

GEOCHEMICAL SURVEY OF MISSOURI

Geochemical Survey of Waters of Missouri



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By GERALD L. FEDER

GEOCHEMICAL SURVEY OF MISSOURI

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*An examination of statewide
geochemical variations in
surface and ground water*



UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

	Page		Page
Abstract	E1	Ground water—Continued	
Introduction	1	Methods of investigation—Continued	
Hydrologic setting	2	Sampling design	E6
Physiography and climate	2	Sampling techniques	7
Ozark Plateaus	3	Analytical procedures	8
Mississippi Alluvial Plain	3	Ground-water results	10
Central Lowland	3	Chemical variability	10
Climate	3	Composition of geohydrologic units	12
Geohydrologic units	3	Q-mode factor analysis	12
Quaternary alluvium	3	Composition of mine waters	51
Glacial deposits	3	Surface water	57
Cretaceous and Tertiary strata	4	Methods of investigation	57
Pennsylvanian strata	4	Sampling design	57
Mississippian strata	4	Sampling techniques	58
Cambrian and Ordovician strata (southwest Missouri)	4	Analytical procedures	59
Cambrian and Ordovician strata (southeast Missouri)	6	Surface-water results	59
Ground water	6	Summary and conclusions	64
Methods of investigation	6	References cited	65
		Appendix I	67

ILLUSTRATIONS

		Page
FIGURES 1-37. Maps showing:		
1. Physiographic divisions of Missouri		E2
2. Mean annual precipitation		4
3. Locations of seven principal geohydrologic units in Missouri		5
4. Locations of wells from which waters were sampled from different stratigraphic (geohydrologic) units		7
5. Iron concentrations in ground waters from seven geohydrologic units in Missouri		13
6. Silica (SiO ₂) concentrations in ground waters from seven geohydrologic units in Missouri		14
7. Sodium concentrations in ground waters from seven geohydrologic units in Missouri		15
8. Potassium concentrations in ground waters from seven geohydrologic units in Missouri		16
9. Boron concentrations in ground waters from seven geohydrologic units in Missouri		17
10. Strontium concentrations in ground waters from seven geohydrologic units in Missouri		18
11. Magnesium concentrations in ground waters from seven geohydrologic units in Missouri		19
12. Lithium concentrations in ground waters from seven geohydrologic units in Missouri		20
13. Sulfate (SO ₄) concentrations in ground waters from seven geohydrologic units in Missouri		21
14. Barium concentrations in ground waters from seven geohydrologic units in Missouri		22
15. Dissolved solids (residue on evaporation at 180°C) in ground waters from seven geohydrologic units in Missouri		23
16. Calcium concentrations in ground waters from seven geohydrologic units in Missouri		24
17. Bicarbonate (HCO ₃) concentrations in ground waters from seven geohydrologic units in Missouri		25
18. Bromine concentrations in ground waters from seven geohydrologic units in Missouri		26
19. Aluminum in ground waters from seven geohydrologic units in Missouri		27
20. Chlorine concentrations in ground waters from seven geohydrologic units in Missouri		28
21. Manganese concentrations in ground waters from seven geohydrologic units in Missouri		29
22. Sulfide (S ²⁻) concentrations in ground waters from seven geohydrologic units in Missouri		30
23. Molybdenum concentrations in ground waters from seven geohydrologic units in Missouri		31
24. Fluorine concentrations in ground waters from seven geohydrologic units in Missouri		32
25. Iodine concentrations in ground waters from seven geohydrologic units in Missouri		33
26. Nitrate concentrations in ground waters from seven geohydrologic units in Missouri		34
27. Nitrite concentrations in ground waters from seven geohydrologic units in Missouri		35
28. Ammonia concentrations in ground waters from seven geohydrologic units in Missouri		36
29. Organic nitrogen concentrations in ground waters from seven geohydrologic units in Missouri		37

FIGURES 1-37. Maps showing —Continued

30. Orthophosphate concentrations in ground waters from seven geohydrologic units in Missouri-----	E38
31. Total phosphorus concentrations in ground waters from seven geohydrologic units in Missouri-----	39
32. Cadmium concentrations in ground waters from seven geohydrologic units in Missouri-----	40
33. Zinc concentrations in ground waters from seven geohydrologic units in Missouri-----	41
34. Copper concentrations in ground waters from seven geohydrologic units in Missouri-----	42
35. Rubidium concentrations in ground waters from seven geohydrologic units in Missouri-----	43
36. Gross alpha radioactivity in ground waters from seven geohydrologic units in Missouri-----	44
37. Gross beta radioactivity in ground waters from seven geohydrologic units in Missouri-----	45
38. Factor-variance diagram for ground waters of Missouri-----	48
39-43. Maps showing:	
39. Geographic variations in the composition loadings on end member I-----	52
40. Geographic variations in the composition loadings on end member II-----	53
41. Geographic variations in the composition loadings on end member III-----	54
42. Geographic variations in the composition loadings on end member IV-----	55
43. Drainage map of Missouri showing units chosen for surface-water sampling and the locations of sampling sites--	57

TABLES

TABLE 1. Analytical methods used in reconnaissance geochemical study of ground water in Missouri-----	E8
2. Elements looked for in spectrographic analysis of evaporation residues but rarely or never detected in this study-----	11
3. Comparison of estimated logarithmic variance components for chemical constituents for ground waters of Missouri-----	11
4. Summary of analytical data on ground waters from seven geohydrologic units in Missouri-----	46
5. Composition scores for the varimax axes, F_{ej} -----	50
6. Composition loadings (a_{ik}) on the varimax axes for four-factor model-----	50
7. Ground-water analyses from two mining areas in southern Missouri-----	56
8. Comparison of estimated logarithmic variance components for surface waters-----	59

CONVERSION FACTORS

Metric unit	Inch-Pound equivalent	Metric unit	Inch-Pound equivalent
Length		Specific combinations—Continued	
millimeter (mm)	= 0.03937 inch (in)	liter per second (L/s)	= .0353 cubic foot per second
meter (m)	= 3.28 feet (ft)	cubic meter per second	= 91.47 cubic feet per second per square mile [(ft ³ /s)/mi ²]
kilometer (km)	= .62 mile (mi)	meter per day (m/d)	= 3.28 feet per day (hydraulic conductivity) (ft/d)
Area		meter per kilometer (m/km)	= 5.28 feet per mile (ft/mi)
square meter (m ²)	= 10.76 square feet (ft ²)	kilometer per hour (km/h)	= .9113 foot per second (ft/s)
square kilometer (km ²)	= .386 square mile (mi ²)	meter per second (m/s)	= 3.28 feet per second
hectare (ha)	= 2.47 acres	meter squared per day (m ² /d)	= 10.764 feet squared per day (ft ² /d) (transmissivity)
Volume		cubic meter per second (m ³ /s)	= 22.826 million gallons per day (Mgal/d)
cubic centimeter (cm ³)	= 0.061 cubic inch (in ³)	cubic meter per minute (m ³ /min)	= 264.2 gallons per minute (gal/min)
liter (L)	= 61.03 cubic inches	liter per second (L/s)	= 15.85 gallons per minute
cubic meter (m ³)	= 35.31 cubic feet (ft ³)	liter per second per meter [(L/s)/m]	= 4.83 gallons per minute per foot [(gal/min)/ft]
cubic meter	= .00081 acre-foot (acre-ft)	kilometer per hour (km/h)	= .62 mile per hour (mi/h)
cubic hectometer (hm ³)	= 810.7 acre-feet	meter per second (m/s)	= 2.237 miles per hour
liter	= 2.113 pints (pt)	gram per cubic centimeter (g/cm ³)	= 62.43 pounds per cubic foot (lb/ft ³)
liter	= 1.06 quarts (qt)	gram per square centimeter (g/cm ²)	= 2.048 pounds per square foot (lb/ft ²)
liter	= .26 gallon (gal)	gram per square centimeter	= .0142 pound per square inch (lb/in ²)
cubic meter	= .00026 million gallons (Mgal or 10 ⁶ gal)	Temperature	
cubic meter	= 6.290 barrels (bbl) (1 bbl= 42 gal)	degree Celsius (°C)	= 1.8 degrees Fahrenheit (°F)
Weight		degrees Celsius (temperature)	= [(1.8 × °C) + 32] degrees Fahrenheit
gram (g)	= 0.035 ounce, avoirdupois (oz avdp)		
gram	= .0022 pound, avoirdupois (lb avdp)		
metric tons (t)	= 1.102 tons, short (2,000 lb)		
metric tons	= 0.9842 ton, long (2,240 lb)		
Specific combinations			
kilogram per square centimeter (kg/cm ²)	= 0.96 atmosphere (atm)		
kilogram per square centimeter	= .98 bar (0.9869 atm)		
cubic meter per second (m ³ /s)	= 35.3 cubic feet per second (ft ³ /s)		

GEOCHEMICAL SURVEY OF MISSOURI

GEOCHEMICAL SURVEY OF WATERS OF MISSOURI

By GERALD L. FEDER

ABSTRACT

A reconnaissance geochemical survey of surface and ground waters of the State of Missouri was made to provide epidemiologists with information on the state-wide distribution and variability of chemical constituents. The information obtained also may be useful as background information for studies in environmental pollution and mineral exploration.

Results from the state-wide sampling program, based on a hierarchical analysis of variance design and randomly chosen sampling sites, show that the concentrations of many chemical constituents in waters of Missouri vary both among and within the major geohydrologic units by statistically significant amounts.

The chemical constituents in surface waters show fewer statistically significant differences between geohydrologic units than the ground waters, and in some geohydrologic units the surface water is chemically quite different from the ground water, especially in its trace element content. Where geohydrologic units overlie one another, there may be large differences in the quality of water obtained from closely spaced wells pumping water from different geohydrologic units.

Analysis of the ground-water data by Q-mode factor analysis indicates that general chemical character of the waters can be moderately well described in terms of four theoretical water types. These include: (1) a Ca-Mg-HCO₃ water with relatively high Cu, (2) a Na-HCO₃-Cl water with high K, Li, Al, B, Rb, Sr, F, and Br, (3) a Ca-HCO₃-SO₄ water with high Fe and Mn, and (4) a water low in total dissolved solids and with low concentrations of trace elements. This last water type was necessary to account for dilution of ground water due to precipitation and the lowering of dissolved solids in ground water due to membrane filtration processes.

INTRODUCTION

This report describes the results of a survey of the chemical characteristics of surface and ground water in the State of Missouri which was undertaken as a part of a general survey of the geochemical environment of the State. The general objective of the study has been to provide unbiased estimates of the "natural" chemical character and regional variability among the ground and surface water of the seven major geohydrologic units. The survey was undertaken in cooperation with medical scientists of the Environmental Health Surveillance Center of the University of Missouri, and all results have been made available to them in support of their studies of the possible effects of environmental geochemistry on health and disease. A preliminary description of the survey and

its implications for epidemiologic research was published by Connor and others (1972), and a general statement of the goals and methods was given by Miesch (1972 and 1976). Much of the work on which this report is based has appeared in a series of progress reports (U.S. Geological Survey, 1972a-1972f, 1973) issued at intervals of 6 months during the 4 years of the study.

The role of trace elements in health and disease has been of interest to medical researchers for a long time, but an increasing public awareness of trace-element hazards in the environment has focused attention on the need for data on the expected concentrations and ranges of many trace elements in ordinary components of the environment, such as water, dusts, plants, and foods, under natural conditions.

Water often has been implicated in human disease caused by microorganisms or by toxic doses of certain trace elements, but little is known about the possible subtle health effects of long-term exposure to low or moderate, or perhaps insufficient, concentrations of water-borne trace elements relative to recommended levels. The trace-element character of potable water is regarded as a factor of possible major importance by epidemiologists, not only because water is directly consumed by humans but also because of possible concentrations of water-borne trace elements in the edible parts of plants and animals. Perhaps the most widely known relation between water chemistry and human disease is that of fluoride and tooth decay, but some investigators suspect there is a relation between water hardness and heart disease (Schroeder, 1966; Sauer, 1974). In addition, Voors (1971) implicates strontium, barium, nitrate, lithium, and cadmium as possible determinants of atherosclerotic heart disease. Shamberger and Frost (1969) reported on the possible protective effect of selenium against cancer.

Trace-element variations in surface and ground water may reflect both pristine environmental conditions and pollution that has resulted from human activities. Throughout this study, primary emphasis is placed on establishing the natural background concentrations of trace elements in the major types of surface and ground

water in Missouri. In addition to providing data for baseline epidemiological studies, such data may be useful for assessing the extent of pollution of surface and ground water and in identifying anomalies in geochemical prospecting surveys. Areas of known or expected anomalous water chemistry purposely were excluded from the main sampling program, although a few special areas were sampled later to establish whether or not they should actually be considered anomalous. Because the emphasis of this study was on potable water, deep saline ground water found in many areas of the State was excluded from the study.

In order to maximize the efficiency of the sampling program and to permit objective evaluation of the data, rigorous statistical procedures were followed as much as possible throughout the study. Although the major purpose of the work described herein is to support epidemi-

logical research, this study also is one of a series aimed at evaluating sample design and techniques of the data analysis in geochemical surveys. General discussions of sampling problems encountered in environmental geochemistry were given by Miesch (1972) and Feder (1972).

I acknowledge with gratitude the facilities and services provided by Dr. Carl J. Marienfeld and his associates of the Environmental Health Surveillance Center, University of Missouri.

HYDROLOGIC SETTING

PHYSIOGRAPHY AND CLIMATE

Missouri contains parts of three physiographic provinces as defined by U.S.G.S. (1968) and shown in figure 1.

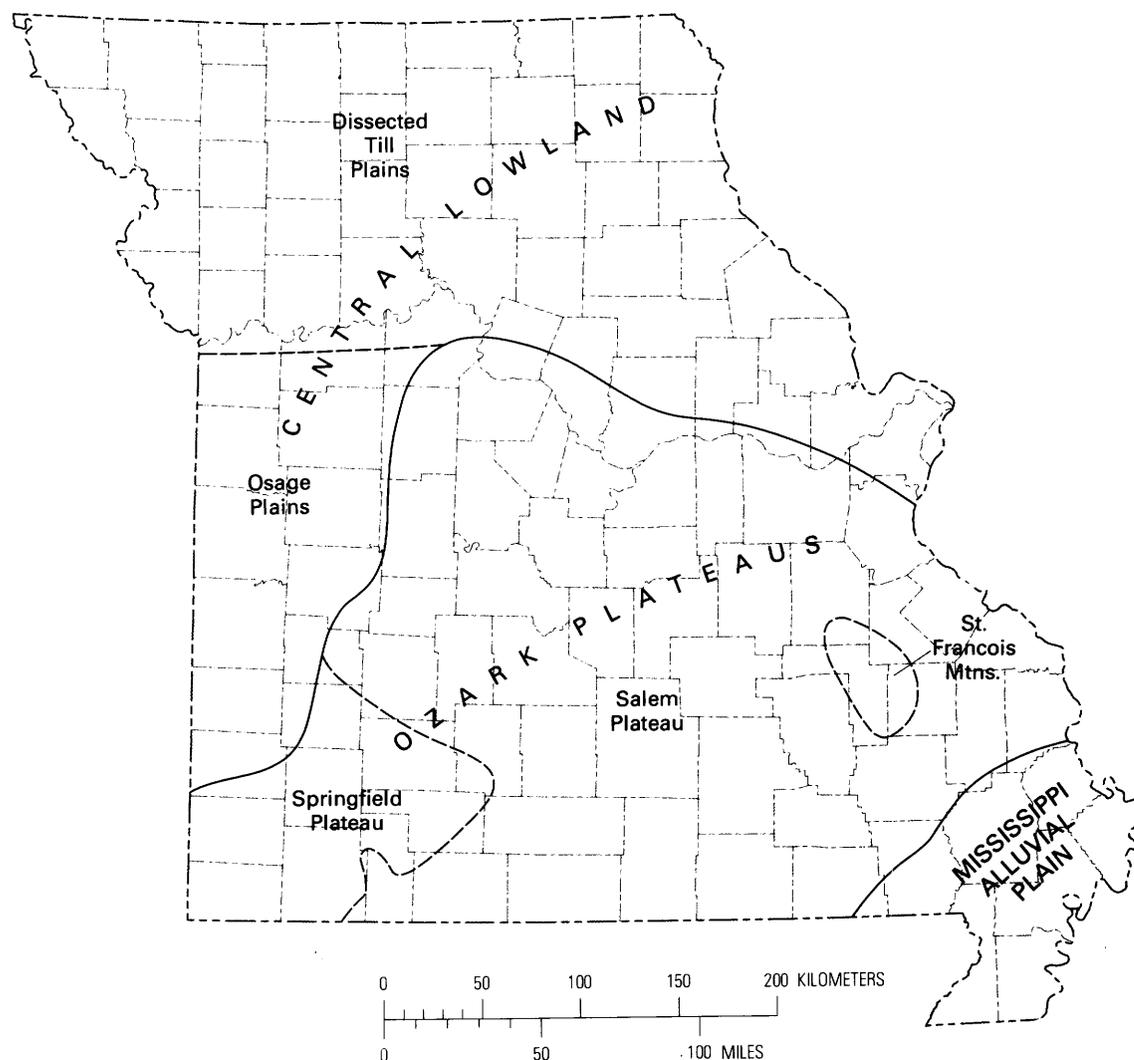


FIGURE 1.—Map showing the physiographic divisions of Missouri.

OZARK PLATEAUS

The Ozark Plateaus province is mostly a rugged area of deep, narrow valleys, and is dissected most strongly in the southern part of the State. Ridgetop altitudes vary from 300 to more than 500 m above sea level and maximum local relief is about 150 m. The region is divided into the Springfield Plateau, Salem Plateau, and St. Francois Mountains.

The St. Francois Mountains contain the highest point in the State, Taum Sauk Mountain, at 540 m above sea level. The area is underlain largely by Precambrian igneous rocks and consists of rugged hills with a local topographic relief commonly exceeding 150 m. A few outlying hills exist where Precambrian rocks have been exposed by erosion in areas surrounding the St. Francois Mountains, and some buried hills are known from geophysical studies and drilling.

The Salem Plateau is underlain predominantly by dolomitic rocks of Cambrian and Ordovician ages. Located at the southern part of the State, the Salem Plateau is dissected thoroughly with valleys that are separated by sharp ridges. Solution of the dolomitic rocks has had an important effect on the landforms and drainage characteristics in the area. Sinkholes, caves, losing streams, dry valleys, and large springs are common in this area.

The Springfield Plateau is underlain by limestones of Mississippian age. It is characterized by gently rolling topography and an abundance of small springs and caves.

MISSISSIPPI ALLUVIAL PLAIN

The Mississippi Alluvial Plain is the northwestern part of the Mississippian embayment, and it is underlain largely by Quaternary age alluvial deposits of the Mississippi River flood plain. The region is relatively flat, with altitudes ranging from 70 to 90 m above mean sea level. Crowleys Ridge, in which rocks of Paleozoic, Cretaceous, and Tertiary age, are exposed, lies diagonally across the area and reaches an altitude of about 150 m above sea level.

CENTRAL LOWLAND

The Central Lowland province includes almost all of the area north of the Missouri River (Dissected Till Plains) and a large area south of the river in the western part of the State (Osage Plains).

The Dissected Till Plains are underlain mostly by Pleistocene glacial deposits. The eastern part of the area is generally an undulating prairie with rolling hills, whereas the western part is more hilly. Altitudes range from 140 m above sea level near the Mississippi River to about 300 m above sea level near the western border of the area.

The Osage Plains are underlain by strata of Pennsylvanian age. The area is south of the limit of glaciation and is characterized by rolling plains of low relief.

CLIMATE

The climate in Missouri is continental and is characterized by large variations in temperature and precipitation. The average annual air temperature ranges from 12° C in the north to 16° C in the south.

Average annual precipitation is 86 cm in the north and 117 cm in the southeast.

Figure 2 shows the distribution of precipitation in Missouri.

GEOHYDROLOGIC UNITS

The principal objective of this study was to describe the variability in trace-element concentrations among the ground and surface waters of the major hydrologic systems in Missouri. The surface and ground waters of the State were divided into conceptual units that are believed to be hydrologically distinct. The conceptual units chosen are referred to in this report as geohydrologic units (Maxey, 1964). Eight such geohydrologic units containing potable ground water were defined on the basis of stratigraphy (Howe and Koenig, 1961): (1) Quaternary alluvium in the Missouri and Mississippi River Valleys, (2) materials deposited by glacial and associated activity, (3) rocks of Cretaceous and Tertiary age, (4) rocks of Pennsylvanian age, (5) rocks of Mississippian age, (6) rocks of Cambrian and Ordovician age in southwestern Missouri, (7) rocks of Cambrian and Ordovician age in southern and southeastern Missouri, and (8) rocks of Precambrian age. Because the rocks of Precambrian age contain too few wells of acceptable construction for sampling, this last unit was not included in this study. The distribution of the other seven units is shown in figure 3.

QUATERNARY ALLUVIUM

The quaternary alluvium includes the sandy and clayey alluvial fill up to about 100 m thick in both the Missouri and Mississippi River Valleys (fig. 3), most of which is considered to be of Wisconsin age. The sandy layers in the Quaternary alluvium throughout most of these valleys yield large supplies of water to wells. (Yields of more than 50 L/s are common.)

Many large towns, including North Kansas City and Columbia, obtain water supplies from this source. In addition, the Quaternary alluvium supplies large amounts of irrigation water.

GLACIAL DEPOSITS

Glacial deposits of Quaternary age, consisting of bouldery clay, sand, gravel, and loess, cover most of the

GEOCHEMICAL SURVEY OF MISSOURI

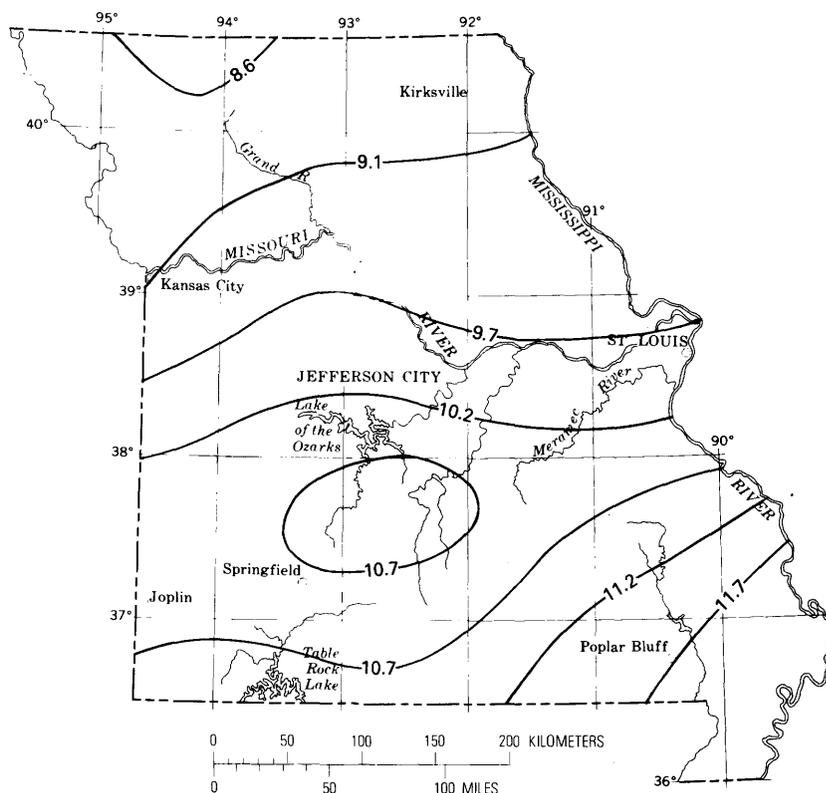


FIGURE 2.—Mean annual precipitation, in centimeters.

State north and east of the Missouri River. The thickness of this geohydrologic unit reaches more than 100 m in places.

Throughout most of this area, ground-water yields to wells are small (<3 L/s), and the water often contains more than 1,000 mg/L dissolved solids.

CRETACEOUS AND TERTIARY STRATA

Cretaceous and Tertiary strata consist of up to about 700 m of predominantly unconsolidated clays, marls, and sands; these sediments underlie most of the southeastern lowlands. The unit crops out in Crowleys Ridge and from there dips to the southeast under the Mississippi River alluvial sediments. Some aquifers that are exposed on Crowleys Ridge are as much as 600 m deep in the southeast corner of the State adjacent to the Mississippi River. Wells yielding more than 25 L/s are common. The quality of water is highly variable, and most concentrations of dissolved solids range from 100 to 1,000 mg/L.

PENNSYLVANIAN STRATA

Pennsylvanian strata consist of up to about 600 m of sandstone, shale, limestone, and coal, and lie beneath most of the west-central part of the State. Most wells in

this unit have small yields (<3 L/s), and the water often contains more than 1,000 mg/L dissolved solids.

MISSISSIPPIAN STRATA

Mississippian strata are up to about 300 m thick and consist predominantly of limestone, with a few interbedded dolomites and shales; these rocks underlie most of southwest Missouri. These strata generally yield moderate amounts (5 L/s) of water to wells. Extensive zinc and lead mineralization is present, and ground water in some parts of this unit has a high dissolved-solids content. However, outside of mineralized areas, the water generally contains less than 300 mg/L dissolved solids.

CAMBRIAN AND ORDOVICIAN STRATA (SOUTHWEST MISSOURI)

Cambrian and Ordovician strata (southwest Missouri) consist of approximately 500 m of predominantly dolomite with a few interbedded sandstones, and these rocks underlie the Mississippian strata. Most towns in southwest Missouri obtain water supplies from this unit. Wells penetrating this unit generally yield between 6 and 30 L/s. The water generally contains less than 300 mg/L dissolved solids.

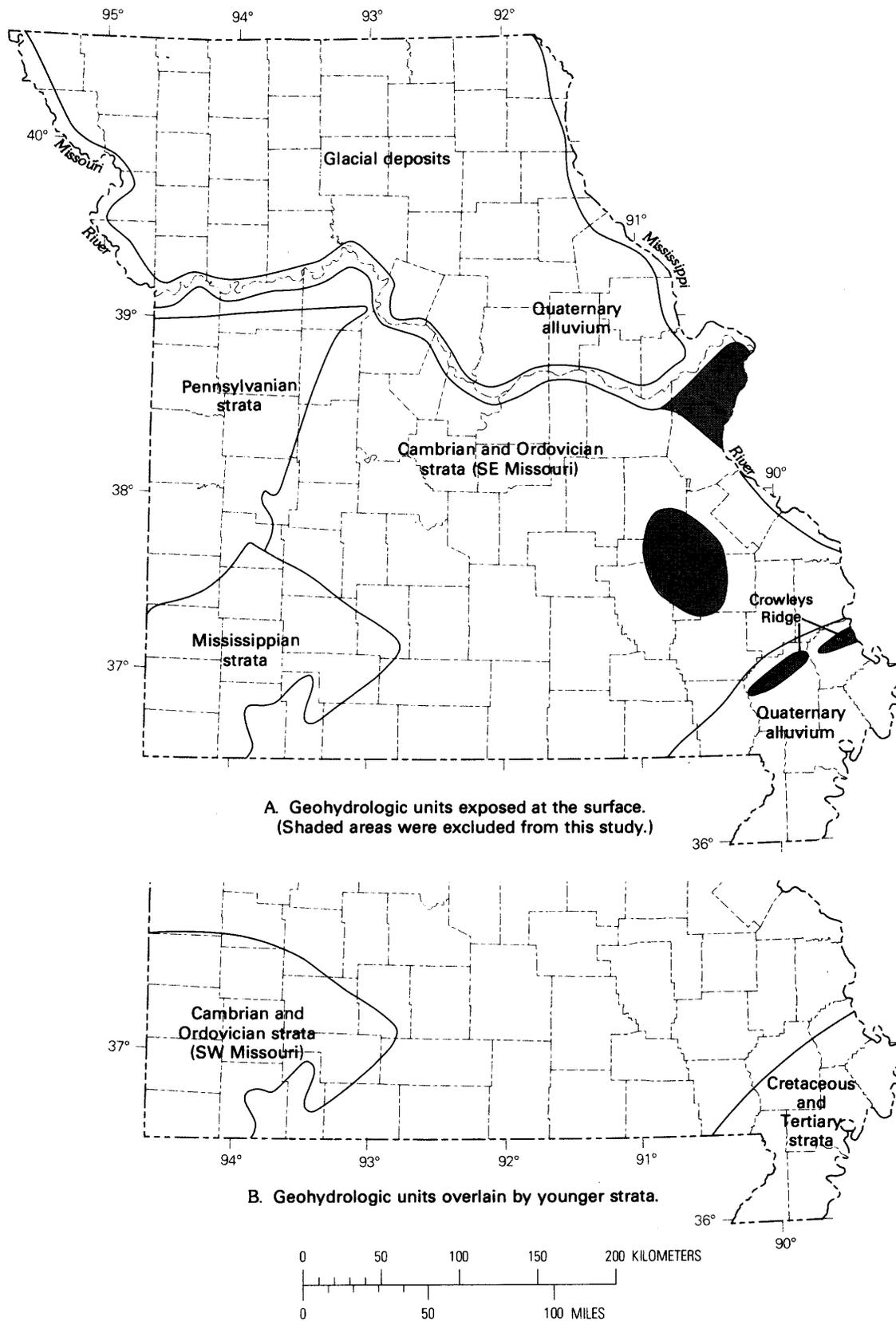


FIGURE 3.—Locations of seven principal geohydrologic units in Missouri.

CAMBRIAN AND ORDOVICIAN STRATA (SOUTHEAST MISSOURI)

Cambrian and Ordovician strata (southeast Missouri) are lithologically similar to the Cambrian and Ordovician (southwest Missouri) unit, except that, in southeast Missouri, these strata are exposed at the surface. The unit is up to about 700 m thick and underlies most of the Missouri Ozarks, except in southwest Missouri. Wells fully penetrating this unit generally yield between 6 and 30 L/s. The water generally contains less than 300 mg/L dissolved solids. Adjacent to the St. Francois Mountains, the Cambrian formations contain extensive lead deposits, and there are numerous mines in the area.

Even though the seven geohydrologic units described here served as a basis for sampling both ground and surface water, the methods of investigation and data analysis were distinct enough to warrant separate treatment of ground and surface water in this report.

GROUND WATER

METHODS OF INVESTIGATION

SAMPLING DESIGN

Sampling of ground water in this study was based on a four-level hierarchical (nested) analysis-of-variance design in which the first three levels are associated with specific ranges of geographic scales; the fourth level is included to measure variation arising from both temporal changes in water quality and errors associated with laboratory and sampling procedures. The top level of this design consists of the seven geohydrologic units described previously. The second and third levels, respectively, consist of 4-km² sites within geohydrologic units and wells within sites. Fifty-six samples were collected and analyzed in a completely randomized sequence from 49 wells throughout the State. The sampling plan consisted of (1) dividing the potable ground waters of Missouri into seven geohydrologic units, (2) sampling one well in each of five sites within each of the seven geohydrologic units, (3) sampling a second well within each of two of the five sites in each geohydrologic unit, and (4) resampling one well in each of the seven geohydrologic units after a random interval of time. The sites and wells within sites were selected for sampling by formal randomization procedures (Miesch, 1976) in an attempt to avoid sampling bias. The duplicate sampling of wells at the fourth level was done at random intervals over a 3-month period.

Wherever possible, wells approved by the Missouri Division of Health for public water supplies were used

because they are constructed to meet rigid State specifications, they are generally of high capacity, and well logs are available at the Missouri Division of Geological Survey and Water Resources. Selecting large capacity and properly constructed wells and collecting a sample from a faucet at the pump minimizes the chances of contamination of samples from the plumbing.

The locations of sampling sites are shown in figure 4. The limited numbers of acceptable sampling sites within the glacial drift and Pennsylvanian geohydrologic units resulted in clustering of sample localities in these units.

The sampling plan was designed to fit the following statistical model (Miesch, 1976):

$$\text{Log } X_{ijkl} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} + \delta_{ijkl} \quad (1)$$

where X_{ijkl} is the amount of a given chemical constituent measured in an individual ground-water sample, μ is the grand mean of the log concentrations of the constituent in all areas of the State, α_i represents the difference between the average log concentration in the i th geohydrologic unit and the grand mean. β_{ij} represents the difference between the average for the j th site and the average for the i th geohydrologic unit, γ_{ijk} represents the difference between the k th well and the average for the j th site, and δ_{ijkl} represents the difference between the l th sample and the average for the k th well. For this study, the last term (δ_{ijkl}) reflects variation arising from both analytical and sampling errors that arise partly from time-dependent changes within a well during the sampling period.

According to the above model, the total observed logarithmic variance in X , estimated as s_x^2 , may be partitioned into four components, each an estimate of a scale-related variance (Miesch, 1976, table 1)

$$s_x^2 = s_\alpha^2 + s_\beta^2 + s_\gamma^2 + s_\delta^2, \quad (2)$$

where s_α^2 represents variation observed among geohydrologic units, s_β^2 represents variance among sites within geohydrologic units (large-scale differences within a geohydrologic unit), s_γ^2 represents variance between wells within sites (small-scale differences within a geohydrologic unit), and s_δ^2 represents the "error" variance. With the exception of pH data, all variance components in this study were estimated following logarithmic transformation of reported concentrations because the analytical data for most chemical constituents tended to have marked positive skewness in their frequency distributions, and log transformations resulted in data better approximating a normal distribution. Log transformation also yielded means and variances for geohydrologic units, sites, and wells that tended to be uncorrelated (Miesch, 1976).

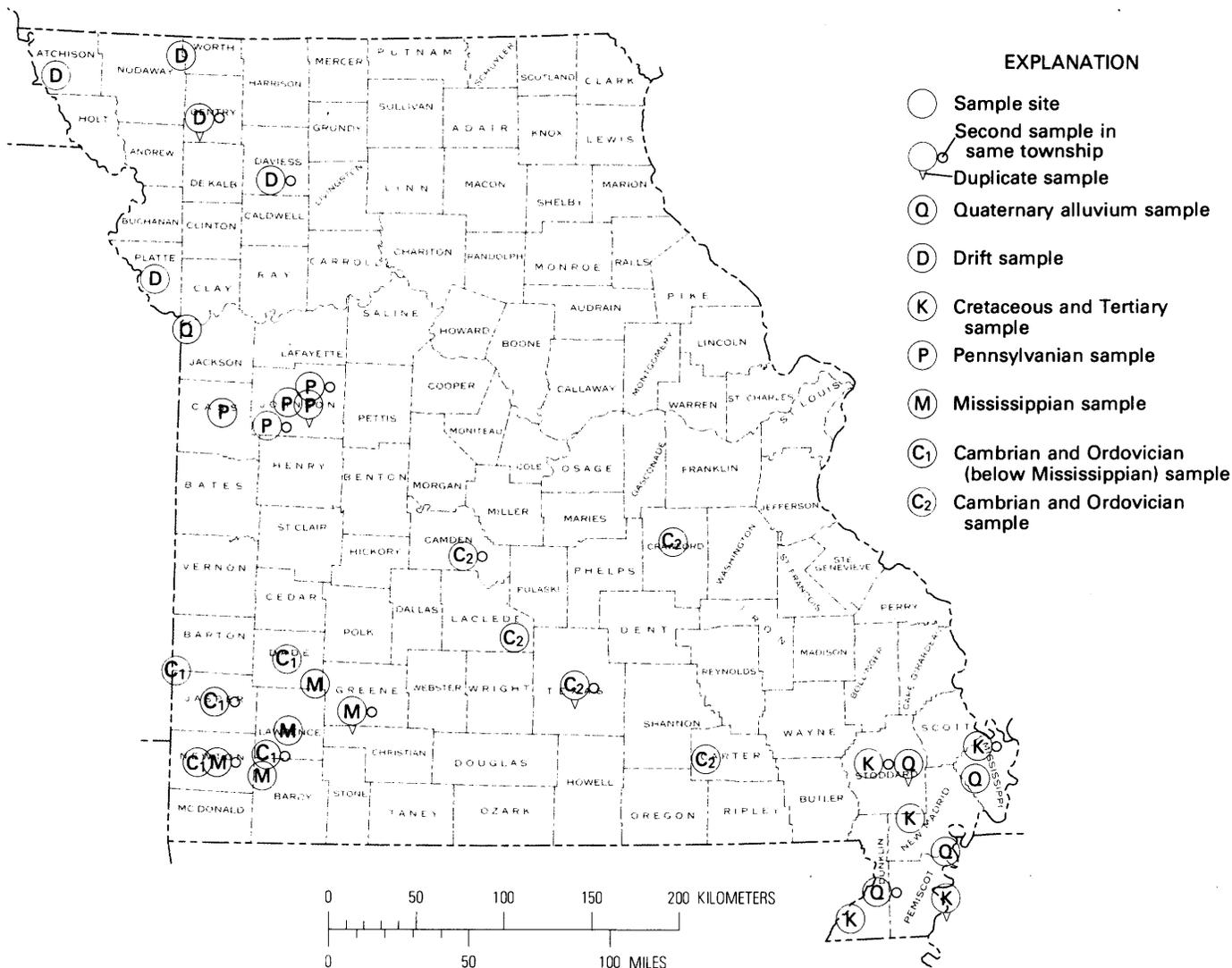


FIGURE 4.—Locations of wells from which waters were sampled from different stratigraphic (geohydrologic) units.

