ENVIRONMENTAL GEOCHEMISTRY

Geochemical survey of Missouri
Plans and progress for fourth six-month period
(January - June, 1971)

Branch of Regional Geochemistry
U.S. Geological Survey
Denver, Colorado

1972

Preface

This is the fourth of a series of progress reports to the Environmental Health Center of the University of Missouri; each report covers a six-month period in our reconnaissance geochemical survey of the State of Missouri that is designed to provide epidemiologists of the Environmental Health Center with data on the variability in the geochemical environment throughout the State. The survey is being directed at geologic units (bedrock), both agricultural and uncultivated soils, native vegetation and farm crops, and both ground and surface waters. Emphasis is on the environment in its natural state; artificial pollution of the environment is being investigated in a few small areas--principally where such pollution is thought to complicate our efforts to determine the natural environmental character. Adequate knowledge of the natural environmental character is necessary in order to establish a background for judging the degree and extent of environmental pollution.

The three previous reports in this series have served principally to describe approaches being considered and tried in this first attempt to conduct an environmental geochemical survey of so large an area (69,420 sq. mi.). Some of the approaches tried have been rejected, but others have proved practical and successful. It appears now that the survey has assumed its final form, and the major task remaining is to continue its execution through to completion.

Data presented in the three previous reports have been largely fragmentary. The present report contains some final, and some near final, data on the chemical characteristics of groundwaters throughout the State and on agricultural and uncultivated soils. Forthcoming reports, however, will contain closer examinations of these data and will perhaps present the data in alternative ways. They will also, of course, contain much other data pertaining to sample collections still in our laboratories.

Nevertheless, this fourth report contains the first systematic data on variation in the geochemical environment throughout the State and will allow epidemiologists of the Environmental Health Center to begin searching for correlations between health data and geochemical factors.

The geochemical survey of Missouri would not be possible without the cooperation and assistance of many individuals. We have continued to enjoy the help of the Environmental Health Center of the University of Missouri, the Missouri Division of Geological Survey and Water Resources and the Soil Conservation Service of the U.S. Department of Agriculture. Special acknowledgment is due to a number of individuals and organizations who helped us assemble a small collection of samples from economic mineral commodities from some of the major mining regions of the State--these include Mr. Peter Sweeney of Cominco American Incorporated, Dr. James Davis and Missouri Lead Operating Company, Messrs. Kenneth Larsen and Harold Krueger of Ozark Lead Company, Mr. Paul Gerdemann of St. Joe

Minerals Corporation, and Messrs. James Martin, Charles Robertson, and Heywood Wharton of the Missouri Division of Geological Survey and Water Resources.

Finally, we wish to acknowledge the continued support of the Branch of Analytical Laboratories and the Plant Laboratory of the Branch of Exploration Research. These units of the U.S. Geological Survey are headed, respectively, by Mr. Irving May, who has succeeded Dr. Frank Grimaldi as Chief Chemist, and by Mr. Fred Ward.

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INTRODUCTION AND SUMMARY

This is the fourth six-month progress report on a reconnaissance geochemical survey of the State of Missouri. The survey was initiated in July, 1969, to provide epidemiologists of the Environmental Health Center of the University of Missouri with data on the variability in the geochemical environment throughout the State. It is a pilot program in that it is the first attempt to provide information of this kind for so large an area (69,420 sq. mi.), and it is expected that the approaches being developed will be applicable to other reconnaissance investigations designed for similar purposes. The general approach--common to all four phases of the program (rocks, soils, vegetation, and water)--now appears to have taken a final form. The approach to sampling has been described in a following section of the present report. The principal task remaining in the reconnaissance geochemical survey is to follow the general approach through to completion. Some special investigations of selected small areas have been completed (Connor, Shacklette, and Erdman, 1971; Connor, Erdman, Sims, and Ebens, 1971), others are underway, and still others may be started--depending on local situations, or problems, that are identified by us or brought to our attention by others. One important purpose of the reconnaissance survey is to provide background data on the general geochemical setting which may allow more meaningful assessments of local geochemical conditions.

This is the first report of the series that presents systematic final, or near final, data from any of the four principal phases of the program. The report also presents the first part of the basic data that is intended for use by epidemiologists in searching for broad-scale geochemical variations throughout the State that may correlate with variations in human or animal health. These final, or near final, data pertain, in particular, to uncultivated soils and the major groundwater systems. Near-final data are also given on the average composition and compositional variability of agricultural soils; but, except for mercury, no examination has yet been made of the geographic patterns of variation among agricultural soils.

Before proceeding with a summary review of each phase of the program, the reader is reminded that the laboratory methods used for analyzing rocks, soils, plants, and water were summarized in the second report of this series (U.S. Geological Survey, 1970a, p. 4-16). The statistical methods used were described in the same report (p. 17-18) and in references cited therein.

Drs. Ebens and Connor completed the first stage_/ on their sampling

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_/ See the following discussion on general sampling designs for surveys in environmental geochemistry for explanation of stages in the sampling program.

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program designed to assess the nature and degree of geochemical variability in particular rock types within the major stratigraphic units of the State. None of the laboratory results on these samples have been received to date, but all results are expected to be in hand later this year. Whether or not the second stage of sampling will be necessary and the extent of the second stage of sampling if it is necessary will depend on the kind of variability present in the substrata, as revealed by the first stage results. Much of the past six months has been spent on mineralogical studies of splits of the same samples that were submitted to the laboratories for chemical and spectrographic determinations. The mineralogy of the samples is important because the chemical elements of importance in health and disease are originally contained in minerals, and the nature of the minerals determines the tendency for the elements to be released into soils and water. Moreover, it is expected that the nature of the variability in the mineral composition of the rocks will be similar to that of the trace elements in the rocks. Ebens and Connor have found that sandstones of Pennsylvanian age, underlying much of northern and western Missouri, are rather uniform in mineral composition on a broad scale. That is, the variation across the entire northern and western parts of the State is not much greater than the variation within a single sandstone outcrop. Similarly, the loess deposits that cover much of northern Missouri, well-exposed along the Missouri and Mississippi Rivers, were found to be rather uniform in mineral composition over broad areas of the State. If this observed uniformity holds true for trace elements, and if true for other groups of rocks and surficial deposits, the implication is that epidemiologists searching for correlations between geochemistry and health should use geologic maps and lithologic data pertaining to geologic map units. In other words, the only pronounced geochemical variations would be among rock types within geologic units--not within rock types. The occurrence of this kind of variation is a distinct possibility that will be examined further.

Drs. Ebens and Connor also describe special sampling of selected geologic materials in the State, such as Precambrian crystalline rocks in the St. Francois Mountains region, coals from western and northern Missouri, and other mineral commodities such as barite and ores of lead, zinc, and copper. They present a small amount of trace element data on Missouri coals taken from a previous study of the U.S. Geological Survey.

Since abandoning the Seventh Approximation system of soils classification as a framework for sampling the soils of the State (Tidball, 1971), Dr. Tidball has concentrated his investigations on parent material as related to chemical variability in soils. He is currently executing a sampling program which involves intensive sampling of soil profiles over a variety of parent material types including loess, glacial till, sandstones, and carbonate rocks. If it can be demonstrated that parent material is an important control on the trace element character of soils, we will have a much better understanding of how geologic and soils investigations should be coordinated in environmental geochemistry and will be better able to judge the degree to which soil characteristics can be inferred from geologic data.

Dr. Tidball is also overseeing the analytical program for the agricultural soil samples collected mostly by the Missouri Agricultural Extension Agents last year. All 1,140 of the samples have been scanned for mercury, and the results are given as symbols on a state map. The map shows no identifiable pattern of geographic variation across the State. Such patterns, if present, are either too subtle to be identified with the analytical method used, or are comprised of local variations that cannot be identified with the samples available. At least, there is no evidence to suggest that agricultural soils vary much in mercury content over broad regions of the State, even though the soils are underlain by a wide variety of geologic materials. Analytical determinations for other chemical elements in the 1,140 samples have been only partly completed, but preliminary summary statistics on the available data are given. Because the samples are being analyzed in a sequence that has been randomized with respect to the locations from which they were taken, the available data comprise a random subset of the whole, and it is not expected that the final summary statistics will be substantially different. The summary statistics indicate that the agricultural soils of Missouri are not greatly variable in composition and that they do not differ greatly from other soils of the eastern U.S. Geographic patterns of variation will be examined when the analytical work is completed, in the same manner as used to examine mercury.

Drs. Shacklette and Erdman, and Mr. Keith, have completed the first and second stages of their sampling program to investigate geochemical variability in uncultivated soils and native vegetation of the State. They plan to initiate a first stage sampling of cultivated plant crops this September. Comparison of their results, for uncultivated soils, from the first and second sampling stages, which were entirely independent, is quite encouraging because it shows that the estimations of variability arising from various sources are satisfactorily reproducible. Estimates of variability are important because they are necessary to determine the adequacy of the data and to plan efficient steps to accomplish the required improvement in the data. We are now satisfied that our estimates of variance components at various levels of the hierarchical sampling designs are adequate for our purposes. Most of the laboratory work on the native plants from the second sampling stage has been completed, but statistical examination of the data has not been started; and no results for native plants are given in the present report. For data on some native plants obtained in the first sampling stage, see the second report in this series (U.S. Geological Survey, 1970a, p. 36-42).

Shacklette, Erdman, and Keith present in this report some final estimates of the geochemical characteristics of the uncultivated soils of the State and show how these differ among the six vegetation-type areas. They also show the amount of geochemical variability in the soils within each of these areas. The data summaries for 4 elements (zinc, chromium, cobalt, and mercury) are presented on maps that show

at a glance the very broad features of the geochemical patterns in the uncultivated soils of the State. Data for these elements, and for others, indicate that some elements tend to be present in the soils in very different amounts from one vegetation-type area to another, whereas other elements are rather evenly distributed in the soils over the major part of the State. Maps for other elements will be given in forthcoming progress reports, but all of the basic data to be used are given here in tabular form. The logical next step in examination of the geochemical variability among the uncultivated soils and the native vegetation of Missouri would be to design and execute the third and fourth stages of the general sampling plan in order to describe the geographic patterns of geochemical variation within each of the six vegetation-type areas. However, two factors must first be considered: 1) the desirability of doing this from the viewpoint of the epidemiologist, and 2) the availability of resources with which to do it. The second factor can only be considered after careful consideration of the first.

Shacklette, Erdman, and Keith also present estimates of the degree to which elemental constituents in uncultivated soils correlate with each other. These estimates are important in the interpretation of the geochemical processes that control the abundance and distribution of the elements and in identifying groups of elements that display similar patterns of geographic variation.

Knowledge of the geochemical character of uncultivated soils is important in environmental studies because these soils support vegetation grazed upon by livestock and because these soils influence to some unknown degree the chemical characteristics of ground and surface waters. Also, understanding of the geochemical characteristics of uncultivated soils will be important in interpretation of the factors that have influenced the agricultural soils, particularly in judging the relative influences of natural geochemical variability and such artificial factors as cultivation and fertilization.

Mr. Feder has completed the first sampling stage in his investigation of the variability in the geochemical characteristics of groundwaters throughout the State and, because statistically significant differences were identified for all constituents among the major groundwater systems, has concluded that a second sampling stage may not be required. However, it was also found that the individual groundwater systems (geohydrologic units) vary in geochemical character to a significant degree over distances of several miles or more, and it would seem desirable to consider sampling to describe this within-unit variation. The cost of such a program appears prohibitive at the present time, however, and the consideration is being deferred until the possible epidemiological usefulness can be assessed. The program would consist of executing the third and fourth sampling stages of the general sampling program described in the following section of this report.

Feder's analysis of variance of the data on the groundwaters of the State shows that most of the geochemical variability is between geohydrologic units and between townships within these units. Only small variation occurs between wells within the same township or between water samples taken from the same well at randomized intervals over a period of several months. Except for the possibility of compositional changes in the groundwater over periods longer than several months, this indicates that the groundwater supplies within a township can be adequately characterized by the collection and analysis of relatively few samples and analyses, as a general rule. It also indicates that the laboratory methods being used in analysis of the water samples are, in general, entirely adequate for the purpose of describing geochemical variations over the State. It even raises the possibility that less precise methods may be more efficient to use if available and if the corresponding reduction in laboratory costs were sufficient.

Feder's table of mean concentrations and variability of chemical constituents in the groundwaters of Missouri, along with the maps showing the distributions of the various geohydrologic units throughout the State, should receive the immediate attention of epidemiologists of the Environmental Health Center in attempts to find broad scale correlation between epidemiological and geochemical factors.

GENERAL SAMPLING DESIGNS FOR SURVEYS IN ENVIRONMENTAL GEOCHEMISTRY

In a discussion of the objectives and plans for the geochemical survey of Missouri, given in the first reports of this series (U.S. Geological Survey, 1969, p. 1), it was pointed out that one important objective was to learn how to make such a survey most efficiently and, of course, in a way that will be useful and meaningful to the epidemiologist. We still have more questions than answers in this regard, but some phases of the problem appear to be very clearly defined now that we are approaching the final phases of the sampling program. The problems of efficiency of geochemical sampling designs and of stability (or reproducibility) in geochemical maps have not received proper attention in geochemistry. These problems have been of utmost concern in the Missouri program, partly because such a large area is involved and partly because we see a need for such concern in many other areas of earth science and in field geochemistry and petrology in particular.

The first normal inclination in attempting a geochemical survey of any region is to collect as many samples, from more or less equally spaced localities, as time and available laboratory resources allow. This approach is often valid and, indeed, has been used in the Missouri program in investigation of the agricultural soils. With 1,140 samples we have approximately one sample per 60 square miles of the State, and

there is no great concern here that the agricultural soils have been oversampled or that laboratory resources have been wasted. It is realized, on the other hand, that the data may be inadequate to describe the geographic patterns of geochemical variability that may be present, unless such variability is either very pronounced or on a very broad scale. We have developed the technique to determine the limitations that must be placed on the interpretation of the agricultural soil data, but have yet to apply it to this problem.

Even if we regarded the design used to sample the agricultural soils as appropriate to use in sampling other soils, rocks, vegetation, and water, the costs of both sampling and laboratory analysis would be entirely prohibitive. Sampling of the agricultural soils in this manner would also have been prohibitive without the assistance of the Missouri Agricultural Extension Agents. Alternatively, we have recognized within each of these media (rocks, soils, vegetation, and water) some previously defined or obvious categories, each of which is thought to be more or less geochemically distinct from one or more of the others. A first sampling stage, in each case, has served to determine whether or not this is true. In one case, it was found that the categories, in general, were not geochemically distinct, and alternative categories are being used; the problem has been described by Tidball (1971). The categories currently being used for sampling the various media of interest are as follows:

Rocks: lithologic types within major stratigraphic units. Examples are sandstones within the Pennsylvanian System and carbonate rocks within the Sauk (Cambro-Ordovician) Sequence.

Uncultivated soils: the B horizon within vegetation-type areas. Examples are B horizon soils of the Glaciated Prairie in the northern part of the State, or of the Oak-hickory-pine Forest area in the southeastern part of the State.

Vegetation: species within each of six vegetation-type areas. Examples are sumac within the Unglaciated Prairie of the west-central part of the State, or soybeans in the Glaciated Prairie area in the northern part of Missouri.

Water: ground or surface water within each of seven geohydrologic units. Examples are groundwater from glacial till in the northern part of the State, or surface water from strata of Cambrian and Ordovician ages in the southern part of the State.

The first sampling stage has been executed for each of these media. In each case the sampling was designed to determine 1) the degree to which the various categories are geochemically distinct and 2) the extent of sampling required to adequately define the geochemical differences among

them. In some cases it may be found that the various categories are sufficiently distinct so that no further sampling is required. In other cases the geochemical variations among the categories may be small, and the extent of sampling in the first stage may be judged inadequate. The first sampling stage, however, is designed in such a way that the results can be used to design an adequate and efficient second sampling stage. This was the case in the investigation of the uncultivated soils described by Shacklette, Erdman, and Keith in a later section of the present report. The basic product of their second sampling is a table showing the average concentrations of elements and the amount of geochemical variability in the B horizon soils of each of the six vegetation-type areas of the State. Next, statistically significant differences among these averages are identified, and the vegetation-type areas are grouped accordingly. Finally, a map is prepared for each chemical element showing the vegetation-type areas that are similar with respect to that element and those that are different. A composite mean concentration of the element is given for each group of similar vegetation-type areas. Maps of this kind show only the broadest features of the geochemical variation patterns over the State, but they are a logical first step in a geochemical survey of a broad region and can be produced at relatively little cost in both field sampling and laboratory analysis. The maps of Shacklette, Erdman, and Keith, for example, are based on only 300 samples--approximately one sample per 230 square miles of the State. If the same number of samples had been collected without regard to the geochemically distinct categories, and were taken simply from localities more or less equally spaced over the State, the resulting geochemical maps would likely fail to indicate the subtle differences among the soils of the different vegetation-type areas, and patterns displayed by the resulting maps would be unstable and misleading. The advantage of describing differences among soil categories, rather than among single points on a map, stems from the well-known statistical principle that the variance of an average of n independent individuals is one nth of the variance of the individuals.

While it is important to recognize the advantages of sampling by categories, and of presenting the results in the form of maps such as those given by Shacklette, Erdman, and Keith, it is also important to recognize the limitations of these maps. They discuss these limitations later in the present report. In brief, the maps show the categories having similar and significantly different averages; they do not show the patterns of geochemical variability within each category. The latter information is sacrificed in the interest of costs.

Where the need to show the patterns of geochemical variability within each category of the media being sampled can justify the costs, third and fourth stages of sampling are required. The third stage is needed to determine an efficient spacing among sampling localities and the number of samples required from each. The fourth stage, of course, is the execution of the final sampling plan designed on the basis of the results from stage three. It is possible that, in some cases, the same information

obtained from the third sampling stage may be obtained from the results of the first and second stages. If this is true, stage three may be unnecessary.

The general sampling plan for surveys of large regions in environmental geochemistry, therefore, as we presently see it, begins with the recognition of various categories of the sampling media (rocks, soils, vegetation, and water) that may be expected to be geochemically distinct. The sampling then proceeds in as many as 4 stages:

Stage 1: Preliminary sampling designed to determine the extent to which the categories are geochemically distinct, and to provide a basis for designing an efficient second stage sampling plan if this is necessary.

Stage 2: Final sampling to estimate mean concentrations, differences among categories, and the amounts of compositional variability within each of the categories. The extent of sampling and the sampling design are based on information obtained from stage 1 and are sufficient to adequately define the major differences among the categories.

Stage 3: Preliminary sampling to determine the sampling locality spacing that would be most efficient for describing the geochemical variation patterns within each category, and the number of samples required from each locality.

Stage 4: Final sampling to describe the geochemical patterns within each category. The sampling design is based on information obtained from stage 3, or, in some cases, from stages 1 and 2.

