and springs are shown in Figure 3

Host rocks of the primary mineralization are the Fernvale Limestone and, to a limited extent, the Cason Shale and St. Joe Limestone. The manganese ore of the Batesville district consists mainly of oxides, six of which were identified by Branner (1940) as psilomelane,  $K(Mn^{+2}, Mn^{+4})_8 O_{16}$ ; hausmannite,  $Mn^{+2}Mn^{+4}O_4$ ; manganite,  $Mn_2O_3 \cdot H_2O$ ; pyrolusite,  $MnO_2$ ; and wad,  $nMnO \cdot H_2O$ . Coffey (1981) has identified additional manganese minerals of lithiophorite,  $Li_2Mn^{+2}Al_8Mn^{+4}O_{35} \cdot 14H_2O$ ; braunite,  $Ca(Mn, Fe)_{14}^{+3}SiO_{24}$ ; bixbyite,  $(Mn, Fe)_2O_3$  and rancieite,  $(Ca, Mn^{+2})Mn_4^{+4}O_9 \cdot 3H_2O$ . In addition to the oxides, the manganese carbonate, rhodochrosite,  $MnCO_3$ ; and the manganese silicates of bemenite,  $Mn_8Si_6O_{15}(OH)_{10}$ , and neotocite,  $Mn_2Fe_2Si_4O_{13} \cdot 6H_2O$  have also been identified by Miser (1922) and McMahan (1957). The primary minerals in their order of abundance are oxides, carbonates and silicates (Kline and Ryan, 1956)

The principle types of manganese deposits in this district are:

1. Unaltered or slightly altered deposits of the primary minerals rhodochrosite, hausmannite, and braunite. These minerals are disseminated in the Cason Shale and the upper 15 to 50 feet of the Fernvale Limestone and the St. Joe Limestone under the protective



LEGEND

- WIDE OR PROSPECT
- × MINES PRODUCING IN 1933 &
- ▲ BENEFICIATION PLANTS OPERATING IN 1934

nd

mile  
70

mu

bei

mantle of densely bedded Boone chert.

2. Irregularly distributed deposits of secondary oxides in residual clay caused by the weathering of the Cason Shale and the Fernvale Limestone. The deposits are in place under shattered and partly weathered Boone chert (Miser, 1922).

3. Deposits in residual clay and talus usually representing both vertical slumpage and downslope creep of secondary oxide deposits.

4. Placer deposits (Miser, 1922).

Stroud (1964) and McMahon (1957) suggest that synclines within the district were favorable sites of deposition for manganese mineralization with the structural high being unfavorable. McGowen 1981 concluded that these synclinal areas contain the greatest concentration of manganese and he also concluded the important synclines are confined to the west Lafferty basin in the southwestern part of IZARD County and to the Glen Creek basin located on the southwest flank of the East Lafferty arch in the southwestern part of Independence county.

#### Water Quality

The spring water in the Batesville area is primarily a calcium-bicarbonate type water with a hardness value of about 150 mg/L as  $\text{CaCO}_3$  on the average; however, several of the springs (e.g., M66-M75) contain considerable magnesium and would be classed as calcium-magnesium, bicarbonate type water (Tables 5 and 5A). These values are consistent with the fact that most of the springs issue from carbonate rock or the contact between carbonate rock, and shale or sand-

TABLE 5. SPRING WATER FIELD AND ANION ANALYSES FOR THE BATESVILLE DISTRICT. ID-SAMPLE NUMBER COND-SPECIFIC CONDUCTIVITY, MICROMHOS/CM 25 C ALK-ALKALINITY, MG/L AS CaCO3 NO3-NO3 AS N, MG/L. ALL OTHER MEASUREMENTS ARE GIVEN IN MG/L EXCEPT FOR PH. MISSING VALUES ARE INDICATED BY (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	DATE	TEMP	COND	ALK	PH	P04	CL	NH4	NO3	S04	SI02
M01	10/07/83	19.0	508	275	8.9	0.06	2.1	0.08	0.59	10.1	16.0
M02	10/07/83	22.0	480	270	8.7	0.11	3.0	0.12	1.45	11.2	14.6
M03	10/07/83	19.5	377	215	8.0	0.12	11.3	0.09	0.57	8.5	15.6
M04	10/07/83	18.5	136	65	6.5	0.14	1.4	0.07	0.68	8.5	11.6
M05	10/07/83	19.5	433	215	7.0	0.08	17.4	0.07	2.00	11.9	15.6
M06	10/07/83	21.5	402	220	7.3	0.08	10.5	0.08	1.70	10.1	16.6
M07	10/07/83	18.0	353	205	7.4	0.11	9.8	0.08	0.66	10.1	16.6
M08	10/07/83	16.0	342	195	7.5	0.07	4.2	0.07	0.66	9.5	16.6
M09	10/07/83	19.0	510	265	.	0.01	25.6	0.07	1.40	8.5	15.6
M10	11/25/83	14.0	122	70	6.5	0.08	1.8	0.02	0.19	10.1	16.0
M11	11/25/83	14.0	234	120	7.3	0.03	4.7	0.02	0.10	9.5	13.2
M12	11/25/83	11.0	147	85	6.8	0.19	2.4	0.20	0.17	11.2	11.4
M13	11/25/83	14.0	268	135	6.8	0.10	17.3	-0.01	0.30	8.5	14.5
M14	11/25/83	12.0	88	20	5.8	0.06	14.2	0.03	0.68	7.6	14.1
M15	11/25/83	12.0	435	235	6.6	0.03	3.3	-0.01	0.18	8.5	15.5
M16	11/25/83	12.0	410	225	6.9	0.09	3.1	-0.01	0.10	8.5	16.0
M17	11/25/83	14.0	232	120	6.4	0.01	12.2	0.04	0.33	10.1	14.1
M18	11/26/83	13.0	229	75	7.3	0.01	4.4	-0.01	0.63	8.5	12.5
M19	11/26/83	14.0	220	120	7.1	0.04	4.0	-0.01	0.33	9.5	13.2



TABLE 5. SPRING WATER FIELD AND ANION ANALYSES FOR THE BATESVILLE DISTRICT. ID=SAMPLE NUMBER COND=SPECIFIC CONDUCTIVITY, MICROMHOS/CM 25 C  
 ALK=ALKALINITY, MG/L AS CaCO<sub>3</sub> NO<sub>3</sub>=NO<sub>3</sub> AS N, MG/L. ALL OTHER MEASUREMENTS  
 ARE GIVEN IN MG/L EXCEPT FOR PH. MISSING VALUES ARE INDICATED BY (.) AND  
 VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	DATE	TEMP	COND	ALK	PH	PO <sub>4</sub>	CL	NH <sub>4</sub>	NO <sub>3</sub>	SO <sub>4</sub>	SI02
M20	11/26/83	15.0	216	155	7.3	0.06	1.6	-0.01	0.12	6.2	14.1
M21	11/26/83	14.0	146	75	7.3	-0.01	3.6	-0.01	0.19	14.8	8.3
M22	11/26/83	14.0	145	268	7.0	0.11	4.0	-0.01	0.74	8.5	10.5
M23	11/26/83	15.0	140	258	7.2	0.02	4.4	-0.01	0.74	10.1	8.6
M24	11/26/83	16.0	313	190	7.2	0.03	3.1	-0.01	0.94	8.5	14.1
M25	11/26/83	15.0	185	330	7.1	0.07	3.1	-0.01	1.09	7.6	14.1
M26	11/26/83	16.0	215	378	7.1	0.20	3.6	-0.01	0.91	10.1	14.5
M27	11/26/83	15.0	195	336		0.14	3.3	-0.01	0.98	8.5	16.0
M28	11/26/83	16.0	330	205	7.7	0.07	3.6	-0.01	0.88	8.5	14.1
M29	11/26/83	26.0	235	160	7.5	0.06	4.2	-0.01	0.14	10.1	15.0
M30	11/26/83	14.0	171	75	5.7	0.20	3.1	-0.01	1.14	10.1	9.6
M31	11/26/83	14.0	366	210	6.5	0.10	2.2	0.15	1.14	8.5	14.1
M32	11/26/83	14.0	458	255	6.2	0.06	0.9	0.44	0.14	8.5	11.4
M33	01/13/84	14.0	238	135	7.2	-0.01	5.5	0.04	0.60	11.2	11.6
M34	01/13/84	6.0	117	60	7.7	0.03	10.0	0.06	0.01	12.5	
M35	01/13/84	13.0	125	186	7.0	0.03	1.3	0.07	0.83	10.1	18.8
M36	01/13/84	13.0	223	140	6.8	0.01	2.5	0.05	0.86	10.6	16.7
M37	01/13/84	11.0	269	155	6.5	0.01	4.0	0.06	0.80	11.9	12.3
M38	01/13/84	10.0	234	145	6.6	0.04	4.8	0.11	0.78	10.1	17.8



TABLE 5. SPRING WATER FIELD AND ANION ANALYSES FOR THE BATESVILLE DISTRICT. ID=SAMPLE NUMBER COND=SPECIFIC CONDUCTIVITY, MICROMHOS/CM 25 C ALK=ALKALINITY, MG/L AS CaCO<sub>3</sub> NO<sub>3</sub>=NO<sub>3</sub> AS N, MG/L. ALL OTHER MEASUREMENTS ARE GIVEN IN MG/L EXCEPT FOR PH. MISSING VALUES ARE INDICATED BY (.). AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	DATE	TEMP	COND	ALK	PH	PO4	CL	NH4	NO3	SO4	SI02
M39	01/14/84	12.0	176	100	7.2	0.05	2.5	0.05	0.08	10.1	13.0
M40	01/14/84	12.0	315	180	7.0	0.20	4.3	0.17	0.10	13.6	17.8
M41	01/14/84	4.5	144	80	7.3	0.05	9.5	0.01	0.14	10.1	12.6
M42	01/14/84	11.0	179	110	7.5	0.06	4.8	0.06	0.22	11.9	12.8
M43	01/14/84	12.0	290	135	7.1	0.17	2.8	0.10	0.11	10.6	15.8
M44	01/14/84	4.0	227	25	7.6	0.01	53.5	-0.01	0.18	17.7	13.0
M45	01/14/84	7.0	367	180	.	0.05	6.0	0.02	0.32	13.6	10.7
M46	04/12/84	21.0	313	245	6.6	0.20	1.2	0.07	0.08	8.5	9.2
M47	04/12/84	16.0	177	85	7.0	-0.01	4.4	0.07	0.58	10.1	10.2
M48	04/12/84	20.0	154	80	7.8	0.33	4.7	0.07	0.38	12.5	11.3
M49	04/12/84	14.0	207	125	6.2	0.04	3.0	0.07	0.27	10.1	9.2
M50	04/12/85	8.0	221	115	7.4	0.03	3.0	0.06	0.36	7.6	10.6
M51	04/13/84	20.0	55	30	7.5	0.06	7.7	0.12	0.17	10.1	10.6
M52	04/13/84	18.0	171	100	6.6	0.01	4.7	0.11	0.88	10.1	9.9
M53	04/13/84	18.0	376	230	7.2	0.14	2.1	0.11	0.35	11.2	12.4
M54	04/13/84	16.0	295	150	7.2	0.05	1.4	0.09	0.35	10.6	7.0
M55	04/13/84	18.0	3	10	7.8	0.03	1.9	0.09	0.02	11.2	9.9
M56	04/13/84	21.0	194	110	.	0.11	1.9	0.10	0.27	10.1	8.6
M57	04/13/84	16.0	106	5	6.4	0.02	12.8	0.12	1.09	10.1	7.9