The data for many of the chemical constituents include values reported as “less than” the laboratory detection levels. Only those chemical constituents with fewer than 20 percent of the values reported as “less than” were chosen for the analysis of variance. As discussed by Miesch (1976, p. A26), a value equal to seven-tenths of the detection level was substituted for reports of “less than.”

The sample design used constitutes a “stage 1a design” as described by Connor and others (1972) and Miesch (1976) for use in geochemical surveys of large regions. For most chemical constituents, this sampling appears to be sufficient to provide the desired degree of stability (Miesch, 1976) in any geochemical maps constructed to show differences among geohydrologic units. “Phase-2” sampling (Miesch, 1976), used for mapping smaller-scaled features, was not conducted.

SAMPLING TECHNIQUES

All water samples were collected in acid-washed polyethylene bottles, and the bottles were filled either by immersing them in springs or from a faucet connected to a well pump. Where wells were sampled, the pump was run for at least 10 min before sampling. A 2-liter sample for spectrographic, radiochemical, and selected chemical analyses was first filtered through a 0.45- μ m filter, then acidified with 3 mL of double redistilled reagent-grade concentrated HNO₃. In addition, a 1-liter sample of untreated water was collected for laboratory determination of pH, specific conductance, alkalinity, and arsenic. A sample for sulfide determination also was collected in a separate 100-mL bottle, and about 0.1 g of zinc acetate was added immediately to precipitate the sulfide. A sample for nitrogen determinations was collected in a 500-

mL bottle, immediately treated with 30 mg HgCl₂, chilled to approximately 4° C, and sent to the laboratory for immediate analysis. This procedure minimized changes in the nitrogen forms.

ANALYTICAL PROCEDURES

Owing to the possibility of rapid changes in certain chemical properties of water, some determinations were made at the well or spring at the time of collection. These determinations included temperature, pH, alkalinity, and

specific conductance. A description of the procedures for making these determinations is given in Skougstad and Feder (1976).

All laboratory determinations were made in U.S. Geological Survey laboratories according to methods listed in table 1. More detailed descriptions are given in Skougstad and Feder (1976), Barnett (1976), and Janzer (1976). Table 2 lists those elements routinely looked for in spectrographic analysis of evaporation residues but rarely or never detected in the present study.

TABLE 1.—Analytical methods used in reconnaissance geochemical study of ground water in Missouri

[AAS, atomic-adsorption spectrophotometer]

Determination	Method	Reported as
Aluminum	Spectrographic	Micrograms per liter.
Alkalinity	Electrometric titration	Milligrams per liter as HCO ₃ and CO ₃ .
Arsenic	Silver diethyldithiocarbamate	Micrograms per liter.
Boron	Spectrographic	Do.
Barium	-----do-----	Do.
Bromine	Catalytic oxidation	Milligrams per liter.
Calcium	AAS--direct	Do.
Cadmium	AAS--direct, spectrographic	Micrograms per liter.
Chlorine	Mercurimetric	Milligrams per liter.
Cobalt	Spectrographic	Micrograms per liter.
Chromium	-----do-----	Do.
Copper	-----do-----	Do.
Fluorine	Zirconium-eriochrome cyanide R	Milligrams per liter.
Iron	AAS--direct, spectrographic	Micrograms per liter.
Hardness	Complexometric	Milligrams per liter as CaCO ₃ .

TABLE 1.—Analytical methods used in reconnaissance geochemical study of ground water in Missouri—
Continued

Determination	Method	Reported as
Hardness, noncarbonate	-----do-----	Do.
Mercury	Flameless AAS	Micrograms per liter.
Iodine	Ceric-arsenious	Do.
Potassium	AAS-direct	Milligrams per liter.
Lithium	-----do-----	Micrograms per liter.
Magnesium	-----do-----	Milligrams per liter.
Manganese	AAS--direct, spectrographic	Micrograms per liter.
Molybdenum	Spectrographic	Do.
Nitrogen (ammonia) ¹	Distillation, titration, or nesslerization.	Milligrams per liter as nitrogen.
Nitrogen (nitrate) ¹	Brucine	Milligrams per liter as nitrate.
Nitrogen (nitrite) ¹	Diazotization	Milligrams per liter as nitrite.
Nitrogen (organic) ¹	Kjeldahl digestion	Milligrams per liter as nitrogen.
Sodium	AAS--direct	Milligrams per liter.
Nickel	Spectrographic	Micrograms per liter.
Phosphorus (total)	Acid-persulfate hydrolysis	Milligrams per liter as phosphorus.
Phosphate	Phosphomolybdate	Milligrams per liter as phosphate.
Lead	Spectrographic	Micrograms per liter.
Hydrogen-ion concentration	Electrometric, glass electrode	Standard units.
Radioactivity (alpha)	Counter	Picocuries per liter.
Radioactivity (beta)	-----do-----	Do.

TABLE 1.—Analytical methods used in reconnaissance geochemical study of ground water in Missouri—
Continued

Determination	Method	Reported as
Rubidium	Spectrographic	Micrograms per liter.
Selenium	Diaminobenzidine	Do.
Silica (as SiO ₂)	Molybdate blue	Milligrams per liter.
Sulfate	Thorin	Do.
Solids (dissolved)	Gravimetric; residue on evaporation at 180°C	Do.
Specific conductance	Wheatstone bridge ²	Micromhos per centimeter at 25°C.
Strontium	Spectrographic	Micrograms per liter.
Temperature	Thermometer ²	Degree Celsius(°C).
Zinc	AAS--direct	Micrograms per liter.

¹Determinations made in Little Rock, Ark., laboratories of the Water Resources Division.

²Determined in field at time of collection.

GROUND-WATER RESULTS

CHEMICAL VARIABILITY

Estimates of the logarithmic variance components s_{α}^2 , s_{β}^2 , s_{γ}^2 , s_{δ}^2 , and of their corresponding percentages of the total variance s_x^2 are given in table 3. They were derived using computational procedures outlined by Anderson and Bancroft (1952, p. 327) for hierarchial designs with unequal subclasses.

The most notable feature of these estimates is that those representing compositional variation among wells within a site and between samples from the same well are generally small when compared to those representing the larger scaled geographic variation (s_{α}^2 and s_{β}^2). This indicates that a single water sample (or at most two or three) is generally satisfactory for characterizing the chemistry of ground water within a geographic area (a few kilometers across). Only Mg, Li, and Br exhibit important variation within sites. Moreover, all of the sampling and analytical methods used, with the possible exception of those for Cl and Al, appear to be suitably

precise. Most of the variation among the chemical constituents in Missouri ground waters is on a broad scale. For the most part, the variation occurs between wells or springs more than several kilometers apart and between geohydrologic units. It is this latter variation that is of primary interest in this study.

The components of logarithmic variance in table 3 serve not only to quantify the nature of the chemical variability among the ground waters of Missouri, but, also, may be used to derive an index of stability for maps that are based on the geohydrologic unit means. The index is (Miesch, 1976)

$$V_m = N_v/E_s, \quad (3)$$

where N_v is equal to s_{α}^2 and E_s is an estimate of the variance of the geohydrologic unit means if computed from the available data, that is, without further sampling. This variance is given by

$$E_s = \frac{s_{\beta}^2}{n_{\beta}} + \frac{s_{\gamma}^2}{n_{\beta}n_{\gamma}} + \frac{s_{\delta}^2}{n_{\beta}n_{\gamma}n_{\delta}} \quad (4)$$

TABLE 2.—Elements looked for in spectrographic analysis of evaporation residues but rarely or never detected in this study

Element	Lower limit of detection (ppm)	Element	Lower limit of detection (ppm)
Be	4	Sn	15
Bi	15	Ti	10
Ga	6	V	15
Ge	15	Zr	20
Ag	2		

site, and because duplicate samples were not taken from each well, the quantities of n_γ and n_δ can be either one or two, depending on the particular site or well. However, because the corresponding estimated variances, s_γ^2 and s_δ^2 , generally are small in comparison with s_β^2 (table 3), the additional error is of little consequence; the values of n_α and n_β were both set to 1, giving

$$E_s = (s_\beta^2 + s_\alpha^2 + s_\delta^2)/5. \tag{5}$$

The computed values of V_m for each chemical constituent are given in table 3. Computer simulation studies (Connor and others, 1972) have indicated that regional patterns are almost impossible to describe (or map), even though present, if the variance ratio, V_m , is less than one. As V_m increases, such maps exhibit increasing reliability of the means. All of the values of V_m given in table 3, except that for pH, are 1.0 or greater and range up to 9.3. Moreover, conventional F -tests indicate that the variances among geohydrologic units, except for pH, are all significant at the 0.05 probability level. Consequently, the means for the geohydrologic units are regarded as adequate for representation on geochemical maps, and the maps are expected to depict the general nature of the regional geochemical character of ground waters of the State. However, the analysis of variance also indicates that an important variation occurs within geohydrologic units over distances of more than a few kilometers, and description of the geographic configuration represented by this variance component (s_β^2) requires a great deal of additional sampling and laboratory analysis.

where n_β , n_γ , and n_δ are, respectively, the numbers of sites sampled within geohydrologic units (five), the number of wells sampled within each site (one or two), and the number of samples from each well (one or two). Because unequal numbers of wells were sampled in each

TABLE 3.—Comparison of estimated logarithmic variance components for chemical constituents for ground waters of Missouri

[All variance components are significantly greater than zero at the 0.05 probability level, except as noted by asterisks. Constituents are ranked in order of decreasing V_m variance mean ratio]

Variable	Total log variance ($s^2 \log_{10} \bar{x}$)	Between geohydrologic units		Between sites		Between wells within sites		Between samples		V_m
		s_β^2	Percent of total	s_α^2	Percent of total	s_γ^2	Percent of total	s_δ^2	Percent of total	
Fe (µg/L)	1.6867	1.0934	65	0.3276	19	0.2621	16	*0.0036	<1	9.3
SiO ₂ (mg/L)	.0616	.0375	61	.0233	38	*.0005	<1	*.0003	<1	7.8
Na (mg/L)	.5699	.3391	60	.1749	31	.0552	10	*.0008	<1	7.5
K (mg/L)	.1803	.0943	52	.0677	38	.0154	9	*.0028	2	5.4
B (µg/L)	.3639	.1872	50	.1370	38	.0415	11	*.0027	<1	5.0
Sr (µg/L)	.3140	.1570	50	.1402	45	.0150	5	*.0018	<1	5.0
Mg (mg/L)	.2593	.1264	49	*.0725	28	.0592	23	*.0013	<1	4.8
Li (µg/L)	.7243	.3421	47	*.1939	27	*.1793	25	*.0090	1	4.4
SO ₄ (mg/L)	.9056	.4096	45	.3711	41	.1246	14	*.0002	<1	4.1
Temperature (°C)	.0022	.0010	43	.0009	40	*0	<1	*.0004	17	3.8
Ba (µg/L)	.2828	.1202	43	.1314	47	.0302	11	*.0011	<1	3.8
Dissolved solids (mg/L)	.0768	.0299	39	.0390	51	.0074	10	*.0005	<1	3.2
Specific conductance (field) (µmho/cm at 25°C)	.0766	.0277	36	.0398	52	.0067	9	*.0024	3	2.8
Ca (mg/L)	.1669	.0546	33	.1050	63	.0056	3	*.0017	1	2.4
Carbonate hardness (mg/L as CaCO ₃)	.1518	.0479	32	.0954	63	.0081	5	*.0004	<1	2.4
HCO ₃ (mg/L)	.0354	.0112	32	.0197	56	.0040	11	*.0005	1	2.4
Br (mg/L)	.3727	.0989	27	*.0490	13	*.1455	39	*.0793	21	1.8
Al (mg/L)	.0438	.0099	23	.0146	33	*0	<1	*.0193	44	1.5
Cl (mg/L)	1.0460	.1715	16	.3937	38	*0	<1	*.4808	46	1.0
pH ¹	.1961	*.0070	4	.1516	77	*.0125	6	*.0250	13	.2

¹pH, by definition, is a logarithmic value and was not transformed for this analysis.

COMPOSITION OF GEOHYDROLOGIC UNITS

Each map (figs. 5–20) distinguishes three gross compositional units, two of which are the geohydrologic units displaying the highest and lowest mean concentrations, and the third (unpatterned) consisting of the five geohydrologic units having mean compositions intermediate to these extremes. Although the statistical significance of the difference between the highest and lowest mean concentrations was demonstrated by the analysis of variance (s_{α}^2 was significant for all constituents, except pH, at the 0.05 level), applications of Duncan's (1955) multiple-range test, as used in a geochemical survey of the plants and soils of Missouri by Erdman, Shacklette, and Keith (1976), generally failed to identify significant differences among means other than those between the highest and lowest means. The geometric mean concentration, the geometric deviation, and the observed range of concentrations are shown for each of the seven units.

Many chemical constituents were below the limits of analytical determination in all of the samples from one or more geohydrologic units, but were detected in most or all samples from the other units. Even though the data could not be examined by analysis of variance methods, it seems apparent that these observed differences among geohydrologic units are important, and hydrogeochemical maps were prepared (figs. 21–37). The chemical constituents include NO_3 , NO_2 , NH_3 , organic N, Cd, Cu, F, I, Mn, Mo, Rb, Zn, PO_4 , total P, and sulfide in addition to Gross Alpha activity and Gross Beta activity.

The chemical properties of the seven geohydrologic units are summarized in table 4. The detection ratio in table 4 is the ratio of the number of water samples in which the chemical constituent was determined to the number of independent samples analyzed from the particular geohydrologic unit. The number analyzed is given as five in most instances because two of the eight samples from each unit were from wells or springs in the same site where other samples had been taken, and one sample was a duplicate from a previously sampled well or spring. For each constituent, the expected value is given as the geometric mean (GM), which is the antilog of the mean logarithm of concentrations in five wells (one in each site) in each unit. The chemical variability was estimated as the geometric deviation (GD). The GD is the antilog of the standard deviation of the logarithmic values, and it is a factor that may be used to estimate the expected range of the constituent (Miesch, 1976). Where concentrations less than the lower limits of analytical determination were encountered, Cohen's (1959) method, as discussed by Miesch (1976, p. A28), was used to estimate both GM and GD.

Q-MODE FACTOR ANALYSIS

Because the concentrations of chemical constituents in water are rarely independent of one another, the varia-

tion of a multitude of chemical properties can be viewed as reflecting the variation of some fewer number of fundamental effects of "factors." The chemical data obtained in this study were analyzed by techniques of *Q*-mode factor analysis as described by Miesch (1976). In this application, the goal was to describe each observed sample composition in terms of a minimum number of fundamental water types. These water types are regarded as hypothetical samples that can be combined in various proportions to approximate the chemical compositions of each of the actual samples. The goal of the analysis is to derive a relation of the form

$$X_{ij} = a_{i1}F_{1j} + a_{i2}F_{2j} + \dots + a_{im}F_{mj}, \quad (6)$$

where X_{ij} is an estimate of the concentration of the j th constituent in the i th sample, the F 's are hypothetical water compositions (the factors), and the a 's are coefficients giving the proportions for combining the hypothetical end members to approximate the composition of the i th sample. In *Q*-mode factor-analysis terminology, the F values are the composition scores and the a values are the composition loadings. In this study, m (the number of factors) was found to be equal to 4. Miesch (1976) described the mathematical basis and procedures in detail.

Q-mode factor-variance diagrams for the chemical data are given in figures 38A and 38B. Only the five within geohydrologic unit samples from the seven geohydrologic units were used for this analysis. These diagrams show the proportions of the total variance in the chemical data for each constituent that can be accounted for by mixing 2–10 hypothetical end members. It is apparent from the diagrams that mixtures of four end members can account for about one-half or more of the variance in each constituent.

An initial *Q*-mode factor analysis included all of the chemical and spectrographic determinations represented in table 4 except those with low detection ratios. A few other constituents (NO_3 , NH_4 , I, and radiochemical data) were eliminated from the final analysis because they were found not to respond to the common factors to which the other variables appeared related; their variances could not be accounted for by models with fewer than eight or nine end members.

The data for the 18 remaining constituents represented on the factor-variance diagrams were expressed as parts-per-million values and summed. The difference between 10^6 and this sum was taken as H_2O . The sum of the 19 variables then was 10^6 for each sample as required for this form of *Q*-mode factor analysis (Miesch, 1976). Although the values for H_2O were overwhelmingly larger than the values for any other constituent, all values were brought into the same range by scaling the values for each constituent to range from zero to one. The factor

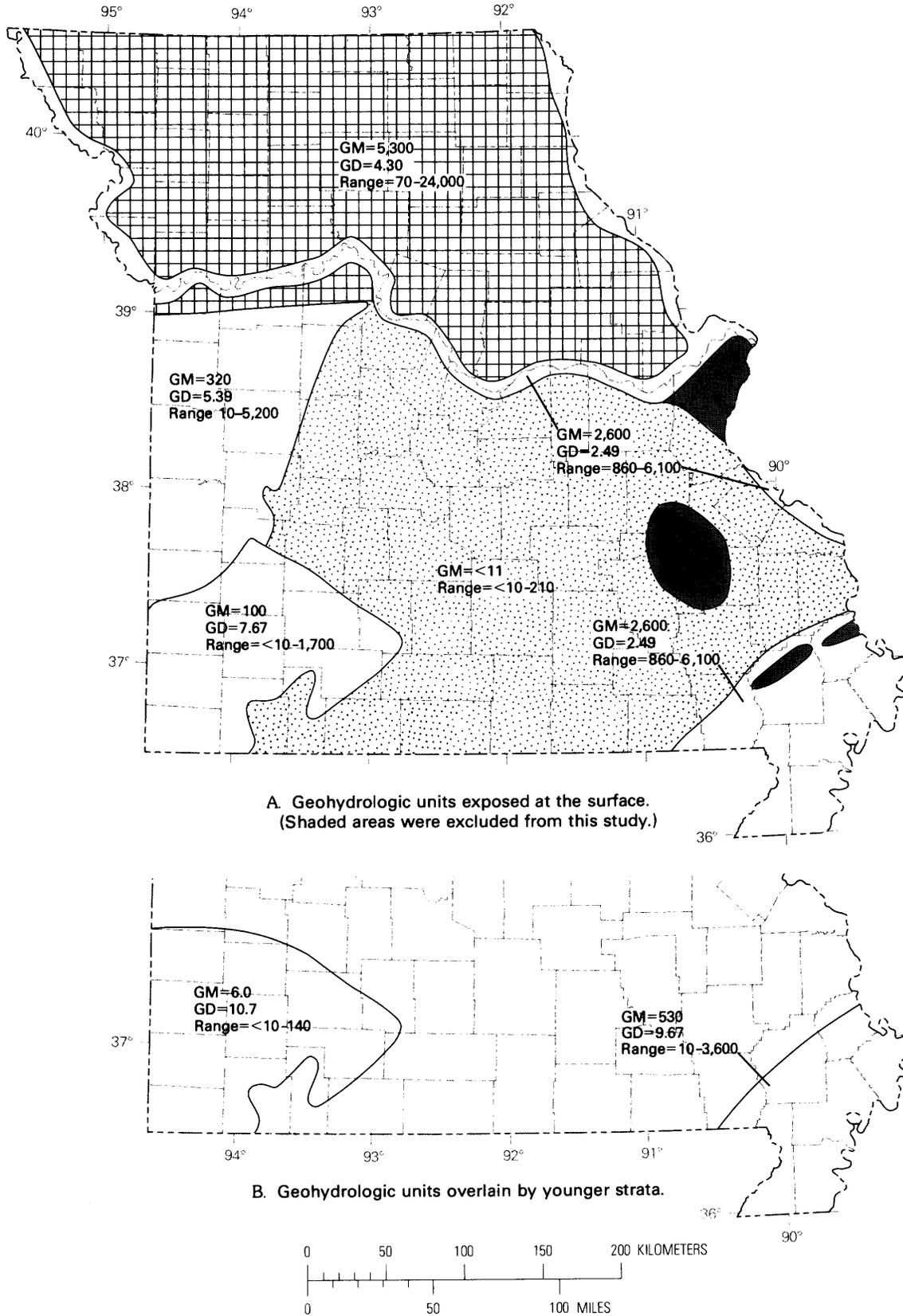


FIGURE 5.—Iron concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in eight samples from the geohydrologic unit.

GEOCHEMICAL SURVEY OF MISSOURI

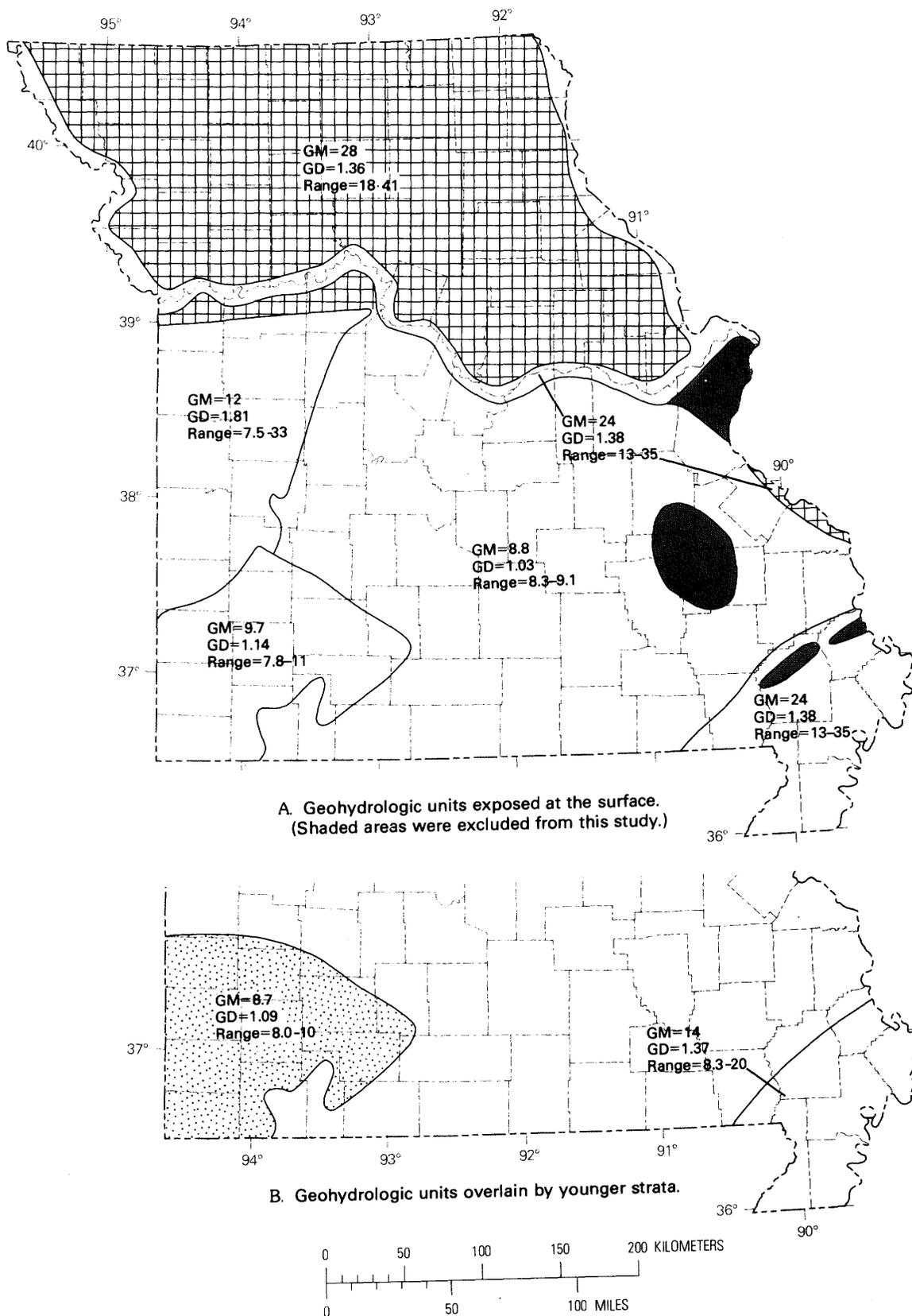


FIGURE 6.—Silica (SiO_2) concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

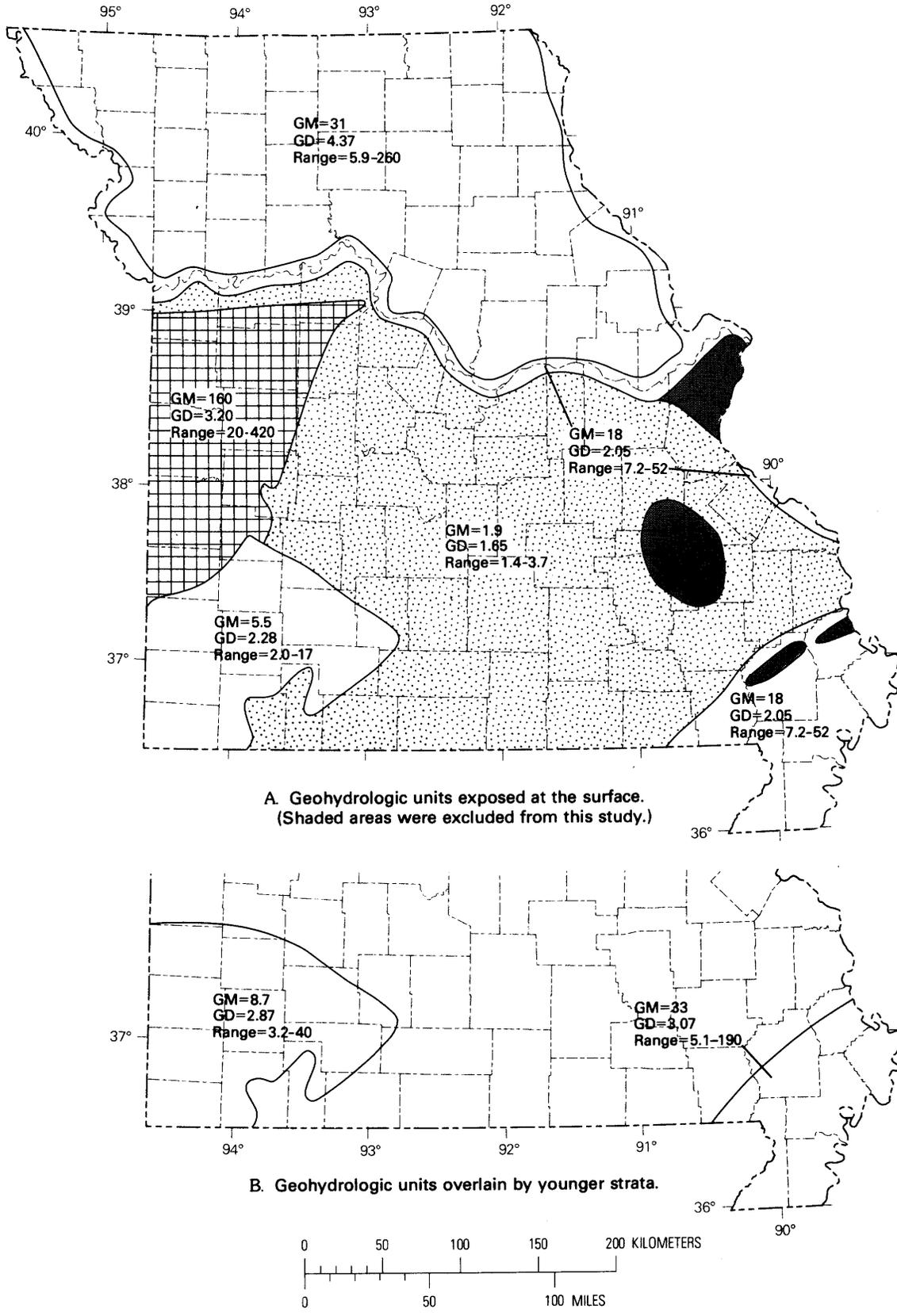


FIGURE 7.—Sodium concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

GEOCHEMICAL SURVEY OF MISSOURI

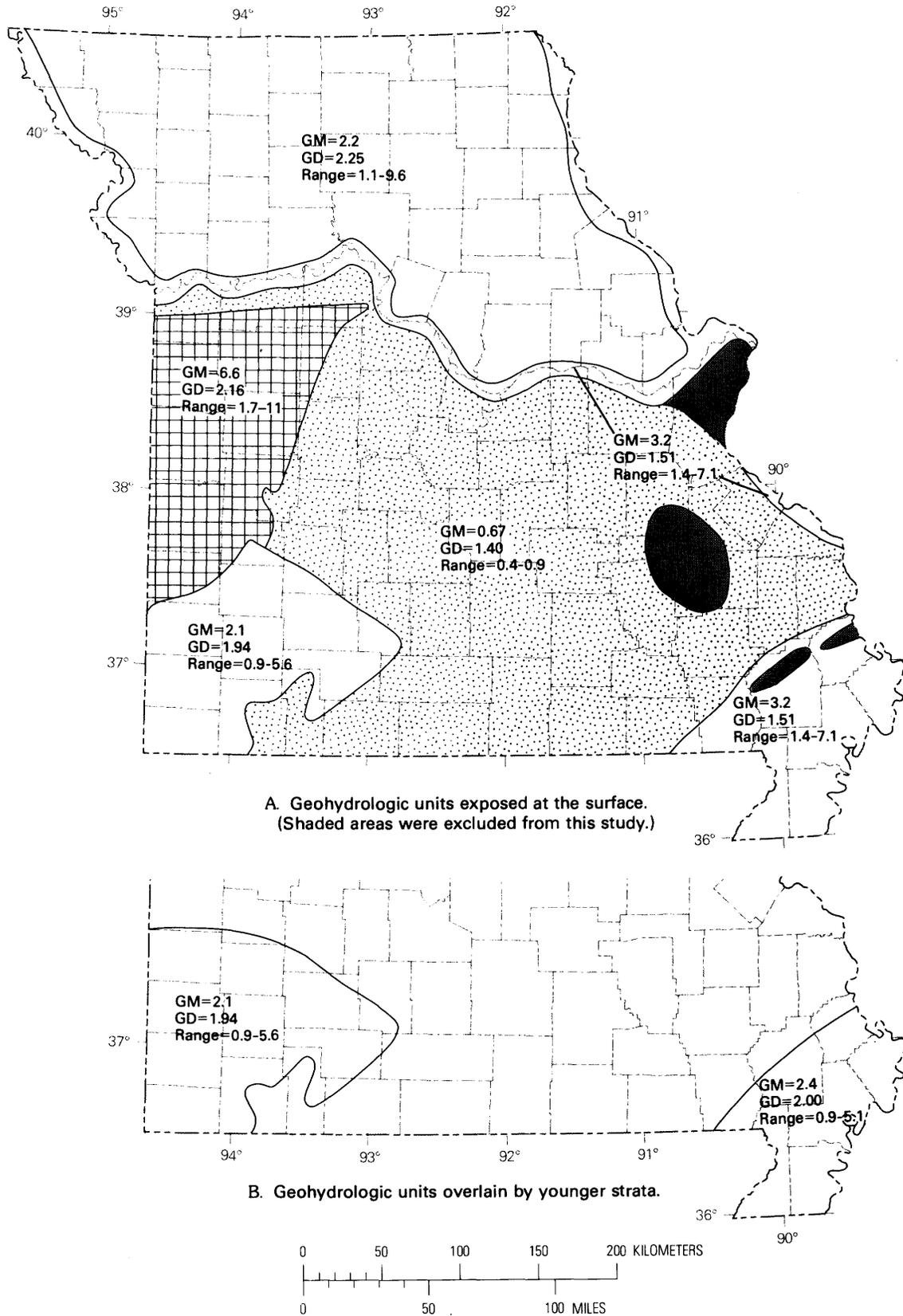


FIGURE 8.—Potassium concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviations; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