All 4 stages of this general sampling plan are not always required, and cost factors may make some of them prohibitive. However, it would not be reasonable to undertake stage 2 without having conducted stage 1, and stage 4 would be unreasonable without having conducted stages 1, 2, or 3. Stage 1 is being conducted in all phases of our geochemical survey of Missouri. Stage 2 has been found necessary in the survey of uncultivated soils and native vegetation, but it will not be required for groundwaters. Stage 2 may or may not be required for sampling of geologic units. At the present time, stages 3 and 4 are not being planned for any of the environmental media being investigated in the Missouri program.

Geochemical survey of geologic units
by R. J. Ebens and J. J. Connor

Present status.--Work on this phase of the Missouri studies during the report period consisted of two preliminary mineralogical studies, library research on and initial drafting of the geologic description section of the final report, and special sampling of the State's economic mineral deposits and Precambrian granitic rocks.

The designs used in sampling the geologic units and economic mineral deposits in Missouri are aimed at estimation of the characteristic compositions and chemical variability of the major stratigraphic and other rock units underlying the State and of the mineral deposits that are sufficiently widespread and compositionally unique to have a possibly significant effect on the chemical character of the environment. Some of the major stratigraphic units in Missouri are best exposed in neighboring states. Figure 1 shows the locations where the stratigraphic units were sampled within Missouri, as well as locations where samples of coal, lead-zinc-copper and barite deposits were collected. The numbers of samples of various types collected to date are summarized in table 1, where they are classified by type of material and geologic map unit in which the material occurs.

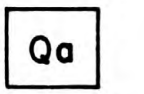
Relatively little of the laboratory work on the samples represented in figure 1 and table 1 has been completed. Some results were reported in previous progress reports in this series. It is anticipated that most of the analytical work will be completed during 1971.

Preliminary mineralogy.--Preliminary mineralogical studies have been completed on two of those groups of samples represented in table 1; sandstones from the Pennsylvanian map unit and loess. The mineralogy of the sandstones was studied in thin section using petrographic microscope techniques; and the loess, because of its fine grain size, was studied using X-ray diffraction techniques.

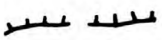
Pennsylvanian rocks crop out at the surface of the midcontinent region in a broad north-south trending belt which extends from southern Iowa to eastern Oklahoma and includes the northwestern one-third of Missouri (fig. 1). The part of the belt that occurs in Missouri is as much as 200 miles wide. The rocks in this belt dip gently to the west so that exposures to the west represent rocks stratigraphically above exposures to the east. Such confounding of the geographic and stratigraphic effects complicates efforts to understand the geologic nature of the compositional variability in the rocks, but does not preclude characterization studies of the near-surface geochemical environment of the area underlain by these rocks.

Generalized geologic map of Missouri
showing sampling localities

EXPLANATION



River alluvium



Dashed line indicates limits of significant amounts of loess deposits, hachures on side of significant deposits. In southern part of Missouri, significant amounts of carbonate residuum occur south of dashed line (● = loess sampling locality; ○ = residuum sampling locality; + = barite sampling locality).

Mostly limestone, shale, and sandstone (▲ = sampling locality) with minor amounts of coal (▲ = sampling locality).

Limestone, minor amounts of shale and sandstone (△ = sampling locality).

Limestone, dolomite, minor amounts of shale and sandstone (■ = sampling locality).

Dolomite, minor amounts of limestone, shale, and sandstone (□ = sampling locality); contains subsurface Pb-Zn-Cu ores (× = sampled mine).

"Granitic" rocks (scale too small to show sampling localities).

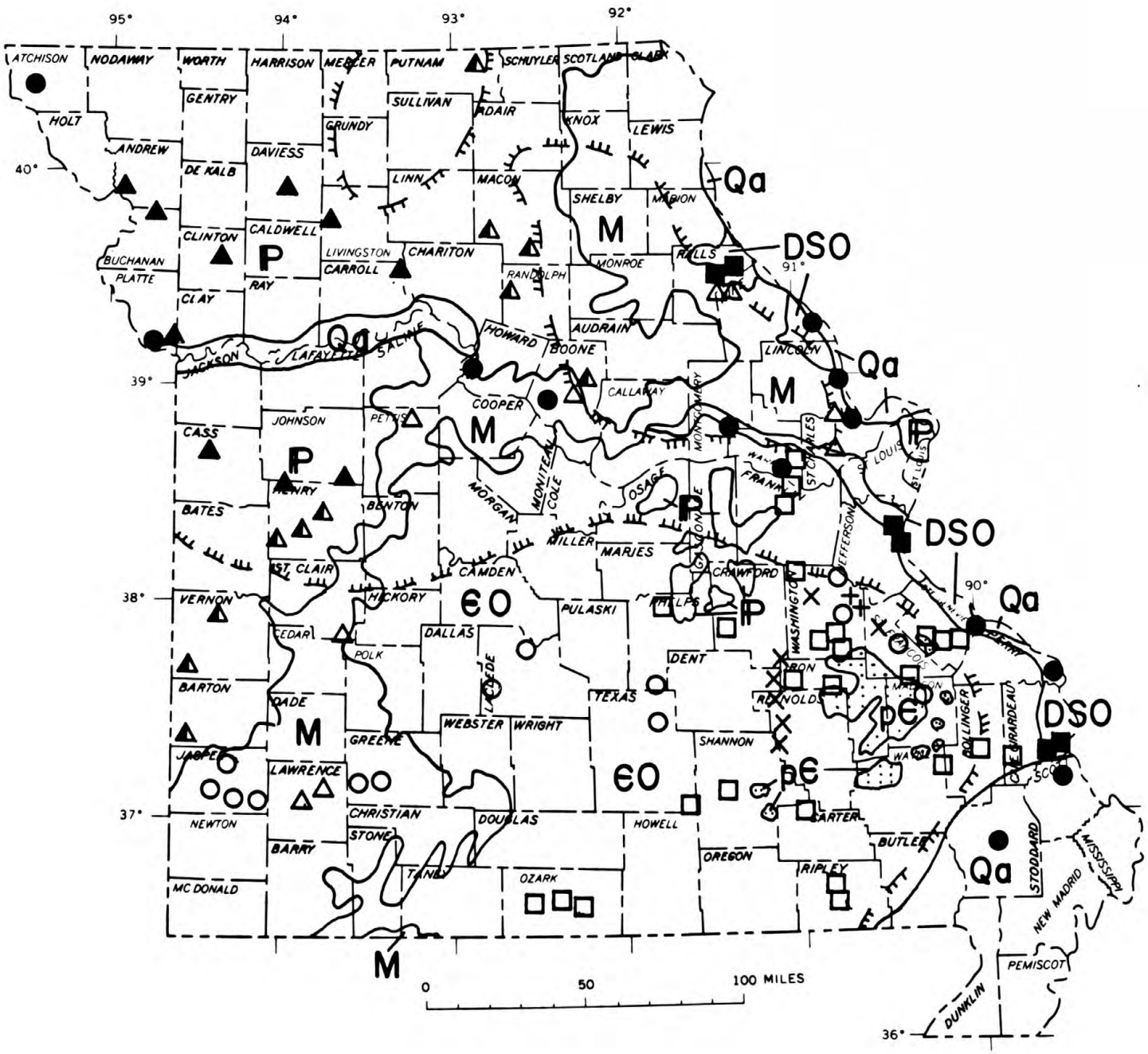


Figure 1.--Generalized geologic map of Missouri showing sampling localities.

[Adapted from American Association of Petroleum Geologists, 1966, and Geological Society of America, 1952]

Table 1.--Numbers of samples collected to date of various geologic materials, classified by type and by geologic map unit (figure 1) in which the material occurs.

Map unit	Type of material									
	Limestone and Dolomite (Ca, Mg-rich)	Sandstone and Chert (Si-rich)	Shale (Si, Al-rich)	Clay (Si, Al-rich)	Loess (Si, Al-rich)	Granite and Rhyolite (Si, Al-rich)	Lead-zinc-copper deposits	Barite deposits	Coal deposits	Total
Loess					26					26
Residuum				42[1/]				8		50
Pennsylvanian	32	32	32						30	126
Mississippian	40	24	22							86
Devonian, Silurian, and Upper Ordovician	12	4	6							22
Lower Ordovician and Cambrian	48	28	6				30			112
Precambrian						60				60
Total	132	88	66	42	26	60	30	8	30	482

1/ A sample of bedrock (limestone, dolomite, or sandstone) was collected at each of 28 localities where residuum was sampled. These 28 samples are not represented on this table.

The outcrop belt was sampled in surface exposures along four east-west traverses, in 1) northern Missouri and northeastern Kansas, 2) western Missouri and eastern Kansas roughly along Interstate 70, 3) northeastern Oklahoma near the Kansas border, and 4) eastern Oklahoma roughly along Interstate 44. The four traverses were selected so as to provide a sequence of exposures representing as near as possible a completely accessible cross section of the Pennsylvanian strata. For purposes of sampling, each traverse was divided into ten equal parts (deciles). Two deciles were selected at random within each traverse and divided into ten equal parts (percentiles). Two percentiles were selected at random, and two random specimens of sandstone were taken from each. In general, the two random specimens from the same percentile were taken from a single exposure. A total of 32 specimens of sandstone was collected.

The statistical model employed in the Pennsylvanian sandstone study is a hierarchical one and similar to that described in the third Missouri progress report (U.S. Geological Survey, 1970b, p. 5-10). It may be written:

$$X_{ijkl} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} + \delta_{ijkl}; \quad \begin{matrix} 1 \le i \le 4 \\ 1 \le j \le 2 \\ 1 \le k \le 2 \\ 1 \le l \le 2 \end{matrix} \qquad (1)$$

where X_{ijkl} is the concentration of the mineral in the lth specimen from the kth percentile exposure of the jth decile of the ith traverse. μ is the average concentration of the mineral in all Pennsylvanian sandstones in the area of study, α_i is the deviation of the ith traverse average from the grand average, β_{ij} is the deviation of the jth decile average from the ith traverse average, γ_{ijk} is the deviation of the kth percentile average from the jth decile average, and δ_{ijkl} is the deviation of the lth specimen (thin section) from the kth percentile average. According to this model, the total variability of the mineral, X, estimated as s_X^2, may be partitioned into four components of variance:

$$s_X^2 = s_\alpha^2 + s_\beta^2 + s_\gamma^2 + s_\delta^2 \qquad (2)$$

where s_α^2 represents the regional (large-scale geographic) variation among traverses from north to south over the belt of outcrop, s_β^2 represents variation along the traverses (large-scale stratigraphic variability), s_γ^2 represents the small-scale stratigraphic variation among percentiles, and s_δ^2 represents variation among specimens from a single exposure (sampling and analytical errors).

Mineral concentrations in the sandstones were estimated from analyses of thin sections cut from each specimen. Two hundred points were counted on each thin section under the petrographic microscope using a mechanical stage. The analytical error arising from this technique was not estimated separately, but minimal values may be approximated from the binomial

theory where the expected variance of a mean, s_a^2, based on n points is given by (Snedecor and Cochran, 1967, p. 207):

$$s_a^2 = \frac{p(100 - p)}{n} \qquad (3)$$

where p is the expected concentration of the mineral in percent. The estimate is minimal because the validity of equation (3) depends on a random selection of points from the thin section and conventional petrographic point-counting is a systematic process. The non-random distribution of mineral grains in rocks will in general result in an effectively smaller n and a larger analytical error than that given in (3).

The petrographic analysis demonstrates that the Pennsylvanian sandstone is composed predominantly of quartz but exhibits varying amounts of feldspar, rock fragments and mica, commonly set in a clay matrix and locally stained with secondary iron oxide cement. Carbonate cement was observed in seven of the 32 specimens. In the northern part of the outcrop belt, exposures of sandstone are scarce and sandstone represents probably less than five percent of the outcrop. In eastern Oklahoma, however, sandstone seems to be the predominant rock type, constituting in places up to 75 percent of the observed outcrops.

The analysis of variance of the Pennsylvanian sandstone mineralogy, based on the model in (1), is given in table 2. These results indicate that no significant compositional variation exists in these rocks on scales larger than the small-scale stratigraphic (between percentile) level. This level consists of specimens separated by a maximum of a few miles geographically and a maximum of a few hundred feet stratigraphically. Over half of the variance of all mineral constituents measured may be attributed to a combination of the small-scale stratigraphic effects with the total (sampling plus analytical) error effects. Although weak components of geographic (regional) variance may exist for quartz, feldspar, and clay matrix, they are not demonstrably significant at the 95 percent confidence level. Larger, though still insignificant, variance components for quartz and rock fragments appear at the large-scale stratigraphic level suggesting the possibility of variation across the outcrop belt. Such variation, of course, may be both geographic and stratigraphic.

Although the analytical error (s_a^2) is underestimated by an unknown amount, an interesting aspect of the total error (s_δ^2) is evident. The error in estimating mica concentrations, for example, appears to be virtually all analytical. This means that within a single exposure of the sandstone, mica tends to be distributed in an essentially uniform fashion. Similarly, at least half of the error for rock fragments and over a third for feldspar appears to be analytical.

Table 2.--Variance components and averages of mineral constituents in sandstones of Pennsylvanian age.

Measured property	Percent of total variance ascribed to different sampling levels				Arithmetic means (in percent)
	Total (sampling plus analytical) error[1/] (s_δ^2)	Stratigraphic variance		Geographic variance (s_α^2)	
		Small-scale (s_γ^2)	Large-scale (s_β^2)		
Framework Grains	25.2 (4.9)	44.7* [2/]	9.1	21.0	---
Quartz	18.8 (4.9)	31.7*	35.8	13.7	62.89
Feldspar	80.3 (31.3)	7.1	0	12.6	2.09
Rock fragments	21.0 (10.6)	44.7*	34.4	0	6.86
Mica	31.5 (25.3)	45.4*	23.0	0	1.68
Cement-matrix					
Clay matrix	7.9 (2.0)	64.3*	0	27.8	14.47
Carbonate cement	18.0 (1.4)	81.2*	0.7	0	4.20
Iron oxide cement	96.1 (3.5)	0	2.5	1.5	6.90

1/ Value in parentheses is minimal estimate of percent analytical error, s_a^2, from equation (3).
2/ * Indicates that the variance component at this level is significantly greater than zero at the 0.05 probability level.

Loess is a fine-grained, wind-blown deposit of sand, silt, and clay which is widespread over much of northern and eastern Missouri. The loess deposits were sampled in bluffs overlooking the Missouri and Mississippi Rivers where they attain their maximum thickness. The bluffs were arbitrarily divided into six segments, each approximately 100 miles in length. Along the west bank of the Mississippi River these segments are 1) Cape Girardeau to the Arkansas border, 2) Cape Girardeau to St. Louis, and 3) St. Louis to the Iowa border. Along the Missouri River the segments are 4) St. Louis to Jefferson City, 5) Jefferson City to Kansas City, on both sides of the river, and 6) Kansas City to the Iowa border on the east side of the river.

Within each of these segments, two random exposures (localities) of loess were selected, and from each locality two random specimens were collected in a vertical section. Each specimen was split into two parts and pulverized to approximately minus two microns. The resulting 48 bulk powders were X-rayed in a randomized sequence on a Norelco diffractometer using CuK alpha nickel-filtered radiation generated at 48 kilovolts and 20 milliamperes. A diffraction pattern, like that in figure 2, was recorded for each powder over the range $2\theta = 2^{o}$ to 60^{o} at a rate of 2^{o} per minute, and peak heights representing various minerals or mineral mixtures were measured in inches. Angular position in degrees 2θ of peak heights and their mineralogical interpretation are given in table 3.

The statistical model employed in the loess study is similar to that used in the Pennsylvanian sandstone study and may be written:

$$X_{ijkl} = \mu + \alpha_i + \beta_{jk} + \gamma_{ijk} + \delta_{ijkl}; \qquad \begin{matrix} 1 \le i \le 6 \\ 1 \le j \le 2 \\ 1 \le k \le 2 \\ 1 \le l \le 2 \end{matrix} \qquad (4)$$

where, in this case, X_{ijkl} is some particular peak height for a given mineral measured in the diffraction pattern of the lth split of the kth specimen from the jth locality in the ith segment. α_i represents the difference between the average peak height in the ith segment and the average height for all segments, μ. β_{ij} is the deviation of the average peak height in the jth locality from the mean of the ith segment, γ_{ijk} is the peak height of the kth specimen from the mean of the jth locality and δ_{ijkl} is the deviation of the lth split from the kth specimen. According to this model, the total observed variation in X, estimated as s_X^2, may be partitioned into four components of variance:

$$s_X^2 = s_\alpha^2 + s_\beta^2 + s_\gamma^2 + s_\delta^2 \qquad (5)$$

where s_α^2 represents the statewide geographic variation (differences among segments), s_β^2 represents small-scale geographic variance (differences among localities), s_γ^2 represents sampling variance (differences among specimens from a vertical exposure), and s_δ^2 represents analytical error.

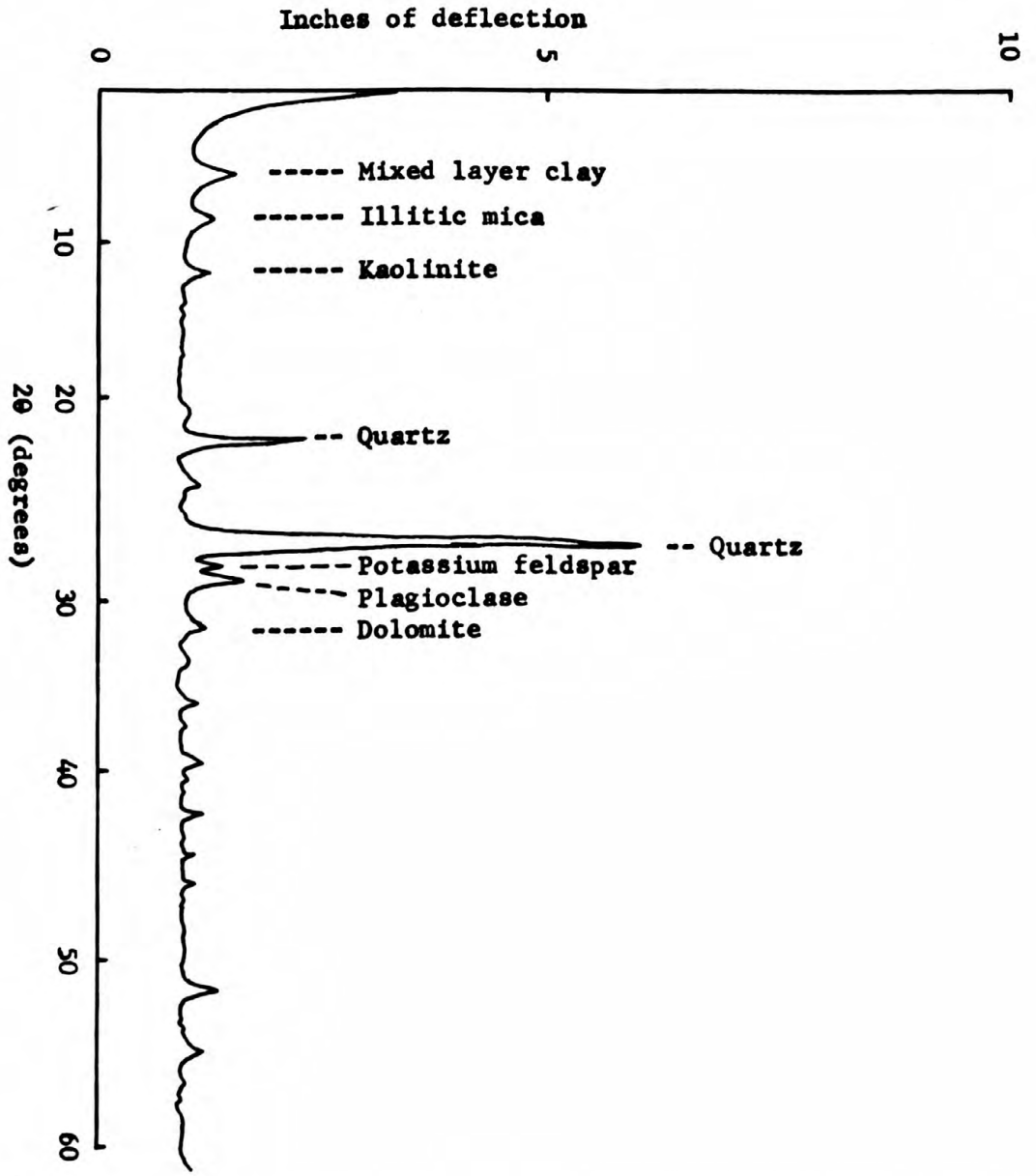


Figure 2.--X-ray diffraction pattern of a specimen of loess.