TABLE 5. SPRING WATER FIELD AND ANION ANALYSES FOR THE BATESVILLE DISTRICT. ID-SAMPLE NUMBER COND-SPECIFIC CONDUCTIVITY, MICROMHOS/CM 25 C ALK-ALKALINITY, MG/L AS CaCO3 NO3-NO3 AS N, MG/L. ALL OTHER MEASUREMENTS ARE GIVEN IN MG/L EXCEPT FOR PH. MISSING VALUES ARE INDICATED BY (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	DATE	TEMP	COND	ALK	PH	PO4	CL	NH4	NO3	SO4	SI02
M58	04/13/84	18.0	342	185	6.8	0.16	2.8	0.11	0.64	11.2	7.9
M59	04/13/84	17.0	290	180	6.2	0.10	3.0	0.10	0.80	8.5	12.8
M60	06/11/84	11.0	288	105	7.8	0.01	11.0	-0.01	0.70	9.2	12.2
M61	06/11/84	18.0	251	160	7.5	0.17	2.3	0.78	0.22	7.4	11.8
M62	06/11/84	14.0	289	180	7.6	0.15	2.8	0.66	0.70	5.7	14.0
M63	06/11/84	15.0	252	150	8.0	-0.01	1.6	0.64		6.3	11.4
M64	06/11/84	17.0	81	45	7.1	-0.01	2.4	-0.01	0.42	10.3	9.8
M65	06/11/84	12.0	271	150	8.0	0.05	1.5	-0.01	0.08	9.8	11.8
M66	06/11/84	26.0	294	170	8.3	0.03	2.3	-0.01	0.17	7.4	9.8
M67	06/11/84	26.0	289	165	8.4	0.05	2.0	0.08	0.18	7.9	9.1
M68	06/11/84	25.0	400	295	8.3	0.02	3.3	-0.01	0.22	9.2	14.0
M69	06/12/84	14.0	317	155	6.5	0.84	4.0	-0.01	0.10	10.3	18.4
M70	06/12/84	21.0	356	210	7.1	1.90	10.5	0.01	0.10	9.8	13.5
M71	06/12/84	12.5	331	165	7.7	0.74	2.5	0.05	0.07	9.2	11.8
M72 <sup>1</sup>	06/12/84	17.0	336	165	7.1	3.62	11.0	-0.01	0.06	6.3	14.9
M73	06/12/84	16.0	260	85	7.1	1.60	3.5	0.01	0.06	4.2	9.1
M74	06/12/84	17.0	331	165	7.6	1.39	2.0	-0.01	0.01	11.0	9.8
M75	06/12/84	17.0	371	175	7.5	1.30	2.5	-0.01	0.05	9.8	11.8

TABLE 5A. CATION ANALYSES. SPRING WATER SAMPLES FROM THE BATESVILLE DISTRICT. NA, K, CA, AND MG VALUES ARE IN MG/L AND ALL OTHER VALUES ARE IN UG/L. MISSING VALUES ARE GIVEN AS (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

	MN	FE	CU	ZN	CD	MG				
M01	108	21		-3		2.0	70		3.5	0.070
M02	670	71	30		25	.5	2.00	04.0	2.3	0.054
M03	20					3.0	.00	78.0	.5	0.039
M04	27		-5			.1	0.80	.0	5.3	0.020
M05	33					5.0	0.70		4.3	0.040
M06				24		3.	.20	76.0	5.3	0.040
M07		-8	-3	10		5.0	2.60	72.0	2.6	0.036
M08			-5			2.3	1.	72.0	3.	0.038
M09		427		20			0.40	.0	30.7	0.034
M10			-5			3.3	0.70	23.0	.9	0.019
						3.5	.00	.0	.6	0.045
M12	907	958	41			3.3	3.	30.0	.4	0.021
M1						10.0	.20	45	.5	0.039
	164	327	25		254	7.2	1.00	8.0	.5	0.021
						2.8	2.30	74.0	14.	0.047
M16				20		2.4	0.90		3.8	0.050
					30	5.3	2.00		3.	0.026
M18						3.1	1.	.8	3.1	0.030
M19								46.0		0.027
					-1	3.	0.07			

TABLE 5A. CATION ANALYSES OF SPRING WATER SAMPLES FROM THE BATESVILLE DISTRICT. NA, K, CA, AND MG VALUES ARE IN MG/L AND ALL OTHER VALUES ARE IN UG/L. MISSING VALUES ARE GIVEN AS (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	MN	FE	NI	CO	CU	PB	ZN	CD	NA	K	CA	MG	SR
M20	4	56	49	3	7	5	15	2	2.2	0.9	51	2.4	0.026
M21	4	13	6	-3	3	13	10	2	1.3	0.6	20	7.6	0.019
M22	6	47	-5	3	5	5	3	-2	2.8	1.3	39	12.8	0.033
M23	6	15	-5	-3	7	10	3	-2	2.8	1.2	39	13.2	0.030
M24	141	35	3	14	3	38	23	6	2.5	1.0	76	5.0	0.036
M25	13	31	-5	-3	7	15	14	1	2.5	0.7	102	4.2	0.033
M26	32	71	-5	3	5	25	8	1	2.5	1.0	70	8.8	0.039
M27	4	21	9	8	13	30	19	5	2.7	0.9	70	4.1	0.036
M28	64	24	19	8	10	21	16	5	2.4	0.8	70	4.7	0.039
M29	150	59	19	3	17	38	27	6	2.4	0.7	64	3.8	0.039
M30	10	13	9	3	7	13	12	4	1.6	2.3	28	6.2	0.019
M31	15	47	-5	3	2	5	5	1	1.6	0.6	69	6.8	0.036
M32	11	8	-5	3	7	10	19	-1	1.6	0.7	80	21.6	0.047
M33	20	47	-5	-3	7	10	17	2	2.2	1.0	39	12.0	0.030
M34	11	55	10	3	9	30	11	1	0.8	0.3	20	6.6	0.017
M35	3	47	5	3	16	20	19	1	1.6	0.6	25	11.8	0.021
M36	-2	-4	-3	-3	-3	-5	3	-2	1.4	0.6	29	14.6	0.027
M37	-2	31	-5	3	5	10	3	1	2.4	1.3	33	16.4	0.030
M38	12	13	3	3	3	13	12	3	3.5	2.6	29	15.4	0.036

TABLE 5A. CATION ANALYSES OF SPRING WATER SAMPLES FROM THE BATESVILLE DISTRICT. NA, K, CA, AND MG VALUES ARE IN MG/L AND ALL OTHER VALUES ARE IN UG/L. MISSING VALUES ARE GIVEN AS (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	MN	FE	NI	CO	CU	PB	ZN	CD	NA	K	CA	MG	SR
M39	2	47	5	3	14	10	5	1	2.5	1.2	38	3.0	0.030
M40	3	7	-3	-3	3	5	27	-2	2.4	0.3	80	1.1	0.027
M41	6	18	6	3	3	21	15	6	2.0	1.5	34	1.2	0.021
M42	3	10	-3	3	3	5	7	2	3.5	1.5	36	2.6	0.026
M43	4	7	-3	3	-3	-5	7	-2	1.9	0.9	62	2.2	0.030
M44	6	13	3	-3	3	-5	6	-2	30.0	1.4	10	3.0	0.019
M45	18	13	3	3	3	13	10	-2	2.2	0.7	66	3.7	0.039
M46	-2	26	5	-3	5	5	5	-1	1.0	0.5	90	0.1	0.034
M47	-2	20	-5	-3	5	5	-3	-1	3.4	2.0	29	2.0	0.033
M48	198	108	40	20	2	71	19	4	2.4	1.4	27	1.3	0.044
M49	30	26	10	6	9	20	11	1	1.8	0.9	28	8.8	0.036
M50	6	13	-5	-3	7	-5	3	-1	1.8	1.1	39	2.0	0.024
M51	3	26	-5	-3	2	-5	-3	-1	1.0	0.9	7	0.1	0.024
M52	30	37	6	5	-2	8	4	1	1.6	1.1	33	1.1	0.032
M53	7	30	-6	5	2	4	14	1	1.4	0.6	85	2.5	0.046
M54	10	15	6	2	2	-4	29	1	1.4	0.7	42	15.2	0.032
M55	-1	28	-6	2	7	-4	11	1	1.2	0.5	2	0.1	0.018
M56	39	-8	-6	2	2	-4	4	-1	1.4	0.3	26	10.4	0.022
M57	39	-8	6	13	2	4	14	-1	7.4	0.9	-1	5.9	0.024

TABLE 5A. CATION ANALYSES OF SPRING WATER SAMPLES FROM THE BATESVILLE DISTRICT. NA, K, CA, AND MG VALUES ARE IN MG/L AND ALL OTHER VALUES ARE IN UG/L. MISSING VALUES ARE GIVEN AS (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	MN	FE	NI	CO	CU	PB	ZN	CD	NA	K	CA	MG	SR
M58	5	15	-6	5	2	8	5	-1	1.6	0.4	59	15.2	0.044
M59	4	15	-6	5	2	4	7	1	1.8	0.6	64	2.0	0.046
M60	2	8	-6	2	2	-4	4	-1	6.2	1.5	50	6.3	0.024
M61	1	8	-6	-2	2	8	6	-1	1.4	0.6	32	16.0	0.026
M62	-1	8	-6	-2	2	13	4	1	1.4	0.8	34	16.8	0.031
M63	7	8	-2	-4	1	1	-1	-1	1.0	0.8	29	16.0	0.042
M64	1	-8	-6	-2	2	-4	3	-1	1.8	1.0	7	4.1	0.020
M65	32	15	12	5	2	21	8	1	2.1	1.3	50	4.1	0.030
M66	11	15	6	-2	2	13	4	-1	2.1	1.1	37	17.2	0.034
M67	67	22	23	2	-2	13	5	-1	1.6	0.9	37	17.6	0.032
M68	75	15	17	5	-2	30	8	2	2.1	0.6	61	20.8	0.040
M69	4	8	12	-2	2	13	10	1	2.1	0.9	26	16.8	0.025
M70	2	-8	-6	2	2	13	4	-1	5.1	0.8	45	23.6	0.044
M71	-1	-8	-6	-2	2	13	8	1	1.4	0.9	39	20.0	0.034
M72	4	8	17	-2	7	13	11	-1	10.0	3.1	36	16.8	0.048
M73	4	8	6	2	2	4	6	4	1.8	0.6	31	13.2	0.038
M74	2	-8	-6	2	2	4	3	-1	1.4	0.6	42	16.4	0.044
M75	5	8	-6	2	2	8	7	1	1.8	1.2	41	20.8	0.042



stone.

Generally the spring water of this area is of good quality based on the chemical analyses performed. However, 11 springs out of 75, exceed drinking water limits (Tables 4, 5 and 5A). All 11 springs (Number 1, 2, 9, 12, 14, 24, 28, 29, 48, 67 and 69) exceed the limits for manganese and/or iron. It should be noted, however, that the manganese and iron limits are set because of staining problems rather than for health reasons. Additionally spring 48 with a lead concentration of 71 ppb exceeds the 50 ppb drinking water limit (Tables 4 and 5A).

#### Comparison of Water Chemistry

Although there is an overall general similarity of the spring water chemistry in the Batesville district and other carbonate areas there are some slight differences. Tables 6 and 6A give the range of values and median values for spring water samples from several areas in northern Arkansas and Joplin, Missouri. The Ponca, Rush, Zinc and Joplin areas are all lead-zinc mineralized areas. Also it should be noted that data for carbonate units 1 and 2 are based on unfiltered water (Tables 6 and 6A).

The Batesville district spring water is slightly higher in orthophosphate, based on median values, than the other areas listed in Table 6. This slightly higher phosphate value might be indicative of some contamination; however, as ammonia, chloride and nitrate values do not appear to be elevated, this interpretation does not seem warranted. Another explanation of the slightly higher phosphate could

TABLE 6. COMPARISON OF SPRING WATER FIELD AND ANION DATA. THE TOP VALUES ARE THE RANGE AND THE BOTTOM VALUE IS THE MEDIAN VALUE. SEE FOOTNOTE FOR JOPLIN DATA. NUMBERS IN ( ) ARE THE NUMBER OF SAMPLES FROM EACH AREA.