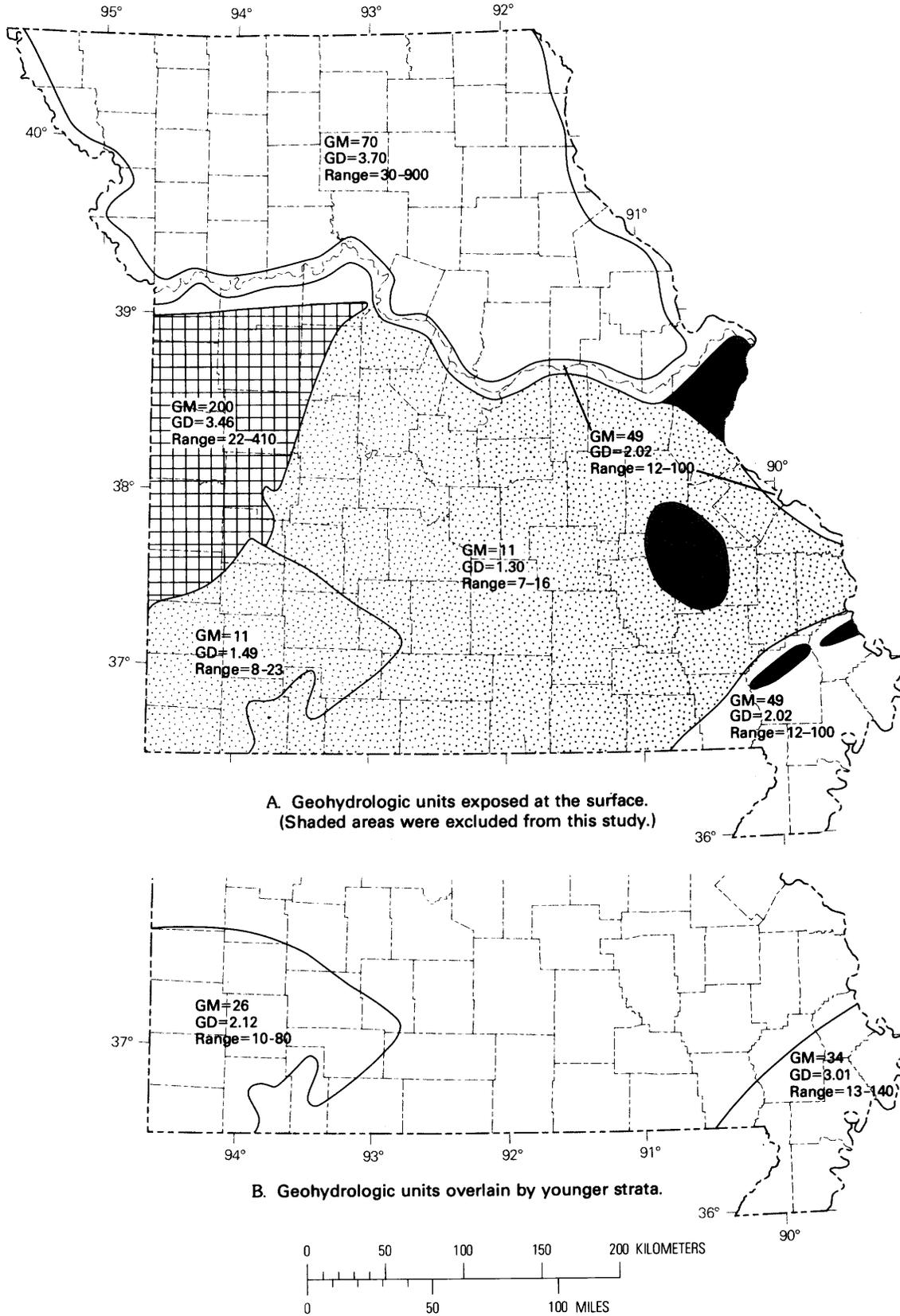


FIGURE 9.—Boron concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

GEOCHEMICAL SURVEY OF MISSOURI

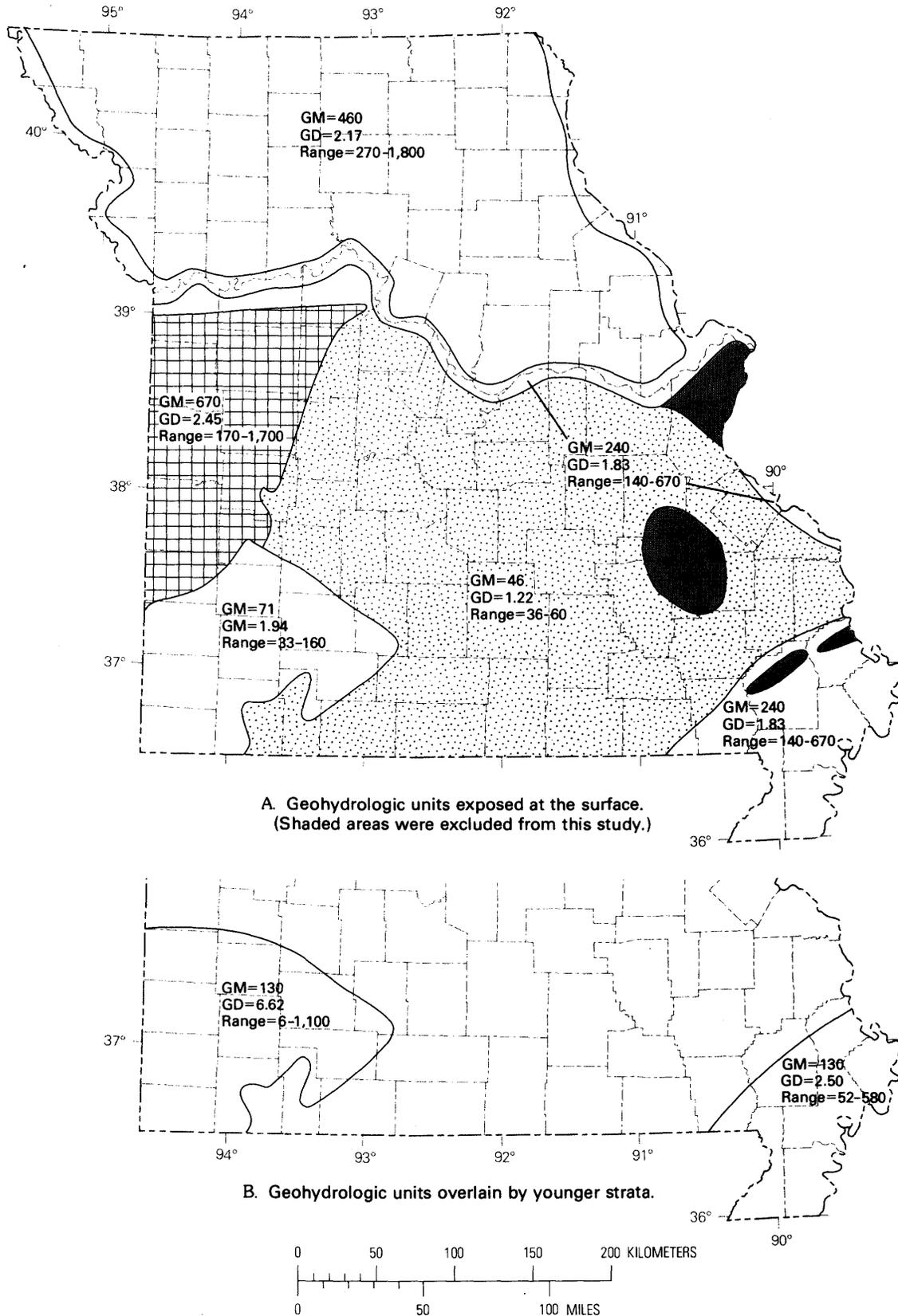


FIGURE 10.—Strontium concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

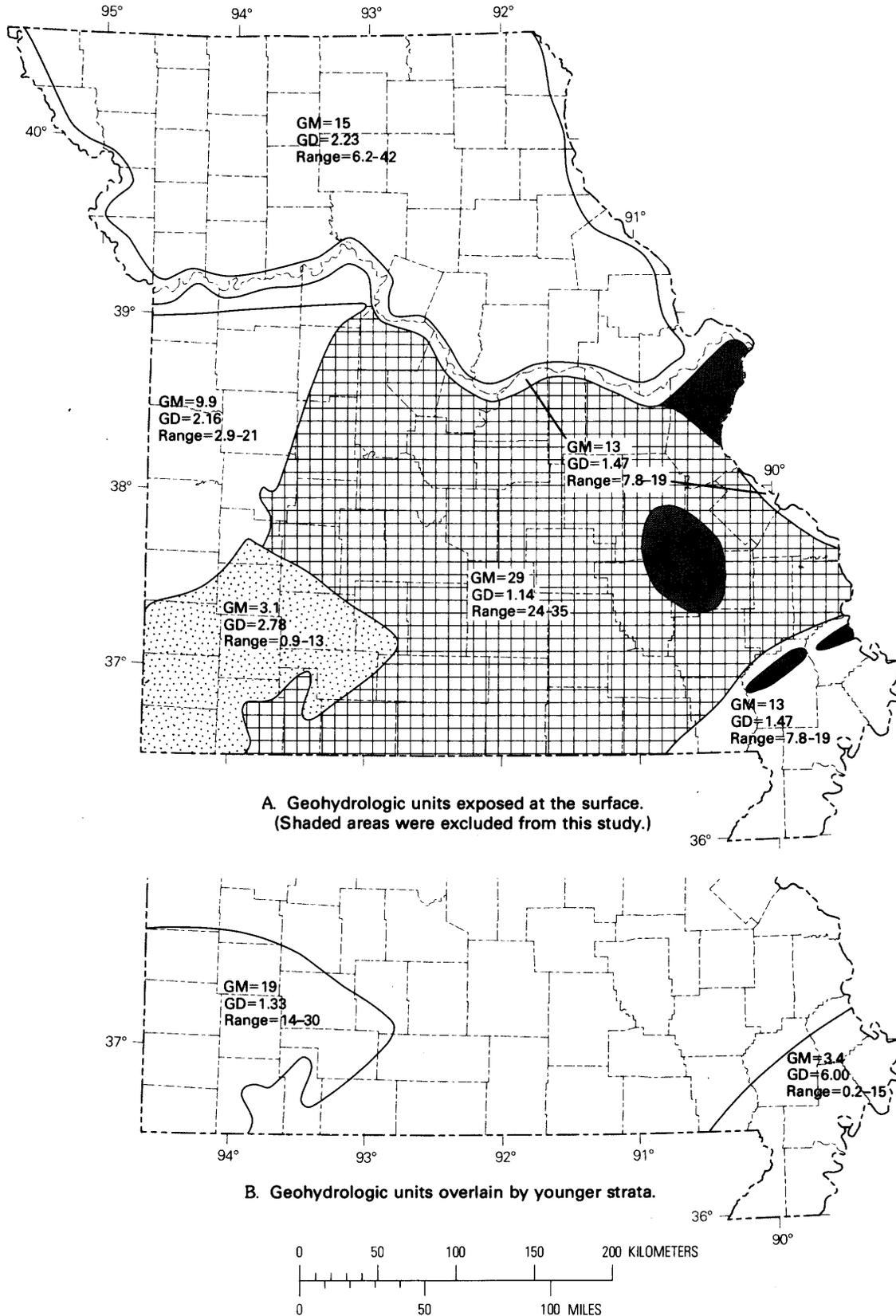


FIGURE 11.—Magnesium concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

GEOCHEMICAL SURVEY OF MISSOURI

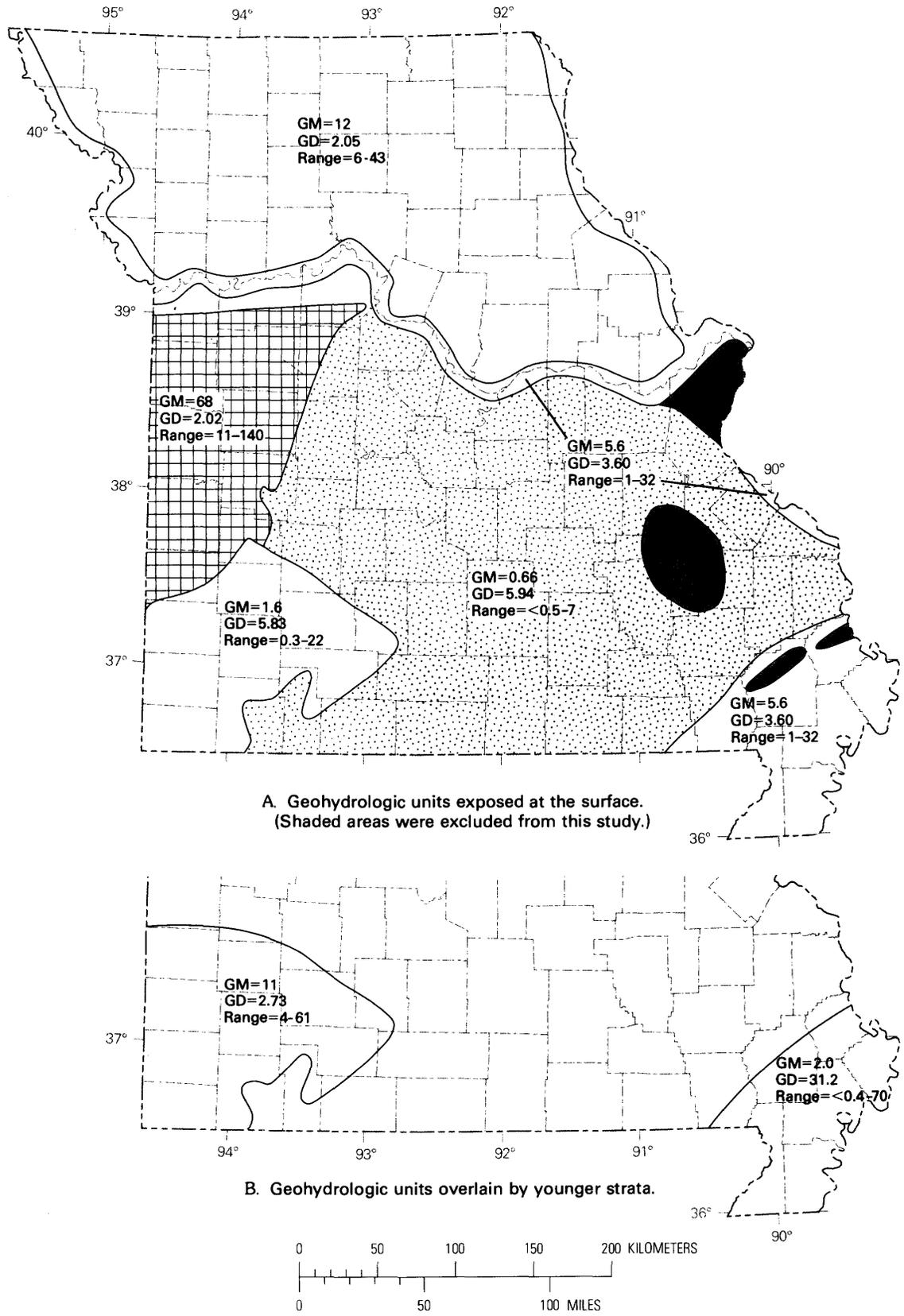


FIGURE 12.—Lithium concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

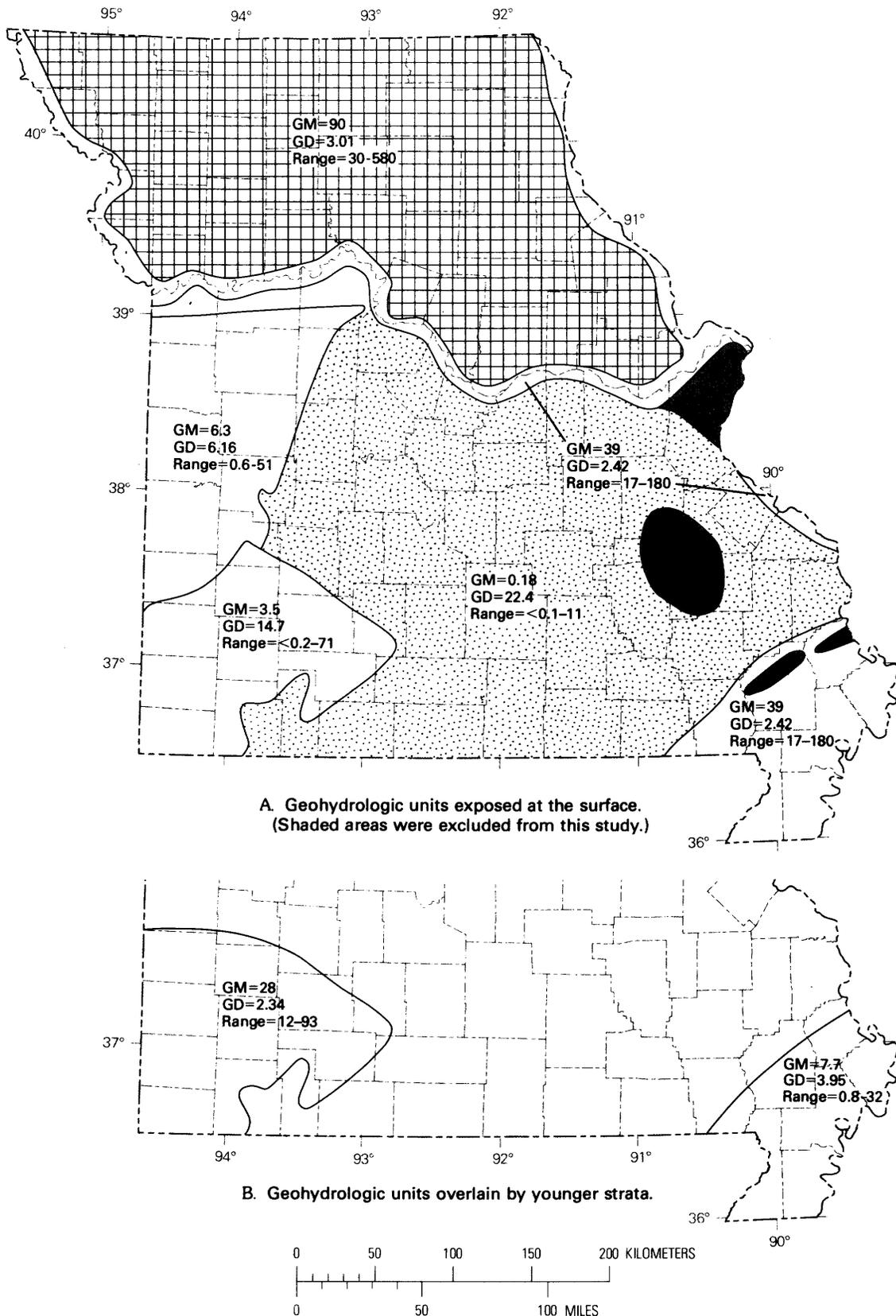


FIGURE 13.—Sulfate (SO₄) concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

GEOCHEMICAL SURVEY OF MISSOURI

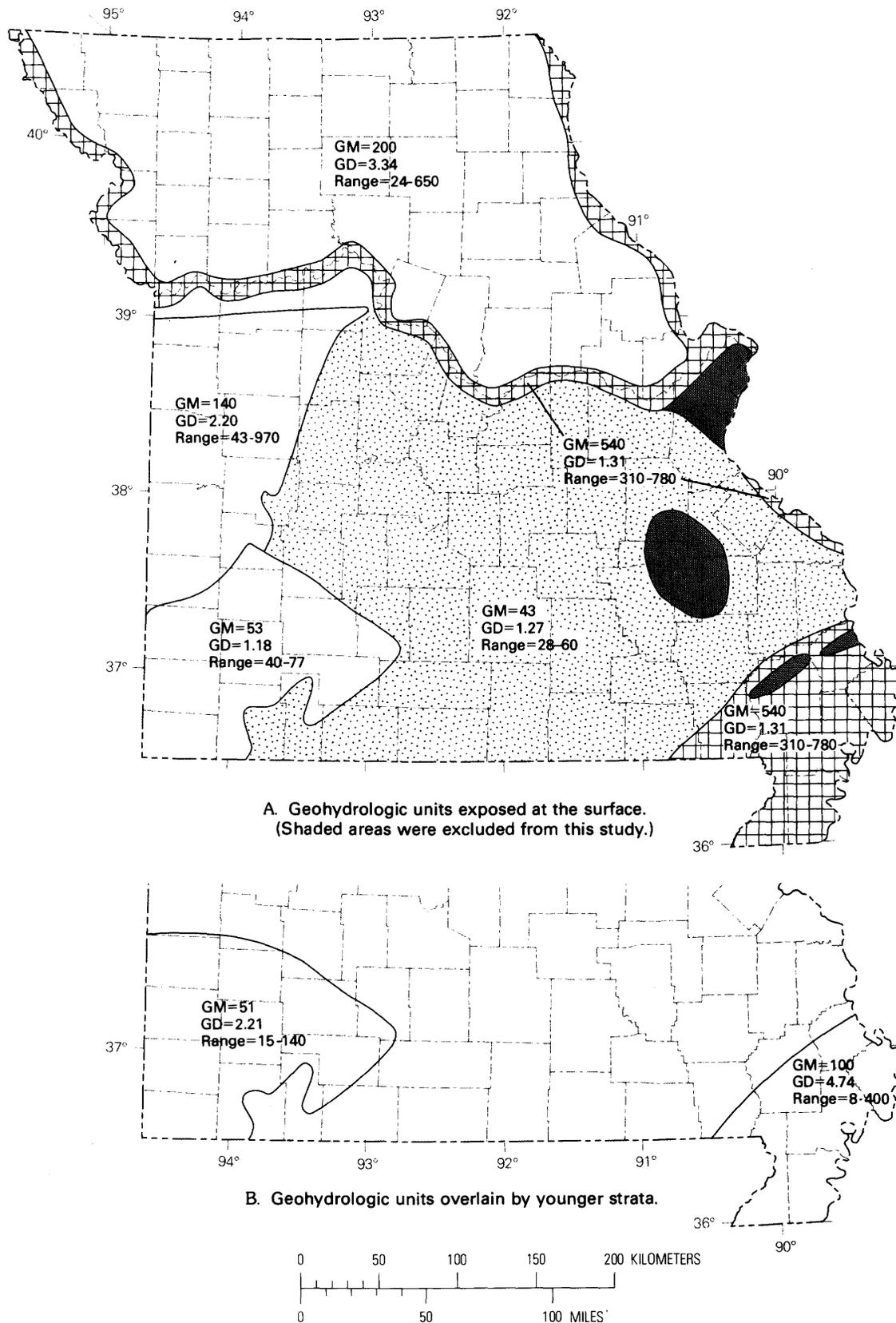


FIGURE 14.—Barium concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

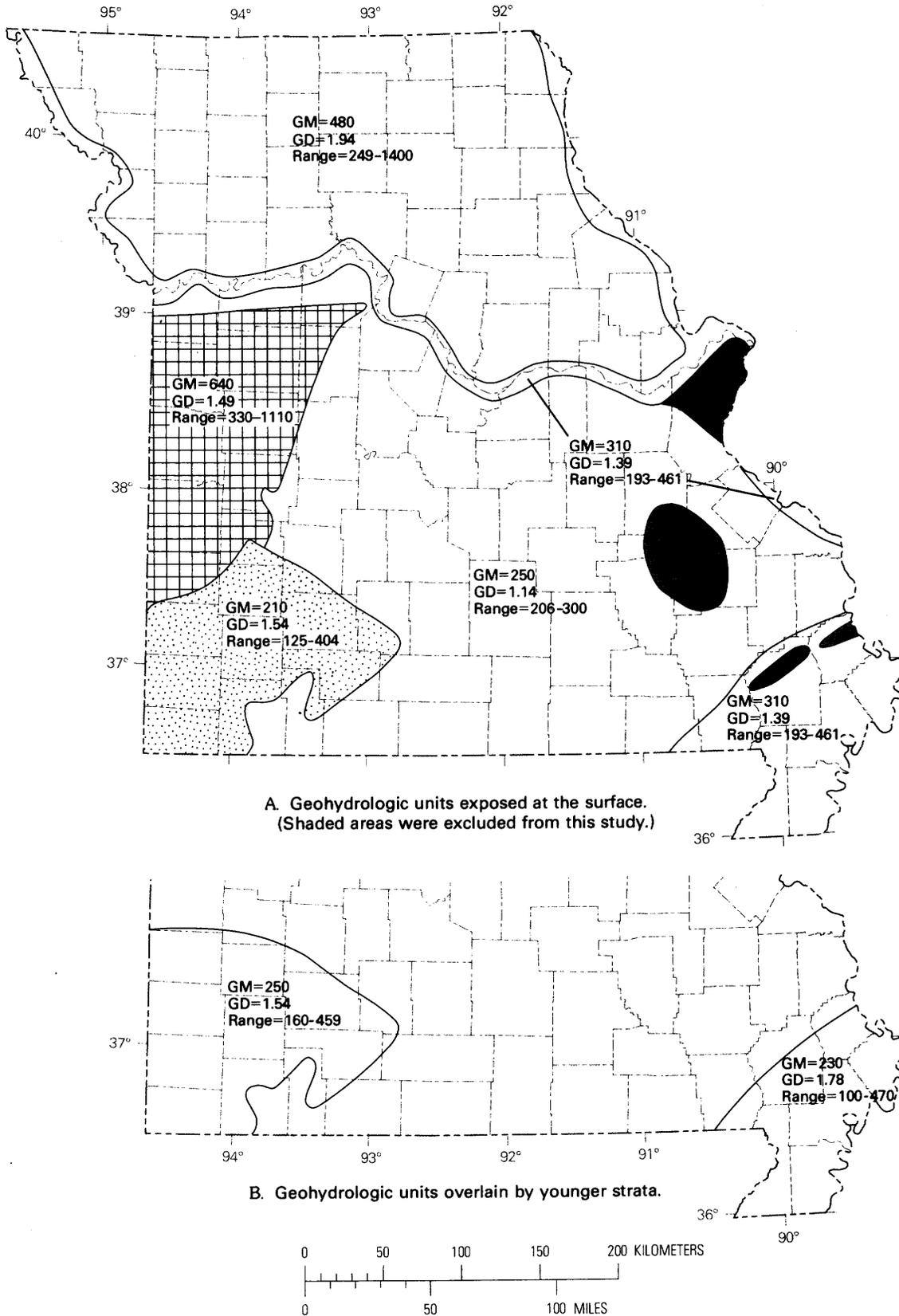


FIGURE 15.—Dissolved solids (residue on evaporation at 180°C) in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

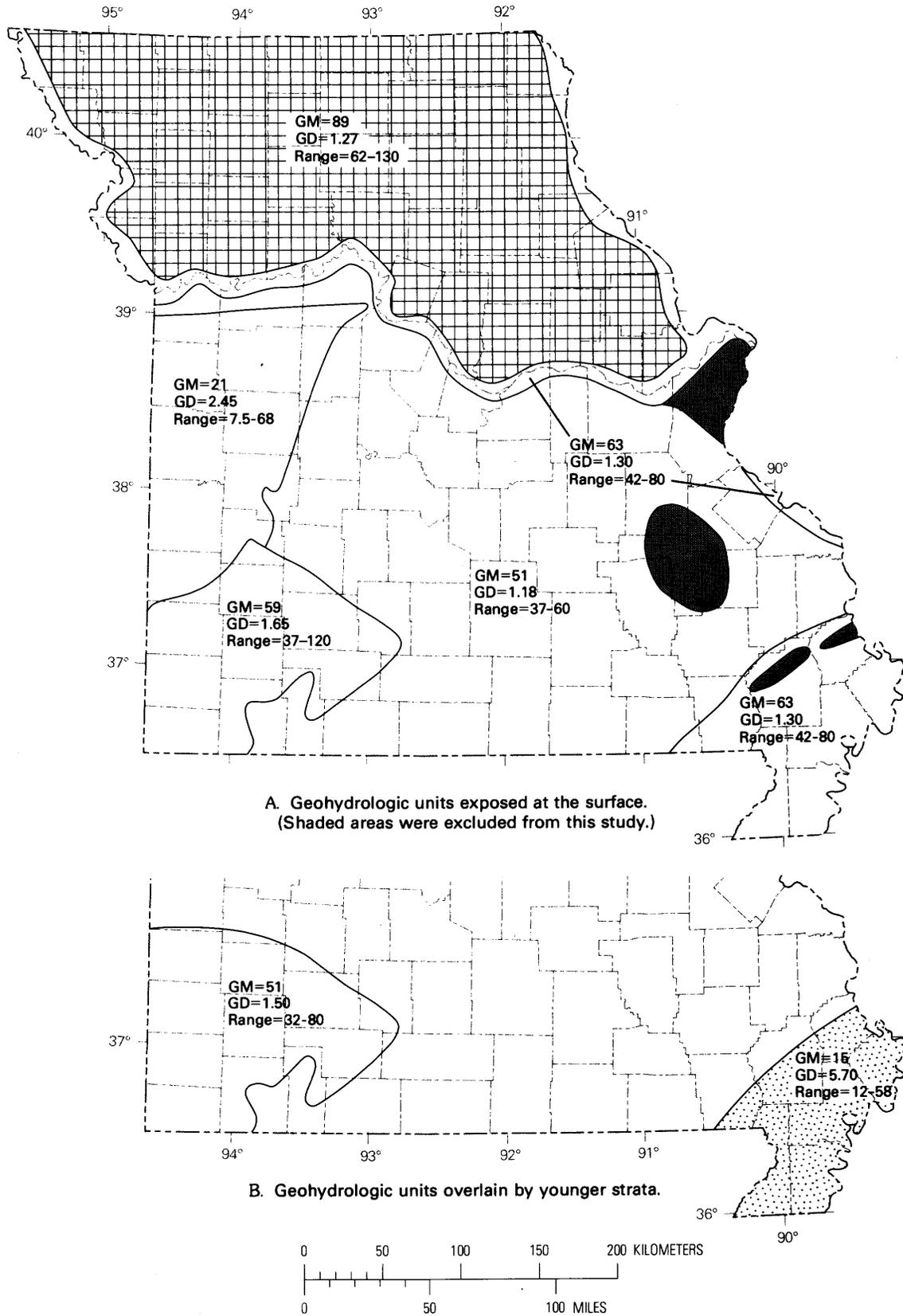


FIGURE 16.—Calcium concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

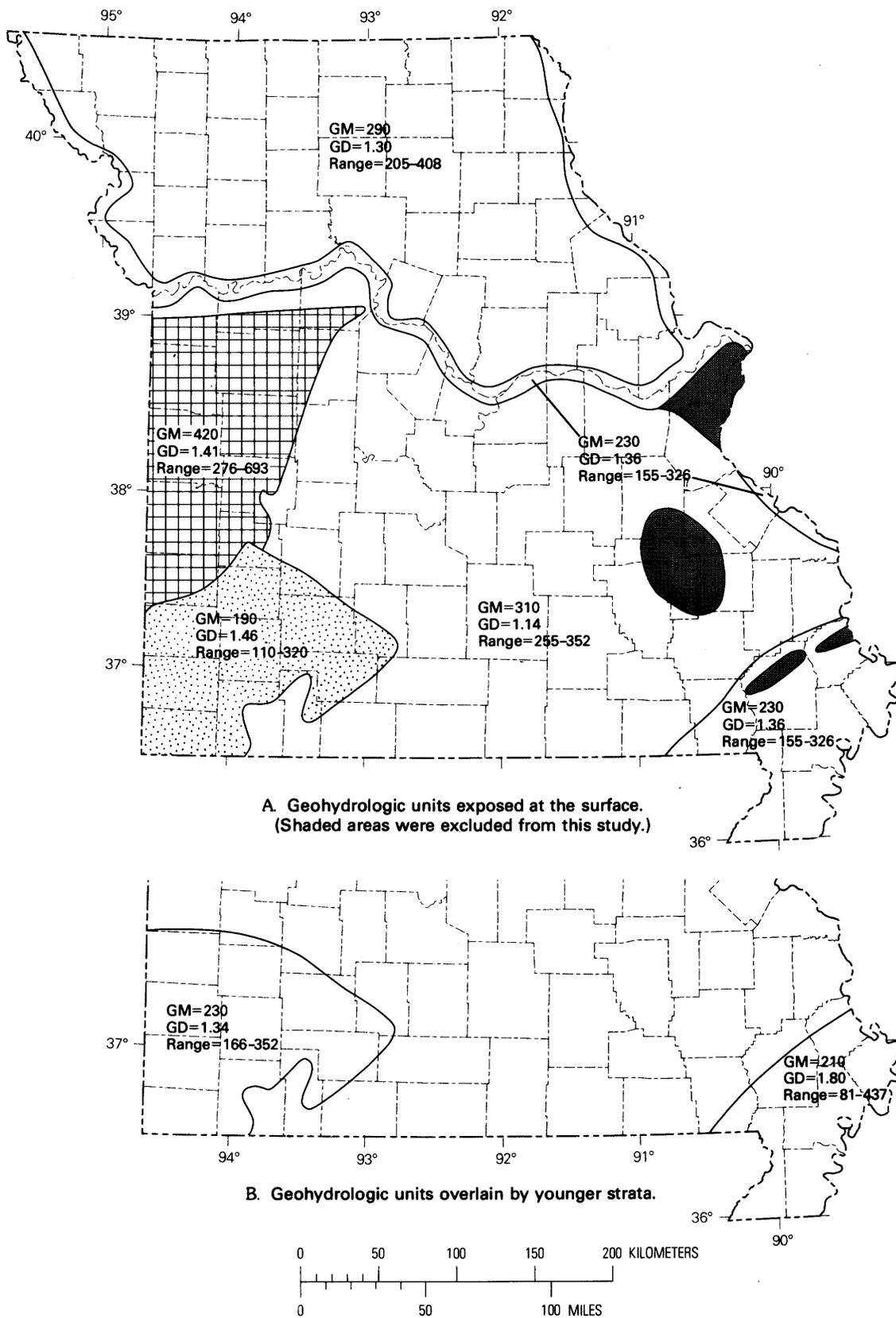


FIGURE 17.—Bicarbonate (HCO_3) concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

