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By R. C. SEVERSON *and* R. R. TIDBALL

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GEOCHEMICAL SURVEY OF THE WESTERN ENERGY REGIONS

SPATIAL VARIATION IN TOTAL ELEMENT CONCENTRATION IN SOIL WITHIN THE NORTHERN GREAT PLAINS COAL REGION

By R. C. SEVERSON and R. R. TIDBALL

ABSTRACT

To objectively determine the changes in chemical character of an area subjected to mining and reclamation, prior information is needed. This study represents a broadscale inventory of total chemical composition of the surficial materials of the Northern Great Plains coal region (western North and South Dakota, eastern Montana, and northeastern Wyoming); data are given for 41 elements in A and C soil horizons.

An unbalanced, nested, analysis-of-variance design was used to quantify variation in total content of elements between glaciated and unglaciated terrains, for four increasingly smaller geographic scales, and to quantify variation due to sample preparation and analysis. From this statistical study, reliable maps on a regional basis (>100 km) were prepared for C, K, and Rb in A and C soil horizons; for Na, Si, Th, U, and Zn in A-horizon soil; and for As, Ca, Ge, and Mg in C-horizon soil. The distribution of variance components for the remaining 29 elements did not permit the construction of reliable maps. Therefore, a baseline value for each of these elements is given as a measure of the total element concentration in the soils of the Northern Great Plains coal region. The baseline is expressed as the 95-percent range in concentration to be expected in samples of natural soils.

INTRODUCTION

The present and future role of the Northern Great Plains in supplying coal and other minerals to meet energy requirements dictates the need for timely information on the chemical character of the soils that will be disturbed by mining and reclamation. In order to evaluate the chemical character of soil, or any other natural material, its variability needs to be quantified so that inferences having known degree of certainty can be made from the data that are collected.

Most previous studies to determine variability in soil constituents have been related to agronomic or taxonomic problems (Beckett, 1967; Beckett and Webster, 1971; Crosson and Protz, 1974; Drees and Wilding, 1973; Jansen and Arnold, 1976; McCormack and Wilding, 1969; McKenzie, 1955; Oertel, 1959; Protz, Presant, and Arnold, 1968; Reynolds, 1975; Walker, Hall, and Protz, 1968; Webster and Butler, 1976; and Wilding, Jones, and Schafer, 1965). These studies considered different soil properties at different geographic scales from those considered in this study. Therefore, their conclusions could not be applied directly at the planning stages of, or to the results of, the present investigation. However, their results indicate, in general, that soil properties tend to exhibit a large local variability within the context of the many different sampling designs.

Studies by Connor, Keith, and Anderson (1976); Erdman, Shacklette, and Keith (1976); Tidball (1976); Tidball and Ebens (1976); and Tourtelot and Miesch (1975) addressed variability of total element concentration in soil on the basis of large mapping-units. Information from these studies was used in planning the present study. In general, these studies also indicated that variability at local scales is large.

The objectives of the present study were three-fold: (1) To provide background information on element concentrations in soil of the Northern Great Plains coal region before mining and reclamation. (2) To evaluate the magnitude of the variability in element concentration in soil at different geographic scales. Knowing the variability, inferences can be made about the soils with a known degree of confidence, and the sample load that would be needed to make inferences at a specified level of certainty can be determined. (3) Either to prepare reliable maps of element concentrations in soil on a regional basis, or to determine the number of samples that would be required to prepare reliable maps for those elements for which adequate data are not available.

STUDY AREA

The study area consists of the part of the Northern Great Plains (fig. 1) whose surface is underlain by geologic formations that contain large resources of

strippable coal. This area is underlain mainly by fine-grained, nonmarine sediments in the Wasatch and Fort Union Formations of early Tertiary age (Keefer, 1974). The boundaries of this area are modified from a U.S. Geological Survey map (1974) for the part within the United States, and from Whitaker and Pearson (1972) for the part in Canada (fig. 1).

Within this area, the greatest contrast in surface features and soil-parent materials is between glaciated and unglaciated areas. Glacial drift generally occupies the area to the north and east of the Missouri River (fig. 1). The glaciated area is an undulating plain having local relief of less than 10 m; closed depressions are common and a well-developed stream drainage is lacking. Nearly level areas of glacial outwash and locally-occurring glacial lake deposits are widespread throughout the glaciated areas. Compared to the drift plain, areas of moraines have steeper slopes, deeper depressions, and a veneer of gravel and boulders; glacial moraines rise above the subdued topography of the drift plain, with local relief of 15 to 30 m. Eolian sediments that are generally found east of and adjacent to major drainages blanket the glacial drift and tend to smooth the undulating surface. Some small areas that were not covered by glacial drift or from which the glacial drift has been removed by erosion are interspersed throughout the drift plain.

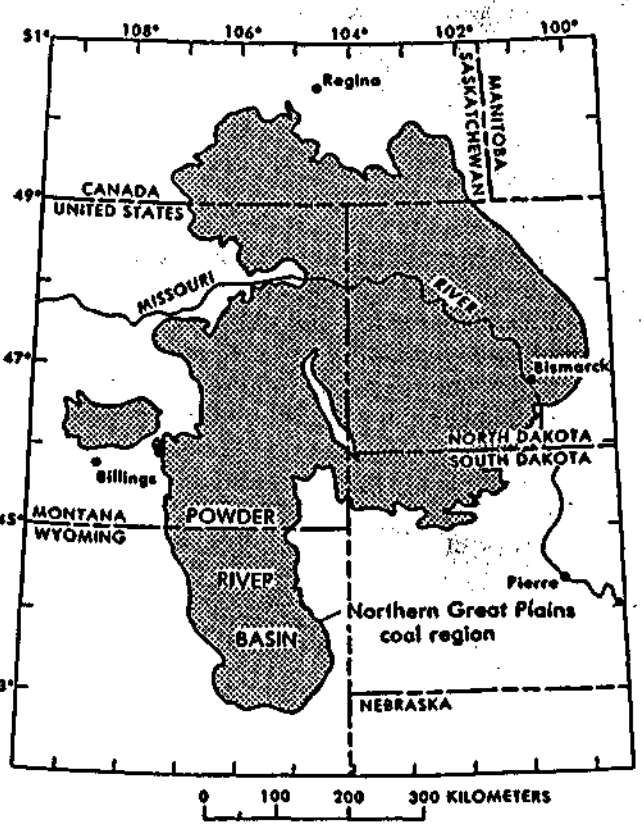


FIGURE 1.—Location of the Northern Great Plains coal region; area containing coal deposits of Tertiary age indicated by stipple pattern.

The transitional area between the glaciated and unglaciated landscapes is generally delineated by the Missouri River Valley. This area has erosion extending as much as 180 m into the soft sediments of the adjacent uplands. The valley is generally less than 3 km wide, and severely dissected canyons impinge upon the surrounding uplands. The valley contains thick deposits of recent alluvium flanked by older terrace deposits.

On the unglaciated plain to the south and west of the Missouri River a parallel drainage pattern has formed, and some stream valleys are as much as 60 m deep. The upland is a gently rolling plain with isolated to closely spaced buttes as much as 200 m higher than the adjacent surface. In some localities, mountain outliers are flanked with pediments and merge with alluvial fans and terraces in the adjacent upland. Between the mountain outliers broad anticlines and synclines control the topographic character of the unglaciated plain. Where thick units of shale are near the surface, they are highly dissected to form "badlands." Spontaneous combustion of some lignite beds in the Tertiary formations has baked the overlying sediments to form reddish colored clinker beds, which are a distinctive feature of the unglaciated area.

The paleogeography of the sediments of Late Cretaceous age in the Northern Great Plains is outlined by Gill and Cobban (1973). Paleogeography of deposits of Tertiary and Pleistocene ages for northeastern Montana and northwestern North Dakota is detailed by Howard (1960). Mineralogy of the major stratigraphic units of Tertiary age in the Northern Great Plains is presented by Denson and Chisholm (1971).

A general description of soil-development gradients by Hunt (1967, p.85–93) indicated that temperature and moisture interactions, as they influence the depth of water penetration in soil, are the major factors that determine the degree of soil development in the Northern Great Plains. Soil moisture and soil temperature were also the major criteria used by Aandahl (1972) to map major taxonomic soil classes in the Great Plains region. The climate of the Northern Great Plains is cool-temperate-subhumid to semiarid, and is not conducive to intense soil development. Depth of solum, horizonation, and accumulation of salts are properties that indicate the intensity of soil development in the Northern Great Plains. Soil development and soil pedons are described by Dunnewald (1957) for Wyoming, by Omodt and others (1968) for North Dakota, by Southard (1969) for Montana, and by Westin, Puhr, and Buntley (1967) for South Dakota.

SAMPLE COLLECTION, PREPARATION, AND ANALYSIS

Samples of A- and C-horizons of soils were collected in the Northern Great Plains coal region (fig. 1) in the fall of 1974. An A-horizon sample consisted of a channel composite of the top 10 cm. A C-horizon sample consisted of a channel composite at a depth of from 100 to 120 cm; if consolidated rock was encountered before this depth was reached, the sample consisted of the 10 cm of material immediately above the rock zone. All samples were collected using a barrel auger that was 10 cm in diameter.

The samples were dried at ambient temperature under forced air and then were disaggregated in a motor-driven ceramic mortar-and-pestle to pass a 2-mm stainless steel sieve. These samples were further ground to minus-100 mesh (minus 149 μm) in a ceramic mill, and splits of this material were used for all chemical determinations.

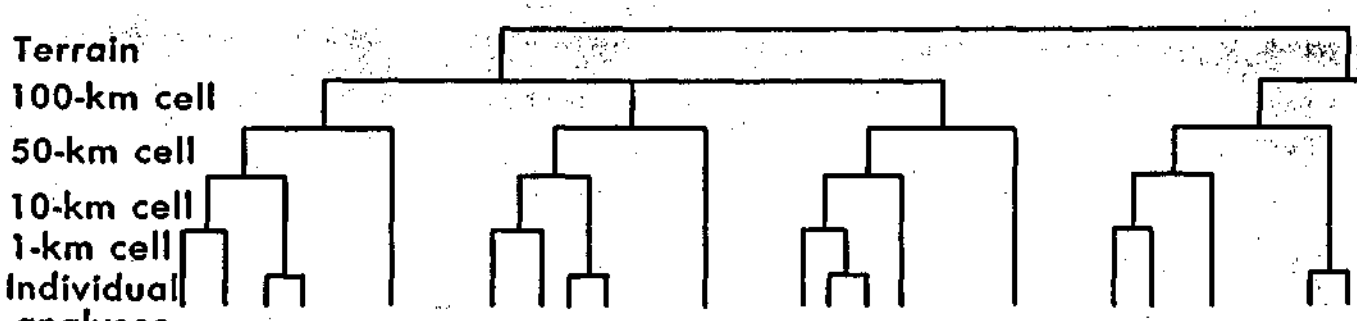
All analyses were done in the laboratories of the U.S. Geological Survey at Denver, Colorado. Analyses were performed by James W. Baker, Leon A. Bradley, Isabelle Davidson, Andrew Drenick, Jefferey England, Johnnie M. Gardner, Patrica Gayle Guest, Raymond G. Havens, Claude Huffman, Jr., J. O. Johnson, Lorraine Lee, R. M. Lemert, R. E. McGregor, H. T. Millard, Jr., Wayne Mountjoy, Farris D. Perez, Van E. Shaw, George D. Shipley, Arthur L. Sutton, Jr., James A. Thomas, Michele L. Tuttle, Richard E. Van Loenen, James S. Wahlberg, and Thomas L. Yager. The analytical methods employed are described in U.S. Geological Survey (1975) by James S. Wahlberg (p. 69), Claude Huffman, Jr. (p. 71), H. T. Millard, Jr. (p. 79), and in U.S. Geological Survey (1976) by Arthur L. Sutton, Jr. (p. 131).

