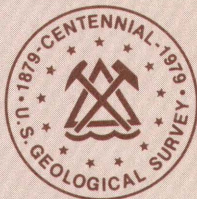
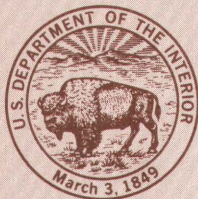


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Geochemical Variation in Soils in the Piceance Creek Basin, Western Colorado

GEOLOGICAL SURVEY BULLETIN 1479



Geochemical Variation in Soils in the Piceance Creek Basin, Western Colorado

By WALTER E. DEAN, CHARLES D. RINGROSE,
and RONALD W. KLUSMAN

G E O L O G I C A L S U R V E Y B U L L E T I N 1 4 7 9

*A geochemical baseline study of the
composition of soils in a
major oil-shale area*



UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, *Secretary*

GEOLOGICAL SURVEY

H. William Menard, *Director*

Library of Congress Cataloging in Publication Data

Dean, Walter E.

Geochemical Variation in Soils in the Piceance Creek Basin, Western Colorado
(Geological Survey Bulletin 1479)

Includes bibliographical references.

1. Soils—Colorado—Piceance Creek watershed—Composition. 2. Oil—Shales—Colorado—
Piceance Creek watershed. I. Ringrose, Charles D., joint author. II. Klusman, Ronald W.,
joint author. III. Title. IV. Series: United States Geological Survey Bulletin 1479
QE75.B9 no. 1479 [S599.C6] 557.3'08s [631.4'7'788] 79-15666

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402
Stock No. 024-001-03240-6

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GEOCHEMICAL VARIATION IN SOILS IN THE PICEANCE CREEK BASIN, WESTERN COLORADO

By WALTER E. DEAN, CHARLES D. RINGROSE¹,
and RONALD W. KLUSMAN¹

ABSTRACT

The magnitude and pattern of natural (baseline) variations in chemical composition of soils from the Piceance Creek basin of western Colorado, a major oil-shale region, were studied using 108 soil samples that were analyzed for 39 elements. These variations also provide a scale by which to measure deviations in soil composition resulting from oil-shale production, processing, and subsequent land recovery. Most of the variation in elemental abundance in soils occurs between samples separated by several kilometers or less. However, 14 of the 39 elements (calcium, iron, magnesium, silicon, titanium, boron, beryllium, chromium, copper, gallium, lithium, yttrium, ytterbium, and zinc) show significant variation on a regional scale (samples separated by distances greater than 19 kilometers), and baselines can be represented by regional maps of element concentration. Most of these elements have regional concentration gradients from north to south across the basin.

Q-mode factor analysis was used to group soils on the basis of similar chemical characteristics. Soils in the southern part of the basin contain relatively high concentrations of trace and major elements largely derived from marlstone (oil shale) of the Parachute Creek Member of the Eocene Green River Formation. Soils in the central part of the basin are mostly developed on sandstone of the Eocene Uinta Formation and therefore tend to contain relatively high concentrations of silicon and low concentrations of trace elements. Soils in the northern part of the basin are also developed on sandstone but contain relatively high concentrations of calcium, magnesium, strontium, and sodium.

Oil shale of the Green River Formation tends to be enriched in a number of trace elements that can be toxic, especially arsenic, mercury, selenium, and molybdenum, relative to soils of the Piceance Creek basin. Land reclamation after the development of an oil-shale industry, using untreated or spent oil shale as fill, could result in increases in a number of environmentally sensitive trace elements in the landscape.

INTRODUCTION

The oil-shale regions of Colorado hold promise for providing a substantial amount of liquid hydrocarbons within the next decade. Leasing of the first tracts in the Piceance Creek basin of western Colorado has been completed, and detailed development plans have been approved for prototype oil-shale lease-tracts C-a and C-b. As a part of the development plans, baselines for concentrations of seven elements (arsenic, antimony, mercury, selenium, cadmium, fluorine,

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and boron) in soils and plants have been established by the tract lessees. These seven elements were chosen because they occur in unusually high concentrations in oil-shale and(or) they are easily mobilized under high-temperature reducing conditions. However, the tracts are relatively small, only seven elements were analyzed, and data for these areas do not provide regional baselines for the entire Piceance Creek basin. In this report the Piceance Creek basin includes the Wasatch, Green River, and Uinta Formations.

Concentrations of trace elements and their variances in the soils of the basin are unknown. Establishing a regional baseline for surficial materials is an essential step in determining which elements may be potential environmental hazards during development of an oil-shale industry and subsequent land rehabilitation. Knowledge of the regional scale of variation of trace-element concentrations, in particular, would allow the determination of the sampling interval required in order to construct a useful geochemical baseline map for the critical trace elements in this and adjacent areas. Maps would be required for those elements that vary regionally, but if regional variation is minor or absent, estimates of mean and total variance alone would provide sufficient baseline information.

The main objective of this study was to estimate the magnitude of regional variations of major and trace elements in soils within the basin. The sampling design was established to test geochemical variability at a number of geographic levels (distances between samples) as well as the variation between two physiographic types (ridgetop vs. valley bottom). Our goal was to provide an approximation of natural (baseline) variations in soil composition within the basin and to provide a scale by which to measure deviations from the baseline during the course of oil-shale production, processing, and land recovery.

ACKNOWLEDGMENTS

R. J. Ebens and R. R. Tidball provided valuable assistance with the sampling design. A. T. Miesch and R. R. Tidball helped with the statistical analyses. J. G. Boerngen did much of the data processing. G. J. Saulnier, Jr., provided valuable information on the water chemistry of the Piceance Creek basin.

SAMPLING DESIGN

The basic sampling plan for the study of soils in the Piceance Creek basin is a partially unbalanced nested analysis-of-variance design. The design is illustrated diagrammatically in figure 1 and is shown with sampling localities identified in figures 2 and 3. The highest

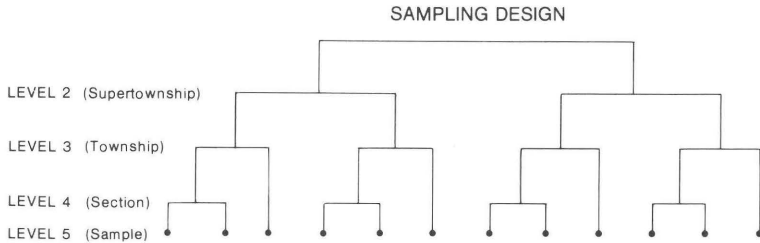


FIGURE 1.—Sampling design for soils from the Piceance Creek basin.

geographic sampling level contains nine supertownships, each of which consists of four adjacent townships (fig. 3). Within each of the 36 townships, two sections were chosen at random. Within one of these two sections, two samples of soil (A-horizon or the top 10 centimeters (cm) where horizons are not developed) were collected at a distance of 100 meters (m) from each other. Only one sample was collected from the other section in each township, for a total of three samples per township. All three samples within a township were collected either from ridgetops or valley bottoms. Ridgetop and valley-bottom sampling alternated according to a checkerboard design (fig. 3). The decision as to which of the two sections in each township would have two samples and which would have only one was made by a simple flip of the coin. From the final suite of 108 samples, 32 were chosen at random to be replicated in analysis. All 140 samples (108 samples plus 32 duplicates) were submitted for analysis in a randomized sequence. The analytical design, therefore, consisted of six levels, one physiographic (level 1, ridgetop and valley bottom), four geographic (level 2, supertownship; level 3, township; level 4, section; and level 5, sample), and one analytical (level 6, 32 duplicate analyses). Level 1 was used to examine differences between soils on ridgetops and those in valley bottoms according to the checkerboard design illustrated in figure 3. This level contained 54 samples plus 16 analytical duplicates from ridgetops and 54 samples plus 16 analytical duplicates from valley bottoms. Level 2 was used to examine differences between supertownships; that is, differences in soils separated by distances greater than about 19 kilometers (km).

Level 3 shows differences in soils between townships, within supertownships (samples separated by distances of 3 to 19 km). Level 4 shows differences between sections, within townships (distances of 0.1 to 3 km), and level 5 shows differences between samples collected 0.1 km (100 m) apart. Level 6 was used to estimate total analytical variance based on 32 pairs of duplicate analyses. The total analytical variance includes contributions from sample inhomogeneity and sample preparation, as well as actual analysis.