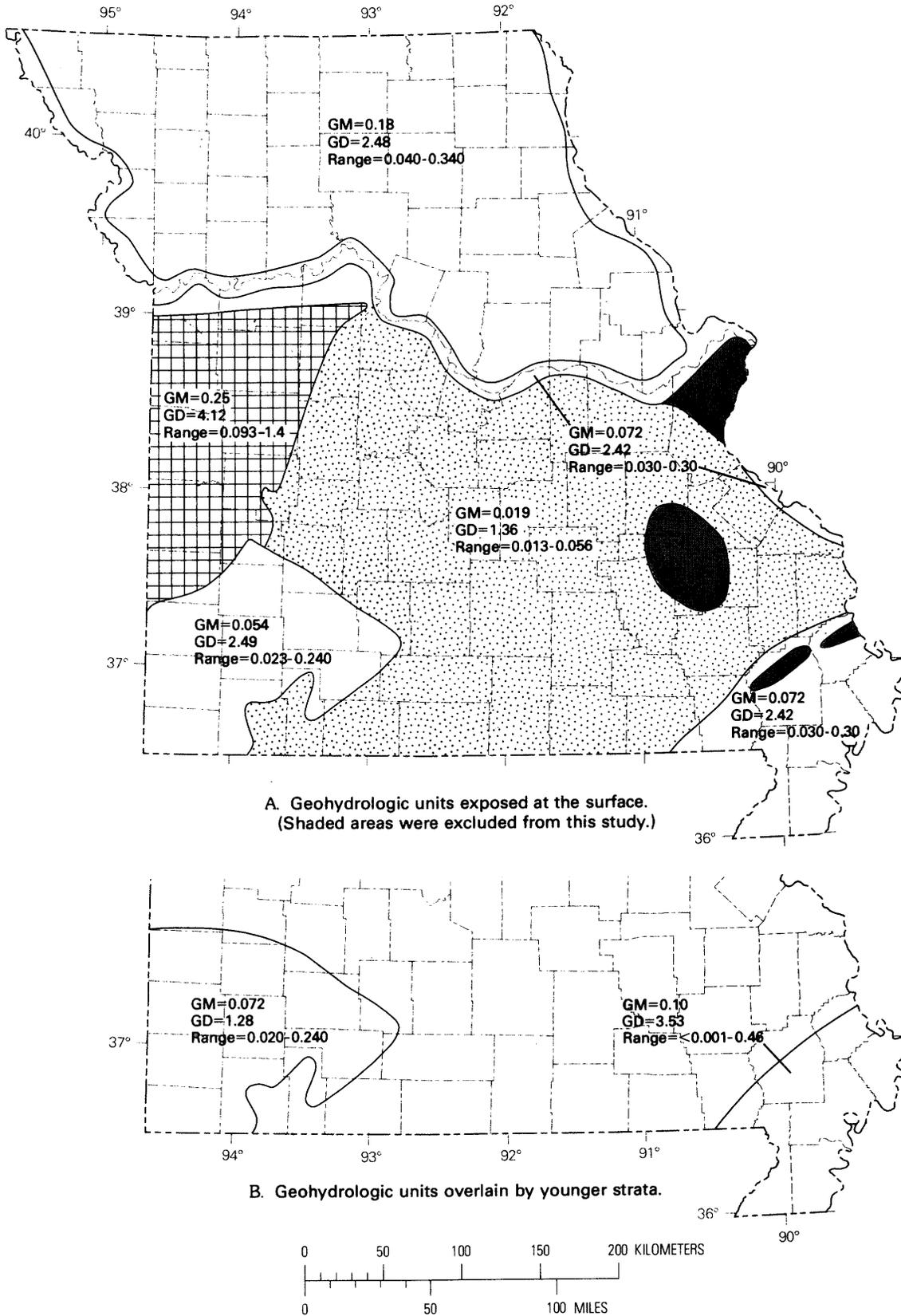


FIGURE 18.—Bromine concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

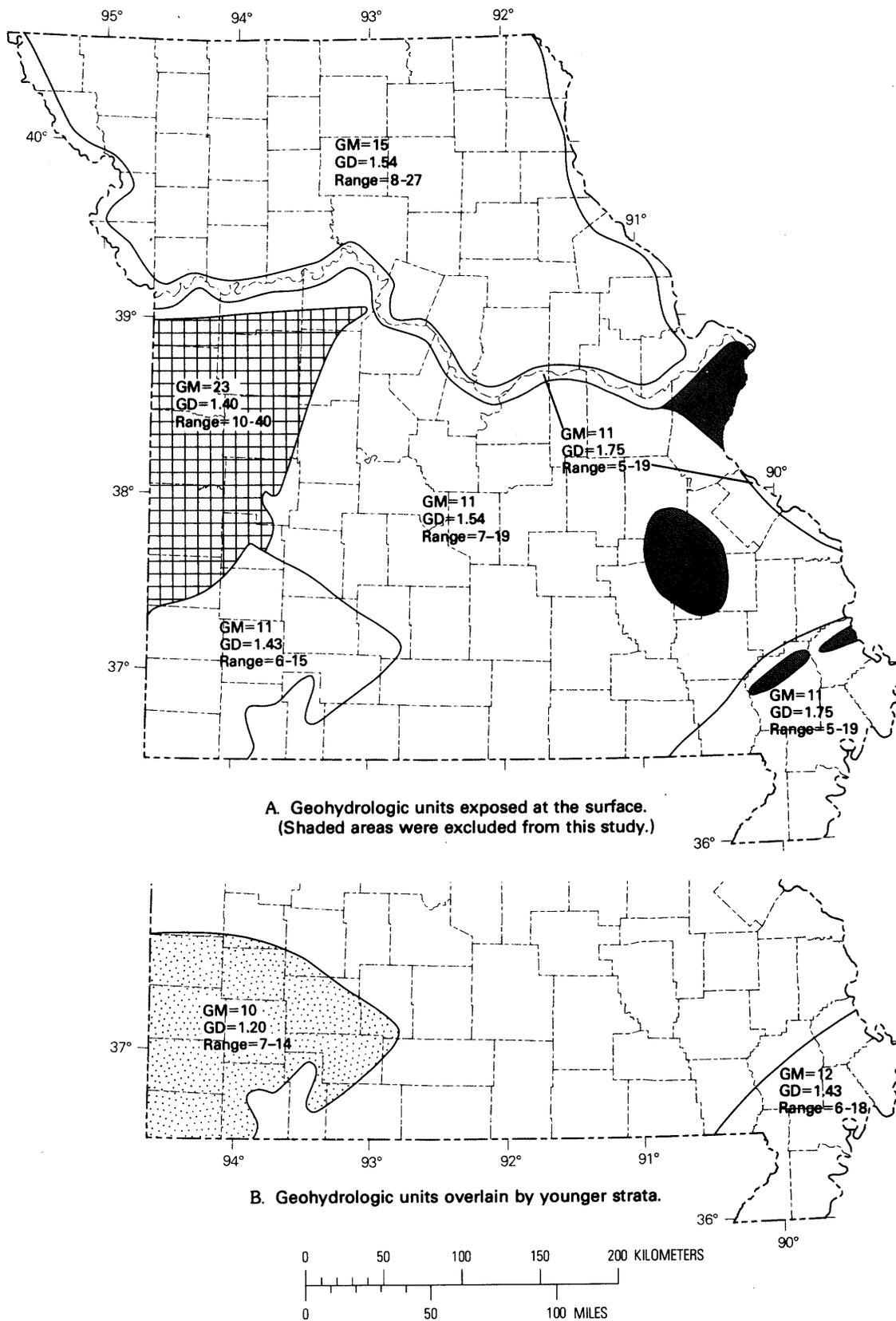


FIGURE 19.—Aluminum in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

GEOCHEMICAL SURVEY OF MISSOURI

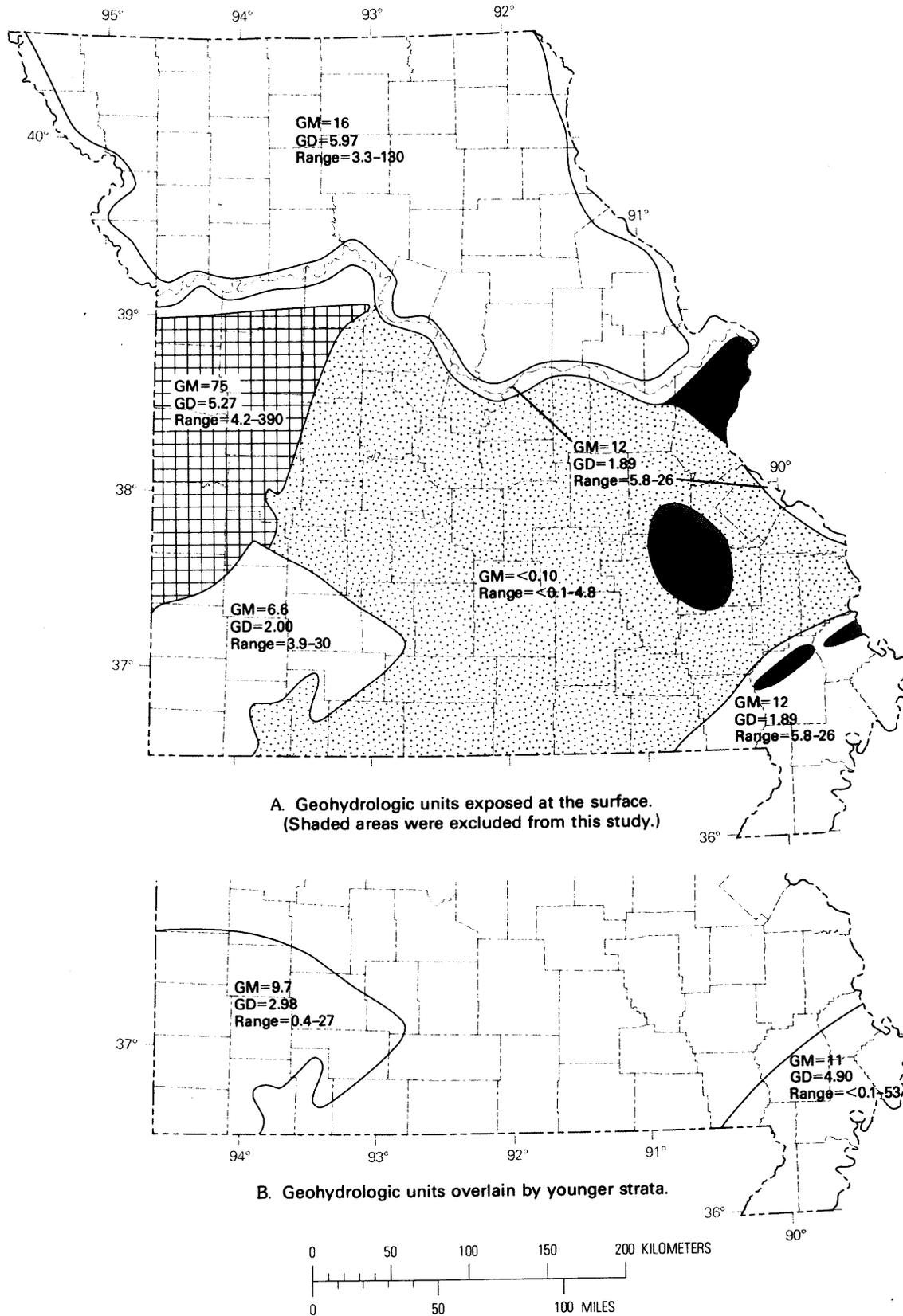


FIGURE 20.—Chlorine concentrations in ground waters from seven geohydrologic units in Missouri. Patterns show units having the significantly different extreme high (crosshatched) and low (stippled) mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples from the geohydrologic unit.

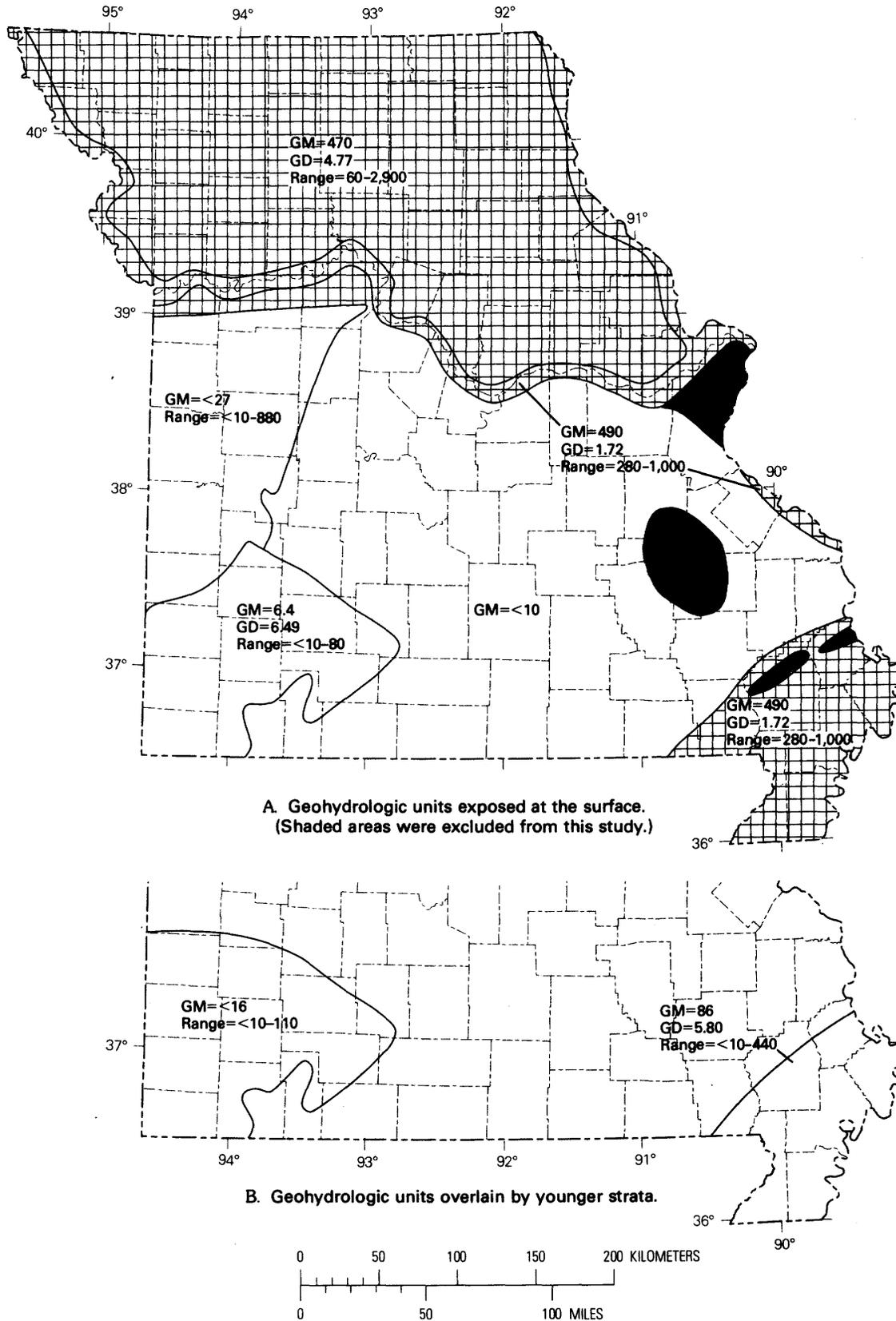


FIGURE 21.—Manganese concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the units having the highest observed mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

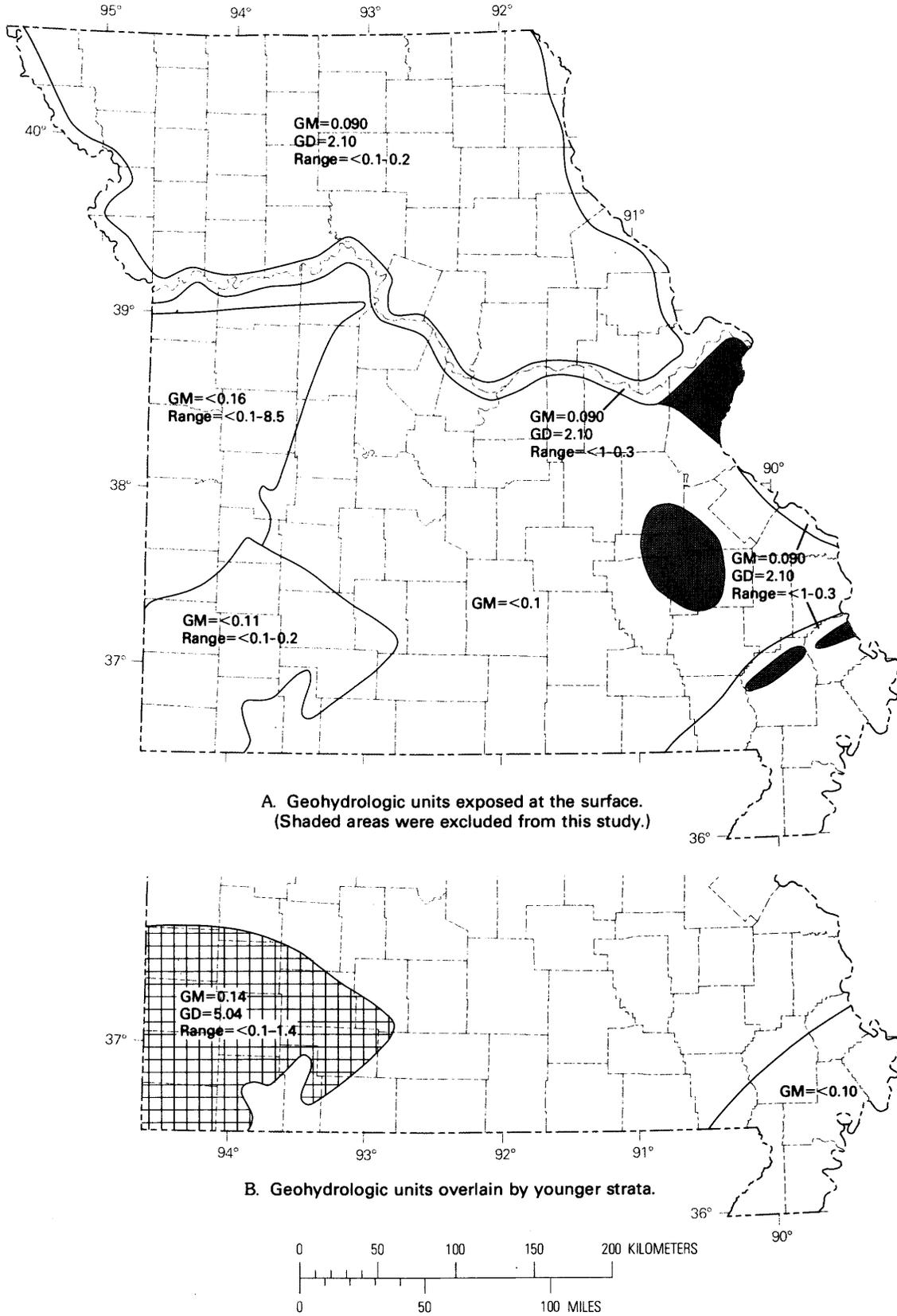


FIGURE 22.—Sulfide (S^{--}) concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

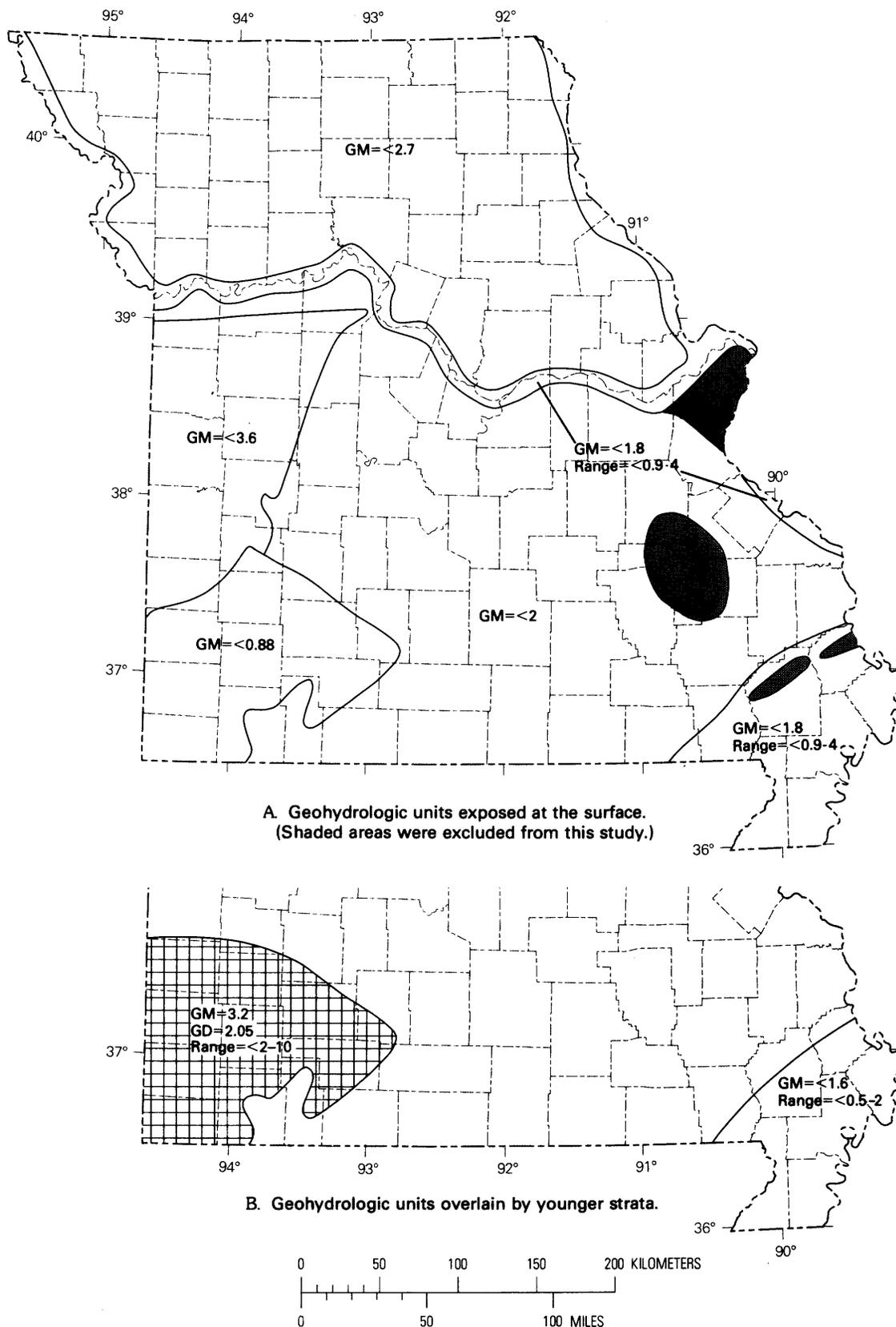


FIGURE 23.—Molybdenum concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

GEOCHEMICAL SURVEY OF MISSOURI

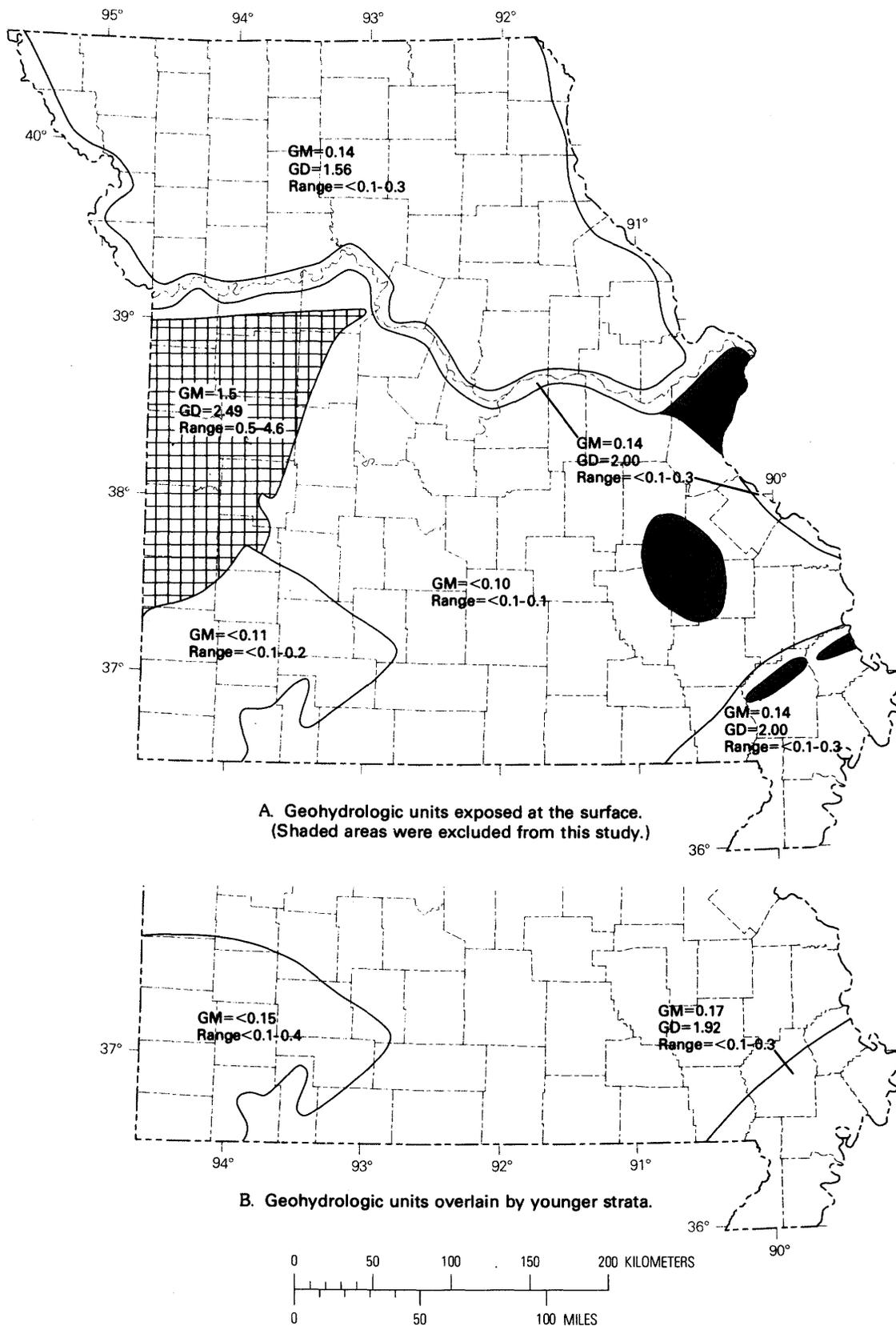


FIGURE 24.—Fluorine concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

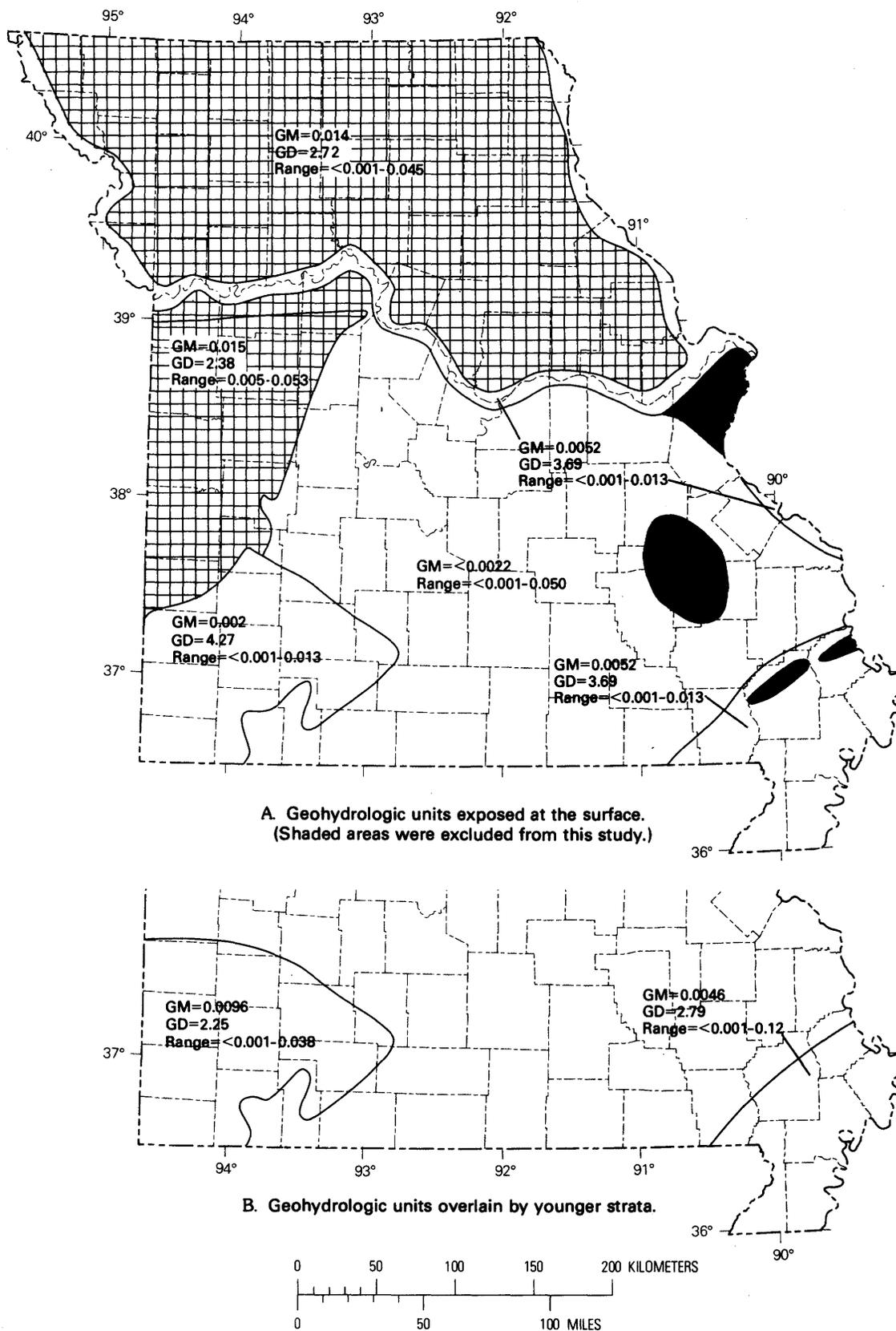


FIGURE 25.—Iodine concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the units having the highest observed mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

GEOCHEMICAL SURVEY OF MISSOURI

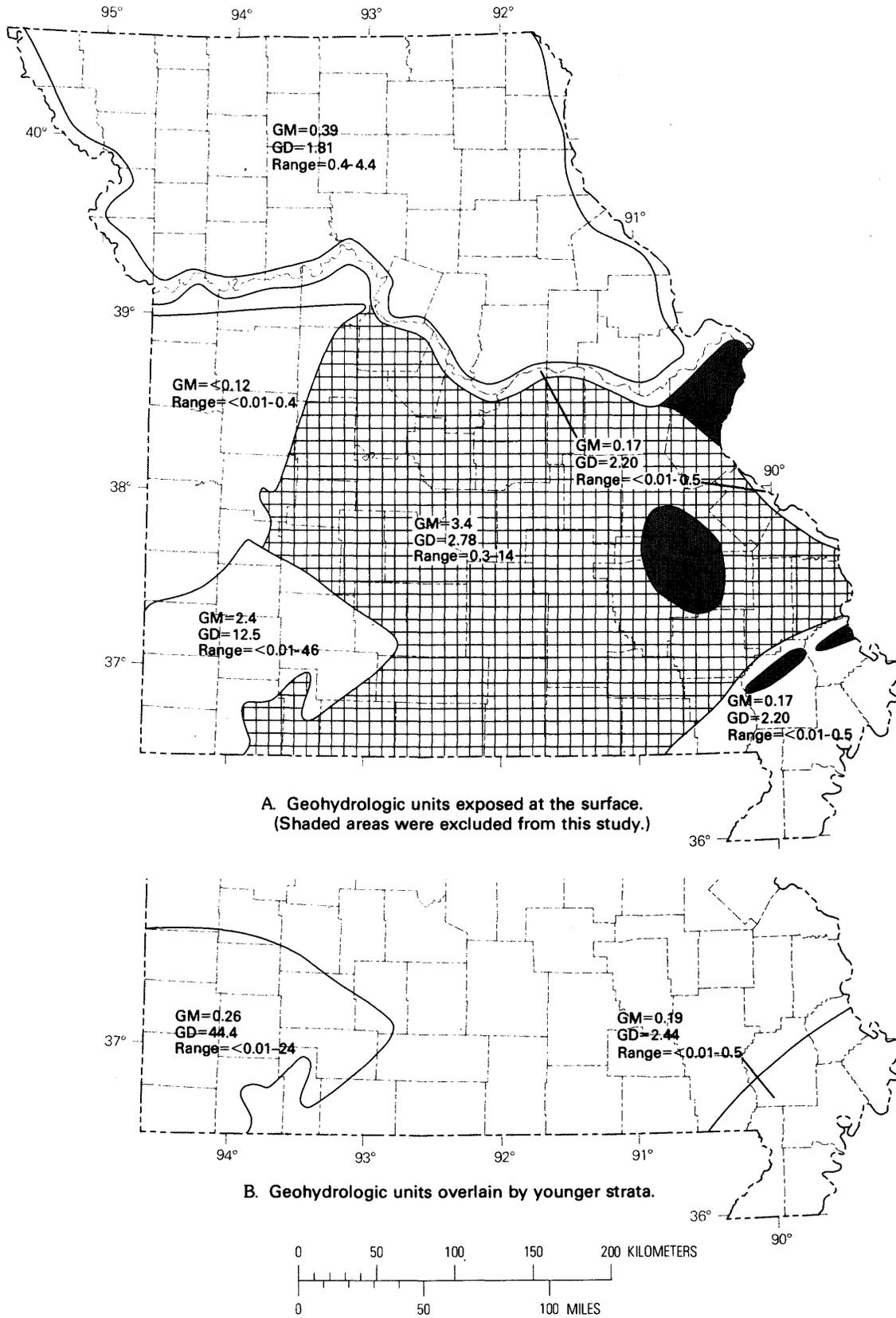


FIGURE 26.—Nitrate concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

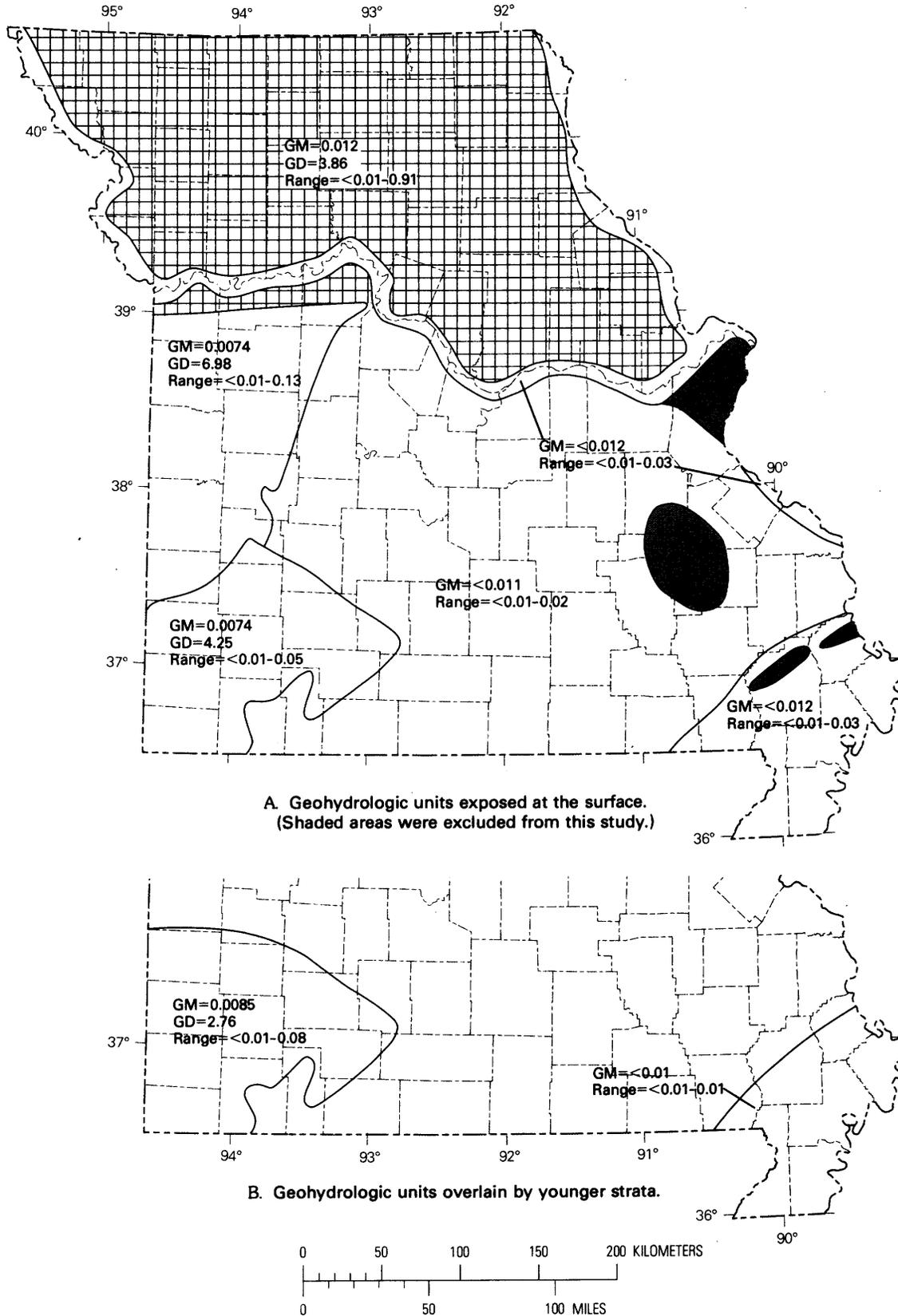


FIGURE 27.—Nitrite concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentration. GM, geometric mean, in milligram per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

GEOCHEMICAL SURVEY OF MISSOURI

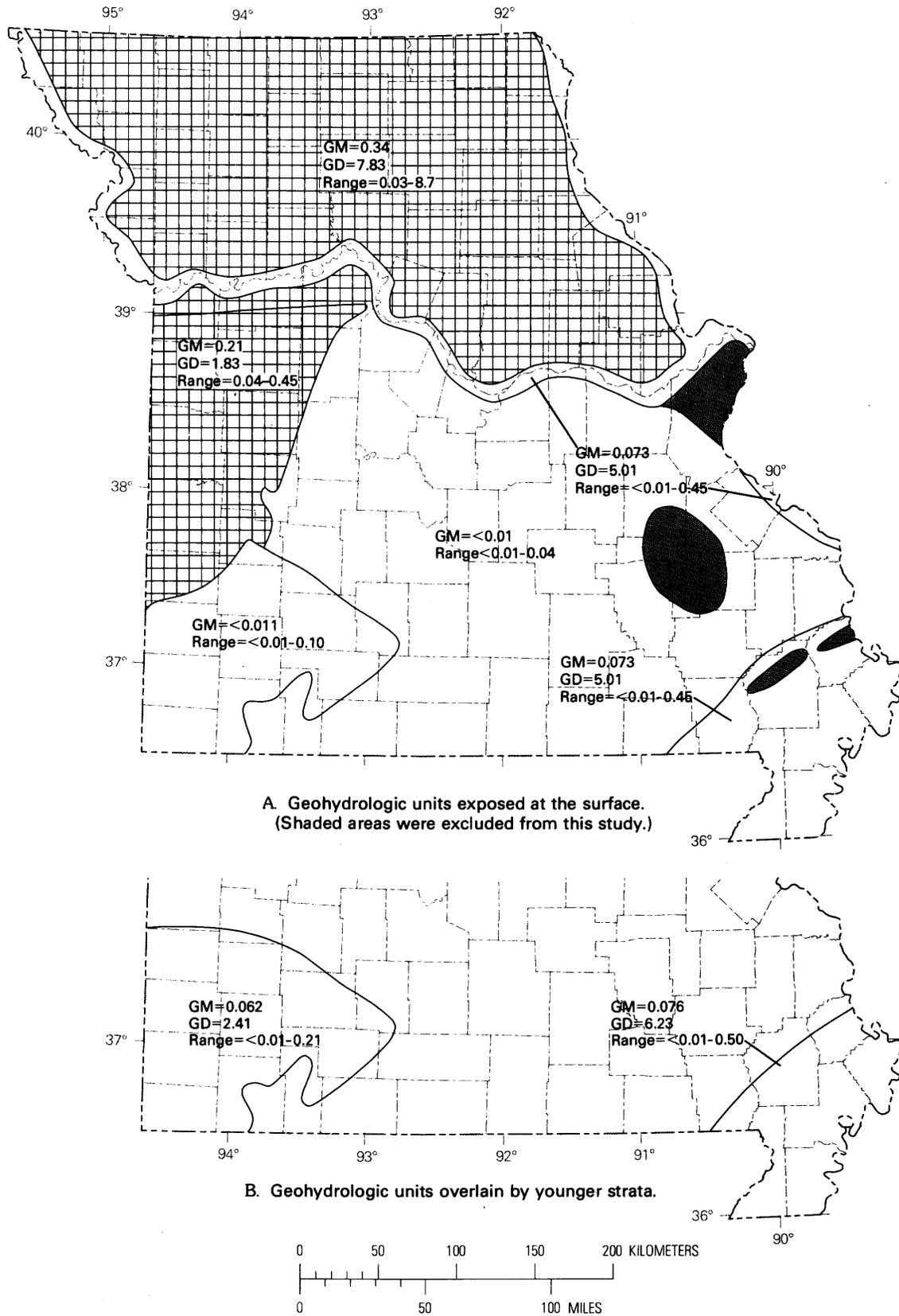


FIGURE 28.—Ammonia concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the units having the highest observed mean concentrations. GM, geometric mean, in milligram per liter; GD, geometric deviation; Range, range of concentrations observed in all eight samples.