SAMPLING DESIGN AND STATISTICAL METHODS

The pattern adopted for collecting soil samples for this study (fig. 2) is a six-level, unbalanced, nested, analysis-of-variance design (Leone and others, 1968). The highest level compares variation in element composition of soil from glaciated terrain with soil from unglaciated terrain. Within the irregular boundaries of each terrain, cells 100 km on a side were arranged to include as much of each terrain as possible (figs. 3 and 4). This arrangement resulted in 12 100-km cells within the glaciated terrain and 22 100-km cells within the unglaciated terrain.

Each of the 100-km cells was partitioned into areas of decreasing size, as follows: four 50-km cells, each of which was divided into 25 10-km cells, which were then divided into 100 1-km cells. Cells to be sampled were randomly selected, as follows: two 50-km cells, two 10-km cells in one 50-km cell and one 10-km cell in the other 50-km cell, two 1-km cells in one 10-km cell and one 1-km cell in each of the two other 10-km cells. This resulted in samples of A and C horizons from each of 136 locations—48 in the glaciated terrain and 88 in the unglaciated terrain.

An estimate of variance due to all laboratory procedures (analytical error) was made from data on 28 randomly selected samples (out of a total of 272)—12 A-horizon samples and 16 C-horizon samples—that were



Number of units sampled at each level

Terrain	Cell size, on a side: 100 km	50 km	10 km	1 km	Analytical units: A-horizon	C-horizon
Glaciated	12	24	36	48	12	16
Unglaciated	22	44	66	88		
Total	34	68	102	136	148	152

FIGURE 2.—Diagram of the unbalanced, nested, analysis-of-variance sampling design.

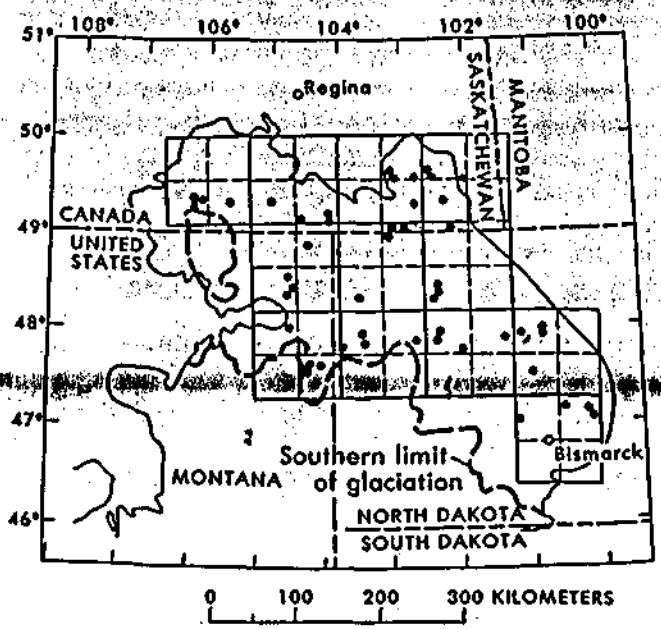


FIGURE 3.—Soil-sample localities in the glaciated terrain of the Northern Great Plains coal region. Large squares (solid lines) are 100 km on a side; smaller squares (dashed lines) are 50 km on a side. Dots are sampling sites. The limit of glaciation is modified from Colton, Lemke, and Lindvall (1963) for North Dakota and from Colton, Lemke, and Lindvall (1961) for Montana.

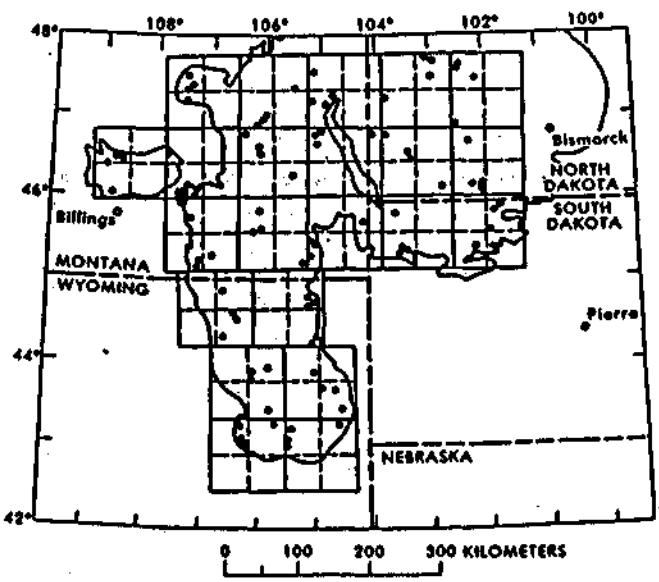


FIGURE 4.—Soil-sample localities in the unglaciated terrain of the Northern Great Plains coal region. Large squares (solid lines) are 100 km on a side; smaller squares (dashed lines) are 50 km on a side. Dots are sampling sites. Modified from U.S. Geological Survey (1974). The limit of glaciation is modified from Colton and others (1963) for North Dakota and from Colton and others (1961) for Montana.

split and analyzed twice. These duplicate samples were randomly interspersed among the original samples, and the entire suite of 300 samples was analyzed in a randomized sequence; thus, any systematic analytical error would be transformed into a random error.

The components of variance estimated by the sampling design are as follows: the level 1 (terrains) component is s_α^2; the level 2 (100-km cells) component is s_β^2; the level 3 (50-km cells) component is s_γ^2; the level 4 (10-km cells) component is s_δ^2; the level 5 (1-km cells) component is s_η^2; and the level 6 (analytical error) component is s_ϵ^2.

The statistical model is represented by the following equation:

$$x_{ijklmn} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} + \delta_{ijkl} + \eta_{ijklm} + \epsilon_{ijklmn} \quad (1)$$

where x_{ijklmn} is a measure of element concentration in a single sample (the nth analysis, of the mth sample, of the lth 1-km cell, and so forth): μ is the mean for the population sampled; and α, β, ψ, δ, η, and ϵ are deviations from the mean associated, respectively, with terrains, distances of 100, 50, 10, and 1 km, and random errors related to sample preparation and analysis. The variance components, as estimated by the analysis-of-variance computation methods following Anderson and Bancroft (1952), are expressed as follows:

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

where s_x^2 is an estimate of the total observed variation for an element in soil, and the remaining terms are the variance components described above. All computations were done on a computer using statistical programs in the U.S. Geological Survey's STATPAC Library (Van Trump and Miesch, 1977).

The unbalanced design was chosen in preference to a balanced design, because it has the advantage of spreading the degrees of freedom almost equally over levels 2–6. Also, the number of degrees of freedom achieved in the higher levels of the unbalanced design is comparable to that achieved in the balanced design, but with only one-half the number of samples. Therefore, the power of the F-test at the higher levels of the unbalanced design is equivalent to that for a balanced design, and yet the cost for sample collection and analyses is only about one-half as much.

Concentrations of some elements are below the limit of determination by a given analytical method, so they are omitted, or "censored." When more than 20 percent of the determinations for an element are below the limit of detection, the element is omitted from further consideration. Elements omitted include Ag, Au, Bi, Br, Cd, Ce, Cl, Cs, Dy, Er, Gd, Hf, Ho, I, In, Ir, La, Nd, Os, Pd, Pr, Pt, Re, Rh, Ru, S, Sm, Ta, Tb, Te, Tl, Tm, and W. For elements with less than 20 percent censored values, the censored

values were replaced by small, arbitrary values. These replacement values can be justified because their small number neither alters the statistical tests nor affects the final interpretation of the data.

The data for all elements except Na, Si, Th, and Zn were transformed by taking the common logarithm, because frequency distributions of the data were more nearly log-normal than normal. All data are reported in terms of either logarithmic (transformed data) or arithmetic variance, means, and deviations. Unless a statistical term is prefixed by "arithmetic," the term refers to logarithmically transformed data.

SAMPLED POPULATION

The population sampled in this study is in the Northern Great Plains coal region and consists of all soils developed either from glaciated materials or from rocks in the Fort Union and Wasatch Formations of early Tertiary age. The 136 sample localities that represent the population were randomly selected within the several nested cells. The diversity of sedimentary parent materials for the soils sampled is shown in figure 5. If indeed the random sampling procedure was unbiased and if the number of samples was sufficiently large, then figure 5 would also show the proportional distribution of parent materials for soils in the Northern Great Plains coal region.

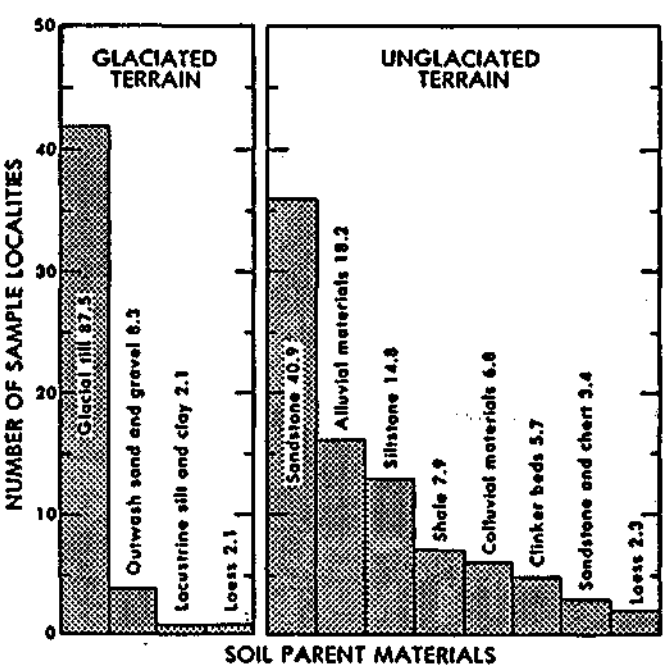


FIGURE 5.—Frequency distribution, in percent, of soil parent materials sampled in glaciated and unglaciated terrains of the Northern Great Plains coal region.