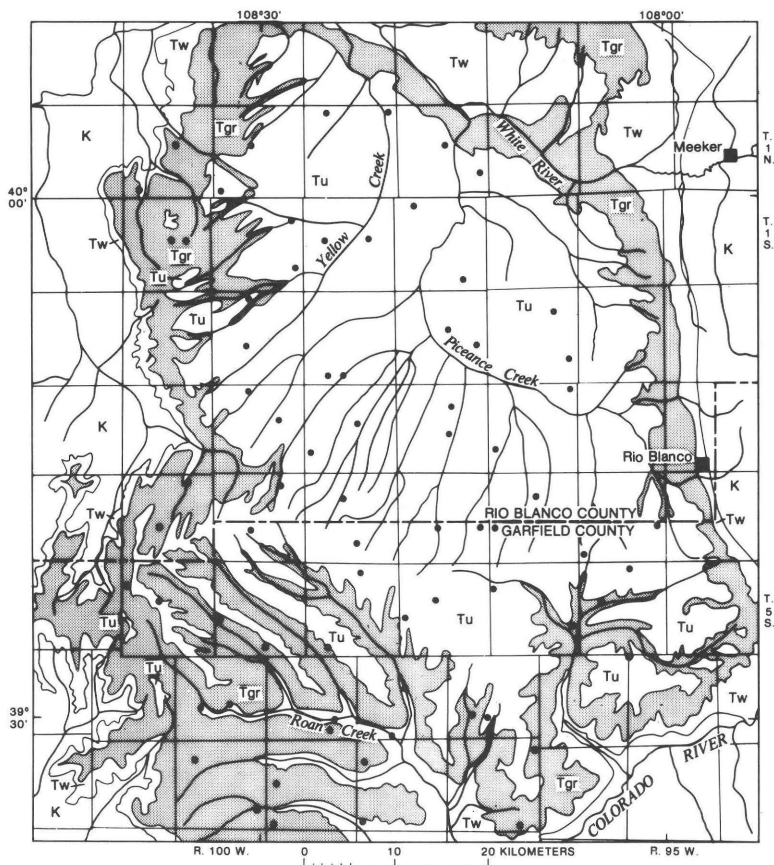


FIGURE 2.—Generalized geologic map of the Piceance Creek basin showing outcrop patterns of the Uinta (Tu), Green River (Tgr, stippled), and Wasatch (Tw) Formations, Cretaceous formations (K), major streams, and soil-sample localities (dots) (from Tweto, 1976). In this report the Piceance Creek Basin includes the Wasatch, Green River, and Uinta Formations.

CHEMICAL ANALYSES

The 140 samples (108 samples plus 32 duplicates) were analyzed in a randomized sequence for 39 elements. The samples were ground in a ceramic mill to pass a 100 mesh (less than 149 micrometers or μ) sieve. Details of analytical methods used were described by Wahlberg (1976), Huffman and Dinnin (1976), Neiman (1976), and U.S. Geological Survey (1976).

Summary statistics for each of 39 elements in the entire sample suite are given in table 1. The results in table 1 and in subsequent

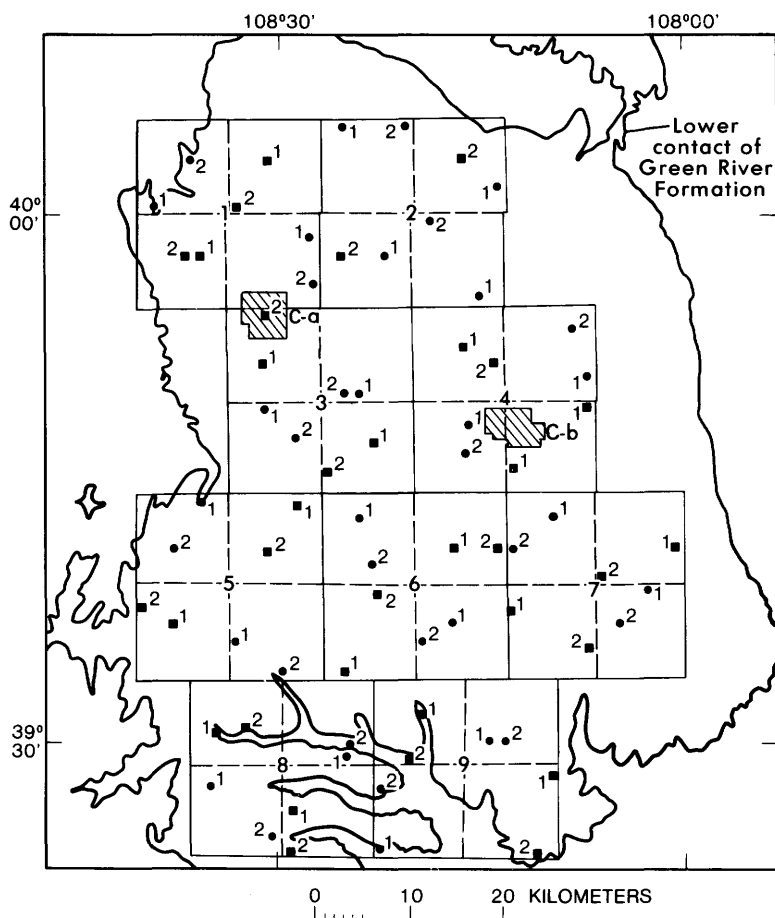


FIGURE 3.—Locations of samples, townships (dashed lines), supertownships (solid lines) used in the analysis-of-variance design, and prototype oil-shale lease tracts C-a and C-b, Piceance Creek basin. Numbers by sample localities denote whether one or two samples were collected from that locality. Dots indicate ridgetop samples; squares indicate valley-bottom samples.

tables and discussions were derived after \log_{10} transformation of the analytical data, although the Q -mode factor analyses were performed on the original data (in percent or parts per million). Skewness and kurtosis statistics showed that some elements, based on the analyses reported here, are approximately normally distributed in soils whereas most are approximately log-normally distributed. However, all results of statistical analyses obtained from original data were closely similar to those obtained from \log_{10} -transformed data.

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TABLE 1.—*Summary statistics for concentrations of nine major and 30 trace elements in 108 samples of soil*

[N is the total number of samples, out of 108 that contained measurable element concentrations greater than the detection limit for that element. Analytical methods used are: 1, X-ray fluorescence by J. S. Whalberg, Michael Goff, and J. W. Baker; 2, optical emission spectroscopy by A. L. Sutton and R. M. Lemert; 3, atomic absorption by V. M. Merritt, Wayne Mountjoy, J. G. Crock, and G. O. Riddle; 4, specific ion electrode by J. M. Gardner and P. G. Guest; 5, combustion V. E. Shaw; 6, flameless atomic absorption by J. A. Thomas and G. O. Riddle; 7, neutron-activation analysis by H.T. Millard, Jr., R. J. Knite, A. J. Bartel, J. P. Hemming, R. J. White, R.J. Vinola, and E. L. Brandt]

Element	Analytical Method	Observed range		Geometric mean	Geometric deviation	N
Percent						
Al-----	1	3.4 -	7.8	5.5	1.17	108
Ca-----	1	.46-	9.8	1.9	2.51	108
Fe-----	1	1.1 -	2.9	1.8	1.22	108
Mg-----	1	.51-	2.7	1.9	1.48	108
K-----	1	.77-	3.2	2.3	1.22	108
Si-----	1	15 -	34	26	1.15	108
Na-----	3	.18-	3.5	1.4	1.65	108
Ti-----	1	.15-	.38	.28	1.20	108
C, total	5	.87-	12	3.0	1.71	108
Parts per million						
As-----	1	<2.0 -	21	6.2	2.01	107
B-----	2	25 -	102	61	1.35	108
Ba-----	2	600 -	13,000	1,400	1.50	108
Be-----	2	.88-	4.4	2.4	1.45	108
Co-----	2	1.2-	16	7.9	1.78	108
Cr-----	2	12 -	110	59	1.63	108
Cu-----	2	<8.7 -	122	30	1.93	108
F-----	4	<400 -	1,600	500	1.52	85
Ga-----	2	<2.2 -	39	18	1.82	107
Ge-----	1	<.14-	2.5	.87	2.35	105
Hg-----	6	.01-	.22	.041	2.53	108
Li-----	3	16 -	140	34	1.55	108
Mn-----	2	82 -	1,200	480	1.65	108
Mo-----	2	<1.04-	14	5.4	2.05	102
Nb-----	2	<2.2 -	21	7.0	2.11	97
Ni-----	2	<3.4 -	42	21	1.83	107
Pb-----	2	<3.3 -	56	26	2.09	107
Rb-----	3	40 -	190	105	1.29	108
Sb-----	1	<.14-	4.6	.90	2.70	103
Sc-----	2	<2.1 -	13	6.8	1.66	99
Se-----	1	<.11-	1.2	.28	2.03	97
Sn-----	1	<.11-	11	.82	3.90	92
Sr-----	2	61 -	660	280	1.54	108
Th-----	7	6.1 -	19	12	1.23	108
U-----	7	1.9 -	5.4	3.3	1.21	108
V-----	2	7.5 -	120	56	1.58	108
Y-----	2	4.9 -	36	16	1.52	108
Yb-----	2	<.28-	6.2	2.1	2.06	107
Zn-----	3	45 -	140	80	1.23	108
Zr-----	2	54 -	700	260	1.55	108

Because there was no clear reason for using original data for some elements and transformed data for others, all statistical analyses were based on log 10-transformed data except where specifically stated otherwise.

ANALYSIS OF VARIANCE

Estimates of variance components from the six-level nested analysis of variance of concentrations of the 39 elements (table 1) are given in table 2 and compared graphically in figure 4. Table 2 and figure 4 show that most of the geographic variation for most elements occurs between sections (distances of 0.1 to 3 km). This result is in accord with analysis-of-variance results for soils from other areas, which indicate that most of the variability in soil composition occurs locally (Tidball, 1975; Tidball and Severson, 1975; Tidball, 1976; Connor and others, 1976). Of the 39 elements listed in table 2, 28 have significant variance components at the section level (aluminum, calcium, iron, magnesium, potassium, silicon, sodium, titanium, arsenic, boron, barium, beryllium, cobalt, chromium, copper, gallium, mercury, lithium, molybdenum, lead, rubidium, scandium, strontium, vanadium, yttrium, ytterbium, zinc, and uranium).