Area	Specific Alkalinity Cond. 25 C	as mg/l CaCO <sub>3</sub>	pH	PO <sub>4</sub> <sup>-3</sup> as P ppm	Cl <sup>-</sup> ppm	NH <sub>4</sub> <sup>+</sup> as N ppm	SiO <sub>2</sub> ppm <sup>2</sup>	SO <sub>4</sub> <sup>=</sup> ppm	NO <sub>3</sub> <sup>-</sup> as N ppm
Ponca <sup>1</sup> (48)	12-447 302	15-358 183	5.2-8.0 7.4	<.01-.47 .01	.6-4.3 2.0	<.01-1.56 .07	3.1-7.8 5.7	<5.0-23.5 5.9	<.02-1.30 .14
Rush <sup>1</sup> (52)	136-546 348	70-410 195	6.8-8.3 7.6	<.01-.17 <.01	.9-45.1 4.2	<.01-.50 .02	4.2-7.9 5.9	<5.0-55.0 8.5	<.03-20.23 .33
Zinc <sup>1</sup> (43)	168-552 348	90-315 205	6.5-7.8 7.3	<.01-.07 .01	1.3-6.5 2.2	<.01-2.34 .04	4.6-8.5 7.0	<4.2-11.9 5.0	<.02-2.20 .3
Northern Arkansas <sup>2</sup>									
Carbonate unit 1 (16)	192-451 270	85-207 140	7.0-8.4 7.5		1.5-16.0 3.4		6.0-11.0 7.4	<.4-9.0 2.5	.02-13.0 3.4
Carbonate unit 2 (15)	320-600 329	140-282 169	7.6-8.4 7.9		1.5-4.2 3.5		8.2-14.0 11.1	<.4-8.0 2.2	1.4 - 3.9 2.6
Joplin <sup>3</sup> (3)	-	136	7.2	-	-	-			
Washington <sup>4</sup> Co., AR (10)	-		-	<.01-.09 .01	-	-			11.0-4.6 5.6
Batesville <sup>5</sup> (75)	3-510 252	5-378 155	5.7-8.9 7.2	<.01-3.62 .06	.9-53.5 3.3	<.01-.78 .05	7-18.8 12.8	4.2-17.7 10.1	.01-2.00 .34

<sup>1</sup>Data from Steele (1983).

<sup>2</sup>Data from Lammonds and Stephens (1969).

<sup>3</sup>Data from Proctor et al., (1977). Average values for alkalinity and pH. Maximum values for metals.

<sup>4</sup>Data from Coughlin (1975).

<sup>5</sup>Data from this study.

TABLE 6A. COMPARISON OF SPRING WATER CATIONS, THE TOP VALUES ARE THE RANGE AND BOTTOM VALUE IS THE MEDIAN  
SEE FOOTNOTE FOR JOPLIN DATA. NUMBERS IN ( ) ARE THE NUMBER OF SAMPLES FROM EACH AREA.

Area	Zn ppb	Pb ppb	Cd ppb	Fe ppb	Mn ppb	Ni ppb	Co ppb	Cu ppb	Na ppm	K ppm	Ca ppm	Mg ppm	Sr ppb
Ponca <sup>1</sup> (48)	<1- 63 10	<4-100 13	<1-2 2	<3.373 18	<1- 57 4	<3-33 11	<1-27 4	<2-13 3	.1-6.7 1.4	.4-1.4 7	2-98 65	.5-11.9 2.4	22-272 42
Rush <sup>1</sup> (52)	4-252 12	<4-40 6	<1-3 2	<3-36 6	<3-22 <4	<1-16 5	<1-18 8	<2-11 <3	.8-20.0 1.9	.4-4.1 .7	22-118 64	.7-34.5 1.6	17- 90 41
Zinc <sup>1</sup> (43)	6-214 25	<8-48 24	<2-6 <2	<11-50 12	<1-97 4	<4-18 7	<5-21 9	<2-2 <6	1.2-4.2 1.8	.5-2.5 1.0	35-100 68	1.1-30.8 3.1	22-70 46
North. Arkansas <sup>2</sup> Carbonate Unit 1 (16)	-	-	-	<10-200 30	<10-10 <10	-	-	-	1.6-12.0 2.0	.6-1.5 .8	41-105 52	.9-10.0 1.2	-
Carbonate Unit 2 (15)	-	-	-	<10-100 80	- <10	-	-	-	1.8-2.0 2.0	.8-1.5 1.2	26-65 53	5.2-37.0 25.0	-
Joplin <sup>3</sup> (3)	200	6	-	11	-	-	-	1.5	-	-	-	-	-
Wash Co, AR <sup>4</sup> (10)	<2-381 20	<1-2 <1	<.2-1.0 <1	<1-46 <2	< 4-36 1	<2-5 <2	2-6 4	<1-9 <1	3-18 5	.9-3.5 1.8	30-75 54	1-2 2	25-41 38
Batesville <sup>5</sup> (75)	<1-254 10	1-80 10	<1-15 1	2-958 15	<1-907 6	1-49 3	1-29 3	1-20 2	.8-30.0 2.2	.1-3.7 0.9	<1-111 39	.1-30.7 5.0	17-70 33

- 1 Data from Steele (1983).  
2 Data from Lammonds and Stephens (1969).  
3 Data from Proctor et al. (1977). Average values for alkalinity and pH. Maximum values for metals.  
4 Data from Coughlin (1975).  
5 Data from this study.

Note: ppb =  $\mu\text{g/l}$

be the phosphate in the rocks of the district. Slightly higher median sulfate and silica values suggest that some of the water may have had contact with shale. Calcium and higher magnesium values are explained by the shale, but the lower calcium and higher magnesium values can be explained due to the influence of shale, the sandstones and/or the dolomite. In the Batesville district, the median values, but the values are higher than the upper range values for manganese, iron and nickel. Geochemical Exploration

Although the concentration of heavy metals in the carbonate-type groundwater in northern Arkansas is very low, hydrogeochemical exploration has shown promising veins of the lead-zinc area (Steele, 1984 & 1993). The Eh-pH diagram (Figure 4) indicates that the phase controlling  $Mn^{2+}$  concentration of the spring water from the Batesville district, based on the median pH (7.2) and a reasonable estimate of  $Eh$  (about +0.2V) for these waters under these conditions and a carbonate concentration of  $10^{-5.6}$  M (calculated from median alkalinity and pH values), the maximum concentration of  $Mn^{2+}$  possible is 10,974 ppb. Equations 1-3 outline these calculations. Alkalinity of these pH values is essentially due to bicarbonate.

1.  $155 \text{ mg/L CaCO}_3 \text{ (alkalinity)} = 155 \text{ mg/L} \div 50 \text{ mg/meq} = 3.1 \text{ meq/L} \times 61 \text{ mg/meq} = 190 \text{ mg/L}$  or  $10^{-2.5} \text{ M HCO}_3^-$
2.  $(H^+) (CO_3^{2-}) / (HCO_3^-) = 10^{-10.3} = (10^{-7.2}) (CO_3^{2-}) / 10^{-2.5} \cdot 5$   
 $(CO_3^{2-}) = 10^{-10.3} \times 10^{2.5} / 10^{-7.2} = 10^{-5.6} \text{ M}$
3.  $(Mn^{2+}) (CO_3^{2-}) = 10^{-9.3}$   
 $(Mn^{2+}) = 10^{-9.3} / 10^{-5.6} = 10^{-3.7} \text{ M or } 10,974 \text{ } \mu\text{g/L}$

1.32.Al-th30155sulfate conditions reasonable Geochemical Lower

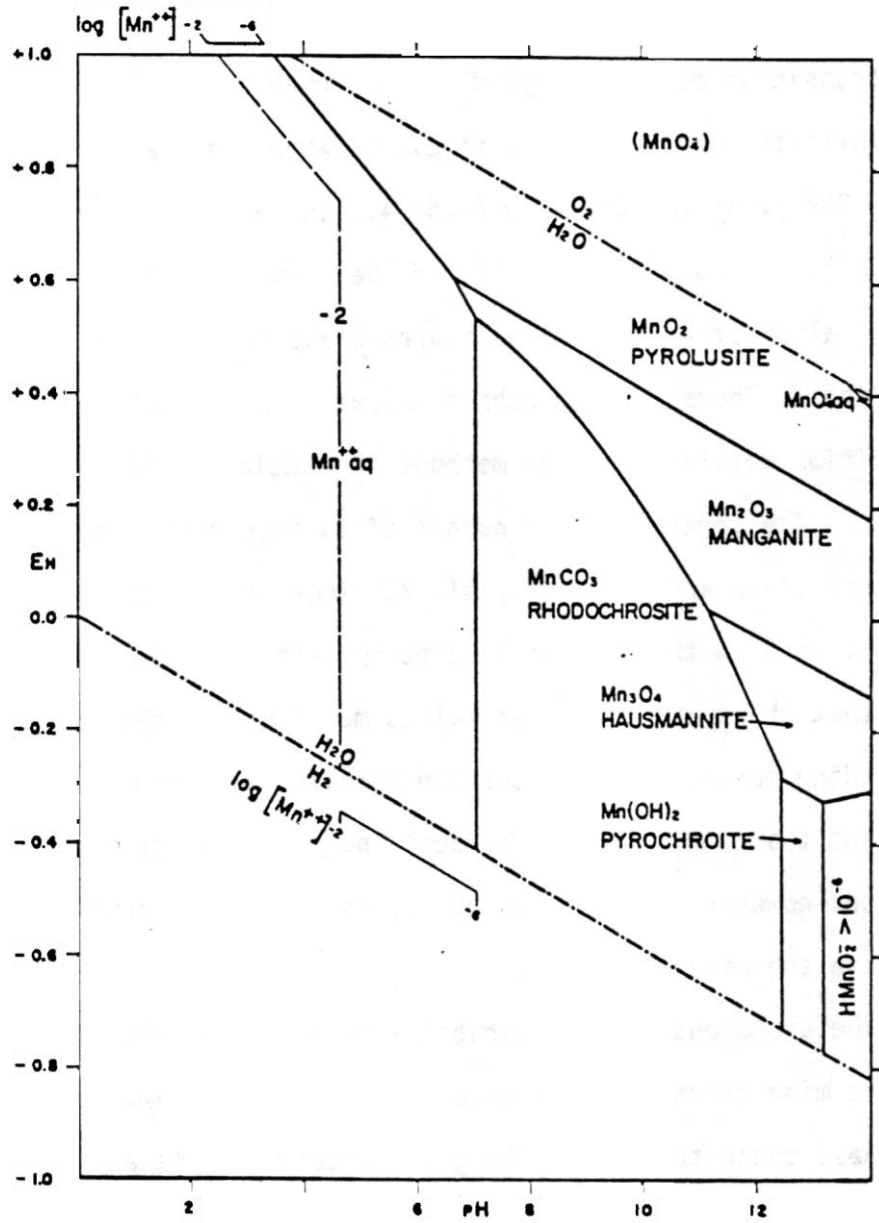


Figure 4.4 Stability relations among some manganese compounds in water at 25°C and at 25 mcs and total sphere total dissolved carbonate species = 10<sup>-4</sup> M. From Garrels and Christ (1965).

"-O..!!Mn10. ■



Other transition metals are present in the manganese-bearing district, especially Ni, Co and Cu (Coffey, 1981). All of the transition metals analyzed in the groundwater (Table 5A) yielded the following correlation coefficients when regressed against manganese:

Fe (0.7490), Ni (0.6085), Co (0.6684), Cu (0.4284), Pb (0.6155), Zn

(0.2089), and Cd (0.5237). All of these correlation coefficients have alpha values of  $< 0.0001$ . See Figures 5 and 5A as examples of these regressions.