Table 3.--Interpretation of X-ray diffraction patterns of loess.

Angle 2θ (degrees)	Probable mineral(s)
6 - 8	Largely mixed layer clays, may include montmorillonite, chlorite, and illite-montmorillonite mix.
9.0	Illitic mica, may include mixed layer clays.
12.	Kaolinite, may include chlorite.
20.8	Quartz.
27.4	Potassium feldspar.
28.	Plagioclase.
31.	Dolomite.

Estimates of the relative magnitudes of the variance components are given in table 4. It is apparent from these estimates that over half of the total observed variation in peak heights may be ascribed to sampling and analytical error. Less than a fifth of the total observed variation can be ascribed to differences occurring on a statewide scale; that is, distances over a few hundred miles. Except for quartz and dolomite, even less variation is noted over shorter range distances of a few tens of miles. These results emphasize the apparent mineralogic homogeneity of Missouri loess across the State. However, the analytical error of the method is high, particularly for plagioclase, and the use of more precise measuring techniques may help in assessing the amount and nature of the statewide variation.

Geochemical implications of the results of both these preliminary studies are difficult to assess, because the mineralogical phases, except quartz and carbonate (including dolomite), tend to be complicated chemical mixtures. SiO_2, as the sole component of quartz, may exhibit a distribution similar to that shown by quartz in tables 2 and 4. But other common rock-forming oxides (Al_2O_3 or the alkalies and iron oxides, for example) generally occur in more than one mineral, as do the trace or minor elements, and their probable distribution in these materials remains speculative. Although important regional differences in the element content of either the Pennsylvanian sandstone or the loess cannot be ruled out, the large components of local mineral variation exhibited in both studies will probably be paralleled by a similarly large local variation in many, if not all, of the chemical elements. If this is borne out, then the average composition of loess given in the second Missouri progress report (U.S. Geological Survey, 1970a, p. 24-25) may be accepted as the expected composition of loess throughout the State.

Special sampling.--Sampling for the general geochemical survey of geologic units has been concentrated to date in the broad bedrock units or widespread surficial geologic materials which, collectively, are the major geological constituents and element sources of the State's natural geochemical environment. During the report period, a minor amount of special sampling was undertaken in a number of geographically restricted units which nevertheless may be highly important element sources. These units are the Precambrian crystalline rocks of the St. Francois Mountains region and deposits of several important mineral commodities throughout the State.

Two major subdivisions of exposed Precambrian igneous rocks in southeastern Missouri (extrusive rhyolitic rocks and intrusive granitic rocks) were each sampled at fifteen randomly selected sites using the Precambrian geologic map of Tolman and Robertson (1969, pl. 1). Two specimens were collected at each site, giving a total of 60 specimens.

Table 4.--Components of variance in the mineralogic data on loess as determined from peak heights on X-ray diffractograms.

Mineral	Percent of total variance ascribed to different sampling levels			
	Analytical error (s^2_δ)	Sampling error (stratigraphic) (s^2_γ)	Geographic variance	
			Small-scale (s^2_β)	Statewide (s^2_α)
Mixed-layer clay	35.7	41.0* 1/	4.8	18.5
Illitic mica	33.9	46.5*	0	19.6
Kaolinite	51.7	35.9*	0	12.4
Quartz	34.0	21.5*	44.5*	0
Potassium feldspar	57.2	37.4*	0	5.4
Plagioclase	73.1	19.1	0	7.9
Dolomite	3.2	54.0*	42.8	0

1/ * Indicates that the variance component at this level is significantly greater than zero at the 0.05 probability level.

The collection of these samples means that a preliminary sample set has now been obtained from all major geologic units in the State except glacial till in the northern part of the State and the limited Cenozoic deposits of the Mississippi Delta region.

Special sample sets of three mineral commodities produced in Missouri were also collected. These sample sets comprise 30 specimens of coal from 11 operating fields in northern and western Missouri, eight samples of barite concentrate from four milling sites in southeastern Missouri, and 30 samples of Pb-Zn-Cu ore and concentrate from seven mining and milling operations, also in southeastern Missouri. These materials are of special environmental interest because of their unusually high concentrations of particular elements, some of which may have significance in epidemiological studies. By the processes of mining, milling, and industrial use they are being introduced into the environment in large quantities, and a survey of their total element content seems desirable.

Zubovic and others (1967, table 6) have published data on the minor element content of five Missouri coal beds. Their averages, in parts per million of bulk coal, are reproduced here in table 5 along with estimates of the average concentrations of the elements in shale, a rock type closely associated with coal and its depositional regime. These data suggest that bulk coal contains up to 15 times as much Ge and up to 6 times as much Mo as shale but noticeably less of the other elements. Nevertheless, the widespread transportation and burning of coal probably results in the potential contact of most of these amounts to plants and animals whereas the metals in shale are much less available for such contact. Zubovic and others (1967, p. 25-26) also note that weathered coal appears to contain appreciably more Be, Ti, V, Cr, Co, Ni, Cu, Ga, Y, and La and less Zn, Ge, and Sn than unweathered coal. This information suggests that, even if natural oxidation of coal should result in a greater availability of these metals, most of them apparently tend not to be released into surface waters. The oxidation process itself may not be materially distributing the metals. Until more is known about the effects of weathering, estimates of the minor element contents of coals should be obtained on samples from fresh exposures.

Table 5.--Trace element concentrations in five composite samples of Missouri coals.
[All averages in parts per million, except as noted.]
(From Zubovic and others, 1967, table 6)

Coal bed	Ash (percent)	Be	B	Ti	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	Mo	Sn	Y	La
Bevier[1/]	8.01	3.1	76	290	16	9.6	3.8	14	10	< 100	3.9	8.2	2.2	0.78	15.0	< 30
Bevier[2/]	5.41	2.6	100	220	13	13	3	13	14	< 100	4.2	24	3.8	< 10	7.7	< 30
Mulky[3/]	7.09	3.4	110	310	71	61	6.6	23	22	< 100	2.6	11	16	< 10	12	< 30
Tebo[4/]	16.72	.53	61	250	39	22	3	40	12	< 100	4.3	13	12	< 10	10	< 30
Bandera[5/]	13.50	1.4	25	430	27	31	4.7	16	16	< 100	6	23	2.5	< 10	10	< 30
Average[6/] for shales		3	100	4600	130	90	19	68	45	95	19	1.6	2.6	6	26	92

1/ Sample collected from Bevier Mine, Bevier Coal Co., Macon County, Missouri.

2/ Sample collected from south pit of the Bevier Mine, Bevier Coal Co., Macon County, Missouri.

3/ Sample collected from north pit of the Bevier Mine, Bevier Coal Co., Macon County, Missouri.

4/ Sample collected from the Power Coal Co. Mine, 2 miles north of Germantown, Henry County, Missouri.

5/ Sample collected from the Tiger Mine, Sinclair Coal Co., near Hume, Bates County, Missouri.

6/ From Turekian and Wedepohl, 1961, table 2.

Geochemical survey of soils
by R. R. Tidball

Present status.--The study of Missouri soils is currently divided into two activities--analysis and interpretation of soil specimens (agricultural soils) collected by the Missouri Agricultural Extension Agents and collection of soil specimens to evaluate the influence of parent material on soil composition.

Agricultural soils.--The laboratory work on the sample set of 1,140 agricultural soils has been only partly completed (except for mercury), and the results shown in table 6 are, therefore, preliminary. However, it is not expected that final estimates of geometric mean concentrations and geometric deviations will change substantially from these preliminary estimates because the specimens analyzed to date are a randomly selected subset of the entire sample suite. The estimates of the mean concentration of mercury and the variance of mercury are based on scanning of the total sample set.

The calculation of a mean concentration based on the whole sample set (grand mean) is thought to be useful to the epidemiologist in that it establishes a point of reference, thereby defining the most typical concentration. Thus, future analyses may be put into proper perspective by classifying specimens as high, low, or normal. The grand mean does not, however, necessarily characterize any limited geographic locality within the State of Missouri, but rather the State as a whole.

The estimate of the deviation about the mean is perhaps even more important than the mean itself. This estimate provides a measure of the variability in concentration that can be expected within the population of soils, and it also provides a basis for determining the reliability in the estimate of the mean.

The detection ratio (specimens with measurable concentration compared to number of specimens examined) is a crude measure of the adequacy of an analytical method to detect concentrations throughout the normal range of concentrations which occur in these materials. For example, the detection ratios shown in table 6 for cadmium and tin show that the analytical methods used are not sufficiently sensitive to detect the very low concentrations in most specimens.

Estimates of mean concentrations for most elements in the Missouri agricultural soils are in the same order of magnitude as the corresponding averages of 371 soil specimens collected extensively from the United States east of the 97th meridian (Shacklette and others, 1971). However, the concentrations of barium, manganese, phosphorus, potassium, and sodium are about twice as high in Missouri soils as in soils of the eastern U.S.,

Table 6.--Preliminary estimates of the mean chemical composition and variation of selected agricultural soils of Missouri. [The means are estimated by a method which also considers censored concentrations below the lower limit of analytical sensitivity. Geometric mean (GM) and geometric deviation (GD) are the antilogarithms of the mean logarithm and standard deviation of the logarithms, respectively. Detection ratio is the number of specimens with measurable concentrations compared to the number of specimens examined.]

Element	GM	GD	Detection Ratio	Element	GM	GD	Detection Ratio
Percent							
SiO_2	76[1/]	5.6[2/]	480:480	Na_2O	0.65	1.7	720:720
Al_2O_3	7.7	1.4	480:480	K_2O	1.7	1.3	480:480
Total Fe as Fe_2O_3	3.0	1.4	480:480	TiO_2	0.58	1.3	480:480
MgO	.27	1.6	720:720	C-carbonate	0.03	3.0	720:720
CaO	.47	2.0	464:480	C-organic	1.2	1.5	720:720
				C-total	1.3	1.5	720:720
Parts per million							
B	32	1.3	475:480	Nd	62	1.2	300:478
Ba	600	1.4	480:480	Ni	15	1.6	478:480
Be	0.8	1.4	234:480	P	600	1.6	472:480
Cd	1.8	-	5:720	Pb	20	1.4	480:480
Ce	110	1.3	165:480	Sc	8	1.4	456:480
Co	10	1.5	480:480	Se	0.4	2.0	450:480
Cr	55	1.4	480:480	Sn	19	-	9:480
Cu	13	1.5	480:480	Sr	110	1.6	480:480
Ga	11	1.5	462:480	V	69	1.5	480:480
Hg	0.039	1.8	1127:1140	Y	32	1.3	479:480
La	42	1.4	478:480	Yb	3	1.3	478:479
Li	22	1.3	720:720	Zn	50	1.5	720:720
Mn	740	1.8	480:480	Zr	320	1.5	480:480
Nb	7	1.4	136:480				

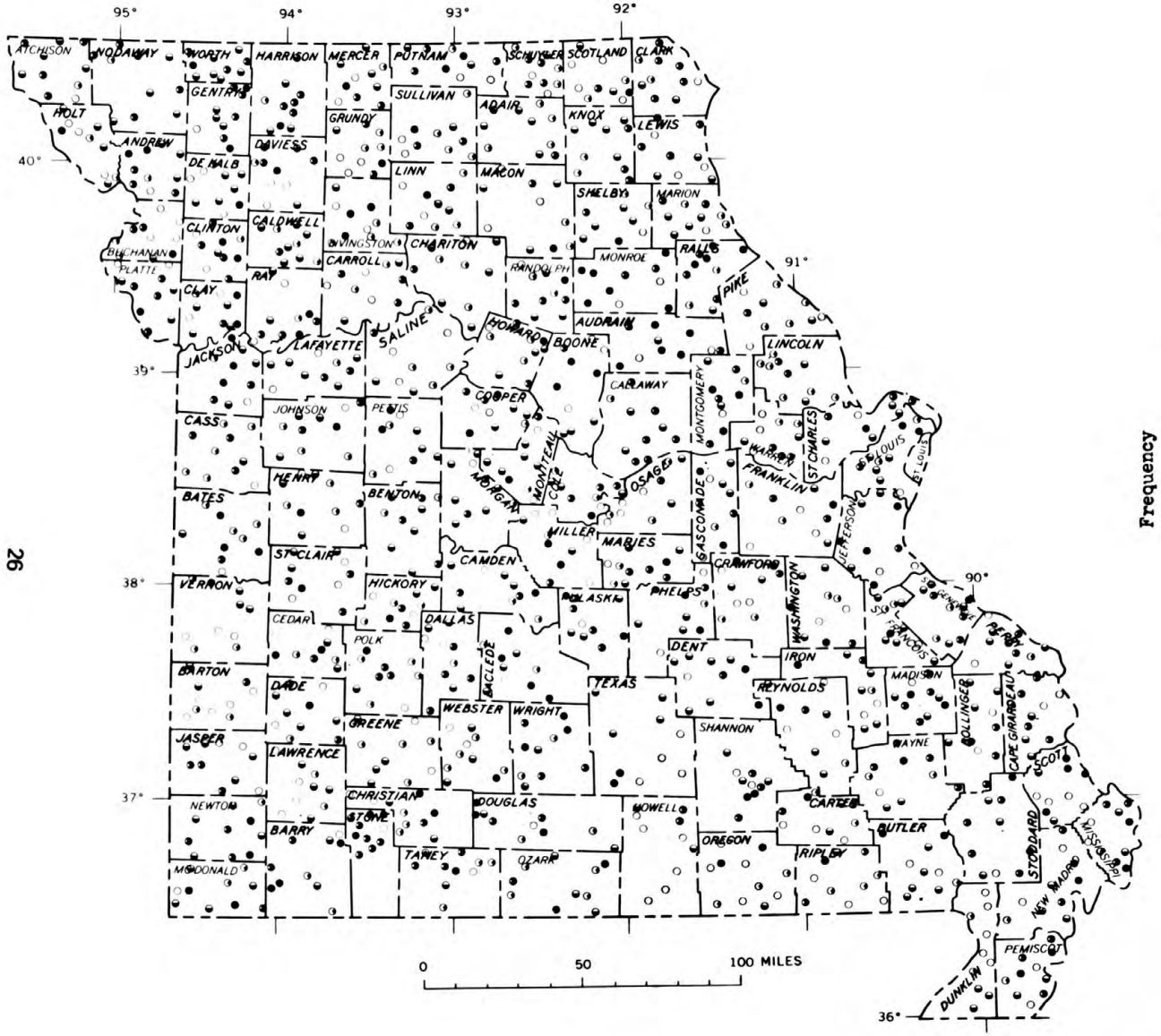
1/ Arithmetic mean rather than geometric mean.

2/ Standard deviation rather than geometric deviation.

and niobium is about one-half that of eastern U.S. soils. Estimates of the geometric deviation are generally less than 2.0, indicating that concentrations of most elements in these soils are not highly variable.

All of the 1,140 specimens have been scanned for mercury, and the results are shown in figure 3 as a distribution map. The frequency distribution, which tends toward a lognormal form, has been divided into 5 frequency classes, each containing approximately 20 percent of the total area under the frequency curve. Symbols shown on the map at the points of collection correspond to the appropriate frequency class that contains the observed concentration. The open circle and the full dot correspond to the lowest and highest frequency classes, respectively. The results do not demonstrate a geographic pattern that would suggest anomalous areas of mercury concentration; rather, the pattern appears to be without order--essentially random. This apparent randomness is the result of both the degree of reproducibility of the analytical method and the very small variation in mercury among sampling localities. The analysis of variance of duplicate laboratory analyses shows that 57 percent of the total variance is due to the analytical method. Differences in mercury concentration among soils developed on diverse parent materials, such as glacial materials in the northern half of the State, the very old carbonate-rock-residuum landscape of the Ozark Plateau, or the Mississippi River floodplain of southeast Missouri, if present, cannot be demonstrated with the data presently available and may be so small as to be unimportant epidemiologically.

Parent material study.--Collection of soil specimens for the study of soil parent materials (U.S. Geological Survey, 1970b, p. 16) is now in progress and will be finished during the summer of 1971. Concurrent collections of earthworms are being made for Dr. Bill Lower, Geneticist with the Environmental Surveillance Center, University of Missouri. Dr. Lower's study will attempt to investigate the composition of animal tissue as a function of the composition of the soil habitat.



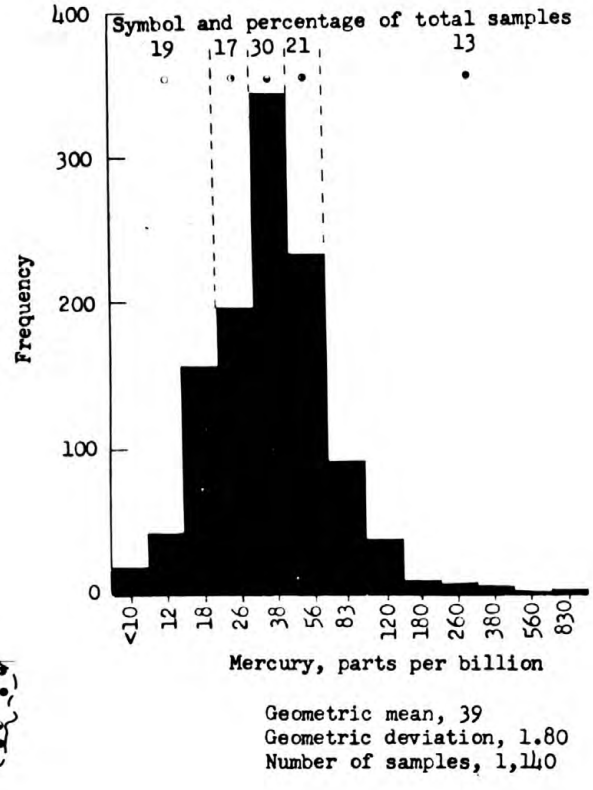


Figure 3.--Concentrations of mercury in 1,140 selected samples of Missouri soils.