Only 11 elements (aluminum, potassium, silicon, sodium, titanium, fluorine, lithium, nickel, zinc, total carbon, and uranium) have significant variance components between samples within sections (100 m), and only seven elements (calcium, sodium, mercury, strontium, total carbon, uranium, and thorium) have significant variance components between townships within supertownships (distances of 3 to 19 km). More than one-third of the elements listed in table 2 (14 of 39) have significant variability between supertownships (distances greater than 19 km). These 14 elements are calcium, iron, magnesium, silicon, titanium, boron, beryllium, chromium, copper, gallium, lithium, yttrium, ytterbium, and zinc. No significant variation was found between samples collected on ridgetops and those collected in valley bottoms. This lack of variation means that the ridgetop and valley-bottom samples can be regarded as part of the same statistical population, and they have been considered as such in all subsequent statistical analyses.

The analysis-of-variance results at the four geographic levels (levels 2-5) indicate that most of the geochemical variability in soils in the Piceance Creek basin can be described by measuring variability between sections within townships and between supertownships. An efficient sampling design for future investigations in this area would involve sampling at intervals of 3 km within townships that are spaced 19 km apart (that is, every other township).

The significant variance at the supertownship level for 14 elements

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TABLE 2.—*Analysis of variance of soil chemistry*

[Distances (in meters or kilometers) are average distances between randomly selected points within each level]

Element	Total logarithmic variance	Variance components as percentage of total variance					Analytical error
		Between ridge tops and valley bottom	Between super townships (>19 km)	Between Townships within super townships (3-19 km)	Between sections within townships (0.1-3 km)	Between samples (100 m)	
Al-----	0.0044	0	¹ 8	0	¹ 58	¹ 14	10
Ca-----	.1596	0	¹ 28	¹ 15	¹ 48	9	0
Fe-----	.0080	0	¹ 27	0	¹ 38	2	33
Mg-----	.0291	0	¹ 28	3	¹ 57	¹ 1	11
K-----	.0075	2	7	0	¹ 80	6	5
Si-----	.0038	0	¹ 22	0	¹ 46	¹ 22	10
Na-----	.0473	0	4	¹ 41	¹ 46	¹ 6	3
Ti-----	.0064	1	¹ 28	0	¹ 54	¹ 9	8
C, total	.0535	1	14	¹ 26	19	¹ 31	10
As-----	.0914	0	0	0	¹ 81	6	13
B-----	.0173	0	¹ 18	0	¹ 57	5	21
Ba-----	.0313	0	0	0	¹ 35	6	58
Be-----	.0264	0	¹ 24	0	¹ 37	0	39
Co-----	.0624	0	12	0	¹ 33	0	55
Cr-----	.0452	0	¹ 17	0	¹ 37	0	46
Cu-----	.0821	0	¹ 28	0	¹ 18	¹ 1	52
F-----	.0331	3	7	0	15	¹ 34	41
Ga-----	.0677	0	¹ 10	0	¹ 59	0	32
Ge-----	.1378	0	0	11	0	27	62
Hg-----	.1631	2	10	¹ 36	¹ 31	4	17
Li-----	.0363	5	¹ 23	0	¹ 58	¹ 10	5
Mn-----	.0476	0	0	8	4	0	88
Mo-----	.0976	0	11	0	¹ 48	7	33
Nb-----	.1055	0	1	0	17	0	82
Ni-----	.0694	0	10	0	24	¹ 36	30
Pb-----	.1029	0	6	0	¹ 39	0	55
Rb-----	.0127	0	6	0	¹ 77	6	11
Sb-----	.1867	1	2	0	0	10	86
Sc-----	.0491	0	5	0	¹ 37	0	59
Se-----	.0947	1	0	15	0	25	59
Sn-----	.3488	0	2	0	0	33	65
Sr-----	.0350	1	19	¹ 18	¹ 31	5	27
Th-----	.0080	2	0	¹ 20	20	7	52
U-----	.0071	0	0	¹ 44	¹ 23	¹ 27	6
V-----	.0396	0	7	0	¹ 52	0	41
Y-----	.0330	0	¹ 9	0	¹ 42	0	49
Yb-----	.0986	0	¹ 8	0	¹ 38	0	54
Zn-----	.0083	1	¹ 31	12	¹ 32	¹ 19	5
Zr-----	.0359	2	1	0	28	2	66

¹Significantly different from zero at 95-percent probability level.

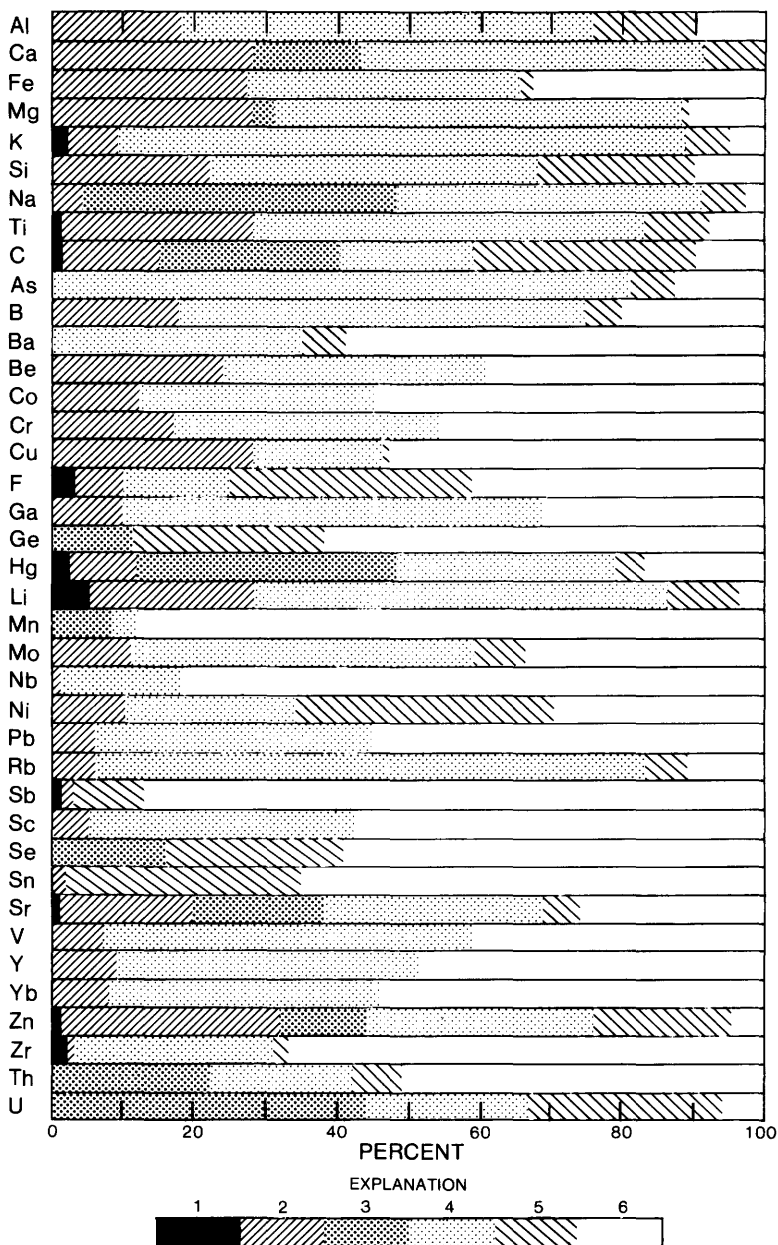


FIGURE 4.—Percent of total logarithmic variance at each of six analysis-of-variance levels for concentrations of 39 elements in soils from the Piceance Creek basin.

suggests that these elements vary regionally across the Piceance Creek basin, and that baselines for these elements can be shown best by a map based on supertownship means. To explore this possibility further, several tests of variance of supertownship means were applied to these 14 elements, and results are presented in table 3. Although strontium did not have significant supertownship variance at the 95-percent probability level, it was close to being significant. For this reason, and because of the significant association of strontium with carbonate-related elements (discussed later), strontium was included with the 14 elements having significant variance at the supertownship level.

The variance ratio, v , is an inverse measure of the relative difficulty of a geochemical-sampling program to describe the variation between map units of a particular size (supertownships in this study). It is defined (Miesch, 1976a) as the ratio of the variance among map units to the sum of the variances at all levels within the units:

$$v = \frac{s_{\alpha}^2}{s_{\beta}^2 + s_{\gamma}^2 + s_{\delta}^2 + s_{\eta}^2}, \quad (1)$$

where s_{α}^2 , s_{β}^2 , s_{γ}^2 , s_{δ}^2 , and s_{η}^2 are the logarithmic variances at the supertownship, township, section, sample and analytical levels, respectively. Once v has been calculated for each element, the number of *random* samples that must be collected within each supertownship to insure that the map pattern is reproducible can be determined, at a given probability level, based on mean values for that element. This effective number of samples has been defined as n_r by Miesch (1976a), and he presented curves for the 80- and 95-percent probability levels for determining n_r knowing the value of v . The n_r values listed in table 3 indicate that from as few as 2 to as many as 14 samples would have to be collected at random from within a supertownship, depending upon the element, to distinguish between supertownships at the 80-percent probability level, based on supertownship means. For example, a mean of analyses of only four random samples from within each supertownship would be required to map the differences between supertownships based on iron concentrations in soils, but a mean of analyses of 14 random samples from each supertownship would be required to confidently map the differences in ytterbium among supertownships.

