ENVIRONMENTAL GEOCHEMISTRY

Geochemical Survey of Missouri
Plans and progress for third six-month period
(July - December, 1970)

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

1972

[redacted]

Preface

This third six-month progress report to the Environmental Health Center of the University of Missouri marks the midway point in our studies of the environmental geochemistry of the State. Over 4,000 samples of rocks, soils, vegetation, and groundwater have been collected from throughout the State; most of these are currently in the Geological Survey laboratories under various stages of preparation and analysis. Some preliminary results have been reported in the two previous progress reports, and others are presented here. It is expected that the major part of the analytical task will be completed in the next 6 to 12 months, however, and forthcoming reports should include information of direct application to the epidemiological investigations of the Environmental Health Center. The present report is intended to inform those concerned of our progress, our plans for the forthcoming final field season of the investigation, and to offer some additional preliminary results. Of specific interest to the Environmental Health Center will be the maps showing localities throughout the State where samples, or groups of samples, of rocks, soils, vegetation, and water have been collected so far; the sampling plans have been discussed briefly in the previous progress reports, and will be described in detail, of course, in forthcoming reports along with analyses and interpretations of the laboratory data.

We wish to thank Dr. Carl J. Marienfeld and his staff at the Environmental Health Center for their continued cooperation in this study, and for the many courtesies extended us while in Missouri. Special acknowledgement is made of the assistance given to us by Dr. Walter F. Heidlage and county agents of the University of Missouri Extension Division in the collection of a large suite of samples of agricultural soils from throughout the State.

A. T. Miesch, Chief
Branch of Regional Geochemistry
U.S. Geological Survey

Contents

Illustrations

Tables

INTRODUCTION AND SUMMARY

This is the third six-month progress report on studies in environmental geochemistry in the State of Missouri in cooperation with the Environmental Health Center of the University of Missouri. As pointed out in the two previous progress reports, the studies are intended to describe the abundance and distribution of chemical elements in rocks, soils, vegetation, and waters of the State. A major purpose is to provide this basic information to the Environmental Health Center for the bearing it may have on their epidemiological investigations. It will also serve to establish a geochemical framework, or background, about which more detailed studies of areas of special interest can be planned and interpreted. Also, the current widespread concern over the presence of elements that may be hazardous to human health in the environment leads us to believe that studies of this kind will be in increasing demand, and we regard this work as a pilot program, or initial experiment, into methods for conducting geochemical surveys over large regions.

We have come to view the studies in two separate parts: 1) a general geochemical survey of the rocks, soils, vegetation, and water of the State, and 2) detailed investigations of any epidemiological anomalies that may be identified by the Environmental Health Center. Having the results of the general survey in hand, the detailed investigations that may be done can be planned with better perspective, and the results can be interpreted in a more meaningful way than would be possible without knowledge of the general geochemical setting of the area of interest.

All currently planned sampling programs directed at the general geochemical survey are expected to be completed by late fall of 1971.

As discussed by Drs. Connor and Ebens in the following section of this report, a total of 382 rock samples have been collected to date from six major geologic units in the State. Chemical variation within each of these tabular units is both stratigraphic (from top to bottom) and geographic, and it is important to identify the magnitude of each. For example, if a large part of the variation in one or more of the units is stratigraphic, then the geochemical character of the unit may be determined adequately by detailed sampling within only a few small areas, and the results may be correctly extrapolated to other areas in which the unit occurs. On the other hand, if most of the variation in a unit is geographic, such extrapolation would be erroneous and more extensive field sampling would be required to define the geochemical characteristics of the unit. Consequently, Connor and Ebens have designed their sampling program around a statistical model that will allow them to partition the total geochemical variability of each unit into one geographic component, one stratigraphic component, and another component which, by necessity, is a combination of both geographic and stratigraphic variation. They discuss the model in detail.

Drs. Connor and Ebens also present some preliminary estimates of the geochemical characteristics of some common rock types in the State. These estimates may be useful in conjunction with geologic maps in considering the sources of chemical elements present in the environment, but they are almost certainly subject to major revision when analytical work on samples presently in the laboratory has been completed. We are particularly anxious to compile more comprehensive data on the trace element characteristics of loess deposits, which cover much of the northern half of the State, and carbonate residuum, which covers much of the southern half (See columns 9 and 10 of table 3.).

Consideration will be given to further sampling of the major geologic units of the State when data on those samples presently in the laboratory have been received and synthesized. Tentative plans are also being made to investigate some less widely distributed rock types that may be geochemically unique.

Dr. Tidball shows the distribution of localities from which agricultural soil samples were either received through the cooperation of the county agents of the University of Missouri Extension Division or collected by him as needed to complete the sample suite. All of these 1,140 samples are being processed in our sample preparation laboratory at the time of this writing. The data will be used to construct maps showing the geochemical characteristics of agricultural soils of the State (See figure 3.).

As described in the second six-month progress report, it has been determined that taxonomic groups of the soil classification system currently in use by soil scientists are not sufficiently different in trace element composition to serve as a good basis for a soil sampling program. Classification of the soils by vegetation-type areas (See U.S. Geological Survey, 1970, figure 3.) appears to be better for this purpose, and Tidball has now turned his major effort toward an investigation of the relations between soil composition and the compositions of soil parent materials within vegetation-type areas. The study is expected to provide information that will be needed to interpret the meaning and significance of data pertaining to the agricultural soils.

In this report, Dr. Tidball presents summary data on 5 chemical elements that may be of particular concern in environmental health--arsenic, fluorine, mercury, iodine and selenium. He has shown that all of these elements, like most of the others studied so far, are more highly concentrated in soils of the Bosworth Series than in those of the Coulstone Series. It was pointed out previously that these two soil Series appear to be the compositional extremes within the total range of soil Series present in Missouri (U.S. Geological Survey, 1970, p. 30-34).

Dr. Tidball also describes the concept of the variance ratio as used in much of sampling program planning. The concept serves to design a sampling program so that sufficient data are collected to insure statistically stable results, but not so much data that field and laboratory resources are wasted.

Dr. Shacklette, Dr. Erdman, and Mr. Keith collected nearly 1,000 plant samples and 300 soil samples the past field season, and have submitted them to our laboratories. The plant samples will be reduced to ash before analysis for most elements. Their report describes the species sampled within each of the six major vegetation-type areas in the State and gives some field observations.

Mr. Feder has successfully completed initial sampling of groundwater from seven broad geohydrologic units throughout the State. In order to randomize the effects of possible changes of water composition with time, he has sampled all wells in a randomized sequence and has obtained duplicate samples from selected wells to measure the possible importance of these effects. About one-half of the laboratory work on his samples has been completed, but all of the determinations on NO_2, NO_3, NH_4, and organic nitrogen have been received. Specific conductance and pH of the samples were measured at the well, or spring, at the time of collection. Analysis of the data shows that there are statistically significant differences among the seven geohydrologic units with respect to NO_3, NH_4, organic nitrogen, total nitrogen, and specific conductance. No significant difference could be demonstrated with respect to pH. Preliminary inspection of the partial results for metallic ions suggests that molybdenum may occur in detectable quantities in only one of the seven geohydrologic units.

As is standard procedure in these investigations, all samples were randomized with respect to the localities from which they were collected before submitting them to the laboratory. The purpose here is to guard against the effects of time-dependent errors in the laboratory and to effectively convert any such systematic errors into errors that are essentially random. Moreover, a given number of "hidden" duplicate samples are included within each group of samples in order to assess analytical precision. It is also standard procedure to enter coded descriptions of the samples into our computer files wherein the laboratory data are also stored on receipt from the laboratories. The data, then, can be selectively retrieved from these files and processed entirely by automatic procedures.

The analytical methods used in these investigations were tabulated in the second six-month progress report (U.S. Geological Survey, 1970). Sufficient results have now been received to identify those elements for which the methods are sufficiently sensitive, and those for which more sensitive methods may be needed. Elements for which the methods seem adequate, for rocks and soils at least, are aluminum, arsenic, boron, barium, carbon, calcium, cobalt, chromium, copper, fluorine, iron, gallium, mercury, potassium, lanthanum, magnesium, manganese, sodium, nickel, phosphorus, lead, silicon, selenium, scandium, strontium, titanium, vanadium, yttrium, ytterbium, zinc and zirconium. The instrumental activation method for selenium, by which we had expected to analyze the large majority of our samples, proved impractical and an x-ray fluorescence method is now being used to determine selenium concentrations as low as 0.05 parts per million. A revised activation method is being used for iodine, but its relatively high cost will severely limit the number of iodine determinations that can be made; the method is sensitive to 0.03 parts per million. Cadmium is being detected only in samples where it is present in concentrations greater than 1 part per million; this seems to be about 20 percent of the rock and soil samples being analyzed. At least cadmium will be reported where it occurs in concentrations high enough to present a potential health hazard. Two elements of possible interest in epidemiological studies that are not being adequately determined with the methods tabulated in the last report are molybdenum and antimony. Other elements that are being detected in enough samples to provide some potentially useful information about their distributions in the rocks and soils of the State are beryllium, cerium, niobium, and neodymium. No results of analyses for lithium have been received as yet.