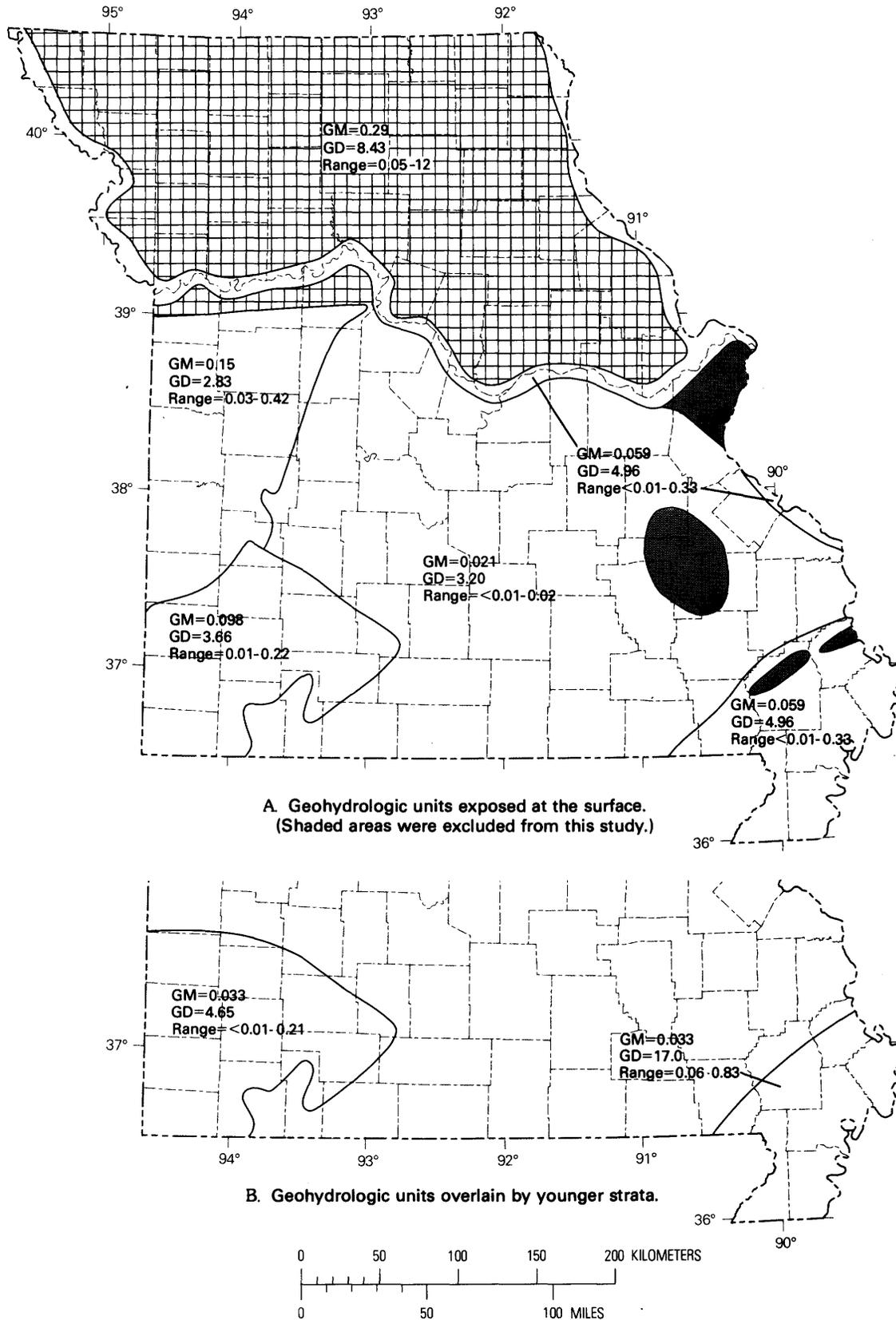


FIGURE 29.—Organic nitrogen concentrations in ground waters from seven geohydrologic units in Missouri. Cross-hatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in milligrams per liter as N; GD, geometric deviation; Range, range of concentrations observed in eight samples.

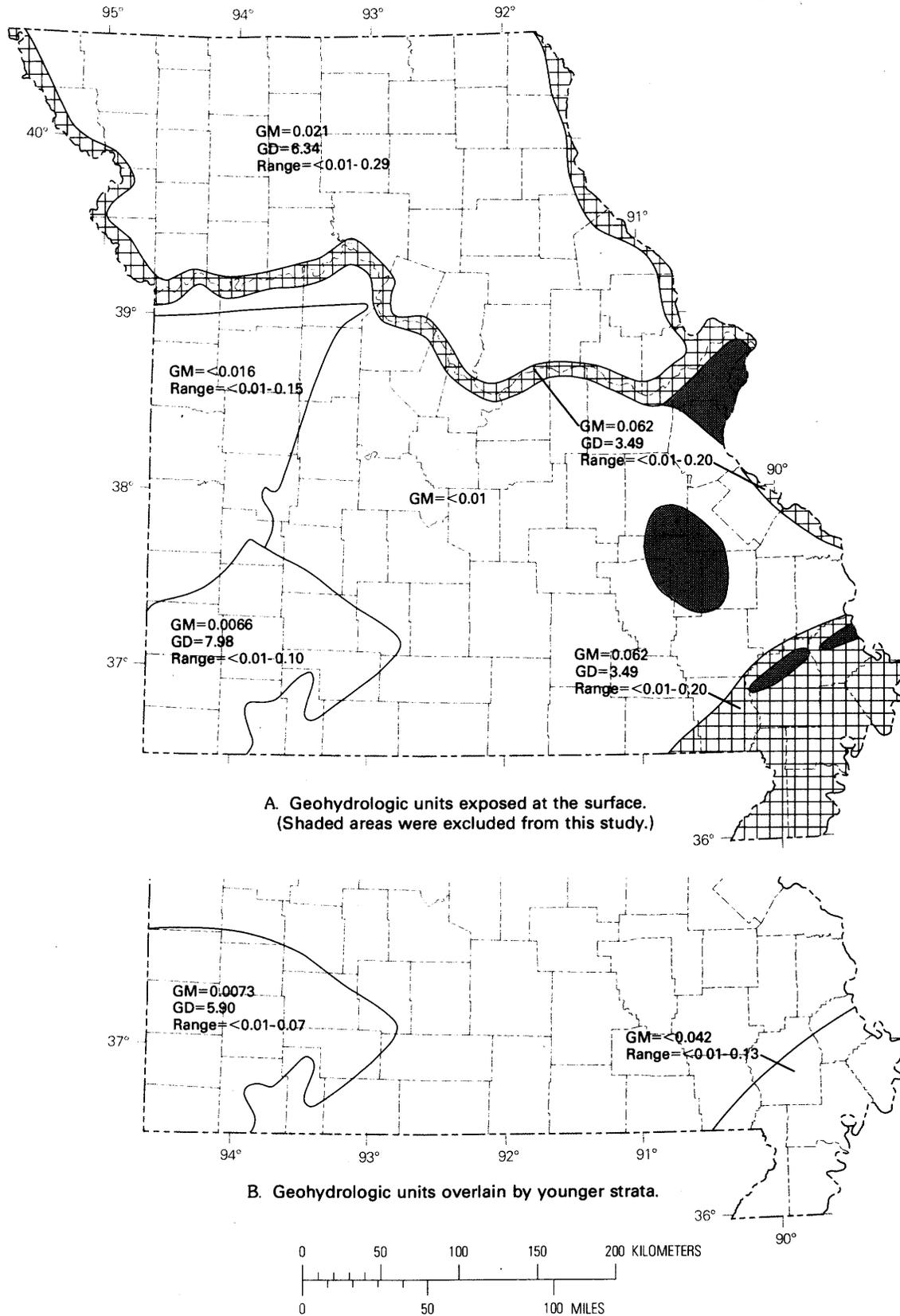


FIGURE 30.—Orthophosphate concentrations in ground waters from seven geohydrologic units in Missouri. Cross-hatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in eight samples.

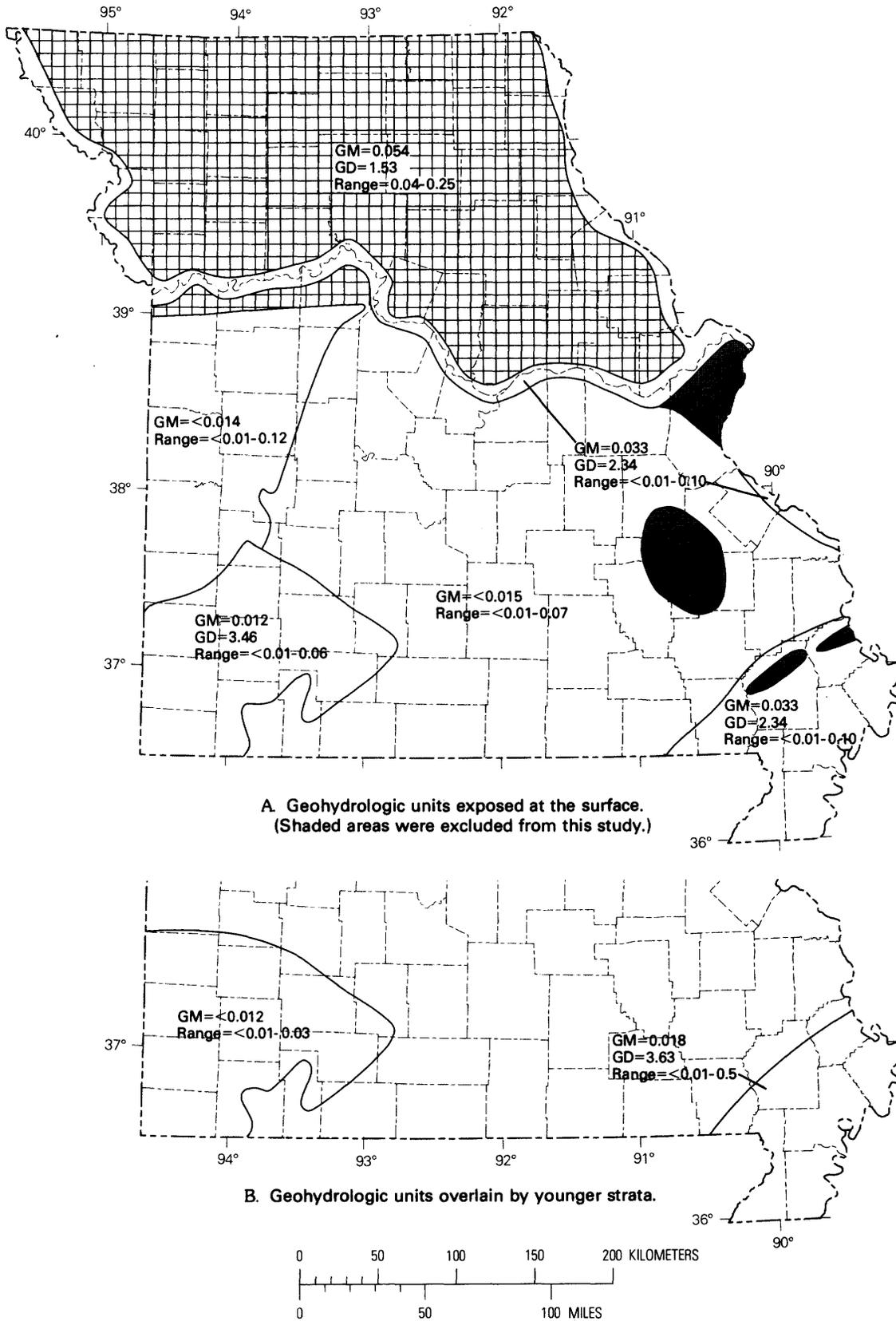


FIGURE 31.—Total phosphorus concentrations in ground waters from seven geohydrologic units in Missouri. Cross-hatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in milligrams per liter; GD, geometric deviation; Range, range of concentrations observed in eight samples.

GEOCHEMICAL SURVEY OF MISSOURI

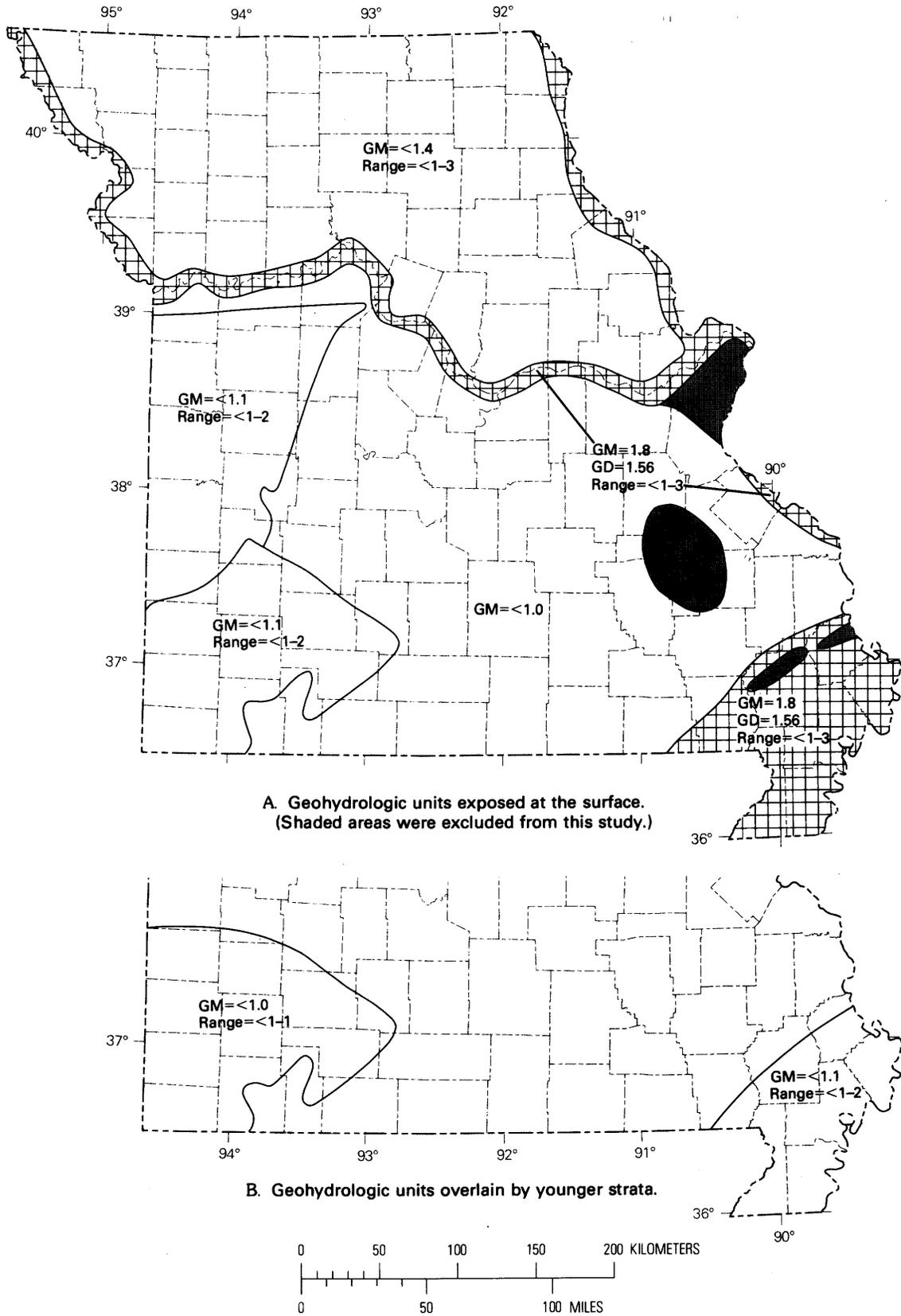


FIGURE 32.—Cadmium concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in eight samples.

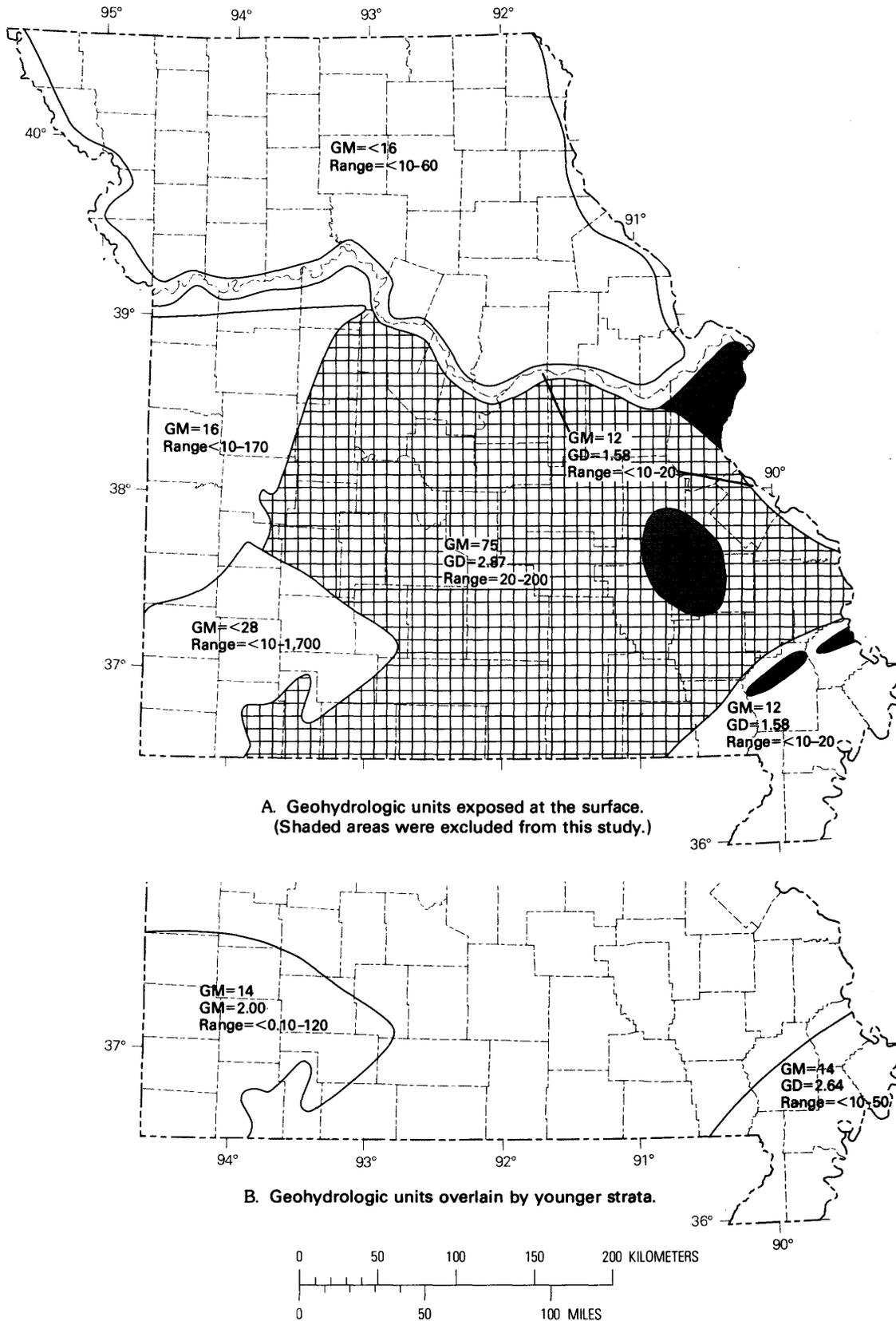


FIGURE 33.—Zinc concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in eight samples.

GEOCHEMICAL SURVEY OF MISSOURI

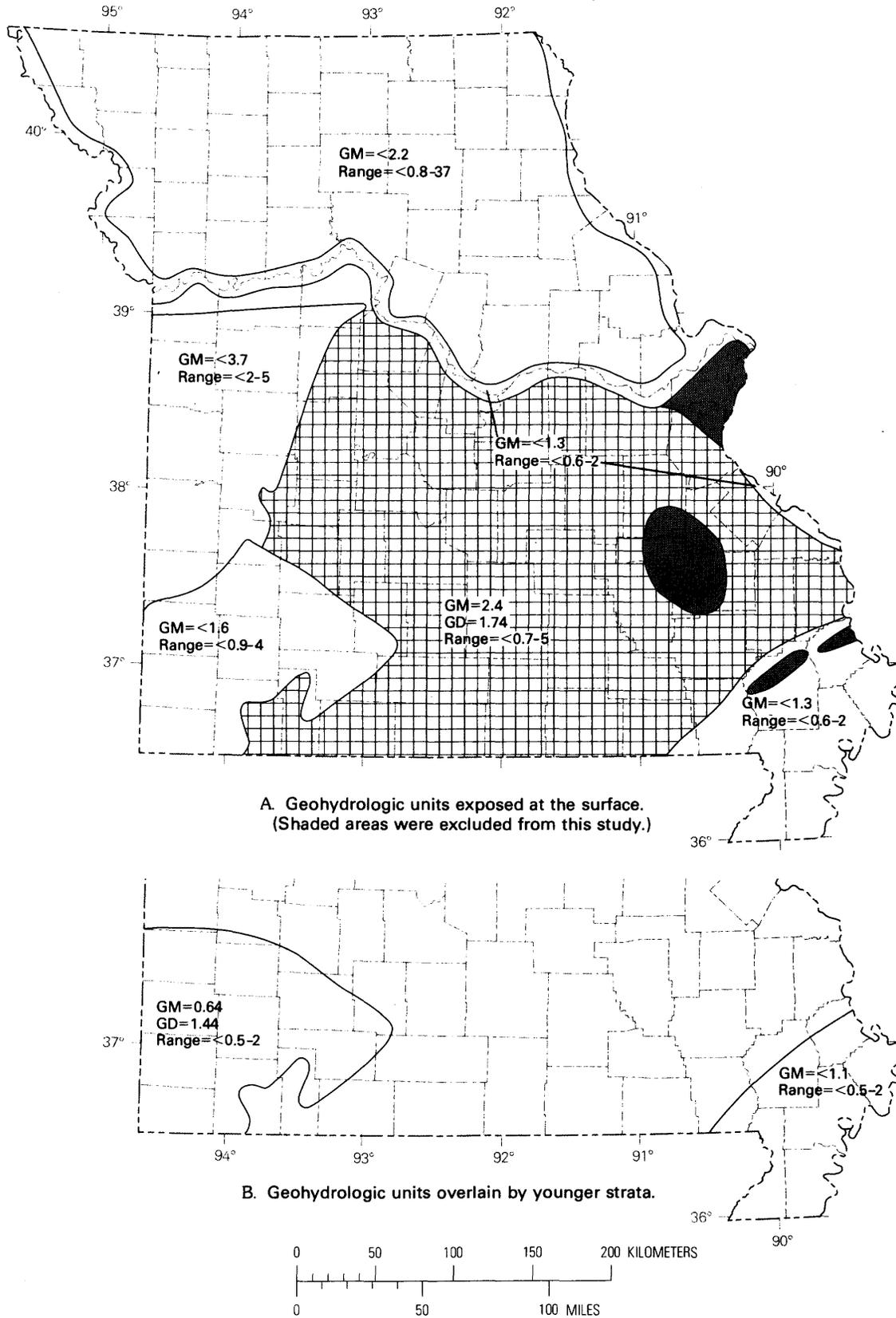


FIGURE 34.—Copper concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in eight samples.

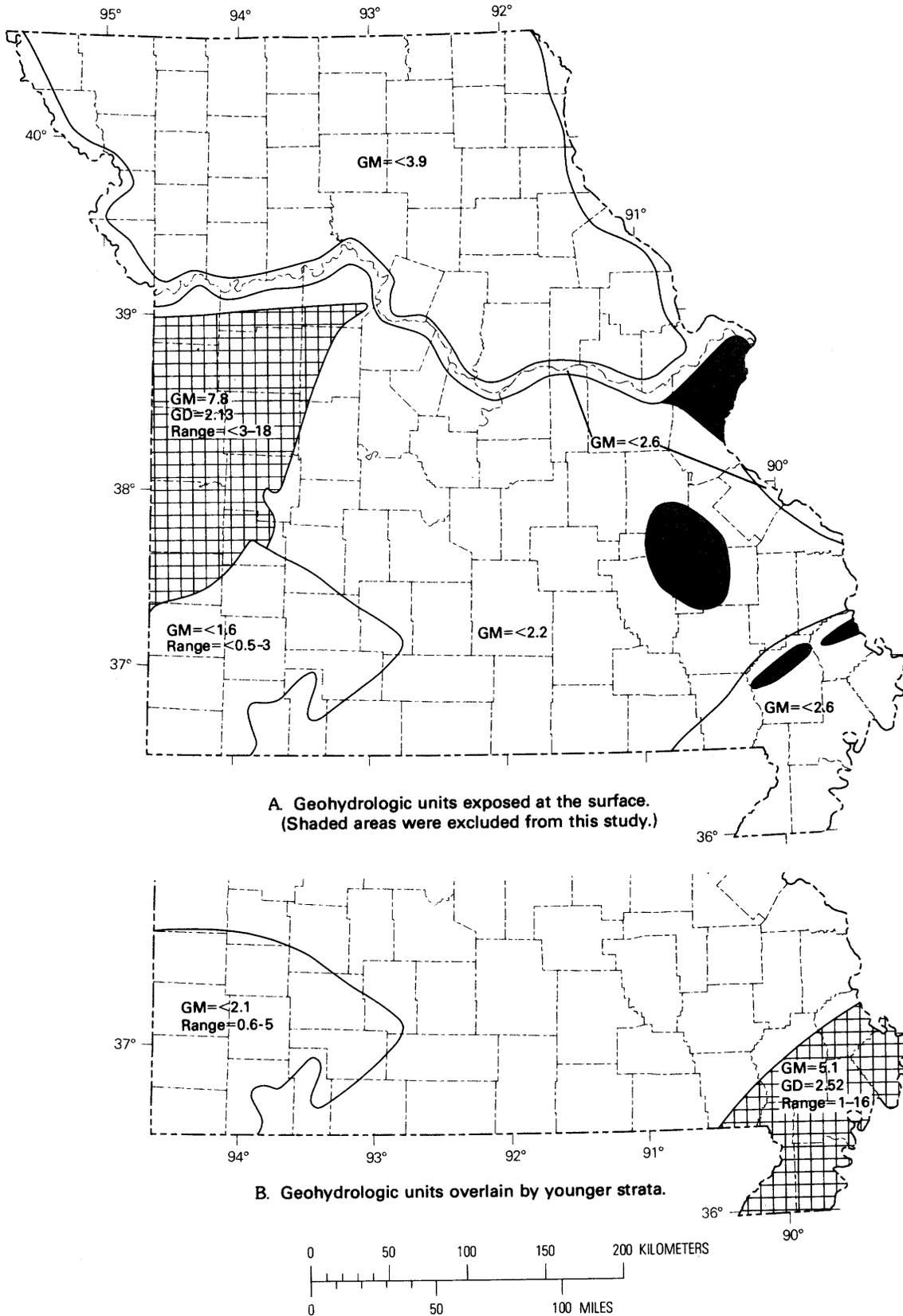


FIGURE 35.—Rubidium concentrations in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the units having the highest observed mean concentrations. GM, geometric mean, in micrograms per liter; GD, geometric deviation; Range, range of concentrations observed in eight samples.

GEOCHEMICAL SURVEY OF MISSOURI

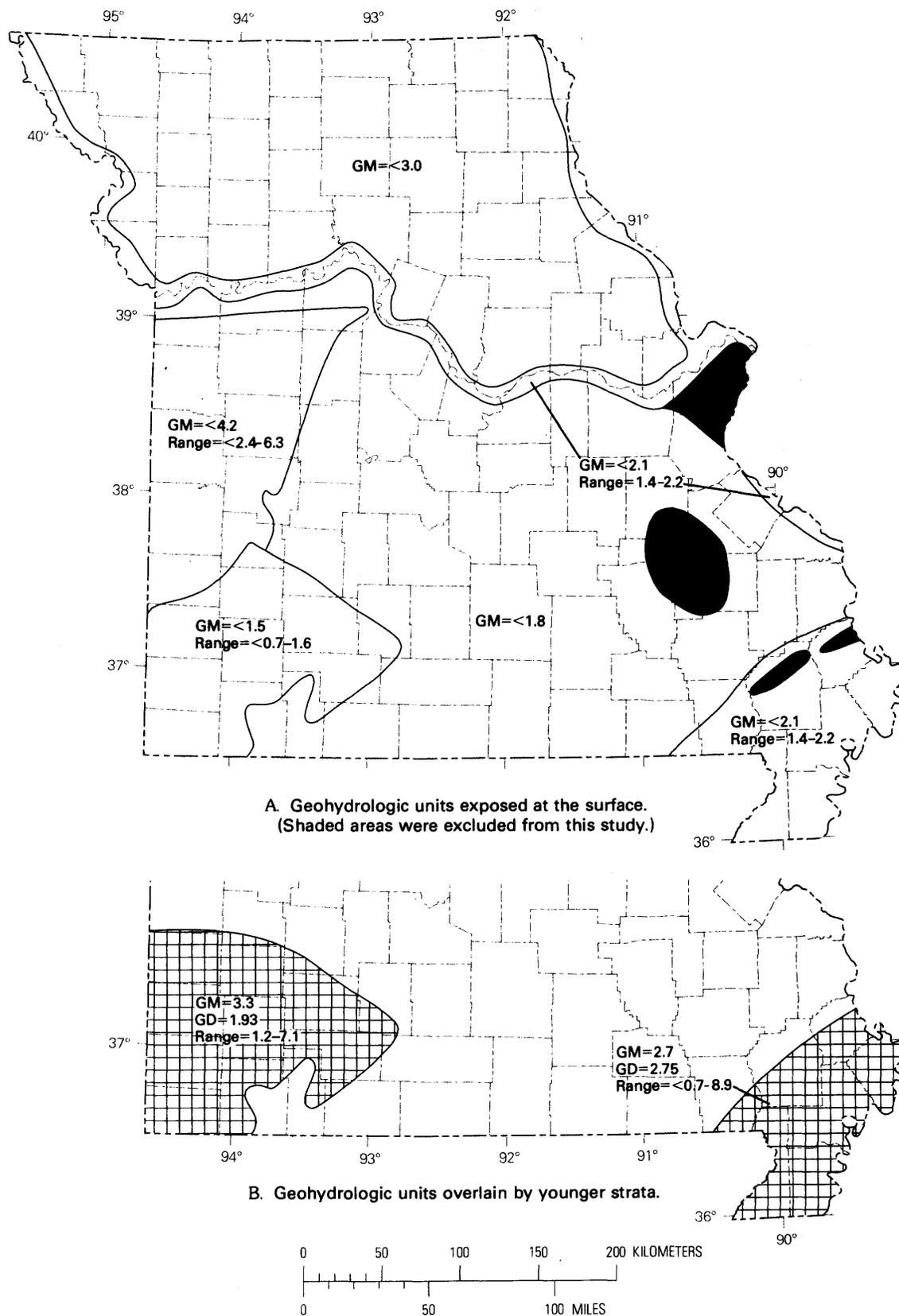


FIGURE 36.—Gross alpha radioactivity in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the units having the highest observed mean radioactivity. GM, geometric mean, in picocuries per liter as uranium-natural; GD, geometric deviation; Range, range of radioactivity observed in eight samples.

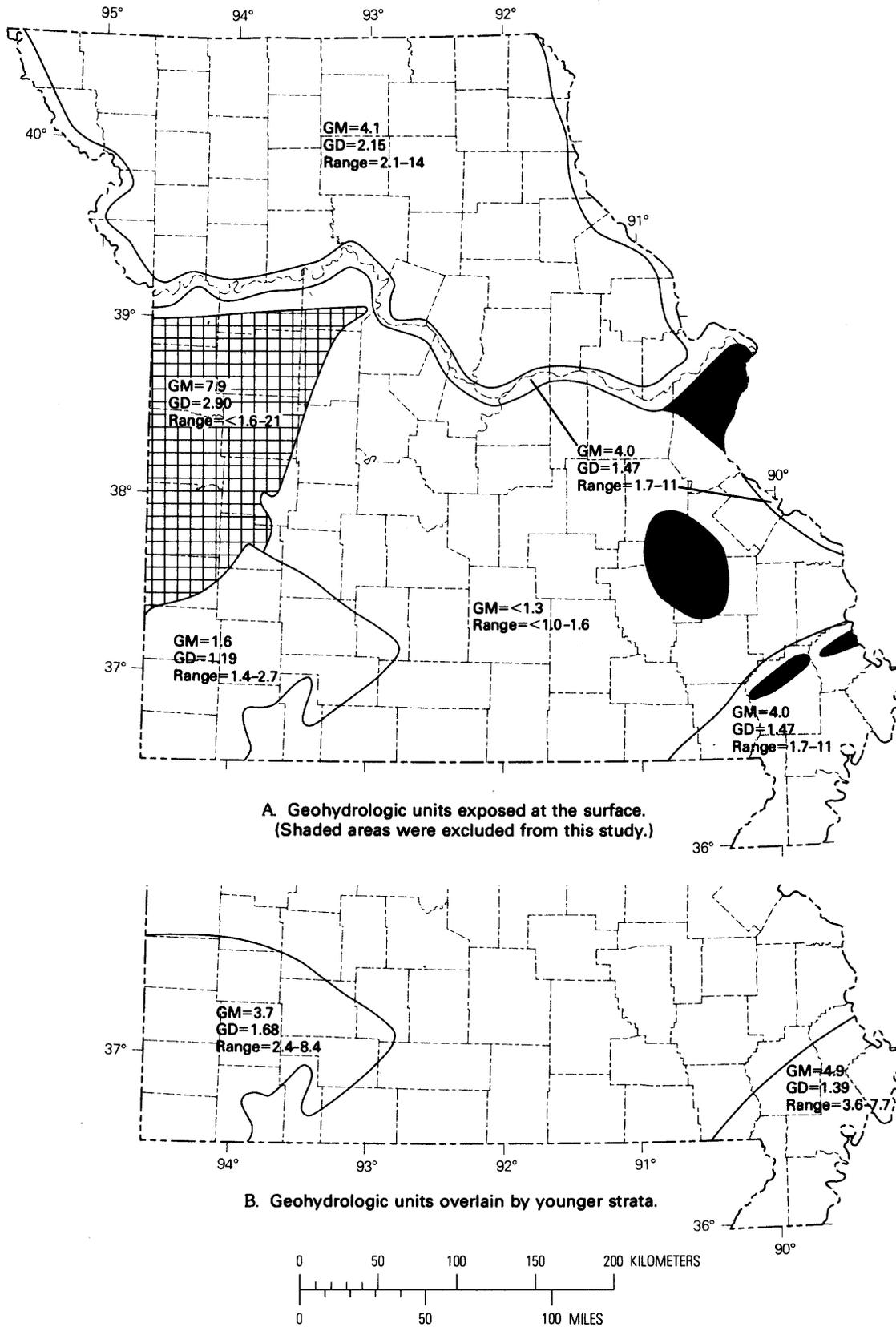


FIGURE 37.—Gross beta radioactivity in ground waters from seven geohydrologic units in Missouri. Crosshatched pattern shows the unit having the highest observed mean radioactivity. GM, geometric mean, in picocuries per liter as cesium-137; GD, geometric deviation; Range, range of radioactivity observed in eight samples.