TABLE 3.—*Comparison of the observed variance of the mean within supertownships with the maximum acceptable variance of the mean for concentrations of elements that show significant variance components at the supertownship level*

[v, observed variance ratio; n_r , required minimum number of randomly selected soil samples within each supertownship for the 80 percent probability level; E_r , maximum acceptable value of the variance of the supertownship means; E_s , observed variance of the mean within supertownships; v_m , variance mean ratio. See text for equations used to calculate these values]

Element	v	$n_r(80)$	E_r	E_s	v_m
Ca-----	0.30	1	0.0285	0.0325	1.38
Fe-----	.33	4	.0015	¹ .0013	1.66
Mg-----	.33	4	.0053	.0060	1.36
Si-----	.24	5	.0006	.0008	1.05
Ti-----	.33	4	.0011	.0013	1.38
B-----	.22	5	.0028	.0038	.82
Be-----	.22	5	.0046	¹ .0044	1.44
Cr-----	.20	6	.0063	.0080	.96
Cu-----	.40	3	.0197	¹ .0104	2.21
Ga-----	.11	9	.0068	.0155	.44
Li-----	.34	3	.0088	¹ .0076	1.10
Sr-----	.18	6	.0047	.0067	1.00
Y-----	.10	11	.0027	.0065	.46
Yb-----	.08	14	.0065	.0188	.42
Zn-----	.51	2	.0029	¹ .0016	1.63

¹ E_s is greater than or equal to E_r , and, therefore, the observed variance is below the maximum acceptable variance of supertownship means.

Once values of n_r have been determined, the maximum acceptable error variance (E_r) of the means of the mapping units (supertownships) can be calculated according to the following equation (Miesch, 1976a):

$$E_r = \frac{s\beta^2 + s\gamma^2 + s\delta^2 + s\eta^2}{n_r} \quad (2)$$

Because n_r was determined at the 80-percent probability level, the values of E_r listed in table 3 are also at the 80-percent level. The E_r value is the upper limit of error variance for supertownship means. The variance of the mean for a supertownship cannot be estimated from equation 2 because the samples from within supertownships were nested within townships and sections rather than chosen at ran-

dom. The variance is estimated as E_s and is either less than, equal to, or greater than the required E_r . If the observed error variance for any particular element is less than or equal to the E_r limit (that is, $E_s \leq E_r$), then we can assume that the results of our sampling can adequately describe differences between supertownships for that element. If $E_s > E_r$, then some additional sampling is needed to reduce the observed variance to a level below the E_r limit. For a balanced hierarchical sampling design, the observed error variance, E_s , is computed according to the following equation (Miesch, 1976a):

$$E_s = \frac{s_\beta^2}{n_\beta} + \frac{s_\gamma^2}{n_\beta n_\gamma} + \frac{s_\delta^2}{n_\beta n_\gamma n_\delta} + \frac{s_\eta^2}{n_\beta n_\gamma n_\delta n_\eta}, \quad (3)$$

where n_β , n_γ , n_δ , and n_η are the number of selected townships within supertownships, the number of sections within townships, the number of samples within sections, and the number of analyses within samples. For the sampling design used in this study, a better estimate of E_s is obtained using finite population-correction terms (Cochran, 1963, p. 23 and 286). These terms are used when a large fraction of the sample unit (township, section, and so forth) available for sampling is actually sampled. When these correction terms are applied, equation 3 becomes

$$E_s = 0.5 \frac{s_\beta^2}{n_\beta} + 0.944 \frac{s_\gamma^2}{n_\beta n_\gamma} + \frac{s_\delta^2}{n_\beta n_\gamma n_\delta} + \frac{s_\eta^2}{n_\beta n_\gamma n_\delta n_\eta}. \quad (3a)$$

Because the actual design was unbalanced, the effective n values at each level are somewhat less than if the design were completely balanced. The effective n values were calculated according to techniques described by Leone, Nelson, Johnson, and Eisenstat (1968). For this particular design, E_s was calculated according to the equation,

$$E_s = \frac{s_\beta^2}{3.78} + \frac{s_\gamma^2}{3.15} + \frac{s_\delta^2}{5.89} + \frac{s_\eta^2}{7.71}. \quad (4)$$

This equation also incorporates finite population-correction terms. E_s values for each of the 14 elements having significant regional variability, plus strontium, are listed in table 3. The condition $E_s \leq E_r$ is satisfied for five elements—iron, beryllium, copper, lithium, and zinc.

A final measure of the suitability of supertownship means to distinguish between supertownships is the variance-mean ratio, v_m , defined by Miesch (1976a) as,

$$v_m = \frac{s_\alpha^2}{E_s} \quad (5)$$

This equation is another way of examining the variance between map units (supertownships in this study) relative to the variance at all levels within the map unit. A v_m value equal to 1 is approximately equivalent to a significant F test of the relationship between v and n_r at the 80-percent probability level ($F=1+n_r v$; Miesch, 1976a). This statement essentially means that the variance between supertownships should be at least as great as the observed error variance, E_s , which itself is a proportioned sum of the variances within the map unit (supertownship). The v_m value is thus a measure of the stability of a geochemical map based on means within a map unit (supertownship). The greater the value of v_m , the greater will be the stability (reproducibility) of the map for that particular element. The v_m values listed in table 3 show that those for 10 elements are greater than or equal to 1. In order of increasing v_m , these elements are strontium, silicon, lithium, magnesium, calcium, titanium, beryllium, zinc, iron, and copper.

To summarize, we have used several measures of the sufficiency of supertownship means for distinguishing between supertownships, and, therefore, the adequacy of the supertownship means as map values in describing regional geochemical variability in the composition of soils in the Piceance Creek basin. The results of the analysis of variance showed that 14 elements have significant variance components at the supertownship level (distances greater than 19 km). An additional element, strontium, is close to being significant at the level tested and was included with the other 14 elements for further testing. Of these 15 elements, 10 (calcium, iron, magnesium, silicon, titanium, beryllium, copper, lithium, strontium, and zinc) have variance-mean ratios greater than or equal to 1 at the supertownship level, indicating that geochemical maps based on supertownship means of these elements are sufficiently stable (reproducible) according to the criterion used. Of these 10 elements, 5 (iron, beryllium, copper, lithium, and zinc) have observed variances of supertownship means that are less than or equal to the maximum acceptable error variance, indicating that the sampling was adequate for these elements and that no additional sampling is necessary.

REGIONAL GEOCHEMICAL BASELINES

The analysis of variance indicates that geochemical baselines for individual elements in soils from the Piceance Creek basin are of four different types: (1) that consisting of elements showing no regional components of variability; (2) that consisting of elements showing significant regional variability, increasing in concentration from northeast to southwest; (3) that consisting of elements showing significant regional variability with concentrations lowest in the central part of the basin; and (4) that consisting of elements showing significant regional variability with highest concentrations in the central part of the basin. Baselines for the last three types for the 10 elements in table 3 that have variance-mean ratios greater than or equal to 1 ($v_m \geq 1.0$) are represented as maps based on supertownship means in figure 5.

Another way of illustrating a geochemical baseline is to plot variation in element concentration as a function of geographic distance (Tidball and Ebens, 1976). Graphs of element concentrations versus distance across the Piceance Creek basin, illustrating the four baseline types mentioned above, are shown in figure 6. In figure 6, supertownships (fig. 3) were ordered geographically from south to north. The original data, geometric mean, and central range (68 percent) are plotted for each supertownship and for each of the four elements used as examples. The central range is that in which approximately 68 percent of the sampled population of soils is estimated to occur and is within the range of GM/GD and $GM \times GD$, where GM and GD are the geometric mean and geometric deviation, respectively (Ebens and others, 1973; Tidball and Ebens, 1976).

The first type of baseline, illustrated by potassium in figure 6A, shows local variability but no regional components of variation. Summary statistics based on a grand mean and deviation are sufficient to describe the variability of an element such as potassium for the entire Piceance Creek basin. The other three types of baselines do have significant regional components of variance that can be described either by maps of element concentration (fig. 5) or by graphs of concentration vs. geographic distribution (figs. 6B-D).

Three elements (zinc, lithium, and copper) have baselines of the second type, showing marked increases in concentration from northeast to southwest across the basin. The concentration patterns of these elements are shown in figures 5A-C, and a concentration vs. distance graph for zinc is shown in figure 6B. Zinc increases from 68 parts per million (ppm) in the northeastern part of the basin to almost 100 ppm in the southwestern part. Concentrations of lithium increase from 25 to 57 ppm, and copper concentration increase from 18 to 50 ppm, in the same direction.

Calcium, magnesium, and strontium have baselines of the third type, with lowest concentrations in an east-west band across the central part of the basin, especially in supertownships 5, 6, and 7 (figs. 5D-F and 6C). Iron, silicon, beryllium, and titanium show the opposite trend and have baselines of the fourth type; that is, concentrations of these elements are generally higher in the central supertownships (figs. 5G-J and 6D). Of the elements that have significant variance components at the supertownship level (table 2) but that do not have v_m values greater than 1 (table 3), most (boron, chromium, gallium, yttrium, and ytterbium) have concentration patterns similar to those of silicon, iron, beryllium, and titanium (that is, concentrations are higher in the central townships).

SOIL GROUPS BY Q-MODE FACTOR ANALYSIS

STATISTICAL METHODS

The results of analysis of variance demonstrate that a number of elements showed a significant variability on a regional scale (distances greater than 19 km). A Q-mode factor analysis was performed to determine if there were any multivariate groupings of individual soil samples.