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

Present status of the sampling program.--Work on this phase of the Missouri studies during the report period consisted principally of the collection of a preliminary set of 382 rock samples from surface exposures of six major rock units. The approximate geographic boundaries of these units in Missouri and the sampled localities are shown on the geologic map in figure 1. Each locality symbol represents at least two rock samples. The number of samples taken from each lithologic type in each rock unit is given in table 1. The only major rock unit not sampled is the Precambrian crystalline core of the St. Francois Mountains (unit p€).

Each sampled unit consists of a nearly flat-lying, tabular rock layer of variable thickness and extent. The two components of element variability of most interest in such tabular layers are those corresponding to variation from top to bottom (stratigraphic variation) and variation between geographically distant parts (geographic variation). The stratigraphic component of element variability is, in turn, subdivided into two parts; one part represents variation over large stratigraphic intervals and the other represents variation over smaller intervals. The preliminary sampling of the major lithologic types in each major rock unit was undertaken according to an experimental design specifically chosen to permit estimation of at least these three components of element variability.

The statistical model employed is:

$$X_{ijk} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} \qquad (1)$$

where X_{ijk} represents the concentration of an element in the kth rock sample taken from the jth part of the ith stratigraphic section, μ is the average concentration of the element in the entire rock unit. α_i represents the difference between the true mean concentration of an element in the ith stratigraphic section and the grand mean μ; β_{ij} represents the large-scale difference between the true mean concentration of the jth part of a stratigraphic section and the mean of the ith section, and γ_{ijk} represents, in part, the smaller-scale difference between the element concentration of the kth specimen and the mean of the jth part of the section. The last term (γ_{ijk}) also includes all variation attributed to post-sampling (laboratory and analytical) procedures. That part of γ_{ijk} due to the post-sampling procedures is referred to as the "analytical error" variance and can be independently estimated through replicate analysis. Once identified it may be subtracted, leaving the final term in (1) to represent only the small-scale stratigraphic variation.

Generalized geologic map of Missouri showing sampling localities

EXPLANATION

Qa		River alluvium
┴┴┴ ┴┴┴	QUATERNARY	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).
P	PENNSYLVANIAN	Limestone, shale, sandstone, minor amounts of coal and clay (▲ = sampling locality).
M	MISSISSIPPIAN	Limestone, minor amounts of shale and sandstone (△ = sampling locality).
DSO	DEVONIAN, SILURIAN, UPPER ORDOVICIAN	Limestone, dolomite, minor amounts of shale and sandstone (■ = sampling locality).
ЄO	LOWER ORDOVICIAN, CAMBRIAN	Dolomite, minor amounts of limestone, shale, and sandstone (□ = sampling locality).
pЄ	PRECAMBRIAN	"Granitic" rocks

MISSOURI

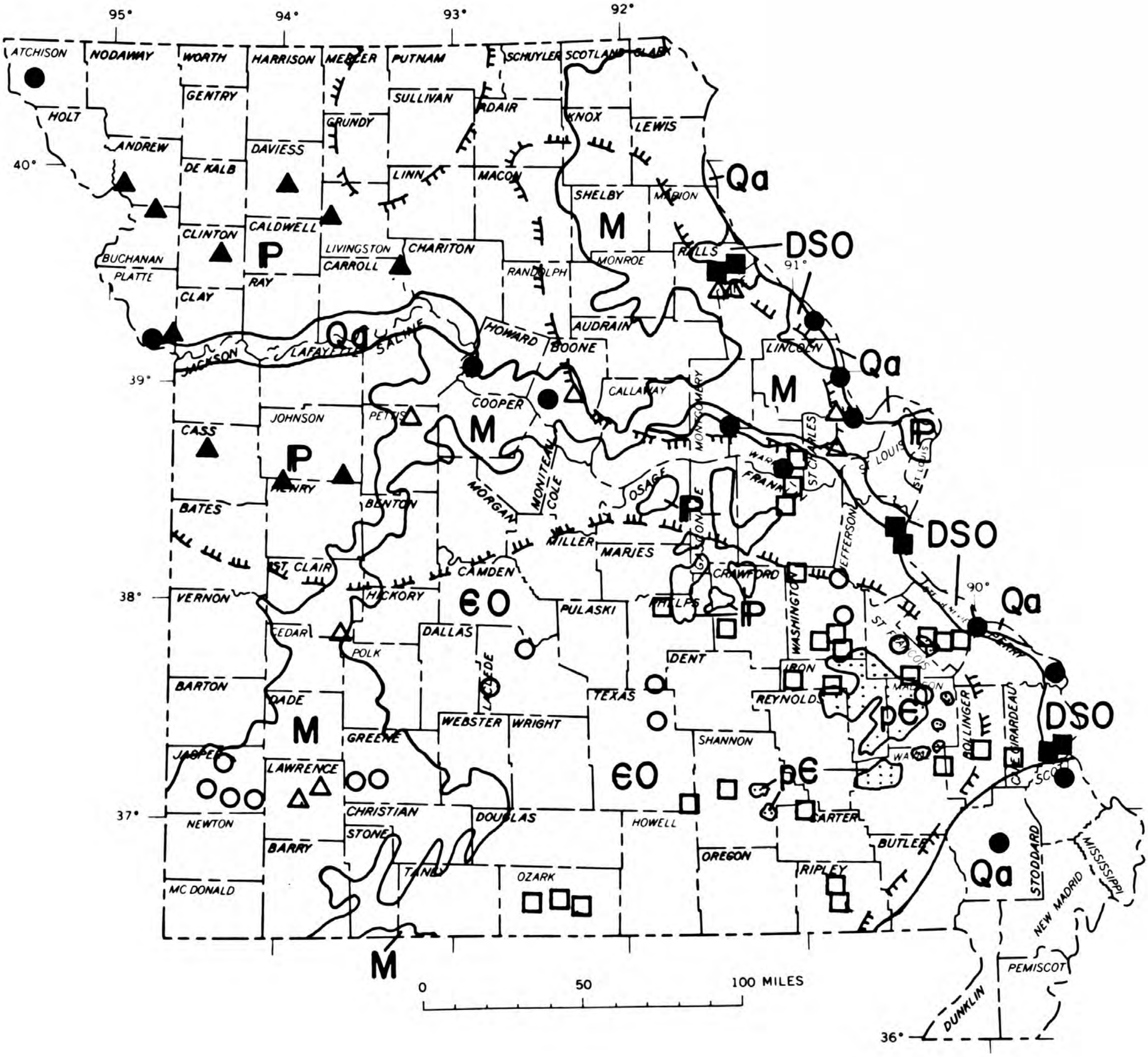

Figure 1. Generalized geologic map of Missouri showing sampling localities.

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

Table 1. Number and type of rock samples collected during report period.

Map Unit	Limestone and Dolomite	Sandstone and Chert	Shale, Siltstone and Claystone
Loess			26
Residuum	24 1/	4 1/	42
Pennsylvanian	32	32	32
Mississippian	40	24	22
Devonian, Silurian, and Upper Ordovician	12	4	6
Lower Ordovician and Cambrian	48	28	6
Total	156	92	134

1/ A bedrock sample (limestone, dolomite or sandstone) was collected at each residuum sample site.

The model in (1) is a specific case of the analysis of variance termed the hierarchical or "nested" case. This particular type of analysis was first applied to a problem in field geology by Potter and Olsen (1954) and is discussed in mathematical detail by Krumbein and Slack (1956). α_i, β_{ij}, and γ_{ijk} are assumed to be random variables with means of zero and variances of σ^2_α, σ^2_β and σ^2_γ. The goal of the sample design used in Missouri is to obtain unbiased estimates of these variances. Estimates of σ^2_α, σ^2_β, and σ^2_γ are obtained by procedures outlined in table 2.

The three-level sampling design outlined in table 2 formed the basis for the preliminary sampling that was executed in Missouri last fall, although it was slightly modified to meet the exigencies of many of the major sampled units. The most common modification was that of adding another level at the top of the design (to estimate the effects of large-scale geographic variability) or another level at the bottom (to estimate very small-scale stratigraphic variability).

The variance component representing large-scale stratigraphic variability (σ^2_β) actually contains an unknown amount of geographic variability. This confounding of stratigraphic and geographic variability in σ^2_β is unavoidable because of the geologic setting of the central part of the United States, which consists of generally flat-lying rocks over areas of generally low relief. The effect is illustrated in figure 2 using the Lower Ordovician-Cambrian rock unit (map unit θO). A generalized geologic cross section from St. Joseph in the northwest to Cape Girardeau in the southeast is shown in this figure.