GEOCHEMICAL SURVEY OF MISSOURI

TABLE 4.—Summary of analytical data on ground

[GM, geometric mean; GD, geometric deviation; Ratio, detection ratio=(number of

Variable	Quaternary alluvium			Glacial Deposits			Strata of Cretaceous and Tertiary age		
	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio
Miscellaneous									
Temperature at time of collection (°C)---	15.4	1.12	5:5	12.7	1.00	5:5	20.9	1.37	5:5
Dissolved solids calculated (mg/L)----	310	1.39	5:5	480	1.94	5:5	230	1.78	5:5
Hardness (Ca, Mg), as CaCO ₃ (mg/L)-----	210	1.32	5:5	290	1.43	5:5	51	5.61	5:5
Noncarbonate hardness (mg/L)-----	<8.2	----	4:5	44	2.90	5:5	<2.0	----	1:5
Specific conductance, laboratory (µmho/cm at 25°C)-----	470	1.46	5:5	740	1.88	5:5	400	1.80	5:5
Specific conductance at time of collection (µmho/cm at 25°C)---	560	1.38	5:5	960	2.18	5:5	500	1.85	5:5
pH-----	7.6	7.3	5:5	7.1	7.3	5:5	7.5	7.8	5:5
Chemical									
SiO ₂ (mg/L)-----	24	1.38	5:5	28	1.36	5:5	14	1.37	5:5
Fe (µg/L)-----	2600	2.49	5:5	5300	4.30	5:5	530	9.67	5:5
Mn (µg/L)-----	490	1.72	5:5	470	4.77	5:5	86	5.80	4:5
Ca (mg/L)-----	63	1.30	5:5	89	1.27	5:5	15	5.70	5:5
Mg (mg/L)-----	13	1.47	5:5	15	2.23	5:5	3.4	6.00	5:5
Na (mg/L)-----	18	2.05	5:5	31	4.37	5:5	33	3.07	5:5
K (mg/L)-----	3.2	1.51	5:5	2.2	2.25	5:5	2.4	2.00	5:5
HCO ₃ (mg/L)-----	230	1.36	5:5	290	1.30	5:5	210	1.80	5:5
Sulfide (mg/L)-----	.090	2.10	2:5	.090	2.10	2:5	<.10	----	0:5
SO ₄ (mg/L)-----	39	2.42	5:5	90	3.01	5:5	7.7	3.95	5:5
Cl (mg/L)-----	12	1.89	5:5	16	5.97	5:5	11	4.90	5:5
F (mg/L)-----	.14	2.00	3:5	.14	1.56	4:5	.17	1.92	4:5
Br (mg/L)-----	.072	2.42	5:5	.18	2.48	5:5	.10	3.53	5:5
I (mg/L)-----	.0052	3.69	4:5	.014	2.72	5:5	.0046	2.79	5:5
Organic N (mg/L), as N-NO ₂ (mg/L)-----	.059	4.96	4:5	.29	8.43	5:5	.0033	17.0	3:5
NO ₂ (mg/L), as N-----	<.012	----	2:5	.012	3.86	3:5	<.01	----	1:5
NH ₃ (mg/L), as N-----	.073	5.01	4:5	.34	7.83	5:5	.076	6.23	4:5
NO ₃ (mg/L)-----	.17	2.20	4:5	.39	1.81	5:5	.19	2.44	4:5
PO ₄ (mg/L), as PO ₄ -----	.062	3.49	4:5	.021	6.34	3:5	<.042	----	3:5
Total P (mg/L), as P-----	.033	2.34	4:5	.054	1.53	5:5	.018	3.63	3:5
Cd (µg/L)-----	1.8	1.56	4:5	<1.4	----	4:5	<1.1	----	1:5
Zn (µg/L)-----	12	1.58	4:5	<16	----	4:5	14	2.64	3:5
Spectrographic									
Al (µg/L)-----	11	1.75	5:5	15	1.54	5:5	12	1.43	5:5
Ba (µg/L)-----	540	1.31	5:5	200	3.34	5:5	100	4.74	5:5
B (µg/L)-----	49	2.02	5:5	70	3.70	5:5	34	3.01	5:5
Cu (µg/L)-----	<1.3	----	3:5	<2.2	----	0:5	<1.1	----	3:5
Pb (µg/L)-----	<3.5	----	1:5	<5.7	----	0:5	<2.8	----	2:5
Li (µg/L)-----	5.6	3.60	5:5	12	2.05	5:5	2.0	31.2	4:5
Mo (µg/L)-----	<1.8	----	1:5	<2.7	----	1:5	<1.6	----	1:5
Ni (µg/L)-----	<4.7	----	3:5	<8.6	----	3:5	<3.4	----	2:5
Rb (µg/L)-----	<2.6	----	2:5	<3.9	----	0:5	5.1	2.52	4:5
Sr (µg/L)-----	240	1.83	5:5	460	2.17	5:5	130	6.62	5:5
Radio--									
Gross alpha (µg/L as U-nat)-----	<6.4	----	2:5	<8.9	----	0:5	8.2	2.75	3:4
Gross alpha (pCi/L as U-nat)-----	<2.1	----	2:5	<3.0	----	0:5	2.7	2.75	3:4
Gross beta (pCi/L as Sr-90/Y-90)-----	3.3	1.45	5:5	3.4	2.10	5:5	4.0	1.38	4:4
Gross beta (pCi/L as Cs-137)-----	4.0	1.47	5:5	4.1	2.15	5:5	4.9	1.39	4:4

¹Arithmetic mean.

²Standard deviation.

GEOCHEMICAL SURVEY OF WATERS OF MISSOURI

E47

waters from seven geohydrologic units in Missouri

samples in which variable could be measured) : (total number of samples analyzed)]

Strata of Pennsylvanian age			Strata of Mississippian age			Strata of Cambrian and Ordovician age (SW Missouri)			Strata of Cambrian and Ordovician age (SE Missouri)		
GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio
determinations											
15.5	1.16	5:5	14.4	1.00	5:5	18.6	1.01	5:5	14.6	1.00	5:5
640	1.49	5:5	210	1.54	5:5	250	1.54	5:5	250	1.14	5:5
97	2.30	5:5	170	1.54	5:5	210	1.39	5:5	250	1.15	5:5
<1.6	----	1:5	13	3.04	3:5	13	4.10	5:5	<1.4	----	1:5
1000	1.52	5:5	360	1.51	5:5	420	1.57	5:5	460	1.13	5:5
1300	1.60	5:5	400	1.48	5:5	470	1.48	5:5	520	1.14	5:5
17.8	1.6	5:5	17.3	1.4	5:5	17.6	1.2	5:5	17.5	1.1	5:5
determinations											
12	1.81	5:5	9.7	1.14	5:5	8.7	1.09	5:5	8.8	1.03	5:5
320	5.39	5:5	100	7.67	5:5	6.0	10.7	2:5	<11	----	1:5
<27	----	3:5	6.4	6.49	2:5	<16	----	1:5	<10	----	0:5
21	2.45	5:5	59	1.65	5:5	51	1.50	5:5	51	1.18	5:5
9.9	2.16	5:5	3.1	2.78	5:5	19	1.33	5:5	29	1.14	5:5
160	3.20	5:5	5.5	2.28	5:5	8.7	2.87	5:5	1.9	1.65	5:5
6.6	2.16	5:5	.75	1.64	5:5	2.1	1.94	5:5	.67	1.40	5:5
420	1.41	5:5	190	1.46	5:5	230	1.34	5:5	310	1.14	5:5
<.16	----	1:5	<.11	----	1:5	.14	5.04	3:5	<.1	----	0:4
6.3	6.16	5:5	3.5	14.7	4:5	28	2.34	5:5	.18	22.4	3:5
75	5.27	5:5	6.6	2.00	5:5	9.7	2.98	5:5	<.10	----	0:5
1.5	2.49	5:5	<.11	----	----	<.15	----	4:5	<.10	----	0:5
.25	4.12	5:5	.054	2.49	5:5	.072	1.28	5:5	.019	1.36	5:5
.015	2.38	5:5	.002	4.27	2:5	.0096	2.25	5:5	<.0022	----	1:5
.15	2.83	5:5	.098	3.66	5:5	.033	4.65	4:5	.021	3.20	4:5
.0074	6.98	2:5	.0074	4.25	2:5	.0085	2.76	2:5	<.011	----	1:5
.21	1.83	5:5	<.011	----	1:5	.062	2.41	5:5	<.01	----	0:5
<.12	----	2:5	2.4	12.5	4:5	.26	44.4	3:5	3.4	2.78	5:5
<.016	----	1:5	.0066	7.98	2:5	.0073	5.90	2:5	<.01	----	0:5
<.014	----	1:5	.012	3.46	3:5	<.012	----	1:5	<.015	----	2:5
<1.1	----	1:5	<1.1	----	1:5	<1.0	----	0:5	<1.0	----	0:5
<16	---	4:5	<28	---	2:5	14	2.00	3:5	75	2.87	5:5
determinations											
23	1.40	5:5	11	1.43	5:5	10	1.20	5:5	11	1.54	5:5
140	2.20	5:5	53	1.18	5:5	51	2.21	5:5	43	1.27	5:5
200	3.46	5:5	11	1.49	5:5	26	2.12	5:5	11	1.30	5:5
<3.7	----	1:5	<1.6	----	2:5	.64	1.44	3:5	2.4	1.74	3:5
<7.3	----	0:5	<2.2	----	2:5	<2.6	----	0:5	<2.6	----	0:5
68	2.02	5:5	1.6	5.83	5:5	11	2.73	5:5	.66	5.94	3:5
<3.6	----	0:5	<.88	----	0:5	3.2	2.05	4:5	<2.0	----	0:5
<8.0	----	1:5	<3.3	----	2:5	<3.0	----	0:5	<5.6	----	1:5
7.8	2.13	4:5	<1.6	----	1:5	<2.1	----	4:5	<2.2	----	0:5
670	2.45	5:5	71	1.94	5:5	130	2.50	5:5	46	1.22	5:5
activity											
<13	----	1:5	<4.5	----	1:5	9.9	1.92	5:5	<5.5	----	0:5
<4.2	----	1:5	<1.5	----	1:5	3.3	1.93	5:5	<1.8	----	0:5
6.5	2.91	4:5	1.4	1.14	4:5	3.0	1.69	5:5	<1.2	----	1:5
7.9	2.90	4:5	1.6	1.19	4:5	3.7	1.68	5:5	<1.3	----	1:5

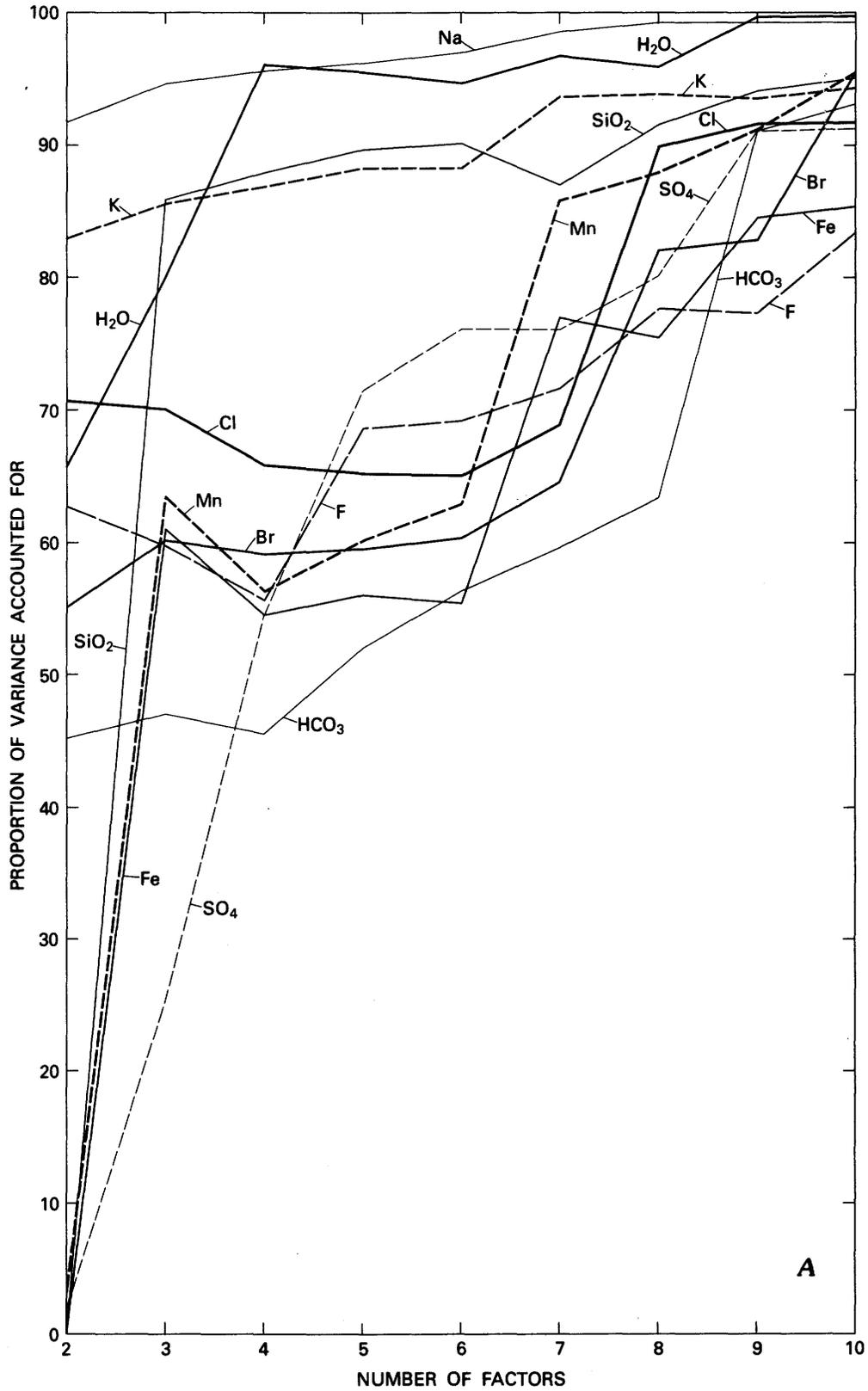


FIGURE 38.—Factor-variance diagram for ground waters of Missouri.

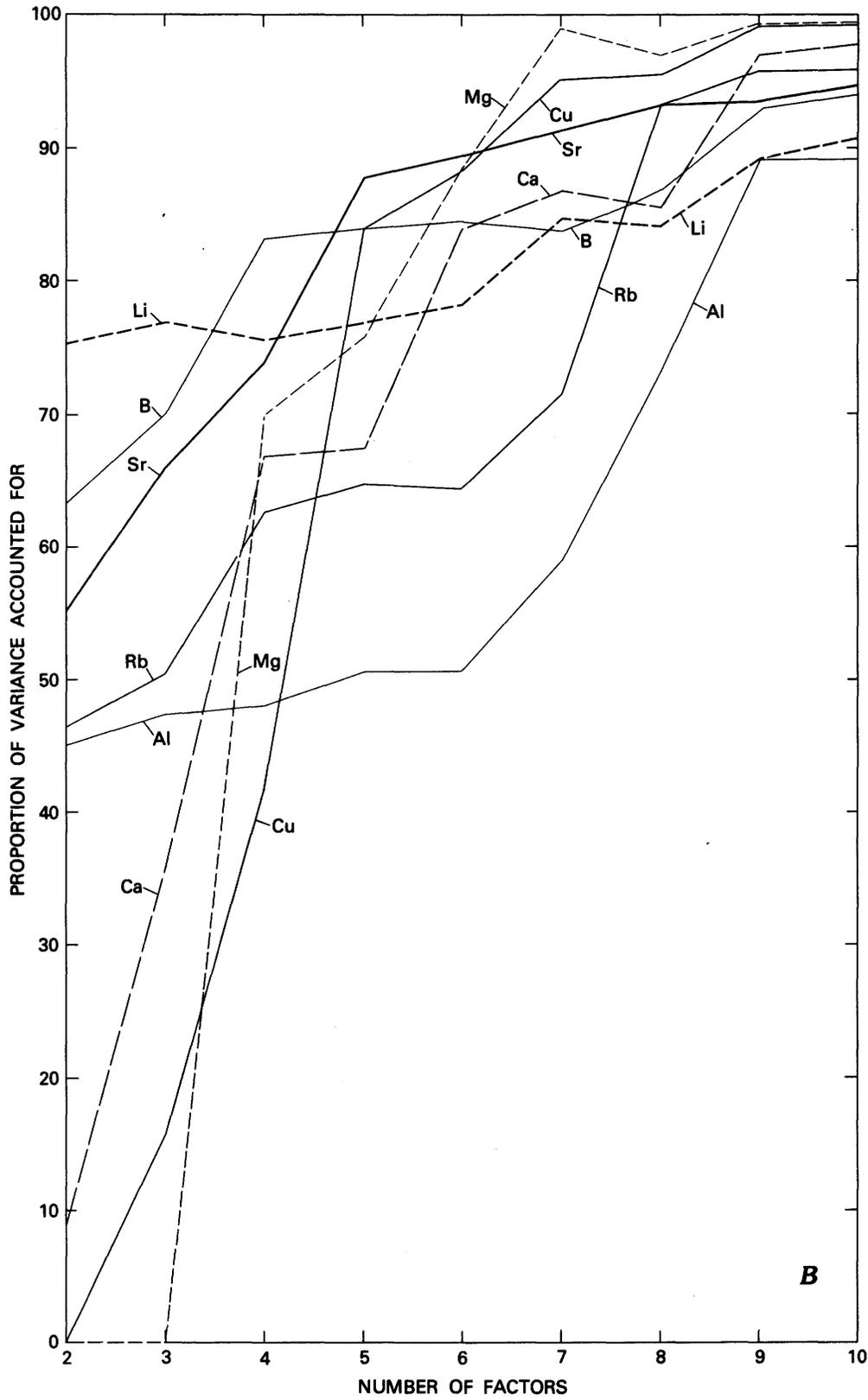


FIGURE 38.—Continued.

analysis was performed on the scaled data and the derived factor model was transformed back to units of parts per million by means of the constant sum (10^6).

One sample, from the glacial drift geohydrologic unit, was found in the initial factor analysis to be an outlier anomalous with respect to the others and was not used.

This sample came from an area of probable ground-water contamination, as evidenced by high ammonia and organic nitrogen contents (NH_3 (as N), 8.7 mg/L, organic N (as N), 12 mg/L).

Although the factor-variance diagrams indicate that the compositions of all but one (see above) of the ground-water samples can be approximated by mixtures of four end members, they give no indication of the chemical natures of the end members. By convention, the samples can be regarded as being represented by vectors within a four-dimensional vector system. The angle between any two vectors is related inversely to the overall compositional similarity between the samples they represent. The end-member compositions can be represented by any four sample vectors or any four hypothetical vectors. The purpose here is merely to summarize the multivariate chemical data and not to develop an actual mixing model. Consequently, the end-member vectors were taken as the four-varimax axes. These reference vectors (axes) have the property of being orthogonal to each other and, therefore, represent four water compositions that are as divergent from each other as possible. The four end-member compositions (composition scores) are given in table 5; some of the composition scores are negative but, inasmuch as the scores are used only to summarize the compositional natures of the samples, they suffice.

TABLE 5.—Composition scores for the varimax axes, F_{ej}

Variable, j	End member, k			
	I	II	III	IV
Al-----	0.011	0.032	0.016	0.006
B-----	-.042	.475	.002	.015
Cu-----	.004	.002	.000	.000
Li-----	-.001	.144	-.013	.003
Rb-----	-.003	.017	-.005	.006
Sr-----	-.061	1.513	.345	-.003
Ca-----	79.921	-8.410	150.445	-3.100
Mg-----	52.567	7.708	9.151	-12.362
Na-----	-54.328	399.709	-16.490	14.064
K-----	-.653	13.386	1.784	1.408
Fe-----	-5.792	-1.497	20.552	-1.888
Mn-----	-.428	-.235	2.302	-.135
SiO_2 -----	-7.590	4.657	64.023	6.839
HCO_3 -----	372.175	627.610	281.962	24.593
SO_4 -----	9.400	27.851	149.180	-28.692
Cl-----	-9.437	255.216	8.818	-16.740
F-----	-.097	2.964	-.322	.063
Br-----	-.105	.769	.209	.033
H_2O -----	999564	998668	999328	1000015

The composition loadings for each sample are given in table 6 and show the degree of similarity between the sample and the respective end-member composition of table 5. Each of the water-sample compositions can be approximated by mixing the four end-member compositions in the proportions indicated by the composition loadings. The degree of approximation is as indicated by the factor-variance diagrams in figure 38, A and B. In situations where a sample has a high loading on one of the end members, that sample tends to contain high concentrations of those constituents for which the score values are high, and low concentrations of those constituents for which the composition score values are low or negative.

Perusal of the scores (table 5) suggests the chemical character of the respective end members (axes). The highest positive scores for axis I indicate a Ca, Mg, HCO_3 water with relatively high Cu compared to other end members. The second appears to be a Na, HCO_3 , Cl water with high K, Li, Al, B, Rb, Sr, F, and Br; and the third a Ca, HCO_3 , SO_4 water with SiO_2 , Fe, and Mn. The

TABLE 6.—Composition loadings (a_{ik}) on the varimax axes for four-factor model

Sample No., i	Geohydrologic unit	End member, k			
		I	II	III	IV
71 1512	Quaternary alluvium-----	0.24	0.11	0.40	0.26
71 1483	-----do-----	.21	.10	.28	.41
71 1672	-----do-----	.31	.21	.32	.16
71 1791	-----do-----	.25	.08	.43	.24
71 1892	-----do-----	.16	.04	.29	.50
71 1326	Glacial deposits-----	.37	.18	.48	-.02
71 1508	-----do-----	.25	.11	.39	.24
71 1674	-----do-----	.24	.07	.39	.29
71 1887	-----do-----	.04	.04	.57	.35
71 1309	Cretaceous and Tertiary strata.	.24	.06	.20	.50
71 1310	-----do-----	.09	.33	.17	.41
71 1484	-----do-----	.08	.13	.07	.72
71 1591	-----do-----	.22	.25	.13	.40
71 1794	-----do-----	.25	.04	.27	.43
71 1324	Pennsylvanian strata----	.03	.82	.07	.08
71 1386	-----do-----	.15	.66	.04	.15
71 1481	-----do-----	.13	.59	.10	.18
71 1511	-----do-----	.24	.09	.41	.26
71 1890	-----do-----	.16	.68	.13	.03
71 1307	Mississippian strata----	.37	.03	.14	.46
71 1510	-----do-----	.32	.06	.12	.50
71 1793	-----do-----	.23	.01	.16	.60
71 1850	-----do-----	.31	.11	.26	.32
71 1888	-----do-----	.21	.00	.12	.67
71 1509	Cambrian and Ordovician strata (southwest Missouri).	.36	.03	.12	.48
71 1593	-----do-----	.38	.07	.17	.37
71 1596	-----do-----	.31	.04	.12	.52
71 1597	-----do-----	.37	.08	.17	.37
71 1847	-----do-----	.43	.24	.21	.12
71 1323	Cambrian and Ordovician strata (southeast Missouri).	.56	.06	.13	.25
71 1482	-----do-----	.59	.08	.14	.18
71 1679	-----do-----	.71	.07	.12	.10
71 1844	-----do-----	.43	.04	.13	.39
71 1849	-----do-----	.49	.03	.15	.32

scores for the fourth end member tend to be generally low in absolute value, except for H_2O , indicating an end member more chemically pure than the first three.

The composition loadings can be used to construct maps that show the regional variability in the general geochemical characteristics of the ground waters (figs. 39–42). Each map shows the loadings for all the samples with respect to one of the theoretical end members. The factor loadings are given to one decimal place on the maps. Those samples represented by the highest values on the map are compositionally most similar to the respective theoretical end member.

Most of the samples with high loadings on the first end member (fig. 39) are from the dolomite of the Cambrian and Ordovician (southeastern Missouri) geohydrologic unit, as is to be expected for Ca, Mg, HCO_3 water. The relatively high Cu concentrations of waters in this geohydrologic unit probably reflect the widespread mineralization of the rapidly circulating oxygenated ground waters. Samples with high loadings on the second end member (fig. 40) were collected from the Pennsylvanian unit and are relatively rich in NaCl and most of the trace elements. The high concentrations of trace elements are probably due to the abundance of trace-element-rich shales and coals in this aquifer (Feder and others, 1972). However, it is noteworthy that despite the high concentrations of many trace metals in the shales, including Fe, Zn, Mo, Pb, Cu, and Hg, they are present in relatively low concentrations in the ground water. Presumably, this is due to the presence of H_2S , and the low solubilities of the metal sulfides in equilibrium with H_2S . The one sample from the Pennsylvanian geohydrologic unit that does not have a high loading on this end member (sample 1511) was obtained from a spring flowing out of a large channel-sandstone deposit. Samples with high loadings on the third member (fig. 41) were collected from the glacial deposits and Quaternary alluvium units.

Samples with high loadings on the fourth end member (fig. 42) are from different geohydrologic units, and the relatively low dissolved solids content of the end member suggests that the samples with high loadings reflect simple dilution either as a result of precipitation or some membrane processes. For example, samples 1510, 1888, and 1979, which have high loadings on the fourth end member, are all from springs or wells in the Mississippian geohydrologic unit and, characteristically, ground water in this geohydrologic unit may contain a high proportion of recently recharged water derived from local precipitation (Feder and others, 1969). The sample with the highest loading on this end member is from a deep well in the Cretaceous and Tertiary geohydrologic unit. The ground water from this well contains a much lower dissolved solids content than ground water from the same formations at shallower depths. The lower dis-

solved solids in water from this well cannot be ascribed to dilution resulting from infiltration of local precipitation, but rather is interpreted as having resulted from membrane processes at depth as discussed by Hanshaw and Coplen (1973).

COMPOSITION OF MINE WATERS

Within the ground-water sampling program, areas within geohydrologic units believed to have unusual ground-water chemistry (for example, mineralized or polluted areas) were not sampled because the emphasis of the program was to describe the chemistry of the "normal" ground water in the units. Wherever these unusual areas were selected in the random selection process, they were rejected and alternative areas were selected by the same process. As a followup to this program, two areas of suspected anomalous ground-water chemistry were sampled.

The first area sampled was the New Lead Belt, which lies in the Cambrian and Ordovician geohydrologic unit in southeastern Missouri. Ground-water samples were collected from flowing drill holes at the faces of new underground mine workings. The samples were believed to have been uncontaminated by mine operations. A single filtered ($0.45 \mu m$) sample was collected at each of two mines.

The second area sampled was the Joplin Lead-Zinc District in the Mississippian geohydrologic unit. This area is no longer actively mined, but water is still being pumped for industrial use from some of the abandoned mines. One sample was collected from the discharge of one such pump, and the other sample was collected from a continuous flow from a mine shaft. Both samples were filtered through a $0.45\text{-}\mu m$ membrane filter.

The analyses of these four samples are listed in table 7. In order to assess just how anomalous these waters may be, any observed value that lies outside the effective range of values for "normal" ground water from the respective geohydrologic units is tagged with an H (higher than the upper limit of the expected range) or with an L (lower than the lower limit of the expected range). The expected range is from GM/GD^2 to $GM \times GD^2$, where the values of GM and GD are from table 4; the expected range is estimated to include the concentrations in 95 percent of the normal ground waters of the geohydrologic unit. In situations where GM and GD could not be estimated, a concentration in mine water was judged to be anomalously high if the value was 10 or more times greater than the geometric mean in "normal" water. Such values are tagged with an (H) in table 7.

The ground-water samples from mines in the Joplin area are distinctly different from the "normal" ground water of the Mississippian geohydrologic unit. The "nor-

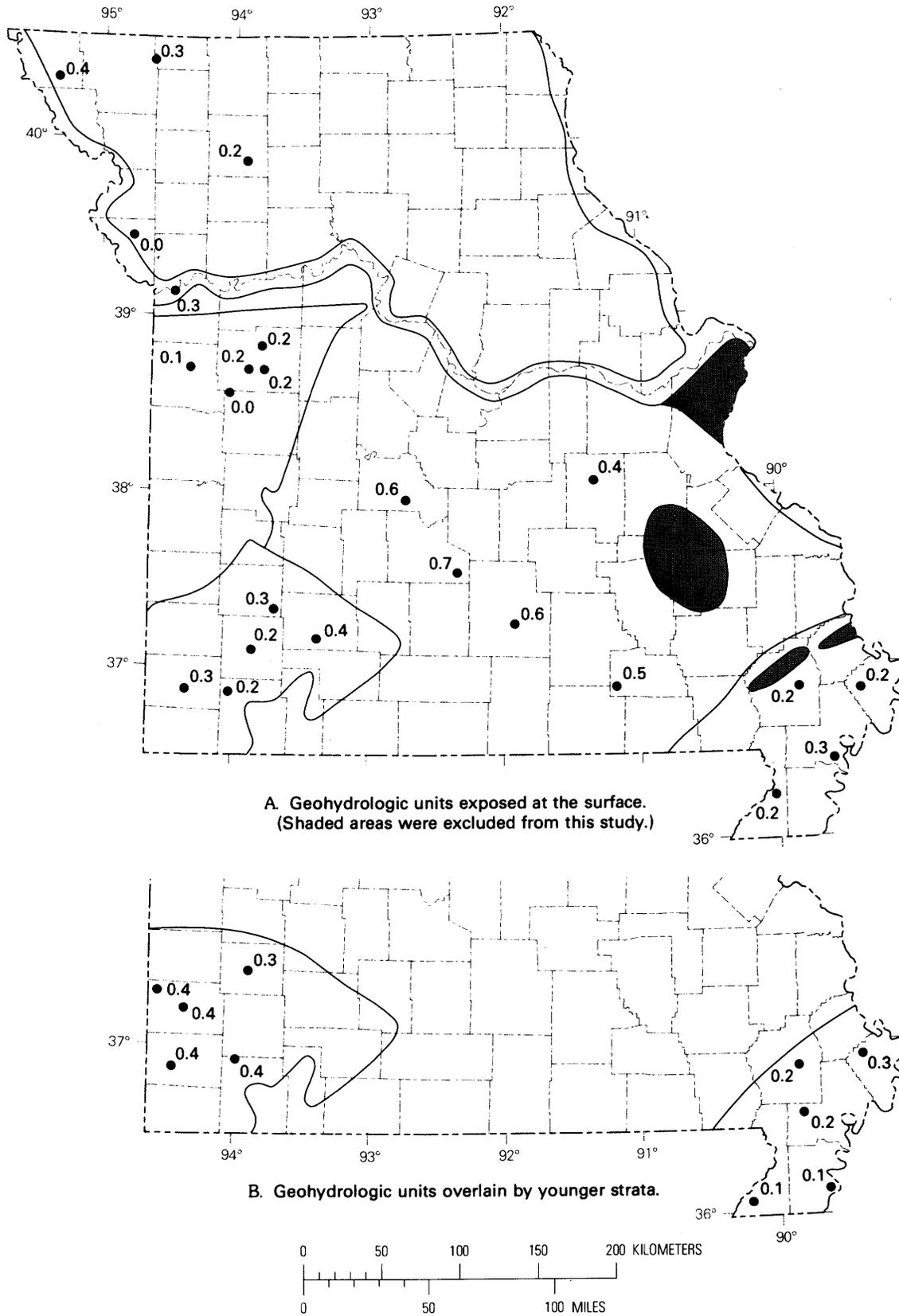


FIGURE 39.—Geographic variation in the composition loadings on end-member I.

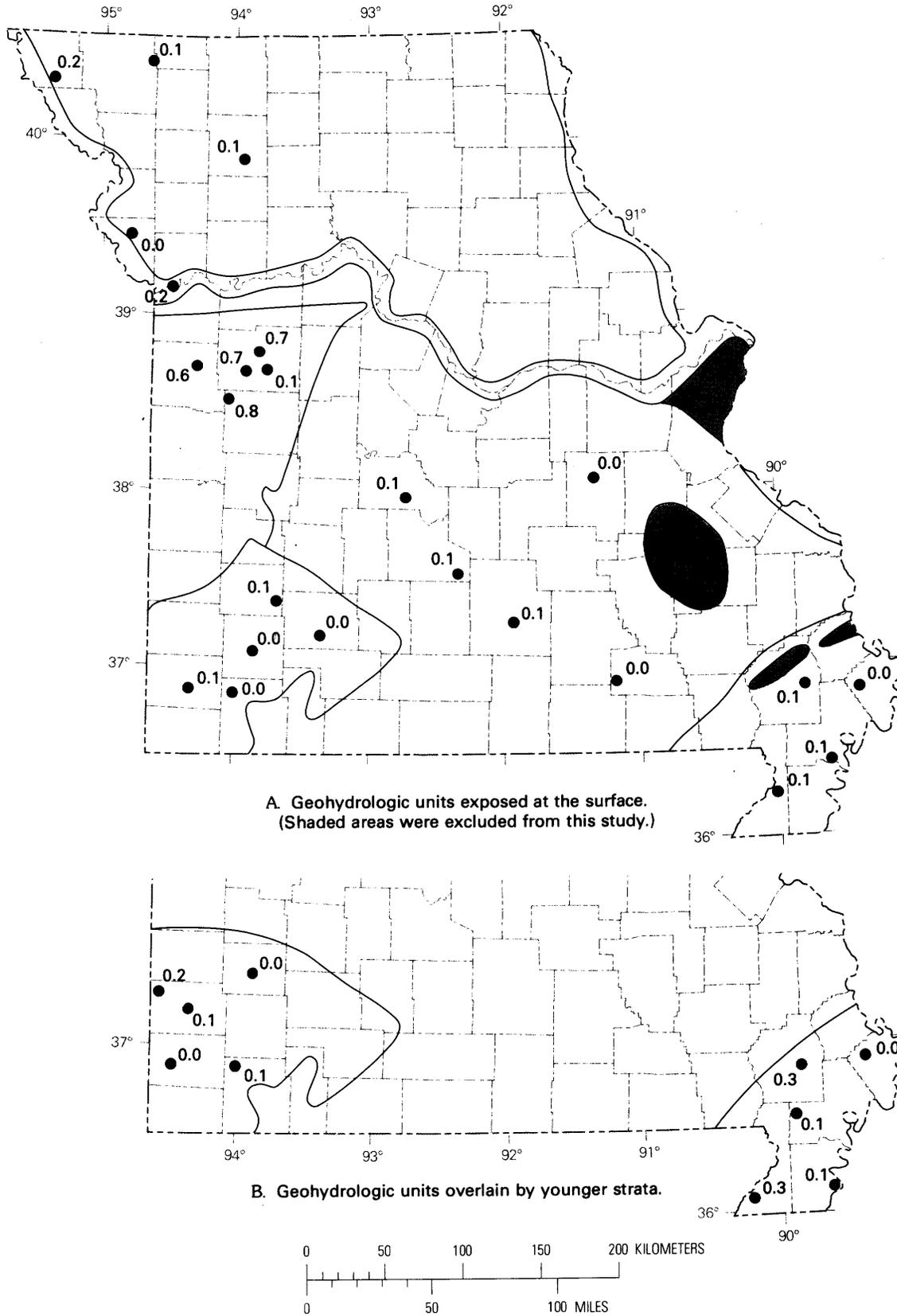


FIGURE 40.—Geographic variation in the composition loadings on end-member II.

GEOCHEMICAL SURVEY OF MISSOURI

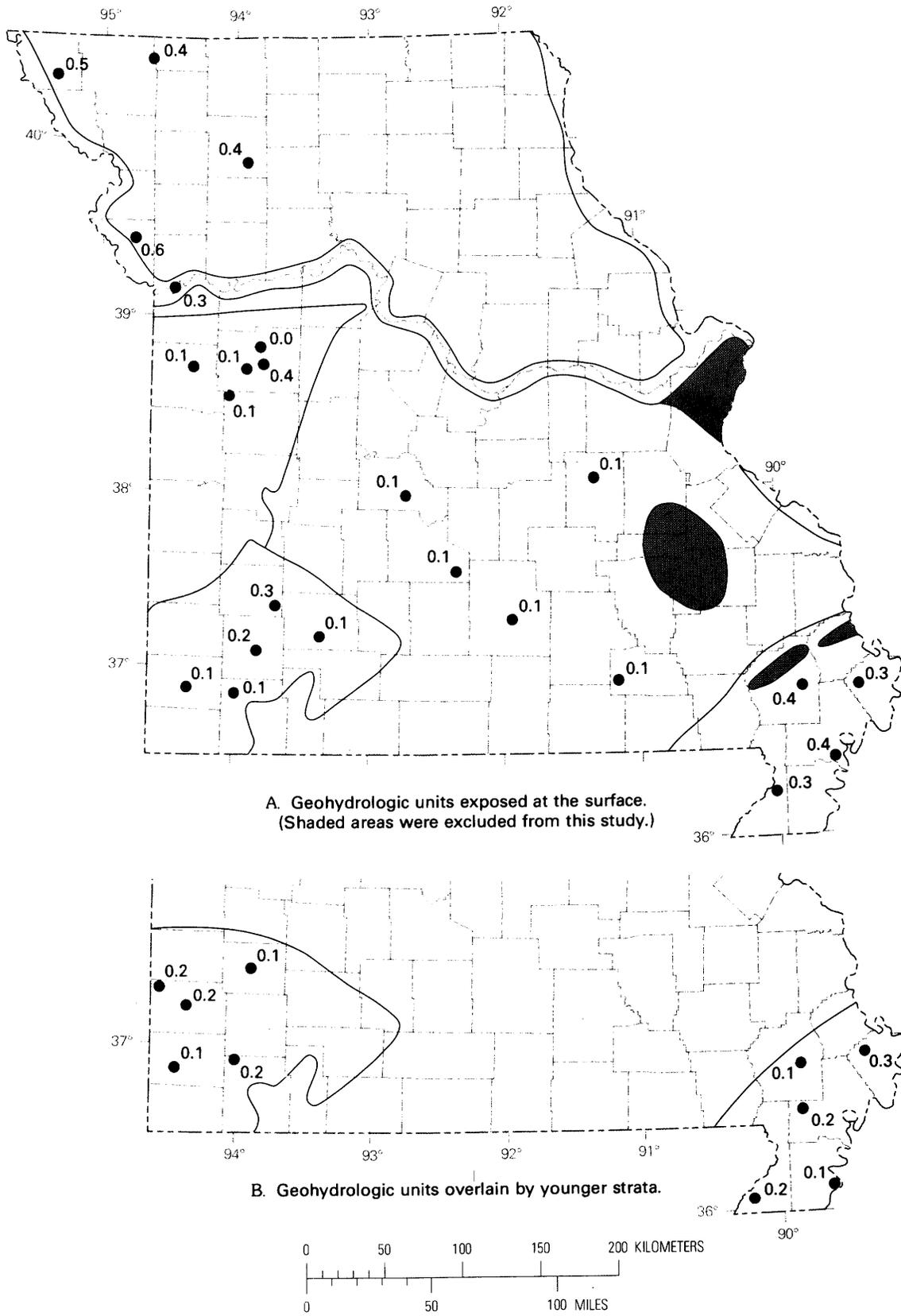


FIGURE 41.—Geographic variation in the composition loadings on end-member III.