The main computer program used for the factor analysis is a remote-terminal-oriented interactive version of the extended CABFAC program described by Klován and Miesch (1976) that is applicable when the row-sums of the data matrix are constant. Detailed descriptions and applications of the interactive Q-mode programs are in Miesch (1976b, 1976c). In this study, the original data make up a two-dimensional matrix of element concentrations in weight percent or parts per million (columns) for each of 140 samples (rows). A brief outline of the steps in the analysis is given below:

1. Form a two-dimensional matrix of element concentrations in weight percent or parts per million (columns) for each of the samples (rows).
2. Convert element concentrations to appropriate oxides in percent.
3. Adjust the data so that the sum of all oxides for each sample (row) is 100 percent.
4. Transform the data so that the concentration of each oxide is expressed as a proportion of the total range of concentrations for that oxide. All data are now on a scale of 0.0 to 1.0.
5. Construct a factor-variance diagram for each element. Choose the smallest number of factors that will account for a satisfactorily large proportion of the total variance for the largest number of oxides. These factors are used in the Q-mode factor model as reference axes. Eliminate those oxides for which the number of factors chosen will explain only a small proportion of the total variance.

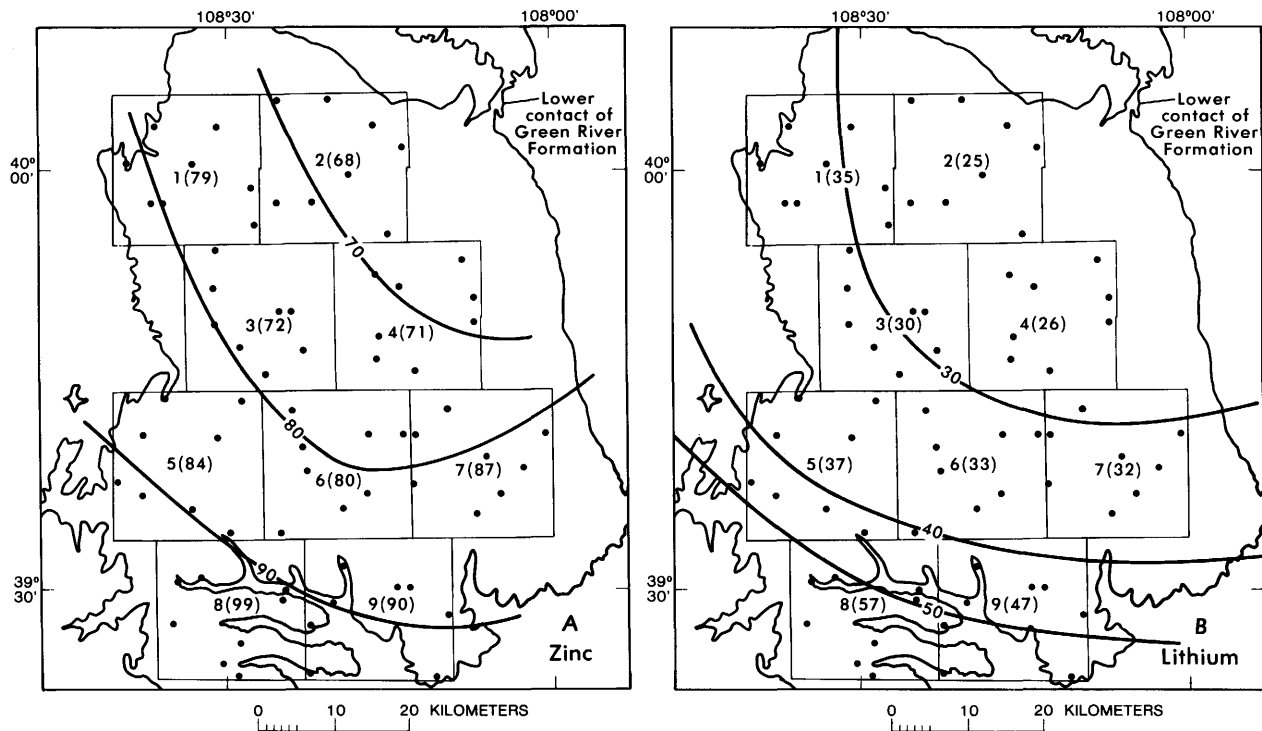


FIGURE 5.—Regional distribution of elements having variance-mean ratios greater than or equal to 1. Numbers in parentheses are mean values for samples in each supertownship. Supertownship numbers are outside parentheses. Dots are sample localities. A, Zinc (parts per million). Contour interval 10 parts per million. B, Lithium (parts per million). Contour interval 10 parts per million.

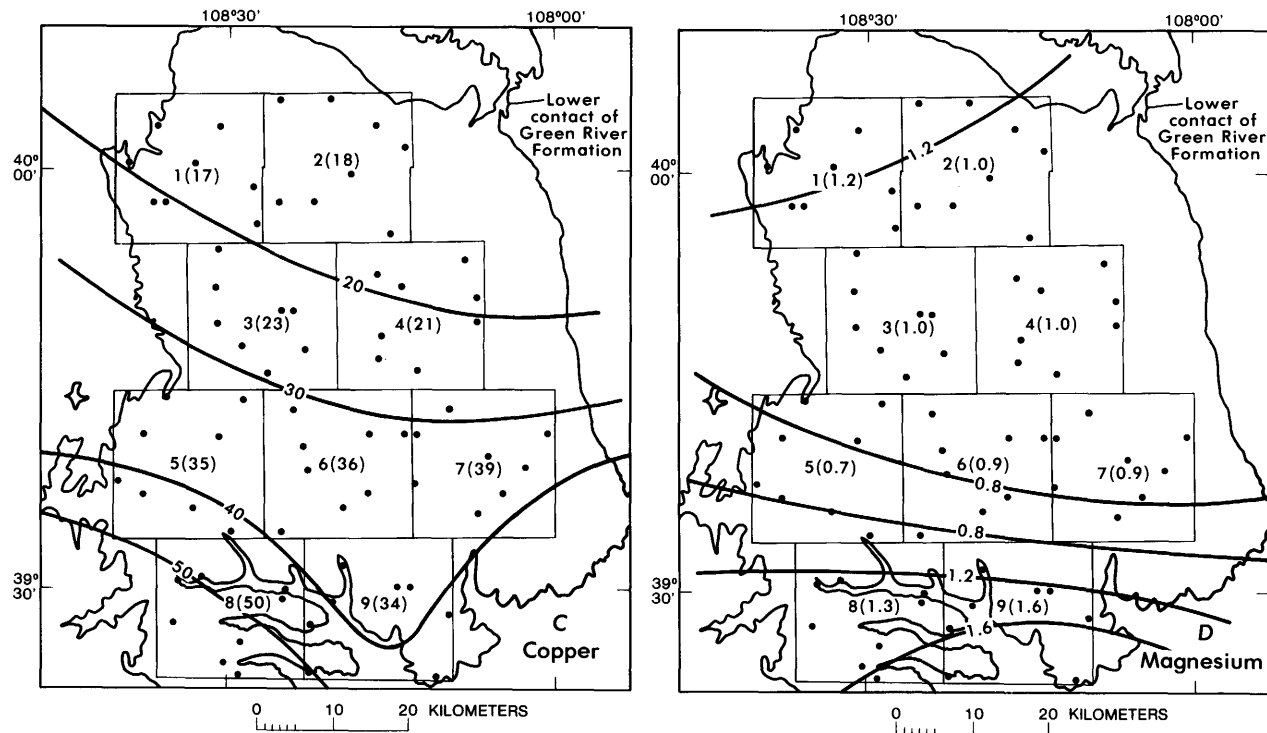


FIGURE 5.—Continued. C, Copper (parts per million). Contour interval 10 parts per million.
D, Magnesium (percent). Contour interval 0.4 percent.