Geochemical survey of vegetation
by H. T. Shacklette, J. A. Erdman, and J. R. Keith

Present status.--The major native plant and uncultivated soil sampling in the natural vegetation-type areas has been completed. In September, 1971 we plan to search for some small outlier prairie areas that were mapped by Küchler (1964) but have not been sampled, and also to examine an isolated area of Oak-Hickory-Pine Forest in southwestern Missouri (fig. 4). If these areas are judged likely to be geochemically distinct, a limited sampling program will be undertaken as an adjunct to the major study. We plan also in September to sample cultivated crop plants and associated soils according to a sampling plan similar to, but not as extensive as, the plan used for native vegetation and uncultivated soils.

Chemical analyses except for iodine, fluorine, and arsenic, have been completed for all samples of uncultivated soils, and statistical analyses of the results are presented in this report. Chemical analyses of the native plant samples are approximately 40 percent complete.

Validation of the sampling plan for soils in the vegetation-type areas.--Comparison of results for preliminary and final sampling of the uncultivated soils enabled us to evaluate the theoretical basis of the sampling plans as applied to this investigation--the purpose of which is to define the geochemical differences among the soils from different vegetation-type areas in Missouri. The preliminary soil sampling plan, conducted in the summer of 1969 (U.S. Geological Survey, 1969, p. 44-45), involved the collection of 2 randomly-selected soil samples in each of 5 randomly-selected 7½-minute quadrangles in each of the 6 vegetation-type areas. The 60 soil samples obtained were analyzed spectrographically and the results were used to estimate variance components at the three levels of the sampling design. Consideration of the between-vegetation-type variance in comparison with the variance within vegetation types indicated that the sampling of 5 sites in each of 10 quadrangles in each of the 6 vegetation-type areas would constitute the most efficient final sampling plan. This plan was executed in the summer of 1970 and resulted in the collection of 300 B-horizon soil samples.

Chemical and spectrographic analyses of samples from the preliminary and the final soil sampling plans were evaluated by an analysis of variance technique in which variance components between vegetation types, quadrangles, sites, and chemical analyses were estimated. These components, and the percentage of the total variance that each component comprises, are presented in table 7. Samples from the preliminary sampling plan were analyzed only by semi-quantitative spectrographic methods. Only those soil constituents for which we have analyses of samples from both the preliminary and the final sampling plan are included in the table. Estimates of the analytical precision for samples of the preliminary study are based on measures of this precision in analyzing Missouri soils as determined by R. R. Tidball (written communication, 1970).

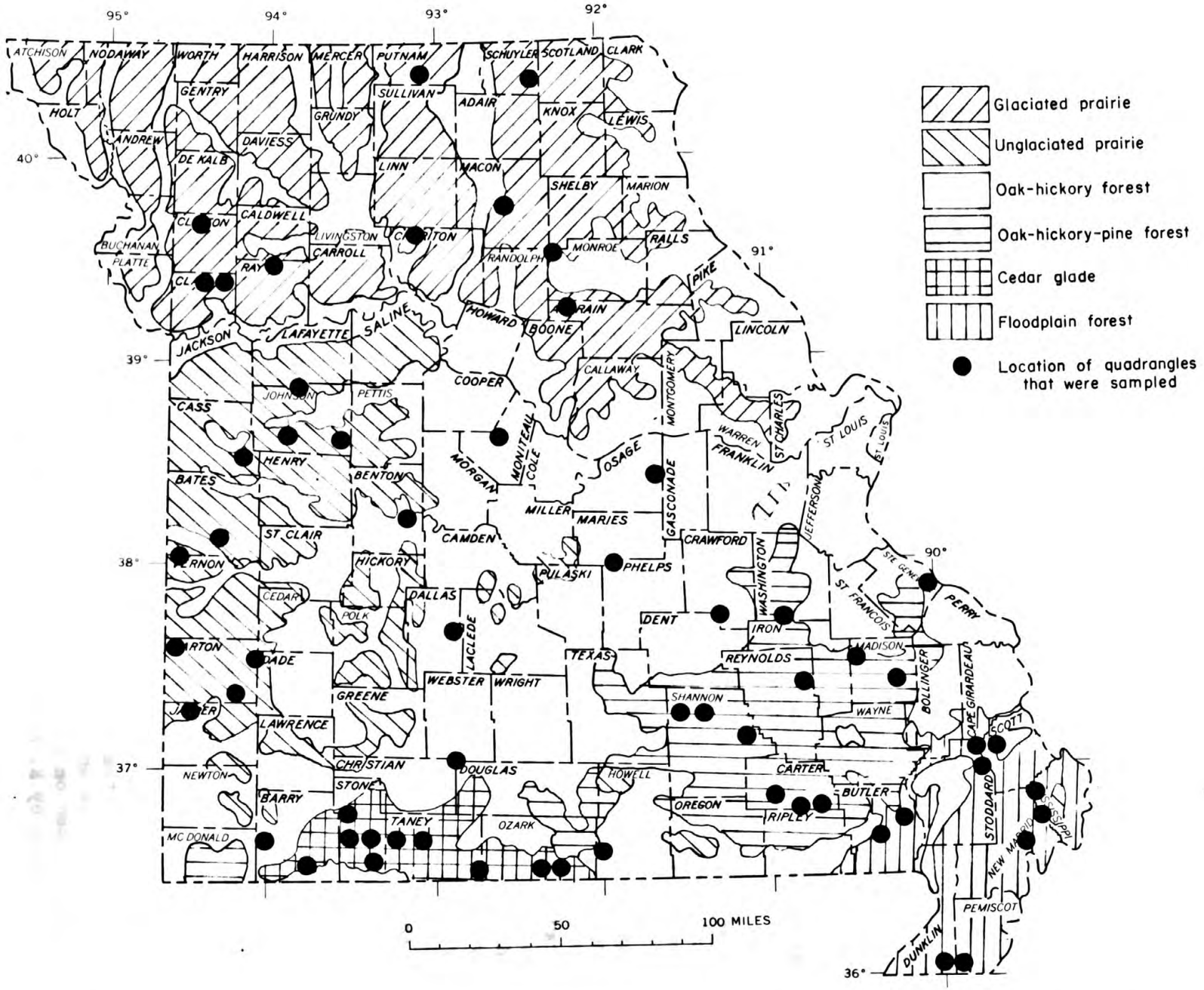


Figure 4.--Vegetation types in Missouri, and location of quadrangles in which plants and soils were sampled.

The generally close accord between variance components at all levels of the sampling design is apparent in table 7. The logarithmic variances for strontium in soils at the vegetation-type level, for example, are 0.0301 and 0.0305 from the preliminary and final sampling programs, respectively. The closeness of the variance estimates for this and other chemical constituents of the soils, obtained from sampling experiments that were entirely independent, verifies the validity of the estimates. Without valid estimates of the variance components it would be impossible to determine the minimum degree of sampling required to accomplish the major goal of the investigation--the characterization of soil geochemistry in the six vegetation types in Missouri. This study provided the first actual field test of the theoretical basis used in designing the sampling programs for the Missouri geochemical projects.

The percent of variance that each level of the sampling design (table 7) contributes to the total variance indicates that, for most constituents, the greatest variability occurs between vegetation types (the largest scale of the design), and between sites (the smallest scale of the design). Nearly all of the variance components between vegetation types are statistically significant, and the geochemical distinctiveness of the different vegetation-type soils, therefore, is adequately demonstrated. From the standpoint of sampling efficiency, sampling more quadrangles would not be advisable in seeking to more closely define the geochemical differences among the soils of the vegetation types because the least variability lies at the quadrangle level. Further definition of the distinctiveness of vegetation-type soils could be achieved, if desired, by taking more samples within each quadrangle at a relatively small increase in field expenses.

Analytical error is shown in table 7 to be a major source of variability for only a few soil constituents. This variability cannot be reduced by any kind of modification of the sampling plan.

Average compositions and compositional variability of soils classified by vegetation-type area.--Results of chemical and spectrographic analyses of soils from the six vegetation types in Missouri (fig. 4) that were collected in the final sampling program, expressed as geometric mean concentrations, geometric deviations, and detection ratios for each constituent, are given in table 8. The highest and lowest mean concentrations for each constituent among the six vegetation-type areas are marked in this table for easy identification.

Some variation in the concentrations of chemical constituents of Missouri soils, among the vegetation-type areas, is apparent by inspection of table 8. For example, relatively high concentrations of many elements occur in the soils of the Glaciated Prairie, the Unglaciated Prairie, and the Cedar Glades, and the lowest concentrations of many elements occur in soils of the Oak-Hickory-Pine Forest.

Table 7.--Comparison of logarithmic variance components derived from analysis of soils collected in the preliminary (upper value for each element, n = 60) and the final (lower value for each element, n = 300) sampling programs in Missouri

[*, significantly greater than zero at the 0.05 probability level.]

Element	Total $\log_{10}$ variance	Variance components							
		Between vegetation types		Between quadrangles		Between sites		Between analyses	
		Component	Percent of total	Component	Percent of total	Component	Percent of total	Component	Percent of total
Al	0.0753	0.0386*	51	0.0044	6	0.0315	42	0.0008	1
	.0643	.0223*	35	.0090*	14	.0266	41	.0064	10
B	.0359	0	0	.0036	10	.0213	59	.0110	31
	.0260	.0026*	10	.0014	5	.0081	31	.0139	53
Ba	.0588	.0177*	30	.0063	11	.0292	50	.0056	9
	.0693	.0212*	31	.0163*	24	.0187	27	.0131	19
Ca	.4278	.2627*	61	.0046	1	.1555	36	.0050	1
	.3086	.1768*	57	.0169*	6	.0979	32	.0170	5
Co	.0574	.0064	11	.0044	8	.0402	70	.0064	11
	.0575	.0044*	8	.0044*	7	.0366	64	.0122	21
Cr	.0344	.0097*	28	.0044	13	.0124	36	.0079	23
	.0485	.0172*	36	.0055*	11	.0171	35	.0087	18
Cu	.0640	.0085	13	.0270*	42	.0171	27	.0114	18
	.0814	.0091*	11	.0090*	11	.0285	35	.0349	43
Fe	.1022	.0567*	56	.0014	1	.0435	42	.0006	1
	.0629	.0241*	38	.0022	4	.0258	41	.0109	17
Ga	.0718	.0363*	51	.0094	13	.0211	29	.0050	7
	.0679	.0282*	42	.0069*	10	.0203	30	.0125	18
K	.0667	.0275*	41	.0093	14	.0306	46	.0003	0
	.0587	.0178*	30	.0119*	20	.0204	35	.0086	15
Mg	.2228	.1263*	57	.0119	5	.0683	31	.0163	7
	.2306	.0957*	42	.0219*	9	.0964	42	.0166	7
Mn	.1751	.0167*	10	0	0	.1444	82	.0140	8
	.1320	.0153*	12	.0160*	12	.0781	59	.0226	17
Ni	.0647	.0119*	18	.0193*	30	.0226	35	.0109	17
	.0983	.0286*	29	.0156*	16	.0442	45	.0099	10
Pb	.0253	.0080*	32	.0028	11	.0105	42	.0040	16
	.0347	.0026*	7	.0034*	10	.0205	59	.0082	24
Sc	.0575	.0314*	55	.0030	5	.0208	36	.0023	4
	.0523	.0206*	40	.0065*	12	.0168	32	.0084	16
Sr	.0803	.0301*	38	.0166*	21	.0290	36	.0046	6
	.0681	.0305*	45	.0114*	17	.0107	16	.0154	23
Ti	.0496	.0198*	40	.0041	8	.0202	41	.0055	11
	.0382	.0124*	32	.0044	12	.0156	41	.0058	15
V	.0742	.0345*	47	.0062	8	.0275	37	.0060	8
	.0676	.0287*	42	.0074*	11	.0264	39	.0052	8
Y	.0348	.0112*	32	0	0	.0196	56	.0040	12
	.0435	.0060	14	.0102	23	.0212	49	.0061	14
Zr	.1020	.0420*	41	0	0	.0506	50	.0094	9
	.0748	.0255*	34	.0108*	14	.0095	13	.0291	39

Table 8.--Mean chemical composition and chemical variation of B-horizon soils or lithosols from major vegetation-type areas in Missouri

[Dry soil used for chemical analyses; soil slurry used for pH determinations. GM, geometric mean; GD, geometric deviation; Ratio, number of samples in which detected:total number of samples; - - -, no data available. Tests using analysis of variance techniques indicated that differences in mean concentrations of pH and each element (except Be, Ce, Mo, Nb, and Nd) and oxide in soils from the vegetation-type areas having the highest and lowest concentrations were significant at the 0.05 probability level; these highest and lowest concentrations are shown in **boldface** and *italic*, respectively.]

Oxide, element, or pH	Vegetation type: Floodplain Forest			Glaciated Prairie			Unglaciated Prairie			Cedar Glade			Oak-hickory Forest			Oak-hickory-pine Forest		
	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio
	Percent																	
SiO_2 [1/]	76	7.70	50:50	69	5.06	50:50	73	6.82	50:50	*62*	17.4	50:50	83	7.43	50:50	**87**	5.68	50:50
Al_2O_3	8.3	1.29	50:50	**11**	1.21	50:50	8.9	1.34	50:50	6.0	1.42	50:50	5.1	1.47	50:50	*4.1*	1.63	50:50
Total Fe as Fe_2O_3	3.0	1.69	50:50	5.0	1.26	50:50	**5.0**	1.53	50:50	2.7	1.43	50:50	2.7	1.43	50:50	*2.2*	1.51	50:50
MgO	.52	1.80	50:50	.89	1.38	50:50	.58	1.57	50:50	*1.4*	3.06	50:50	.30	2.25	50:50	*.18*	1.67	50:50
CaO	.59	1.75	50:50	.54	1.36	50:50	.33	1.79	49:50	**2.4**	4.52	49:50	.21	2.80	46:50	*.091*	2.44	28:50
Na_2O	**.84**	1.65	50:50	.67	1.45	50:50	.51	1.62	50:50	*.17*	1.70	50:50	.38	2.01	50:50	.26	1.86	50:50
TiO_2	.43	1.51	50:50	.62	1.30	50:50	**.65**	1.34	50:50	*.32*	1.43	50:50	.58	1.44	50:50	.55	1.61	50:50
K_2O	2.0	1.14	50:50	1.8	1.28	50:50	1.6	1.45	50:50	**2.0**	1.50	50:50	1.3	1.61	50:50	*1.0*	1.96	50:50
P_2O_5	.16	1.86	49:50	.075	1.58	44:50	.086	1.56	47:50	*.19*	1.73	50:50	.076	1.88	40:50	**.070**	1.67	42:50
Total C	.98	1.93	50:50	.94	1.54	50:50	1.1	1.44	50:50	**4.2**	1.79	50:50	1.1	1.72	50:50	*.80*	1.67	50:50
Carbonate C	.046	3.06	45:50	.055	2.95	44:50	**.046**	3.34	42:50	*.40*	8.43	47:50	.054	4.14	44:50	.055	3.11	45:50
Organic C	.89	2.09	50:50	.83	1.69	50:50	.98	1.48	50:50	**2.8**	1.64	50:50	.96	1.69	50:50	*.70*	1.81	50:50
	Parts per million																	
B	29	1.44	46:50	33	1.38	49:50	35	1.40	50:50	*27*	1.48	43:50	**39**	1.41	49:50	32	1.43	49:50
Ba	**660**	1.43	50:50	560	1.46	50:50	490	1.58	50:50	*250*	1.61	50:50	390	1.78	50:50	340	1.96	50:50
Be	.99	1.46	33:50	1.2	1.29	46:50	1.3	1.27	47:50	*.88*	1.47	27:50	.77	1.42	20:50	.77	1.47	21:50
Ce	*<150*	- - -	0:50	97	1.36	11:50	110	1.34	16:50	*<150*	- - -	5:50	78	1.45	6:50	*<150*	- - -	2:50
Co	**8.3**	1.72	50:50	11	1.55	50:50	**14**	1.83	50:50	9.5	1.48	50:50	10	1.71	49:50	9.5	1.89	50:50
Cr	39	1.80	50:50	**66**	1.15	50:50	65	1.23	50:50	42	1.51	50:50	43	1.45	50:50	**30**	1.67	50:50
Cu	15	1.99	50:50	**24**	1.66	50:50	18	1.63	50:50	17	1.94	50:50	13	1.99	50:50	**12**	1.88	50:50
Ga	12	1.53	50:50	**19**	1.40	50:50	**14**	1.51	50:50	11	1.64	47:50	8.4	1.54	48:50	*5.9*	1.92	37:50
Hg	.057	2.07	50:50	.068	1.70	50:50	**.046**	1.76	50:50	*.36*	2.39	50:50	.055	1.91	50:50	**.045**	2.05	50:50
La	32	1.24	46:50	39	1.35	50:50	**45**	1.37	50:50	33	1.36	45:50	35	1.37	46:50	*30*	1.31	40:50
Li	20	1.63	50:50	**32**	1.21	50:50	29	1.33	50:50	23	1.55	50:50	18	1.33	50:50	*15*	1.41	50:50
Mn	710	2.72	49:50	**430**	2.25	50:50	780	2.29	50:50	**1,200**	1.57	50:50	730	2.16	50:50	660	2.09	50:50
Mo	*<3*	- - -	1:50	*<3*	- - -	4:50	*<3*	- - -	1:50	*<3*	- - -	3:50	*<3*	- - -	2:50	*<3*	- - -	1:50
Nb	5.8	1.38	7:50	7.9	1.24	19:50	8.1	1.26	22:50	*<10*	- - -	1:50	8.0	1.38	22:50	7.9	1.36	21:50
Nd	46	1.36	11:50	60	1.21	27:50	61	1.18	30:50	37	1.55	8:50	47	1.35	12:50	36	1.47	5:50
Ni	19	1.65	50:50	23	1.49	50:50	20	1.88	49:50	**23**	2.31	49:50	12	1.82	47:50	*8.8*	1.75	47:50
Pb	19	1.56	49:50	19	1.31	50:50	24	1.50	50:50	**25**	1.52	50:50	23	1.50	50:50	*18*	1.64	49:50
Sc	7.1	1.58	42:50	**12**	1.34	50:50	10	1.33	50:50	6.8	1.59	43:50	5.4	1.49	37:50	*4.7*	1.78	30:50
Se	.31	2.78	42:50	**.73**	2.11	49:50	.67	1.64	50:50	*.31*	2.10	46:50	.31	1.90	48:50	**.27**	2.01	46:50
Sr	**120**	1.32	50:50	120	1.35	50:50	95	1.51	50:50	72	1.51	50:50	66	1.66	50:50	*42*	1.90	50:50
V	64	1.87	50:50	**110**	1.34	50:50	92	1.39	50:50	59	1.58	50:50	53	1.48	50:50	*37*	1.70	50:50
Y	23	1.63	48:50	30	1.30	50:50	**37**	1.35	50:50	22	1.79	49:50	27	1.50	50:50	*22*	1.69	49:50
Yb	2.1	1.56	48:50	3	1.27	50:50	**3.4**	1.42	49:50	*2*	1.66	49:50	2.8	1.44	50:50	2.4	1.69	50:50
Zn	54	1.67	50:50	**67**	1.41	50:50	51	1.41	50:50	54	1.71	50:50	36	1.59	50:50	*30*	1.62	50:50
Zr	160	1.93	50:50	210	1.42	50:50	**300**	1.52	50:50	*120*	1.68	50:50	300	1.63	50:50	260	1.74	50:50
	Standard units																	
pH [1/]	5.8	.68	50:50	**5.3**	0.50	50:50	5.3	0.38	50:50	*7.3*	0.51	50:50	5.6	0.81	50:50	5.5	0.65	50:50

1/ Arithmetic mean and standard deviation.