The base of the unit is exposed in the St. Francois Mountains region but the top is exposed some 100 miles away to the northwest. A stratigraphic section measured at the surface must be "pieced" together using available outcrops over this interval. For example, the beds at the base of the unit (up to horizon Y) may be sampled in the St. Francois Mountains region at C. The beds between horizons X and Y may be sampled in the Osage River bluffs at B and the topmost beds may be sampled at A. Because it is necessary to piece together geographically separated outcrops in order to obtain a complete stratigraphic section across the rock unit, the large-scale stratigraphic effects (σ^2_β) will contain an unknown amount of geographic variation. Such confounding of the variation at this level of the design in no way invalidates the model in (1), the analysis of variance method in table 2, or the resulting judgements as to number and location of additional sampling, but it does require that this confounding be considered in the geologic interpretation of the geochemical results.

Table 2. Analysis of variance table for three-level hierarchical design.[1]

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Mean Square is estimate of
1. Among stratigraphic sections	$SS_1 = \frac{1}{bc}\sum_{i}^{a}(\sum_{j}^{b}\sum_{k}^{c}X_{ijk})^2 -$ $\frac{1}{abc}(\sum_{i}^{a}\sum_{j}^{b}\sum_{k}^{c}X_{ijk})^2$	a-1	$\frac{SS_1}{a-1}$	$\sigma_\gamma^2 + c\sigma_\beta^2 + bc\sigma_\alpha^2$
2. Within stratigraphic sections A. Large-scale effects	$SS_2 = \frac{1}{c}\sum_{i}^{a}\sum_{j}^{b}(\sum_{k}^{c}X_{ijk})^2 -$ $\frac{1}{bc}\sum_{i}^{a}(\sum_{j}^{b}\sum_{k}^{c}X_{ijk})^2$	a(b-1)	$\frac{SS_2}{a(b-1)}$	$\sigma_\gamma^2 + c\sigma_\beta^2$
B. Small-scale effects	$SS_3 = \sum_{i}^{a}\sum_{j}^{b}\sum_{k}^{c}(X_{ijk})^2 -$ $\frac{1}{c}\sum_{i}^{a}\sum_{j}^{b}(\sum_{k}^{c}X_{ijk})^2$	ab(c-1)	$\frac{SS_3}{ab(c-1)}$	σ_γ^2

---

[1] Adapted from Krumbein and Slack (1956, p. 753). X_{ijk} is the analytical value on the kth sample taken from the jth part of the ith stratigraphic section, a is the number of stratigraphic sections, b is the number of sampled parts in each section and c is the number of samples from each sampled part. The indices i, j and k increase from 1 to a, 1 to b and 1 to c, respectively.

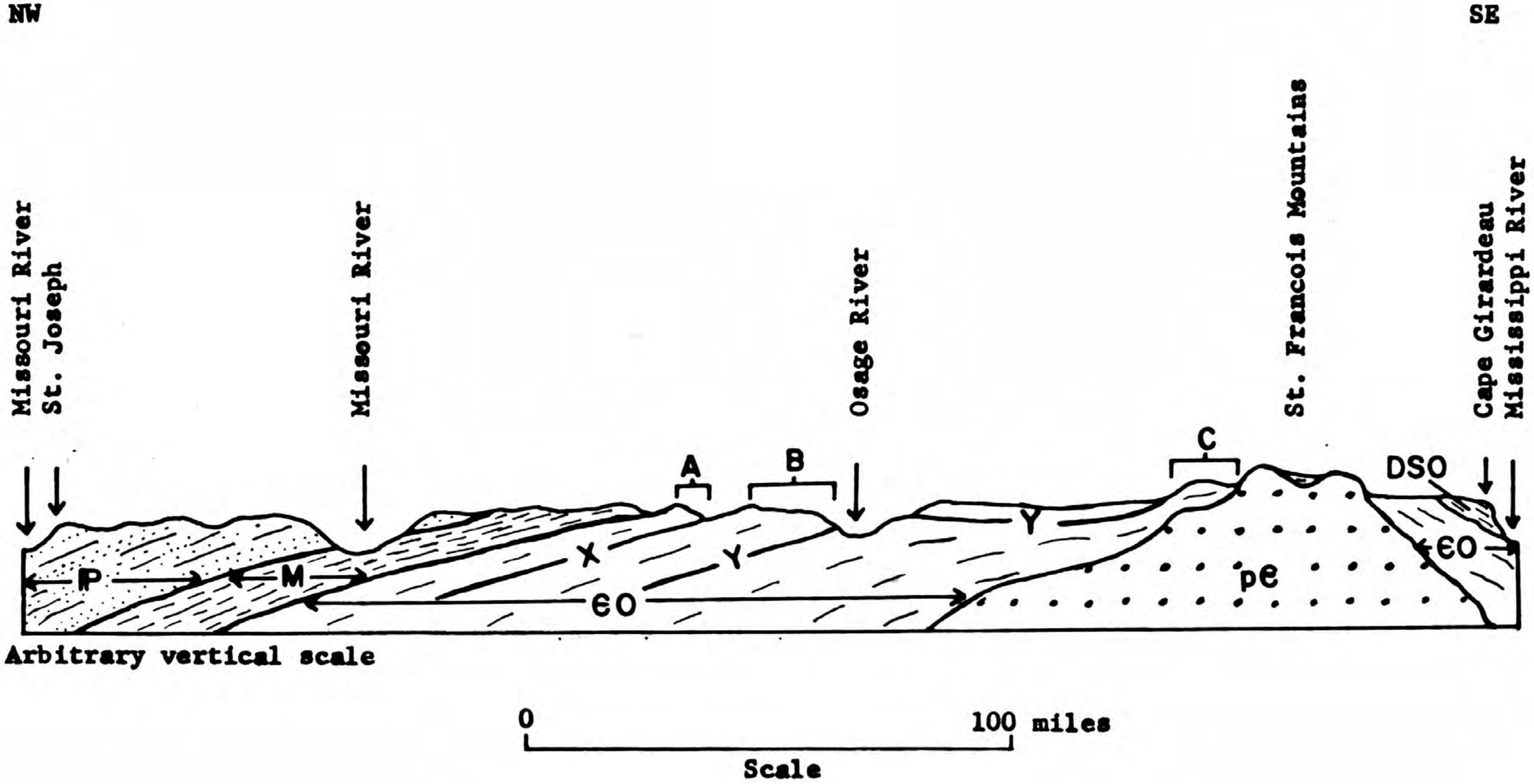

Figure 2. Generalized geologic cross section across Missouri from St. Joseph to Cape Girardeau illustrating the confounding of geographic and stratigraphic variation. Rock Units are those represented in figure 1.

Table 3. Average minor and trace element concentrations (expressed as geometric mean concentrations in parts per million) in miscellaneous geologic materials from Missouri. 1/

Element	Limestone and Dolomite			Sandstone			Shale, Siltstone and Claystone				"Granite"	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Ag	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.22 2/	< 0.5	< 0.5	< 0.5	< 0.5
As	< 1	1.1	< 5 2/	< 0.5	< 5 2/	1.9	2.8	< 5 2/	18	9.3	1.5	1.3
B	20	< 20	< 10	< 10	< 10	30	20	40	< 20	43	< 20	< 10
Ba	15	7.1	< 1.5	20	< 1.5	150	150	43	200	1000	70	300
Be	< 1	< 1	< 1	< 1	< 1	< 1	< 1	.98	2.6	.88	1	1
Cd	--	--	--	< 1	< 5 2/	< 1	< 1	.44 2/	.66	.93	< 1	< 1
Ce	< 150	< 150	< 150	< 150	< 150	< 150	< 150	< 150	< 150	110	100	< 150
Co	< 3	< 3	2.9	< 3	< 3	5	< 3	13	10	8.6	< 3	< 3
Cr	2.3	2.3	39	1	< 1	70	20	159	59	58	< 1	1
Cu	< 1	.94	2.5	< 1	2.5	2	10	15	47	16	< 1	2
F	200	140	650 2/	40	650 2/	200	< 40	1700 2/	620	320	1400	100
Ga	< 5	< 5	--	< 5	--	5	10	--	24	13	20	30
Hg	0.025	0.033	0.032 2/	0.02	0.017 2/	1.2	< 0.01	0.052 2/	0.10	0.063	0.02	< 0.01
I	< 0.5	< 0.5	1.7 2/	< 0.5	0.033 2/	< 2	< 0.5	0.21 2/	< 0.5	< 0.5	< 0.5	< 2
La	< 30	< 30	< 20	< 30	< 20	< 30	< 30	15	53	49	50	30
Mn	550	110	780	3	62	100	15	290	310	740	70	700
Nb	< 10	< 10	< 10	< 10	< 10	< 10	< 10	8.5	< 10	8.2	< 10	10
Nd	< 70	< 70	--	< 70	--	< 70	< 70	--	< 70	< 70	70	< 70
Ni	< 5	< 5	6.0	< 5	< 5	20	< 5	85	48	27	< 5	< 5
P	< 130	< 130	370	< 130	< 130	< 170	< 130	660	96	350	< 130	< 130
Pb	< 10	< 10	< 10	< 10	< 10	10	15	14	20	15	10	50
Se	--	--	< 5 2/	0.3	< 5 2/	0.1	--	2.0 2/	--	--	0.2	< 0.1
Sc	< 5	< 5	< 5	< 5	< 5	5.0	5.0	15	11	9.0	3.0	7.0
Sr	160	140	690	15	< 5	30	30	99	70	240	20	30
Ti	65	26	191	380	150	2400	2700	4600	1100	2100	380	980
V	< 7	1.6	21	< 7	< 7	30	50	130	140	86	< 7	< 7
Y	< 10	< 10	13	< 10	< 10	10	10	17	38	28	30	50
Yb	< 1	< 1	--	1.5	--	1	1	--	3.1	2.8	3	5
Zn	< 10	< 10	46 2/	< 10	< 10 2/	32	15	55 2/	140	72	26	125
Zr	< 10	< 10	12	200	24	< 10	< 10	125	< 10	< 10	70	700

