ENVIRONMENTAL GEOCHEMISTRY

Geochemical Survey of Missouri
Plans and progress for second six-month period
(January - June, 1970)

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

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Preface

A survey of the environmental geochemistry of Missouri is being conducted by the Branch of Regional Geochemistry of the U.S. Geological Survey in support of statewide epidemiological studies by the Environmental Health Surveillance Project of the University of Missouri. The Surveillance Project studies are under the direction of Carl J. Marienfeld, M.D. This progress report, the second in a series, briefly describes the results of the first year of the survey and outlines plans for the forthcoming field season. This first year has been spent principally in orientation studies--gaining a better familiarity with the geology, the soils, and the vegetation of the State, and a somewhat better understanding of procedures that may lead us closer to the goals of the project.

The emphasis in this work is on determining the chemical characteristics of the natural environment, although certain effects of environmental pollution must necessarily be examined as they bear on our primary objectives. We note from the popular news media that nearly all of the public concern for environmental quality is directed at pollution problems. There seems to be little or no acknowledgement of the fact that environmental quality may vary greatly from one place to another independently of pollution effects. Because of large, and presumably important, differences in the chemical character of the natural environment, studies of environmental quality must include examination of natural variation. It is conceivable, for example, that the cadmium contents of vegetables may depend more on whether they are grown in soils derived from shale or limestone than on whether they are grown near industrialized areas. Our work in Missouri is directed primarily at problems of this kind. It is also directed at the development of efficient field and laboratory methods for this type of work.

We are indebted to the staff of the Environmental Health Surveillance Project for their continued support of our work and for the many courtesies extended to us. We feel fortunate to be associated with the Surveillance Project, for, as stated in the Preface of our report on the first six-month period of the project, the systematic and comprehensive approach being taken in their epidemiological studies of an area that is large enough to be geologically diverse offers an opportunity for parallel studies in environmental geochemistry that has not been previously available.

We are also indebted to the staffs of the Missouri Division of Geological Survey and Water Resources and of the Soil Conservation Service, U.S. Department of Agriculture, for their cooperation and assistance in the design and execution of our sampling programs.

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

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INTRODUCTION AND SUMMARY

This is the second six-month progress report on studies in environmental geochemistry in the State of Missouri initiated on behalf of the Environmental Health Surveillance Project in July, 1969. The studies are being made in support of epidemiological investigations of the Surveillance Project to provide general information pertaining to the occurrence and distribution of chemical elements in rocks, soils, plants, and water throughout the State. Emphasis is placed on the occurrence and distribution of elements in the natural environment, though studies of the effects of some types of chemical pollution are necessarily included. The objectives and plans for the three phases of the Survey that are directed at the rocks, soils, and vegetation are described in the progress report for the first six-month period; those for the phase of the project concerned with the water are described by Gerald L. Feder in a later section of the present report. The addition of this latter phase significantly expands the scope of our study and increases its relevance to studies of human and animal health. Mr. Feder has a valuable background in the geology and hydrology of Missouri, and we are most pleased that he has joined us in this effort.

Our preliminary studies this past year have increased our familiarity with the geology, soils, and vegetation of the State, and the results of preliminary sampling will serve to guide us in the further extensive sampling that is planned. One result of immediate special interest was obtained during the course of this preliminary work. This was the identification of extraordinarily high concentrations of metals, principally lead, in cedar trees near a highway in Reynolds County. This was reported in the progress report for the first six-month period, but since then we have been informed by Dr. Arthur Case of the Environmental Health Surveillance Project that several horses died from lead poisoning in this general region of the State; the specific location was along the same highway about 18 miles east of the area on which we reported.

Progress in the study of the occurrence and distribution of elements in geologic units--the bedrock--of the State has consisted largely of the compilation of stratigraphic information and gaining familiarization with the stratigraphy and the occurrence of outcrops. Valuable assistance was provided by personnel of the Missouri Division of Geological Survey and Water Resources. One important result of some preliminary sampling has been the determination of the fact that rock samples collected from outcrops along highways do not reflect trace element contamination from highway sources if the samples are trimmed in the manner that is customary in geologic sampling. This is an important determination because the best exposures of the geologic units are in cuts along major highways. Some other preliminary data have been obtained showing some of the compositional differences between loess and carbonate residuum--the two parent materials from which most of the soils of the State have been derived. Plans for the forthcoming field season include the initiation of a sampling program designed to estimate the geochemical characteristics of all major geologic units of the State.

Initial sampling of the soils of the State has shown that the conventional system of soil classification may not provide an ideal framework on which to base a major sampling program. The results have shown that the chemical characteristics of soil types, as defined by the soil classification system, overlap by considerable amounts. It is expected that some alternative scheme of soil classification may be more suitable for geochemical studies. The Soil Conservation Service and Mr. H. E. Grogger, in particular, have provided valuable guidance in this preliminary work. We sincerely appreciate their cooperative assistance. The Extension Division of the University of Missouri has completed the collection of 10 representative soil samples from nearly all of the 114 counties of the State, and laboratory work on the samples will begin as soon as they can be sorted and prepared for analysis.

Six broad areas of the State exhibiting characteristic vegetation types have been sampled in reconnaissance fashion to obtain estimates of the volume of sampling that will be required to adequately describe the differences among the areas. Samples were taken of several plant species and of associated soils. Study of the laboratory data on the soils indicates that the soils of the areas of different vegetation type are somewhat distinct in some compositional aspects, and that the differences among the areas may be adequately defined with a moderate amount of further sampling. The extent to which this will hold true for the plant species has not been finally determined. It has been determined, however, that various species of the same plant genera may vary widely in trace element content and that the conventional scheme of plant classification, like that of soil classification, may not be an ideal framework for sampling in geochemical studies. But, unlike the situation with the soils, there seems to be little likelihood that plants may be studied within some alternative framework. It will be more likely that representative species of plants will be selected for study from the more than 3,000 species present throughout the State. The species selected will include both agricultural crops and natural vegetation.

The phase of the project directed at the water of the State was initiated only within the past several months. The principal accomplishment to date has been the development of some general plans and objectives. Most of the concern so far has been with the problems of sampling underground waters as these are expected to best represent the geochemical environment. Surface waters are generally less reliable indicators of the geochemical environment due to susceptibility to man-made pollution, dramatic effects of organisms on water chemistry, and frequent rapid changes in quality due to surface runoff. The ground waters may be generally classified according to the geologic system in which the waters occur and the depth below the surface. Viewing the ground water in this way leads to the recognition of 7 general geohydrologic units throughout the State. Preliminary sampling of each of these systems, and of selected surface waters, will begin within the next six months. Samples will be taken of both raw and finished water, and analyses will be made in the Denver laboratories of the Geological Survey. The primary goal of the water investigations will be to determine the gross geochemical character, including the trace element content, of major geohydrologic units throughout the State and to identify the geochemical relations between water chemistry and the chemistry of aquifers and drainage areas. Special investigations of water composition will be made where they may have bearing on epidemiological problems identified by the Environmental Health Surveillance Project.

An airborne gamma-ray survey was made during this report period across parts of Iron, St. Francois, and Ste. Genevieve Counties. The flight path was selected to cross geologic features of particular interest and because of certain epidemiological characteristics of St. Francois County. The predominant feature of the gamma-ray profile along the flight path is a radiometric "high" over the granitic rocks of the St. Francois Mountains, which reflects a higher concentration of potassium in these rocks than in the surrounding sedimentary rocks. Detailed sampling of rocks and soils along the flight path will be conducted this summer. Alpha-radioactivity, believed by Masironi (1970) to be negatively correlated with the occurrence of heart disease, cannot be measured in airborne surveys. We may speculate, however, that the granitic rocks of the St. Francois Mountains contain more uranium and thorium than the surrounding sedimentary rocks, and, therefore, emit more alpha radiation. This may be of interest in view of a conclusion by Herbert I. Sauer (written communication, 1969) that St. Francois County rates in the upper octile for the entire United States in adjusted death rates due to cardiovascular causes.

Selection of analytical methods

Because the environmental geochemistry studies in Missouri may extend over a considerable period of time, perhaps 5 years, it is important that an effort be made to maintain consistency in laboratory methods from the beginning of the project to the end. This will insure that observed geochemical variation reflects actual variation in the materials sampled rather than changes in laboratory methodology. Conferences with Dr. F. S. Grimaldi, Chief Chemist of the U.S. Geological Survey, and his staff have led to the establishment of procedures that will be used for the analysis of rocks and soils throughout the duration of the project. Specified in the procedures for the determination of each chemical element are 1) the analytical method, 2) the lower limit of analytical determination, and 3) the specific Geological Survey laboratory (table 1).

Table 1. Analytical methods for rocks and soils.

Element	Selected analytical methods	Lower limit of determination (parts per million)	Laboratory
Ag	Spectrographic [1/]	0.5	Denver
Al	Spectrographic X-ray fluorescence	10 10,000	Denver Denver
As	Spectrographic Dithio carbamate-colorimetric	1,000 0.2	Denver Washington
Au *	Spectrographic	20	Denver
B	Spectrographic	20	Denver
Ba	Spectrographic	1.5	Denver
Be	Spectrographic	1	Denver
Bi *	Spectrographic	10	Denver
C (total)	Leco gasometric	500	Denver
C (in CO_3)	Gasometric	100	Denver
C (organic)	Calculated as the difference between C (total) and C (in CO_3)	1,000	Denver
Ca	Spectrographic X-ray fluorescence	20 1,000	Denver Denver
Cd	Spectrographic Atomic absorption [2/]	20 1	Denver Denver
Ce *	Spectrographic	150	Denver
Co	Spectrographic	3	Denver
Cr	Spectrographic	1	Denver
Cu	Spectrographic	1	Denver
Dy *	Spectrographic	50	Denver
Er *	Spectrographic	50	Denver

Table 1. Analytical methods for rocks and soils.--Continued.

Element	Selected analytical methods	Lower limit of determination (parts per million)	Laboratory
Eu *	Spectrographic	100	Denver
F	F selective ion electrode	40	Washington
Fe	Spectrographic	10	Denver
	X-ray fluorescence	1,000	Denver
Ga	Spectrographic	5	Denver
Gd *	Spectrographic	50	Denver
Ge *	Spectrographic	10	Denver
Hf *	Spectrographic	100	Denver
Hg	Mercury detector	0.01	Denver-GX
Ho *	Spectrographic	20	Denver
I	I_2 colorimetric	1	Washington
	Neutron activation	0.05 (?)	Denver
In *	Spectrographic	10	Denver
Ir *	Spectrographic	50	Denver
K	Spectrographic	7,000	Denver
	X-ray fluorescence	1,000	Denver
La	Spectrographic	30	Denver
Li	Spectrographic	50	Denver
	Atomic absorption	5	Denver
Lu *	Spectrographic	30	Denver
Mg	Spectrographic	20	Denver
	Atomic absorption	300	Denver
Mn	Spectrographic	1	Denver
Mo	Spectrographic	3	Denver
Na	Spectrographic	500	Denver
	Atomic absorption	100	Denver

Table 1. Analytical methods for rocks and soils.--Continued.

Element	Selected analytical methods	Lower limit of determination (parts per million)	Laboratory
Nb *	Spectrographic	10	Denver
Nd *	Spectrographic	70	Denver
Ni	Spectrographic	5	Denver
Os *	Spectrographic	50	Denver
P	Spectrographic X-ray fluorescence	2,000 300	Denver Denver
Pb	Spectrographic	10	Denver
Pd *	Spectrographic	1	Denver
Pr *	Spectrographic	100	Denver
Pt *	Spectrographic	30	Denver
Re *	Spectrographic	30	Denver
Rh *	Spectrographic	2	Denver
Ru *	Spectrographic	10	Denver
Sb *	Spectrographic	150	Denver
Si	Spectrographic X-ray fluorescence	20 10,000	Denver Denver
Se	Activation analysis [3] Instrumental activation	0.03 1	Washington Denver
Sc	Spectrographic	5	Denver
Sn *	Spectrographic	10	Denver
Sr	Spectrographic	5	Denver
Sm *	Spectrographic	100	Denver
Ta *	Spectrographic	200	Denver
Tb *	Spectrographic	300	Denver

Table 1. Analytical methods for rocks and soils.--Continued.

Element	Selected analytical methods	Lower limit of determination (parts per million)	Laboratory
Te *	Spectrographic	2,000	Denver
Th *	Spectrographic	200	Denver
Ti	Spectrographic	2	Denver
Tl *	Spectrographic	50	Denver
Tm *	Spectrographic	20	Denver
U *	Spectrographic	500	Denver
V	Spectrographic	7	Denver
W *	Spectrographic	100	Denver
Y *	Spectrographic	10	Denver
Yb *	Spectrographic	1	Denver
Zn	Spectrographic	200	Denver
	Atomic absorption	10	Denver
Zr	Spectrographic	10	Denver

1/ The spectrographic method being used is essentially that described by Myers, Havens, and Dutton (1961), but the analytical results are given in six steps per order of magnitude rather than three. That is, results are reported in the geometric series, 1, 1.5, 2, 3, 5, 7, 10, 15 . . . etc., parts per million. These values are approximate midpoints of geometric brackets having the boundaries 0.83, 1.2, 1.8, 2.6, 3.8, 5.6, 8.3, 12, 18 . . . etc., parts per million. For example, a reported analytical value of 2 ppm indicates the range 1.8 to 2.6 ppm as the analyst's best estimate of the concentration of the element present in the sample. This system of reporting is used because the standard error of the analytical method for a given type of sample material is approximately proportional to the amount of the element present. The standard error is an inverse measure of the reproducibility and, for most elements, is nearly equal to one geometric bracket. Although 65 elements are sought in each sample analyzed, many of the limits of detection are too high to detect the element in common soils and rocks. These elements are identified by an asterisk (*) on the above list and will be detected only where they are present in concentrations that are extremely high for these types of materials.