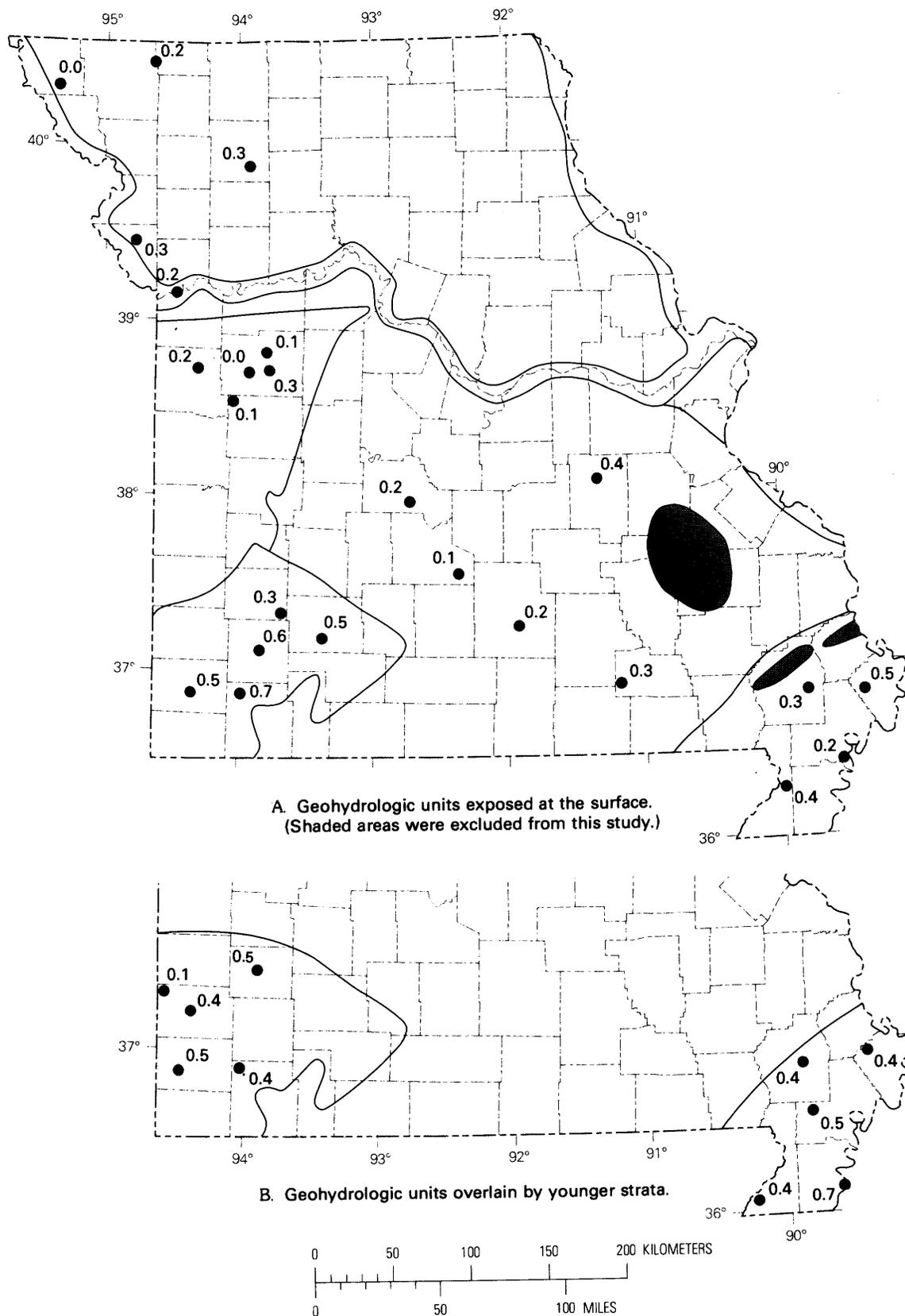


FIGURE 42.—Geographic variation in the composition loadings on end-member IV.

TABLE 7.—Ground-water analyses from two mining areas in southern Missouri

[H, analytical value exceeds estimated upper limit of 95-percent range of constituent in "normal" water; L, analytical value exceeds estimated lower limit of 95-percent range of constituent in "normal" water; (H), 95-percent range not estimated but analytical value is 10 times or more greater than geometric mean in "normal" water]

Constituent	Geohydrologic unit and sample location			
	Strata of Mississippian age		Strata of Cambrian and Ordovician age (southeast Missouri)	
	Joplin area No. 1	Joplin area No. 2	New Lead belt No. 1	New Lead belt No. 2
Al ($\mu\text{g/L}$)-----	180 H	160 H	30 H	35 H
Ba ($\mu\text{g/L}$)-----	<60	<35 L	<10 L	<10 L
B ($\mu\text{g/L}$)-----	<25	19	65	50
Cd ($\mu\text{g/L}$)-----	35 (H)	3	<1	<1
Cr ($\mu\text{g/L}$)-----	<30	<17	<5	<5
Co ($\mu\text{g/L}$)-----	<20	<12	<4	<4
Cu ($\mu\text{g/L}$)-----	12	2	1	4
Fe ($\mu\text{g/L}$)-----	50	20	<10	20
Pb ($\mu\text{g/L}$)-----	11	1	44 (H)	3
Li ($\mu\text{g/L}$)-----	10	20	10	<10
Mn ($\mu\text{g/L}$)-----	120	<10	<10	<10
Mo ($\mu\text{g/L}$)-----	<9	<6	4	2
Ni ($\mu\text{g/L}$)-----	50 (H)	30	<5	<5
Sr ($\mu\text{g/L}$)-----	100	110	200 H	120 H
Zn ($\mu\text{g/L}$)-----	13,000 (H)	2,800 (H)	20	<10
Hg ($\mu\text{g/L}$)-----	.7	.5	<.5	<.5
Se ($\mu\text{g/L}$)-----	<1	<1	<1	<1
Br ($\mu\text{g/L}$)-----	51	63	26	9 L
I ($\mu\text{g/L}$)-----	10	14	3	4
F ($\mu\text{g/L}$)-----	1,200 (H)	400	700	300
Cl (mg/L)-----	76 H	12	7.4 (H)	1.4 (H)
SO ₄ (mg/L)-----	920 H	490	18	16
HCO ₃ (mg/L)-----	180	272	197	192
NO ₃ (mg/L)-----	.3	<.1 L	<.1 L	<.1 L
NO ₂ (mg/L)-----	<.1	<.1	<.1	<.1
NH ₄ (mg/L)-----	.04	.09	.02	.03
Organic N (mg/L)	.09	.01	.02	.03
P-total (mg/L)---	.02	.02	.02	.04
Ca (mg/L)-----	460 H	260 H	31 L	32 L
Mg (mg/L)-----	9.7	14	16 L	18 L
Na (mg/L)-----	7.8	12	17 H	6.5 H
K (mg/L)-----	1.6	1.8	3.9 H	2.5 H
SiO ₂ (mg/L)-----	11	9.6	9.0	8.5
pH (field)-----	7.09	7.10	7.92 H	7.83 H
Dissolved solids (mg/L)-----	1,580 H	934 H	200	179 L
Noncarbonate hardness (mg/L)	1,000 H	480 H	0	0
Total hardness (mg/L)-----	1,200 H	710 H	140	150
Gross alpha as U-nat. (pCi/L)	<21	22	7.2	9.1
Gross beta as Ca-137 (pCi/L)	5.6 H	2.7 H	4.7	3.6

mal" water is a calcium bicarbonate type and generally has the lowest trace-element content of any ground waters sampled. The mine waters, on the other hand, have high calcium and sulfate concentrations and high concentrations of several trace elements, including the highest values for Cd, Zn, and Ni encountered in the entire study. The reasons why the mine water in the Joplin area is of such poor quality are probably: (1) large amounts of iron sulfide are present in the mineral deposits; (2) the mining was near the surface and attendant collapse resulted in good hydrologic connection between the surface and the mine workings; and (3) the extensive tailings piles that cover the mine areas contain appreciable amounts of sulfide minerals that are still being leached by well-oxygenated precipitation that drains through the tailings piles into the local ground water.

The calcium-magnesium-bicarbonate type ground water in the New Lead Belt has lower concentrations of these

constituents than "normal" for the geohydrologic unit. In general, the trace-element concentrations are considerably lower than those in mine water from the Joplin area, presumably because mines in the New Lead Belt are comparatively deep and the ground water is poorly oxygenated.

SURFACE WATER

METHODS OF INVESTIGATION

SAMPLING DESIGN

The surface-water part of the study was designed to describe the compositional variations in surface-water chemistry due to variations in geology. Only four of the seven geohydrologic units, which served as the basis for sampling ground waters, also were used for sampling surface waters. These are shown in figure 43. Two of the other three geohydrologic units occur entirely, or almost

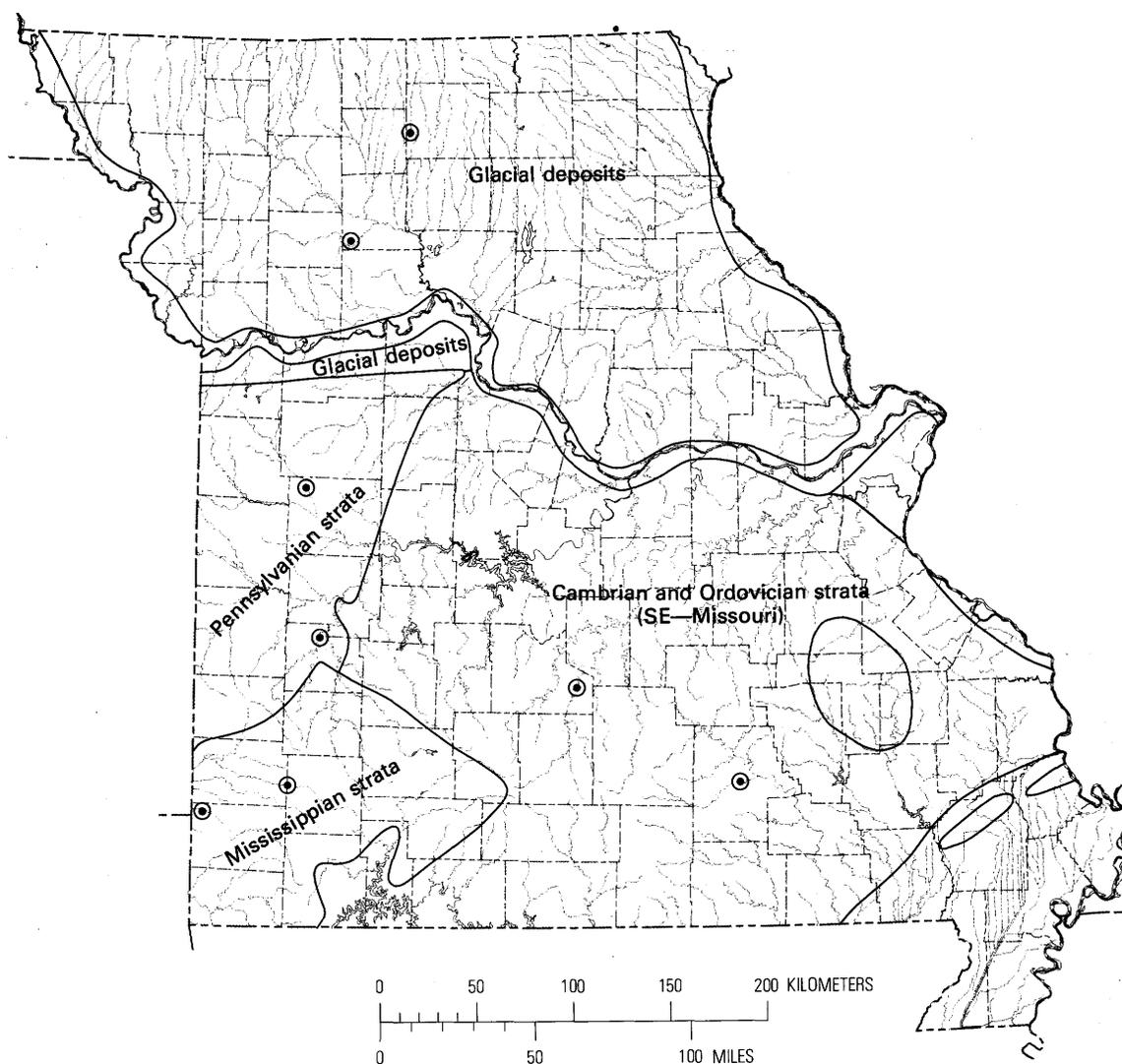


FIGURE 43.—Drainage map of Missouri showing units chosen for surface-water sampling and the locations of sampling sites (dots in circles).

entirely, in the subsurface; the remaining unit consists of the alluvium in the drainages of the Missouri and Mississippi Rivers.

Four criteria were established in selecting stream-sampling sites within the selected geohydrologic units—

1. The drainage basin within which the stream occurs should lie completely within one of the four geohydrologic units.
2. A continuous-recording gaging station should be located on the stream at or near the proposed sampling site.
3. The drainage area above the gage should be 250–1,300 km².
4. The stream should be relatively free of municipal and industrial effluents.

After identifying all streams meeting these criteria, two sampling sites were selected from each of the four geohydrologic units (fig. 43).

Each of the selected streams was sampled during a low-flow period in the fall and again during high flows in the spring. All low-flow samples were collected during the fall of 1972, and the high-flow samples were collected during runoff events in 1972 and 1973. The low-flow samples were collected to represent base-flow conditions when the major contribution to streamflow is from ground water. The sampling plan was designed to consider the possibility of significant changes in stream-water quality resulting from adsorption of trace elements on suspended sediments or removal of trace elements by aquatic organisms. An estimate of the effects of aquatic organisms on water quality was obtained by collecting predawn and late-afternoon samples at each low-flow sampling site. This was done to observe any differences in stream-water quality resulting from photosynthetic activity during the day (late-afternoon samples) and respiration during the night (predawn samples). In order to estimate the amounts of adsorption of trace elements on suspended sediments, filtered and unfiltered samples were collected during a single event consisting of a large rise in stream discharge following a spring rainfall.

The estimates of the effects on surface-water chemistry due to diel fluctuations in activity of aquatic organisms, high flow versus low flow, and variations between filtered and unfiltered water were obtained as differences in the chemistry of sampled sites. The geographic aspect of variation in water chemistry was determined by sampling in a standard (nested) analysis-of-variance design. This permitted the estimation of

$$s_x^2 = s_\alpha^2 + s_\beta^2, \quad (7)$$

where s_α^2 is a regional component of variance (between geohydrologic units) and s_β^2 is a component that includes both the local variance (between streams) and the "error" variance.

SAMPLING TECHNIQUES

The unfiltered low-flow samples were collected by immersing acid-washed polyethylene bottles in the center of the streams after rinsing them several times with the stream water. The filtered low-flow samples were collected by filling a Skougstad-type filter (Brown and others, 1970) with stream water and 1.4 kg/cm² nitrogen pressure from a pressure tank to force the water through a 0.1- μ m filter.

In order to sample during a stream-flow rise, most sites had to be visited during a rainfall event. The multiple-vertical depth-integrated (composite) stream-sampling method was abandoned in favor of a single depth-integrated sample from the center of the stream using a weighted 5-gal acid-washed polyethylene carboy. The composite sampling method was abandoned because of two reasons: The large number of stream-sampler fillings required to furnish sufficient water for laboratory analysis required too much time and there was danger of extending the sampling period into widely variable conditions. Another reason was the possibility of contamination of samples from precipitation during the numerous emptyings of the sampler bottles into the 5-gal carboy.

After filling the 5-gal carboy at the stream site, individual sample bottles for laboratory determinations were filled nearby in a covered area. The unfiltered samples were poured out of the carboy after giving it a vigorous shaking. The filtered samples were handled in the same way as the low-flow samples, except that a 1.2- μ m pre-filter was used in conjunction with the 0.1- μ m final filter.

The following samples were collected during each site visit:

- (1) one 2-L filtered acidified¹ for spectrographic analysis
- (2) one 2-L unfiltered acidified¹ for spectrographic analysis
- (3) one 2-L unfiltered unacidified for radiochemical analysis
- (4) two 1-L filtered acidified¹ for wet chemical analysis
- (5) one 1-L filtered unacidified for wet chemical analysis
- (6) two 1-L unfiltered acidified¹ for wet chemical analysis
- (7) one 1-L unfiltered unacidified for wet chemical analysis
- (8) one 1-L filtered acidified² for NO₃, NO₂, NH₃, organic N, PO₄
- (9) one 500-mL unfiltered acidified² for total P.

Samples for determination of the various forms of nitrogen and phosphorous were kept in an ice-filled cooler

¹ 1 mL/L of double-redistilled, reagent-grade concentrated HNO₃.

² 2 mL/L of 1N H₂SO₄.

and shipped by bus each week to the U.S. Geological Survey laboratory in Little Rock, Ark., where they were analyzed on the same day they were received.

ANALYTICAL PROCEDURES

In order to minimize changes due to shipping of certain chemical constituents, certain water-quality determinations were made at the sampling site. These determinations included pH, alkalinity, temperature, and dissolved oxygen. Dissolved oxygen was not determined during high-flow sampling because of intense rainfall. A description of the procedures for making these determinations is given in Skougstad and Feder (1976).

All laboratory determinations were made in U.S. Geological Survey laboratories according to methods listed in table 1. More detailed descriptions of laboratory analytical procedures are given in Miesch (1976). Table 2 lists those elements routinely looked for in spectrographic analysis but are rarely or never detected in evaporation residues of 0.1- μ m filtered waters. However, several of these elements are detected in unfiltered waters.

Analytical results for total determinations by the spectrographic method represent true totals. All other reported totals are for aliquots of unfiltered samples after 0.1N HCl-digestions for approximately 24 hr.

SURFACE-WATER RESULTS

Results of the analysis of variance to estimate the logarithmic variance components s_a^2 and s_b^2 and of their corresponding proportions of the total variance s_x^2 are given in table 8. Separate estimates were made on low-flow predawn and late afternoon samples, filtered and unfiltered low-flow samples for each of the above categories, and for filtered and unfiltered high-flow samples. These results show that Ca, I, Mg, Mn, Na, and Sr exhibit statistically significant regional variation (at the 95-percent confidence level) in either predawn or late afternoon (or both) low-flow samples, regardless of filtration treatment. In addition, Fe, SiO₂, total solids on evaporation, and Gross Alpha activity exhibit significant regional variation in either the predawn or late afternoon filtered samples. For the high-flow samples Ba, B, K, Mg, NO₃, SO₄, Na, Sr, and dissolved solids on evaporation exhibit significant regional variation in the filtered samples.

TABLE 8—Comparison of estimated logarithmic variance components for surface waters

[a.m., p.m. denote predawn and late-afternoon samples, respectively. *, denotes significantly greater than zero at the 0.05-probability level. I, insufficient data above detection level. ND, not determined]

Constituent	Flow	Filtration	Total log variance	Between geohydrologic units		Within geohydrologic units	
				Component	Percent	Component	Percent
					of total		of total
Aluminum (Al)	Low:						
	a.m.	Filtered	0.1696	0.1199	72	0.0497	28
	p.m.	Filtered	.2225	.0000	0	.2225	100
	a.m.	Raw	.4418	.2314	53	.2105	47
	p.m.	Raw	.3124	.0582	19	.2542	81
	High	Filtered	.0516	.0238	46	.0278	54
		Raw	.2651	.1455	55	.1196	45
Ammonia (NH ₃)	Low:						
	a.m.	Filtered	.0453	.0000	0	.0453	100
	p.m.	Filtered	.1138	.0000	0	.1138	100
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
	High	Filtered	I	----	--	----	---
	Raw	ND	----	--	----	---	
Arsenic (As)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
	High	Filtered	I	----	--	----	---
	Raw	.2610	.0000	0	.2610	100	
Barium (Ba)	Low:						
	a.m.	Filtered	.0614	.0125	20	.0489	80
	p.m.	Filtered	.0553	.0027	5	.0526	95
	a.m.	Raw	.0942	.0196	21	.0746	79
	p.m.	Raw	.0773	.0122	16	.0651	84
	High	Filtered	.0608	*.0475	78	.0133	22
		Raw	.2621	.1341	51	.1280	49

TABLE 8.—Comparison of estimated logarithmic variance components for surface waters—Continued

Constituent	Flow	Filtration	Total log variance	Between geohydrologic units		Within geohydrologic units	
				Component	Percent of total	Component	Percent of total
Bicarbonate (HCO ₃)	Low:						
	a.m.	Filtered	0.0099	0.0058	58	0.0041	42
	p.m.	Filtered	.0095	.0032	34	.0063	66
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
	High	Filtered	.1124	.0826	74	.0297	26
		Raw	ND	----	--	----	---
Boron (B)	Low:						
	a.m.	Filtered	.0947	.0581	61	.0366	39
	p.m.	Filtered	.0766	.0464	61	.0302	39
	a.m.	Raw	.1117	.0662	59	.0454	41
	p.m.	Raw	.1191	.0661	55	.0530	45
	High	Filtered	.0755	*.0594	79	.0161	21
		Raw	.1905	.0786	41	.1119	59
Bromine (Br)	Low:						
	a.m.	Filtered	.1218	.0328	27	.0889	73
	p.m.	Filtered	.3284	.1792	55	.1491	45
	a.m.	Raw	.2092	.1413	68	.0669	32
	p.m.	Raw	.3021	.0000	0	.3021	100
	High	Filtered	.1199	.0702	58	.0498	42
		Raw	.1761	.0000	0	.1761	100
Cadmium (Cd)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
	High	Filtered	I	----	--	----	---
		Raw	.1801	.1077	60	.0740	40
Calcium (Ca)	Low:						
	a.m.	Filtered	.0115	*.0094	82	.0021	18
	p.m.	Filtered	.0107	*.0082	77	.0025	23
	a.m.	Raw	.0105	*.0091	86	.0014	14
	p.m.	Raw	.0114	*.0091	79	.0024	21
	High	Filtered	.1416	.0909	64	.0507	36
		Raw	.1908	.0000	0	.1908	100
Chromium (Cr)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
	High	Filtered	I	----	--	----	---
		Raw	.2603	.1622	62	.0981	38
Chlorine (Cl)	Low:						
	a.m.	Filtered	.0548	.0235	43	.0313	57
	p.m.	Filtered	.0474	.0176	37	.0298	63
	a.m.	Raw	.0686	.0236	34	.0450	66
	p.m.	Raw	.0509	.0178	35	.0331	65
	High	Filtered	.1321	.0751	57	.0570	43
		Raw	ND	----	--	----	---
Cobalt (Co)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
	High	Filtered	I	----	--	----	---
		Raw	.3927	.1126	29	.2801	71
Copper (Cu)	Low:						
	a.m.	Filtered	.0576	.0337	59	.0238	41
	p.m.	Filtered	.0441	.0227	52	.0214	48
	a.m.	Raw	.0624	.0000	0	.0624	100
	p.m.	Raw	.0578	.0000	0	.0578	100
	High	Filtered	.0078	.0000	0	.0078	100
		Raw	.1708	.0232	14	.1476	86

TABLE 8.—Comparison of estimated logarithmic variance components for surface waters—Continued

Constituent	Flow	Filtration	Total log variance	Between geohydrologic units		Within geohydrologic units	
				Component	Percent of total	Component	Percent of total
Fluorine (F)	Low:						
	a.m.	Filtered	0.0598	0.0200	33	0.0398	67
	p.m.	Filtered	.0664	.0379	57	.0285	43
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
High	Filtered	.0804	.0481	60	.0323	40	
	Raw	.2785	.0393	14	.2391	86	
Iodine (I)	Low:						
	a.m.	Filtered	.3659	.2452	67	.1206	33
	p.m.	Filtered	.3545	*.2694	76	.0851	24
	a.m.	Raw	.1833	*.1602	87	.0231	13
	p.m.	Raw	.3602	.2859	79	.0743	21
	High	Filtered	.1586	.0122	8	.1464	93
Raw	Filtered	.4719	.0000	0	.4719	100	
	Raw						
Iron (Fe)	Low:						
	a.m.	Filtered	.0566	*.0453	80	.0113	20
	p.m.	Filtered	.1284	.0944	74	.0340	26
	a.m.	Raw	.4472	.3208	72	.1264	28
	p.m.	Raw	.3858	.2670	69	.1188	31
	High	Filtered	.0754	.0537	71	.0217	29
Raw	Filtered	.2248	.1171	52	.1077	48	
	Raw						
Lead (Pb)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
High	Filtered	I	----	--	----	---	
Raw	Filtered	.2494	.0547	22	.1946	78	
	Raw						
Magnesium (Mg)	Low:						
	a.m.	Filtered	.1202	*.1172	98	.0030	2
	p.m.	Filtered	.1196	*.1161	97	.0035	3
	a.m.	Raw	.1268	*.1226	97	.0042	3
	p.m.	Raw	.1241	*.1199	97	.0042	3
	High	Filtered	.1938	*.1756	91	.0182	9
Raw	Filtered	.1755	.0814	46	.0940	54	
	Raw						
Manganese (Mn)	Low:						
	a.m.	Filtered	.8237	*.7239	88	.0998	12
	p.m.	Filtered	.6783	*.5940	88	.0844	12
	a.m.	Raw	.5539	*.4373	79	.1166	21
	p.m.	Raw	.5816	.4074	70	.1742	30
	High	Filtered	.3587	.0000	0	.3587	100
Raw	Filtered	.1361	.0733	54	.0628	46	
	Raw						
Mercury (Hg)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
High	Filtered	I	----	--	----	---	
Raw	Filtered	.4743	.3611	76	.1133	24	
	Raw						
Nickel (Ni)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
High	Filtered	I	----	--	----	---	
Raw	Filtered	.1685	.0633	38	.1052	62	
	Raw						
Nitrate (NO ₃)	Low:						
	a.m.	Filtered	.3717	.0000	0	.3717	100
	p.m.	Filtered	.6757	.4569	68	.2188	32
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
	High	Filtered	.1076	*.1020	95	.0056	5
Raw	Filtered	ND	----	--	----	---	
	Raw						
Organic nitrogen N(Organic)	Low:						
	a.m.	Filtered	.1547	.0000	0	.1547	100
	p.m.	Filtered	.1490	.0775	52	.0715	48
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
	High	Filtered	.3072	.0121	4	.2951	96
Raw	Filtered	ND	----	--	----	---	
	Raw						

TABLE 8.—Comparison of estimated logarithmic variance components for surface waters—Continued

Constituent	Flow	Filtration	Total log variance	Between geohydrologic units		Within geohydrologic units	
				Component	Percent	Component	Percent
					of total		of total
Potassium (K)	Low:						
	a.m.	Filtered	0.0759	0.0550	72	0.0209	28
	p.m.	Filtered	.0816	.0593	73	.0223	27
	a.m.	Raw	.0749	.0550	74	.0198	26
	p.m.	Raw	.0841	.0550	65	.0292	35
	High	Filtered	.0402	*.0326	81	.0076	19
		Raw	ND	----	--	----	---
Selenium (Se)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
	High	Filtered	0.0189	.0053	28	.0137	72
		Raw	ND	----	--	----	---
Silica (SiO ₂)	Low:						
	a.m.	Filtered	.0044	*.0034	78	.0010	22
	p.m.	Filtered	.0044	*.0035	78	.0010	22
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
	High	Filtered	.0131	.0051	39	.0080	61
		Raw	ND	----	--	----	---
Sodium (Na)	Low:						
	a.m.	Filtered	.1426	*.1156	81	.0270	19
	p.m.	Filtered	.1317	*.1134	86	.0183	14
	a.m.	Raw	.1424	*.1178	83	.0246	17
	p.m.	Raw	.1364	*.1155	85	.0209	15
	High	Filtered	.2740	*.2276	83	.0463	17
		Raw	ND	----	--	----	---
Strontium (Sr)	Low:						
	a.m.	Filtered	.2362	*.2004	85	.0357	15
	p.m.	Filtered	.1993	*.1670	84	.0323	16
	a.m.	Raw	.2156	*.1748	81	.0408	19
	p.m.	Raw	.2279	*.1985	87	.0294	13
	High	Filtered	.2444	*.1854	76	.0590	24
		Raw	.3574	.2300	64	.1274	36
Sulfate (SO ₄)	Low:						
	a.m.	Filtered	.5517	.3664	66	.1853	34
	p.m.	Filtered	.2449	.1559	64	.0891	36
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
	High	Filtered	.2831	.2642	*93	.0189	7
		Raw	ND	----	--	----	---
Titanium (Ti)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	.6520	.4504	69	.2016	31
	p.m.	Raw	.5400	.1635	30	.3765	70
	High	Filtered	I	----	--	----	---
		Raw	.2375	.1258	53	.1117	47
Vanadium (V)	Low:						
	a.m.	Filtered	I	----	--	----	---
	p.m.	Filtered	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
	High	Filtered	I	----	--	----	---
		Raw	.2558	.1306	51	.1252	49
Zinc (Zn)	Low:						
	a.m.	Filtered	.0674	.0000	0	.0674	100
	p.m.	Filtered	.0424	.0272	64	.0152	36
	a.m.	Raw	.1562	.0000	0	.1562	100
	p.m.	Raw	.1938	.0828	43	.1110	57
	High	Filtered	.1717	.0818	48	.0899	52
		Raw	.1759	.0000	0	.1759	100
Zirconium (Zr)	Low:						
	a.m.	Filtration	I	----	--	----	---
	p.m.	Filtration	I	----	--	----	---
	a.m.	Raw	I	----	--	----	---
	p.m.	Raw	I	----	--	----	---
	High	Filtration	I	----	--	----	---
		Raw	.1910	.0000	0	.1910	100
pH	Low:						
	a.m.	Filtered	.0355	.0000	0	.0355	100
	p.m.	Filtered	.0474	.0080	17	.0395	83
	a.m.	Raw	ND	----	--	----	---
	p.m.	Raw	ND	----	--	----	---
	High	Filtered	.2132	.1471	69	.0661	31
		Raw	ND	----	--	----	---

TABLE 8.—Comparison of estimated logarithmic variance components for surface waters—Continued

Constituent	Flow	Filtration	Total Log variance	Between geohydrologic units		Within geohydrologic units	
				Component	Percent	Component	Percent
					of total		of total
Total solids on evapora- tion	Low:						
	a.m.	Filtered	0.0075	0.0053	70	0.0022	30
	p.m.	Filtered	.0120	*.0106	88	.0014	12
	a.m.	Raw	ND	-----	--	-----	---
	p.m.	Raw	ND	-----	--	-----	---
	High	Filtered	.0952	*.0721	76	.0231	24
		Raw	.1719	.0261	15	.1458	85
Gross alpha activity	Low:						
	a.m.	Filtered	.4642	.2998	65	.1644	35
	p.m.	Filtered	.5036	.2531	50	.2505	50
	a.m.	Raw	I	-----	--	-----	---
	p.m.	Raw	I	-----	--	-----	---
	High	Filtered	I	-----	--	-----	---
		Raw	.1939	.0697	36	.1245	64
Gross beta activity	Low:						
	a.m.	Filtered	.0901	*.0817	91	.0083	9
	p.m.	Filtered	.0961	*.0817	85	.0145	15
	a.m.	Raw	.1404	.0587	42	.0816	58
	p.m.	Raw	.1883	.1214	65	.0668	35
	High	Filtered	.0489	.0278	57	.0212	43
		Raw	.1619	.0890	55	.0728	45

None of the chemical constituents for the unfiltered high-flow samples showed significant regional variation. In addition fewer low-flow unfiltered samples than filtered samples showed significant regional variation. This is a result of the large variations in suspended material in the streams at the time of sampling, and as would be expected, this variability is especially pronounced during periods of high flow.

The analysis-of-variance results for filtered low-flow samples show considerable differences from the high-flow samples in the numbers and types of chemical constituents that show significant regional variability. This is due to the low-flow samples representing predominantly ground-water discharge to the streams, while the high flow samples represent mostly rapid chemical reactions near the land surface during overland runoff. In the karst terranes associated with Cambrian and Ordovician (southeastern Missouri) and the Mississippian geohydrologic units (fig. 43), surface runoff to streams is limited, and much of the precipitation falling on the land surface travels through sinkholes and caverns and eventually discharges to the streams. This results in closer and longer contact of the streamflow with the rocks of the geohydrologic unit, thereby reducing the differences both in concentrations and ratios of chemical parameters between high-flow and low-flow water quality, and even between surface water and ground water. In contrast, the precipitation runoff from the shales, sandstones, and unconsolidated glacial deposits of the Pennsylvanian and glacial deposits geohydrologic units respectively (fig. 43)

remains mostly at or close to the land surface and reaches the streams rapidly. This results in a marked difference in the high-flow and low-flow chemical composition of the stream water, and it also results in a relatively large difference between low-flow surface water and ground-water chemical composition. This is especially evident in the Pennsylvanian geohydrologic unit. For example, the ground water from the Pennsylvanian geohydrologic unit had the highest mean lithium value, (68 $\mu\text{g/L}$) of all geohydrologic units, yet both the low-flow and high-flow samples for both streams sampled in this unit had lithium values below the 10- $\mu\text{g/L}$ detection limit for both filtered and unfiltered samples. This indicates that even during low-flow periods, there is little contribution to streamflow by aquifers in the Pennsylvanian geohydrologic unit. Most of the streamflow probably comes from strongly leached near-surface aquifers and saturated residuum. The two streams sampled in this geohydrologic unit have drainage areas of 1,087 and 1,072 km^2 , yet their median 7-day low flows are 20 and 6 L/s, respectively (Skelton, 1966). The flow rates contrast with those of the two streams sampled in the Cambrian and Ordovician (southeastern Missouri) geohydrologic unit, which have drainage areas of 1,046 and 1,031 km^2 , but have median 7-day low flows of 765 and 3,455 L/s. This difference in base flow of streams between the two geohydrologic units is caused by many factors, but the most important are believed to be related to the permeability and thickness of the aquifers and the extent of hydraulic connection between the aquifers and the streams. These factors

are also important in determining, within a geohydrologic unit, how closely the major-ion and trace-element composition of surface waters during low flow reflects the trace-element content of the ground water. By comparing the concentrations of chemical constituents for filtered low-flow samples (Appendix I) with the summary data for ground water (table 4) it can be seen that ground water and low-flow surface water in the Cambrian and Ordovician (southeastern Missouri) geohydrologic unit are quite similar in quality, whereas in the Pennsylvanian geohydrologic unit they are quite different.

Comparisons of the analysis-of-variance results for surface waters and ground waters should be made with caution, due to the fewer degrees of freedom for the surface-water data. Also, because only two streams were sampled in each geohydrologic unit, summary statistics for the data are not given; instead, the entire sample analyses are tabulated in Appendix I.

SUMMARY AND CONCLUSIONS

1. The concentrations of many chemical constituents in ground waters of Missouri show statistically significant variation between the major geohydrologic units over distances of a few kilometers or more. The nature of the chemical variability of Missouri ground water may have important implications in epidemiology. Populations in cities and farms in different parts of the State using water from different geohydrologic units will be exposed to some very different assemblages of major-ion and trace-element constituents. However, the water-quality characteristics of supplies from widely spaced towns within the same geohydrologic unit also may differ significantly. Cities and farms located within a few kilometers of each other and drawing water from the same geohydrologic unit will, in general, be using water of about the same chemical properties, unless greatly different plumbing systems and methods of water treatment are in use.