1/ Averages based on analyses of the following samples:

(1) Bonneterre Dolomite, 11 samples, from Belleview, Mo. (Cambrian-Lower Ordovician map unit).

(2) Potosi Dolomite, 13 samples from Centerville, Mo. (Cambrian-Lower Ordovician map unit).

(3) Westerville Limestone, 30 samples from Kansas City, Mo. (Pennsylvanian map unit).

(4) Lamotte Sandstone, 1 sample from Farmington, Mo. (Cambrian-Lower Ordovician map unit).

(5) St. Peter Sandstone, 30 samples from Pacific, Mo. (Devonian-Silurian-Upper Ordovician map unit).

(6) Bluejacket Sandstone, 1 sample from a rock asphalt deposit at Deerfield, Mo. (Pennsylvanian map unit).

(7) Cheltenham Formation(?), 1 sample from a late Paleozoic sinkhole deposit near Centerville, Mo. (Pennsylvanian map unit).

(8) Quivira Shale, 30 samples from Kansas City, Mo. (Pennsylvanian map unit).

(9) Carbonate Residuum, 5 samples from Centerville, Mo. Data in part from Connor and Ebens (1970).

(10) Loess, 7 samples from Missouri River bluffs. Data in part from Connor and Ebens (1970).

(11) Granite, 1 sample from Iron Mountain, Mo. (Precambrian map unit).

(12) Rhyolite, 1 sample from Fredericktown, Mo. (Precambrian map unit).

2/ Geometric mean based on 5 (instead of 30) samples.

Preliminary minor element analyses.--During the first year of these studies, a number of small, separate investigations of various facets of Missouri bedrock geochemistry were undertaken (cf. U.S. Geological Survey, 1969, p. 5-8, and 1970, p. 22-29). Although the results of these studies can shed little light on the magnitude and source of geochemical variability present (the preliminary sample set described above is specifically designed to do this), they may offer some preliminary information on the minor or trace element content of these rocks. A summary of the geochemical data obtained to date in our studies is given in table 3 (p. 12).

Most elements, as expected, are more highly concentrated in the fine-grained sedimentary rocks (shales, siltstones and claystones). This reflects two basic geochemical facts. Of the common rock-forming minerals, only the clays (which are concentrated in shales, siltstones, and claystones) are crystallographically capable of abundant, large-scale metal substitution. That is, their crystal structure tends to be flexible enough to accommodate a large variety of metallic ions. Secondly, the generally fine-grain size and layered structure of the clay minerals results in rocks with large and electrostatically versatile mineral surfaces onto which metallic ions or complexes may adhere. It is for these reasons that clay-bearing rocks are sometimes viewed as "element trash baskets."

Limestones, dolomites and sandstones are generally trace-element poor compared with clay-bearing rocks. The major exceptions in table 3 are Sr in limestone (column 3) and Hg in sandstone (column 6). The high Sr value reflects the common tendency for the Sr^{++} ion to substitute for the Ca^{++} ion in the crystal lattice of calcite, the common mineral of limestone. The high Hg value is due to the fact that this particular sandstone sample has been impregnated with natural asphalt which, because of its organic nature, has a strong affinity for many metals, including Hg. Note that many metals are much more abundant in this sample (column 6) than in the other two sandstones, (column 4) and (column 5). These high contents also largely reflect the asphalt content of the sandstone in column 6. We emphasize that this sample (and the stratigraphic unit it represents) is a geological rarity. The granitic rocks also tend to be rich in trace elements although not as much so as the clay-bearing rocks. Their limited geographic extent (p€ map unit, fig. 1) makes them perhaps less interesting in the environmental sense than the widespread clay-rich rocks.

In general, minor or trace elements not listed in table 3 occur in very small amounts in ordinary rocks. Au, Bi, Ge, Hf, In, Li, Mo, Pd, Pt, Sb, Sn, Ta, Te, Th, Tl and U are commonly looked for during spectrographic analysis of rocks but are hardly ever detected. Concentrations of these elements in the rocks listed in table 3 are below the limits of analytical detection given in U.S. Geological Survey, 1970, p. 5-8.

Plans for 1971.--No further rock sampling is planned until the results of the chemical analyses on the preliminary sample set have been received and submitted to statistical analysis (as outlined in table 2). At such time as the statistical analysis is completed, a decision will be made as to the amount and location of any additional sampling required for satisfactory geochemical characterization of the map units. No firm date for completion of the chemical analysis is available but it is anticipated that results will be forthcoming no sooner than summer, 1971. The first half of 1971 will be spent in part on mineralogical examination of the preliminary sample set (using techniques of optical microscopy and x-ray diffraction) and in part on tasks preparatory to statistical analysis and report preparation.

Geochemical survey of soils

by R. R. Tidball

Present status of the sampling program.--The 1970 field season was devoted to two sampling projects. The first project was to complete the sample set of 10 specimens per county originally submitted by the Missouri Agricultural Extension Agents. Because, in some cases, we received either too small a specimen or no specimen at all, 125 new specimens were collected in 31 counties. A total of 1,140 specimens, from the localities shown in figure 3, have been submitted for chemical analysis.

In the second project, a study was initiated to examine the possible chemical grouping of soil profiles as a function of parent materials from which the soils were derived. This study includes soils developed on four landscape types, each a combination of prairie vegetation developed on either glacial till, loess, Pennsylvanian limestones of the Kansas City group, or Pennsylvanian sandstones and shales of the Cherokee group (fig. 4). A hierarchical sampling design is being used which consists of the following: 4 landscape types, 10 7½-minute quadrangles per type, and 2 soil profiles per quadrangle for a total of 80 soil profiles. Each profile is being sampled according to morphologic horizons to a depth of 65 inches; the procedure commonly yields 5 or 6 specimens per profile.

The average concentrations of arsenic, fluorine, iodine, mercury, and selenium in 188 soil specimens from the preliminary sampling project of 1969 (U.S. Geological Survey, 1969, p. 8-10; 1970, p. 30) are given in table 4. The detection ratios indicate that out of 188 specimens examined, As, F, Hg, and Se were detected in virtually all of them. With regard to iodine, the usual limit of detection for the colorimetric method is one ppm. At this concentration, however, errors can be as high as 100 percent. Concentrations above 0.5 ppm and below one ppm have been reported by the analyst with the understanding that individual values may be questionable, and a statistical summary should be viewed with caution.

Principal components analysis (previously reported in U.S. Geological Survey, 1970, p. 31) showed that the compositions of all of the soils studied (each with 28 elements reported) could be expressed as some combination of two soil series having extreme trace-element compositions, one the Bosworth Series, the other the Coulstone Series. The contrasting concentrations of arsenic, fluorine, iodine, mercury, and selenium in these two end-member soil Series are given in table 5. The results for these elements (except iodine) correspond to the general pattern previously established (U.S. Geological Survey, 1970, p. 33) that the Bosworth Series, developed on recent river alluvium, has higher concentrations of elements than the Coulstone Series which developed from carbonate rocks and weathered for a much longer time.