Table 1. Analytical methods for rocks and soils.--Continued.

2/ Determination of cadmium by atomic absorption is inapplicable to Ca-rich samples such as limestone or dolomite.

3/ Due to the high cost of the activation analysis for selenium, only selected samples will be analyzed by this method.

The same spectrographic method will be used for the analysis of plant ashes, supplemented by special determinations on plant ashes and dried plants as shown in table 2.

Analyses of water, for both major and minor constituents, will be made in the Denver laboratories of the Geological Survey. Some of the minor constituents will be determined by spectrographic analysis of water residues, using a method comparable to that being used for the rocks, soils, and plant ashes. The methods for water analysis are tabulated in table 3.

All spectrographic analyses of rocks, soils, and plant ashes in the Denver laboratories are being made by Harriet Neiman under the supervision of A. T. Myers. Other plant analyses are being made by Thelma Harms and Clara Papp under the direction of F. N. Ward. Most other analytical work in the Denver laboratories on rocks and soils is under the direction of Claude Huffman, Jr.; X-ray fluorescence analyses are being made by James Wahlberg. Spectrographic analyses of water will be by Paul R. Barnett; other water analyses will be under the direction of Dr. Marvin W. Skougstad. Analytical work in Washington will be under the direction of the Chief, Branch of Analytical Laboratories.

Mobile laboratories of the Geological Survey were used on the Columbia campus during the 1969 field season. These laboratories are designed primarily for investigations in mineral exploration and are under the direction of A. P. Marranzino, Chief of Field Services Section, Branch of Exploration Research. Future use of mobile laboratories will depend on their availability and on the need to obtain analytical determinations concurrent with field activities.

Table 2. Analytical methods for plants excluding spectrographic methods. (All plant analyses will be made in the Denver laboratories.)

Element or constituent [1]	Analytical method	Lower limit of determination (in parts per million except where noted)
Ag	Atomic absorption	0.1
As *	Colorimetric	1.
Ash	Gravimetric	1000.
Au	Atomic absorption	0.04
Bi	do.	10.
Br	Selective-ion electrode	2.[2]
Ca	Atomic absorption	100.
Cd	do.	0.5
Cl	Selective-ion electrode	2.[2]
Co	Atomic absorption	4.
Cu	do.	2.
F	Selective-ion electrode	0.02 [2]
Fe	Colorimetric	50.
I	Selective-ion electrode	0.01 [2]
I *	Catalytic	1.
K	Atomic absorption	100.
Li	do.	4.
Mg	do.	100.
Mn	do.	10.
Mo	Colorimetric	4.
Na	Atomic absorption	100.

Table 2. Analytical methods for plants excluding spectrographic methods.--Continued.
(All plant analyses will be made in the Denver laboratories.)

Element or constituent 1/	Analytical method	Lower limit of determination (in parts per million except where noted)
Ni	Atomic absorption	4.0
NO_3 *	Colorimetric	100.
P	do.	50.
Pb	Atomic absorption	10.
Se *		1.
Si		500.
SO_4	Colorimetric	200.
U	Colorimetric Fluorimetric	1. 1.
Water soluble salts	Gravimetric	100.
Zn	Atomic absorption	10.

1/ Elements or constituents will be determined on plant ash, except where noted by asterisk (*). These elements or constituents will be determined on dried plant.

2/ Units of micrograms per milliliter of solution.

Table 3. Analytical methods for water.

(All determinations will be 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 $CaCO_3$
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
Eh **	Electrometric [3]	millivolts
F	Zr-Eriochrome cyanide R	mg/l
Fe (total)	AAS--Direct Spectrographic	µg/l
Fe (ferrous)	Bipyridine	µg/l

Table 3. Analytical methods for water.--Continued.

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

Determination [1]	Method	Reported as:
Fe (ferric)	Bipyridine	µg/l
Ga *	Spectrographic	µg/l
Ge *	do.	µg/l
Hardness	Complexometric	mg/l as $CaCO_3$
Hardness, carbonate	Calculation	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)	Distillation, titration or nesslerization	mg/l
N (nitrate)	Brucine	mg/l as N
N (nitrite)	Diazotization	mg/l as N
N (organic)	Kjeldahl digestion	mg/l
Na	AAS--Direct	mg/l
Ni	Spectrographic	µg/l

Table 3. Analytical methods for water.--Continued.

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

Determination [1]	Method	Reported as:
O (dissolved) **	Alsterberg-azide [3]	mg/l
P (total)	Acid-persulfate hydrolysis	mg/l
P (in dissolved orthophosphate)	Phosphomolybdate	mg/l as P
Pb	Spectrographic	µg/l
pH	Electrometric, glass electrode	Standard units
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 [3]	µmhos/cm at 25°C.
Sr	Spectrographic	µg/l
Temperature	Thermometer [3]	Degrees C
Ti *	Spectrographic	µg/l
V *	do.	µg/l

Table 3. Analytical methods for water.--Continued.

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

Determination [1]	Method	Reported as:
Y *	Spectrographic	µg/l
Yb *	do.	µg/l
Zn	AAS--Direct Spectrographic	µg/l
Zr *	Spectrographic	µg/l

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[1] Elements indicated by asterisk (*) will be detected and measured only in water samples containing unusually high concentrations. Determinations indicated by double asterisk (**) are tentative.

[2] Direct analysis by atomic absorption spectrophotometry.

[3] Determined in field at time of collection.

Statistical methods

The frequency distributions of the concentrations of minor, and frequently of major, elements in natural materials tend in most cases to be closer to lognormal than to normal. Moreover, the variances of the concentrations are always at least approximately proportional to the corresponding means. Consequently, the statistical methods used in this program in Missouri are generally based on assumed lognormal distributions in the populations from which the data are drawn. The matter of the validity of this assumption is of varying degrees of importance, depending on the statistical method being used. It is generally of greater importance in tests of significance, where lognormal probability theory is employed, than it is in the selection of statistics to estimate averages and variability. However, analysis of variance methods, which are used in significance tests, are generally regarded as robust, and therefore rather insensitive to small departures of the data from the normal form; all of our ANOV tests are performed on logarithms of the observed data.

The principal measure of average used in this program is the geometric mean (GM) which is computed as the antilogarithm of the arithmetic mean of the logarithms of the observed element concentrations. Arithmetic means (AM) of observed concentrations are used in some instances where the frequency distributions are closer to normal than to lognormal, or where a measure of geochemical abundance, as used by Miesch (1967) is required.

The geometric mean is the appropriate measure of central tendency for a lognormal distribution, and, therefore, is the best conventional estimate of the most typical, or characteristic, concentration in most geochemical populations. The arithmetic mean, however, is necessary to derive an estimate of element abundance, which, in turn, is required to estimate the amount of an element (in pounds, tons, etc.) present in a given volume of rock, soil, water, or plant material.

The principal measure of variability used is the geometric deviation (GD) which is computed as the antilogarithm of the standard deviation of the logarithms of the observed element concentrations. Where the underlying parent distribution from which the data were drawn is lognormal, two-thirds of the distribution is estimated to fall within the range from GM ÷ GD to GM x GD; 95 percent is estimated to fall within the range from GM ÷ $(GD)^2$ to GM x $(GD)^2$.

For example, R. R. Tidball (table 5 of this report) gives GM = 44 and GD = 1.29 as the geometric mean and geometric deviation for boron in soils of the Bosworth Series. It is estimated, therefore, that two-thirds of all potential samples of the Bosworth Series have concentrations of boron that fall in the range 34 (44 ÷ 1.29) to 57 (44 x 1.29) parts per million; 95 percent of the potential samples have boron contents in the range 26 ($44 \div 1.29^2$) to 73 (44×1.29^2) parts per million.

Every analytical method used in the laboratory has a limited range of application and, therefore, lower and upper limits on concentrations of elements that may be detected and measured. The frequency distributions of measured element concentrations, consequently, are commonly censored, especially at the lower limit of analytical detection. In some such cases, the samples in which the element was not detected are assumed for statistical calculations to contain concentrations equal to seven-tenths of the lower limit of detection--providing that the element was actually detected and measured in the large majority of the samples under study. The only justification for this arbitrary assignment of values to unknown quantities is that the final statistical estimates are insensitive to the differences among any reasonable values that may be assigned. Where the statistics are sensitive--to any important degree--to the values assigned, this method is not employed. In these cases, tests of significance using ANOV techniques are not made, and geometric means and geometric deviations are derived from censored distribution techniques developed by Cohen (1961) as used by Miesch (1967) and by Shacklette, Sauer, and Miesch (1970).

Personnel

Vitae and bibliographies of the personnel conducting these studies in Missouri, except for support personnel who provide laboratory services and computer processing, were included in the first six-month progress report. Since that report, one geologist, John D. Sims, has been reassigned to another Geological Survey program, but another, Richard J. Ebens, has been acquired on a full-time, rather than part-time basis. Dr. Ebens has resigned from the Geology Department faculty of Emory University in Atlanta, Georgia, and has transferred to Denver to assist Dr. Connor in geologic aspects of the project. We are most pleased to have Dr. Ebens join us full time in this work.

Another recent addition to our staff is Mr. Gerald L. Feder of the Water Resources Division of the Geological Survey. Mr. Feder is permanently headquartered in Rolla, Missouri, where he has been engaged in hydrologic studies of the State for the past seven years. He is now devoting his full attention to the environmental geochemistry of Missouri, and will have complete responsibility for the studies directed at the major and minor element chemistry of ground and surface waters. His broad experience in the hydrology of Missouri, and his particular experience in past studies of Missouri springs and of the Joplin mining area, make him a welcome addition to our group. Mr. Feder is currently completing requirements for the PhD degree in geology and geochemistry at the University of Missouri in Columbia. His vita and bibliography follow:

<u>Name and title</u>: Gerald L. Feder, Hydrologist, Water Resources Division
U.S. Geological Survey

<u>Date and place of birth</u>: December 9, 1937 - New York, N. Y.

<u>Education</u>: City College of New York - Geology - BS 1960
University of Tennessee - Geology - MS 1963
University of Missouri at Columbia - Hydrology

<u>Honors and awards</u>: Research Assistantship
University of Missouri at Columbia, 1969

<u>Research interests</u>: Geochemical processes in hydrology
Statistical methods in hydrology
Carbonate hydrology
Environmental hydrogeochemistry

<u>Experience</u>: Hydrologist, U.S. Geological Survey, 1963 - present

Teaching assistant in geology, University of Missouri at Columbia, 1968 - 1969

Bibliography:

Feder, G. L., 1964, Cause of hachured weathering patterns produced on dolomite: Jour. Sed. Petrology, v. 34, no. 1, p. 197-198.

Feder, G. L., Skelton, J., Jeffery, H. G., Harvey, E. J., 1969, Water resources of the Joplin area, Mo.: Mo. Geol. Survey and Water Resources, Water Resources Report No. 24, 97 p.

Feder, G. L., 1970, A semi-quantitative method for determining the source of springflow in the Missouri Ozarks: U.S. Geol. Survey Prof. Paper 700-C, p. C214-C217.

One other participant should be mentioned for his significant contribution to these studies. This is James A. Pitkin of the Branch of Regional Geophysics of the Geological Survey, who has directed the airborne radiometric survey across parts of Ste. Genevieve, St. Francois, and Iron Counties described in a later section of this report. We are grateful to Mr. Pitkin and to Don R. Mabey, Chief of the Branch of Regional Geophysics, for making this survey possible.

Participation in Fourth Annual Conference on Trace Substances in Environmental Health

All members of the project attended this conference sponsored by the Environmental Health Surveillance Project on the Columbia campus on June 22-24, 1970. The Geochemistry Session of the conference was chaired by A. T. Miesch, and the following papers were delivered by project personnel:

R. R. Tidball: Geochemical variation in Missouri soils.

J. J. Connor*, J. A. Erdman, J. D. Sims, and R. J. Ebens: Roadside effects on trace metal content of some rocks, soils, and plants of Missouri.

H. T. Shacklette: A U.S. Geological Survey study of the elements in soils and other surficial materials in the United States.

* Denotes speaker.

These papers will appear in a proceedings volume entitled "Trace Substances in Environmental Health - IV" to be published near the end of the year by the University of Missouri.

Other members of the Branch of Regional Geochemistry attending were Dr. Michael Fleischer from Washington, D.C., Dr. Charles L. Christ from Menlo Park, California, and Mrs. Helen L. Cannon from Denver, Colorado, who, with Dr. Howard C. Hopps, presented an account of the activities of the U.S. Subcommittee on Environmental Geochemistry in Relation to Health and Disease.

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

Present status.--Work on this phase of the project during the report period consisted primarily of continuing reconnaissance stratigraphic studies, including both field and library research, in preparation for the design of a sampling program. These studies support the earlier contention that the most efficient way to characterize the chemical nature and variability of the bedrock of Missouri, for the purposes of this project, is to direct the sampling at a number of broad scale, compositionally distinct rock groups. Preliminary estimates indicate that the first stage of the sampling program will result in approximately 500 specimens; the results of the first stage will be used to determine the extent of sampling required for the second stage.

All but one of the rock groups to be sampled is sedimentary in origin, and each of these consists of a tabular layer of variable thickness that extends over a major portion of the State. As is common in sedimentary rock units, the compositional variability from top to bottom is generally much greater than its variation geographically over hundreds of square miles. Consequently, samples will be collected along stratigraphic sections--traverses across the units--spaced some distance apart. Results of preliminary sampling will serve to indicate the proportions of the total compositional variability that occur both within stratigraphic sections and between them. This information can then be used to form an efficient design for the next sampling stage--a design that will be sufficient to identify the compositional differences among the rock units with an acceptable degree of confidence.