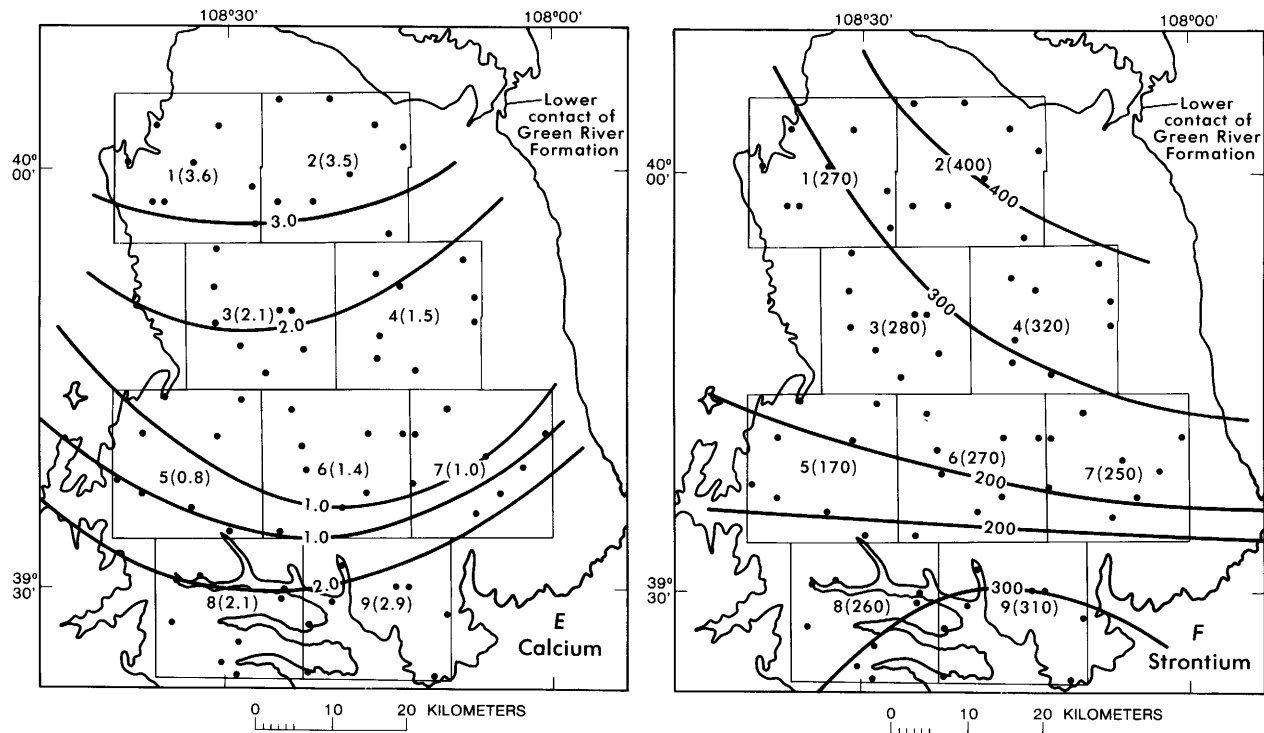


FIGURE 5.—Continued. *E*, Calcium (percent). Contour interval 1.0 percent. *F*, Strontium (parts per million). Contour interval 100 parts per million.

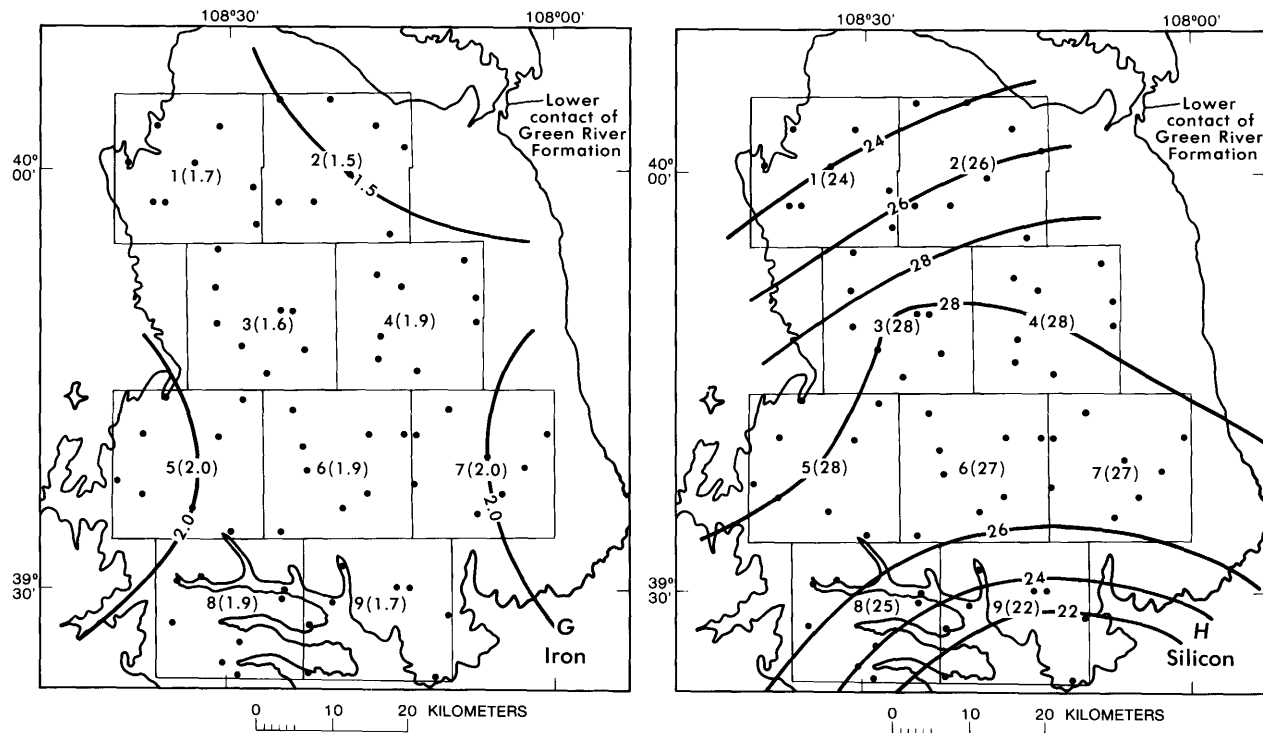


FIGURE 5.—Continued. G, Iron (percent). Contour interval 0.5 percent. H, Silicon (percent). Contour interval 2 percent.

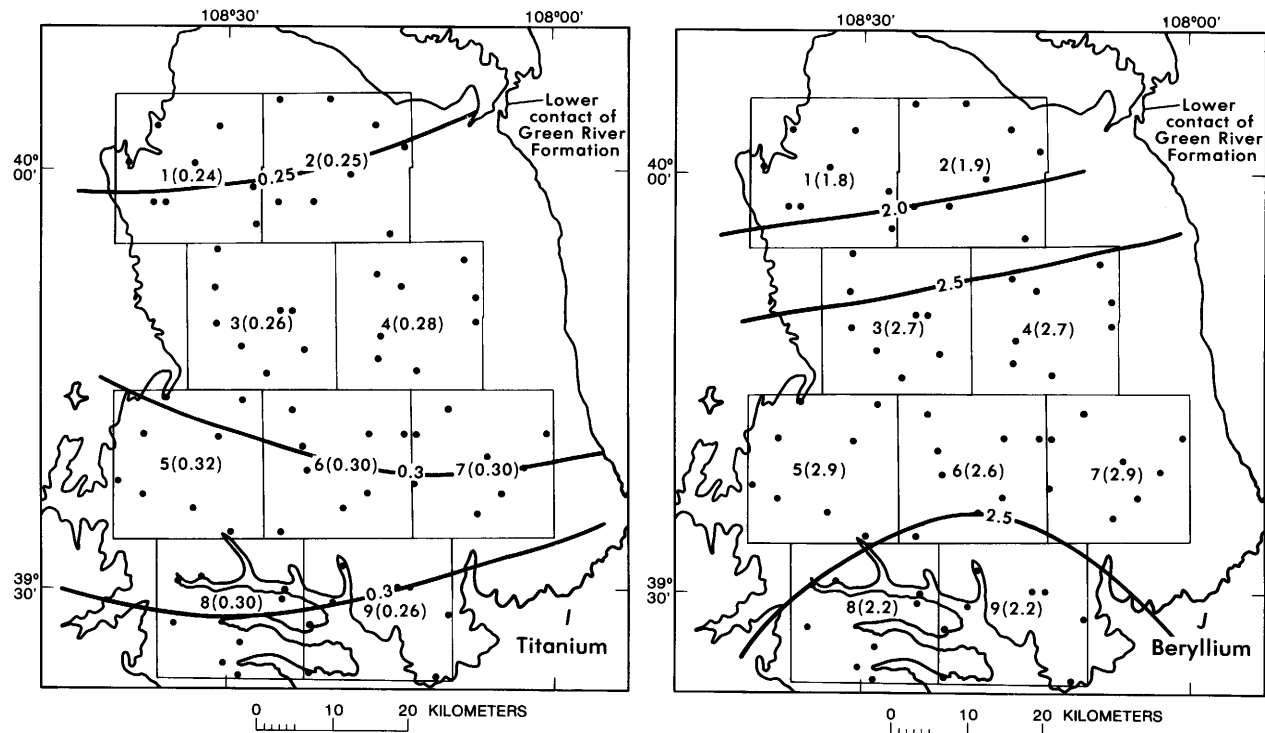


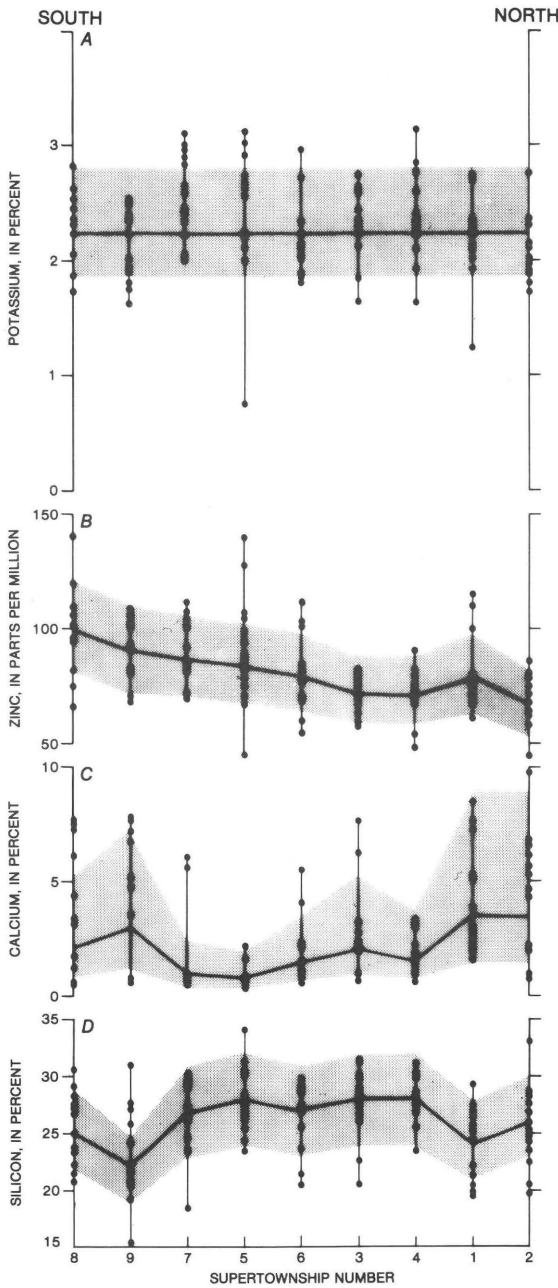
FIGURE 5.—Continued. *I*, Titanium (percent). Contour interval 0.05 percent. *J*, Beryllium (parts per million). Contour interval 0.5 parts per million.