As suggested by figure 5, a natural division exists between glaciated and unglaciated terrains in terms of the character of the parent materials. The division is significant for two reasons: (1) The total chemical character of the soils of the different terrains should be distinct because of the different amounts of time over which pedologic processes have been acting. (2) The mineralogy, source areas, and mode of deposition of parent materials of glacial origin are distinctly different from those of the Tertiary sediments. These differences should be reflected in the chemical variation between the soils of the two terrains. The highest level of the sampling design is, therefore, intended to estimate differences in chemical variation between the two terrains. Before discussing terrain differences, however, it will be helpful to discuss variance components.

VARIANCE COMPONENTS

Within each terrain, sampling was designed to measure variation over increments of distance expressed in terms of cell size. Thus, the total variance was subdivided into components, each associated with a given cell size. The distribution of variance components for 41 elements in both A and C horizons (82 combinations), each expressed as a percentage of the total variance, is shown in table 1.

Of the 82 entries in table 1, 21 exhibit an analytical-error-variance component that is greater than 50 percent of the total observed variance. This amount is excessive and these elements are excluded from further interpretation. Reduction of the analytical-error-variance component to an acceptable level requires a more precise analytical method or repeated analyses of the sample. Generally, as analytical precision or number of analyses is increased, the cost rises. It is necessary, therefore, to balance the value of the results against the increased cost of more precise or repeated analyses for each element.

The variance distribution indicates that, for most elements, the largest variance occurs at a local level; that is, within areas 10 km or less on a side. In fact, it is not uncommon for most of the variance to occur within distances of 1 km. This could logically be expected where a variety of different sample materials are found in a small area (for example, outwash gravel and lacustrine silt and clay in glacial terrain, or sandstone and shale in unglaciated terrain). Naturally, the variance in element distribution between soils developed from diverse materials would be greater than variances between soils from the same type of material. Independent studies by Tidball (1975), Tidball and Ebens (1976), and Keith, Anderson, and Connor (1974) of soil in the Powder River

TABLE 1.–*Variance components (expressed as percent of total variance) for 41 elements in A and C horizons of soils from the Northern Great Plains coal region, and the variance mean ratio for 100-km cells. An asterisk indicates significance at the 0.05 probability level*

Element	Soil horizon	Total log variance	Between terrains	Between 100-km cells	Between 50-km cells	Between 10-km cells	Between 1-km cells	Analytical error	v_m[1]
Al	A	0.0069	11.7*	0	32.3*	3.3	31.7*	21.0	0.34
	C	.0106	11.0*	0	16.2	0	66.9*	5.9	.39
As	A	.1336	0	11.9	0	0	83.7*	4.4	.52
	C	.1290	0	31.0*	0	7.4	56.0*	4.0	1.66
B	A	.0446	0	8.6	0	40.9*	18.4	23.9	.30
	C	.0466	.7	10.2	0	12.1	69.7*	7.3	.46
Ba	A	.0175	0	4.3	0	3.1	3.2	87.5	.26
	C	.0629	0	9.0*	0	21.9*	0	69.1	.35
Be	A	.0340	6.4*	.03	6.4	0	55.7*	31.4	.25
	C	.0477	1.3	0	52.1*	0	28.9*	17.4	.03
C	A	.0444	35.4*	20.7*	0	4.7	48.5*	.5	3.3
	C	.1293	31.2*	12.5*	0	13.6	32.1*	.6	1.8
Ca	A	.1304	0.6	18.6*	[illegible]	21.3	59.5*	.4	[illegible]
	C	.1158	26.6*	4.0	4.6	7.2	57.4*	.4	1.5
Co	A	.0400	0	0	49.0*	3.5	25.0	22.5	0
	C	.0411	.6	0	24.9	0	58.5*	16.0	.02
Cr	A	.0434	0	17.2*	0	0	15.3	67.5	.63
	C	.0679	.7	0	32.2*	0	41.0*	25.1	.02
Cu	A	.0470	.7	0	22.7	2.6	44.5*	29.4	.02
	C	.0877	0	0	17.8	0	48.2*	34.0	0
F	A	.0827	2.4*	11.6*	5.4	0	0	80.4	.40
	C	.0493	.1	0	0	26.2*	0	73.7	<0.01
Fe	A	.0329	0	18.1*	0	62.9*	18.6*	.4	.64
	C	.0291	0	0	20.2*	0	79.5*	.3	0
Ga	A	.0287	3.0	0	10.4	0	42.5	44.0	.11
	C	.0565	2.0*	0	29.2*	0	41.3*	27.6	.06
Ge	A	.1546	0	14.4*	0	29.6	54.5*	1.7	.55
	C	.0746	0	29.2*	0	0	65.5*	5.3	1.56
Hg	A	.0672	6.4*	4.6	0	55.0*	2.9	30.9	.39
	C	.0736	3.8	3.7	6.3	0	82.9	3.3	.29
K	A	.0038	43.7*	0	13.3	4.4	36.6*	2.0	2.2
	C	.0063	39.6*	0	21.6*	2.4	35.9*	.5	1.7
La	A	.0353	2.7	0	0	9.4	30.3	57.5	.11
	C	.0508	.4	0	15.9	0	45.3*	38.4	.01
Li	A	.0209	3.0	4.1	11.1	.1	79.1	2.6	.26
	C	.0440	0	0	25.4	0	68.2*	6.4	0
Mg	A	.0477	0	5.2	40.3	18.6	35.5*	.2	.13
	C	.0620	10.7*	17.2*	0	27.6*	44.4*	.1	1.3
Mn	A	.1451	22.6*	0	0	31.0*	8.2	36.2	.96
	C	.2361	10.6*	0	34.1*	4.2	24.3	26.8	.30
Mo	A	.1068	0.5	7.8*	11.1	0	44.6	36.2	.31
	C	.1840	0	0	32.5*	0	25.7	41.8	0
Na	A	.0374	7.7	19.5*	10.1	0	62.2*	.5	1.2
	C	.1249	1.6	7.3	0	29.2	61.1*	.9	.33
Nb	A	.0510	.7	0	19.1*	0	24.5	55.7	.02
	C	.0600	0	0	21.3	18.8	0	59.9	0
Ni	A	.0275	0	11.0*	0	12.3	40.6	36.0	.46
	C	.0519	3.8*	0	20.8	0	58.2*	17.2	.12
P	A	.0319	0	1.1	5.9	0	0	93.2	.06
	C	.0281	0	0	17.9	0	4.9	77.2	0
Pb	A	.0396	1.9	0	9.9	0	26.6	61.6	.07
	C	.0826	.1	0	38.4*	0	35.4*	24.9	<0.01
Rb	A	.0093	25.0*	11.1*	0	29.2*	24.8*	9.9	1.6
	C	.0186	31.2*	0	3.3	9.4	49.3*	6.8	1.6
Sb	A	.4064	0	0	0	14.8	0	85.2	0
	C	.4374	.8	0	3.1	0	39.2	56.9	.03
Sc	A	.0622	0	9.1	0	6.9	21.3	62.2	.39
	C	.0772	2.2	0	22.9	0	5.6	69.1	.07
Se	A	.3418	3.2*	0	1.9	0	41.3*	33.4	.13
	C	.3549	2.1	0	6.6	0	7.6	83.7	.06
Si[2]	A	9.331	0	27.0*	0	7.6	32.0*	13.4	1.4
	C	12.61	6.9*	9.3	0	7.3	64.7*	11.8	.74
Sn	A	.1490	.9	3.3	0	43.4*	34.5*	18.8	.18
	C	.1462	5.1	8.3	0	0	71.5*	15.1	.60
Sr	A	.0295	8.8*	2.1	0	37.5*	33.4*	16.3	.40
	C	.0372	9.3*	6.1	0	0	75.0*	8.8	.73
Th	A	.0096	17.7*	5.5	0	39.2*	23.5	24.1	1.0
	C[2]	.0200	13.3*	0	2.2	16.5	17.1	50.9	.54
Ti[2]	A	.0023	0	11.2	0	39.9*	32.2*	16.7	.41
	C	.0041	1.3	0	6.4	0	57.4*	6.9	.05
U	A	.0131	31.7*	10.2*	0	16.0	37.6*	2.5	2.5
	C	.0286	17.7*	0	10.6	11.5	57.9*	2.3	.68
V	A	.0171	7.3*	0	3.1	12.6	22.1	54.9	.28
	C	.0449	10.7*	0	17.5*	0	60.6*	11.2	.37
Y	A	.0369	3.3	7.1	0	0	47.2	43.5	.41
	C	.0361	0	0	0	30.9*	29.1	40.1	0
Yb	A	.0396	6.4*	0	9.0	0	3.3	81.3	.26
	C	.0347	1.2	0	0	26.7*	24.5	47.6	.04
Zn	A	340.2	3.3	19.0*	0	13.4	62.4*	1.9	1.1
	C	413.5	0	0	18.7	0	74.9*	14.4	0
Zr	A	.0594	4.4*	6.6	0	10.0	0	78.4	.59
	C	.0406	0	5.0	4.2	0	23.9	67.9	2.0

[1]Variance mean ratio of Hinsch (1976a).

[2]Variance computed on arithmetic basis.

Basin of Wyoming (fig. 1) showed a significant portion of the total variation to be at distances of from 0.3 to 1 km for many of the elements evaluated in this study.

Each variance component was tested against the null hypothesis that the component does not significantly differ from zero using the conventional F-test at the 0.05 probability level (table 2). If a component fails to differ from zero, then it is impractical to map the observed variation over intervals associated with that component because of the high probability that no variation exists. On the other hand, a significant variance component at the terrain level suggests that the concentrations of elements in samples from one terrain differ from those of the other terrains.

Our principal interest is in using variance components to calculate the variance mean ratio, to calculate the minimum number of samples required to estimate a cell mean with a given degree of certainty, and to determine the presence and magnitude of regional variance as a basis for making regional maps. (We define "regional variance" as variation that occurs between areas of 100-km on a side or greater.) The large local variation indicates that mapping within smaller areas would require an excessive number of samples and would result in more map detail than is necessary.