From the results of the analysis of variance, as given in tables 7 and 8, we are assured that significant differences in concentrations of constituents do occur between at least the two vegetation types that have the extreme mean values. A further step in the data analysis is the identification of other significant differences among means. For this purpose we used the Duncan Multiple Range test (Duncan, 1955), which is one of several multiple comparison tests that could have been used.

The Duncan Multiple Range test is applied as follows: The vegetation-type areas are ranked by order of geometric mean concentration of the element (for example, zinc) in the uncultivated soils, from table 8.

Vegetation-type area	Mean concentration of Zn (ppm)
Glaciated Prairie	67
Floodplain Forest	54
Cedar Glade	54
Unglaciated Prairie	51
Oak-Hickory Forest	36
Oak-Hickory-Pine Forest	30

The location and extent of each of the vegetation-type areas are identified on figure 4. On the basis of the Duncan Multiple Range test, the bracketed means shown above cannot be demonstrated to be significantly different at the 0.05 level of probability. Only one clear discontinuity can be identified in the ranked means--between the Unglaciated Prairie and the Oak-Hickory Forest. Therefore, the 6 vegetation-type areas are classed into two groups with respect to zinc concentrations in the soils. One of these, relatively high in zinc, is formed by the Glaciated Prairie, the Floodplain Forest, the Cedar Glade, and the Unglaciated Prairie. The other group, relatively low in zinc, is formed by the Oak-Hickory Forest and the Oak-Hickory-Pine Forest. The vegetation-type areas are classed in this manner in figures 5, 6, 7, and 8. Thus, zinc, for example (see figure 5), tends on a broad scale to be about equally abundant in the prairie soils in the northern and western parts of the State, and in the soils of the Cedar Glade and Floodplain Forest areas. The geometric mean zinc concentration for this entire area was derived from the weighted mean logarithms for the individual vegetation-type areas and is given on figure 5 as 60 parts per million. As also shown on figure 5, the mean zinc concentration of soils in the Oak-Hickory and Oak-Hickory-Pine areas is significantly lower--estimated to be only 35 ppm.

Thus, the presentation of data on maps such as that given in figure 5, except for pointing out the significance of differences among vegetation-type areas, offers little more information beyond that given in table 8. In fact, table 8 gives the information in more detail. However, maps such as that given in figure 5 present the very broad features of the element distribution pattern at a glance and may be useful for direct comparison with maps showing variation in epidemiological characteristics over the State.

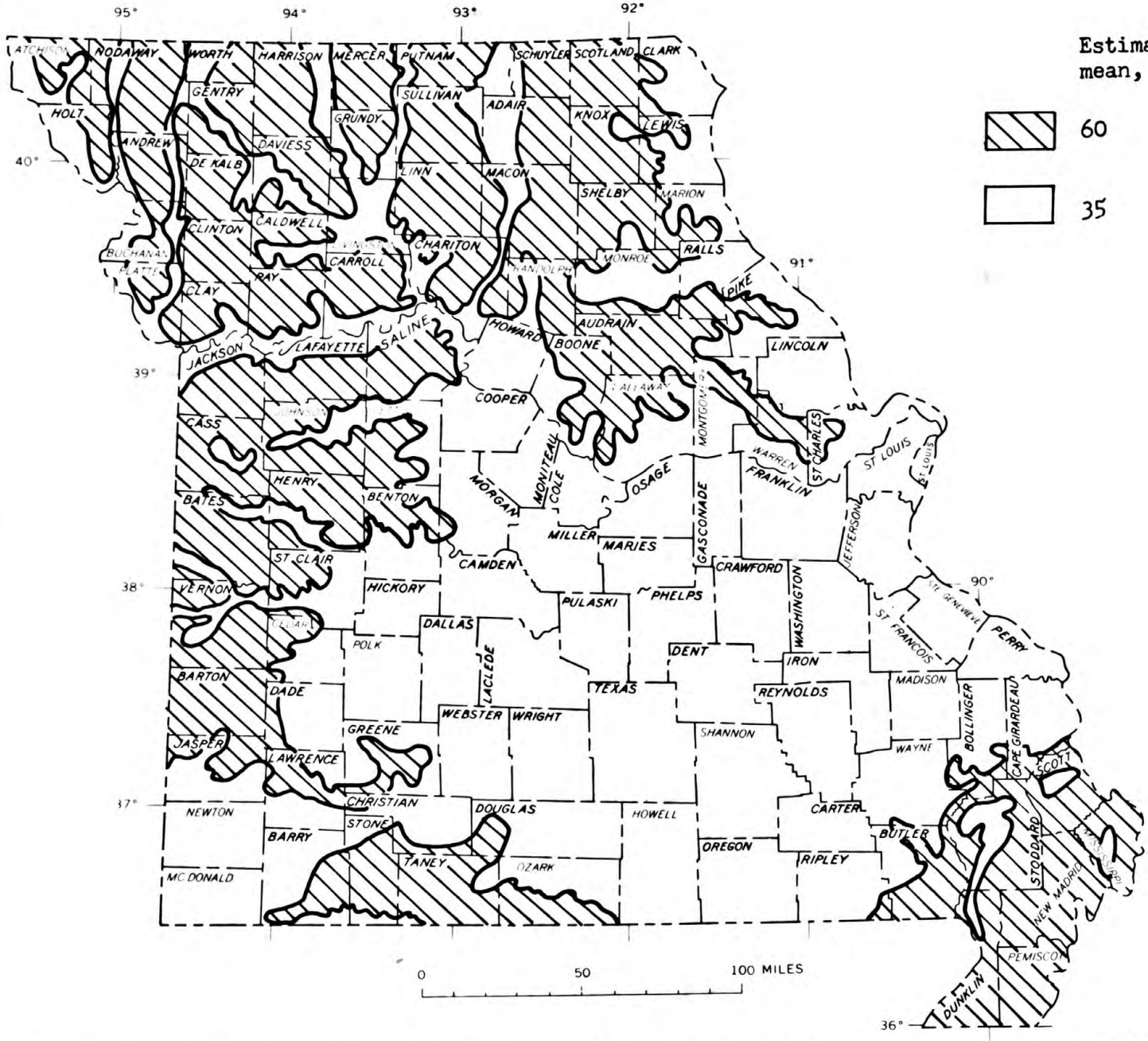


Figure 5.--Vegetation-type areas in Missouri that have distinctive mean concentrations of zinc in the B horizon of uncultivated soils.

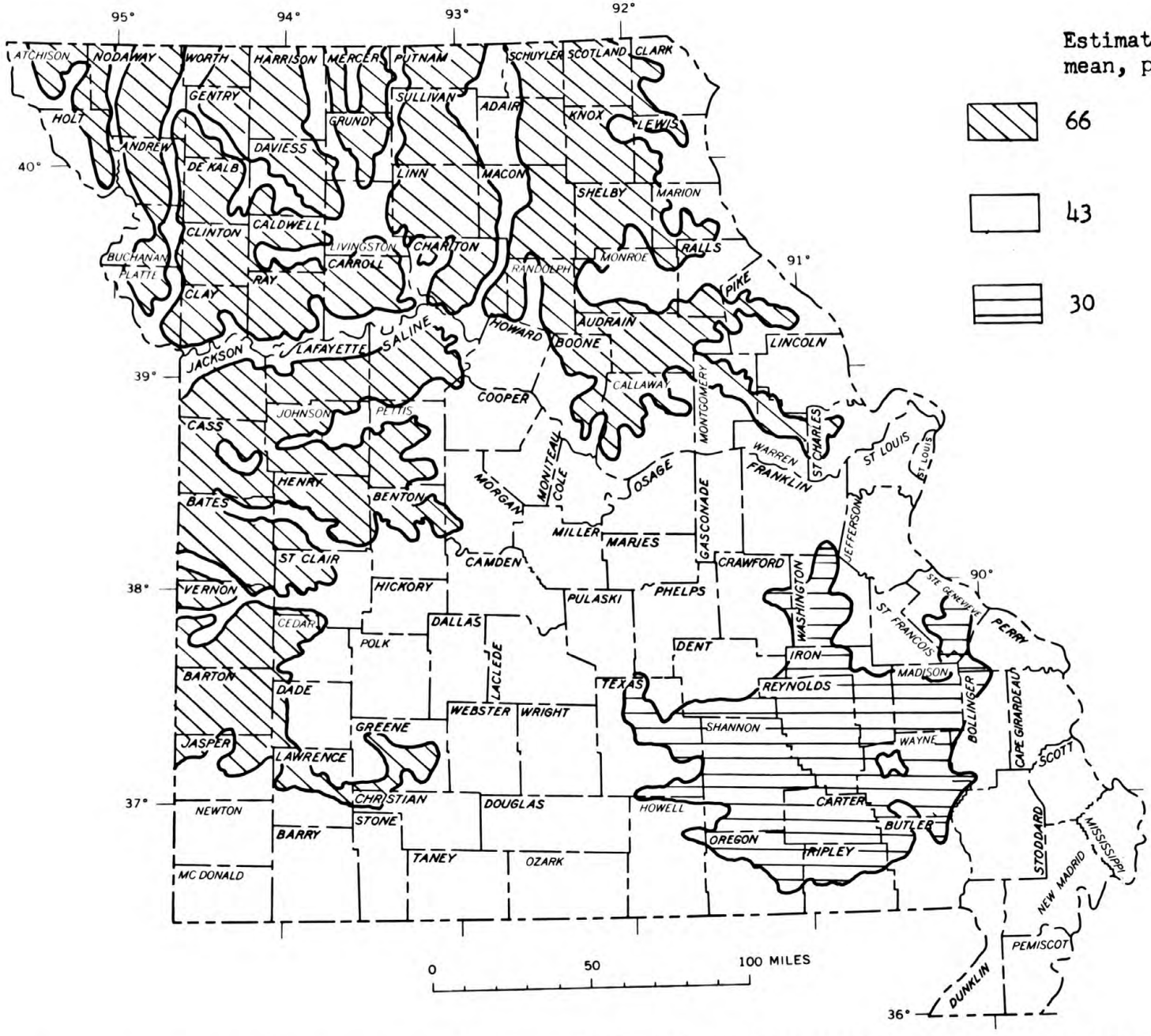


Figure 6.--Vegetation-type areas in Missouri that have distinctive mean concentrations of chromium in the B horizon of uncultivated soils.

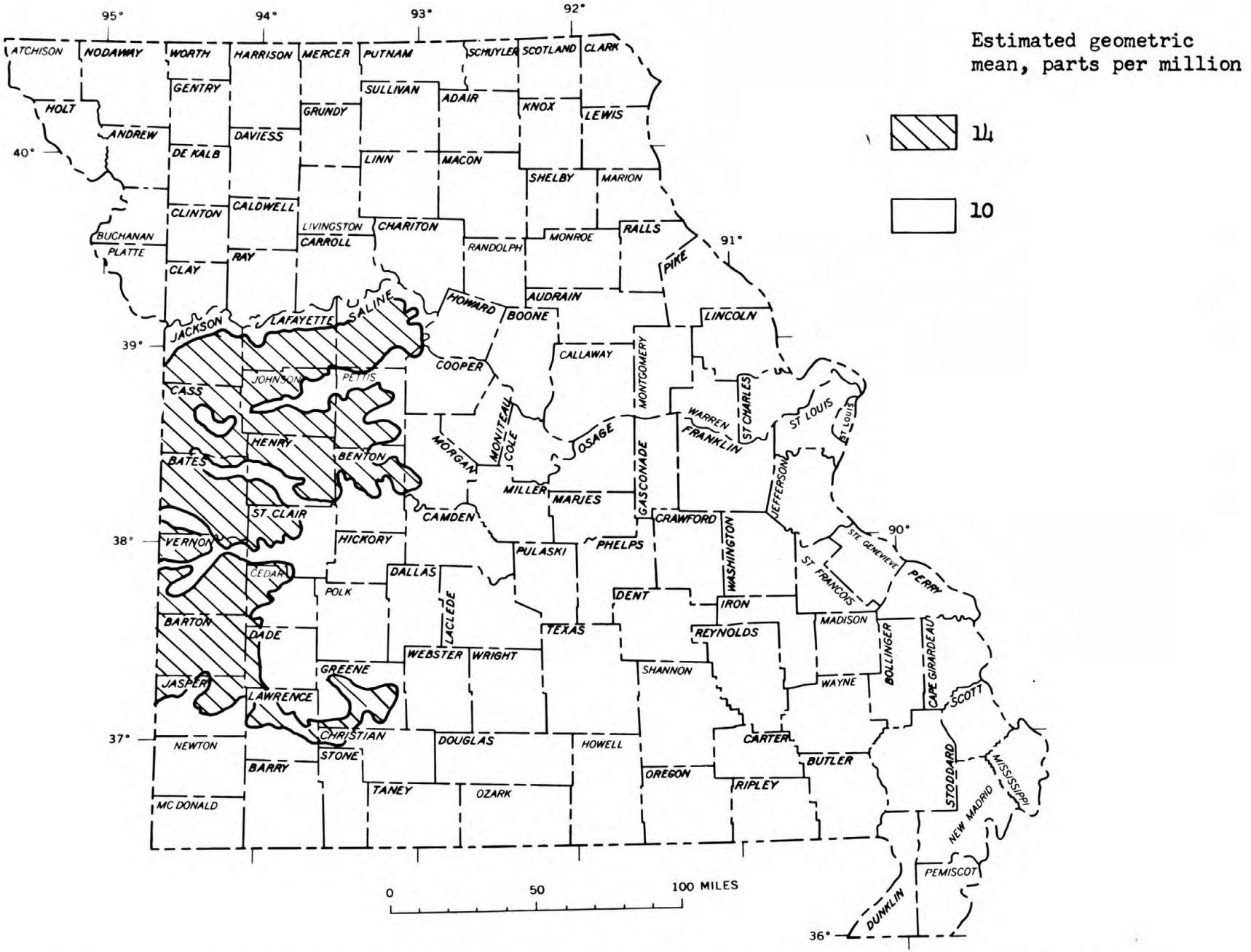


Figure 7.--Vegetation-type areas in Missouri that have distinctive mean concentrations of cobalt in the B horizon of uncultivated soils.

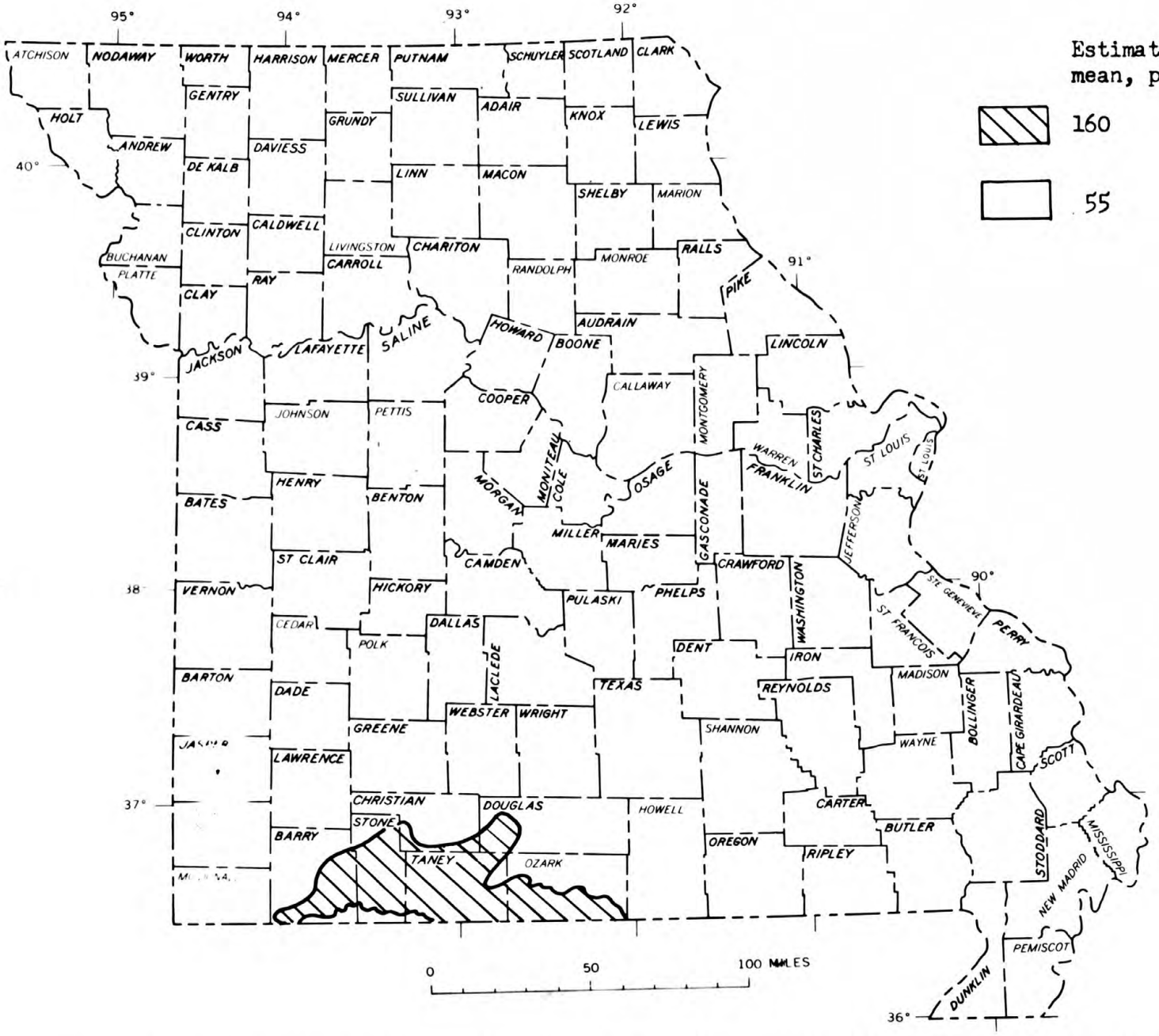


Figure 8.--Vegetation-type areas in Missouri that have distinctive mean concentrations of mercury in the B horizon of uncultivated soils.