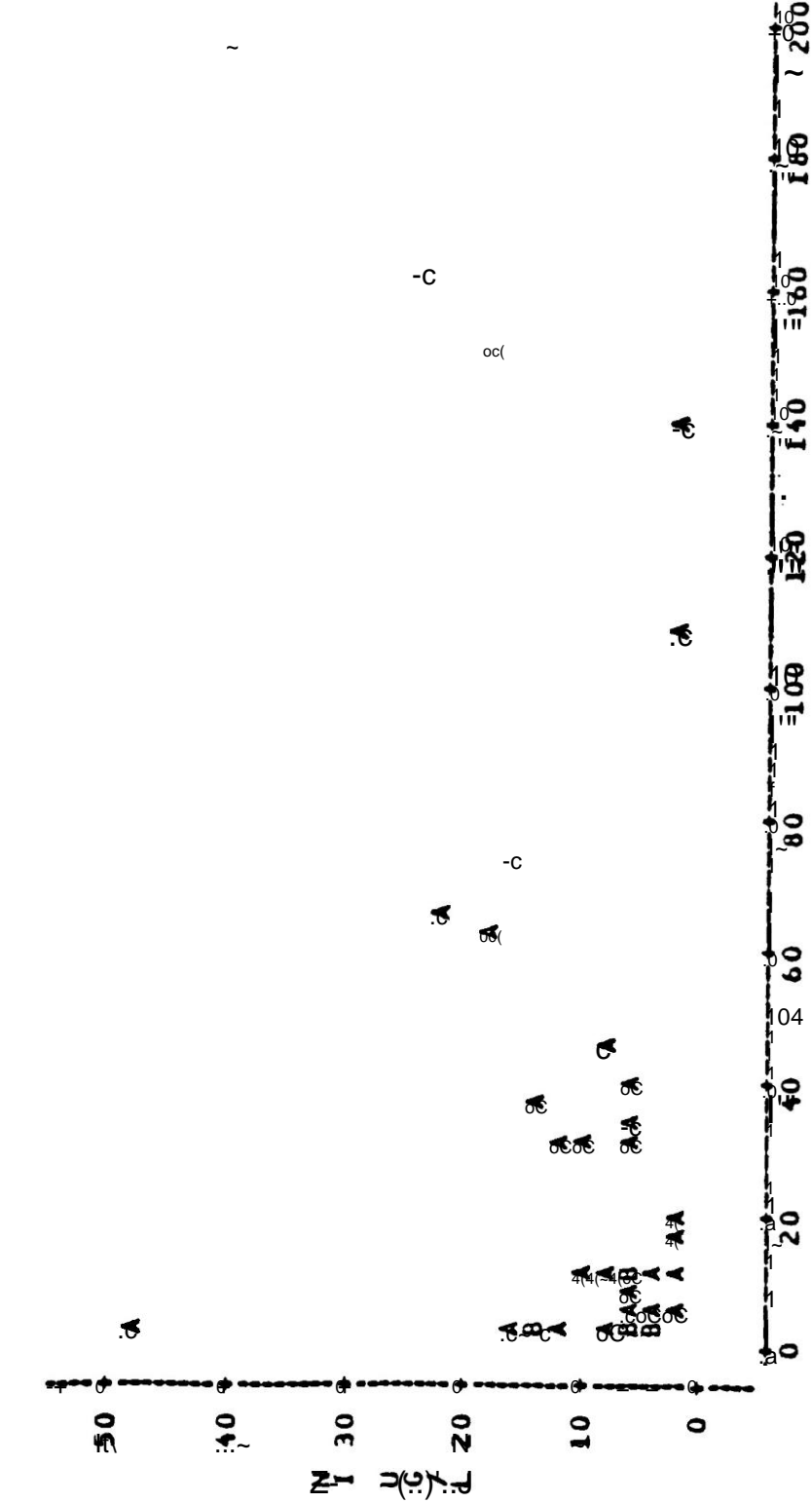
Therefore, threshold values were determined for all the transition metals using the methods of Sinclair (1976) and Lepeltier (1969). The thresholds and number of springs with anomalous metal concentrations are given in Table 7. There are 25 springs out of the 75 collected in the Batesville district with anomalous values; however, note that there are only 8 anomalous metal values that do not have corresponding manganese concentrations. From Table 7 it is apparent that, manganese is the best responding manganese anomalous concentrations. From Table 7 it is apparent that manganese is the best indicator of the manganese mineralization; however, nickel and cobalt, especially in combination, also indicate the mineralization

The anomalous springs exhibit a relationship with distance to nearest mineralization (Tables 8 and 9 and Figure 6).

Dilution of the manganese concentration in the groundwater would be expected if the water from mineralization due to mixing with "non-unique" water. Only 44 percent of the springs within 2000 feet of known mineralization were

anomalous. Thus, hydrologic and chemical factors such as solubility of the various manganese minerals, kinetics, groundwater flow rate, and recharge, as well as groundwater flow path (i.e., the groundwater

i.e., anomalous.(0.2089)Table ,



NOTE: 36 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

A A

z 0 ■ N

z 0 ■ N

FIGURE 5.1 PLOT OF NEI VS MN.

LEGEND: A = 1 OBS, B = 2 OBS, ETC

FIGURE 5.2 PLOT OF NEI VS MN.

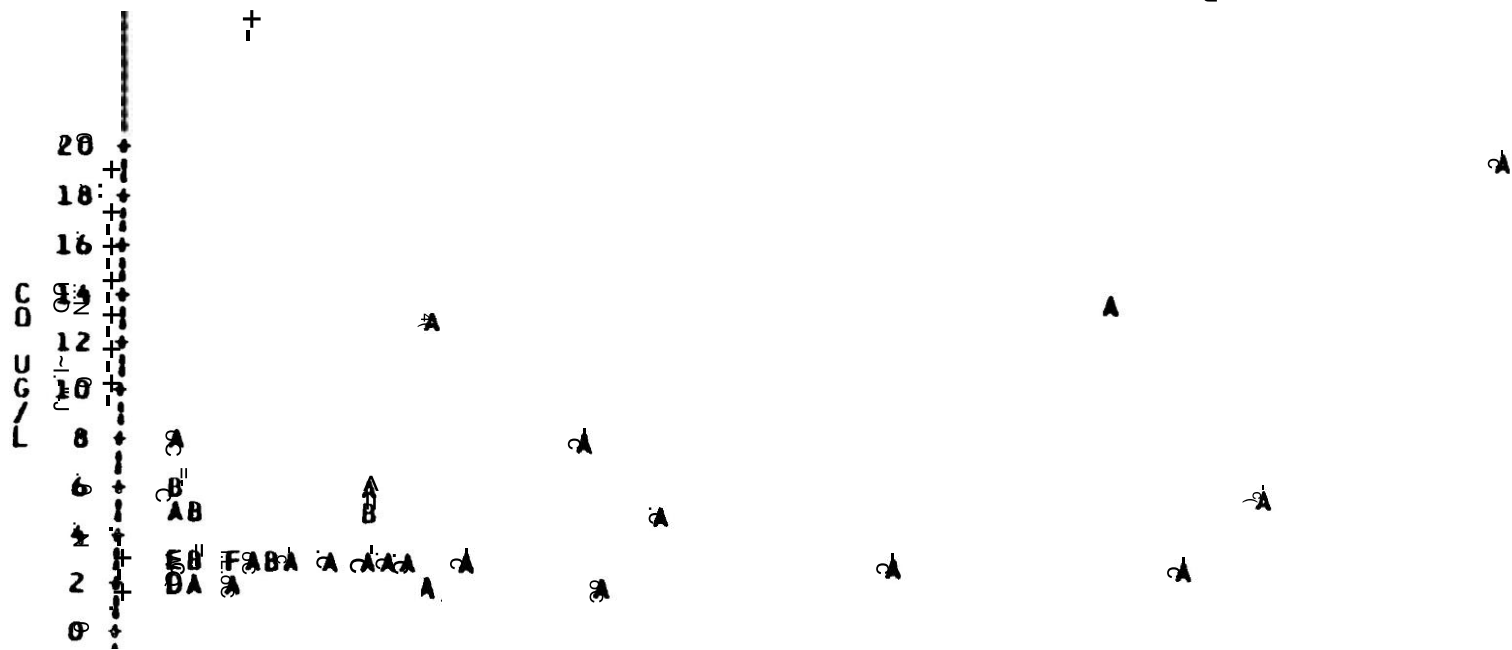
...Jcx

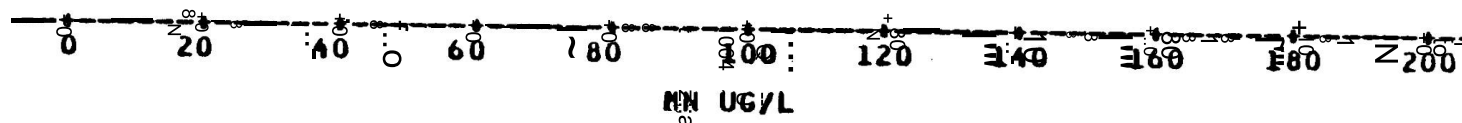
Z

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50



FIGURE 5A. PLOT OF CO VS MN  
 PLOT OF CO+MN LEGEND: A = 1 OBS, B = 2 OBS, ETC.





NOTE: 26 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

TABLE 7. THRESHOLD VALUES AND NUMBER OF ANOMALIES BY ELEMENT FOR THE BATESVILLE DISTRICT.  
 CONCENTRATIONS ARE  $\mu\text{g/L}$ .

Element	Mn	Fe	Ni	Co	Cu	Pb	Zn	Cd
Threshold	32	186	14	4	16	41	46	9
# of Anomalous Springs	17	3	11	9	3	2	2	2
# of Anomalous Springs Without Mn Anomalies		0	2	3	1	0	1	1



TABLE 8. RELATIONSHIP BETWEEN NUMBER OF ANOMALOUS SPRINGS AND DISTANCE TO NEAREST MINERALIZATION IN THE BATESVILLE DISTRICT.

	Distance to Nearest Mineralization (feet)		
	0-2000	2000-4000	>4000
Number of Anomalous Springs	15	7	3
Number of Springs	34	26	15
Percent Anomalous Springs	44	27	20

1

TABLE 9. LIST OF SPRINGS IN THE BATESVILLE AREA WITH ANOMALOUS HEAVY METAL CONCENTRATIONS. ALL UNITS ARE IN UG/L. DIST-DISTANCE IN FEET TO NEAREST MINERALIZATION AND FORM REPRESENTS FORMATION WITH 1-COTTER, 2-EVERTON, 4-KIMMSWICK, 6-LAFFERTY/ST. CLAIR, AND 7-BDOONE.