VARIANCE MEAN RATIO

The variance mean ratio, v_m, of Miesch (1976a) provides an index of the relative stability of an estimate of the mean for any cell size on the basis of the data already collected. In particular, we use v_m (table 1) to evaluate the feasibility of mapping the regional distribution of total concentration of elements in soil. The equation for v_m has been modified from that of Miesch (1976a) to account for the unbalanced, nested design, as follows:

$$v_m = \frac{s_\alpha^2 + s_\beta^2}{n_\gamma s_\gamma^2 + n_\delta s_\delta^2 + n(s_\eta^2 + s_\epsilon^2)} \qquad (3)$$

where the numerator is the variance between 100-km cells and the denominator is the variance within 100-km cells. The s_i's are the variance components at each level,

TABLE 2.—*Unbalanced, nested, analysis-of-variance design used in the Northern Great Plains coal region*

Level	Source of variation	Degrees of freedom	Mean square estimates[1]	F-ratio[2]	Variance component
1	Between terrains	1	$MS_1 = s_\epsilon^2+1.2s_\eta^2+1.8s_\delta^2+2.8s_\gamma^2+4.5s_\beta^2+68.6s_\alpha^2$	MS_1/MS_2	$s_\alpha^2 = \frac{MS_1 - MS_2}{68.6} \cong \sigma_\alpha^2$
2	Between 100-km cells within terrains	32	$MS_2 = s_\epsilon^2+1.1s_\eta^2+1.7s_\delta^2+2.7s_\gamma^2+4.3s_\beta^2$	MS_2/MS_3	$s_\beta^2 = \frac{MS_2 - MS_3}{4.3} \cong \sigma_\beta^2$
3	Between 50-km cells within 100-km cells	34	$MS_3 = s_\epsilon^2+1.1s_\eta^2+1.3s_\delta^2+1.6s_\gamma^2$	MS_3/MS_4	$s_\gamma^2 = \frac{MS_3 - MS_4}{1.6} \cong \sigma_\gamma^2$
4	Between 10-km cells within 50-km cells	34	$MS_4 = s_\epsilon^2+s_\eta^2+1.4s_\delta^2$	MS_4/MS_5	$s_\delta^2 = \frac{MS_4 - MS_5}{1.4} \cong \sigma_\delta^2$
5	Between 1-km cells within 10-km cells	34	$MS_5 = s_\epsilon^2+1.1s_\eta^2$	MS_5/MS_6	$s_\eta^2 = \frac{MS_5 - MS_6}{1.1} \cong \sigma_\eta^2$
6	Between analyses of:				
	A-horizons within 1-km cells	12	$MS_6 = s_\epsilon^2$	-------	$s_\epsilon^2 \cong \sigma_\epsilon^2$
	C-horizons within 1-km cells	16	$MS_6 = s_\epsilon^2$	-------	$s_\epsilon^2 \cong \sigma_\epsilon^2$

[1]Mean-square estimates are for A horizons; the coefficients for C horizons may vary by 0.1 unit because of the different numbers of samples for A and C horizons at the "Between analyses" level.

[2]Leaders (--), no F-ratio exists.

and the n_i's are coefficients that represent the average number of samples in each level. These coefficients are developed from a more general expression of Leone and others (1968, p. 725). A value of 1.0, which is taken as a threshold value, is approximately equivalent to an F-test at the 80 percent probability level. For values of v_m less than about one, a map of total concentration of an element in soil, based on limited sampling, tends not to faithfully reproduce the true chemical pattern (Miesch, 1976b, p. 102). As v_m increases beyond 1.0, however, a map based on limited sampling reveals more clearly the true chemical pattern. The observed values of v_m range from a low of zero to a high of 3.3 (table 1). Eight elements in the A horizon and eight in the C horizon have a v_m greater than one and, therefore, these data are presented cartographically.

ELEMENT-DISTRIBUTION SUMMARIES

The decision as to which method of reporting the distributions of element concentrations is best depends on the magnitude of variation present in the data. A distribution map based on the means of rather small areas is the most ideal display, because the element concentrations can be related to geographic locations. However, this requires highly reproducible data. Where such data are not available, then the means must be summarized over larger areas, with the result that local differences tend to disappear. The data have been subdivided, therefore, into five groups on the basis of variance components at the terrain, 100-km-cell, and analytical-error levels, and on the basis of whether or not the variance-mean ratio exceeds the threshold of 1.0.

The five distinct groups of elements are presented in table 3. Group-1 elements are those that exhibit a significant variance component at either the terrain or the 100-km-cell level and that have a $v_m > 1.0$. For these elements, we can prepare reliable maps of their concentration in soil on the basis of the means of samples within each 100-km cell. These maps represent values from a minimum of 22 percent of the total observed arithmetic variation (Zn in A horizons) to a maximum of 46 percent of the total observed logarithmic variation (C in A horizons). Maps showing regional distribution of amounts of 15 elements in soil are presented in figures 6A through 6Q. The resolution, or the amount of detail, is dependent on the sampling interval (cell size) shown on the map. Greater resolution and increasing detail of element distributions in soil can be obtained if the mapping interval is decreased to 50, 10, and 1 km, respectively, and if a significant variance component is associated with each of these smaller geographic scales. However, the reliability of data on maps of smaller areas will depend on the variance mean ratio (Eq. 3). For example, mapping Ge in the C horizon of a 10-km unit would result in no increase in either reliability or resolution over mapping a 100-km unit, because the components of variance at 50 and 10 km are both zero (table 1). However, mapping K in the C horizon at a 50- rather than a 100-km unit should enhance both the reliability and the resolution of the map, because the variance component at 50 km is significant and it accounts for an additional 21.6 percent of the total variation. The value of v_m is increased from 1.7 (100-km unit) to 5.3 (50-km unit); the resulting map of K in the C horizon would be much more reliable. The variation explained by the map based on 100-km units is 39.6 percent of the total variation and would be 61.2 percent of the total variation for a map based on a 50-km unit. In addition, the map of a 50-km unit would show more detail of the element distribution than the map of a 100-km unit. However, maps of less than 100-km units are not presented because of the nature of our unbalanced sampling design and the resulting distribution of data points.

The entries in Groups 2, 3, and 4 (table 3) have a $v_m < 1.0$ and, therefore, the lines on a map for any of these elements would not be considered reliable when compiled for a 100-km unit using the present data. Group-2 elements exhibit significant variance components at the terrain level but not at the 100-km-cell level (table 3). For these elements, the means and expected ranges in concentration of the samples within each terrain give the best estimate of element distribution in soil for the area. This type of estimate has been referred to as a "regional geochemical baseline" by Tidball and Ebens (1976). The baselines for elements of Group 2 are presented in table 4 for each of the two terrains, glaciated and unglaciated. The expected range is computed after adjusting the gross deviation for analytical error, which makes up a portion of the gross deviation (Connor, 1976). An estimate was also computed for n_r, the number of random samples needed within each 100-km cell to raise the value of v_m to 1.0 and, thereby, provide data that can be expressed by a reliable map.

Group-4 elements have no significant variance component at either the terrain or the 100-km-cell levels (table 3). A single estimate of the mean and expected range for each of these elements over the entire study area is the best estimate of a baseline. The estimates are presented in table 5. The value of the baseline for each element in Groups 2 and 4 represents an expected range in concentration that we consider to be of use in making extrapolations from one location to another, either over the entire study area (Group-4 elements) or within the area of each terrain (Group-2 elements). In addition, any new data may be compared to the baseline to identify extreme values in element concentration.

TABLE 3.—*Grouping of elements based on significant variance components ($s_{\alpha,\beta}^2$), variance mean ratios (v_m), and analytical-error variance (s_ϵ^2)*

[Asterisk indicates significance at the 0.05 probability level. (---) indicates no element included in that grouping]

100-km cell	Soil horizon	v_m>1.0	v_m<1.0			s_ϵ^2>50 pct.
		Group 1	Group 2	Group 3	Group 4	Group 5
				Terrain, s_α^2*		
s_β^2*	A	C, Rb, U	---	---	---	F
	C	C, Mg	---	---	---	---
s_β^2	A	K, Th	Al, Be, Hg, Mn, Se, Sr,	---	---	Yb, Zr
	C	Ca, K, Rb	Al, Ga, Mn, Ni, Si, Sr, U, V	---	---	Th, V
				Terrain, s_α^2		
s_β^2*	A	Na, Si, Zn	---	Ca, Fe, Ge	---	Cr
	C	As, Ge	---	Mo, Ni	---	Ba
s_β^2	A	---	---	---	As, B, Ca, Co, Ga, Li, Mg, Sn, Ti, Y	Ba, La, Nb, P, Pb, Sb, Sc
	C	---	---	---	B, Be, Co, Cr, Cu, Fe, Hg, La, Li, Mo, Na, Pb, Sn, Ti, Y, Yb, Zn	F, Nb, P, Sb, Sc, Se, Zr

Group-3 elements (table 3) exhibit a significant component of variance between 100-km cells but not between terrains. The regional distribution of these elements, therefore, is best estimated by each 100-km-cell mean. These means are both given in table 5 and plotted on maps in figures 6*P*–6*T*. The values on the maps are not contoured because the data are judged to be unreliable (v_m<1.0).

Group-5 elements (table 3) exhibit excessive analytical error. Therefore, no interpretation is presented for these elements.

FIGURE 6 (following pages).—Regional distribution of elements in A and C horizons of soils of the Northern Great Plains coal region. Values are means of cells 100-km on a side. Contour lines for figures *A* through *O* are the geometric mean (GM) or the arithmetic mean (AM) and the upper or lower expected 95-percent values. No contours are given for figures *P* through *T* because the analysis of variance indicates that such contour lines would tend not to be reproducible.