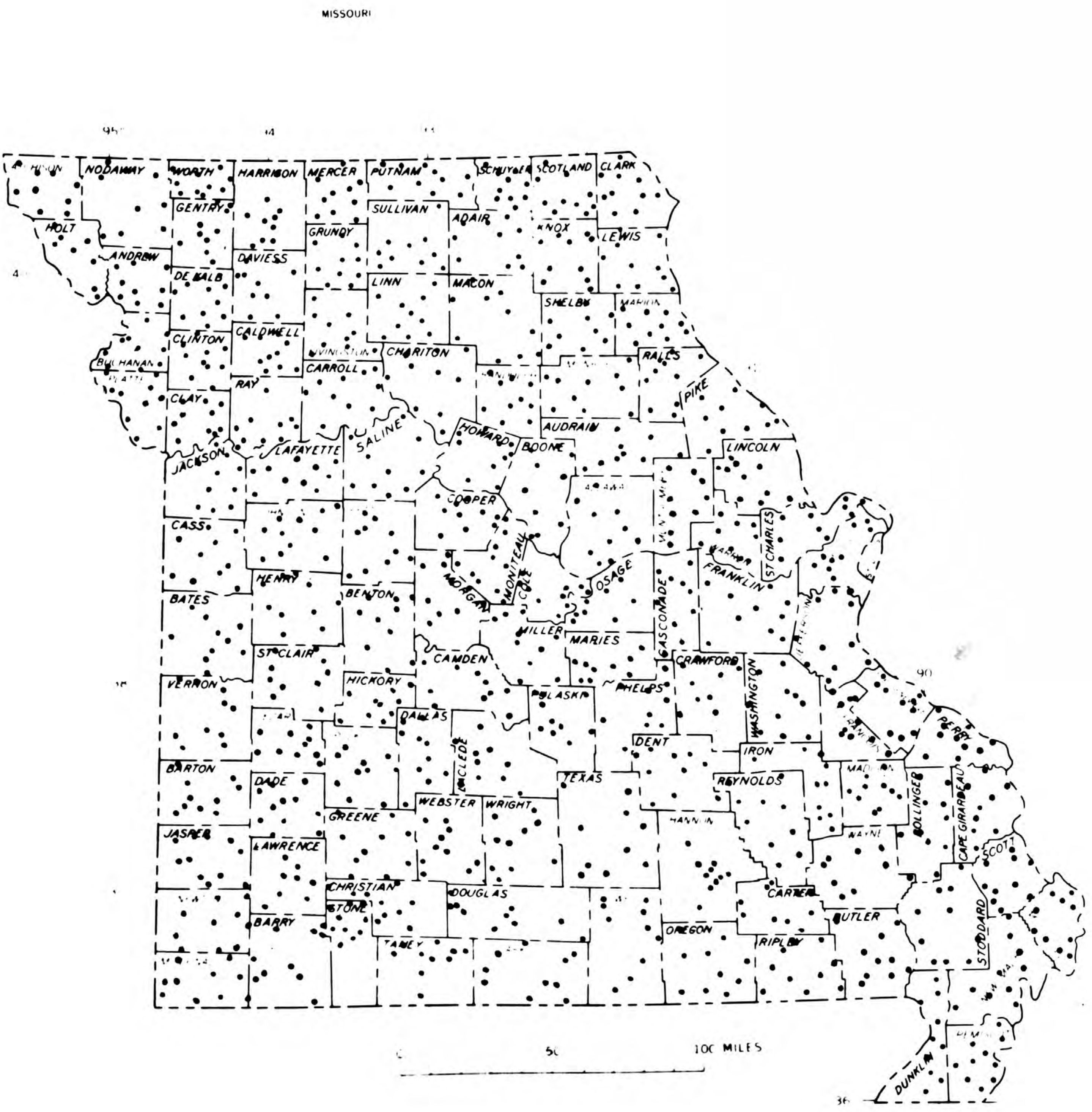

Figure 3. Map of Missouri showing localities where agricultural soils were sampled.

Table 4. Element concentration in surface horizons of soils collected for preliminary sampling project of 1969.

[All values are in parts per million. The geometric mean (GM) and geometric deviation (GD) are explained in U.S. Geological Survey, 1970, p. 17.]

Element	GM	GD	Detection Ratio[1]	Lower limit of detection
As	7.2	1.42	188 : 188	0.2
F	250	2.02	187 : 188	10
Hg	.052	1.94	188 : 188	.01
I	.64	1.35	111 : 188	.5
Se	.33	2.19	180 : 188	.05

1/ First number indicates number of specimens in which the element was detected. Second number indicates number of specimens analyzed.

Table 5. Average compositions of soil samples from the Bosworth and Coulstone Series. These series are end members of overall contrasting composition.

[Means are in parts per million. The geometric mean (GM) and geometric deviation (GD) are explained in U.S. Geological Survey, p. 17. Leadered entries (-) mean no data available.]

	Series			
	Bosworth (4 samples)		Coulstone (4 samples)	
Element	Geometric mean	Geometric deviation	Geometric mean	Geometric deviation
As	12.0	1.00	6.2	1.01
F	680	1.01	115	1.51
Hg	.067	1.00	.027	1.02
I	.65	1.01	----	----
Se	.69	1.01	.12	3.81

Discussion of efficiency in sampling designs.--Of 33 elements studied in soils to date, the analytical procedures used for 31 of them are sufficiently precise to describe differences among individual specimens. The analytical procedures used for iodine and mercury, however, tend to be too imprecise for general use in soil studies. The iodine procedure has been abandoned principally because iodine concentrations in soils are commonly below the limit of analytical detection. Mercury, on the other hand, is nearly always detected but the analysis needs to be at least 16 times as precise in order to detect differences among individual soil specimens at the 95 percent confidence level. In spite of this analytical imprecision, the mercury method may be sufficient to measure differences among groups of specimens (representing Suborders, for example) that have regional importance.

The following discussion describes a procedure for designing an efficient sampling plan to determine the distribution of mercury among soil Suborders. Analytical precision was estimated by selecting a random subset of 25 specimens from the total sample of 188. Each of the 25 specimens was split into two parts, each part was randomized among the 188 specimens, and the entire group was analyzed in a random sequence. Analysis of variance of the 25 duplicate analyses permitted estimation of the variance component due to laboratory imprecision. This estimate is compared with all of the variance components arising from other sources to determine the adequacy of the laboratory method for specific purposes.

The objective of the preliminary sampling program is to estimate the number of specimens that are necessary to provide a stable estimate of the group mean, however the group is defined. Groups (such as Suborders) may may be distinguished from one another only if differences within groups are small enough so as not to obscure differences between them. These respective differences (measured by the variance) are compared by the variance ratio, V,

$$V = \frac{S_b^2}{S_w^2} \tag{1}$$

where S_b^2 is the estimated variance between groups, and S_w^2 is the estimated variance within groups. V cannot be changed (it is a fundamental property of the soils) but if S_w^2 is replaced by the variance of the mean within groups, $S_{\bar{x}}^2$, an adjustable variance ratio, V_m, is defined

$$V_m = \frac{S_b^2}{S_{\bar{x}}^2} \tag{2}$$

where $$S_{\bar{x}}^2 = \frac{S_w^2}{N} \tag{3}$$

and N is the number of random samples within each group used to estimate a group mean.

The estimated variance components for log mercury, along with the associated percentage of total variance, are:

1 - Between Suborders (S_1^2)	.0070	6 percent
2 - Between Subgroups (S_2^2)	0.	0 "
3 - Between Series (S_3^2)	.0126	12 "
4 - Between localities (S_4^2)	0.	0 "
5 - Between specimens (S_5^2)	0.	0 "
6 - Between analyses (S_6^2)	.0876	82 "

Clearly, a large percentage (82 percent) of the total variance is due to analytical variation.

If we focus on distinguishing among the Suborders, V becomes:

$$V = \frac{S_1^2}{S_2^2 + S_3^2 + S_4^2 + S_5^2 + S_6^2} = \frac{.007}{.100} = .07 \qquad (4)$$

Recent investigations by A. T. Miesch, J. J. Connor, and the writer have shown that in order to describe differences among groups with any acceptable degree of confidence, N in equation 3 must be such that V_m in equation 2 is equal to at least unity. Thus, if N = 15, V_m becomes adequately large:

$$V_m = \frac{S_1^2}{\dfrac{\sum\limits_{i=2}^{6} S_i^2}{N}} = \frac{.007}{\dfrac{.100}{15}} = 1.05 \qquad (5)$$

Equation (5) may be expanded to:

$$V_m = \frac{S_1^2}{\dfrac{S_6^2}{n_6 n_5 n_4 n_3 n_2} + \dfrac{S_5^2}{n_5 n_4 n_3 n_2} + \dfrac{S_4^2}{n_4 n_3 n_2} + \dfrac{S_3^2}{n_3 n_2} + \dfrac{S_2^2}{n_2}} \geq 1.05 \qquad (6)$$

where the n_i represents the number of items collected at each level of the design. The n_i may be adjusted in any manner whatsoever in order to keep $V_m \geq 1.05$. It is apparent that, in general, V_m can be most effectively increased by increasing n_2 (the number of Subgroups within each Suborder). In this example, however, $S_2^2 = 0$ while $S_3^2 = .0126$. It is impractical to attempt to measure differences among Subgroups, but not among Series. Therefore, increasing n_3, the number of Series within Subgroups, is in this case the most effective way of increasing V_m.