ID	MN	FE	NI	CO	CU	PB	ZN	CD	DIST	FORM
M01	108	21	3	3	7	-5	-3	4	850	1
M02	670	71	30	3	7	30	25	3	300	7
M05	33	18	6	3	-3	5	15	2	1000	2
M06	10	15	5	3	2	24	73	2	1600	2
M09	36	427	15	3	14	20	42	2	1800	2
M10	-2	-8	-5	-3	2	-5	-3	15	9200	7
M11	4	13	14	6	-3	17	14	4	9800	7
M12	907	958	41	29	20	80	32	14	3900	7
M13	47	13	9	3	-3	5	14	4	1300	6
M14	164	327	25	6	5	10	254	2	800	7
M18	4	7	14	6	-3	21	8	4	400	6
M20	4	56	49	3	7	5	15	2	2200	1
M24	141	35	3	14	3	38	23	6	1200	2

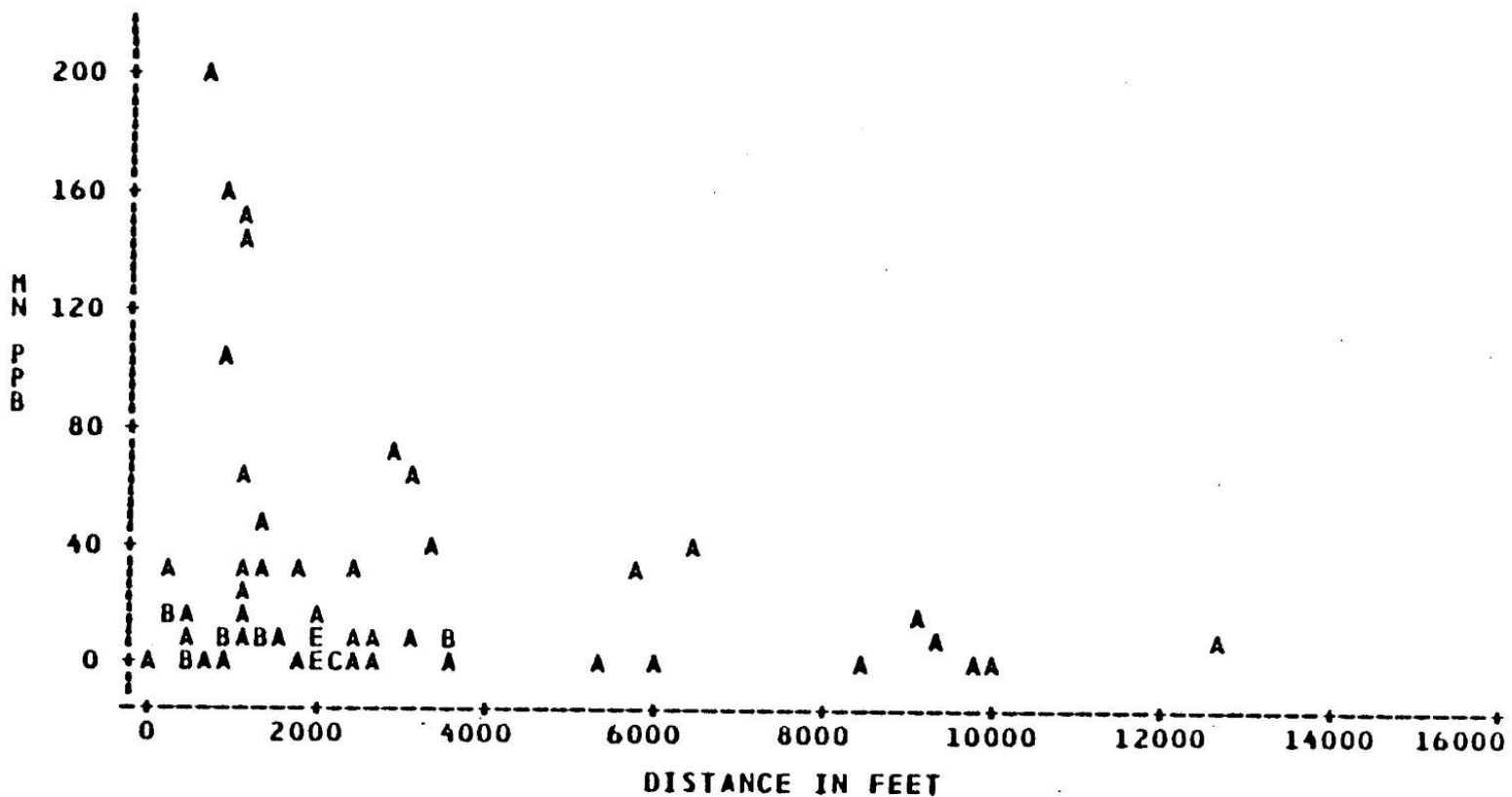
TABLE 9. LIST OF SPRINGS IN THE BATESVILLE AREA WITH ANOMALOUS HEAVY METAL CONCENTRATIONS. ALL UNITS ARE IN UG/L. DIST-DISTANCE IN FEET TO NEAREST MINERALIZATION AND FORM REPRESENTS FORMATION WITH 1-COTTER, 2-EVERTON, 4-KIMMSWICK, 6-LAFFERTY/ST. CLAIR, AND 7-BOONE.

ID	MN	FE	NI	CO	CU	PB	ZN	CD	DIST	FORM
M26	32	71	-5	3	5	25	8	1	1400	2
M27	4	21	9	8	13	30	19	5	100	2
M28	64	24	19	8	10	21	16	5	1200	1
M29	150	59	19	3	17	38	27	6	1200	2
M35	3	47	5	3	16	20	19	1	3500	2
M48	198	108	40	20	2	71	19	4	600	7
M56	39	-8	-6	2	2	-4	4	-1	3300	2
M57	39	-8	6	13	2	4	14	-1	6500	2
M65	32	15	12	5	2	21	8	1	200	1
M67	67	22	23	2	-2	13	5	-1	3200	2
M68	75	15	17	5	-2	30	8	2	2900	7
M72	4	8	17	-2	7	13	11	-1	2500	4

~N~E

FIGURE 6. PLOT OF THE MN CONCENTRATION OF SPRING WATER VS DISTANCE TO NEAREST MINERALIZATION FOR THE BATESVILLE DISTRICT.

PLOT OF MN\*DIST LEGEND: A = 1 OBS, B = 2 OBS, ETC.



NOTE: 10 OBS HAD MISSING VALUES OR WERE OUT OF RANGE

may never have come in contact with the mineralization) are important factors in controlling anomalous metal concentrations of the groundwater.

The latter statement above indicates that there could be a relationship between the formation from which a spring issues and anomalies. Fifty percent ( $4/8$ ) of the springs from the Cotter Formation have anomalous values, 29 percent ( $12/42$ ) from the St. Peter-Everton, 29 percent ( $2/7$ ) from the Silurian Formations and 50 percent ( $7/14$ ) from the Boone-St. Joe. Although there are not a sufficient number of springs from some of the formations to allow conclusive interpretation, there appears to be a relationship between the anomalous springs and formation (Table 9).

There are no unusually high silica values for springs in this area that would suggest a geothermal source of some of the water.

#### Four Mineralized Areas

##### General Geology

There are two phosphate mineralized areas in the Peyton Creek vicinity of Highway 65 south of Leslie (Figure 7). The most southerly and less mineralized deposit is the smaller of the two and has been referred to as the Marshall deposit. The results of drilling at the Marshall deposit indicate that this deposit is associated with a black, oolitic, limestone conglomerate that marks the base of the Cane Hill Formation and in a cross-bedded brownish sandstone. The outcrop of a single continuous bed of phosphate dissipates into a series of thin, discontinuous, phosphate layers at depth (Stroud, 1961).

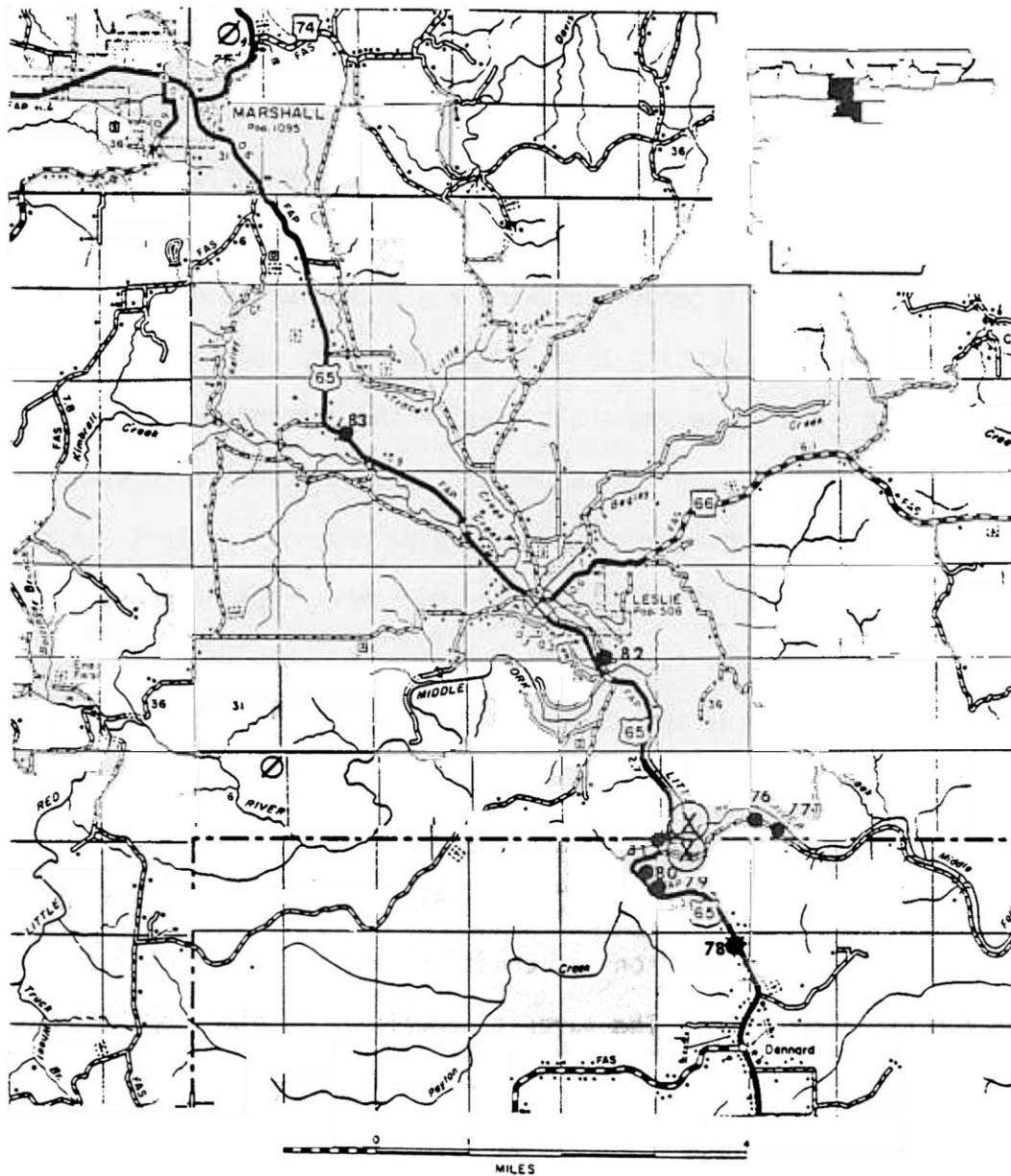


Figure 7. Location of groundwater sites (solid circles) sampled in the vicinity of the Peyton Creek phosphate deposit (circle X). Samples 78, 80 and 81 are from wells and 82 and 83 are from springs. All other samples are from springs.

The typical P<sub>2</sub>O<sub>5</sub> content of the rocks at this site is about 8 percent

(1964)

The larger and more mineralized Ferguson phosphate deposit was deposited during the same time as the enclosing sandstone in the Boone Formation. The deposit has a tongue shape that extends southward a distance of about 2700 feet from the outcrop, suggesting that it may have been deposited from a bay or estuary. Sandstone and shale overlie the phosphate-bearing sandstone. The ore-bearing zone has an oolitic texture, calcite cement, carbonized wood fragments, pyrite and varying amounts of quartz sand. Ore reserves are estimated to be 2,800,000 short tons of phosphate rock averaging 19 percent P<sub>2</sub>O<sub>5</sub> and occurring in a bed of at least five feet thick. Variations in grade are due primarily to dilution by sand grains.