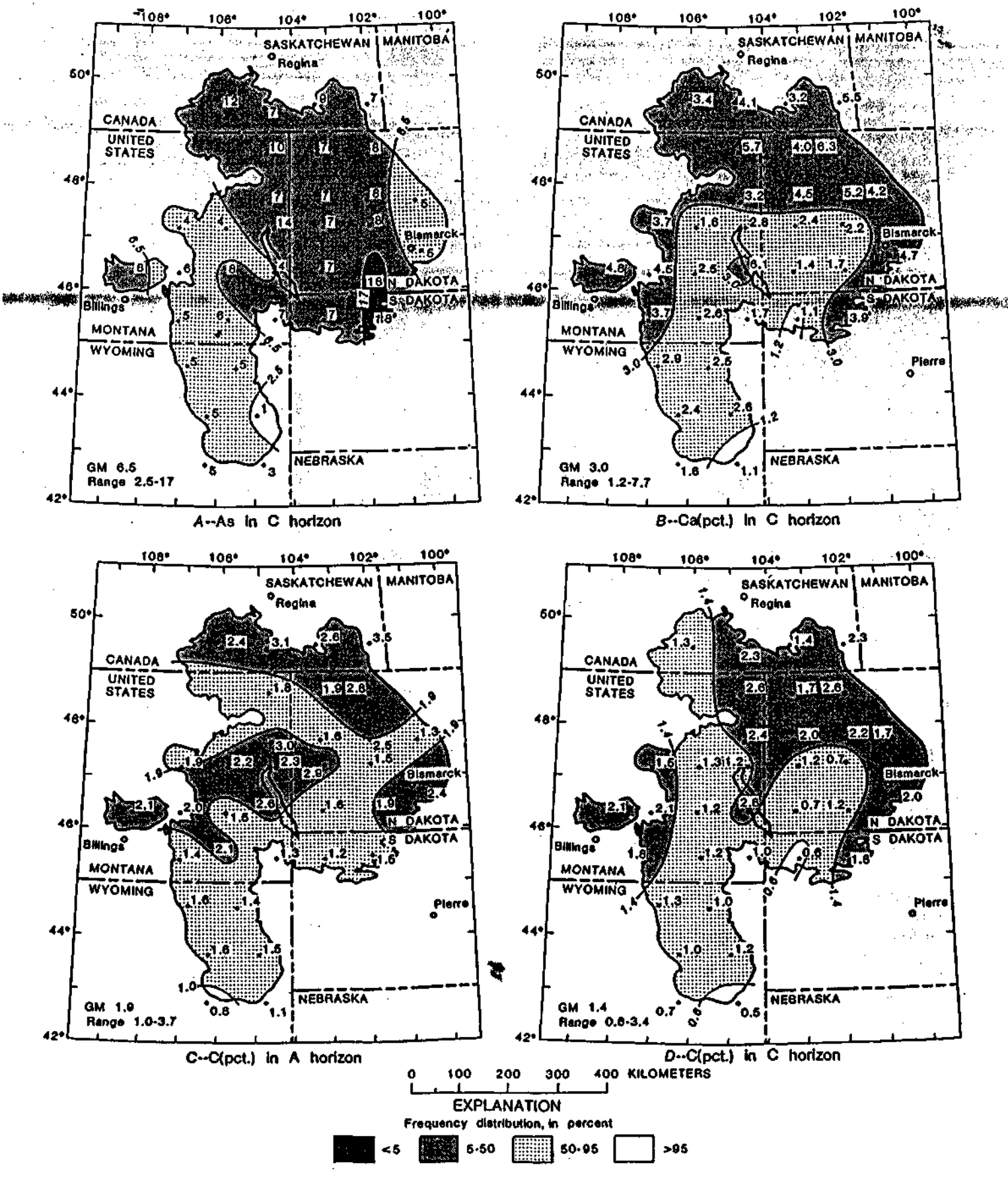


FIGURE 6.—Continued

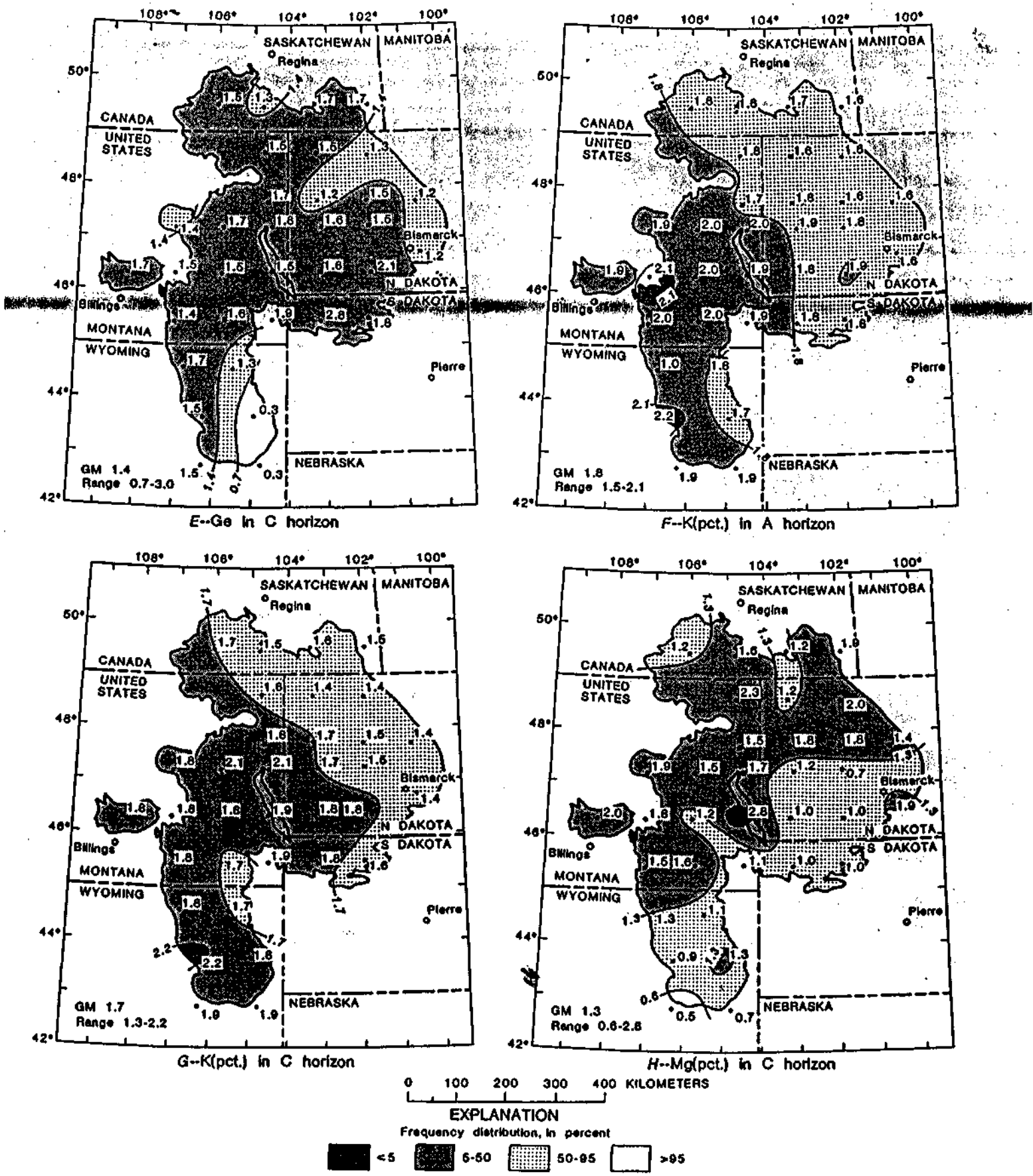


FIGURE 6.—Continued

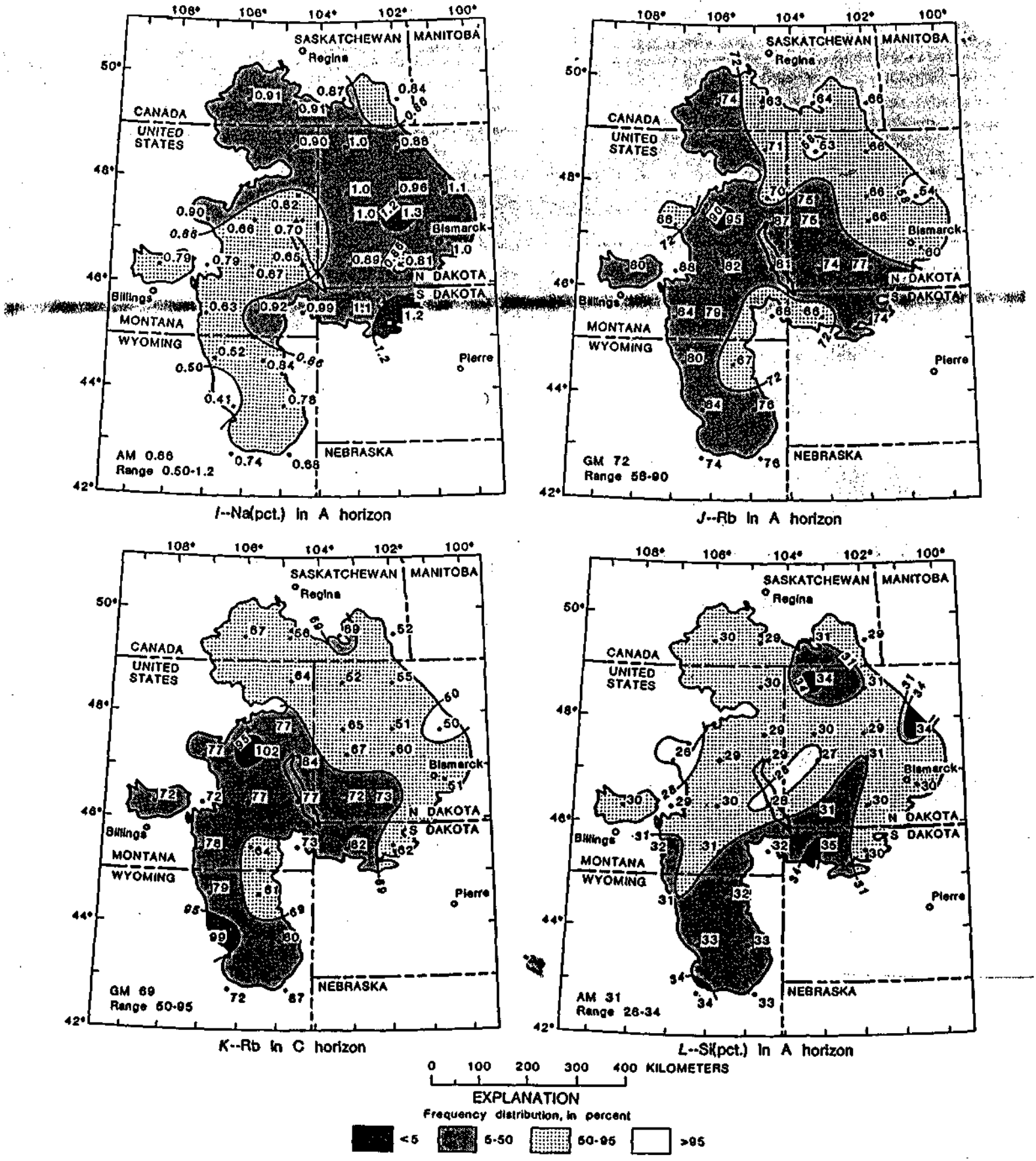
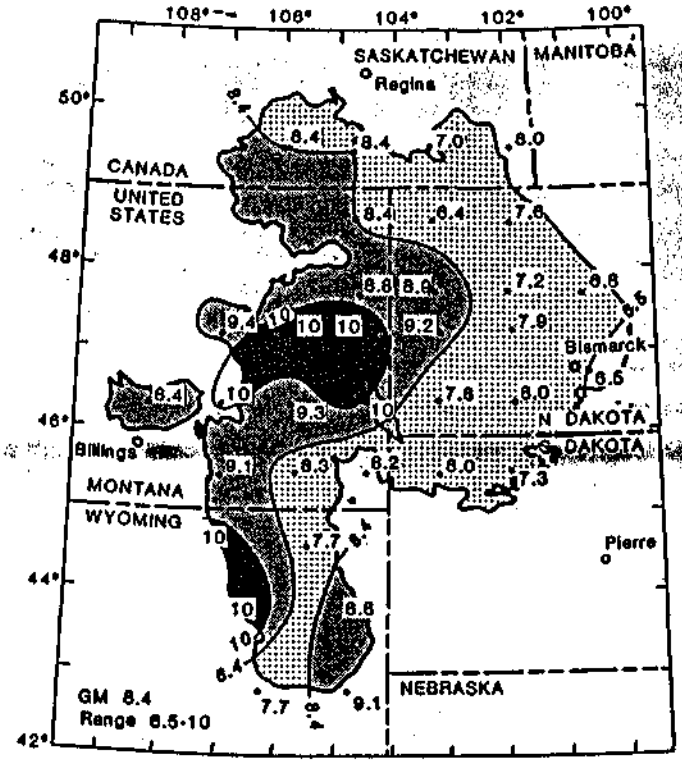
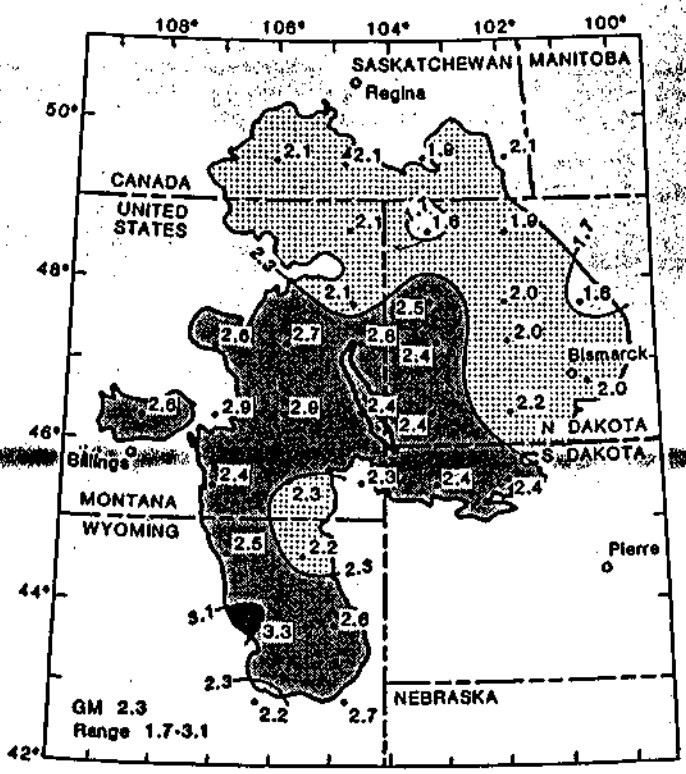