The map in figure 5 shows only that the soils in the Oak-Hickory Forest and Oak-Hickory-Pine Forest areas tend to contain less zinc than soils elsewhere in the State. This does not mean that all soils in the Oak-Hickory Forest and Oak-Hickory-Pine Forest areas contain less zinc than soils elsewhere. Information regarding the amount of geochemical variability in each of the vegetation-type areas is presented as geometric deviations in table 8.

Figure 6 shows a similar map for chromium. It indicates that the uncultivated soils of Missouri may be classed into three categories on the basis of their chromium contents: 1) soils of the Glaciated and Unglaciated Prairies (relatively high in Cr), 2) soils of the Oak-Hickory Forest, Cedar Glade, and Floodplain Forest areas (intermediate in Cr content), and 3) soils of the Oak-Hickory-Pine Forest area (relatively low in Cr).

Figures 7 and 8 give similar maps for cobalt and mercury. With regard to cobalt, only the Unglaciated Prairie area in western Missouri is unique. Statistically significant differences among the other vegetation-type areas cannot be demonstrated with available data.

With regard to mercury, only the Cedar Glade area is unique. Significant differences cannot be demonstrated among the other vegetation-type areas. Tidball (this report) has found that mercury in cultivated soils, similarly, varies locally but not regionally over the State.

Similar maps representing other chemical constituents are in preparation.

Of the six vegetation-type areas considered in this study, both the Glaciated Prairie and the Unglaciated Prairie have high average concentrations of Al_2O_3, Ba, Co, Cr, Cu, total Fe as Fe_2O_3, Ga, La, Li, Ni, Sc, Se, Sr, TiO_2, V, Y, and Yb. For many constituents, soils of the two prairie types are indistinguishable. Those chemical constituents in which both prairie types appear to form a single soil population are Cr, total Fe as Fe_2O_3, Li, Sc, Se, and V. However, the prairie types do differ from one another in that the Glaciated Prairie soils tend to be higher in Al_2O_3, CaO, Ga, and MgO, whereas the Unglaciated Prairie soils tend to have greater concentrations of Co and Mn. The discovery of these geochemical differences between the two prairie vegetation types justifies our decision, made at the beginning of the Missouri studies, to divide Küchler's (1964) prairie-mosaic type (which was established on the basis of plant species composition) into two types for conducting geochemical studies of soils and vegetation.

The Cedar Glade soils are distinct from soils of the other vegetation-type areas in Missouri in that they have significantly higher average pH and concentrations of CaO, total C, carbonate C, organic C, Hg, and MgO. On the other hand, they tend to be lowest in concentrations of Na_2O, TiO_2, and Zr.

The notable feature of the Oak-Hickory-Pine Forest soils is that, for the most part, they have the lowest concentrations of many constituents. Soils of this vegetation type are unique in their low concentrations of Al_2O_3, CaO, Cr, total Fe as Fe_2O_3, Ga, Li, MgO, Sr, and V.

Covariation among constituents in soil samples from the B horizon in six vegetation-type areas.--Comparison of typical concentrations of chemical constituents, if examined by means of product-moment correlation coefficients (r), serves to identify covariation in abundance of these constituents. The correlation coefficients are based on logarithms of the element concentrations in soils of each vegetation type. Correlations that were significant at the 95-percent confidence level were identified by reference to tables of critical values of r; these correlations are given in table 9.

Each correlation coefficient within a vegetation type appears twice in table 9. For example, in the Glaciated Prairie K_2O and Ba have a correlation of 0.77, and this correlation appears after both K_2O and Ba as listed under the column heading "chemical constituents."

Possible causal factors of covariation in concentrations include the original chemical composition of bedrock or regoliths from which the soil was derived, the effects of varying climate on chemical activity and mobility of elements, selective absorption and concentration of elements by vegetation, and the length of time that has been available for the elements to reach their present concentrations in soils. Because of the complexity of interrelations among these factors and the constituents of soils, and because of the large number of significant correlations that were found, only a few of the most obvious relationships will be discussed.

One of the covariations most likely to be causally related is that of pH and Ca in five of the six vegetation-type soils. In the sixth area--the Oak-Hickory-Pine Forest--Ca is present in only minor amounts (table 8).

The Cedar Glade soils have the highest concentrations of organic C and are the only vegetation-type soils that exhibit a significant correlation of any constituent with Hg. This covariation suggests that organic materials in this area may serve as a "sink" for mercury that moves through the environment.

In general, there are many more pairs of constituents that vary similarly in concentrations in the Unglaciated Prairie soils than in those of the Glaciated Prairie. This contrast in number of correlations may reflect the youthfulness of Glaciated Prairie soils and the fact that chemical and physical equilibria have not been attained in the B horizon to the same degree as in the older Unglaciated Prairie soils.

Table 9.--Significant correlations (at 95 percent confidence level) between chemical constituents of soils from six vegetation-type areas in Missouri.
[- - -, no significant correlations in the vegetation type.]

Chemical constituents	Vegetation types					
	Floodplain Forest	Glaciated Prairie	Unglaciated Prairie	Cedar Glades	Oak-Hickory Forest	Oak-Hickory-Pine Forest
SiO_2------	Al_2O_3 -0.86; total Fe as Fe_2O_3 -.84; Ga -.80; Li -.74; MgO -.84; Ni -.61; Sc -.78; Se -.60; V -.72; Zn -.87	Cu -0.64; total Fe as Fe_2O_3 -.72; MgO -.83; Sc -.64; V -.73; Zn -.71; Zr .68	Al_2O_3 -0.83; total Fe as Fe_2O_3 -.72; Ga -.74; Li -.77; MgO -.73; Ni -.83; Sc -.74; Sr -.61; V -.79	Total C -0.86; Carbonate C -.84; CaO -.92; MgO -.69; pH -.69	CaO -0.81; MgO -.92; Zn -.76	Al_2O_3 -0.84; Cr -.67; Total Fe as Fe_2O_3 -.74; Ga -.82; K_2O -.74; Li -.70; MgO -.82; Sc -.71; Sr -.68; TiO_2 -.63; V -.78; Yb -.67
Al_2O_3-----	Cr .70; Total Fe as Fe_2O_3 .70; Ga .83; Li .87; SiO_2 -.86; V .87; Zn .90	Total Fe as Fe_2O_3 .69; Li .80; MgO .78; Sc .62; V .64; Zn .70; Zr -.62	Cr .61; Ga .72; Li .81; MgO .90; Ni .81; Sc .78; SiO_2 -.83; Sr .68; V .71; Zn .65	Organic C .67; Cr .74; Total Fe as Fe_2O_3 .90; Ga .80; K_2O .69; Li .82; Ni .62; V .86	Ga .84; K_2O .70; Li .84; MgO .68; Sc .66; Sr .65; V .65; Zn .70	Ba .65; Cr .71; Total Fe as Fe_2O_3 .71; Ga .82; K_2O .86; Li .75; MgO .83; Na_2O .69; Sc .72; SiO_2 -.84; Sr .84; TiO_2 .68; V .80; Y .63; Yb .70
Total Fe as Fe_2O_3--	Al_2O_3 .70; Co .67; Cu .64; Ga .73; Li .67; MgO .65; Sc .84; SiO_2 -.84; V .67; Zn .77	Al_2O_3 .69; Li .68; MgO .69; Sc .60; SiO_2 -.72; V .70; Zn .62; Zr .67	Li .66; Se .74; SiO_2 -.72	Al_2O_3 .90; Cr .72; Ga .78; Li .82; Ni .63; V .82	V .61	Al_2O_3 .71; Cr .80; Ga .65; Li .71; MgO .62; Sc .74; Se .65; SiO_2 -.74; TiO_2 .64; V .88; Yb .65

Table 9.--Continued.

Chemical constituents	Vegetation types					
	Floodplain Forest	Glaciated Prairie	Unglaciated Prairie	Cedar Glades	Oak-Hickory Forest	Oak-Hickory-Pine Forest
MgO------	Cr .64; Total Fe as Fe_2O_3 .65; Ga .81; Li .80; Sc .72; SiO_2 -.84; V .83; Zn .88	Al_2O_3 .78; Cu .65; Total Fe as Fe_2O_3 .69; Sc .64; SiO_2 -.83; V .74; Zn .84	Al_2O_3 .90; Ba .67; CaO .63; Ga .75; K_2O .74; Li .63; Ni .80; Sc .77; SiO_2 -.73; Sr .72; V .69	Total C .77; Carbonate C .73; CaO .77; SiO_2 -.69; pH .79	Al_2O_3 .68; CaO .77; K_2O .65; Li .67; SiO_2 -.92; V .61; Zn .80	Al_2O_3 .83; Cr .68; Total Fe as Fe_2O_3 .62; Ga .69; K_2O .65; Li .80; SiO_2 -.82; Sr .67; V .68
CaO------	pH .69	Sr .63; pH .63	Ba .72; Total C .65; Organic C .64; K_2O .76; MgO .63; Na_2O .67; Sr .61	Total C .87; Carbonate C .92; MgO .77; SiO_2 -.92; pH .78	Carbonate C .62; MgO .77; P_2O_5 .65; SiO_2 -.81; Zn .73	- - - - - - -
Na_2O-----	- - - - - -	- - - - - -	Ba .68; CaO .67; K_2O .72	- - - - - - -	Ba .85; K_2O .88; Sr .88; TiO_2 .63; Y .66; Yb .65	Al_2O_3 .69; Ba .64; K_2O .78; Sr .80
TiO_2-----	Cr .66; Y .70; Yb .63; Zr .70	- - - - - -	- - - - - - -	Yb .65	Ba .65; Na_2O .63; Sr .62; Y .62; Yb .66; Zr .73	Al_2O_3 .68; Cr .75; Total Fe as Fe_2O_3 .64; K_2O .71; Li .73; Se .62; SiO_2 -.63; Sr .68; V .71; Yb .71; Zr .72

Table 9.--Continued.

Chemical constituents	Vegetation types					
	Floodplain Forest	Glaciated Prairie	Unglaciated Prairie	Cedar Glades	Oak-Hickory Forest	Oak-Hickory-Pine Forest
K_2O------	- - - - - -	Ba .77; Mn.64; Sr .74	Ba .82; CaO .76; MgO .74; Na_2O .72; Sr .72	Al_2O_3 .69; Organic C .71; Se .62	Al_2O_3 .70; Ba .82; Ga .67; Li .71; MgO .65; Na_2O .88; Sr .89	Al_2O_3 .86; Ba .73; Ga .71; MgO .65; Na_2O .78; SiO_2 -.74; Sr .85; TiO_2 .71; V .64; Y .76; Yb .78
P_2O_5-----	- - - - - -	- - - - - -	- - - - - - -	Total C .61	CaO .65	- - - - - - -
Total C--	Organic C .98	Organic C .97	Organic C .98; CaO .65	Carbonate C .76; CaO .87; MgO .77; P_2O_5 .61; SiO_2 -.86; pH .74	Organic C .88	Organic C .97
Carbonate C----	- - - - - -	- - - - - -	- - - - - -	Total C .76; CaO .92; MgO .73; SiO_2 -.84; pH .66	CaO .62	- - - - - - -
Organic C	Total C .98	Total C .97	Total C .98; CaO .64	Al_2O_3 .67; Hg .63; K_2O .71	Total C .88	Total C .97
Ba-------	- - - - - -	K_2O .77; Sr .73	CaO .72; K_2O .82; MgO .67; Na_2O .68; Sr .68	Yb .62	Cr .61; Ga .60; K_2O .82; Na_2O .85; Sr .84; TiO_2 .65; Y .75; Yb .65	Al_2O_3 .65; K_2O .73; Na_2O .64; Sr .82; Y .67; Yb .61

Table 9.--Continued.

Chemical constituents	Vegetation types					
	Floodplain Forest	Glaciated Prairie	Unglaciated Prairie	Cedar Glades	Oak-Hickory Forest	Oak-Hickory-Pine Forest
Co-------	Total Fe as Fe_2O_3 .67; Mn .77	Mn .78	Mn .80	Ni .79; Sc .75; Y .69; Yb .74	- - - - - -	Mn .66; Ni .66
Cr-------	Al_2O_3 .70; Cu .68; Ga .70; Li .84; MgO .64; TiO_2 .66; V .85; Zn .72	- - - - - -	Al_2O_3 .61	Al_2O_3 .74; Total Fe as Fe_2O_3 .72; Li .63; V .69	Ba .61; Ga .64; V .68; Y .63	Al_2O_3 .71; Total Fe as Fe_2O_3 .80; Li .85; MgO .68; SiO_2 -.67; Sr .60; TiO_2 .75; V .87; Yb .61
Cu-------	Cr .68; Total Fe as Fe_2O_3 .64; Ga .72; Li .70; V .69; Zn .65	MgO .65; Sc .66; SiO_2 -.64; Zn .69	Ni .68	- - - - - -	- - - - - -	- - - - - - -
Ga-------	Al_2O_3 .83; Cr .70; Cu .72; Total Fe as Fe_2O_3 .73; Li .77; MgO .81; Ni .67; Sc .70; SiO_2 -.80; V .81; Zn .81	Sc .63	Al_2O_3 .72; Li .69; MgO .75; Ni .72; Sc .78; SiO_2 -.74; V .69	Al_2O_3 .80; Total Fe as Fe_2O_3 .78; Li .62; V .75	Al_2O_3 .84; Ba .60; Cr .64; K_2O .67; Li .74; Sc .62; Sr .70; V .68	Al_2O_3 .82; Total Fe as Fe_2O_3 .65; K_2O .71; MgO .69; Sc .71; SiO_2 -.82; V .69
Hg-------	- - - - - -	- - - - - -	- - - - - -	Organic C .63	- - - - - -	- - - - - - -
La-------	- - - - - -	- - - - - -	- - - - - -	Ni .66; Sc .78; Y .66	Y .66	Y .65

Table 9.--Continued.

Chemical constituents	Vegetation types					
	Floodplain Forest	Glaciated Prairie	Unglaciated Prairie	Cedar Glades	Oak-Hickory Forest	Oak-Hickory-Pine Forest
Li-------	Al_2O_3 .87; Cr .84; Cu .70; Total Fe as Fe_2O_3 .67; Ga .77; MgO .80; Sc .87; SiO_2 -.74; V .93; Zn .88	Al_2O_3 .80; Total Fe as Fe_2O_3 .68; Zr -.71	Al_2O_3 .81; Total Fe as Fe_2O_3 .66; Ga .69; MgO .63; Ni .75; Sc .75; SiO_2 -.77	Al_2O_3 .82; Cr .63; Total Fe as Fe_2O_3 .82; Ga .62; Ni .70; V .76	Al_2O_3 .84; Ga .74; K_2O .71; MgO .67; V .70 Zn .63	Al_2O_3 .75; Cr .85; Total Fe as Fe_2O_3 .71; MgO .80; SiO_2 -.70; TiO_2 .73; V .79
Mn-------	Co .77	Co .78; K_2O .64	Co .80	- - - - - - -	- - - - - -	Co .66
Ni-------	Ga .67; SiO_2 -.61; Zn .66	- - - - - -	Al_2O_3 .81; Cu .68; Ga .72; Li .75; MgO .80; Sc .80; SiO_2 -.83; Sr .61; V .65; Zn .63	Al_2O_3 .62; Co .79; Total Fe as Fe_2O_3 .63; La .66; Li .70; Sc .85; Y .73; Yb .64	- - - - - -	Co .66; Zn .68
Sc-------	Total Fe as Fe_2O_3 .84; Ga .70; Li .87; MgO .72; SiO_2 -.78; V .80; Zn .73	Cu .66; Total Fe as Fe_2O_3 .60; Ga .63; MgO .64; SiO_2 -.64; V .64	Al_2O_3 .78; Ga .78; Li .75; MgO .77; SiO_2 -.74; Sr .63; V .70	Co .75; La .78; Ni .85; V .71; Y .82; Yb .76	Al_2O_3 .66; Ga .62	Al_2O_3 .72; Total Fe as Fe_2O_3 .74; Ga .71; SiO_2 -.71; V .73
Se-------	SiO_2 -.60; Zn .63	- - - - - -	Total Fe as Fe_2O_3 .74	K_2O .62	- - - - - -	Total Fe as Fe_2O_3 .65; TiO_2 .62; V .65

Table 9.--Continued.

Chemical constituents	Vegetation types					
	Floodplain Forest	Glaciated Prairie	Unglaciated Prairie	Cedar Glades	Oak-Hickory Forest	Oak-Hickory-Pine Forest
Sr-------	- - - - - -	Ba .73; CaO .63; K_2O .74	Al_2O_3 .68; Ba .68; CaO .61; K_2O .72; MgO .72; Ni .61; Sc .63; SiO_2 -.61	- - - - - - -	Al_2O_3 .65; Ba .84; Ga .70; K_2O .89; Na_2O .88; TiO_2 .62; Y .65	Al_2O_3 .84; Ba .82; Cr .60; K_2O .85; MgO .67; Na_2O .80; SiO_2 -.68; TiO_2 .68; V .67; Y .61; Yb .67
V--------	Al_2O_3 .87; Cr .85; Cu .69; Total Fe as Fe_2O_3 .67; Ga .81; Li .93; MgO .83; Sc .80; SiO_2 -.72; Zn .88	Al_2O_3 .64; Total Fe as Fe_2O_3 .70; MgO .74; Sc .64; SiO_2 -.73; Zn .65	Al_2O_3 .71; Ga .69; MgO .69; Ni .65; Sc .70; SiO_2 -.79	Al_2O_3 .86; Cr .69; Total Fe as Fe_2O_3 .82; Ga .75; Li .76; Sc .71; Zn .65	Al_2O_3 .65; Cr .68; Total Fe as Fe_2O_3 .61; Ga .68; Li .70; MgO .61	Al_2O_3 .80; Cr .87; Total Fe as Fe_2O_3 .88; Ga .69; K_2O .64; Li .79; MgO .68; Sc .73; Se .65; SiO_2 -.78; Sr .67; TiO_2 .71; Yb .70
Y--------	TiO_2 .70; Yb .71	- - - - - -	- - - - - - -	Co .69; La .66; Ni .73; Sc .82; Yb .85	Ba .75; Cr .63; La .66; Na_2O .66; Sr .65; TiO_2 .62; Yb .73	Al_2O_3 .63; Ba .67; K_2O .76; La .65; Sr .61; Yb .88
Yb-------	TiO_2 .63; Y .71	- - - - - -	- - - - - - -	Ba .62; Co .74; Ni .64; Sc .76; TiO_2 .65; Y .85	Ba .65; Na_2O .65; TiO_2 .66; Y .73; Zr .70	Al_2O_3 .70; Ba .61; Cr .61; Total Fe as Fe_2O_3 .65; K_2O .78; SiO_2 -.67; Sr .67; TiO_2 .71; V .70; Y .88; Zr .68

Table 9.--Continued.