Deposits of pyrite occur in a highly fractured zone of the Cotter Dolomite in Carroll County (Figure 8). The deposit is estimated to contain 462,000 long tons of Dolomite that averages 24.3 percent sulfur (Figure 8). (The deposit is located in 462,000 long tons of crude ore that averages 24.3 percent sulfur (Strodtgen, 1925). The largest deposits have been noted in the SE 1/4 SW 1/4 sec. 8, T20N R24W and also encountered in occurrences have been noted in the SE 1/4 SW 1/4 sec. 8, T20N R24W and also encountered in wells dug in sec. 7 between these two deposits. The largest deposit is exposed mostly as limonite along the bed of a creek for about 100 feet (Branner, 1940).

Lead and zinc minerals occur in the Boone Formation in Washington County. The Morrow prospect is located on the bank of Fly Creek about feet west of the town of Morrow. The ore minerals, galena and







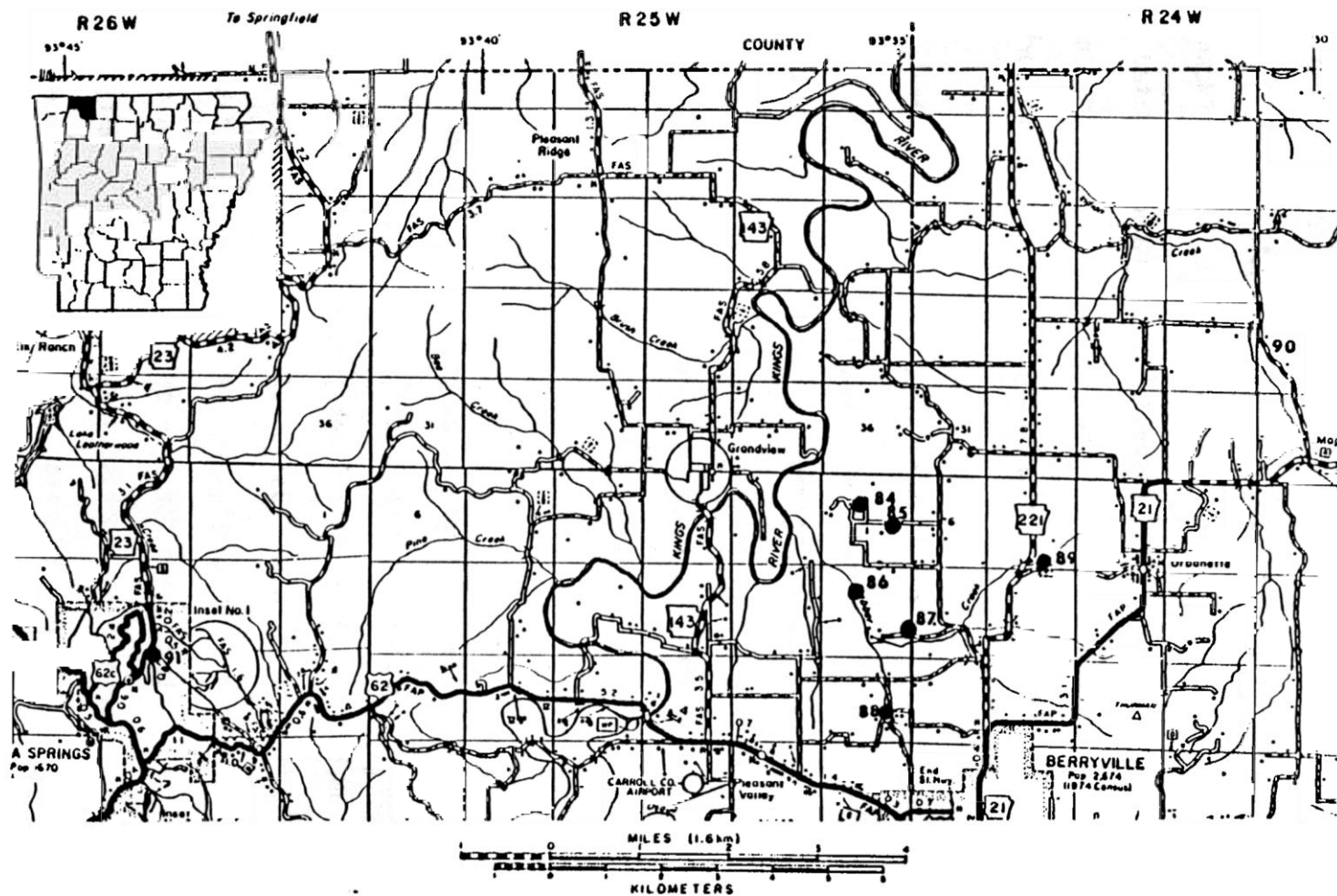


Figure 8. Location of springs (solid circles) sampled in the pyrite mineralized area near Berryville. Pyrite mineralization is located in the NW $\frac{1}{4}$  NE $\frac{1}{4}$  sec. 12, T20N R25W; SE $\frac{1}{4}$  SW $\frac{1}{4}$  sec. 8, T20N R24W; and in sec. 7 between these two sections.

sphalerite in about equal proportions, occurs in scattered pockets and small fractures in the chert, and to a lesser extent, in the limestone (Branner, 1940). Although a mill was erected to handle the ore, the only output was only about 50 tons, half galena and half sphalerite (McKnight, 1935). There is another lead-zinc prospect (Burr prospect) located in the SW 1/4 SW 1/4 sec. 28, T16N R32W of Washington County; however, sampling was confined to the area surrounding the larger and richer Morrow prospect (Figure 9). There is a slightly radioactive anomaly in the sandstone body above the Chattanooga Shale located in Washington County (Figure 10). This sandstone contains about 150 ppm U compared to a range of 17-44 ppm U for the surrounding area (Duncan, 1983). Unfortunately, the springs in the area, issued from the overlying Boone limestone and probably do not come in contact with the uranium mineralization.

### Water Quality

Only a few springs were collected from each of the mineralized areas - phosphate (Peyton Creek), pyrite (Berryville), lead-zinc (Morrow) and uranium (Friendship Creek); thus, these springs may not be representative of the water quality of the entire area. Five (P78-P80 and P83) of the eight springs in the Peyton Creek phosphate area exceed drinking water limits for iron or manganese because of staining problems. Spring P81 also has an extremely high ammonia value, suggestive of nearby waste contamination. The spring water composition in the Peyton Creek area generally reflects the source rocks for the



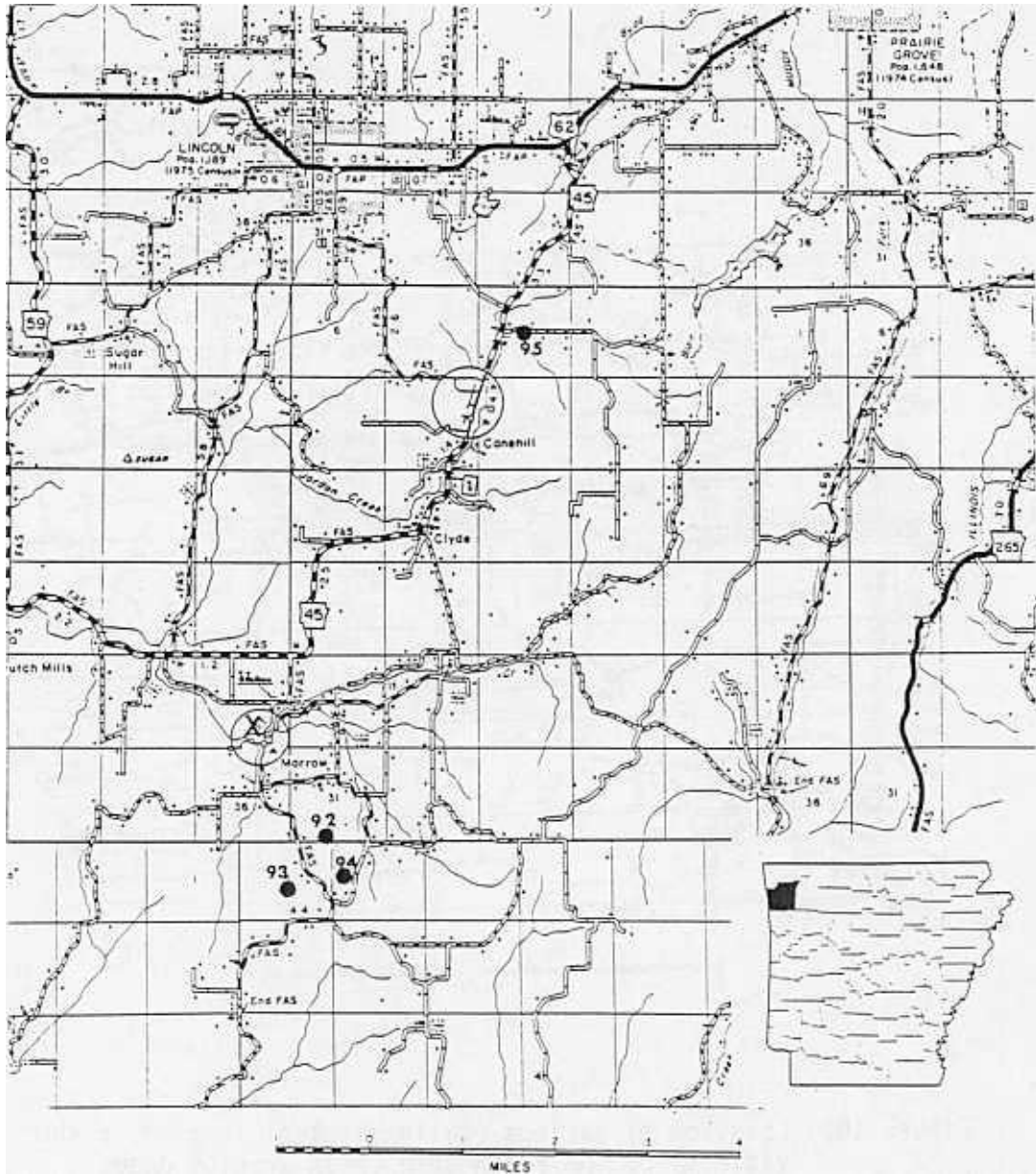


Figure 9. Location of springs (solid circles) sampled in the vicinity of the Morrow lead-zinc deposit (x).