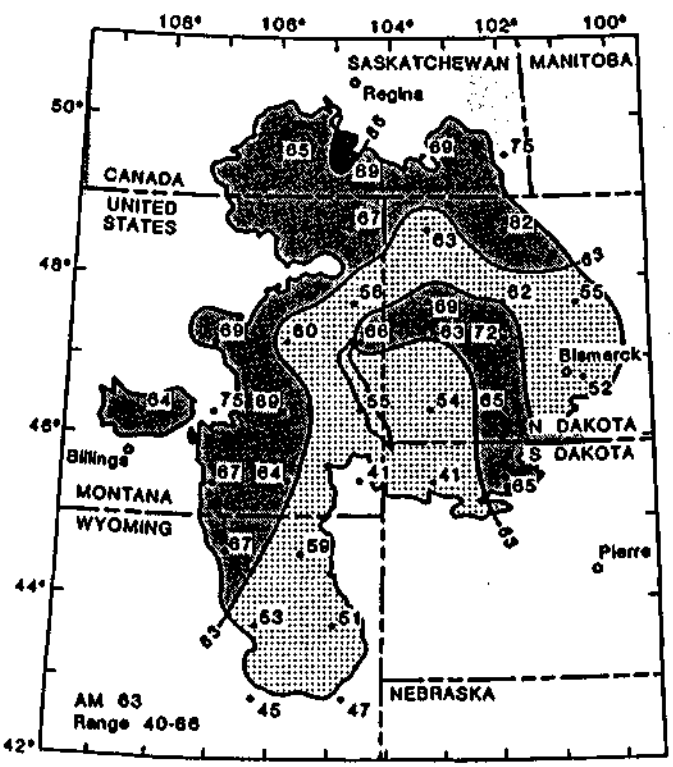
FIGURE 6.—Continued



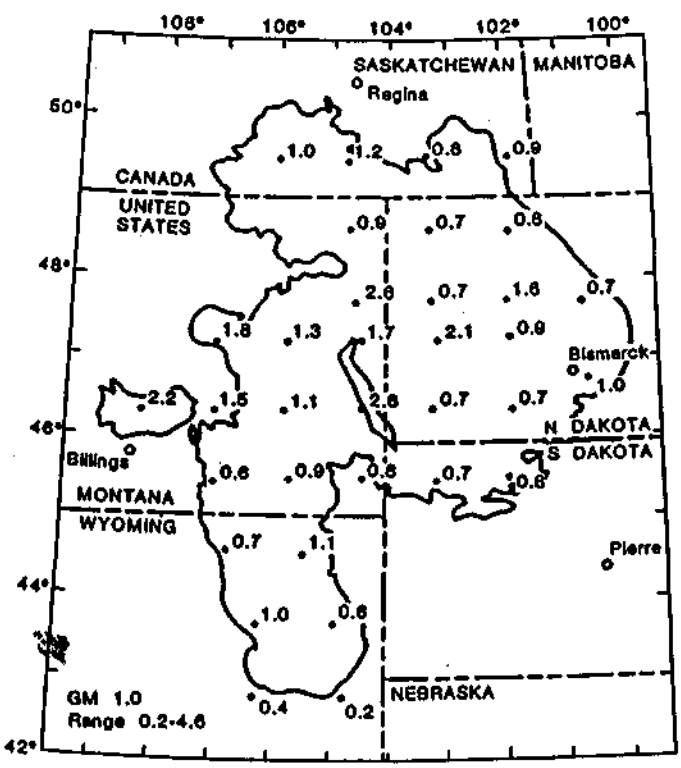
M--Th in A horizon



N--U in A horizon



O--Zn in A horizon



P--Ca(pct.) in A horizon

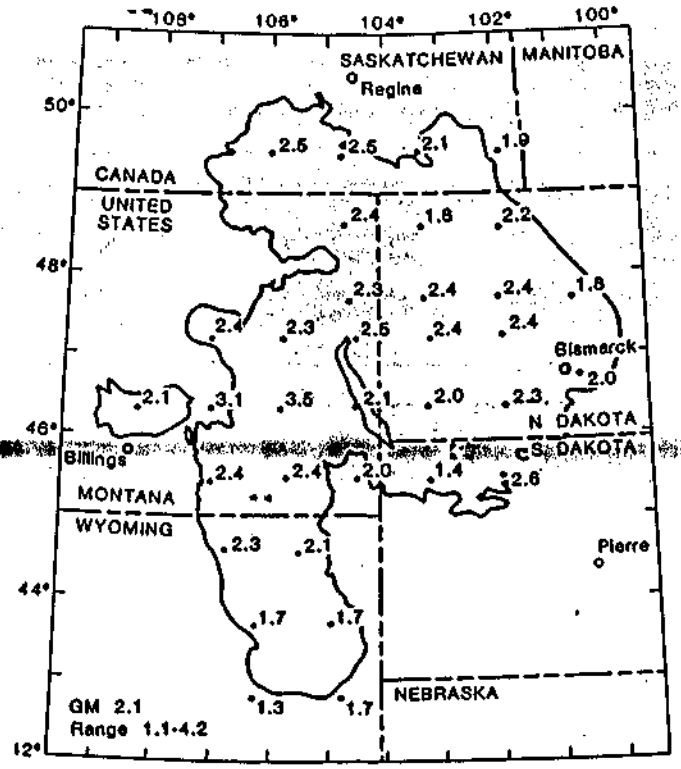
0 100 200 300 400 KILOMETERS

EXPLANATION

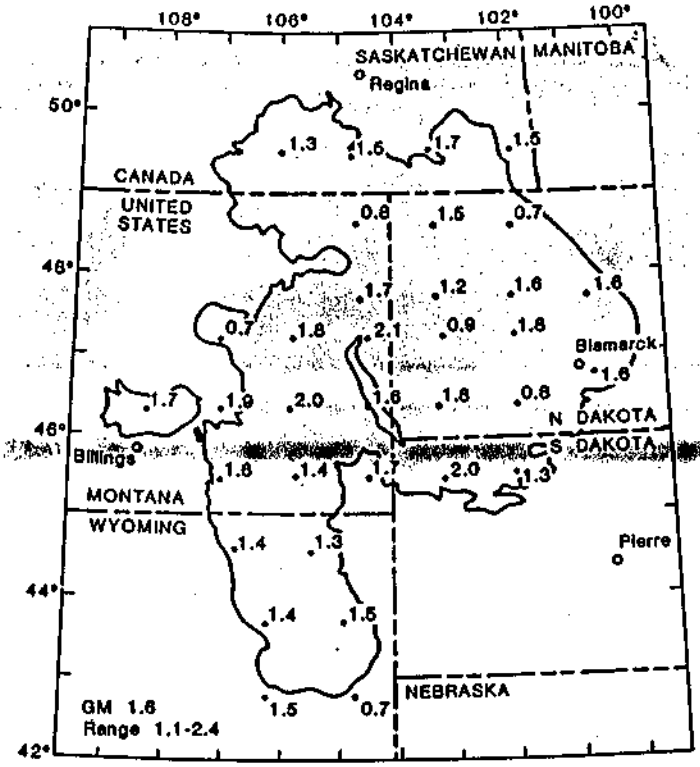
Frequency distribution, in percent

<5 5-50 50-95 >95

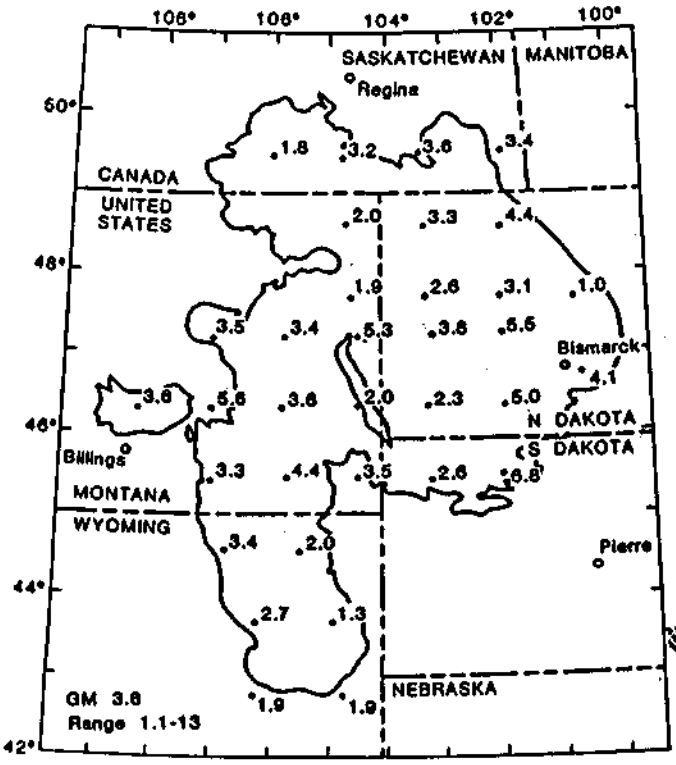
FIGURE 6.—Continued



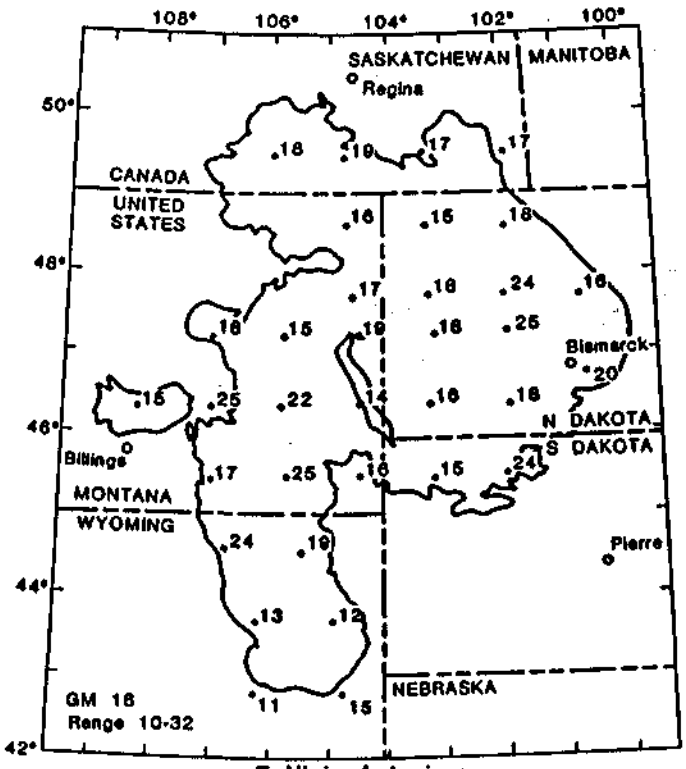
Q--Fe(pct.) in A horizon



R--Ge in A horizon



S--Mo in A horizon



T--Ni in A horizon

0 100 200 300 400 KILOMETERS

FIGURE 6.—Continued

TABLE 4.–*Chemical summaries for elements in soil that exhibit a significant variance component between terrains of the Northern Great Plains coal region (Group-2 elements)*