It is expected that much of the rock sampling, both this year and in the future, must take place in roadside exposures. A study of roadside contamination in rocks, undertaken last summer and described at the Fourth Annual Conference on Trace Substances in Environmental Health, indicates that the roadside environment produces no unusual chemical effects in routinely trimmed rock specimens.

Perhaps the geologic materials of greatest significance to epidemiological studies are the near-surface deposits of unconsolidated clay, silt, and sand covering much of the State. These deposits are the parent materials for most of the soils in Missouri; they are generally grouped into four distinct geologic units: 1) river alluvium, 2) periglacial deposits (principally loess), 3) glacial till, and 4) carbonate residuum. Loess and carbonate residuum together probably comprise three-fourths of these materials.

Loess is a fine-grained, wind-laid deposit, derived from glacial debris, which covers much of northern Missouri and parts of the Mississippi Valley (fig. 1). Carbonate residuum is a chert-bearing, generally red-colored, clay-rich deposit, which covers extensive areas of southern Missouri. It is the accumulated residue of perhaps millions of years of weathering of carbonate bedrock, where the principal weathering process has been solution. Neither of these deposits, particularly loess, is notably water-bearing, although much water entering the underground regimen percolates through these materials. In spite of their wide-spread occurrence, they have been little studied in a geochemical sense.

Some information on the geochemical nature of loess and carbonate residuum is provided in table 4, in which are listed typical element concentrations based on a few preliminary samples of each material. The loess averages are based on samples collected by J. D. Sims at seven random localities in bluffs along the Missouri River. The carbonate residuum averages are based on five samples collected in a roadcut near Centerville, Missouri. Although this particular site is one in which an exceptional accumulation of Pb has been noted in the roadside environment (cf. Shacklette and others, 1969), the residuum here typically contains only 20 parts per million Pb, compared to an average of 20 ppm Pb in clay-rich rocks given by Turekian and Wedepohl (1961, table 2). Thus, the averages listed here for carbonate residuum may be cautiously viewed as at least approximately representative of the geochemical nature of this material. The major geochemical differences in the two materials are the more siliceous nature of loess and the more aluminous nature of residuum. These differences reflect the greater clay content of the residuum. The large difference in Na_2O (20 times as much in the loess as in the residuum) probably reflects the intense leaching of Na from the residuum. To the extent that the averages in table 4 may be viewed as representative, it appears that the major soil parent in most of northern Missouri and the Mississippi River Valley (loess) is richer than that in southern Missouri (carbonate residuum) by a factor of two or more in the alkali metals (Na and K) and alkaline-earth metals (Ca, Sr, and Ba) as well as in P, B, Ga, and Mn. The carbonate residuum is richer by a factor of two or more in the transition metals (Fe, Cu, Ni, V, and Zn) and Be. It is probable that both the element enrichment and depletion in residuum compared to loess reflects the longer period of weathering to which the residuum has been subjected. That is, it reflects a tendency for the more soluble minerals (containing the alkalies and alkaline earths) to be continually depleted and less soluble minerals (containing the transition metals) to be continually accumulated.

Table 4. Element concentrations in loess and carbonate residuum.

[All values are in percent, except where noted as parts per million (ppm)]

Element	Loess		Carbonate residuum	
	Geometric mean (except where noted)	Geometric deviation (except where noted)	Geometric mean (except where noted)	Geometric deviation (except where noted)
SiO_2 --------	77 1/	3.90 1/	52 1/	15.7 1/
Al_2O_3 -------	11	1.05	18	1.38
Total Fe as Fe_2O_3 -----	3.8	1.09	7.7	1.36
MgO ---------	1.2	1.59	.72	2.76
CaO ---------	1.6	2.01	.65	7.21
Na_2O --------	1.4	1.07	.066	1.31
K_2O ---------	2.0	1.03	1.0	1.84
P_2O_5 --------	.081	1.43	.022	1.81
Ag (ppm) ----	< .5	----	< .5	----
B (ppm) -----	43	1.28	< 20	----
Ba (ppm) ----	1000	1.00	200	1.57
Be (ppm) ----	.88	1.17	2.6	1.82
Total C -----	.50	2.07	1.1	2.98
Organic C ---	.23	1.63	.39	3.16
Carbonate C as C ------	.13	5.41	.11	10.23
Cd (ppm) ----	.93	1.13	.66	2.24
Ce (ppm) ----	110	1.32	< 150	----
Co (ppm) ----	8.6	1.21	10	1.57

Table 4. Element concentrations in loess and carbonate residuum.--Continued.

[All values are in percent, except where noted as parts per million (ppm)]

Element	Loess		Carbonate residuum	
	Geometric mean (except where noted)	Geometric deviation (except where noted)	Geometric mean (except where noted)	Geometric deviation (except where noted)
Cr (ppm) ---	58	1.20	59	1.86
Cu (ppm) ---	16	1.15	47	1.53
F ----------	< .004	----	< .004	----
Ga (ppm) ---	13	1.22	2.4	1.37
La (ppm) ---	49	1.28	53	1.16
Mn (ppm) ---	740	1.27	310	2.40
Mo (ppm) ---	< 3	----	< 3	----
Nb (ppm) ---	8.2	1.22	< 10	----
Nd (ppm) ---	< 70	----	< 70	----
Ni (ppm) ---	27	1.40	48	1.67
Pb (ppm) ---	15	1.00	20	1.28
Sc (ppm) ---	9.0	1.19	11	1.61
Sr (ppm) ---	240	1.24	70	1.28
Ti ---------	.38	1.45	.21	1.77
V (ppm) ----	86	1.21	140	1.48
Y (ppm) ----	28	1.17	38	2.19
Yb (ppm) ---	2.8	1.17	3.1	1.38
Zn (ppm) ---	72	1.12	140	1.42

1/ Arithmetic mean and standard deviation.

Plans for 1970 field season.--The 1970 field season will be spent in the execution of various sampling programs which may be grouped into three general studies. These are briefly described below in order of priority. It is felt that only under optimum conditions can all three be completed this field season. Distributions of the major rock groups in Missouri are shown in figure 1.

A. Geochemical variation in sedimentary bedrock units. Highest priority will be given to four broad-scale compositional rock types which together comprise as much as 80 or 90 percent of the total exposed bedrock in Missouri. These compositional types are 1) dolomites of the Cambro-Ordovician group (map unit ꞒO), 2) limestones of the Mississippian group (map unit M), 3) limestones, and 4) shales, both of the Pennsylvanian group (map unit Ꝑ). Both the geographic and stratigraphic chemical variability of each type will be determined. In addition, this field season's work will include detailed sampling in a small number of stratigraphic sections chosen especially to characterize the chemistry of the geographically restricted rock group DSO (fig. 1) and detailed sampling along the path of an airborne radiometric survey in southeastern Missouri, described in a later section of this report.

B. Geochemical variation in surficial deposits. A second important general study to be undertaken this field season is that of investigating the chemical variability of the extensive, unconsolidated surficial deposits of Missouri, to supplement the preliminary data in table 4. Emphasis will be placed on two general categories of surficial material: 1) carbonate residuum, which covers practically all of rock groups ꞒO and M in southern Missouri, and 2) loess (a wind-laid, glacially-related deposit) which covers large areas of northern Missouri. These materials will be sampled on a grid pattern within each of the areas in which they occur.

C. Geochemical variation in Precambrian crystalline rocks. As a third general study but one of relatively low priority because of limited rock distribution, we propose to sample the granitic rocks of the St. Francois Mountains in southeastern Missouri. This study will serve to identify the chemical differences among some 23 named rock units (Tolman and Robertson, 1969, pl. 1).

In addition to the three general studies described here, it may be anticipated that geochemical studies of specific health problem areas will be undertaken as they are delineated by the Environmental Health Surveillance Project.

Figure 1 is shown on the following pages.

Generalized geologic map of Missouri

EXPLANATION

Qa	QUATERNARY	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.
ℙ	PENNSYLVANIAN	Limestone, shale, sandstone, minor amounts of coal and clay
M	MISSISSIPPIAN	Limestone, minor amounts of shale and sandstone
DSO	DEVONIAN, SILURIAN, UPPER ORDOVICIAN	Limestone, dolomite, minor amounts of shale and sandstone
ЄO	LOWER ORDOVICIAN, CAMBRIAN	Dolomite, minor amounts of limestone, shale, and sandstone
pЄ	PRECAMBRIAN	"Granitic" rocks

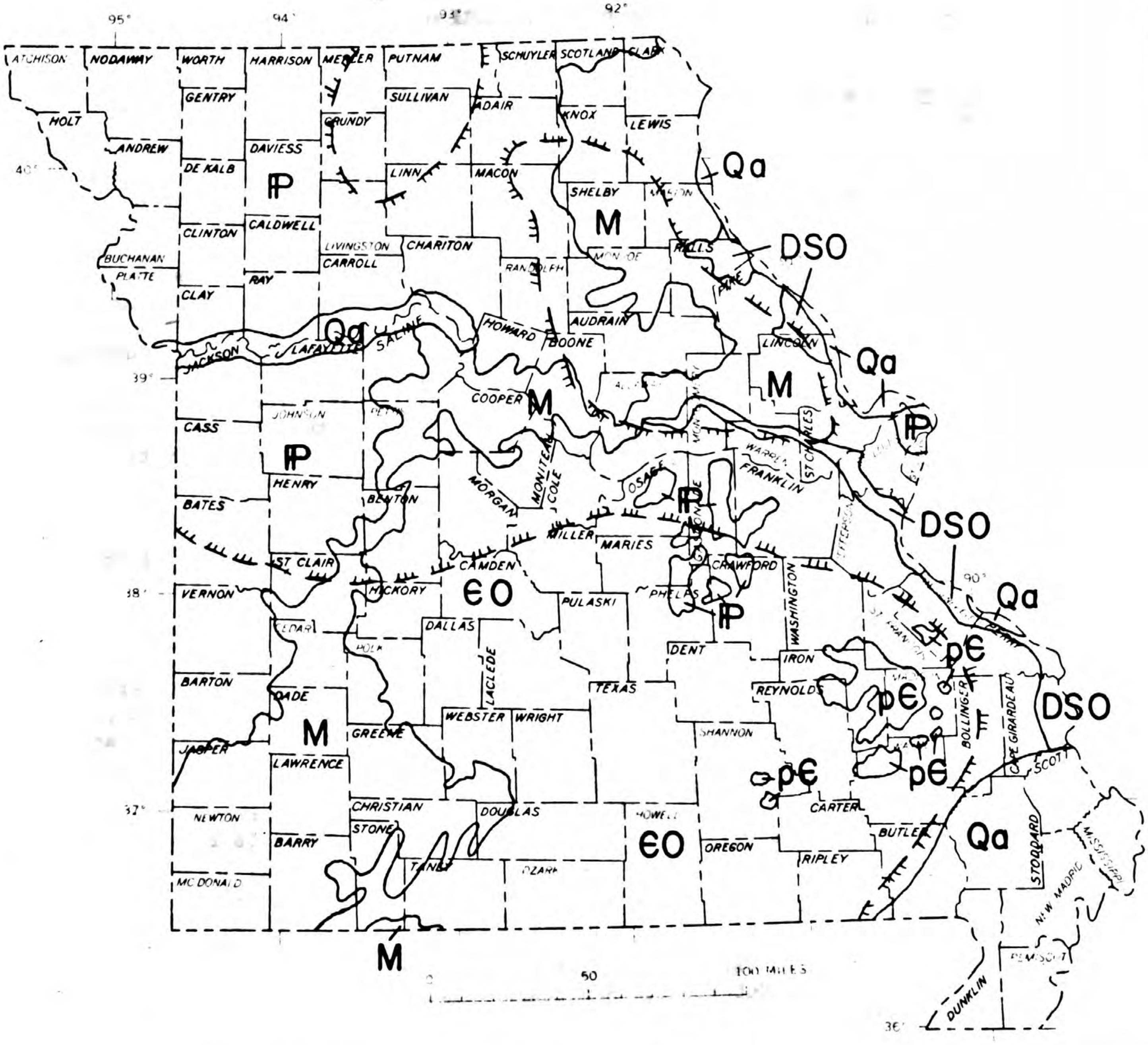


Figure 1.--Generalized geologic map of Missouri.

(Adapted from American Association of Petroleum Geologists, 1966, and Geological Society of America, 1952)

Geochemical survey of soils
by R. R. Tidball

Present status.--Certain quality control standards for the preparation and analysis of soils have been developed. The analytical standards are discussed in a previous section; preparation standards for soil samples are discussed here. Rather consistent differences in the analytical results for soil prepared and analyzed in the field spectrographic laboratory versus the Denver laboratories suggested the need for standard procedures for preparation that are mechanized and reproducible, and ones that will minimize the chances of contamination. A commercial soil grinding machine was obtained and modified so that the initial breakdown of natural soil aggregates (but not primary rock and mineral grains) occurs by passage between two ceramic surfaces. The disaggregated sample then passes over a two-millimeter aluminum sieve. By definition, the "soil material" for this study consists of particles that are less than two millimeters in size; particles greater than two millimeters (gravel) are discarded. All plant parts that can be removed conveniently by hand or on the sieve are discarded. The sample preparation commences with air drying in a forced-draft oven at ambient temperature followed by initial disaggregation and sieving. The soil material is then pulverized in a ceramic mill to a size sufficient to pass a 100-mesh (149 micron) sieve. Finally the soil material is mixed in an end-over-end mixer for two hours.

The results of a preliminary sampling project described in the first six-month progress report were presented in a paper at the Fourth Annual Conference on Trace Substances in Environmental Health. These results were based on all analyses completed to date except those for arsenic, fluorine, iodine, mercury, and selenium. Taxonomic categories of the Soil Classification System (Soil Survey Staff, 1960, 1967, 1968) which are based on morphologic criteria were tested to see whether chemical criteria would result in the same grouping of soils. If so, the classification system would be a useful basis for sampling the great diversity of soils throughout Missouri.