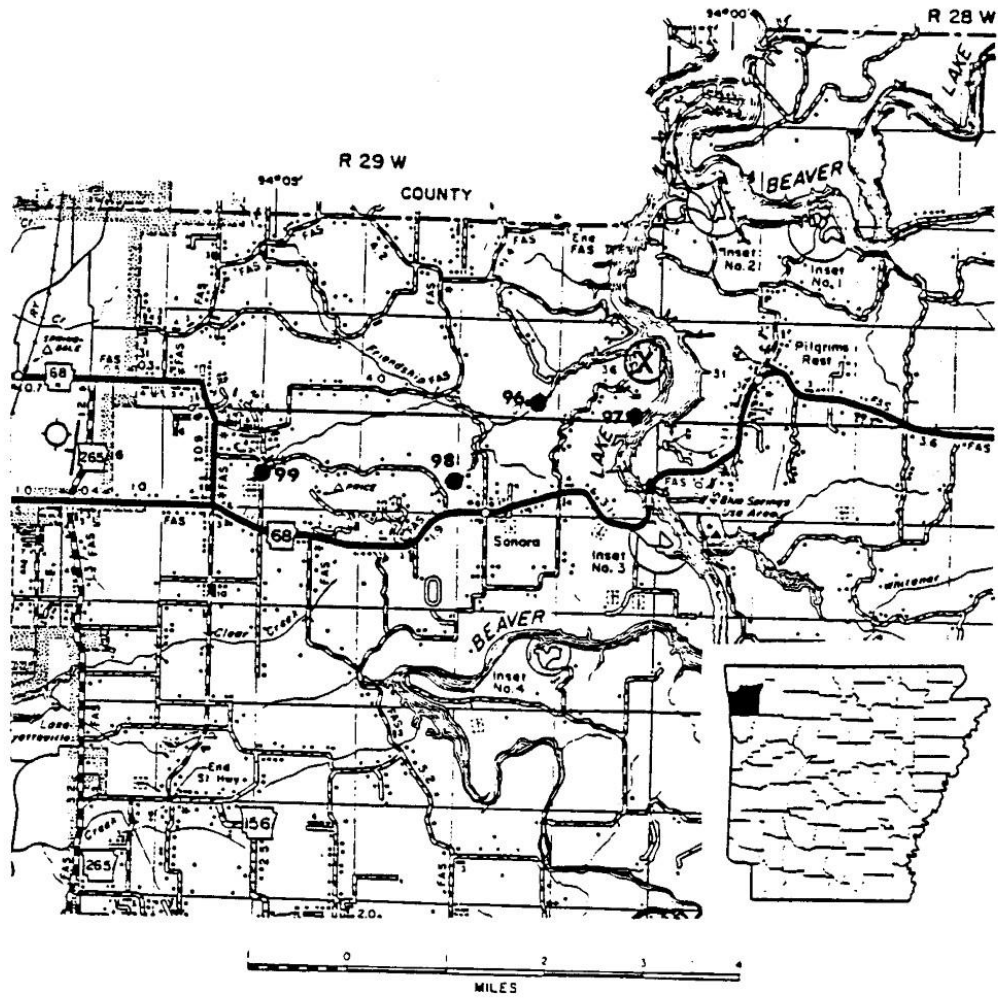


Figure 10. Location of springs (solid circles) sampled in the vicinity of the Friendship Creek uranium deposit (circled x).

groundwater. The springs (P76-P79) issuing from sandstone have lower pH values (about 5.5) and lower hardness (about 20 mg/L as  $\text{CaCO}_3$ ) whereas, those issuing from dolostone (P80-P83) have a calcium or calcium-magnesium type water with pH values about 7.1 and hardness about 300 mg/L as  $\text{CaCO}_3$  (Tables 10 and 10A).

Only one spring (B86) located in the midst of the pyrite deposit near Berryville exceeded drinking water limits, and it only exceeded limits for manganese. The spring water collected in the Berryville area is of a calcium-magnesium bicarbonate type, reflective of the Cotter Dolomite source of the groundwater. Spring F98 in the uranium (Friendship Creek) area exceeded the manganese limits, and no springs in the lead-zinc (Morrow) area exceeded the drinking water limits. The springs in the Friendship Creek and Morrow areas issue from limestone which results in calcium bicarbonate type water (Tables 10 and 10A).

#### Summary of Water Chemistry

Because no more than eight springs, including sites as near as possible to mineralization and background sites, were collected in the Peyton Creek, Berryville, Morrow and Friendship Creek areas, the data from these areas should not be considered as representative of a very wide area. However, with this caution in mind, the spring water chemistry from these areas will be compared below and in Tables 11 and 11A.

The spring water from Peyton Creek is lower in alkalinity, pH and calcium; and higher in silica, zing, iron, manganese, strontium and possibly sodium (Tables 11 and 11A). These observations are indicative of the presence of shale in the Peyton Creek area. Despite



TABLE 10. SPRING WATER FIELD AND ANION ANALYSES FOR PEYTON CREEK (P); BERRYVILLE (B), MORROW (C), AND FRIENDSHIP CREEK (F) MINERALIZED AREAS. ID-SAMPLE NUMBER COND-SPECIFIC CONDUCTIVITY, MICROMHOS/CM 25 C ALK-ALKALINITY, MG/L AS CaCO3 NO3=NO3 AS N, MG/L. ALL OTHER DETERMINATIONS ARE GIVEN IN MG/L EXCEPT FOR PH. MISSING VALUES ARE INDICATED BY (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	DATE	TEMP	COND	ALK	PH	P04	CL	NH4	NO3	S04	SI02
P76	06/26/84	17.5	51	10	5.1	0.02	-0.3	0.12	0.06	10.6	12.2
P77	06/26/84	17.5	45	10	5.1	0.05	2.0	0.10	0.30	10.1	10.6
P78	06/26/84	24.0	105	45	6.0	0.01	5.8	0.10	0.24	8.5	16.3
P79	06/26/84	21.0	42	20	5.8	0.01	1.5	0.12	0.04	10.1	15.9
P80	06/26/84	22.5	735	325	7.1	-0.01	3.0	0.11	0.12	6.2	19.5
P81	06/26/84	22.0	541	305	7.1	0.10	3.8	0.95	0.03	11.9	19.0
P82	06/26/84	20.5	471	260	7.1	0.10	5.3	0.14	0.38	28.2	14.0
P83	06/26/84	20.0	768	345	7.0	0.04	10.5	0.32	0.16	48.5	20.0
B84	07/02/84	23.0	541	295	7.1	-0.01	9.2	0.01	0.87	14.1	13.3
B85	07/02/84	18.0	515	300	7.0	0.01	8.3	0.01	0.94	13.0	12.8
B86	07/02/84	22.0	528	305	7.2	-0.01	2.9	0.07	0.12	21.7	10.9
B87	07/02/84	23.0	417	210	7.0	-0.01	9.2	0.04	0.80	18.2	13.7

TABLE 10. SPRING WATER FIELD AND ANION ANALYSES FOR PEYTON CREEK (PI), BERRYVILLE (B), MORROW (C), AND FRIENDSHIP CREEK (F) MINERALIZED AREAS. ID=SAMPLE NUMBER COND=SPECIFIC CONDUCTIVITY, MICROMHOS/CM 25 C ALK=ALKALINITY, MG/L AS CaCO3 NO3=NO3 AS N, MG/L. ALL OTHER DETERMINATIONS ARE GIVEN IN MG/L EXCEPT FOR PH. MISSING VALUES ARE INDICATED BY (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	DATE	TEMP	COND	ALK	PH	P04	CL	NH4	NO3	S04	SI02
B88	07/02/84	21.0	477	260	7.2	-0.01	9.3	0.10	0.62	14.1	9.8
B89	07/02/84	24.0	610	295	7.6	0.03	9.0	0.04	0.77	21.7	12.5
B90	07/02/84	18.5	407	225	7.1	0.01	4.6	0.07	0.80	10.6	12.1
B91	07/02/84	21.0	200	80	7.1	-0.01	10.2	0.11	1.01	17.7	10.5
C92	07/03/84	25.5	713	310	7.0	0.09	9.1	0.10	0.70	10.1	16.4
C93	07/03/84	26.0	465	265	7.2	0.12	2.1	0.04	0.91	10.1	12.1
C94	07/03/84	26.0	390	220	7.0	0.04	2.5	0.15	0.97	9.5	11.3
C95	07/03/84	24.5	204	105	7.2	0.05	4.0	0.04	1.04	9.5	13.3
F96	07/04/84	23.0	356	160	7.1	0.15	7.9	0.26	1.14	9.5	11.7
F97	07/04/84	22.0	363	150	7.1	0.03	7.9	0.09	7.50	9.5	13.3
F98	07/04/84	23.5	369	180	7.1	0.06	3.6	0.06	0.89	13.0	13.3
F99	07/04/84	23.0	490	205	7.5	0.13	14.4	0.04	4.10	28.9	16.4

TABLE 10A. CATION ANALYSES OF SPRING WATER SAMPLES FROM PEYTON CREEK (P), BERRYVILLE (B), MORROW (C), AND FRIENDSHIP CREEK (F) MINERALIZED AREAS. NA, K, CA, AND MG VALUES ARE IN MG/L AND ALL OTHER VALUES ARE IN UG/L. MISSING VALUES ARE GIVEN AS (-) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	MN	FE	NI	CO	CU	PB	ZN	CD	NA	K	CA	MG	SR
P76	32	53	8	7	5	6	26	10	1.4	1.1	4	1.1	0.020
P77	38	36	8	7	3	23	18	7	1.4	0.9	2	0.8	0.022
P78	63	69	5	7	5	14	36	3	3.7	0.2	16	1.1	0.018
P79	159	165	15	7	18	28	297	5	1.8	1.0	3	1.6	0.014
P80	39	359	8	7	20	6	130	2	26.5	2.0	109	35.6	0.767
P81	16	57	2	4	-3	6	7	2	74.0	0.6	30	17.6	1.967
P82	19	48	5	4	-3	6	17	2	12.0	2.0	83	8.1	0.430
P83	50	31	8	4	1	4	109	2	5.8	1.1	140	16.0	2.333
B84	9	8	8	7	1	14	10	2	3.4	6.8	57	37.2	0.058
B85	7	16	12	4	1	19	10	3	3.7	3.4	58	35.2	0.064
B86	257	28	15	7	1	28	7	7	2.8	1.3	62	28.8	0.043
B87	22	8	8	7	1	14	5	2	2.9	0.8	47	29.6	0.045
B88	7	16	5	4	1	10	-1	2	3.7	1.5	57	32.0	0.046

TABLE 10A: CATION ANALYSES OF SPRING WATER SAMPLES FROM PEYTON CREEK (P), BERRYVILLE (B), HORROR (C), AND FRIENDSHIP CREEK (F) MINERALIZED AREAS. NA, K, CA, AND MG VALUES ARE IN MG/L AND ALL OTHER VALUES ARE IN UG/L. MISSING VALUES ARE GIVEN AS (.) AND VALUES BELOW DETECTION LIMITS ARE INDICATED BY MINUS (-) SIGNS.

ID	MN	FE	NI	CO	CU	PB	ZN	CD	NA	K	CA	MG	SR
B89	9	12	8	4	3	6	1	1	5.8	2.2	64	39.0	0.056
B90	7	16	8	7	1	6	1	2	2.8	1.4	55	24.0	0.038
B91	9	20	12	7	3	19	7	3	4.9	2.8	30	7.7	0.064
C92	9	16	15	15	1	32	7	5	3.4	0.3	144	3.8	0.260
C93	4	12	8	4	-1	10	-1	1	0.1	0.4	105	2.3	0.090
C94	7	12	5	-4	1	6	1	1	4.0	1.1	70	4.7	0.115
C95	-1	-4	-2	-4	-1	-6	-1	-1	2.8	1.5	38	1.8	0.050
F96	3	4	2	4	1	14	5	1	5.1	2.8	66	2.3	0.064
F97	3	4	2	4	-1	10	-1	1	2.6	1.2	69	3.6	0.054
F98	63	24	5	7	10	19	5	2	5.8	2.7	74	2.4	0.058
F99	4	4	8	11	1	23	7	2	14.5	1.5	87	4.6	0.104

TABLE 11. COMPARISON OF SPRING WATER FIELD AND ANION DATA FROM THE PHOSPHATE (PEYTON CREEK), PYRITE (BERRYVILLE), LEAD-ZINC (MORROW) AND URANIUM (FRIENDSHIP CREEK) AREAS. TOP VALUES ARE THE RANGE AND THE BOTTOM ONES ARE THE MEDIAN VALUES. NUMBERS IN ( ) ARE THE NUMBER OF SAMPLES COLLECTED FROM EACH AREA.