6. Perform the *Q*-mode factor analysis (computer program EQMAIN, Miesch, 1976b) by changing the reference axes from an orthogonal (varimax) position to an oblique position coincident with selected extreme sample vectors (the oblique-solution method of Imbrie, 1963), which are hereafter called end-member samples. The actual compositions of these end-member samples are used in the program. Compute composition scores, in weight percent, for each end member. Compute composition loadings for each sample. These loadings may be interpreted as mixing proportions of each of the end members that are required to approximate each sample composition.
7. Use computer program EQCHEK to obtain computed and observed data for each sample and summary statistics for each oxide.

The factor-variance diagram (fig. 7) shows at a glance how much of the total variance for each element can be accounted for by any given number of factors (end members) in a *Q*-mode model. A compromise must be reached in which as much of the variance as possible can be accounted for in as many elements as possible by as few factors as possible. For example, in figure 7, obviously a much higher proportion of the variance for most elements is achieved by increasing the number of factors from three to four, but little is gained by increasing the number of factors from four to five. Also, by increasing the number of factors, the *Q*-mode model becomes more complex, making interpretation more difficult. On the basis of the factor-variance diagrams in figure 7, the decision was made to derive a four-factor model for soils of the Piceance Creek basin.

Factor-variance diagrams also indicate which elements vary almost independently of the others. Factor-variance diagrams of all 39 oxides in the original data matrix showed that very little of the variances of 10 elements (barium, fluorine, germanium, mercury, niobium, antimony, selenium, tin, thorium, and zirconium) could be accounted for by models having fewer than 5 to 10 factors. Because the proportions of the total variance that can be attributed to analysis are large for most of these elements (table 2; fig. 4), these 10 elements were eliminated so that the final *Q*-mode factor model contained 4 factors and accounted for about 40 percent or more of the total variance in 29 oxides.

Each end member in the *Q*-mode model will have certain chemical attributes defined in terms of the compositional variables (29 oxides in this study). Each sample can then be regarded as a mixture of the four end members in varying proportions. The end members may be theoretical samples, or they may represent actual samples from the data matrix. For this study, the four reference axes in the *Q*-mode model represent four actual soil samples. After a number of iterative



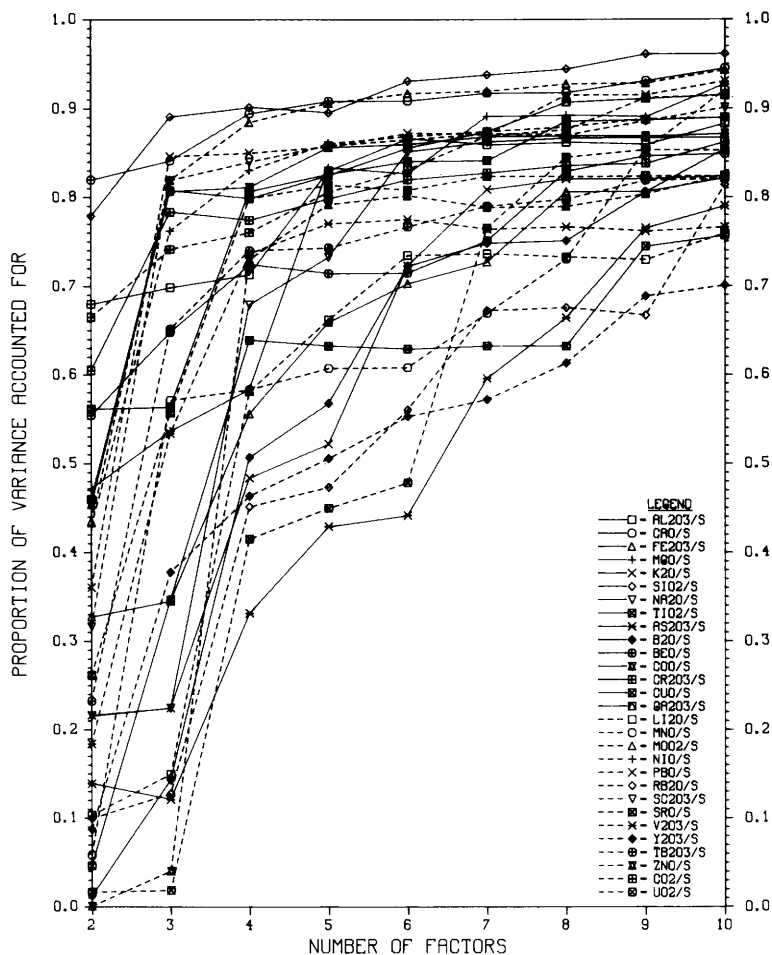


FIGURE 7.—Factor-variance diagrams for 29 oxides in 108 samples and 32 analytical replicate samples of soils from the Piceance Creek basin.

◀ FIGURE 6.—Variations in concentrations of *A*, potassium; *B*, zinc; *C*, calcium; and *D*, silicon in soils within supertownships from south to north across the Piceance Creek basin (see fig. 3 for locations of supertownships). Actual data points within each supertownship are plotted as dots. Solid lines in *B*, *C*, and *D* connect geometric means for supertownships. The shaded area in *A* represents the central range (68-percent expected range) based on the grand geometric mean and deviation. Shaded areas in *B*, *C*, and *D* represent the central range based on geometric means and deviations for supertownships.

runs through the main interactive *Q*-mode program (EQMAIN, Miesch, 1976b and 1976c), beginning with a varimax rotation and then modifying the varimax axes, four vectors representing samples of extreme composition were chosen as factor axes (table 4).

Important advantages of the extended *Q*-mode factor analysis method over conventional methods of factor analysis are that the end-member compositions (factor scores) are expressed in units of the original data (weight percent of oxides), and the end-member mixing proportions (factor loadings) are true mixing proportions that sum to 1.0 for each sample. The computed compositions for each of the four end members listed in table 4 are the factor scores that consist of sample compositions adjusted by projection of vectors from 29- to 4-dimensional space. The factor loadings listed in table 5 are the mixing proportions and indicate how similar each sample is to each of the four end members. For example, the recipe for sample 111111KP (table 5) is to mix 0.65 parts of end-member 1 (sample 252111KP), 0.05 parts of end-member 2 (sample 191111KP), 0.29 parts of end-member 3 (sample 151111KP), and 0.01 parts of end-member 4 (sample 142111KP).

By using the mixing-proportion recipes for each element, compositions based on the *Q*-mode model can be computed for each sample and compared with the observed compositions by goodness-of-fit measures. This computation is done simply by multiplying the matrix of factor loadings (table 5) by the transpose of the matrix of factor scores (computed compositions of end members in table 4). The matrix multiplication and computation of summary statistics for the entire sample population are accomplished using program EQCHEK (Miesch, 1976b). Summary statistics for the four-factor model based on 29 elements in 140 samples from the Piceance Creek basin are given in table 6.

The factor loadings (table 5) are essentially chemical variables expressed as mixing proportions of each of the four end members. In other words, the 29 observed chemical variables used as input to the *Q*-mode model have been reduced to four composite chemical variables (table 5). However, the loadings give no indication of which elements had the most influence on the selection of sample 252111KP for end-member 1, sample 191111KP for end-member 2, and so forth. Some idea of the chemical characteristics of each of the four end members can be obtained by scanning the observed compositions of the end members given in table 4. For example, from table 4 it is readily apparent that end-member 2 is higher in calcium and magnesium carbonates and that end-members 3 and 4 are high in silica. However, it is difficult to evaluate all 29 elements for each end member and impossible to determine which elements had the most influence on the model.