The results on V_m of various combinations of n_i are given in table 6. Note that the data from the preliminary design of 2, 2, 3, 2, 1 (without any analytical duplication) are adequate ($V_m = 1.03$). The same design but with duplicate analyses (2, 2, 3, 2, 2) improves V_m (1.41), but at the expense of doubling the analytical load (N) from 24 to 48 analyses per soil Suborder. The smallest analytical load (N = 15) is achieved at the cost of locating and sampling 15 different soil Series for each Suborder. Here the combination 1, 15, 1, 1, 1 indicates 15 randomly selected Series per Suborder with one analysis per specimen and one specimen per Series. If we assume that the cost of locating a different Series and collecting a specimen from it is greater than that of a duplicate analysis, somewhat better results ($V_m = 1.34$) may be achieved by sampling only 8 Series and performing the laboratory analysis on each specimen in triplicate (1, 8, 1, 1, 3 in table 6).

In spite of the ability to describe the compositional differences in mercury among soil Suborders with imprecise analyses, the variance components for most other elements indicate that compositional variations among Suborders are rather small. It is for this reason that major attention has turned to sources of variation associated with other factors--such as soil parent materials. It should be pointed out here that the analytical error variance components for most elements determined in our laboratories are quite small compared with the naturally occurring variation in the soils. In general, the analytical error is no obstacle in data interpretation.

Plans for 1971.--Sample collection will be continued on the soil parent material study. The map in figure 4 shows the location of existing sampling sites and proposed sites.

Table 6. The variance ratio (V_m) for log mercury concentrations calculated by equation (6) for various combinations of n_i ($i = 2, \ldots 6$).[1]

n_2	n_3	n_4	n_5	n_6	V_m	N
2	2	3	2	1	1.03	24
1	15	1	1	1	1.05	15
1	7	1	1	3	1.18	21
1	10	1	1	2	1.25	20
1	8	1	1	3	1.34	24
1	11	1	1	2	1.37	22
1	20	1	1	1	1.40	20
2	2	3	2	2	1.41	48
1	10	1	1	3	1.68	30

[1] n_2 = number of Subgroups per Suborder.
n_3 = number of Series per Subgroup.
n_4 = number of localities per Series.
n_5 = number of specimens per locality.
n_6 = number of analyses per specimen.
N = total number of analyses required per Suborder to derive estimates of the Suborder means that are sufficiently precise to describe Suborder differences.

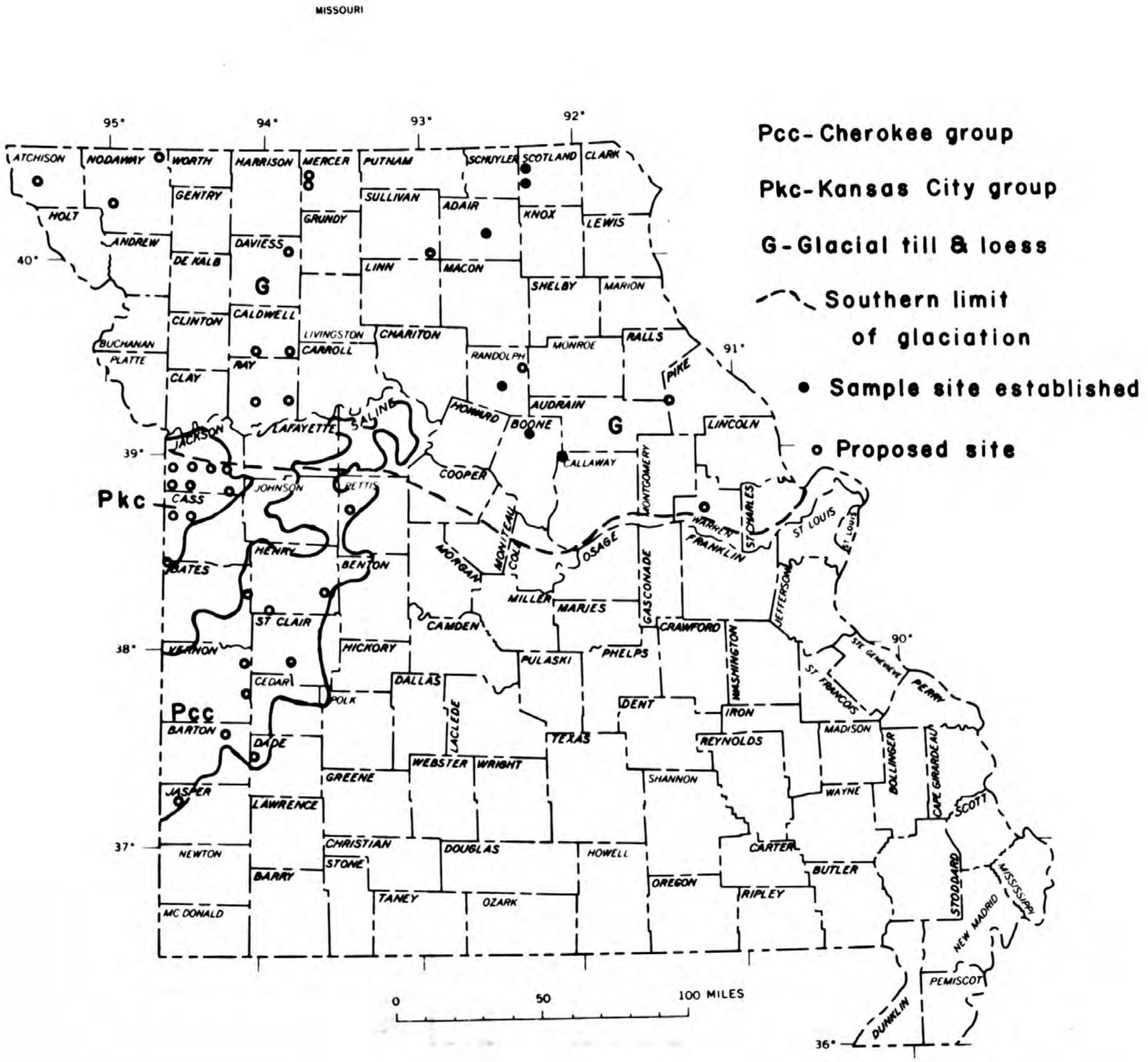

Figure 4. Map of Missouri showing sampling localities for soil parent material study.

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

Present status of the sampling program.--The sampling plan that was executed in September and October, 1970, was based on results of the preliminary sampling program of 1969, as described in U.S. Geological Survey (1970, p. 44-46). This stratified sampling plan required the random selection of 5 sites in each of 10 randomly selected 7½-minute quadrangles within each of the 6 vegetation types in Missouri. These quadrangles and sites were selected and marked on topographic maps before going to the field. In addition, 3 alternate quadrangles with 5 sites each were randomly chosen in each vegetation type for use if some of the originally selected quadrangles did not have the required species. These alternate quadrangles were used in 2 vegetation types--3 in the oak-hickory forest, and 1 in the cedar glade. The extent of these vegetation types, and the locations of quadrangles that were sampled, are shown in figure 5. Because of the restrictions of map scale, individual sampling sites could not be shown in this figure.

The principal difficulties in following the sample program were caused by the lack of 7½-degree topographic maps for some quadrangles in the vegetation type areas, and the obsolescence of other maps. This inadequate map coverage hindered determination of the location and access routes to certain sites. The problem was especially pronounced in areas along the southern border of the State, where artificial lakes produced by damming of streams obliterated roads indicated on the out-of-date maps. It was also noted that many road designations on the topographic maps, as well as on commercially-prepared road maps, do not agree with present road signs.

Field studies.--Notes on sample collecting include the species of plants and number of samples that were collected, and miscellaneous observations made of each vegetation type.

1. Glaciated prairie. Smooth sumac (*Rhus glabra*), 50; buckbush (*Symphoricarpos orbiculatus*), 47; big bluestem grass (*Andropogon gerardi*), 5. The partridge pea (*Cassia fasciculata*) was to be one of a pair of species to be sampled at sites throughout the State; field experience, however, indicated that it was not as ubiquitous as originally believed. Buckbush, therefore, was substituted for it. Big bluestem grass was once a characteristic species of the Missouri prairies, but because it generally grew most abundantly on land that was suitable for cultivation, only isolated stands of this grass can be found at present.