Area	Specific Alkalinity Concd. 25 C	as mg/l CaCO <sub>3</sub>	pH	PO <sub>4</sub> <sup>-3</sup> as P ppm	Cl <sup>-</sup> ppm	NH <sub>4</sub> <sup>+</sup> as N ppm	SiO <sub>2</sub> ppm	SO <sub>4</sub> <sup>=</sup> ppm	NO <sub>3</sub> as N ppm
Peyton Creek (8)	42-768 288	10-345 152	5.1-7.1 6.5	<.01-.10 .03	<.3-10.5 3.4	.10-.95 .12	10.6-20.0 16.1	6.2-48.5 10.4	.03-38 .14
Berryville (8)	200-600 496	80-305 278	7.0-7.6 7.1	<.01-.03 <.01	2.9-10.2 9.1	.01-.11 .06	9.8-13.7 12.3	10.6-21.7 16.9	.12-1.01 .80
Morrow (4)	209-713 427	105-310 243	7.0-7.2 7.1	.04-.12 .07	2.1-9.1 3.3	.04-.15 .07	11.3-16.4 12.7	9.5-10.1 9.8	.9 -9.7 1.0
Friendship Creek (4)	356-490 366	150-205 170	7.1-7.5 7.1	.03-.15 .10	3.6-14.4 7.9	.04-.26 .08	11.7-16.4 13.3	9.5-28.9 11.3	.9-7.5 2.6

TABLE 11A. COMPARISON OF SPRING WATER CATION DATA FROM PEYTON CREEK, BERRYVILLE, MORROW AND FRIENDSHIP CREEK AREAS. TOP VALUES ARE THE RANGE AND THE BOTTOM ONES ARE THE MEDIAN VALUES. NUMBERS IN ( ) ARE THE NUMBER OF SAMPLES COLLECTED FROM EACH AREA.

Area	Zn ppb	Pb ppb	Cd ppb	Fe ppb	Mn ppb	Ni ppb	Co ppb	Cu ppb	Na ppm	K ppm	Ca ppm	Mg ppm	Sr ppb
Peyton Creek (8)	7-297 31	4-28 6	2-10 3	31-359 55	16-159 39	2-15 8	4-7 7	1-20 4	1.4-74.0 4.8	.2-2.0 1.1	2-140 23	.8-35.6 4.9	14-2333 226
Berryville (8)	<1-10 6	6-28 14	1-7 2	8-28 16	7-257 9	5-15 8	4-7 7	1-3 1	2.8-5.8 3.6	.8-6.8 1.9	30-64 57	7.7-39.0 30.8	38-64 51
Morrow (4)	<1-7 1	3-32 8	<1-5 1	2-16 12	<1-9 6	1-15 7	2-15 3	<1-7 1	.1-4.0 3.1	.3-1.5 .8	38-144 88	1.8-4.7 3.1	50-260 103
Friendship Creek (4)	<1-7 5	10-23 17	1-2 2	4-24 4	3-63 4	2-8 4	4-11 6	<1-10 1	2.6-14.5 5.5	1.2-2.8 2.1	66-87 72	2.3-4.6 3.0	54-104 61

NOTE: ppb =  $\mu\text{g/l}$

the phosphate mineralization in the area, there does not appear to be elevated phosphate contents in the spring water nor any other indication of mineralization. However, phosphate is rather insoluble and contamination in the other areas may obscure any slight elevation of phosphate in this area.

The one sample (B86) in the midst of the pyrite deposit near Berryville had higher manganese and perhaps higher nickel values. Sample B85 may also have slightly higher nickel values (Table 11A). The sulfate values are also somewhat higher in this area (Table 11). Thus, groundwater geochemical exploration for pyrite deposits of this type appears to be worthy of additional investigation, especially using a close grid for sampling.

In the Morrow area, sample C92 with a lead concentration of 32 ppb may be reflecting the lead-zinc mineralization in the area (Table 11A). This observation plus the results of other hydrogeochemical studies in lead-zinc mineralized areas (Steele 1984 & 1983) suggests that additional investigation in the Morrow area would be of value.

Although samples from the Friendship Creek were not analyzed for uranium, it was hoped that other elements, e.g., Co and Cu, might be indicative of the mineralization (Tables 11 and 11A). There is no indication of the uranium mineralization; however, it should be noted that it occurs in an anomalous sandstone that is not widespread and therefore, the groundwater issuing from the springs of this area may not have come in contact with the uranium mineralization.

Compared with the spring water from other areas of northern Ar-

kansas (Tables 6 and 6A), the Berryville, Morrow and Friendship Creek areas' springs are apparently higher in nitrate; the Berryville and Friendship Creek areas' springs are higher in chloride; the Morrow and Friendship Creek areas' springs are higher in phosphate; and all of the areas have higher ammonia values (Tables 11 and 11A). These data indicate that these areas, especially Berryville, Morrow and Friendship Creek, are contaminated by animal and/or septic tank wastes (and possibly road salt). Note the generally lower values for phosphate, chloride, ammonia and nitrate values for the lower population (including livestock and poultry) Ponca and Rush areas. The lack of anomalously high silica values rules out any significant geothermal component of these spring waters.

#### CONCLUSIONS

Although 18 of the 99 springs exceeded drinking water limits, most of the springs exceeded only iron and/or manganese limits which were established because of staining problems. Thus, the water in these areas is generally of good chemical quality. However, there is an indication that the Berryville, Morrow, and Friendship Creek areas have higher ammonia and nitrate, chloride or phosphate concentrations than other northern Arkansas areas and these higher values may be due to higher human and animal populations which have caused contamination of the groundwater. The results of this investigation do not indicate any geothermal waters in these areas.

The potential value of hydrogeochemical exploration for phosphate, pyrite, uranium and the small lead-zinc (Morrow) deposits can not be



effectively evaluated due to the small number of springs sampled from each of these areas. However, the small size of the uranium deposit may have contributed significantly to the negative results for this area. The insolubility of the phosphate, plus possible phosphate contamination, gave negative results for the Peyton Creek area. The results from the Berryville and Morrow areas do suggest that additional research would be worthwhile in these areas.

Hydrogeochemical exploration in the Batesville district appears to be effective, with 44 percent of the springs within 2000 feet of mineralization having metal anomalies (especially manganese). Additional work in this area with particular attention to the formation from which the spring issues would be helpful in developing more complete interpretations of the data.

### LITERATURE CITED

- APHA, 1979. Standard Methods for the Examination of Water and Wastewater, 15th ed. American Public Health Association, Washington, D.C., 874 p.
- AGC, 1965. Core drilling project - Peyton Creek phosphate area, Arkansas, Final Report-Phase II. Arkansas Geological Commission, 7 p.
- AGC, 1964. Core drilling project - Peyton Creek phosphate area, Arkansas, Final Report-Phase I. Arkansas Geological Commission, 12 p.
- Branner, George C., 1940. Mineral resources of Benton, Carroll, Madison and Washington Counties. Arkansas Geological Surv., County Mineral Rept. 2, 55p.
- Branner, George C., 1940. Manganese minerals of Arkansas. Arkansas Geological Surv., 20 p.
- Caplan, William M., 1957. Subsurface geology northwestern Arkansas. Arkansas Geological Commission, Information Circ. 19, 14 p.
- Coffey, W. S., 1981. The mineralogy and geochemistry of the Batesville manganese district, Arkansas. Unpub. M.S. Thesis, Univ. of Arkansas, Fayetteville, 82 p.
- Coughlin, T. L., 1965. Geologic and environmental factors affecting ground water in the Boone Limestone of northcentral Washington County, Arkansas. Unpub. M.S. Thesis, Univ. of Arkansas, Fayetteville, 98 p.
- Derring, M. F., Mohr, E.T., Sypniewski, B.F. and Carlson, E.H., 1983. The application of hydrogeochemistry to the exploration for Mississippi Valley-type deposits in northwestern Ohio - Program with Abstracts, 9th International Geochemical Symposium, Saskatoon, Canada, p. 20-21.
- Duncan, Robert C., 1983. Geochemical investigation of the Chattanooga Shale, Arkansas. Unpub. M.S. Thesis, Univ. of Arkansas, Fayetteville, 184 p.
- EPA, 1982. Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency, Washington, D.C., 298 p.
- EPA, 1976. Quality Criteria for Water. U.S. Environmental Protection Agency, Washington, D.C., 256 p.

- Fournier, R. O. and Rowe, J. J., 1966. Estimation of underground temperatures from the silica content of water from hot springs and steam wells. *Am. Jour. Sci.*, vol. 264, p. 685-697.
- Garrels, R. M., and Christ, C. L., 1965. Solutions, Minerals, and Equilibria. Harper and Row Publishers, New York, 450 p.
- Ginzburg, I. I., 1960. Principles of Geochemical Prospecting (translation from Russian by Sokoloff). Pergamon, New York-London, 311 p.
- Gordon, Mackenzie, Jr., and Kinney, Douglas M., 1944. Geological map and structural sections of the Batesville district, Independence, County, Arkansas. U.S. Geol. Surv., Oil and Gas Inventory Prelim. Map. 12.
- Hach Chemical Company, 1975. Water Analysis Handbook. Hach Chemical Company, Ames, Iowa. 186 p.
- Lammonds, A. G. and Stephens, J. W., 1969. Water-resources data for the Ozark Plateaus Province, Arkansas. Unpublished report, available through the U.S. Geological Survey, Water Resources Division, Little Rock, Arkansas.
- Langmuir, D. and Chatham, J. R., 1980. Groundwater prospecting for sand-stone-type uranium deposits: a preliminary comparison of the merits of mineral-solution equilibria, and single-element tracer methods. *Jour. Geochem. Explor.*, Vol. 13, p. 201-219.
- Lepeltier, C., 1969. A simplified statistical treatment of geochemical data by graphical representation. *Econ. Geol.*, Vol. 64, p. 538-550.
- McGowen, M. F., 1981. A structural and stratigraphic study of a portion of the Batesville manganese district, Arkansas. Unpub. M.S. Thesis, Univ. of Arkansas, Fayetteville, 69 p.
- McMahan, T.W., 1957. Geology of representative manganese deposits in the Batesville district, Arkansas. Unpub. M.S. Thesis, Univ. of Arkansas, Fayetteville, 65 p.
- Miser, Hugh D., 1940. Manganese carbonate in the Batesville district, Arkansas. U.S. Geol. Surv. Bull. 921A, p. 1-94.
- Miser, Hugh D., 1922. Deposits of manganese ore in the Batesville district, Arkansas. U.S. Geol. Surv. Bull. 734, 273 p.
- Nix J. and Goodwin, T., 1970. The simultaneous extraction of Fe, Mn, Cu, Co, Ni, Cr, Pb and Zn from natural water for determination by atomic absorption. *At. Absorpt. Newsl.*, Vol. 9, p. 119-122.

- Proctor, P. D., Kisvarsanyi, G., Garrison, E. and Dilamarter, R. R., 1976. Heavy metal additions to waters of the Joplin area, Tri-State mining district, Missouri. in Hydrologic Problems in Karst Regions, R. R. Dilamarter ed., Western Kentucky Univ. Press, Bowling Green, KY, 481 p.
- Public Health Service, 1962. Public Health Service Drinking Water Standards. U.S. Public Health Service, Dept. of Health, Education and Welfare, 61 p.
- Sinclair, A. J., 1976. Applications of probability graphs in mineral exploration. Assoc. of Explor. Geochemists, Special Vol. 4, 93 p.
- Steele, K. F., 1984. Hydrogeochemical exploration for Mississippi Valley-type deposits, Arkansas. Jour. Geochem. Explor. (in press).
- Steele, K. F., 1983. Chemistry of the springs of the Ozark Mountains, Northwestern Arkansas. Arkansas Water Resources Research Center Publication No. 98, Univ. of Arkansas, Fayetteville, 48 p.
- Stroud, R. B., Arndt, R. H., Fulkerson, F. B. and Diamond, W.G., 1969. Mineral resources and industries of Arkansas. U.S. Bureau of Mines, Bull. 645, 418 p.
- Vales, V. and Jurak, L., 1979. Hydrogeochemical prospecting for fluorite and barite in the Zelezne Hory Mts. Jour. of Geological Science, Economic Geology and Mineralogy, Vol. 17, p. 59-94.
- World Health Organization, 1971. International Standards for Drinking Water. 3rd ed., WHO, Geneva, 70 p.