Chemical constituents	Vegetation types					
	Floodplain Forest	Glaciated Prairie	Unglaciated Prairie	Cedar Glades	Oak-Hickory Forest	Oak-Hickory-Pine Forest
Zn-------	Al_2O_3 .90; Cr .72; Cu .65; Total Fe as Fe_2O_3 .77; Ga .81; Li .88; MgO .88; Ni .66; Sc .73; Se .63; SiO_2 -.87; V .88	Al_2O_3 .70; Cu .69; Total Fe as Fe_2O_3 .62; MgO .84; SiO_2 -.71; V .65	Al_2O_3 .65; Ni .63	V .65	Al_2O_3 .70; CaO .73; Li .63; MgO .80; SiO_2 -.76	Ni .68
Zr-------	TiO_2 .70	Al_2O_3 -.62; Total Fe as Fe_2O_3 .67; Li -.71; SiO_2 .68	- - - - - - -	- - - - - - -	TiO_2 .73; Yb .70	TiO_2 .72; Yb .68
pH------	CaO .69	CaO .63	- - - - - - -	Total C .74; Carbonate C .66; CaO .78; MgO .79; SiO_2 -.69	- - - - - - -	- - - - - - -

The correlations of SiO_2 and other soil constituents, if significant, are negative in every case. This relationship doubtless is characteristic of any soil constituent that comprises an overwhelming percentage of the total constituents. Typical concentrations of SiO_2 in these soils range from 62 percent to 87 percent of the total soil constituents. The only other constituents present in amounts greater than one, and less than ten, percent are K_2O, total Fe as Fe_2O_3, and Al_2O_3.

Explanations of all the numerous covariations in constituents of soils from the six vegetation types perhaps never can be provided. Nevertheless, from a descriptive standpoint these combinations of covariation constitute one aspect of the distinctiveness of vegetation-type soils in Missouri, and they may be useful in identifying pairs or groups of elements that display similar patterns in geographic variation within the soils of any of the six vegetation-type areas.

Geochemical survey of water
by G. L. Feder

Present status.--All of the analytical results from the groundwater sampling program, which was outlined in the third progress report (U.S. Geological Survey, 1970b), were received during the report period. It is now possible to describe the differences among the major and trace element characteristics of groundwaters from the seven major geohydrologic units of the State. The methods of sampling and the analytical techniques will be described here in more detail, and some of the notably distinctive characteristics of the waters from each unit will be discussed. The sampling program was carried out over a 3-month period, from September to December, 1970.

Sampling of groundwaters.--The sampling program for groundwaters is described in two parts--the sampling design, or selection of wells and springs for sampling--and the sampling technique used after this selection had been made.

A. Sampling design

A rigorous sampling program, involving complete randomization, was designed to maximize the efficiency of sample collection and laboratory analysis and to provide data suitable for analysis by statistical techniques, including analysis of variance.

The sampling plan consisted of 1) dividing the potable groundwaters of the State into seven geohydrologic units (fig. 9), 2) randomly selecting five sampling sites (townships) within each geohydrologic unit, 3) randomly selecting one well (or spring) within three of the townships and two wells within two townships (the two townships in which a pair of wells were sampled again were selected at random), and 4) randomly selecting one well in each geohydrologic unit to be sampled in duplicate after a random interval of time.

Wherever possible, wells approved by the Division of Health of Missouri for public water supplies were used because they are 1) constructed so as to meet State specifications, 2) generally of high capacity, and 3) because well logs are available at the Missouri Division of Geological Survey and Water Resources. Selecting large capacity, properly constructed wells, and collecting a sample from a faucet at the pump, minimizes the chances of contamination of samples from the plumbing.

A total of 56 samples were collected in a completely randomized sequence from 49 wells throughout the State. The five sites within each geohydrologic unit were sampled to determine the compositional variation within each unit over distances of several miles or more. The two wells

Quaternary alluvium, unconsolidated stratified sands, silts, and clays

Glacial drift, unconsolidated, usually unstratified, gravels, sands, silts, and clays

Cretaceous and Tertiary unconsolidated, stratified sand, silts, and clays

Pennsylvanian consolidated sandstone, shale, limestone, and coal

Mississippian limestone

Cambrian and Ordovician (SW-Missouri) dolomite

Cambrian and Ordovician (SE-Missouri) dolomite

Figure 9.--Maps showing seven major geohydrologic units of Missouri and their lithologies. Shaded areas indicate extent of outcrop area. Dotted areas indicate areal extent of units covered by younger strata.

within selected townships were sampled to determine the compositional variation over distances of several miles or less. The duplicate samples from selected individual wells are necessary to measure the combined sampling and analytical error associated with the characterization of a single well. The sampling error is due, in part, to temporal changes at the well over the 3-month period of sample collection.

The locations of sampling sites are shown in figure 10. The limited numbers of acceptable sampling sites within the glacial drift and Pennsylvanian geohydrologic units led to some clustering of sampling localities. A few areas of suspected anomalous water chemistry within a geohydrologic unit were excluded from the sample design. Later sampling of these areas and comparison of these data with the mean values obtained from the initial sampling program will determine the nature of the anomalies if they do exist.

B. Sampling techniques

All samples were collected in acid-washed polyethelyne bottles at the faucet or pump, after letting the water run for at least 10 minutes. A 2-liter sample for spectrographic and radiochemical analysis was first filtered through a 0.45 micron filter, then acidified with 3 ml (milliliter) of double-redistilled, reagent-grade, concentrated HNO_3. Several element determinations by chemical methods were also made from this sample. A 1-liter sample of untreated water was collected for laboratory determination of pH, specific conductance, alkalinity, and arsenic. Samples for sulfide determination were collected in 100-ml bottles, and about 0.1 gram of zinc acetate was immediately added to precipitate the sulfide. Samples for nitrogen cycle determinations were collected in a 500-ml bottle and immediately treated with 30 mg (milligrams) $HgCl_2$ and placed in an ice-filled cooler. The samples for determination of the various forms of nitrogen were shipped by bus each week in an ice-filled cooler to the Little Rock, Ark., Water Resources Division laboratory where they were analyzed immediately. This procedure minimized changes in the nitrogen cycle components.

Analytical methods for groundwaters

A. Field determinations

Due to the possibility of rapid changes in certain chemical properties of water, some determinations were made in the field at the well or spring. These determinations included temperature, pH, alkalinity, and specific conductance. Procedures for making these determinations are given in Brown, Skougstad, and Fishman (1970).

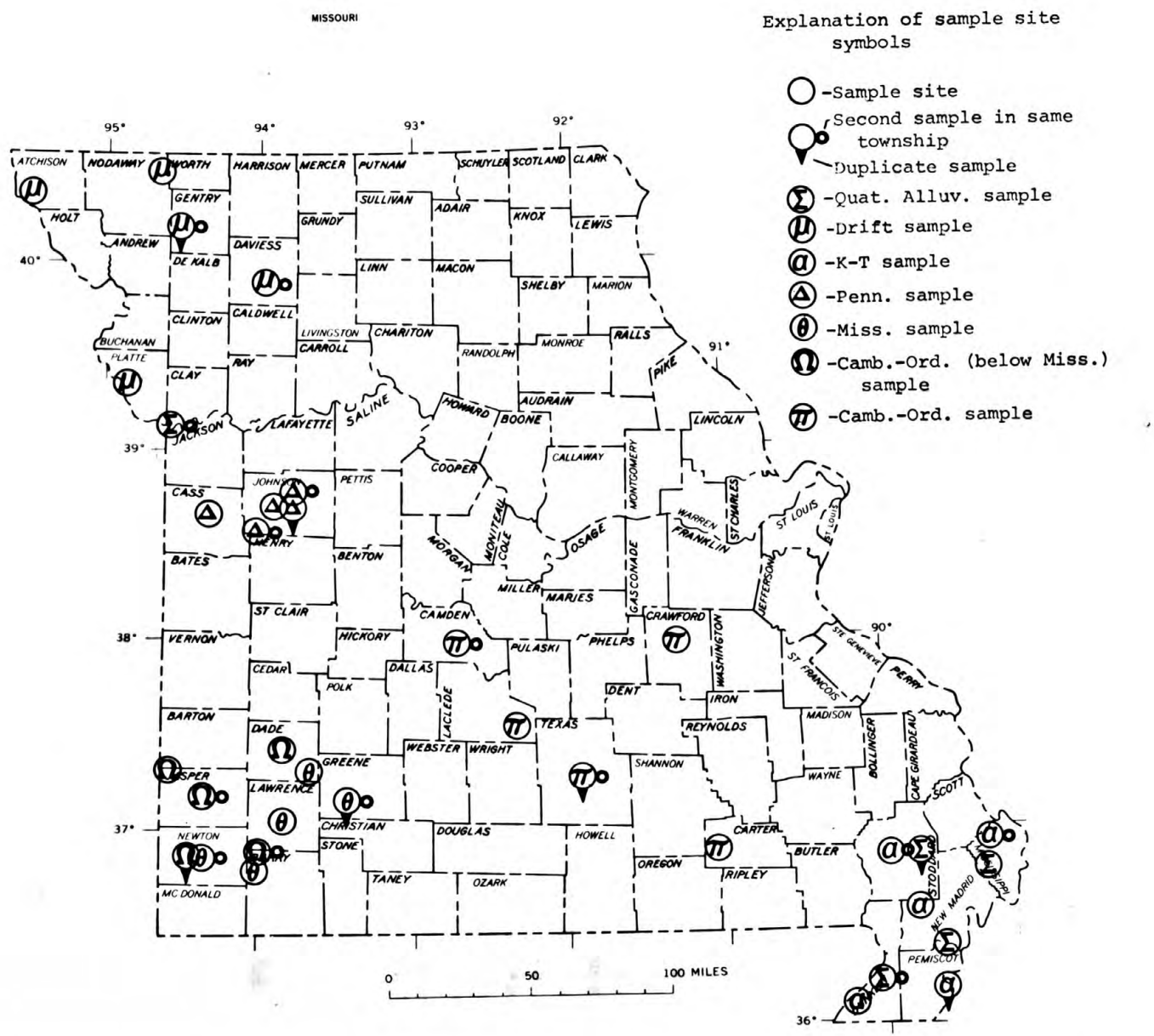


Figure 10.-- Map of Missouri showing locations of wells from which waters were sampled from various stratigraphic (geohydrologic) units.

B. Laboratory determinations

All laboratory determinations, except nitrogen cycle components, were made in the Water Resources Division laboratories in Denver, Colo., under the supervision of Dr. Marvin W. Skougstad. The nitrogen cycle determinations were made in the Water Resources Division laboratories in Little Rock, Ark., under the supervision of Charles T. Bryant.

Table 10 lists the determinations made and the method used. Complete descriptions of the methods are given in Brown, Skougstad, and Fishman (1970), Barker and Robinson (1963), and Barnett and Mallory (1971).

Nature of the chemical variability among groundwaters.--One of the principal findings of this study has been that waters from wells and springs less than a few miles apart (in the same township), and water samples taken from the same well or spring at randomized intervals over a 3-month period, do not differ much in major or trace element characteristics. Moreover, nearly all of the analytical methods used are of more than adequate precision for the purpose at hand. Most of the variation among the chemical characteristics of Missouri groundwaters is on a broad scale--among wells or springs more than several miles apart, and between geohydrologic units. It is this latter variation--between units--that has been of primary interest in this study.

The statistical model which served as the basis for the sampling program and the analysis of variance is the same as that given by Ebens and Connor in a previous section of the present report. Here, however, X_{ijkl} is the log concentration of the particular chemical constituent in the lth sample from the kth well or spring in the jth township in the ith geohydrologic unit. The grand mean, μ, is the average log concentration in all the groundwaters from all seven major geohydrologic units; α_i is the deviation of the mean for the ith geohydrologic unit from the grand mean; β_{ij} is the deviation of the mean for the jth township from the mean for the ith unit $(\mu + \alpha_i)$; γ_{ijk} is the deviation of the mean for the kth well or spring from the mean for the jth township $(\mu + \alpha_i + \beta_{ij})$; and, δ_{ijkl} is the deviation of the analysis of the lth sample from the mean for the kth well $(\mu + \alpha_i + \beta_{ij} + \gamma_{ijk})$.

In accordance with this model, the total log variance, σ_x^2, for a given chemical constituent--among the groundwaters in the seven geohydrologic units--may be partitioned into 4 components:

$$\sigma_x^2 = \sigma_\alpha^2 + \sigma_\beta^2 + \sigma_\gamma^2 + \sigma_\delta^2 ,$$

where σ_α^2 is the variance among the seven units and is the component of variance of primary interest in this study. The remaining variance terms, σ_β^2, σ_γ^2, and σ_δ^2, are, respectively, the components of variance among waters from different townships in the same unit, among waters

Table 10.--Analytical methods for water.

(All determinations were made in the Denver laboratories of the Water Resources Division, except where noted.)

Determination[1/]	Method	Reported as:
Ag	Spectrographic	µg/l
Al	do.	µg/l
Alkalinity	Electrometric titration	mg/l as HCO_3 and CO_3
As	AgDDC	µg/l
B	Spectrographic	µg/l
Ba	do.	µg/l
Be *	do.	µg/l
Bi *	do.	µg/l
Br	Catalytic oxidation	mg/l
Ca	AAS--Direct[2/]	mg/l
Cd	AAS--Direct Spectrographic	µg/l
Cl	Mecurimetric	mg/l
Co	Spectrographic	µg/l
Cr	do.	µg/l
Cu	do.	µg/l
F	Zr-Eriochrome cyanide R	mg/l
Fe (total)	AAS--Direct Spectrographic	µg/l
Ga *	Spectrographic	µg/l
Ge *	do.	µg/l

Table 10.--Continued.

Determination[1/]	Method	Reported as:
Hardness	Complexometric	mg/l as $CaCO_3$
Hardness, noncarbonate	do.	mg/l as $CaCO_3$
Hg	Flameless AAS	µg/l
I	Ceric-arsenious	µg/l
K	AAS--Direct	mg/l
La *	Spectrographic	µg/l
Li	do.	µg/l
Mg	AAS--Direct	µg/l
Mn	AAS--Direct Spectrographic	µg/l
Mo	Spectrographic	µg/l
N (in ammonia)[3/]	Distillation, titration or nesslerization	mg/l as N
N (nitrate)[3/]	Brucine	mg/l as NO_3
N (nitrite)[3/]	Diazotization	mg/l as NO_2
N (organic)[3/]	Kjeldahl digestion	mg/l as N
Na	AAAS--Direct	mg/l
Ni	Spectrographic	µg/l
P (total)	Acid-persulfate hydrolysis	mg/l as P
PO_4	Phosphomolybdate	mg/l as PO_4
Pb	Spectrographic	µg/l
pH	Electrometric, glass electrode	Standard units

Table 10.--Continued.

Determination[1]	Method	Reported as:
Radioactivity (alpha)	Counter	pc/l
Radioactivity (beta)	do.	pc/l
Rb	Spectrographic	µg/l
Sc *	do.	µg/l
Se	Diaminobenzidine	µg/l
SiO_2	Molybdate blue	mg/l
Sn *	Spectrographic	µg/l
SO_4	Thorin	mg/l
Solids (dissolved)	Gravimetric; ROE at 180°C	mg/l
Spec. conductance	Wheatstone bridge[4]	µmhos/cm at 25°C.
Sr	Spectrographic	µg/l
Temperature	Thermometer[4]	Degrees C
Ti *	Spectrographic	µg/l
V *	do.	µg/l
Y *	do.	µg/l
Yb *	do.	µg/l
Zn	AAS--Direct	µg/l
Zr *	Spectrographic	µg/l

1/ Elements indicated by asterisk (*) are detected and measured only in water samples containing unusually high concentrations.
2/ Direct analysis by atomic absorption spectrophotometry.
3/ Determinations made in Little Rock, Ark., laboratories of the Water Resources Division.
4/ Determined in field at time of collection.

from different wells or springs in the same township, and between analyses of samples from the same well. Estimates of these components, and of their corresponding proportions of the total variance, σ_x^2, are given in table 11. They were derived using computational procedures outlined by Anderson and Bancroft (1952, p. 327-330) for hierarchical designs with unequal subclasses.

The most notable feature of these variance component estimates is that those representing variation among closely spaced wells and between samples from the same well are small in comparison to those representing larger scale geographic variation and variation among the geohydrologic units. This indicates that a single water sample--surely no more than a few--is generally satisfactory for determining the chemical characteristics of groundwater from a given geohydrologic unit within an area less than several miles across. The greatest source of error in estimating the average chemical characteristics of the waters within a geohydrologic unit arises from the broad scale variation, between wells more than several miles apart (in different townships). Therefore, the only effective way to improve these averages (see table 12) is to sample more wells or springs at widely spaced locations over the entire unit. No substantial improvement would result from obtaining more samples from closely spaced wells, more samples from the same wells, or from using more precise laboratory procedures. The only foreseeable possibility which might modify these conclusions is that temporal changes over long periods might greatly exceed the changes that occurred during the 3-month period during which the samples were collected in this study.

The nature of the chemical variability of Missouri groundwaters, as revealed in this study, may have important implications in epidemiology. Cities and farms in different parts of the State, drawing water for domestic use from different geohydrologic units, will be exposed to some very different assemblages of major and trace chemical constituents. However, the water supplies from different towns within the same geohydrologic unit may also vary significantly. Cities and farms located within several miles 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.

It is important to recall that this study was purposefully directed at high capacity wells constructed to meet State specifications and at wells in areas where no unusual natural or artificial factors that may affect water composition were present. Further sampling of waters in areas containing local geologic features that may have a bearing on water quality, and cause the water to be of unusual composition, is planned. The added variability that may arise from such sources will be of special interest in epidemiological studies, but it can only be identified and interpreted in light of knowledge about what is normal, or expected, for other waters of the State.

Table 11.-- Comparison of estimated logarithmic variance components for groundwaters of Missouri.

[*, significantly greater than zero at the 0.05 probability level.]