Suborders (a category of regional scope) are chemically unique in 20 out of 28 elements, but only weakly so. On the average, no more than about 25 percent of the total variance among the soils of Missouri may be described by sampling all of the Suborders. Subgroups within a suborder have practically no chemical uniqueness. Chemical grouping at the Series level (a category of local scope) is the most consistent. Sampling all of the Series would allow description of about 60 percent of the total compositional variance in the soils of Missouri. It is concluded that the classification system is quite limited in providing a basis for an efficient sampling plan to evaluate the total chemical composition of soils over the State.

The present data provide some limited insight into geographic differences among the soils studied. On the average, the highest concentrations of most elements are found in soils classed as Aquolls (a Suborder), representatives being situated on the Missouri River floodplain. The lowest concentrations of most elements are found in soils classed as Udults, examples of which are developed from cherty limestone residuum on the Ozark Plateau of south-central Missouri. Principal components analysis (a multivariate statistical procedure) has shown that the compositions of all of the soils studied (each with 28 elements reported) may be expressed in terms of two extreme end members, one the Bosworth Series (an Aquoll), the other the Coulstone Series (a Udult). About 92 percent of the total variance in the soils of Missouri can be accounted for by viewing these soils as conceptual mixtures of the two end members. A plot of the silica-sesquioxide molecular ratio (Jenny, 1941, p. 26)

$$\frac{\text{Moles of } SiO_2}{\text{Moles of } Al_2O_3 + \text{Moles of } Fe_2O_3}$$

against the proportional composition of each soil specimen is shown in figure 2. The Bosworth end member has a low silica-sesquioxide ratio and contains abundant very fine-grained mineral particles derived from many sources that are initially enriched in iron and aluminum (with respect to silica); it also contains numerous trace elements. Soils developed from these materials have weathered in place for only a comparatively brief time--ranging from a few years to several thousand years. The Coulstone end member has a high silica-sesquioxide ratio and is derived from carbonate rocks that are typically devoid of iron, aluminum, and other elements that are relatively abundant in the Bosworth Series. The area in which the Coulstone Series occurs lies beyond the extent of recent glaciation and has been exposed to weathering processes for a long period of time. Thus, silica which is a common residual product from weathered carbonate appears considerably enriched with respect to other elements as compared with the Bosworth Series. A comparison of the average (expressed by the geometric mean) concentrations of 25 elements in the two contrasting soil Series is given in Table 5.

Plans for 1970 field season--The preliminary results suggest a grouping among the soils that relates at least in a general way to geographic location and to the parent material from which the soils have been derived. With this lead, part of the investigations during the 1970 field season will consist of an attempt to evaluate more directly the variation in the composition of soils as a function of parent material. Such studies will include some or all of the major parent material types according to the following (adapted from Scrivner, Baker, and Miller, 1966):

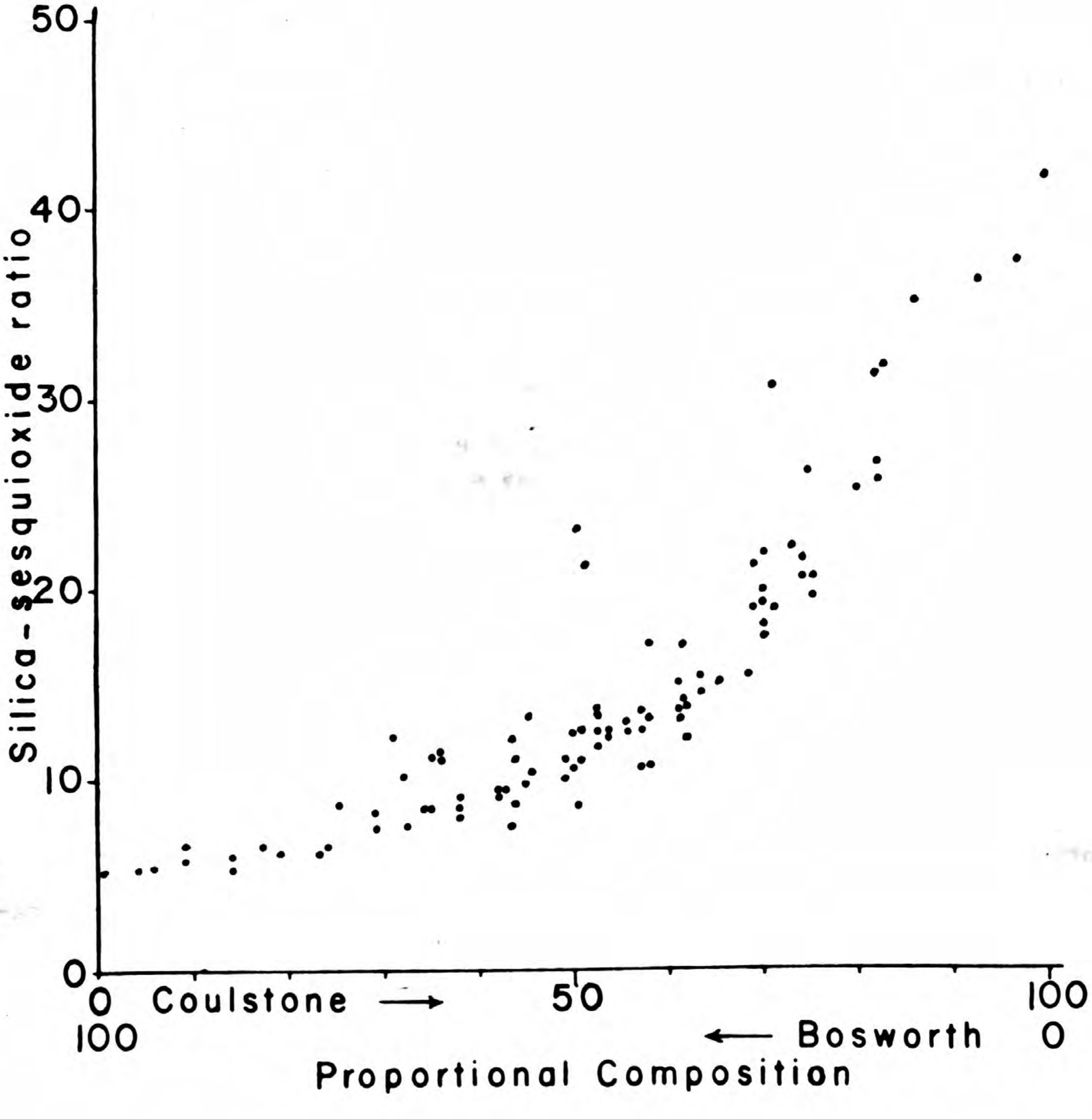


Figure 2.--Graph showing the silica-sesquioxide ratio of all soil specimens as a function of the proportional composition in terms of two extreme end-member specimens.

Table 5. Average compositions of soil samples from the Bosworth and Coulstone Series.
[Means are in parts per million except where noted is in percent]

Element	Series			
	Bosworth (4 samples)		Coulstone (4 samples)	
	Geometric mean	Geometric deviation	Geometric mean	Geometric deviation
Al (%) ---	8.3	1.04	1.3	1.24
B --------	44.	1.29	25.	1.58
Ba -------	1100.	1.23	270.	1.23
Ca (%) ---	1.21	1.15	.05	3.06
Co -------	14.	1.23	3.	1.00
Cr -------	92.	1.20	22.	1.23
Cu -------	54.	1.18	6.	1.21
Fe (%) ---	4.8	1.01	1.8	1.23
Ga -------	30.	1.00	< 5.	----
K (%) ----	2.2	1.04	.41	1.19
La -------	70.	1.00	< 30.	----
Mg (%) ---	.99	1.12	.05	1.10
Mn -------	700.	1.00	230.	1.40
Na (%) ---	.46	1.09	.11	1.25
P --------	530.	1.15	120.	1.53
Pb -------	22.	1.23	11.	1.20
Sc -------	15.	1.00	< 5.	----
Si (%) ---	29.	1.02	44.	1.02
Sr -------	250.	1.26	29.	1.64

Table 5. Average compositions of soil samples from the Bosworth and Coulstone Series.--Continued.

Element	Series			
	Bosworth (4 samples)		Coulstone (4 samples)	
	Geometric mean	Geometric deviation	Geometric mean	Geometric deviation
Ti (%) ---	0.34	1.29	0.28	1.55
V --------	190.	1.16	34.	1.29
Y --------	25.	1.26	12.	1.41
Yb -------	2.7	1.23	1.5	1.33
Zn -------	130.	1.08	15.	1.15
Zr -------	140.	1.23	220.	1.23

1. Loess and glacial till, which covers all of the State north of the Missouri River and borders the Mississippi River Valley.

2. Pennsylvanian shales, limestone, and sandstone, on the Osage Plain of west-central Missouri.

3. Ordovician cherty limestone and dolomite, on the Ozark Plateau of south-central Missouri.

4. Mississippian cherty calcium limestone, southwest Missouri.

5. Granite, St. Francis Mountains.

6. Mixed alluvium, Missouri and Mississippi River Valleys.

The interstream divides of the southern half of the State are further modified by a mantle of loess that diminishes in depth with increasing distance away from the major river valleys.

Practically without exception, agricultural soils under intensive management have a history of fertilization. This may be regarded as a possible adulteration if our interest is in understanding weathering processes in a natural system. However, it may be of little consequence for environmental purposes because no matter what circumstances govern their chemical characteristics, the soils will exercise the same influence. The magnitude of any trace element contamination may be examined by studying certain isolated tracts of virgin prairie that have been brought to our attention by Agricultural Extension Agents in Missouri. Plans are being considered to study both the soils and vegetation on these areas.

The sampling of soils (10 per county) obtained through cooperation with the Missouri Agricultural Extension Agents is nearly complete; 111 out of 114 counties have responded. All of the specimens received as of the end of June were delivered to Denver by automobile and are awaiting processing pending completion of the sample set. Plans are being made to do supplementary sampling where needed to fill in either nonresponses or to replace specimens that are too small. Seventy-four percent of the counties responding either furnished a map of sampling locations, or submitted a hand drawing that will allow estimation of the parent material of the soil at the sampling locality and sufficiently accurate latitude and longitude for the data storage system.

Geochemical survey of vegetation

by H. T. Shacklette, J. A. Erdman, and J. R. Keith

During the period covered by this report, results of the preliminary sampling program were evaluated and sampling programs for future use were developed, insofar as possible at this time. Most chemical analyses of the plant and soil samples that were collected in 1969 were completed, and some of the results have been evaluated statistically. On the basis of these studies, the results which follow are considered noteworthy.

Average concentrations of selected elements in soils of the vegetation types in Missouri.--The B horizons of soils were sampled from randomly selected quadrangles and randomly selected sites within quadrangles in each of the six vegetation type areas that are shown in figure 3. Results of analyses of these samples are given in table 6. The highest and lowest element values for soils are indicated only where the variances among vegetation types are significant at the 95 percent confidence level.

The most striking feature indicated by these extreme element concentrations is that eight elements (Al, Cr, Cu, Fe, Ga, Ni, Sc, V) show their highest average concentration in soils of the Glaciated Prairie and fourteen elements show their lowest average concentration in soils of the Oak-hickory (Al, Cr, Cu, Mn, Pb, Sc, V) and Oak-hickory-pine (Ca, Fe, Ga, K, Mg, Ni, Sr) Forests. Soils of the Floodplain Forest were expected to have the largest concentrations of many elements, but analyses indicate that they are highest only in barium and strontium. Soils of the Cedar Glades were expected, and found, to be high in calcium and magnesium because they are mostly shallow soils over limestone and dolomite bedrock. Soils of the Oak-hickory and Oak-hickory-pine Forests are generally low in concentrations of the elements that were studied; the high average concentration of manganese in soils of the latter region may be of significance in explaining the occurrence of pine in a forest type otherwise similar to the Oak-hickory Forest type.

In general, this preliminary study showed that the amounts of elements found in the B horizon of Missouri soils correspond well with the amounts in the same horizon of soils of the eastern half of the United States as reported by Shacklette and others (in press).