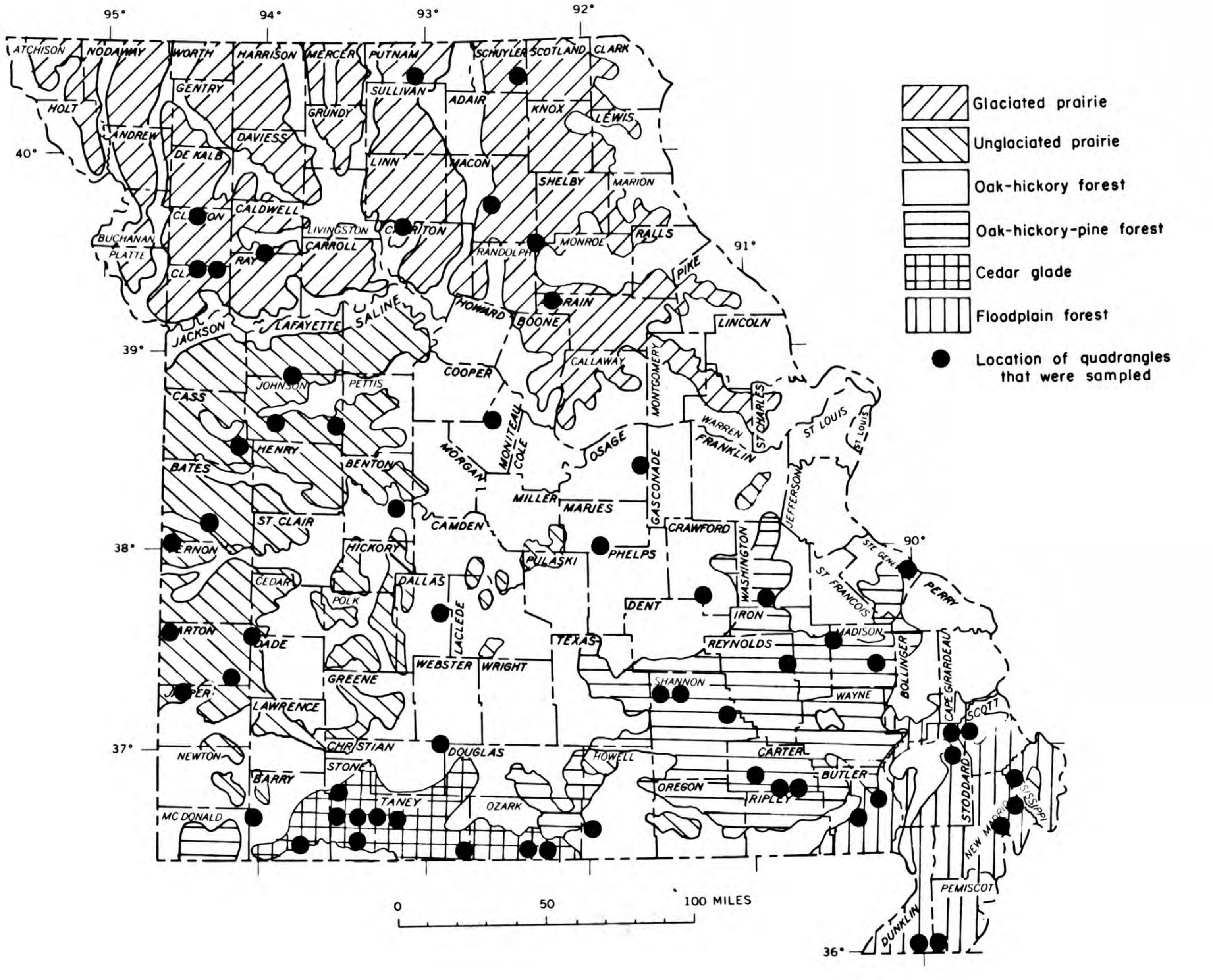

Figure 5. Vegetation types in Missouri, and location of quadrangles in which plants were sampled.

2. Unglaciated prairie. Smooth sumac, 50; buckbush, 47. The same problems in locating and identifying prairie sites existed here as in the glaciated prairie because most prairies are now in cultivation. The area likewise is dissected by fragments of the oak-hickory forest that are common in the drainage systems.

3. Oak-hickory forest. White oak (*Quercus alba*), 50; shagbark hickory (*Carya ovata*), 19; smooth sumac, 50; buckbush, 49. Three randomly selected quadrangles were rejected because of the scarcity of white oak or hickory, and alternate quadrangles were substituted. We found shagbark hickory to be less abundant than was anticipated; perhaps a more complete suite of hickory samples would have been obtained if we had chosen another species of hickory (*Carya tomentosa*).

4. Oak-hickory-pine forest. White oak, 49; shagbark hickory, 7; short-leaf pine (*Pinus echinata*), 49; smooth sumac, 49; buckbush, 41. Shagbark hickory was relatively rare in this vegetation type area; *Carya tomentosa* would have been a better choice for sampling. This vegetation type occurs commonly in areas of highly dissected topography, and the general scarcity of secondary roads and passable trails made some sites difficult to reach. At some places alternate sites were chosen as near the selected site as possible. Isolated areas of this vegetation type too small to be shown on Küchler's (1964) map were found in both the oak-hickory forest and the cedar glade types.

5. Cedar glade. Cedar (*Juniperus virginiana*), 50; post oak (*Quercus stellata*), 50; smooth sumac, 49; buckbush, 50. The area of this vegetation type as shown in figure 5 is misleading,if it is considered to indicate that cedar glades occupy most of the area. The glades consist of many relatively small isolated stands of cedar and other characteristic species surrounded by oak-hickory, or occasionally oak-hickory-pine, forests. The relationships of edaphic factors that lead to the development of cedar glades are not well understood. We observed that glades develop only where either limestone or dolomite bedrock crops out or is near the surface, usually where there is but little slope, and where there are marked periods of summer drought. The glades occur on hill summits, in saddles, and on gently sloping benches, if red residuum is absent. A shallow, azonal, highly organic soil that has only a few chert fragments immediately overlies the carbonate bedrock. The glades have little economic importance; they supply only limited pasture for livestock, and a few cedar posts. The ground cover is sparse and is composed largely of herbaceous species that are entirely, or almost entirely, restricted to this vegetation type. We found no glade sites in one of the chosen quadrangles that was mapped as an area of cedar glades, therefore an alternate quadrangle was sampled. Some of the randomly chosen sites did not fall in cedar glades, hence the glade nearest the chosen site was sampled. These alternate sites commonly were located by following an altitudinal contour where carbonate rocks cropped out.

6. Floodplain forests. Willow oak (Quercus phellos), 46; sweet gum (Liquidambar styraciflua), 47; smooth sumac, 48; buckbush, 4. The area of this vegetation type, as shown in figure 5, is now mostly under cultivation, having been cleared of timber and drained with numerous ditches. Only a few forest stands, therefore, occurred at the selected sample sites. At these sites (many of which fell in very large cultivated fields) the nearest ditch bank, roadside, or small grove in which the selected species grew was chosen for sampling. The highly-developed farm management practices generally followed in this area, including the widespread use of herbicides, made the location of the desired species difficult in some quadrangles. In addition, the numerous drainage ditches prevented access to some selected sites either by vehicle or on foot. We found overcup oak (Quercus lyrata), the species originally selected for sampling, to be restricted to forests, therefore rare. In its place we sampled willow oak, a "weedy" species of roadsides and ditch banks. Buckbush was rare in this vegetation type, although abundant in all others.

In summary, we found the characteristic species in each vegetation type generally to be sufficiently abundant for our sampling plan to be satisfactorily executed. We found smooth sumac at nearly all sites in all vegetation types, and buckbush was adequately sampled in all but the floodplain forest type. The sampling program was accomplished by 2 men in approximately 42 days of field work. A total of 300 soil samples and 950 plant samples was collected.

Laboratory studies.--The samples were shipped to Denver where they were dried in an electric oven. All plant samples were then assigned random numbers from 1 to 950; the soil samples likewise were numbered randomly. The samples were coded for our data storage and retrieval system and submitted to the Geological Survey laboratories for chemical analyses to be performed in random order.

The soil samples were pulverized in a ceramic mill without removing rock fragments that may have been present. The plant samples, when brittle dry, were shredded in a Wiley mill and portions were weighed, burned to ash in an electric muffle, and the percentages of ash calculated. In analyzing some elements the dry plants, not ash, must be used. Although reports of analyses of some soil samples have already been received, several months will be required to complete the analyses.

Plans for 1971.--When completed results of plants and soil analyses are received from the laboratories, they will be analyzed statistically in order to determine the conclusions and to prepare the report on the geochemistry of soils and plants in the vegetation types of Missouri. We plan to sample crop plants and cultivated soils in Missouri in late summer and fall, following the same general plan of sampling as was used in the study of vegetation types.

Geochemical survey of water
by G. L. Feder

Present status of sampling program.--Field work for the preliminary groundwater sampling program in Missouri has been completed. The sampling plan consisted of 1) dividing the groundwater of the State into seven geohydrologic units, 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. A total of 56 samples were collected in a 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. The two wells within selected townships were sampled to determine the compositional variation on a very local scale. The duplicate samples within selected wells are intended to measure the sampling and analytical error associated with the characterization of a single well, error due to both temporal changes at the well and imprecision in the laboratory method.