Variable	Total $\log_{10}$ variance	Between geohydrologic units		Between townships		Between wells		Between samples	
		Component	Percent of total	Component	Percent of total	Component	Percent of total	Component	Percent of total
Temperature	0.0022	0.0010*	43	0.0009*	40	0	< 1	0.0004	17
Dissolved solids	.0768	.0299*	39	.0390*	51	.0074*	10	.0005	< 1
Carbonate hardness	.1518	.0479*	32	.0954*	63	.0081*	5	.0004	< 1
Specific conductance (laboratory)	.0678	.0233*	34	.0374*	55	.0065*	10	.0007	1
Specific conductance (field)	.0766	.0277*	36	.0398*	52	.0067*	9	.0024	3
pH 1/	.1961	.0070	4	.1516*	77	.0125	6	.0250	13
SiO_2 (mg/l)	.0616	.0375*	61	.0233*	38	.0005	< 1	.0003	< 1
HCO_3 (mg/l)	.0354	.0112*	32	.0197*	56	.0040*	11	.0005	1
SO_4 (mg/l)	.9056	.4096*	45	.3711*	41	.1246*	14	.0002	< 1
Cl (mg/l)	1.0460	.1715*	16	.3937*	38	0	< 1	.4808	46
Br (mg/l)	.3727	.0989*	27	.0490	13	.1455	39	.0793	21
Ca (mg/l)	.1669	.0546*	33	.1050*	63	.0056*	3	.0017	1
Mg (mg/l)	.2593	.1264*	49	.0725	28	.0592*	23	.0013	< 1
Na (mg/l)	.5699	.3391*	60	.1749*	31	.0552*	10	.0008	< 1
K (mg/l)	.1803	.0943*	52	.0677*	38	.0154*	9	.0028	2
Al (µg/l)	.0438	.0099*	23	.0146*	33	0	< 1	.0193	44
Ba (µg/l)	.2828	.1202*	43	.1314*	47	.0302*	11	.0011	< 1
B (µg/l)	.3639	.1827*	50	.1370*	38	.0415*	11	.0027	< 1
Fe (µg/l)	1.6867	1.0934*	65	.3276*	19	.2621*	16	.0036	< 1
Sr (µg/l)	.3140	.1570*	50	.1402*	45	.0150*	5	.0018	< 1

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

Chemical properties of groundwaters from the seven major geohydrologic units.--Summaries of the average compositions of the groundwaters, and their variabilities in composition, are given in table 12. The averages are given as geometric means because the frequency distributions tend to be symmetrical on logarithmic scales, and the geometric mean, therefore, is the appropriate measure of central tendency. The variabilities are given as geometric deviations--or the antilogarithms of the standard deviations of the logs. The detection ratio on table 12 is the ratio of the number of water samples in which the constituent was detected to the total number of independent samples analyzed from the particular geohydrologic unit. This denominator is 5 in most instances because 2 of the 8 samples from each unit were from the wells or springs in the same township where other samples had been taken, and 1 sample was a duplicate from a previously sampled well or spring. These 3 samples, therefore, were not independent and their inclusion in the averages would have placed more weight on some townships, wells, or springs than on others; also, the geometric deviations would have tended to be underestimated. The 3 samples were collected for the purpose of estimating variance components among closely spaced wells and between duplicate samples from the same well.

The geometric means and geometric deviations were estimated using techniques described in the second report of this series (U.S. Geological Survey, 1970a, p. 17-18) and in references cited therein.

A. Quaternary alluvium

Gross properties

Waters from the Quaternary alluvium geohydrologic unit, which includes the surficial deposits in the Southeast Lowlands, Mississippi River flood plain and the Missouri River flood plain (fig. 9) tend to be calcium-magnesium bicarbonate in gross chemical character. The geometric mean of the dissolved solids for the sampled wells is 310 mg/l (milligrams per liter) as shown in table 12. The water is generally very hard (see Hem, 1970, p. 225), and contains much iron and manganese. Water from wells in the Quaternary alluvium supplies large populations in suburban St. Louis and Kansas City, Mo., and many smaller communities in Missouri. The City of Columbia is developing a new water supply from this source at present. Large amounts of this type of water are also used for irrigation, especially in the Southeast Lowlands.

Trace elements and radiochemical data

Water in the Quaternary alluvium tends to have significantly higher cadmium and barium contents than that in other geohydrologic units. It is also comparatively high in strontium.

Table 12.--Summary of analytical data on groundwaters from seven geohydrologic units in Missouri

[GM, geometric mean; GD, geometric deviation; Ratio, number of samples in which variable could be measured: total number of samples analyzed]

[Analyses by P. R. Barnett, O. J. Feist, Jr., Darwin Golden, and E. C. Mallory, Jr. Organic-N, NO_2, NH_3-H, and NO_3 determinations by B. F. Lambert, R. D. McKibben, R. L. James; radiochemical determinations by V. J. Janser]

Variable	Quaternary alluvium			Glacial drift			Strata of Cretaceous and Tertiary age			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	GM	GD	Ratio	GM	GD	Ratio	GM	GD	Ratio
Miscellaneous determinations																					
Temperature at time of collection (°C)	15.4	1.12	5:5	12.7	1.00	5:5	20.9	1.37	5:5	15.5	1.16	5:5	14.4	1.00	5:5	18.6	1.01	5:5	14.6	1.00	5:5
Dissolved solids calculated (mg/l)	310	1.39	5:5	480	1.94	5:5	230	1.78	5:5	640	1.49	5:5	210	1.54	5:5	250	1.54	5:5	250	1.14	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	97	2.30	5:5	170	1.54	5:5	210	1.39	5:5	250	1.15	5:5
Noncarbonate Hardness (mg/l)	<8.2	----	4:5	44	2.90	5:5	<2.0	----	1:5	<1.6	----	1:5	13	3.04	3:5	13	4.10	5:5	<1.4	----	1:5
Specific conductance, laboratory (µmhos/cm at 25°C)	470	1.46	5:5	740	1.88	5:5	400	1.80	5:5	1000	1.52	5:5	360	1.51	5:5	420	1.57	5:5	460	1.13	5:5
Specific conductance, at time of collection (µmhos/cm at 25°C)	560	1.38	5:5	960	2.18	5:5	500	1.85	5:5	1300	1.60	5:5	400	1.48	5:5	470	1.48	5:5	520	1.14	5:5
pH	7.6[1]	0.3[2]	5:5	7.1[1]	0.3[2]	5:5	7.5[1]	0.8[2]	5:5	7.8[1]	0.6[2]	5:5	7.3 [1]	0.4[1]	5:5	7.6[1]	0.2[2]	5:5	7.5[1]	0.1[2]	5:5
Chemical determinations																					
SiO_2 (mg/l)	24	1.38	5:5	28	1.36	5:5	14	1.37	5:5	12	1.81	5:5	9.7	1.14	5:5	8.7	1.09	5:5	8.8	1.03	5:5
Fe (µg/l)	2600	2.49	5:5	5300	4.30	5:5	530	9.67	5:5	320	5.39	5:5	100	7.67	5:5	6.0	10.7	2:5	<11	----	1:5
Mn (µg/l)	490	1.72	5:5	470	4.77	5:5	86	5.80	4:5	<27	----	3:5	6.4	6.49	2:5	<16	----	1:5	<10	----	0:5
Ca (mg/l)	63	1.30	5:5	89	1.27	5:5	15	5.70	5:5	21	2.45	5:5	59	1.65	5:5	51	1.50	5:5	51	1.18	5:5
Mg (mg/l)	13	1.47	5:5	15	2.23	5:5	3.4	6.00	5:5	9.9	2.16	5:5	3.1	2.78	5:5	19	1.33	5:5	29	1.14	5:5
Na (mg/l)	18	2.05	5:5	31	4.37	5:5	33	3.07	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
K (mg/l)	3.2	1.51	5:5	2.2	2.25	5:5	2.4	2.00	5:5	6.6	2.16	5:5	.75	1.64	5:5	2.1	1.94	5:5	.67	1.40	5:5
HCO_3 (mg/l)	230	1.36	5:5	290	1.30	5:5	210	1.80	5:5	420	1.41	5:5	190	1.46	5:5	230	1.34	5:5	310	1.14	5:5
Sulfide (mg/l)	.090	2.10	2:5	.090	2.10	2:5	<.10	----	0:5	<.16	----	1:5	<.11	----	1:5	.14	5.04	3:5	<.1	----	0:4
SO_4 (mg/l)	39	2.42	5:5	90	3.01	5:5	7.7	3.95	5:5	6.3	6.16	5:5	3.5	14.7	4:5	28	2.34	5:5	.18	22.4	3:5
Cl (mg/l)	12	1.89	5:5	16	5.97	5:5	11	4.90	5:5	75	5.27	5:5	6.6	2.00	5:5	9.7	2.98	5:5	< .10	----	0:5
F (mg/l)	0.14	2.00	3:5	0.14	1.56	4:5	0.17	1.92	4:5	1.5	2.49	5:5	<.11	----		<.15	----	4:5	<.10	----	0:5
Br (mg/l)	.072	2.42	5:5	.18	2.48	5:5	.10	3.53	5:5	.25	4.12	5:5	.054	2.49	5:5	.072	1.28	5:5	.019	1.36	5:5
I (mg/l)	.0052	3.69	4:5	.014	2.72	5:5	.0046	2.79	5:5	.015	2.38	5:5	.00071	11.8	2:5	.0096	2.25	5:5	<.0022	----	1:5
Organic N (mg/l)-as N	.059	4.96	4:5	.29	8.43	5:5	.033	17.0	3:5	.15	2.83	5:5	.098	3.66	5:5	.033	4.65	4:5	.021	3.20	4:5
NO_2 (mg/l)	<.012	----	2:5	.012	3.86	3:5	<.01	----	1:5	.0074	6.98	2:5	.0074	4.25	2:5	.0085	2.76	2:5	<.011	----	1:5
NH_3 (mg/l)-as N	.073	5.01	4:5	.34	7.83	5:5	.076	6.23	4:5	.21	1.83	5:5	<.011	----	1:5	.062	2.41	5:5	<.01	----	0:5
NO_3 (mg/l)	.17	2.20	4:5	.39	1.81	5:5	.19	2.44	4:5	<.12	----	2.5	2.4	12.5	4:5	.26	44.4	3:5	3.4	2.78	5:5
PO_4 (mg/l)-as PO_4	.062	3.49	4:5	.021	6.34	3:5	<.042	----	3:5	<.016	----	1:5	.0066	7.98	2:5	.0073	5.90	2:5	<.01	----	0:5
Total P (mg/l)-as P	.033	2.34	4:5	.054	1.53	5:5	.018	3.63	3:5	<.014	----	1:5	.012	3.46	3:5	<.012	----	1:5	<.015	----	2:5
Cd (µg/l)	1.8	1.56	4:5	< 1.4	----	4:5	< 1.1	----	1:5	<1.1	----	1:5	<1.1	----	1:5	<1.0	----	0:5	< 1.0	----	0:5
Zn (µg/l)	12	1.58	4:5	< 16	----	4:5	14	2.64	3:5	< 16	----	4:5	<28	----	2:5	14	2.00	3:5	75	2.87	5:5
Spectrographic determinations																					
Al (µg/l)	11	1.75	5:5	15	1.54	5:5	12	1.43	5:5	23	1.40	5:5	11	1.43	5:5	10	1.20	5:5	11	1.54	5:5
Ba (µg/l)	540	1.31	5:5	200	3.34	5:5	100	4.74	5:5	140	2.20	5:5	53	1.18	5:5	51	2.21	5:5	43	1.27	5:5
B (µg/l)	49	2.02	5:5	70	3.70	5:5	34	3.01	5:5	200	3.46	5:5	11	1.49	5:5	26	2.12	5:5	11	1.30	5:5
Cu (µg/l)	<1.3	----	3:5	< 2.2	----	0:5	< 1.1	----	3:5	< 3.7	----	1:5	<1.6	----	2:5	.64	1.44	3:5	2.4	1.74	3:5
Pb (µg/l)	< 3.5	----	1:5	< 5.7	----	0:5	< 2.8	----	2:5	< 7.3	----	0:5	< 2.2	----	2:5	<2.6	----	0:5	< 2.6	----	0:5
Li (µg/l)	5.6	3.60	5:5	12	2.05	5:5	2.0	31.2	4:5	68	2.02	5:5	1.6	5.83	5:5	11	2.73	5:5	.66	5.94	3:5
Mo (µg/l)	<1.8	----	1:5	<2.7	----	1:5	< 1.6	----	1:5	< 3.6	----	0:5	<0.88	----	0:5	3.2	2.05	4:5	< 2.0	----	0:5
Ni (µg/l)	< 4.7	----	3:5	<8.6	----	3:5	< 3.4	----	2:5	< 8.0	----	1:5	< 3.3	----	2:5	<3.0	----	0:5	<5.6	----	1:5
Rb (µg/l)	< 2.6	----	2:5	<3.9	----	0:5	5.1	2.52	4:5	7.8	2.13	4:5	<1.6	----	1:5	< 2.1	----	4:5	< 2.2	----	0:5
Sr (µg/l)	240	1.83	5:5	460	2.17	5:5	130	6.62	5:5	670	2.45	5:5	71	1.94	5:5	130	2.50	5:5	46	1.22	5:5
Radioactivity																					
Gross alpha (µg/l as U-nat)	< 6.4	----	2:5	<8.9	----	0:5	8.2	2.75	3:4	<13	----	1:5	<4.5	----	1:5	9.9	1.92	5:5	< 5.5	----	0:5
Gross alpha (pCi/l as U-nat)	<2.1	----	2:5	<3.0	----	0:5	2.7	2.75	3:4	<4.2	----	1:5	<1.5	----	1:5	3.3	1.93	5:5	<1.8	----	0:5
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	6.5	2.91	4:5	1.4	1.14	4:5	3.0	1.69	5:5	<1.2	----	1:5
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	7.9	2.90	4:5	1.6	1.19	4:5	3.7	1.68	5:5	<1.3	----	1:5

[1] Arithmetic mean

[2] Standard deviation.

B. Glacial drift

Gross properties

Waters from the glacial drift geohydrologic unit, which includes surficial deposits over most of Missouri north of the Missouri River (fig. 9), tend to be calcium-magnesium bicarbonate in gross chemical character, although locally they may be a calcium-sodium bicarbonate type. The geometric mean of the dissolved solids for the sampled wells is 480 mg/l (table 12). The waters are very hard, and may contain high concentrations of iron, manganese, and sulfate. Locally, water in the glacial drift may contain high concentrations of ammonia and organic nitrogen. Due to the low yields of most wells in the glacial drift, they can provide adequate water supplies only for farms and small communities. However, some wells in locally buried river channel deposits may yield over 100 gpm (gallons per minute). Many farms and communities in the glacial drift area use individual cisterns or artificial lakes as sources of water.

Trace elements and radiochemical data

Waters from the glacial drift tend to contain relatively high concentrations of strontium, lithium, boron, barium, iodine, bromine, and total phosphorus.

C. Strata of Cretaceous and Tertiary age

Gross properties

Strata of Cretaceous and Tertiary age underlie most of the Southeast Lowlands of Missouri and are exposed at the surface in the northwestern part of this area (fig. 9). The strata dip to the southeast, and aquifers which are exposed at the surface in the northwestern part of the area may occur 2,000 feet below the surface in the southeast.

The water in the strata in the vicinity of the outcrop area is a calcium-magnesium sodium bicarbonate type. It is hard and locally contains large amounts of iron and manganese. As the water in the strata migrates downdip in a southeasterly direction, it gradually changes to a soft sodium bicarbonate water. In this area the water has a high iron content and the temperature is over 27 degrees C (centigrade).

Many towns in the Southeast Lowlands use water from these strata for municipal supplies. The contrast between the quality of water used in towns near the outcrop area and in towns farther to the southeast, where the strata are deeply buried, is best illustrated by comparing the properties of water from Dexter and Caruthersville, Mo. A water sample from Dexter has a dissolved-solids content of 300 mg/l, total hardness of 170 mg/l (as $CaCO_3$), alkalinity of 257 mg/l, and a sodium content of 42 mg/l. A sample from Caruthersville has a dissolved-solids content of 100 mg/l, total hardness of 18 mg/l (as $CaCO_3$), alkalinity of 86 mg/l, and a sodium content of 26 mg/l.

Trace elements and radiochemical data

Water in the strata of Cretaceous and Tertiary age tends to be the highest of all types in Missouri in rubidium and in gross-alpha radioactivity.

D. Strata of Pennsylvanian age

Gross properties

Wells in strata of Pennsylvanian age that were sampled in this study were all located in the outcrop area in west-central Missouri (fig. 9). The water in the strata tends to be a sodium-bicarbonate type and is moderately hard. The geometric mean concentration of dissolved solids, for the sampled wells, is 640 mg/l. The water locally contains high iron and chloride. Due to the low yields of wells and the general poor quality of the water, strata of Pennsylvanian age provide water for only small private supplies and a few small towns. Most farms and towns use individual cisterns or artificial lakes for water supply.

Trace elements and radiochemical data

Water in the strata of Pennsylvanian age has a significantly higher fluorine, bromine, iodine, boron, lithium, rubidium, and strontium content than that in the other geohydrologic units. It also has the highest average gross-beta radioactivity.

E. Strata of Mississippian age

Gross properties

Springs and wells in strata of Mississippian age sampled in this study were all located in the outcrop area in southwest Missouri (fig. 9). Most of the water is a calcium-bicarbonate type. The geometric mean concentration of dissolved solids for the sampled wells and springs is 210 mg/l. The water is hard and locally contains appreciable amounts of nitrate. Due to the rapid circulation, proximity to the surface, and minimal opportunity for filtration, the Division of Health of Missouri will not approve wells in this aquifer. However, the water is used by most small farms and in many homes throughout this area.

Trace elements and radiochemical data

Water in the strata of Mississippian age has among the lowest trace-element content of that in any of the geohydrologic units included in this study.

F. Strata of Cambrian and Ordovician age (southwest Missouri)

Gross properties

Strata of Cambrian and Ordovician age penetrated by wells sampled in this study were classified into 2 groups--strata overlain by Mississippian and Pennsylvanian rocks in southwest Missouri and other Cambro-Ordovician strata in south-central and southeast Missouri (fig. 9). The water in Cambro-Ordovician strata in southwest Missouri can be characterized as calcium-magnesium bicarbonate in type. The geometric mean concentration of dissolved solids for the sampled wells is 250 mg/l. The water is very hard and may contain appreciable sulfate. Most towns in this area (fig. 9) use water from this aquifer.

Trace elements and radiochemical data

Water in the strata of Cambrian and Ordovician age in southwest Missouri tends to have a significantly higher molybdenum content and higher gross-alpha radioactivity than that in the other geohydrologic units. It also has among the highest concentrations of copper, lithium, and sulfide.

G. Strata of Cambrian and Ordovician age (southeast Missouri)

Gross properties

Wells in the strata of Cambrian and Ordovician age in south-central and southeast Missouri sampled in this study are all located in the outcrop area south of the Missouri River (fig. 9). The water in these strata is calcium-magnesium bicarbonate in type. The geometric mean concentration of dissolved solids for the sampled wells is 250 mg/l. The water is very hard and contains little sulfate or chloride. Almost every town and farm in this area (fig. 9) uses water from these strata.

Trace elements and radiochemical data

Water in the strata of Cambrian and Ordovician age (southeast Missouri) has a significantly higher average zinc content than the water in other geohydrologic units.

Plans for 1971 field season.--During the 1971 field season groundwater samples will be collected from areas where water of anomalous chemical properties may possibly exist, including the "Viburnum trend Lead District" and the Joplin Lead-Zinc District. Some possible trace element anomalies that may be of interest to the Environmental Health Center, identified in the initial sampling program, will be more intensively investigated. Surface-water samples will be collected from two streams in each of four geohydrologic units which have natural surface-water drainage systems.

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