Average concentrations of selected elements in smooth sumac from the vegetation types in Missouri.--After having demonstrated differences in the soil chemistry of vegetation type areas in Missouri, we then attempted to determine if the plant chemistry reflected similar patterns. Different plant types or species can be very disparate in their ability to assimilate chemical elements from the substrate; therefore a species common to most, if not all, vegetation types within the State was required to measure relative element abundances in the vegetation types. Additional requirements were that this target species be perennial, a conspicuous component of the landscape, and easily identified in the field. After scanning the

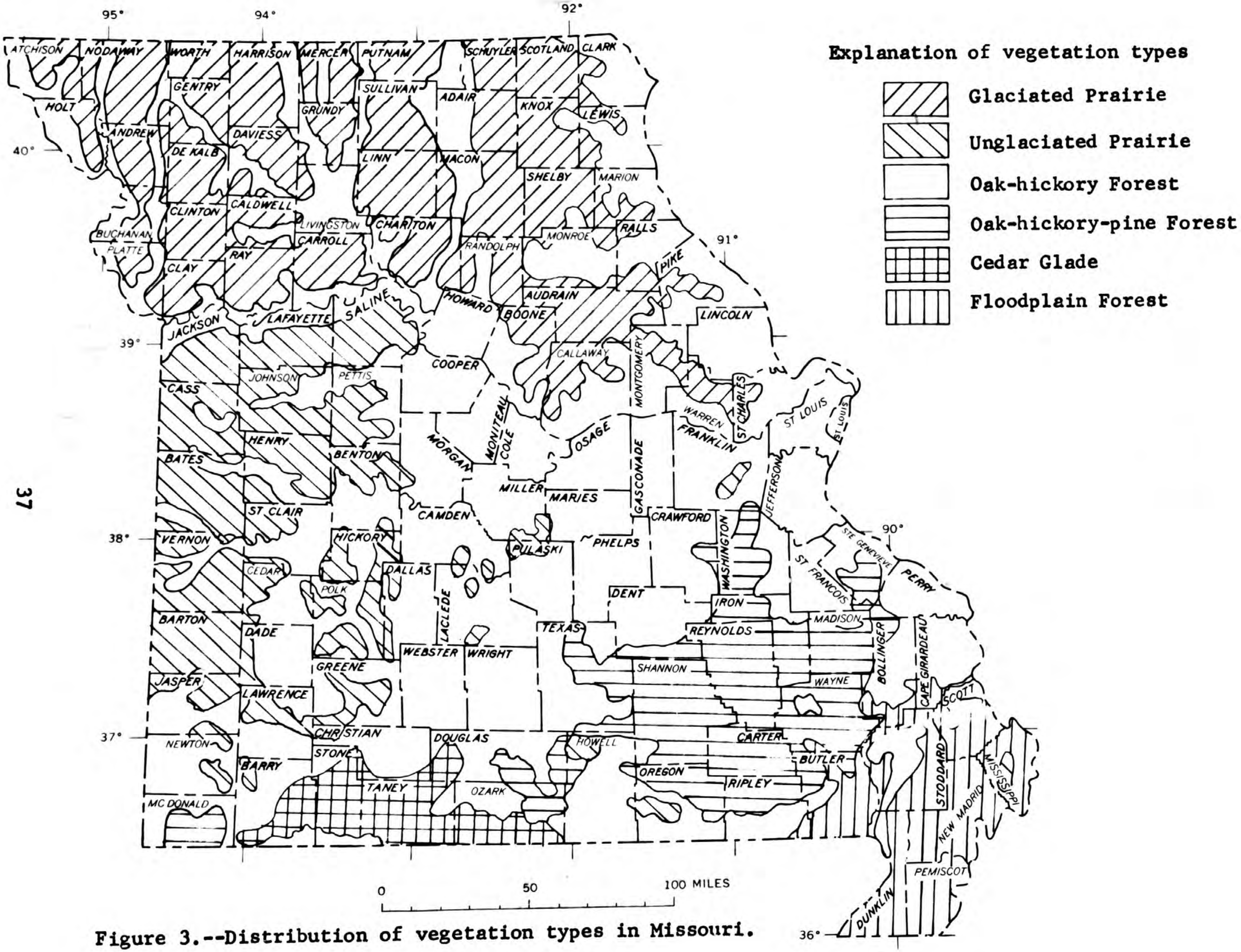


Figure 3.--Distribution of vegetation types in Missouri.

(Modified from Kuchler, 1964)

Table 6.--Average concentrations of selected elements in B horizon soils from six vegetation types in Missouri.

[GM, geometric mean; GD, geometric deviation. Al, Ca, Fe, K, Mg, and Ti are reported in percent, the remaining elements in parts per million, of dry soil. One asterisk (*) indicates the lowest, two asterisks (**) the highest, value for each element. Analyses performed by the methods described earlier in this report.]

Element	Floodplain Forest		Glaciated Prairie		Unglaciated Prairie		Cedar Glade		Oak-hickory Forest		Oak-hickory-pine Forest	
	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD
Al-----	06.5	1.59	07.3**	1.22	05.8	1.75	03.4	1.45	02.5*	1.86	02.6	1.29
B------	35.	1.44	34.	1.76	38.	1.60	27.	1.50	39	1.54	39	1.40
Ba-----	910 **	1.48	670	1.46	490	1.75	320 *	1.57	580	1.83	520	1.39
Ca-----	.40	2.44	.34	1.72	.12	2.15	2.2**	5.79	.13	1.85	.08*	1.33
Co-----	10	1.75	11	1.61	8.9	1.72	7.4	1.49	5.5	2.13	8.4	1.30
Cr-----	64	1.33	75 **	1.16	73	1.36	48	1.42	43 *	1.72	44	1.49
Cu-----	23	1.79	25 **	1.51	18	1.86	16	1.56	12 *	1.99	13	1.38
Fe-----	2.9	1.87	5.2**	1.39	4.1	1.57	2.1	1.44	1.5	1.89	1.2 *	1.57
Ga-----	16	1.71	19 **	1.40	14	1.60	12	1.32	6.4	1.70	6.3 *	1.40
K------	2.1	1.41	1.6	1.40	1	1.85	2.5**	1.53	.93	2.02	.88*	1.63
Mg-----	.44	2.13	.58	1.44	.33	1.80	1.5**	3.46	.17	1.77	.15*	1.39
Mn-----	570	1.53	410	2.81	380	3.00	760	1.32	350 *	3.38	840 **	1.61
Ni-----	20	2.17	24 **	1.35	19	1.90	19	1.40	12	1.66	11 *	1.46
Pb-----	18	1.16	20	1.21	18	1.34	26 **	1.46	13 *	1.57	15	1.29
Sc-----	11	1.56	14 **	1.19	11	1.33	5.7	1.76	4.6 *	2.02	5.0	1.47
Sr-----	190 **	1.56	170	1.40	96	1.57	120	1.53	85	2.14	57 *	1.67
Ti-----	.43	1.28	.35	1.28	.44	1.34	.19*	1.71	.40	1.84	.53**	1.29
V------	97	1.89	120 **	1.23	97.	1.60	63	1.26	41 *	1.86	43	1.44
Y------	29	1.29	28	1.32	30 **	1.24	15 *	1.67	23	1.58	26	1.23
Yb-----	2.7	1.22	2.7	1.22	2.7	1.27	1.2	1.70	2.3	1.47	2.5	1.24
Zr-----	280	1.93	250	1.68	410	1.79	130 *	1.92	450	1.56	480 **	1.33

plant distribution maps in Steyermark's "Flora of Missouri" (1963), we selected several species of woody plants for our initial objective of estimating the sampling density needed to characterize the biogeochemistry of the vegetation of Missouri. These plants were smooth sumac (*Rhus glabra*), red cedar (*Juniperus virginiana*), and three species in the white oak group--white oak (*Quercus alba*), post oak (*Q. stellata*), and overcup oak (*Q. lyrata*). As with the soils, these plants were sampled from randomly selected quadrangles and sites within quadrangles in each of the six vegetation types that are shown in figure 3.

Smooth sumac is the only species in the group that was found in all vegetation types; therefore, data analyses for only the samples of this species are given here. Summary statistics are shown in table 7. The highest and lowest element values for sumac are indicated only if the variance of the element in sumac, among vegetation type areas, is significant at the 95 percent confidence level.

Extremes in element concentrations occur between 1) the Floodplain Forest and the Unglaciated Prairie, which have high values for four (Cu, Mg, Mn, P) and two (Fe, Sr) elements, respectively, and 2) the Cedar Glade type which has low values for five elements (Ba, Cu, Mn, P, Sr). The Oak-hickory Forest and Oak-hickory-pine Forest have low values for one element each (Fe and Mg, respectively). In general, the variation of elements in sumac among the six vegetation type areas of Missouri does not correspond closely to their variation among the soils of these areas. However, because the sampling plan upon which these results are based was a preliminary one, the values presented in tables 6 and 7 only suggest trends in element composition of the soils and plants among the vegetation types. It is quite clear, as we had anticipated, that the prairie and floodplain regions generally are enriched in the elements that were analyzed, whereas the Ozark uplands are considerably lower in content of these elements.

Comparison of element concentrations in two species of sumac.--We have often discussed the question of similarity of element content in closely related plant species, but heretofore have had few opportunities to seek answers. During the initial planning stages of the Missouri biogeochemical investigations we decided, where possible, to collect plant samples whose analyses might provide useful data for answering this question.

In our preliminary sampling in 1969 we collected both smooth sumac (*Rhus glabra*) and winged sumac (*Rhus copallina*) and samples of soils on which they grew at 21 randomly selected sites. These two species were chosen because they have similar morphology and growth habit and because they generally occupy similar habitats, such as roadsides, abandoned fields, and forest borders. The two species were growing either adjacent to or within a short distance of each other at all sites. It might be

Table 7.--Average concentrations of selected elements in dry stems of smooth sumac from six vegetation types in Missouri.

[GM, geometric mean; GD, geometric deviation. Al, Fe, Mg, P, and Ti are reported in percent, the remaining elements in parts per million of plant ash. One asterisk (*) indicates the lowest, two asterisks (**) the highest, value for each element. Analyses performed by the methods described earlier in this report.]

Element	Floodplain Forest		Glaciated Prairie		Unglaciated Prairie		Cedar Glade		Oak-hickory Forest		Oak-hickory-pine Forest	
	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD	GM	GD
Al-----	0.1	1.8	0.087	1.4	0.082	1.6	0.068	1.3	0.074	1.7	0.097	1.7
B------	290	1.4	250	1.4	270	1.2	260	1.2	240	1.3	260	1.2
Ba-----	4000	1.8	2600	1.8	5300	1.9	480 *	3.2	4900	2.3	6500 **	1.7
Cu-----	180 **	1.3	110	1.4	140	1.5	85 *	1.6	90	1.3	120	1.4
Fe-----	.12	1.5	.097	1.3	.15 **	1.6	.084	1.3	.082 *	1.5	.091	1.5
Mg-----	4.9 **	1.2	3.4	1.5	3.8	1.4	2.9	1.7	3.5	1.4	2.6 *	1.4
Mn-----	1200 **	1.8	530	1.9	910	1.6	430 *	1.8	740	1.5	1000	1.4
P------	1.7 **	1.3	1.5	1.4	1.2	1.3	.75 *	1.5	1.2	1.4	.88	1.4
Pb-----	27	1.7	30	1.7	43	1.5	45	1.5	48	1.7	44	1.5
Sr-----	3800	1.4	3500	1.7	4200 **	1.7	670 *	2.0	4000	1.6	3700	1.6
Ti-----	.0081	2.6	.0077	1.8	.0088	1.5	.0071	1.4	.0065	1.9	.0096	2.3

reasonably assumed, therefore, that because of these similarities, the element contents might be similar. If element absorption were shown to be similar in the two species field sampling would be facilitated, because either species could be used as a biogeochemical analog of the other. This freedom to substitute one species for the other would be especially useful at sites where only one of the two was present.

Chemical analyses, however, indicated that the element absorption patterns are quite different in the two species. The results of analyses for 13 elements are shown in table 8. The two species differed significantly in their ability to absorb certain elements from the same soil substrate. We concluded that it is not advisable to use smooth sumac and winged sumac as interchangeable indicators of element content of underlying soils or of biogeochemical differences between vegetation types. Further sampling and analysis of these two species are planned for the 1970 field season.

Roadside contamination as indicated by analyses of mosses and associated soils.--Reports by Rühling (1969) indicate that mat-forming mosses are effective accumulators of heavy metal fallout. As a part of our study of roadside contamination we sampled mosses and soils from paired sites at ten locations in southern Missouri. The occurrence of mat-forming mosses near roads was dependent upon the shade of trees growing on the roadsides in a region of abundant rainfall; the selection of sample sites, therefore, was limited almost entirely to the Ozark plateau. The on-road site at each location was sampled as close as possible (15-25 feet) to the pavement of two-lane blacktop roads, whereas the off-road site was at a distance of 300-400 feet from the road. One or more species of moss, and the upper one inch of soil immediately under the moss mat, were sampled at each site. The moss samples were thoroughly cleaned in the laboratory to remove adhering soil particles, following the method described by Shacklette (1965, p. 8-9). Chemical analyses of the moss samples have not yet been completed and, therefore, are not discussed in this report. The soil analyses, however, have been completed. No evidence was found that the soils beneath the mosses along roads had been contaminated by any of the elements that were examined. This result supports the earlier studies of Connor, Erdman, Sims, and Ebens (in press) who found that roadside soils from a few inches beneath the surface showed little or no effects of highway contamination, even though the roadside plants were greatly contaminated with lead. The effectiveness of moss mats in "filtering out" contaminants that otherwise would have been deposited on the surface soils cannot be evaluated until analyses of the moss plants have been accomplished.

One site of anomalous element values in soil was found during this study. This off-road site was 300 feet from the pavement in an Oak-hickory Forest 1½ miles east of the junction of Route E and State Route 142, in Ripley County. A comparison of amounts of certain elements found in this sample with the range in amounts in other off-road samples is given in table 9.

Table 8.--Geometric mean concentrations of selected elements in two species of sumac from six vegetation types in Missouri.

[Al, Fe, Mg, P, and Ti are reported in percent, the remaining elements in parts per million, of plant ash. An asterisk (*) indicates differences between species that are significant at the 0.05 probability level. Analyses performed by the methods described earlier in this report.]

Element	Smooth sumac	Winged sumac
* Al ------------------	0.088	0.28
B ------------------	250	280
Ba ------------------	4500	3700
* Cr ------------------	2.1	6.7
* Cu ------------------	120	200
* Fe ------------------	.10	.26
Mg ------------------	2.8	2.4
* Mn ------------------	920	2500
Ni ------------------	9.5	12
P ------------------	.93	.94
* Pb ------------------	38	120
Sr ------------------	2800	2700
* Ti ------------------	.0081	.030

Table 9.--Comparison of concentrations of selected elements in sample no. MO-12-1 with the range of concentrations found in other off-road samples.

[Amounts of K, Mg, and Ti are reported in percent; amounts of the other elements are reported in parts per million. N = not detected.]