The locations of the sampling sites are shown in figure 6. The limited numbers of acceptable sampling sites within the glacial drift and Pennsylvanian geohydrologic units led to some clustering of sampling localities.

Some preliminary results.--Most of the laboratory results on the collected samples are pending, but those pertaining to NO_2, NO_3, NH_4, and organic nitrogen have been completed. The total nitrogen in each sample has been computed from these results. In addition, the specific conductance of each sample and its pH were measured at the well at the time of collection. The proportion of the total variance in each of these properties was estimated for each level of the sampling design. These estimates are given in table 7. It will be seen that relatively little of the variance in specific conductance, pH, and NH_4 is due to either temporal changes at the well or measurement error (table 7, column 1). Most of the variation in specific conductance and pH is from one township to another within a geohydrologic unit (table 7, column 3). The proportion of the total variance that is associated with differences among geohydrologic units is statistically significant at the 0.05 level for all properties except pH and NO_2.

It is common practice in the evaluation of groundwater quality to use the nitrate (NO_3) content of the water as an index of organic pollution. This practice is based on the assumption that most forms of nitrogen in potable groundwater will rapidly oxidize to the nitrate form. This assumption is probably true where the water is well-oxygenated, but many groundwaters in Missouri are reducing as indicated by the odors of H_2S.

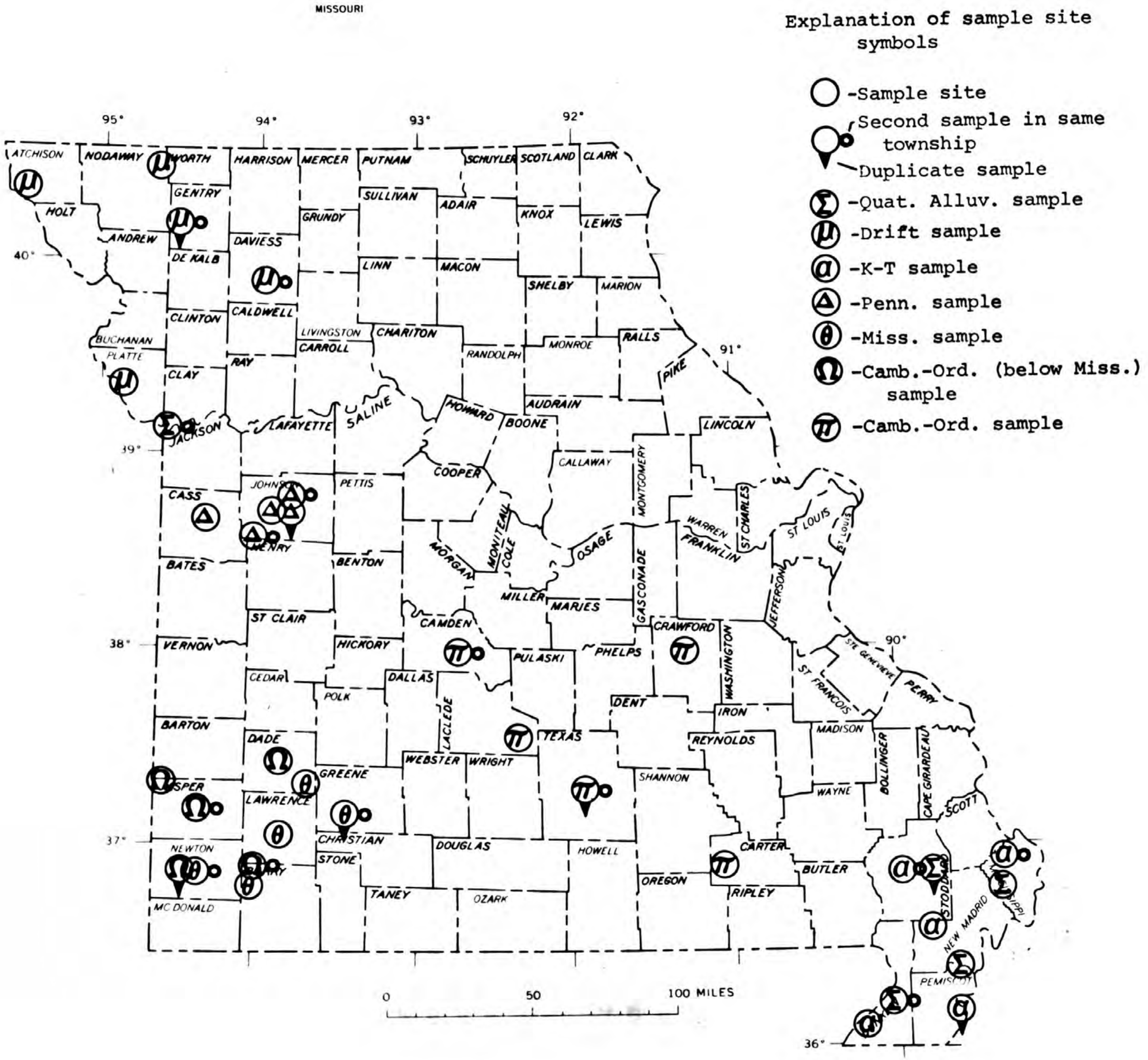

Figure 6. Map of Missouri showing locations of wells from which waters were sampled from various stratigraphic (geohydrologic) units.

Table 7. Distribution of variance in some chemical properties of groundwater in Missouri.

Property	Percent of variance			
	(1)	(2)	(3)	(4)
	Between analyses of water from the same well	Between wells from the same township	Between townships from the same geohydrologic unit	Between geohydrologic units
Specific conductance	3	9*1/	52*	36*
pH	13	7	77*	4
NO_3	46	19	0	35*
NO_2	(33)2/	(60)	(0)	(7)
Organic N as N	32	39	1	28*
NH_4 as N	18	15	10	57*
Total N as N3/	58	0	30	13*

1/ * indicates that the variance component at this level is significantly different from zero at the 0.05 or lower level of probability.

2/ Values in parentheses are uncertain due to the fact that NO_2 was not detected in about one-half of the samples analyzed.

3/ Calculated.

Where conditions are reducing, ammonia and organic nitrogen are chemically stable with respect to nitrate, and total nitrogen, organic nitrogen, or ammonia may serve as more reliable pollution indicators. None of these indicators is totally reliable as each of the constituents may occur in high concentrations through natural processes, but man-made pollution is immediately suspected when high concentrations are encountered.

As an illustration, three water samples collected from one township in Missouri had an average nitrate content of only 0.36 mg/l (as N)--less than the average nitrate content of all samples collected and certainly no cause for concern. However, the high average organic nitrogen and ammonia contents of these samples (7.2 and 7.5 (mg/l) as N, respectively) strongly indicates a possibility of organic pollution.

Cursory examination of the partially completed laboratory results indicates that molybdenum was detected only in the groundwaters from Cambro-Ordovician rocks in the southwestern part of the State. The presence of extensive mineral deposits in this part of the State may be relevant to this observation, but we wish to reserve interpretation until all of the analytical data have been received.

Plans for 1971.--The data from the preliminary sampling program will be analyzed using nested analysis of variance techniques. The results of this analysis will indicate where more sampling is required and which elements need further sampling. Results of water analyses will be compared to results obtained from rock, soil, and plant analyses to determine what relationships exist. Areas of the State found to contain health anomalies by the Environmental Health Center, will be compared with results of water analyses to determine if any relationship exists. If health anomalies are found in areas containing insufficient water data, provisions have been made for a limited number of additional water samples this fiscal year.

If the present samples of groundwaters prove adequate for describing most of the compositional differences among the seven geohydrologic unit, and if all special purpose sampling of groundwaters can be completed this spring, the sampling of surface waters of the State will commence this spring.

References cited

American Association Petroleum Geologists, 1966, Geological highway map of the mid-continent region: U.S. Geol. Highway Map Series, Map no. 1.

Geological Society of America, 1952, Pleistocene eolian deposits of the U.S., Alaska, and parts of Canada (map).

Krumbein, W. C., and Slack, H. A., 1956, Statistical analysis of low-level radioactivity of Pennsylvanian black fissile shale in Illinois: Geol. Soc. America Bull., v. 67, p. 739-762.

Küchler, A. W., 1964, Potential natural vegetation of the conterminous United States: Special Publ. no. 36, Am. Geogr. Soc., 116 p. + map.

Potter, P. E., and Olsen, J. S., 1954, Variance components of cross-bedding directions on some basal Pennsylvanian sandstones of the Eastern Interior Basin: Geological application: Jour. Geol., v. 62, p. 50-73.

U.S. Geological Survey, 1969, Environmental geochemistry, Geochemical survey of Missouri, Plans and progress for first six-month period (July-December, 1969), Denver, Colo., 49 p.

U.S. Geological Survey, 1970, Environmental geochemistry, Geochemical survey of Missouri, Plans and progress for second six-month period (January-June, 1970), Denver, Colo., 59 p.

GPO 834-196