[G, glaciated terrain; U, unglaciated terrain. *, element measured in percent; other elements measured in parts per million except Hg, parts per billion]

Element	Soil horizon	Geometric mean		Geometric deviation		Geometric error	Baseline value[1]		n_r[2]
		G	U	G	U		G	U	
Al*----	A	5.3	5.8	1.17	1.18	1.09	4.1- 6.9	4.4- 7.7	7
	C	5.3	5.9	1.22	1.22	1.06	3.6- 7.8	4.0- 8.6	7
Be-----	A	1.5	1.7	1.46	1.38	1.27	0.8- 2.6	1.1- 2.6	11
Ga-----	C	10	11	1.58	1.51	1.33	5 - 21	6 - 21	34
Hg-----	A	26	21	1.40	1.48	1.05	13 - 51	9 - 44	7
Mn-----	A	720	330	1.83	2.76	1.81	570 - 910	60 -1700	5
	C	440	180	2.37	4.20	1.79	120 -1600	10 -2500	8
Ni-----	C	22	18	1.44	1.67	1.24	12 - 40	7 - 46	16
Se-----	A	.5	.4	2.45	2.93	2.18	0.2- 1.1	0.1- 1.9	n.d.[3]
Si*[4]--	C	27	29	2.74	3.59	1.22	22 - 32	22 - 36	5
Sr-----	A	180	150	1.24	1.54	1.18	140 - 240	70 - 340	7
	C	240	190	1.24	1.56	1.14	170 - 380	80 - 450	6
U------	C	2.2	2.8	1.42	1.41	1.06	1.1- 1.4	1.4- 5.5	5
V------	C	64	50	1.45	1.43	1.18	33 - 120	26 - 99	7

[1] Expected 95-percent range.

[2] Minimum number of random samples per 100-km cell needed to map regional variation.

[3] Not determined.

[4] Values computed on arithmetic basis.

DIFFERENCES BETWEEN SOIL HORIZONS

In the unbalanced, nested, analysis-of-variance design, the sixth (or lowest) level consists of samples that were analyzed in duplicate to estimate variation associated with sample preparation and analysis (table 2). This was done because splits of a single sample, when subjected to repeated chemical analysis, do not yield identical results. The variance associated with sample preparation and analysis should be estimated and included as part of the total variation observed in a sample of a population, because, in some cases, it exceeds the variation from any other source.

Initially each element was assumed to have a common analytical-error variance that could be estimated from sample determinations irrespective of soil horizons. Although the reproducibility of a measured value is subject to interferences that arise from differing matrix effects, these effects were expected to be common to both surface and subsurface horizons. However, the possible analytical errors shown in table 1 suggest that, for many elements, the analytical reproducibility differs widely in the two soil horizons. For most elements, the portion of the total observed variance associated with sample preparation and analysis of the A horizon exceeds that of the C horizon (table 1). In fact, logarithmic variance estimates of analytical error for B, Ba, C, Hg, Li, Na, Th, and Zn differ significantly between horizons as indicated by an F-test at the 5 percent probability level. (The F-ratio is computed by dividing the variance of the A or C horizon, whichever is larger, by the smaller variance.)

Because the data for 29 elements do not show significant differences in analytical error between horizons, it

TABLE 5.—*Chemical summaries for elements in soil that exhibit a non-significant variance component between terrains of the Northern Great Plains coal regions (Group-3 and -4 elements)*

[*, element measured in percent; all others measured in parts per million except Hg, parts per billion]

Element	Soil horizon	Geometric mean	Geometric deviation	Geometric error	Baseline[1] value	n_c[2]
As------	A	7.1	1.69	1.19	2.6 - 19	7
B------	A	41	1.59	1.27	18 - 96	9
	C	43	1.61	1.14	16 -115	7
Be------	C	1.6	1.44	1.23	0.6 - 4.0	n.d.[3]
Ca*-----	A	1.0	2.14	1.06	0.2 - 4.6	5
Co------	A	6.4	1.48	1.24	2.8 - 14	n.d.
	C	6.6	1.49	1.21	2.8 - 16	n.d.
Cr------	C	42	1.66	1.35	15 -120	n.d.
Cu------	A	19	1.64	1.31	8 - 43	n.d.
	C	17	1.82	1.49	6 - 52	n.d.
Fe*-----	A	2.1	1.41	1.02	1.1 - 4.2	5
	C	2.2	1.40	1.02	1.1 - 4.3	n.d.
Ga------	A	11	1.44	1.30	6 - 19	28
Ge------	A	1.6	1.27	1.13	1.1 - 2.4	6
Hg------	C	27	1.74	1.12	10 - 80	10
La------	C	23	1.55	1.38	10 - 51	n.d.
Li------	A	19	1.40	1.06	10 - 37	11
	C	21	1.48	1.13	10 - 46	n.d.
Mg*-----	A	.7	1.67	1.02	0.2 - 1.8	14
Mo------	A	3.8	1.68	1.57	1.1 - 13	9
	C	4.0	1.72	1.90	0.9 - 18	n.d.
Na*[4]---	C	.9	.33	.034	0.2 - 1.5	9
Ni------	A	18	1.46	1.26	10 - 32	7
Pb------	C	15	1.71	1.39	5 - 47	n.d.
Sn------	A	.9	1.86	1.51	0.3 - 2.2	30
	C	.9	1.94	1.44	0.3- 2.8	6
Ti*[4]---	A	.25	.023	.019	0.22- 0.28	7
	C	.25	.058	.014	0.14- 0.36	32
Y------	A	18	1.46	1.34	10 - 36	8
	C	17	1.47	1.32	9 - 33	n.d.
Yb------	C	2.1	1.49	1.34	1.1 - 3.9	n.d.
Zn -----	C	59	19	7.7	23 - 96	n.d.

[1]Expected 95-percent range.

[2]Minimum number of random samples per 100-km cell needed to map regional variation.

[3]Not determined.

[4]Values computed on arithmetic basis.

appears that some properties or factors in addition to matrix composition are affecting the reproducibility of the analytical determinations. If the analytical technique is at fault, then we would expect that a group of elements determined by a single technique should consistently exhibit either significant or nonsignificant variation between horizons. However, the elements that exhibit significant differences between errors in the two horizons were determined by several procedures (see U.S. Geological Survey, 1975, fig. 2). Therefore, differences in analytical reproducibility between soil horizons are related to matrix effects, analytical methods, and other unknown factors. However, from the data it is not clear which effect dominates.

The investigator should be aware of the possibility of significant analytical variability between soil materials and should plan to account for it. The cost of reducing the analytical variability, however, must be balanced against the cost of deriving an adequate estimate of the analytical variation either by repeated analysis of a sample or by a more precise analytical technique.

Discriminate-function analysis of data was also performed between A and C horizons. The results, which are presented in figure 7, show that an adequate function can be obtained to discriminate between A and C horizons using only three variables (Ca, Mg, and C). In general, a discriminate-function analysis using only trace-element data would be of little value in separating A- from C-horizon samples. For future studies that concentrate on describing the geographic distribution of elements occurring in trace amounts, a more productive use of available resources may be to sample and analyze only a single soil horizon or a composite sample of several soil horizons. Just as much, or possibly more, information useful in constructing maps of element concentration in soil may be obtained in this way as is obtained by dividing available resources between samples of more than one soil horizon.

CONCLUSIONS

An attempt has been made to determine the spatial variability of soil chemistry in the Northern Great Plains coal region for 41 elements on the basis of their total concentrations in A and C horizons. Using an unbalanced, nested, analysis-of-variance design, maps showing dependable data were prepared based on 100-km cells (100 km on a side) for three elements (C, K, and Rb) in both A and C horizons, for an additional five elements (Na, Si, Th, U, and Zn) in the A horizon, and C horizon. By doubling the number of random samples from four to eight per 100-km cell, an additional 20 elements in either A- or C-horizon soil would be mappable for the 100-km cell. Baseline values can be assigned, however, for elements that were not dependably mappable. The baseline value is a probable range in concentration to be expected in natural soils. The baseline can be applied to soil materials throughout the study area.

Most of the total observed variation in element concentration for most elements is within cells of less than 10 km on a side. Therefore, while baseline values can be used as an overview, additional sampling is necessary to evaluate local variability.

Repeated analytical determinations on samples of A and C horizons of soils vary significantly for several elements. It is not clear from the data whether the varying matrix compositions of the samples or the analytical techniques, or both, are responsible for these variations.

Discriminate-function analysis shows that analyses for only three elements (Ca, Mg, and C) are needed to adequately distinguish between A- and C-horizon soil samples in the Northern Great Plains coal region.