Element	Concentrations in sample no. MO-12-1, Ripley County	Range in concentrations in other off-road samples of this study
Cr --------------	70	15-50
Ga --------------	10	N-7
Li --------------	17	5-15
Mg --------------	.30	0.03-0.15
Ni --------------	15	5-10
Pb --------------	70	N-50
Sc --------------	7	N-5
Sr --------------	100	10-70
Ti --------------	.7	0.1-0.5
V ---------------	70	15-50
Yb --------------	5	1-3
Zn --------------	236	13-61

The occurrence of anomalous concentrations of zinc in the Ripley County sample, especially when accompanied by concentrations of certain other elements that are also greater than those of other samples in the study, cannot be explained at present. Artificial contamination of the site with this suite of elements seems unlikely; there was no evidence that this forested site had been greatly disturbed by man. Further studies of this site, to include sampling of soils and underlying bedrock, are planned for the current field season.

Proposed sampling programs:

A) Minimum sampling density required to characterize the chemistry of soils and plants of the six vegetation type areas of Missouri.

The sampling design that was used in the preliminary study of the vegetation of the State, Kuchler's "Potential Natural Vegetation of the Conterminous United States," (1964). The top level of this hierarchical design, therefore, consists of six major types of vegetation, as shown in figure 3. From an index map of the topographic quadrangles of the State, five 7½' quadrangles were selected at random from each of the vegetation type areas; two points or sites were then chosen at random within each of the selected quadrangles. These selections constitute, respectively, the second and third levels of the design. At each site in each of the quadrangles, one soil sample from the B horizon and one or more plant samples were collected. By using this procedure a total of 60 soil samples and 57 samples of smooth sumac were collected. Numbers of samples of the other plant species were considerably less because of the absence of the species in some of the vegetation types. Therefore, the sampling density estimate described below is based on only the soil and sumac materials.

A three-level analysis of variance technique was used to demonstrate whether significant differences existed in the amounts of elements that occur among the vegetation type areas, among quadrangles within areas, and among sampling sites within quadrangles. The statistical analysis included only those elements which were detected in measurable concentrations in 90 percent or more of the samples analyzed. Where the element was not detected in measurable concentrations, the concentration was assumed, for purposes of calculation, to be seven-tenths of the lower limit of detection of the analytical method.

Appropriate statistical computations were made by using estimates of the variance components derived from the analysis of variance routine, the number of samples from the preliminary stratified sampling design, and results of a simulation study by R. R. Tidball. This study demonstrated the relationship of the between group: within group variance ratio to the number of samples required to adequately describe the between group differences. From these computations it appears that soils have already been adequately sampled for describing differences in the concentrations of iron, magnesium, calcium, titanium, scandium, strontium, vanadium, yttrium, and zirconium among the vegetation type areas. Barium, chromium, nickel, and lead will require the same site sampling density (two sites per quadrangle), but ten quadrangles per vegetation type area. Description of the differences among cobalt and manganese concentrations in the soils of these areas, however, will require a density of five sites per quadrangle and ten quadrangles per area. In order to study copper adequately, it is estimated that at least ten sites per quadrangle and 15 quadrangles per type would be needed.

Similar computations based on the smooth sumac data indicate that the data already on hand for barium, strontium, and phosphorus are adequate. Iron, magnesium, manganese, and copper will require two sites per quadrangle, ten quadrangles per vegetation type area; lead will require five sites within a quadrangle and ten quadrangles for each area. We could not demonstrate any significant variance of titanium, boron, and aluminum among areas.

Therefore, on the basis of these studies, a stratified sampling plan has been proposed in which five sites will be randomly selected from each of ten randomly selected quadrangles, within each of six major vegetation types that occur in Missouri. Results obtained following this plan should serve to adequately describe the chemical differences among the six areas.

B) Sampling native plant communities.

The final objective of our biogeochemical studies is to characterize, on an areal basis, the relative abundances of elements that are moved from the soil into the plants allowing the elements to exert their beneficial or harmful effects on plants, animals, and man. Chemical analysis of plants is one method of estimating the abundance of elements that occur in soils in an available (soluble) form, or that can be made available by the action of plant roots or microorganisms on compounds generally considered to be insoluble. Analysis for total concentrations of elements in soils, in contrast, measures the total amounts of elements in both soluble and insoluble forms.

In the process of plant sampling it is necessary to choose from the great number of species that grow naturally in Missouri (see Steyermark, 1963). Because of the diversity of the physical environment in this State, there are only a few ubiquitous plant species. Many reports in the literature indicate that plant species commonly have unique genetically-controlled capabilities in element absorption, and that element concentrations can be compared only for samples of the same species--a conclusion that was reached also in our studies of sumac. These two circumstances preclude a simple and direct approach to estimating similarities and differences in biogeochemical characteristics among areas as defined by vegetation type. We propose, therefore, to evaluate two procedures, as follows:

(1) Select one or more ubiquitous species, and interpret their characteristic element contents according to the vegetation type from which the samples originated. This method of regional biogeochemical evaluation is based on the assumption of a rather constant genetic absorption capability within the species, and assumes further that variation in element content of the plant is predominantly controlled by the amount of the element available in the soils. The validity of these assumptions is being tested in our present program.

(2) Select different plant species in the various vegetation type areas according to some criteria such as dominance, abundance, biomass, importance in the animal food chain, etc. This method of regional biogeochemical evaluation is based on the assumption that the selected species is representative, in its importance to element cycling, of the many other species that are also present in the vegetation of the area. The validity of this assumption can be only approximated in our studies, and we anticipate that only qualified statements of the results will be possible. That is, we may be required to conclude a study with statements similar to the following: "The soil-plant cycling of zinc in the Oak-hickory Forest area, *as measured by analyses of white oak*, is more active than that in the Cedar Glades, *as measured by analyses of red cedar*." Further studies will be aimed at determining the appropriateness of this method of estimating biogeochemical characteristics on a regional basis.

The species that have been selected for sampling in each vegetation type area are discussed in the following paragraphs.

The natural vegetation of the Glaciated and Unglaciated Prairies has been so greatly modified by man that it is not possible to sample the grass species which formerly were dominant in these areas. Tentatively, it is planned to sample smooth sumac, *Rhus glabra*, in the prairies, but after examining some virgin prairie sites the selection of species may be changed.

In the Oak-hickory Forest type white oak, *Quercus alba*, and shagbark hickory, *Carya ovata*, will be sampled. These two plants, with the addition of short-leaf pine, *Pinus echinata*, will be sampled in the Oak-hickory-pine Forest type.

Red cedar, *Juniperus virginiana*, and post oak, *Quercus stellata*, are the species that have been chosen for sampling in the Cedar Glades.

The Delta physiographic region (Floodplain Forest type) presents sampling problems similar to those of the Prairie types. Most of the original forest in this region has been cleared for farming, but some remnants of the original vegetation remain. Sweet gum (*Liquidambar styraciflua*, and overcup oak, *Quercus lyrata*, will be sampled in these forest remnants.

Two plant species considered to be nearly ubiquitous in Missouri will be sampled in all six vegetation types. These species are *Rhus glabra* and *Cassia fasiculata*. Data obtained from this sampling will provide a basis for comparing availability of chemical elements in the different vegetation types.

C. Sampling agricultural plant communities.

In order to adequately evaluate the biogeochemical characteristics of the areas mapped according to natural vegetation (fig. 3), the fact must be considered that much of the land area of the State is used for agricultural plants. For this reason, and because of the possibility of a direct relation between minor elements in crops and human or animal health, some measure of the relative concentrations of elements in field crop plants must be made. The principal agricultural plants, defined on the basis of acreage devoted to their production, are judged to be corn, soybeans, small grains, forage plants, and cotton. Less acreage apparently is planted in rice, tobacco, vegetables, orchards, vineyards, and miscellaneous crops. Three plantations will not be considered as cultivated crops. During the current field season we plan to make field observations and notes of these crop plants, but will postpone final sampling until a later field season.

D. Study of the vegetation of virgin prairie areas.

Dr. Walter F. Heidlage, Program Coordinator, Extension Environmental Health of Missouri, has provided the locations and descriptions of several areas of virgin prairies that occur in the State. We plan to examine these areas in order to gain a better understanding of the vegetation and the characteristic species so that the best possible selection of species to sample in the extensive prairie areas, now largely under cultivation, can be made.

Geochemical survey of water

by G. L. Feder

The following excerpts (A through C) have been taken from the Project Description prepared for the "Geochemical Survey of Waters of Missouri" project and submitted to the Geologic Division of the U.S. Geological Survey.

A. Objectives:

The Environmental Health Surveillance Center at the University of Missouri in cooperation with U.S.P.H.S. and the U.S.G.S. is conducting studies on the relation between the environment and health. Water has often been implicated with diseases caused by microorganisms, but little is known about the effects of trace elements in water on health. The existence or lack of trace elements in water is regarded as a factor of possible major importance by epidemiologists because of the direct consumption of water by humans and animals. Water may also indirectly affect health through its consumption by plants with attendant concentration of certain trace elements in the edible portions of plants.

The purpose of this project is to: (a) make a hydrochemical reconnaissance of the potable ground waters in Missouri with special emphasis on their trace element content in support of epidemiological studies of the EHSC; (b) relate the chemical content of the waters to the enclosing rocks and the flow system; (c) develop efficient methods for sampling large areas for trace elements in waters, and analysis of the data using modern statistical methods.

An additional benefit to be derived from this study would be the re-evaluation of tolerance limits established for trace elements in water.

B. Justification:

The project is an integral phase of a team effort to conduct a geochemical survey of the State of Missouri in support of epidemiological studies of the University of Missouri. Other phases are directed at rocks, soils, and vegetation of the State. This project will provide basic information on the chemical composition, including trace elements of the potable waters of Missouri. Because virtually no comprehensive information is available on the areal, vertical, and temporal distribution of trace elements in potable water supplies, this project will provide the Survey and the district with a first in this field. Development of efficient ground-water sampling techniques, and rigorous methods of analysis of data would be of benefit to other district studies. Also, if a relationship is established between the content of various trace elements in water and the occurrence of diseases and birth defects, the project will yield excellent additional dividends.

C. Methods:

A pilot well-sampling program will be undertaken in order to get an idea of the variance of the trace element content within and among water types and aquifer systems. This information will be used to design an efficient and rigorous sampling program to characterize the trace element distribution among the potable ground waters of the State. Due to the complexity of surface-water sampling, it is anticipated that only anomalous areas chosen by the EHSC for intensive study will have their surface waters sampled. In order to accurately relate the trace element distribution in water with the geologic environment, some analysis of precipitation statewide and sources of man-made contaminants will be made. Modern statistical methods will be applied to data obtained in order to relate the chemistry of waters to the natural environment and to environmental health.

It is anticipated that all analytical work except a few necessary field determinations will be performed at the Survey research laboratories in Denver, Colo. Most of the statistical analysis will be done on Survey computers. Interpretive reports on findings will be prepared.

Present status.--A preliminary analysis of trace elements in surface waters of the State indicates that sampling of this source will require large numbers of samples spread over a long period of time. Table 10 shows some selected trace-element analyses for a few streams in Missouri obtained by the Missouri Water Pollution Board in cooperation with the U.S. Geological Survey, Water Resources Division. Due to the high areal and temporal variability of surface-water chemistry, the main emphasis of this study will be on ground-water supplies. There are very few data available on the areal and temporal distribution of trace elements in ground water, but it is believed to be less variable than surface water and to better reflect the geochemical environment. In order to better relate ground-water chemistry to the geochemical environment, the State has been conceptually divided into seven major geohydrologic units (fig. 4). An initial sampling program will be conducted to obtain random samples from each of these units, and a nested analysis of variance will be performed on the resulting data. The results of this analysis will be used to design a more intensive sampling program.

Plans for 1970 field season.--During the 1970 field season an initial program of sampling ground-water wells throughout the State will be undertaken. The seven major geohydrologic units of the State will serve as a basis for the sampling program. Wherever possible only properly constructed wells that have complete logs on file with the Missouri Division of Geological Survey and Water Resources will be sampled. Chemical analysis will be done by the Denver laboratories of the Water Resources Division. The analyses will consist of 1) a "complete analysis" for major ions, 2) a spectrographic analysis for a suite of trace elements, 3) analysis for mercury, and 4) a gross alpha and beta radioactivity analysis (see table 3). Field measurements will be made of pH, alkalinity, Eh, conductance, and temperature. It is estimated that approximately 30 sites will be sampled in this initial program.

Table 10.--Analyses showing some variations with time in the concentrations of barium and zinc in four streams in Missouri.