2. The general chemical character of ground water in the seven geohydrologic units can be moderately well described in terms of various combinations of four theoretical water types. These are viewed as three dominant ground-water types, and a fourth type apparently reflects dilution by relatively rapid infiltration of local precipitation, or reduction in dissolved solids due to membrane filtration through associated clays.

3. Tables of summary statistics provide estimates of typical concentrations and the expected variability of chemical constituents in each of the geohydrologic units. This does not imply that all water from each unit is chemically similar; chemically anomalous water probably occurs in each unit. Geochemical maps based on data from the tables can be used by epidemiologists to observe pat-

terns in chemical composition among ground waters of the State and to compare these with epidemiological patterns to search for possible relationships between ground-water chemistry and health. When using the geochemical maps for epidemiological comparisons, investigators should be aware of the three-dimensional aspect of ground-water supplies and the possible large differences in the chemical compositions of ground waters from different aquifers underlying an area. The tables and maps also can be used to provide base-line information for geochemical exploration or pollution studies. For example, ground water containing 70 $\mu\text{g/L}$ lithium would be considered "normal" if it occurred in the Pennsylvanian geohydrologic unit (table 4), but would be anomalous if found in the Cambrian and Ordovician strata (southeastern Missouri) geohydrologic unit.

4. The presence of high values of ammonia and organic nitrogen in some ground waters from northwest Missouri suggests the presence of organic contamination in this area and the need for a more widespread and thorough study. The abandoned lead-zinc mines in the Joplin mining area contain ground water with anomalously high concentrations of numerous chemical constituents when compared with ground waters in the same geohydrologic unit but outside the mining area. However, without premining base-line values, it is not possible to determine if the high concentrations of many chemical constituents are natural or manmade anomalies.

5. During low flow, many chemical constituents in surface waters of Missouri show significant differences between geohydrologic units.

6. Most of the variability between geohydrologic units in the chemical composition of surface water occurs in filtered water. The chemical composition of unfiltered samples is controlled strongly by the proportion of suspended sediment in streamflow. The large variability of suspended sediment content in samples collected from streams within a geohydrologic unit overwhelms any real variability between geohydrologic units in the chemical composition of unfiltered samples.

7. The chemical composition of filtered low-flow surface waters in the Cambrian and Ordovician (southeastern Missouri) and Mississippian geohydrologic units is similar to that of the ground waters sampled in these units. However, the chemical composition of filtered low-flow surface waters in the Pennsylvanian and glacial deposits geohydrologic units is different from that of the ground waters sampled in these units.

8. During high-flow periods, the differences between filtered surface-water samples and ground-water samples from the same geohydrologic unit are greater than during low flow.

9. There were no significant variations in trace-element concentrations between predawn and late after-

noon filtered samples. However, there were significant differences in pH, alkalinity, and percent oxygen saturation. Any differences in the trace-element concentration in the sampled streams, between predawn and late afternoon, were too subtle to determine by the laboratory methods used. Future studies to determine if such differences do occur will require more precise laboratory methods.

REFERENCES CITED

- Anderson, R. L., and Bancroft, T. A., 1952, *Statistical theory in research*: New York, McGraw-Hill, 399 p.
- Barnett, P. R., 1976, Analysis of water residue by emission spectroscopy, in Miesch, A. T., *Geochemical survey of Missouri—Methods of sampling, laboratory analysis, and statistical reduction of data*: U.S. Geological Survey Professional Paper 954-A, p. A22-A23.
- Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, TWRI 5-A2, 160 p.
- Cohen, A. C., Jr., 1959, Simplified estimators for the normal distribution when samples are singularly censored or truncated: *Technometrics*, v. 1, no. 3, p. 217-237.
- Connor, J. J., Feder, G. L., Erdman, J. A., and Tidball, R. R., 1972, Environmental geochemistry in Missouri—a multidisciplinary study: 24th International Geologic Congress, Symposium 1, p. 7-14.
- Duncan, D. B., 1955, Multiple range and multiple F tests: *Biometrics*, vol. II, no. 1, p. 1-42.
- Erdman, J. A., Shacklette, H. T., and Keith, J. R., 1976, Elemental composition of corn grains, soybean seeds, pasture grasses, and associated soils from selected areas in Missouri: U.S. Geological Survey Professional Paper 954-D, 23p.
- Feder, G. L., 1972, Problems of sampling in trace element investigations, in Cannon, H. L., and Hopps, H. C., eds., *Geochemical environment in relation to health and disease*: Annals of the New York Academy of Science, v. 199, p. 118-123.
- Feder, G. L., Ebens, R. J., and Connor, J. J., 1972, The relationship between lithology and trace-element content of ground water, in Harbaugh, T. E., and Warner, D. L., eds., *Short papers of the Eighth Annual Water Resources Conference*: American Water Resources Association, St. Louis, Missouri, p. 104.
- Feder, G. L., Skelton, John, Jeffery, J. G., and Harvey, E. J., 1969, Water resources of the Joplin area, Missouri: Missouri Geological Survey and Water Resources Report no. 24, 97 p.
- Hanshaw, B. B., and Coplen, T. B., 1973, Ultrafiltration by a compacted clay membrane—II. Sodium ion exclusion at various ionic strengths: *Geochimica et Cosmochimica Acta*, v. 37, p. 2311-2327.
- Howe, W. B., and Koenig, J. W., 1961, The stratigraphic succession in Missouri: Missouri Geological Survey and Water Resources, v. 40, 185 p.
- Janzer, V. J., 1976, Analysis of water for radioactivity, in Miesch, A. T., *Geochemical survey of Missouri—Methods of sampling, laboratory analysis, and statistical reduction of data*: U.S. Geological Survey Professional Paper 954-A, p. A23-A25.
- Maxey, G. B., 1964, Hydrostratigraphic Units: *Journal of Hydrology*, v. 2, p. 124-129.
- Miesch, A. T., 1972, Sampling problems in trace element investigations of rocks, in Cannon, H. L., and Hopps, H. C., eds., *Geochemical environment in relation to health and disease*: Annals of the New York Academy of Science, v. 199, p. 95-104.
- 1976, *Geochemical survey of Missouri—Methods of sampling, laboratory analysis, and statistical reduction of data, with sections on laboratory methods*, by Barnett, P. R., Bartel, A. J., Dinnin, J. I., Feder, G. L., Harms, T. F., Huffman, Claude, Jr., Janzer, V. J., Millard, H. T., Jr., Nieman, H. G., Skougstad, M. W., and Wahlberg, J. S.: U.S. Geological Survey Professional Paper 954-A, 39 p.
- Sauer, H. I., 1974, Relationship between trace element content of drinking water and chronic diseases: Proceedings of the 16th Water-Quality Conference, University of Illinois, Urbana, Illinois, p. 39-48.
- Schroeder, H. A., 1966, Municipal drinking water and cardiovascular death rate: *Journal of the American Medical Association*, v. 185, no. 2, p. 81-85.
- Shamberger, R. J., and Frost, D. V., 1969, Possible protective effect of selenium against human cancer: *Journal of Canadian Medical Association*, v. 100, p. 682.
- Skelton, John, 1966, Low-flow characteristics of Missouri streams: Missouri Geological Survey and Water Resources Report no. 20, 47 p.
- Skougstad, M. W., and Feder, G. L., 1976, Analysis of water by chemical methods, in Miesch, A. T., *Geochemical survey of Missouri—Methods of sampling, laboratory analysis, and statistical reduction of data*: U.S. Geological Survey Professional Paper 954-A, p. A18-A21.
- U.S. Geological Survey, 1968, Landforms of the United States: U.S. Geological Survey pamphlet, 15 p.
- 1972a, *Geochemical survey of Missouri—Plans and progress for first six-month period (July-December, 1969)*: U.S. Geological Survey Open-file Report, 49 p.
- 1972b, *Geochemical survey of Missouri—Plans and progress for second six-month period (January-June, 1970)*: U.S. Geological Survey Open-file Report, 60 p.
- 1972c, *Geochemical survey of Missouri—Plans and progress for third six-month period (July-December, 1970)*: U.S. Geological Survey Open-file Report, 33 p.
- 1972d, *Geochemical survey of Missouri—Plans and progress for fourth six-month period (January-June, 1971)*: U.S. Geological Survey Open-file Report, 63 p.
- 1972e, *Geochemical survey of Missouri—Plans and progress for fifth six-month period (July-December, 1971)*: U.S. Geological Survey Open-file Report, 145 p.
- 1972f, *Geochemical survey of Missouri—Plans and progress for sixth six-month period (January-June, 1972)*: U.S. Geological Survey Open-file Report, 86 p.
- 1973, *Geochemical survey of Missouri—Plans and progress for seventh six-month period (July-December, 1972)*: U.S. Geological Survey Open-file Report, 59 p.
- Voors, A. W., 1971, Atherosclerotic heart disease and drinking water trace metals in North Carolina, in Hemphill, D. D., ed., *Trace substances in environmental health—V*: University of Missouri, Columbia, Missouri, p. 523-533.

APPENDIX

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri

[F, filtrate from 0.1 micrometer filter; R, raw; S, suspended]

Variable	Pennsylvanian strata					
	Cedar Creek near Pleasantville			Big Creek at Blairstown		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Date sampled-----	11-12-71	11-11-71	10-22-72	10-29-71	10-28-71	5-24-72
Discharge (m ³ /s)-----	0.48	0.48	23	0.62	0.76	11.3
Temperature (°C)-----	7.4	8.0	15.5	16.0	18.1	18.6
Total dissolved solids (mg/L)----	220	218	41	196	198	116
Specific conductance (µmhos/cm at 25°C)-----	318	320	70	363	354	165
pH-----	7.71	7.92	6.65	7.80	7.91	7.32
O ₂ (mg/L)-----	7.9	8.6	-----	5.3	7.2	-----
O ₂ (percent saturation)-----	66	73	-----	54	75	-----
NH ₃ , as N (mg/L)-----	<.01	<.01	.03	<.01	<.01	.07
Organic N, as N (mg/L)-----	.12	.31	1.6	.77	.97	.05
NO ₂ , as N (mg/L)-----	<.001	<.001	<.01	.010	.003	.4
NO ₃ , as N (mg/L)-----	.06	.06	.63	1.00	1.20	3.2
HCO ₃ , (mg/L)-----	164	168	22	154	152	56
SiO ₂ , (mg/L), F-----	12	12	4.6	11	11	4.1
Gross alpha (as U natural pCi/L):						
F-----	1.1	<.9	13	2.6	2.4	<.6
S-----	.2	.1	26	1.3	1.7	120
Gross beta (as Sr-90, pCi/L):						
F-----	5.6	5.5	12	9.0	9.2	6.6
S-----	1.1	1.1	37	3.4	3.8	1.7
P (mg/L):						
F-----	.01	.01	-----	.14	.13	.08
R-----	.07	.06	-----	.27	.27	5.9
Ca (mg/L):						
F-----	50	51	5.7	50	49	20
R-----	51	51	8.5	51	50	140
Mg (mg/L):						
F-----	5.0	4.9	1.5	7.0	7.0	3.5
R-----	4.8	4.9	3	7.2	7.3	22
Na (mg/L):						
F-----	5.5	5.4	1.8	11	10	5.1
R-----	5.4	5.2	-----	10	10	7.9
K (mg/L):						
F-----	3.0	3.1	4.2	6.1	6.0	3.8
R-----	3.4	3.4	4.7	6.4	6.1	5.1
SO ₄ (mg/L):						
F-----	25	-----	9.3	36	32	17
R-----	25	16	9.9	39	39	21
Cl (mg/L):						
F-----	5.2	5.2	2.3	11	11	5
R-----	4.4	4.7	3.7	11	11	8
Br (µg/L):						
F-----	80	70	20	100	100	70
R-----	70	70	20	200	90	60
F (µg/L):						
F-----	100	100	200	300	300	300
R-----	100	100	1,000	200	200	5,000
I (µg/L):						
F-----	2	2	8	10	8	50
R-----	10	4	10	20	7	20

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Pennsylvanian strata						
Variable	Cedar Creek near Pleasantville			Big Creek at Blairstown		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Zr ($\mu\text{g/L}$):						
F-----	<9	<9	<2	<10	<10	<3
R-----	<10	<10	200	15	12	1,600
V ($\mu\text{g/L}$):						
F-----	<3	<3	<.9	3	3	<2
R-----	<3	<3	110	13	10	900
Ti ($\mu\text{g/L}$):						
F-----	<2	<2	<.9	<3	<3	1
R-----	7	7	7,000	<3	<3	54,000
Sn ($\mu\text{g/L}$):						
F-----	<5	<5	<.9	<5	<5	<2
R-----	<5	<5	<20	<6	<5	<120
Sr ($\mu\text{g/L}$):						
F-----	70	67	23	190	180	86
R-----	67	74	90	190	160	700
Ag ($\mu\text{g/L}$):						
F-----	<.3	<.3	<.09	<.3	<.3	<.1
R-----	<.3	<.3	<2	<.3	<.3	<8
Ni ($\mu\text{g/L}$):						
F-----	<5	6	3	6	9	<2
R-----	8	7	88	14	13	500
Mo ($\mu\text{g/L}$):						
F-----	<2	<2	<.4	4	3	2
R-----	<2	3	<9	4	3	40
Li ($\mu\text{g/L}$):						
F-----	<10	<10	<1	<10	<10	<10
R-----	<10	<10	<10	<10	<10	10
Pb ($\mu\text{g/L}$):						
F-----	<5	<5	1	<5	<5	<2
R-----	<5	<5	25	<6	<5	190
Ga ($\mu\text{g/L}$):						
F-----	<1	<1	<0.4	<1	<1	<1
R-----	<1	<1	14	<2	<2	250
Cu ($\mu\text{g/L}$):						
F-----	2	3	2	4	5	2
R-----	2	1	36	4	4	200
Co ($\mu\text{g/L}$):						
F-----	<5	<5	<.9	<5	<5	<2
R-----	<5	<5	32	<6	<5	82
Cr ($\mu\text{g/L}$):						
F-----	<5	<5	<.9	<5	<5	<2
R-----	<5	<5	110	7	5	650
B ($\mu\text{g/L}$):						
F-----	17	17	10	45	44	15
R-----	21	16	100	56	58	850
Bi ($\mu\text{g/L}$):						
F-----	<3	<3	<.9	<4	<3	<2
R-----	<3	<3	<18	<4	<4	<80
Be ($\mu\text{g/L}$):						
F-----	<1	<1	<.3	<1	<1	<.6
R-----	<1	<1	<6	<2	<2	<40

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Pennsylvanian strata						
Variable	Cedar Creek near Pleasantville			Big Creek at Blairstown		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Ba ($\mu\text{g/L}$):						
F-----	80	80	36	150	140	60
R-----	90	92	740	190	180	5,800
Al ($\mu\text{g/L}$):						
F-----	57	58	18	15	69	23
R-----	310	250	82,000	4,300	3,500	630,000
Zn ($\mu\text{g/L}$):						
F-----	30	30	8	40	40	30
R-----	20	20	90	30	50	480
Mn ($\mu\text{g/L}$):						
F-----	160	130	290	100	110	7
R-----	200	190	1,100	330	320	7,300
Fe ($\mu\text{g/L}$):						
F-----	40	60	50	20	40	20
R-----	360	620	1,100	1,300	1,500	18,000
Se ($\mu\text{g/L}$):						
F-----	20	20	4	8	6	5
R-----	8	10	3	2	3	-----
As ($\mu\text{g/L}$):						
F-----	1	2	<1	3	1	<1
R-----	<1	<1	1	1	5	20
Hg ($\mu\text{g/L}$):						
F-----	.1	.1	.3	<.1	<.1	<.1
R-----	<.1	<.1	.3	<.1	<.1	.3
Cd ($\mu\text{g/L}$):						
F-----	<1	<1	2	<1	<1	<1
R-----	<1	<1	1	1	1	2
Glacial deposits						
Variable	Shoal Creek near Braymer			Medicine Creek near Galt		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Date sampled-----	9-30-71	9-29-71	4-20-72	9-29-71	9-28-71	4-20-72
Discharge (m^3/s)-----	0.03	0.03	8.5	0.08	0.08	5.4
Temperature ($^{\circ}\text{C}$)-----	21.7	24.2	14.4	21.0	29.0	13.3
Total dissolved solids (mg/L)-----	360	358	364	276	262	296
Specific conductance ($\mu\text{mhos/cm}$ at 25°C)-----	500	495	510	457	441	365
pH-----	7.82	7.99	7.99	7.88	8.40	7.98
O_2 (mg/L)-----	4.8	6.1	-----	6.5	7.1	-----
O_2 (percent saturation)-----	54	73	-----	72	92	-----
NH_3 , as N (mg/L)-----	.04	.09	.08	.01	<.01	<.01
Organic N, as N (mg/L)-----	.60	.47	1.6	.34	.37	2.1
NO_2 , as N (mg/L)-----	.003	.003	.02	.003	.003	.02

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Variable	Glacial deposits					
	Shoal Creek near Braymer			Medicine Creek near Galt		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
NO ₃ , as N (mg/L)-----	.10	.02	.27	.10	.02	.90
HCO ₃ (mg/L)-----	308	302	231	206	186	160
SiO ₂ (mg/L), F-----	9.7	9.6	6.1	11	11	8.7
Gross alpha (as U natural pCi/L):						
F-----	2.3	3.7	2.1	1.8	1.8	1.6
S-----	.7	.9	8.7	.7	.3	35
Gross beta (as Sr-90, pCi/L):						
F-----	7.4	7.3	8.8	8.1	7.2	5.0
S-----	3.4	3.9	20	1.5	2.8	36
P (mg/L):						
F-----	.03	.09	.28	.03	.05	.21
R-----	.16	.17	.39	.11	.12	.42
Ca (mg/L):						
F-----	79	79	79	61	59	53
R-----	77	78	77	62	59	57
Mg (mg/L):						
F-----	12	12	13	12	12	12
R-----	12	12	13	12	12	14
Na (mg/L):						
F-----	11	11	16	17	17	11
R-----	11	11	16	17	17	12
K (mg/L):						
F-----	3.9	4.1	6.4	3.2	3.4	5.7
R-----	4.0	3.9	5.2	3.6	3.3	6
SO ₄ (μg/L):						
F-----	18	18	72	71	71	64
R-----	25	17	72	73	70	64
Cl (μg/L):						
F-----	5.1	5.3	12	5.2	5.3	8
R-----	5.2	5.3	14	5.2	5.3	15
Br (μg/L):						
F-----	30	-----	70	80	100	90
R-----	100	-----	100	200	50	8
F (μg/L):						
F-----	300	300	400	300	300	400
R-----	400	300	1,000	100	300	2,000
I (μg/L):						
F-----	50	40	10	20	20	10
R-----	40	70	40	20	20	4
Zr (μg/L):						
F-----	<15	<15	<10	<14	<13	<12
R-----	<16	<16	110	15	<14	760
V (μg/L):						
F-----	<4	<4	<7	<3	<3	<12
R-----	<4	<4	60	<4	<3	140
Ti (μg/L):						
F-----	<4	<4	<4	<3	<3	<6
R-----	150	74	2,800	150	57	5,900
Sn (μg/L):						
F-----	<4	<4	<7	<3	<3	<6
R-----	<4	<4	<15	<4	<3	<24
Sr (μg/L):						
F-----	410	390	260	270	230	120
R-----	400	400	280	260	250	200

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Variable	Glacial deposits					
	Shoal Creek near Braymer			Medicine Creek near Galt		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Ag ($\mu\text{g/L}$):						
F-----	<.7	<.7	<.4	<.7	<.6	<2
R-----	<.8	<.8	<1	<.7	<.7	<5
Ni ($\mu\text{g/L}$):						
F-----	<15	<15	<7	<14	<13	<6
R-----	<16	16	45	16	13	130
Mo ($\mu\text{g/L}$):						
F-----	8	7	5	5	5	2
R-----	7	5	4	5	5	5
Li ($\mu\text{g/L}$):						
F-----	<10	<10	<10	<10	<10	<10
R-----	<10	<10	<10	<10	<10	<10
Pb ($\mu\text{g/L}$):						
F-----	<7	<7	<7	<7	<6	<6
R-----	<8	<8	13	<7	<7	31
Ga ($\mu\text{g/L}$):						
F-----	<4	<4	<4	<3	<3	<3
R-----	<4	<4	15	<4	<3	65
Cu ($\mu\text{g/L}$):						
F-----	.8	2	2	1	1	3
R-----	1	1	12	3	.8	70
Co ($\mu\text{g/L}$):						
F-----	<4	<4	<7	<3	<3	<3
R-----	<4	<4	16	<4	<3	20
Cr ($\mu\text{g/L}$):						
F-----	<7	<7	<7	<6	<6	<6
R-----	<8	<8	38	<7	<7	99
B ($\mu\text{g/L}$):						
F-----	34	35	40	41	34	31
R-----	45	45	100	48	38	150
Bi ($\mu\text{g/L}$):						
F-----	<7	<7	<5	<7	<6	<6
R-----	<8	<8	<10	<7	<7	<24
Be ($\mu\text{g/L}$):						
F-----	<2	<2	<3	<2	<2	<2
R-----	<2	<2	<5	<2	<2	<5
Ba ($\mu\text{g/L}$):						
F-----	240	240	140	86	76	86
R-----	280	280	480	110	88	930
Al ($\mu\text{g/L}$):						
F-----	7	12	30	12	10	10
R-----	3,300	1,700	34,000	3,700	1,200	68,000
Zn ($\mu\text{g/L}$):						
F-----	10	10	8	30	20	20
R-----	10	10	140	20	10	160
Mn ($\mu\text{g/L}$):						
F-----	780	820	25	770	340	8
R-----	1,000	1,000	670	1,200	600	1,000
Fe ($\mu\text{g/L}$):						
F-----	10	10	10	10	10	10
R-----	940	1,000	15,000	600	340	20,000

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Glacial deposits						
Variable	Shoal Creek near Braymer			Medicine Creek near Galt		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
	Se ($\mu\text{g/L}$):					
F-----	8	8	2	8	8	4
R-----	6	6	2	6	8	4
As ($\mu\text{g/L}$):						
F-----	<1	<1	<1	<1	<1	<1
R-----	<1	<1	8	<1	<1	10
Hg ($\mu\text{g/L}$):						
F-----	.3	.1	.2	.1	.2	.2
R-----	.4	.4	.2	.2	.3	.2
Cd ($\mu\text{g/L}$):						
F-----	1	1	1	1	1	1
R-----	<1	<73	2	<1	<1	2

Mississippian strata						
Variable	Shoal Creek at Joplin			Spring River near La Russell		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
	Date sampled-----	11-13-71	11-12-71	3-10-73	11-16-71	11-15-71
Discharge (m^3/s)-----	2.1	2.2	85	1.3	1.3	140
Temperature ($^{\circ}\text{C}$)-----	11.2	11.8	14.5	14.4	16.5	14.2
Total dissolved solids (mg/L)----	256	220	105	268	264	68
Specific conductance ($\mu\text{mhos/cm}$ at 25°C)-----	335	327	150	363	359	110
pH-----	8.19	8.40	7.50	7.88	8.06	7.26
O_2 (mg/L)-----	8.0	10.5	-----	7.4	9.8	-----
O_2 (percent saturation)-----	73	96	-----	72	100	-----
NH_3 , as N (mg/L)-----	<.01	<.01	<.01	<.01	<.01	<.01
Organic N, as N (mg/L)-----	.19	.14	1.7	.10	.09	2.6
NO_2 , as N (mg/L)-----	.003	.003	.01	.003	.003	.02
NO_3 , as N (mg/L)-----	.10	1.10	1.6	1.60	1.60	1.1
HCO_3 (mg/L)-----	182	170	71	200	196	44
SiO_2 (mg/L), F-----	8.1	8.0	7.7	8.3	8.1	5.1
Gross alpha (as U natural pCi/L):						
F-----	<.7	1.4	<.5	<.6	1.3	<.3
S-----	.2	<.1	14	<.1	<.1	33
Gross beta (as Sr-90, pCi/L):						
F-----	2.5	2.8	3.1	2.1	2.0	4.1
S-----	.7	<.4	13	<.4	.6	30
P (mg/L):						
F-----	.21	.19	.05	.15	.15	.08
R-----	.24	.22	.47	.18	.16	.73

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Mississippian strata						
Variable	Shoal Creek at Joplin			Spring River near La Russell		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Ca (mg/L):						
F-----	53	53	24	60	60	13
R-----	54	54	25	60	60	17
Mg (mg/L):						
F-----	3.5	3.5	1.7	3.9	4.1	1.4
R-----	3.4	3.5	2	3.8	4.0	2
Na (mg/L):						
F-----	10	7.3	2.0	6.6	6.7	1.1
R-----	10	7.0	1.9	6.3	6.4	1.0
K (mg/L):						
F-----	1.5	1.5	2.2	1.5	1.6	3.3
R-----	1.9	1.7	2.5	1.7	-----	4.3
SO ₄ (mg/L):						
F-----	0.5	7.5	6.7	4.5	7.5	3.5
R-----	1.0	7.3	7.2	8.8	8.8	6.3
Cl (mg/L):						
F-----	8.0	7.6	3.4	10.0	9.9	2.4
R-----	7.3	7.1	3.6	9.0	9.2	3.8
Br (μg/L):						
F-----	40	60	20	100	90	10
R-----	80	70	10	100	-----	20
F (μg/L):						
F-----	100	100	100	100	<100	100
R-----	<100	<100	1,000	<100	<100	1,000
I (μg/L):						
F-----	2	3	3	4	1	5
R-----	7	2	<1	8	-----	30
Zr (μg/L):						
F-----	<10	<10	<4	<10	<10	<3
R-----	<10	<10	230	<10	<10	260
V (μg/L):						
F-----	<3	<3	<2	<3	<3	<2
R-----	<3	<3	67	<3	<3	74
Ti (μg/L):						
F-----	<3	<3	<2	<3	<3	<2
R-----	11	11	4,300	8	8	4,600
Sn (μg/L):						
F-----	<5	<5	<2	<5	<5	<2
R-----	<5	<5	<17	<5	<5	<16
Sr (μg/L):						
F-----	42	47	26	55	56	25
R-----	47	44	83	51	51	57
Ag (μg/L):						
F-----	<.3	<.3	<.2	<.3	<.3	<.2
R-----	<.3	<.3	<2	<.3	<.3	<2
Ni (μg/L):						
F-----	17	13	<2	<3	<3	<2
R-----	33	22	78	<3	<3	55
Mo (μg/L):						
F-----	<2	<2	<.9	<2	<2	<.7
R-----	<2	<2	<9	<2	<2	<8
Li (μg/L):						
F-----	10	10	10	10	10	10
R-----	10	10	-----	10	10	-----

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Variable	Mississippian strata					
	Shoal Creek at Joplin			Spring River near La Russell		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Pb ($\mu\text{g/L}$):						
F-----	<3	<3	<2	<3	<3	<2
R-----	3	3	200	<3	<3	33
Ga ($\mu\text{g/L}$):						
F-----	<1	<1	<.9	<1	<1	<.7
R-----	<1	<1	14	<1	<1	14
Cu ($\mu\text{g/L}$):						
F-----	2	2	2	1	2	2
R-----	2	1	28	1	1	28
Co ($\mu\text{g/L}$):						
F-----	<5	<5	<2	<5	<5	<2
R-----	<5	<5	<17	<5	<5	18
Cr ($\mu\text{g/L}$):						
F-----	19	9	<2	<3	<3	<2
R-----	26	12	64	<3	<3	54
B ($\mu\text{g/L}$):						
F-----	22	19	10	12	12	8
R-----	26	20	78	13	11	76
Bi ($\mu\text{g/L}$):						
F-----	<3	<3	<2	<3	<3	<2
R-----	<3	<3	<17	<3	<3	<16
Be ($\mu\text{g/L}$):						
F-----	<1	<1	<.6	<1	<1	<.5
R-----	<1	<1	<6	<1	<1	<6
Ba ($\mu\text{g/L}$):						
F-----	62	66	54	74	75	48
R-----	69	67	620	79	78	690
Al ($\mu\text{g/L}$):						
F-----	60	5	7	63	80	7
R-----	200	250	60,000	230	150	55,000
Zn ($\mu\text{g/L}$):						
F-----	70	30	90	20	30	30
R-----	80	140	520	20	20	100
Mn ($\mu\text{g/L}$):						
F-----	22	20	20	18	17	20
R-----	54	50	480	36	31	920
Fe ($\mu\text{g/L}$):						
F-----	20	10	30	20	20	30
R-----	100	120	5,300	70	70	12,000
Se ($\mu\text{g/L}$):						
F-----	4	6	5	7	2	5
R-----	5	6	5	6	10	5
As ($\mu\text{g/L}$):						
F-----	<1	<1	2	<1	-----	2
R-----	<1	<1	1	<1	<1	3
Hg ($\mu\text{g/L}$):						
F-----	.3	<.1	.1	.6	.4	<.1
R-----	<.1	<.1	.1	.5	-----	.1
Cd ($\mu\text{g/L}$):						
F-----	<1	<1	1	<1	<1	<1
R-----	<1	1	10	<1	<1	10

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Variable	Jacks Fork at Eminence			Osage Fork near Dry Creek		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Date sampled-----	11-2-71	11-2-71	4-16-72	11-3-71	11-2-71	3-10-73
Discharge (m ³ /s)-----	3.1	3.1	280	2.1	2.3	110
Temperature (°C)-----	15.0	16.1	17	13.2	15.2	14.3
Total dissolved solids (mg/L)-----	214	210	130	236	238	-----
Specific conductance (μmhos/cm at 25°C)-----	347	342	145	378	377	140
pH-----	8.38	8.39	7.68	7.75	8.20	7.53
O ₂ (mg/L)-----	6.9	10.3	-----	5.8	7.8	-----
O ₂ (percent saturation)-----	68	104	-----	55	77	-----
NH ₃ , as N (mg/L)-----	<.01	<.01	.03	<.01	.01	<.01
Organic N, as N (mg/L)-----	.28	.08	.97	.06	.27	1.6
NO ₂ , as N (mg/L)-----	<.001	<.001	.01	<.001	<.001	.01
NO ₃ , as N (mg/L)-----	.20	.20	.50	.30	.30	.68
HCO ₃ (mg/L)-----	228	222	85	230	228	74
SiO ₂ (mg/L), F-----	8.8	8.9	6.8	10	10	5.7
Gross alpha (as U natural pCi/L):						
F-----	1.2	<.7	.5	<.8	<.7	<.43
S-----	<.1	<.1	6.9	<.2	<.2	8
Gross beta (as Sr-90, pCi/L):						
F-----	2.0	1.6	4.2	2.7	2.6	2.8
S-----	<.4	<.4	9.9	1.2	1.1	12
P (mg/L):						
F-----	.01	<.01	.04	.02	.02	.03
R-----	.02	<.01	.09	.06	.06	.35
Ca (mg/L):						
F-----	38	39	17	41	41	14
R-----	39	37	15	41	41	16
Mg (mg/L):						
F-----	22	22	8.2	23	23	7.4
R-----	23	23	8	23	24	9
Na (mg/L):						
F-----	1.5	1.6	.7	2.6	2.5	1.3
R-----	1.5	1.5	.6	2.5	2.5	1.4
K (mg/L):						
F-----	1.0	.9	3.0	1.8	1.8	2.0
R-----	1.0	.9	2.3	1.9	1.9	2.6
SO ₄ (mg/L):						
F-----	2.3	2.0	5.9	6.3	6.5	5.7
R-----	2.5	2.8	7.2	-----	5.8	9.7
Cl (mg/L):						
F-----	2.1	2.3	.9	4.9	5.1	3.1
R-----	1.6	2.1	3.4	4.4	4.6	3.7
Br (μg/L):						
F-----	10	20	30	40	30	30
R-----	10	30	60	20	40	30
F (μg/L):						
F-----	200	<100	300	100	100	100
R-----	<100	<100	<1,000	<100	<100	1,000
I (μg/L):						
F-----	3	2	4	1	2	20
R-----	3	2	5	3	4	7

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Cambrian and Ordovician strata (Southeast Missouri)

Variable	Jacks Fork at Eminence			Osage Fork near Dry Creek		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Zr ($\mu\text{g/L}$):						
F-----	<11	<11	<5	<12	<12	<5
R-----	<11	<11	93	<13	<13	110
V ($\mu\text{g/L}$):						
F-----	<4	<4	<5	<3	<3	<2
R-----	<4	<4	22	<3	<3	33
Ti ($\mu\text{g/L}$):						
F-----	<3	<3	<3	<3	<3	<2
R-----	3	<3	1,900	26	32	1,800
Sn ($\mu\text{g/L}$):						
F-----	<5	<5	<3	<6	<6	<2
R-----	<5	<5	<6	<6	<6	<9
Sr ($\mu\text{g/L}$):						
F-----	22	27	12	37	36	18
R-----	23	20	13	45	38	29
Ag ($\mu\text{g/L}$):						
F-----	<.3	<.3	<.5	<.3	<.3	<.2
R-----	<.3	<.3	<2	<.4	<.4	<.9
Ni ($\mu\text{g/L}$):						
F-----	<5	<5	3	<6	<6	<2
R-----	<5	<5	39	<6	<6	25
Mo ($\mu\text{g/L}$):						
F-----	<3	<3	<.5	<2	<2	<1
R-----	<3	<3	<2	<2	<2	<4
Li ($\mu\text{g/L}$):						
F-----	<10	<10	<10	<10	<10	<10
R-----	<10	<10	<10	<10	<10	-----
Pb ($\mu\text{g/L}$):						
F-----	<5	<5	<3	<6	<6	<2
R-----	<5	<5	16	<6	<6	11
Ga ($\mu\text{g/L}$):						
F-----	<2	<2	<2	<2	<2	<1
R-----	<2	<2	15	<2	<2	6
Cu ($\mu\text{g/L}$):						
F-----	2	3	3	2	2	2
R-----	<1	<1	19	2	2	12
Co ($\mu\text{g/L}$):						
F-----	<5	<5	<2	<4	<4	<2
R-----	<5	<5	16	<4	<4	<9
Cr ($\mu\text{g/L}$):						
F-----	<5	<5	<3	<4	<4	<2
R-----	<5	<5	18	<4	<4	23
B ($\mu\text{g/L}$):						
F-----	7	8	17	11	12	9
R-----	7	7	40	14	11	38
Bi ($\mu\text{g/L}$):						
F-----	<4	<4	<3	<4	<4	<2
R-----	<4	<4	<6	<4	<4	<9
Be ($\mu\text{g/L}$):						
F-----	<2	<2	<.5	<2	<2	<.7
R-----	<2	<2	<2	<2	<2	<3
Ba ($\mu\text{g/L}$):						
F-----	37	39	27	80	80	34
R-----	27	34	110	100	90	260

APPENDIX I.—Analyses of surface water from four geohydrologic units in Missouri—Continued

Cambrian and Ordovician strata (Southeast Missouri)						
Variable	Jacks Fork at Eminence			Osage Fork near Dry Creek		
	Low flow		High flow	Low flow		High flow
	a.m.	p.m.		a.m.	p.m.	
Al ($\mu\text{g/L}$):						
F-----	61	55	17	51	15	8
R-----	120	94	13,000	490	600	25,000
Zn ($\mu\text{g/L}$):						
F-----	30	30	8	30	40	<1
R-----	150	60	120	20	80	30
Mn ($\mu\text{g/L}$):						
F-----	3	4	8	22	21	10
R-----	12	7	320	100	90	490
Fe ($\mu\text{g/L}$):						
F-----	10	20	30	10	10	40
R-----	20	30	6,200	160	160	5,000
Se ($\mu\text{g/L}$):						
F-----	20	6	4	8	1	5
R-----	6	8	4	6	6	12
As ($\mu\text{g/L}$):						
F-----	<1	<1	<1	<1	<1	2
R-----	<1	<1	5	<1	<1	2
Hg ($\mu\text{g/L}$):						
F-----	<.1	<.1	.1	.1	<.1	<.1
R-----	<.1	<.1	.1	<.1	<.1	.2
Cd ($\mu\text{g/L}$):						
F-----	<1	<1	1	<1	<1	<1
R-----	1	1	2	<1	1	10