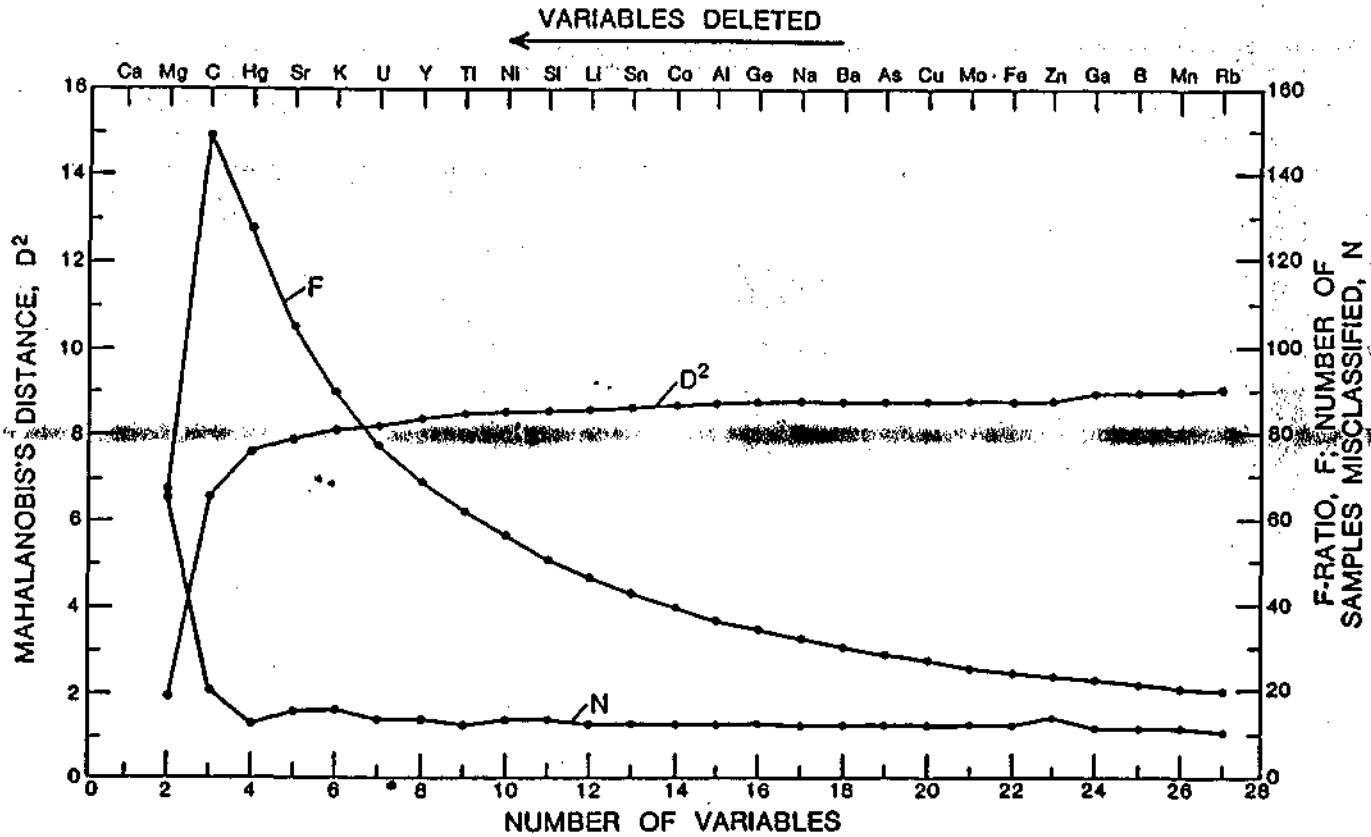


FIGURE 7.—Discriminate function analysis, for elements with analytical error less than 50 percent, between A- and C-horizon samples from the Northern Great Plains coal region.

REFERENCES CITED

Aandahl, A. R., 1972, Soils of the Great Plains: Published by author, P.O. Box 81242, Lincoln, Nebraska 68508, scale 1:2,500,000.

Anderson, R. L., and Bancroft, T. A., 1952, Statistical theory in research: New York, McGraw-Hill, 399 p.

Beckett, P. H. T., 1967, Lateral changes in soil variability: The Australian Institute of Agricultural Science Journal, v. 33, p. 172–179.

Beckett, P. H. T., and Webster, R., 1971, Soil variability—a review: Soils and Fertilizers, v. 34, p. 1–15.

Colton, R. B., Lemke, R. W., and Lindvall, R. M., 1961, Glacial map of Montana east of the Rocky Mountains: U.S. Geological Survey Miscellaneous Geologic Investigations Map I–327, scale 1:500,000.

———, 1963, Preliminary glacial map of North Dakota: U.S. Geological Survey Miscellaneous Geologic Investigations Map I–331, scale 1:500,000.

Connor, J. J., 1976, A note on the use of geochemical summaries in assessing suspected metal pollution, *in* U.S. Geological Survey, Geochemical survey of the western energy regions, 3rd annual progress report, July 1976: U.S. Geological Survey Open-file Report 76–729, inside covers.

Connor, J. J., Keith, J. R., and Anderson, B. M., 1976, Trace-metal variation in soils and sagebrush in the Powder River Basin, Wyoming and Montana: U.S. Geological Survey Journal of Research, v. 4, no. 1, p. 49–59.

Crosson, L. S., and Protz, R., 1974, Quantitative comparison, of two closely related soil mapping units: Canadian Journal of Soil Science, v. 54, p. 7–14.

Denson, N. M., and Chisholm, W. A., 1971, Summary of mineralogical and lithologic characteristics of Tertiary sedimentary rocks in the middle Rocky Mountains and the northern Great Plains, *in* Geological Survey Research 1971: U.S. Geological Survey Professional Paper 750–C, p. 117–126.

Drees, L. R., and Wilding, L. P., 1973, Elemental variability within a sampling unit: Soil Science Society of America Proceedings, v. 37, p. 82–87.

Dunnewald, J. J., 1957, Wyoming soils and soils materials, Wyoming University Agricultural Experiment Station Bulletin 349, 24 p.

Erdman, J. A., Shacklette, H. T., and Keith, J. R., 1976, Elemental composition of selected native plants and associated soils from major vegetation-type areas in Missouri: U.S. Geological Survey Professional Paper 954–C, 87 p.

Gill, J. R., and Cobban, W. A., 1973, Stratigraphy and geologic history of the Montana group and equivalent rocks, Montana, Wyoming, and North and South Dakota: U.S. Geological Survey Professional Paper 776, 37 p.

Howard, A. D., 1960 [1961], Cenozoic history of northeastern Montana and northwestern North Dakota with emphasis on the Pleistocene: U.S. Geological Survey Professional Paper 326, 108 p.

Hunt, C. B., 1967, Physiography of the United States: San Francisco and London, W. H. Freeman and Co., 480 p.

Jansen, I. J., and Arnold, R. W., 1976, Defining ranges of soil characteristics: Soil Science Society of America Journal, v. 40, no. 1, p. 89–92.

Keefer, W. R., 1974, Geologic map of the Northern Great Plains, *in* Regional topography, physiography, and geology of the Northern Great Plains: U.S. Geological Survey Open-file Report 74–50, Plate A–3, scale 1:1,000,000.

Keith, J. R., Anderson, B. M., and Connor, J. J., 1974, Trace metal variation in the Powder River Basin, *in* Geochemical survey of the western coal regions, 1st annual progress report, July 1974: U.S. Geological Survey Open-file Report 74–250, p. 14–29.

Leone, F. C., Nelson, L. S., Johnson, N. L., and Eisenstat, S., 1968, Empirical studies of unbalanced nested designs, pt. 2 *of* Sampling distributions of variance components: Technometrics v. 10, no. 4, p. 719–737.

McCormack, D. E., and Wilding, L. P., 1969, Variation of soil properties within mapping units of soils with contrasting substrata in northwestern Ohio: Soil Science Society of America Proceedings, v. 33, p. 587–593.

McKenzie, R. M., 1955, Sampling variations in the concentrations of elements in soils: Australian Journal of Agricultural Research, v. 6, p. 699–706.

Miesch, A. T., 1976a, Geochemical survey of Missouri—methods of sampling, laboratory analysis, and statistical reduction of data *with sections on* laboratory methods by 11 others: U.S. Geological Survey Professional Paper 954–A, 39 p.

———, 1976b, Sampling designs for geochemical surveys—syllabus for a short course: U.S. Geological Survey Open-file Report 76–772, 138 p.

Oertel, A. C., 1959, Estimation of the trace element status of large areas of soil: Australian Journal of Agricultural Research, v. 10, p. 58–70.

Omodt, H. W., Johnsgard, G. A., Patterson, D. D., and Olson, O. P., 1968, The major soils of North Dakota: North Dakota State University Agricultural Experiment Station Bulletin 472, 60 p.

Protz, R., Presant, E. W., and Arnold, R. W., 1968, Establishment of the modal profile and measurement of variability within a soil landform unit: Canadian Journal of Soil Science, v. 48, p. 7–19.

Reynolds, S. G., 1975, Soil Property variability in slope studies — suggested sampling schemes and typical required samples sizes: Zeitschrift für Geomorphologie, v. 19, no. 2, p. 191–208.

Southard, A. R., 1969, Soils of Montana: Montana State University Agriculture Experiment Station Bulletin 621, 42 p.

Tidball, R. R., 1975, Sampling requirements for mapping soil geochemistry in the Powder River Basin, *in* U.S. Geological Survey, Geochemical survey of the western coal regions, 2nd annual progress report, July 1975: U.S. Geological Survey Open-file Report 75–436, p. 20-28.

———, 1976, Chemical variation of soils in Missouri associated with selected levels of the soil classification system: U.S. Geological Survey Professional Paper 954–B, 16 p.

Tidball, R. R., and Ebens, R. J., 1976, Regional geochemical baselines in soils of the Powder River Basin, Montana-Wyoming, *in* Laudon, R. B., ed., Geology and energy resources of the Powder River: Wyoming Geological Association Guidebook, 28th annual field conference, p. 299–310.

Tourtelot, H. A., and Miesch, A. T., 1975, Sampling designs in environmental geochemistry: Geological Society of America Special Paper no. 155, p. 107–118.

U.S. Geological Survey, 1974, Stripping coal deposits of the northern Great Plains, Montana, Wyoming, North Dakota, and South Dakota: U.S. Geological Survey Miscellaneous Field Studies Map MF–590, scale 1:1,000,000.

———, 1975, Geochemical survey of the western coal regions, 2nd annual progress report, July 1975: U.S. Geological Survey Open-file Report 75–436, 132 p.

———, 1976, Geochemical survey of the western energy regions, 3rd annual progress report, July 1976: U.S. Geological Survey Open-file Report 76–729, 252 p.

VanTrump, George, Jr., and Miesch, A. T., 1977, The U.S. Geological Survey RASS-STATPAC system for management and statistical reduction of geochemical data: Computers and Geoscience, v. 3, no. 3, p. 475–488.

Walker, P. H., Hall, G. F., and Protz, R., 1968, Soil trends and variability across selected landscapes in Iowa: Soil Science Society of America Proceedings, v. 32, p. 97–101.

Webster, R., and Butler, B. E., 1976, Soil classification and survey studies at Ginninderra: Australian Journal of Soil Research, v. 14, p. 1–24.

Westin, F. C., Puhr, L. F., and Buntley, G. J., 1967, Soils of South Dakota rev. ed.: South Dakota State University Agricultural Experiment Station Soil Survey Series 3, 32 p.

Whitaker, S. H., and Pearson, D. E., 1972, Geological map of Saskatchewan: Saskatchewan Department of Mineral Resources, Geologic Science Branch—Saskatchewan Research Council, Geologic Division, scale 1:1,267,200.

Wilding, L. P., Jones, R. B., and Schafer, G. M., 1965, Variation of soil morphological properties within Miami, Celina, and Crosby mapping units in west-central Ohio: Soil Science Society of America Proceedings, v. 29, p. 711–717.