Stream	Date sampled	Discharge (cfs)	Barium (μg/l)	Zinc (μg/l)
Strother Creek near Oates, Mo.	10/17/68	12	90	10
	1/16/69	13	1,600	10
	4/9/69	13	< 50	30
	7/15/69	11	< 50	20
Indian Creek near Anthonies Mill, Mo.	10/16/68	3	1,200	< 2
	1/13/69	15	500	20
	4/7/69	41	< 50	10
	7/17/69	10	< 50	20
Flat River at Flat River, Mo.	10/16/68	5	1,400	60
	1/13/69	12	2,700	260
	4/7/69	27	< 50	50
	7/16/69	6	< 50	80
Big Creek at Chloride, Mo.	10/16/68	1	1,000	70
	1/15/69	6	< 50	10
	4/8/69	38	< 50	20
	7/16/69	1	< 50	100

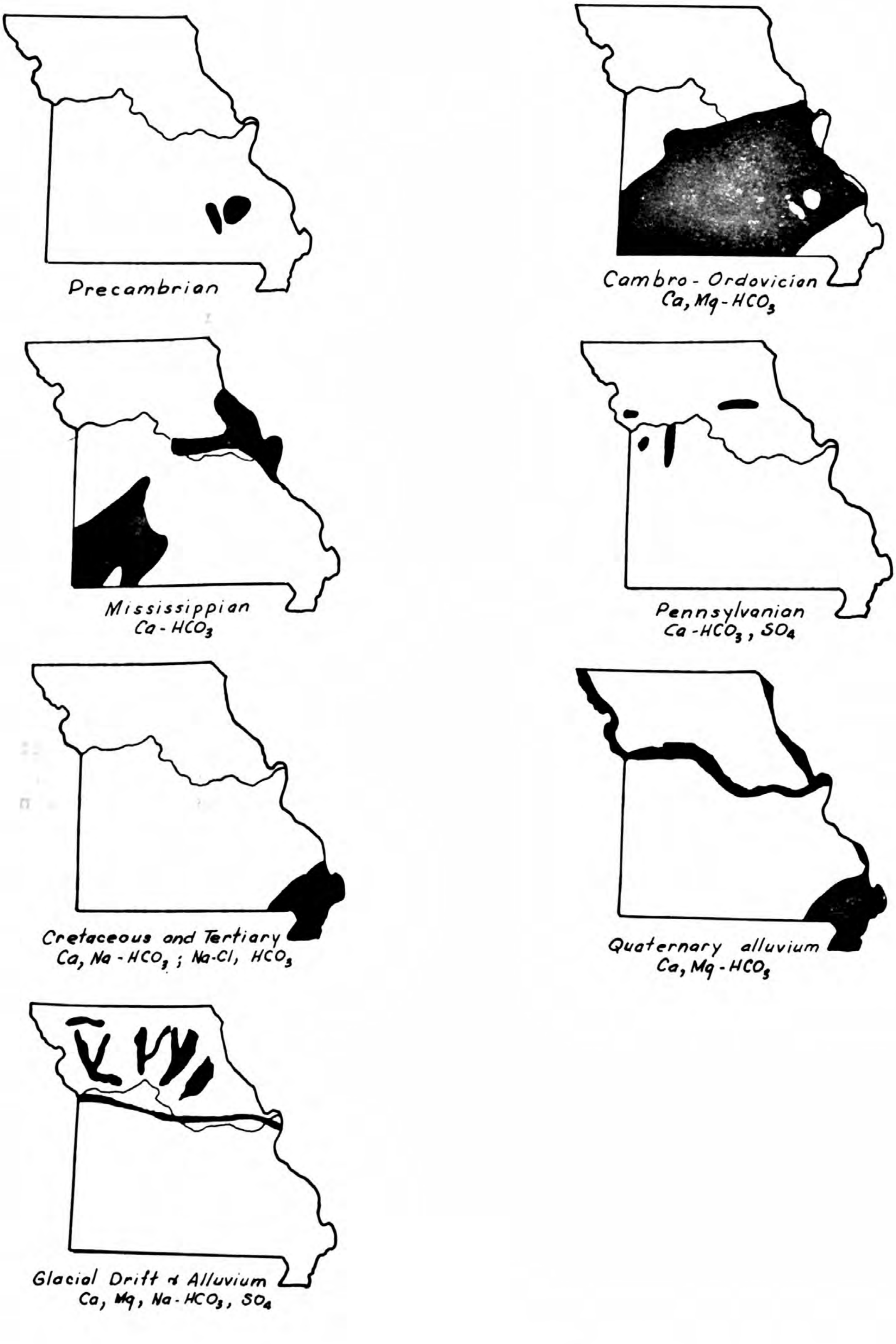


Figure 4.--Maps showing seven major geohydrologic units of Missouri and their major ion contents. Shaded areas indicate areal extent.

Airborne gamma-ray survey

by J. A. Pitkin and J. J. Connor

Purpose.--Gamma radiation is a form of very high energy electromagnetic radiation resulting from the spontaneous transition of atomic nuclei from higher energy or "excited" states to lower energy states. As with all atomic radiation, large quantities are harmful to living tissue. In order to test this aspect of the physical environment in Missouri, a preliminary airborne survey of the terrestrial gamma-ray activity was made in the southeastern part of the State during the report period. The area of the survey, which is shown in figure 5, was selected for a number of reasons. Many of the geologic units occurring in Missouri are present along the line of this survey, so that the radioactive characteristics of a variety of rock types and surficial deposits may be compared. Also, the area immediately to the north and west of Farmington lies in a general area of Pb mining activity thus offering the possibility of assessing the effect of such activity on gamma radiation levels. In addition, St. Francois County, which underlies part of the area of the survey, has for some time been an area of epidemiological interest (C. J. Marienfeld and H. I. Sauer, 1970, unpublished data).

Methods.-- The airborne gamma-ray spectrometer survey described here was flown on May 13, 1970. The survey consisted of three traverses spaced approximately one mile apart. The central traverse was positioned along the center of the shaded area in figure 5. It is located for the most part along State Highway 32, except between Farmington and Belleview, where it is centered on County Highway W and a short segment of State Highway 21. The northern and southern traverses are generally located at the northern and southern margins of the shaded area.

The gamma radiation generally detected in airborne surveys is that produced by the naturally occurring radioisotopes of K, U, and Th. Only those isotopes in the uppermost 8 to 12 inches of rock or soil at the earth's surface can be measured by airborne methods, and their distribution is dependent on original bedrock composition modified by the geologic processes of weathering, solution, and transportation (Pitkin, 1968, p. F7-F-8). Descriptions of geologic applications of gamma-ray spectrometry may be found in recent reports by Adams (1969), Darnley, Bristow, and Donhoffer (1969), and Foote (1969).

The spectrometer used in this study detects gamma energy impinging on four 4" by 5" thallium-activated sodium iodide crystals. The detected energy is electronically sorted into four measurements of natural radioactivity (see figure 6):

1. Total count or total gamma activity in the energy interval 0.4 - 2.8 mev (million electron volts),

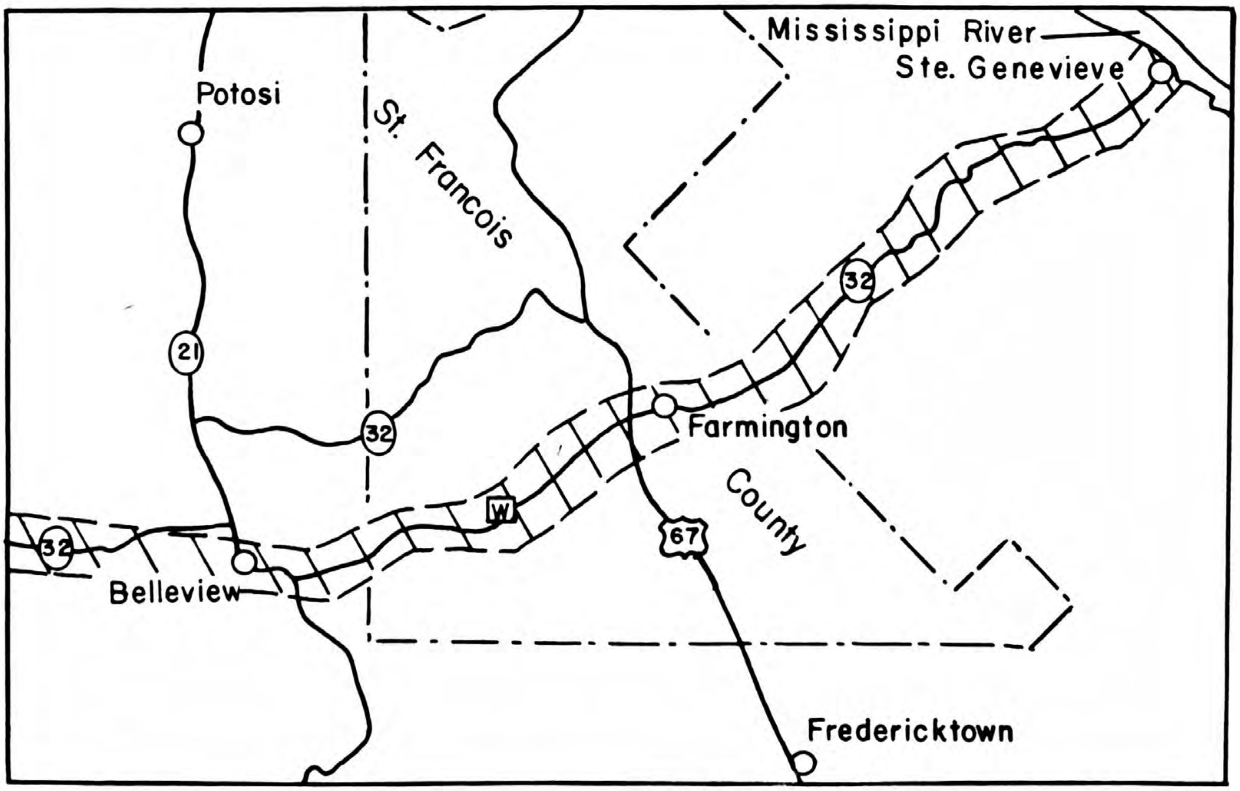
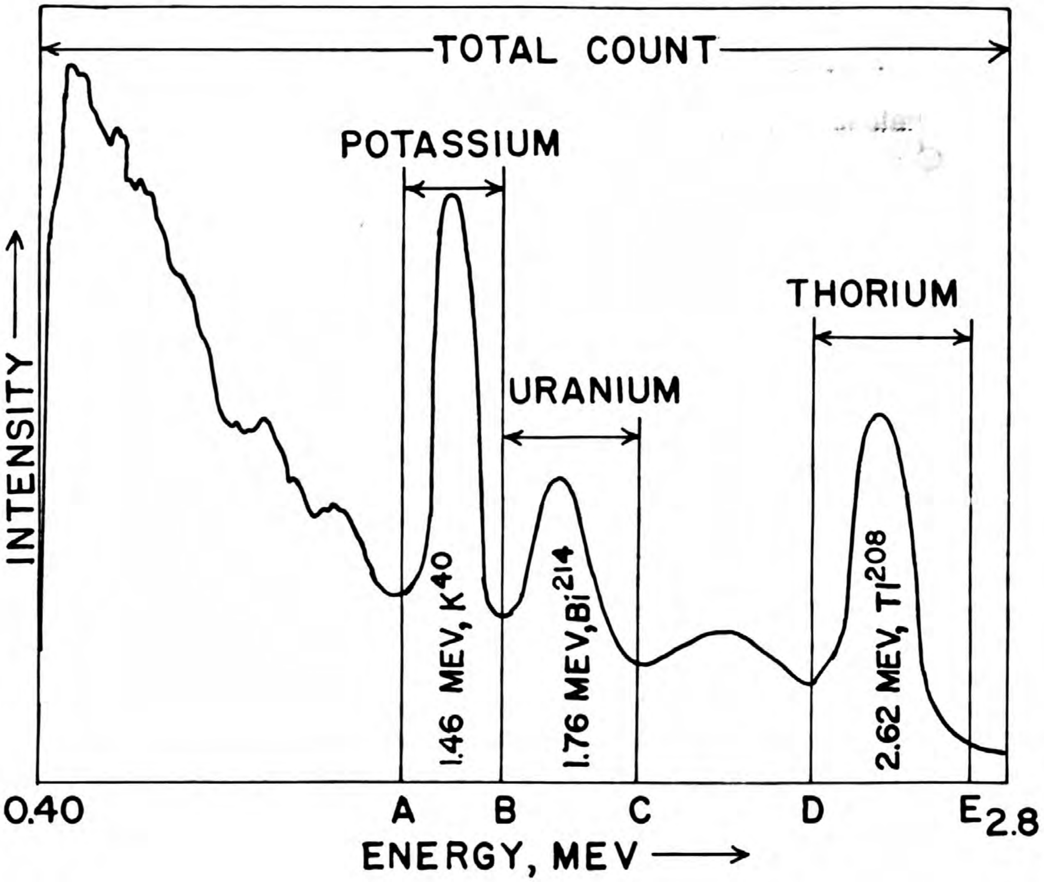


Figure 5. Index map of southeastern Missouri showing area (shaded) of airborne gamma-ray spectrometric survey.



A = low energy edge, K^{40} photopeak, ~ 1.35 mev.
B = high energy edge, K^{40} photopeak, and low energy edge, Bi^{214} photopeak, ~ 1.60 mev.
C = high energy edge, Bi^{214} photopeak, ~ 1.85 mev.
D = low energy edge, Tl^{208} photopeak, ~ 2.50 mev.
E = high energy edge, Tl^{208} photopeak, ~ 2.75 mev.

Figure 6.--Typical spectrum of natural gamma-ray energies.

2) A 0.25 mev interval centered on the 1.46 mev photopeak of K^{40},

3) A 0.25 mev interval centered on the 1.76 mev photopeak of Bi^{214} in the U^{238} decay series, and

4) A 0.25 mev interval centered on the 2.62 mev photopeak of Tl^{208} in the Th^{232} decay series.

The 1.46 mev photopeak of K^{40} is a direct measure of terrestrial K abundance because K^{40} is the only naturally occurring K radioisotope and its gamma emission is monoenergetic. The 1.76 mev photopeak of Bi^{214} and the 2.62 mev photopeak of Tl^{208} are conventionally used in airborne gamma-ray spectrometer surveys to obtain relative measures of U (as U^{238}) and Th (as Th^{232}). Because both the U^{238} and Th^{232} decay series are complex and are frequently in disequilibrium, we will simply refer to U and Th rather than U^{238} and Th^{232}. K^{40} will be referred to simply as K.

The survey was flown at an average elevation of 400 feet above ground. The four measurements of gamma radiation were continuously recorded on a strip chart recorder. Flight paths were recovered from a 35 millimeter frame camera actuated by an intervalometer clock at 1.5 second intervals while surveying. The strip chart recorder and camera were synchronized by a manually-operated fiducial edgemark system. At the surveying elevation of 400 feet, the crystals detect energy from an area approximately 800 feet wide along the flight path. Integrating time constants of 5 seconds for total count and 3 seconds for K^{40}, Bi^{214}, and Tl^{208} were used during this survey.

The spectrometer used in this study does not separate the contribution of nuclear fallout to the total measured terrestrial gamma radiation. Since 1963, only occasional atmospheric tests have contributed to the general level of terrestrial gamma radiation in the northern hemisphere. Experience has shown that nuclear fallout does not in general affect geologic interpretation of airborne gamma radiation measurements (Pitkin, 1968, p. F6).

In this preliminary study, we have assessed the radioactivity data in a qualitative rather than a quantitative manner. This is due in part to the fact that the data presented here have not been adjusted for effects introduced by topography and Compton backscatter. The principal effect of topography on gamma-ray intensity is to enhance the intensity as distance to the ground surface decreases and vice-versa, but such effects in this study are probably localized inasmuch as the general altitude was held at about 400 feet during the survey. Compton backscatter results in slight enhancement of the K radioactivity due to an interfering effect of the U and Th radioactivity. Similarly, a slight enhancement of the U intensity is introduced by backscatter from the Th radioactivity. Nevertheless, qualitative assessment of the near surface gamma-ray environment is possible because variation in radioactive intensity attributed to a specific isotope will in general vary directly with the abundance of that isotope in the surface material studied.

Results.--Radioisotope profiles for four different energy intervals (fig. 6) along each of the three flight lines are shown in figure 7. The profiles have been presented together to allow an easy visual assessment of the data. The profiles labeled B are those measured along the central traverse; those labeled A were measured along the northern traverse, and those labeled C were measured along the southern traverse. For each profile, the vertical scale is relative only; intensity increases upward. The generalized bedrock geology and geographic control points in the study area are shown at the bottom of the figure.

The most noteworthy feature of the radioactivity data is the broad "high", seen on nearly every profile, in the area between Belleview and Farmington. This area lies at the northern tip of the St. Francois Mountains, in an area of abundant K-rich granites and rhyolites. A sample of granite collected in this area contains 4.8 percent K_2O. K-rich igneous rocks tend to be rich also in U and Th. It is likely that the prominent radioactive peaks in this area represent surface exposures of granite and rhyolite, whereas adjoining low-intensity readings reflect surficial geologic deposits in the area.

It is obvious that although there are strong variations in the K profiles, the U and Th profiles are more subdued, which most likely reflects the greater abundance of K in the igneous rocks. For example, the strong K peak at locality X on figure 3 is not associated with a particularly strong U or Th peak. In contrast, localities do exist where strong U and Th peaks are associated with strong K peaks;two such localities are marked W and Y on figure 3. Such localities probably represent local geologic effects of some kind, perhaps small concentrations of U and Th.

Outside of the St. Francois Mountains, the study area is underlain by sedimentary rocks, chiefly limestones and dolomites which normally have low concentrations of natural radioelements. This is evidenced on all of the radioactivity profiles by the low-intensity regions east of the mountains and at the extreme western end of the study area. The prominent radioactive peaks west of Belleview probably reflect occasional exposures of rhyolite in valleys or stream beds.

It should be emphasized that the radioactivity data obtained over some areas of sedimentary rocks may not be representative of the radioactivity of these rocks as they tend to be poorly exposed. Rather, the radioactivity measured in these areas is better viewed as representative

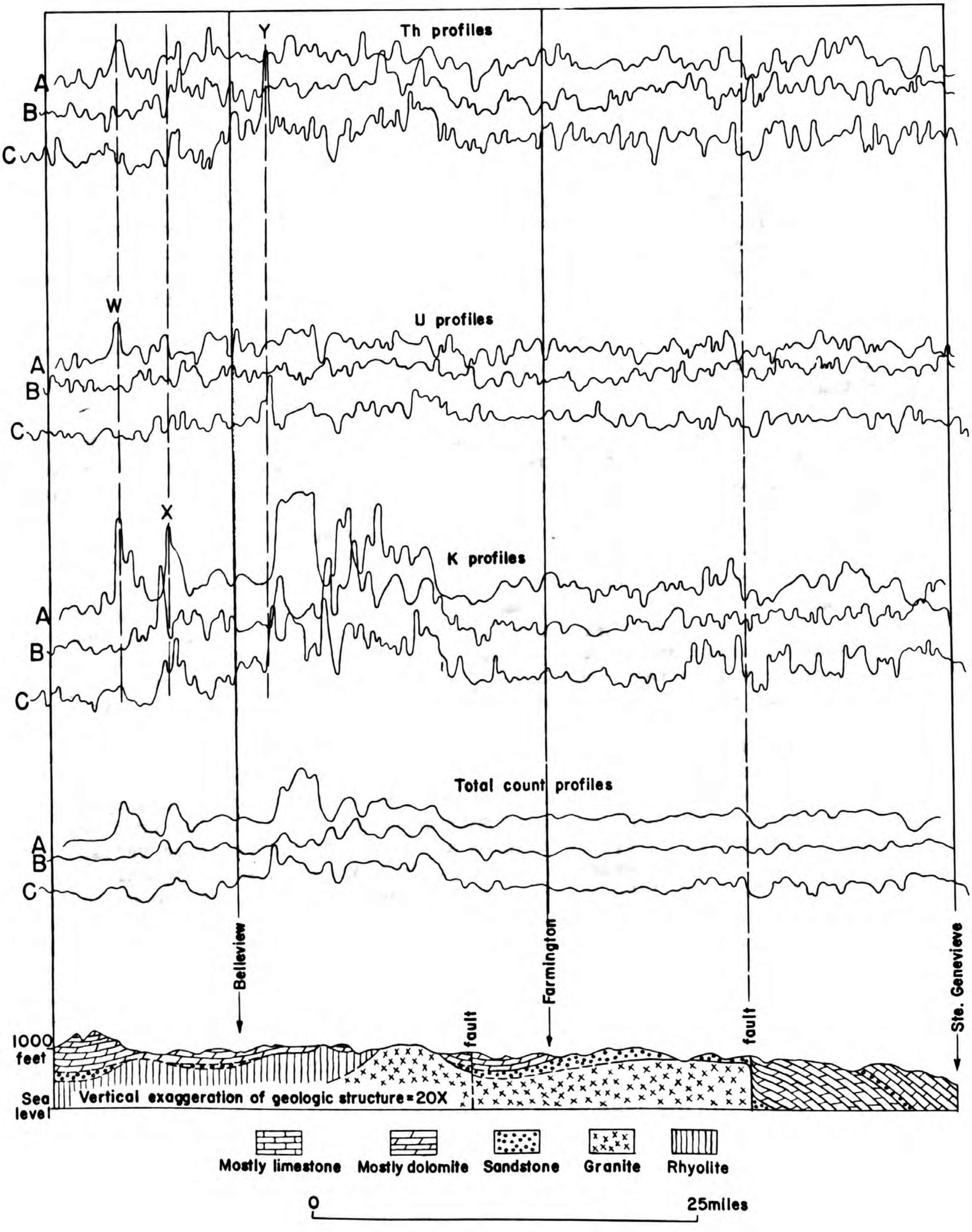


Figure 7. Generalized geologic section and airborne gamma-ray spectrometric profiles

of carbonate residuum, and, near Ste. Genevieve, perhaps of loess. The carbonate residuum is predominantly an Fe-rich siliceous clay containing about 1 percent K_2O; the loess contains an average of 2 percent K_2O (see table 4).

An additional feature of the radioactivity data, requiring additional work for full evaluation, is present on the profiles halfway between Ste. Genevieve and Farmington (see fig. 7). Here a distinct fluctuation in radioactivity levels is apparently associated with a prominent fault along which rocks on the east side have been dropped a vertical distance of perhaps 1000 feet relative to rocks on the west side. This fluctuation appears in the U and Th data nearly as prominently as in the K data, and is best developed in the A and C traverses, and poorly, if at all, in the B traverse.

East of the fault, the low level of radioactivity appears to be associated with dolomite bedrock. However, because these particular rocks are not thought to be different in radioactivity from other nearby dolomite formations, it is tentatively proposed that the radioactivity low reflects the fault in some way. Faults commonly serve as conduits for solution movement through the earth's near-surface rocks, and, to the extent that such solutions may have locally removed or redistributed the radioisotopes, a region of low radioactivity may develop. The radioactivity high on the west side of the fault may be reflecting the presence of arkosic sandstone, a K-rich sedimentary rock. In addition, granite locally crops out here, particularly in stream beds along the southern edge of the study area, and some of the radioactivity measured here may be related to such outcrops.

These major features of the gamma-ray environment show up quite well in the total count data. It seems apparent that the total count data reflects mostly K radioactivity which in turn is reflecting mostly the K-bearing properties of the near surface materials. Judging from the results presented here, the maximum airborne-detectable gamma radiation in Missouri probably exists in the St. Francois Mountains region. Carbonate regions, like those generally present throughout the southern half of the State, will probably exhibit the lowest gamma radiation of any area in the State because of the general paucity of K in such rocks. The northern and western parts of the State, which consist largely of glacial material and loess underlain by intimately intermixed limestone, shale, and sandstone, may exhibit a gamma-ray environment somewhat greater than the carbonate areas but certainly less than the granite areas. The most likely exceptions may be local high intensities over outcrops of organic-rich rocks such as coal or black shale, which may contain higher quantities of U.

References cited

Adams, J. A. S., 1969, Total and spectrometric gamma-ray surveys from helicopters and vehicles, p. 147-161, in Nuclear techniques and mineral resources, Proceedings of a symposium, Buenos Aires, 5-9 November 1968: International Atomic Energy Agency, Vienna, 548 p.

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

Cohen, A. C., Jr., 1961, Tables for maximum likelihood estimates; singly truncated and singly censored samples: Technometrics, v. 3, no. 4, p. 535-541.

Connor, J. J., Erdman, J. A., Sims, J. D., and Ebens, R. J., Roadside effects on trace metal content of some rocks, soils, and plants of Missouri, in D. D. Hemphill, ed., Trace substances in environmental health - IV: Univ. of Missouri 4th Ann. Conf., Trace Substances in Environmental Health Proc., (in press).

Darnley, A. G., Bristow, Q., and Donhoffer, D. K., 1969, Airborne gamma-ray spectrometer experiments over the Canadian Shield, p. 163-186 in Nuclear techniques and mineral resources, Proceedings of a symposium, Buenos Aires, 5-9 November 1968: International Atomic Energy Agency, Vienna, 548 p.

Foote, R. S., 1969, Improvement in airborne gamma-radiation data analyses for anomalous radiation by removal of environmental and pedologic radiation changes, p. 187-196 in Nuclear techniques and mineral resources, Proceedings of a symposium, Buenos Aires, 5-9 November 1968: International Atomic Energy Agency, Vienna, 548 p.

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

Jenny, Hans, 1941, Factors of soil formation, a system of quantitative pedology: New York, McGraw-Hill Book Co., Inc., 281 p.

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

Masironi, Roberto, 1970, Cardiovascular mortality in relation to radio-activity and hardness of local water supplies: World Health Organization, 20 p.

Miesch, A. T., 1967, Methods of computation for estimating geochemical abundance: U.S. Geol. Survey Prof. Paper 574-B, 15 p.

Myers, A. T., Havens, R. G., and Dutton, P. J., 1961, A spectrochemical method for the semiquantitative analysis of rocks, minerals, and ores: U.S. Geol. Survey Bull. 1084-I, p. 207-229.

Pitkin, J. A., 1968, Airborne measurements of terrestrial radioactivity as an aid to geologic mapping: U.S. Geol. Survey Prof. Paper 516-F, p. F1-F29.

Rühling, Åke, 1969, Tungmetalföroreningar inom Oskarshammsområdet (Heavy metal pollution within the limits of the Oskarshamm area): Forskningsrapport, Ekologiske tungmetallundersoknigar, Avd. för Ekologist Botanik, Lunds Universitet, 11 p. [in Swedish]

Scrivner, C. L., Baker, J. C., and Miller, B. J., 1966, Soils of Missouri, a guide to their identification and interpretation: Circular 823, Extension Division, University of Missouri, Columbia, Missouri, 48 p.

Shacklette, H. T., 1965, Element content of bryophytes: U.S. Geol. Survey Bull. 1198-D, 21 p.

Shacklette, H. T., Erdman, J. A., and Keith, J. R., 1969, Geochemical survey of vegetation, in Geochemical survey of Missouri: U.S. Geol. Survey unpublished report, 49 p.

Shacklette, H. T., Sauer, H. I., and Miesch, A. T., 1970, Geochemical environments and cardiovascular mortality rates in Georgia: U.S. Geol. Survey Prof. Paper 574-C, 39 p.

Shacklette, H. T., Hamilton, J. C., Boerngen, J. G., and Bowles, J. M., Elemental composition of surficial materials in the conterminous United States: U.S. Geol. Survey Prof. Paper 574-D. (in press)

Soil Survey Staff, 1960, Soil classification, a comprehensive system, seventh approximation: Washington, D.C., Soil Conservation Service, U.S. Dept. of Agriculture, 265 p.

_____, 1967, Supplement to soil classification system (seventh approximation): Washington, D.C., Soil Conservation Service, U.S. Dept. of Agriculture, 207 p.

_____, 1968, Supplement to soil classification system (seventh approximation), histosols: Washington, D.C., Soil Conservation Service, U.S. Dept. of Agriculture, 22 p.

Steyermark, Julian A., 1963, Flora of Missouri: Ames, Iowa, Iowa State Univ. Press, 1725 p.

Turekian, K. K., and Wedepohl, K. H., 1961, Distribution of the elements in some major units of the Earth's crust: Geol. Soc. Am. Bull., v. 72, p. 175-192.