TABLE 4.—*Observed and computed compositions (in weight percent) for each of the four end members used in the extended Q-mode factor model for soils*

Oxide	Factor 1 end member (sample 252111)		Factor 2 end member (sample 191111)		Factor 3 end member (sample 151111)		Factor 4 end member (sample 142111)	
	Observed	Computed	Observed	Computed	Observed	Computed	Observed	Computed
SiO ₂ ---	57.6	59.2	35.5	39.8	74.7	70.6	67.1	69.2
Al ₂ O ₃ --	12.5	12.8	6.8	7.2	8.2	11.1	14.4	12.3
Fe ₂ O ₃ --	3.3	3.8	2.1	1.9	1.7	2.4	2.9	2.6
MgO----	1.4	2.4	4.8	3.8	.92	1.1	1.9	.92
CaO----	1.0	1.1	11.4	13.8	2.4	2.1	2.1	2.2
Na ₂ O---	1.0	.98	1.7	.48	.24	2.50	5.2	4.3
K ₂ O----	3.7	3.8	2.3	2.3	.94	2.8	2.2	2.8
TiO ₂ ---	.61	.66	.27	.32	.55	.50	.55	.49
Co ₂ ----	18.5	14.8	34.8	30.2	10.5	6.8	3.5	5.0
As ₂ O ₃ --	.0009	.0015	.0022	.0018	.0006	.0010	.0007	.0002
B ₂ O ₃ ---	.0030	.0034	.0211	.0208	.0082	.0134	.0142	.0160
BeO----	.0009	.0011	.0003	.0003	.004	.0005	.0009	.0008
CoO----	.0017	.0020	.0003	.0002	.0003	.0003	.0018	.0015
Cr ₂ O ₃ --	.0016	.0152	.0032	.0015	.0018	.0047	.0137	.0137
CuO----	.0076	.0110	.0034	.0032	.0013	.0000	.0022	.0026
Ga ₂ O ₃ --	.0037	.0043	.0005	.0005	.0003	.0007	.0050	.0040
Li ₂ O----	.0190	.0158	.0155	.0137	.0037	.0043	.0047	.0012
MnO----	.14	.14	.063	.057	.0214	.0039	.063	.106
MoO ₃ ---	.0007	.0020	.0001	.0001	.0001	.0000	.0015	.0012
NiO----	.0049	.0056	.0009	.0007	.0005	.0008	.0040	.0036
PbO----	.0060	.0061	.0008	.0006	.0004	.0000	.0057	.0045
Rb ₂ O---	.019	.019	.010	.010	.0044	.0103	.0054	.0104
Sc ₂ O ₃ --	.0021	.0020	.0003	.0004	.0003	.0002	.0018	.0015
SrO----	.023	.031	.053	.053	.0073	.0107	.053	.049
UO ₂ ----	.0004	.0004	.0004	.0004	.0003	.0003	.0002	.0002
V ₂ O ₃ ---	.0173	.0164	.0042	.0053	.0044	.0031	.0012	.0089
Y ₂ O ₃ ---	.0028	.0034	.0009	.0016	.0012	.0009	.0022	.0021
Yb ₂ O ₃ --	.0005	.0006	.0000	.0001	.0001	.0000	.0002	.0003
ZnO----	.018	.016	.012	.012	.0057	.0096	.0096	.0069
Total	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000

TABLE 5.—*Loadings for the four factors used in the extended Q-mode model*

	Factor 1	Factor 2	Factor 3	Factor 4
Sample	Sample 252111KP	Sample 191111KP	Sample 151111KP	Sample 142111KP
111111KP	0.8133	-0.0349	0.4533	-0.2317
111121KP	.5685	.1482	.5576	-.2744
111122KP	.7086	.1464	.3536	-.2086
111211KP	-.0036	.6703	.3160	.0174
112111KP	-.0374	.1157	.6443	.2774

TABLE 5.—*Loadings for the four factors used in the extended Q-mode model—*
Continued

Sample	Factor 1 Sample 252111KP	Factor 2 Sample 191111KP	Factor 3 Sample 151111KP	Factor 4 Sample 142111KP
112211KP	.0997	.3465	.0266	.5272
112212KP	.1551	.3483	-.0406	.5371
112221KP	.2154	.1265	.2743	.3838
121111KP	.1931	.4415	-.1119	.4773
121211KP	.0086	.5606	-.2714	.7022
121212KP	.0013	.5581	-.1532	.5937
121221KP	-.1125	.4393	.0870	.5861
121222KP	-.1949	.5126	.2986	.3837
122111KP	.2476	-.0337	.4946	.2916
122121KP	.2174	.1648	.4546	.1632
122211KP	.2586	-.0322	.5412	.2323
131111KP	.4052	.0266	.8666	-.2984
131121KP	.1549	.0920	.5161	.2370
131211KP	.0127	.0997	.2248	.6628
131212KP	.0025	.1293	.2411	.6271
132111KP	.4579	.0102	-.0062	.5380
132211KP	.5020	-.1591	.2191	.4380
132221KP	.5134	-.1738	.2783	.3821
132222KP	.4155	-.1533	.5036	.2341
141111KP	.6848	-.0332	.3029	.0455
141112KP	.4600	-.0204	.7628	-.2024
141121KP	.6492	-.0064	.1117	.2455
141122KP	.4370	.0080	.2788	.2762
141211KP	.4633	-.1465	.2478	.4354
142111KP	.0870	-.0589	.0858	.8860
142211KP	.5606	-.0930	.2940	.2385
142221KP	.7351	-.1708	-.0739	.5097
151111KP	.0371	-.0198	1.0646	-.0819
151211KP	.4750	-.1152	.3482	.2920
151221KP	.6265	-.0210	.5354	-.1408
151222KP	.9324	-.0693	.3599	-.2231
152111KP	.7012	-.1089	.2479	.1598
152211KP	.1339	-.0458	.9660	-.0541
152212KP	.4921	-.1566	.1867	.4778
152221KP	.5045	-.0902	.1619	.4238
161111KP	.5211	.2413	.0587	.1789
161112KP	.3210	.2678	.3589	.0523
161211KP	.2195	-.0741	.0997	.7550
161221KP	.1319	-.0456	.0739	.8398
162111KP	.6358	-.1235	.5148	-.0271
162112KP	.6848	-.0929	.4589	-.0507

TABLE 5.—*Loadings for the four factors used in the extended Q-mode model—Continued*

Sample	Factor 1 Sample 252111KP	Factor 2 Sample 191111KP	Factor 3 Sample 151111KP	Factor 4 Sample 142111KP
162211KP	.6159	-.1574	.2422	.2993
162221KP	.5111	-.2113	.3947	.3055
171111KP	.6339	-.1499	.5875	-.0715
171112KP	.7929	-.0690	.0489	.2272
171211KP	.4414	-.2288	.2569	.5305
171221KP	.2177	-.0683	.8023	.0483
172111KP	.6104	-.0590	.3058	.1428
172211KP	.9251	-.2057	.2732	.0074
172221KP	1.0020	-.1821	.1743	.0058
181111KP	.9300	-.0766	.2931	-.1465
181211KP	.4408	.1721	.6516	-.2645
181221KP	.5541	.2235	.2451	-.0227
182111KP	1.0230	-.1170	.5290	-.4350
182211KP	.6722	-.1068	.5094	-.0748
182212KP	.6993	-.1169	.3201	.0976
182221KP	.7052	-.1350	.4251	.0047
191111KP	.0042	1.0055	-.0125	.0029
191211KP	.4882	.3078	.1013	.1027
191221KP	.3433	.7574	-.2682	.1674
192111KP	.5965	-.1042	.3813	.1264
192211KP	.6910	.3888	.0214	-.1012
192221KP	.4895	.5134	.0265	-.0293
211111KP	-.0037	.7783	-.4001	.6255
211112KP	-.0786	.7396	-.1877	.5267
211211KP	.2021	.7027	-.2324	.3277
211221KP	.1207	.5043	.4391	-.0641
211222KP	.3643	.5562	-.1464	.2259
212111KP	.2330	.1840	.7164	-.1334
212121KP	.4067	.1914	.2636	.1382
212211KP	-.0845	.6943	.3444	.0459
221111KP	.1397	.4822	.0853	.2929
221112KP	.1882	.3158	.1693	.3267
221121KP	-.0484	.9157	-.2791	.4118
221211KP	.2190	.0241	-.0463	.8032
222111KP	.1354	.3077	-.0471	.6040
222112KP	.0660	.3517	.2048	.3775
222121KP	.2068	.0945	.1482	.5505
222122KP	.1350	.1366	.3307	.3977
222211KP	.0176	.7552	-.4221	.6492
231111KP	-.0107	.6267	.3730	.0110
231121KP	.1457	.5216	-.0225	.3552

TABLE 5.—*Loadings for the four factors used in the extended Q-mode model—Continued*

Sample	Factor 1 Sample 252111KP	Factor 2 Sample 191111KP	Factor 3 Sample 151111KP	Factor 4 Sample 142111KP
231211KP	.2175	.1346	.1496	.4983
232111KP	.4231	.1582	-.1540	.5726
232112KP	.1993	.1926	.3099	.2982
232211KP	.1642	.0716	.3262	.4380
232212KP	.3126	.0319	-.0633	.7188
232221KP	.0850	.0894	.5522	.2734
232222KP	.2404	.0613	.3650	.3333
241111KP	.3470	.1544	.0154	.4833
241211KP	.0714	.0572	.2774	.5940
241212KP	-.0359	.1360	.5006	.3994
241221KP	.0916	.2098	.4068	.2917
242111KP	.0482	.1197	.6490	.1831
242112KP	.2677	.0478	.1120	.5725
242211KP	.2645	.1371	-.1565	.7550
242212KP	.1090	.1842	.2107	.4962
251111KP	.6257	.0013	.1521	.2209
251112KP	.3911	.0008	.4495	.1586
251211KP	.4924	-.1277	.4857	.1496
251221KP	.8146	-.1705	.2985	.0574
252111KP	1.1566	-.0711	.1589	-.2444
252112KP	.9532	-.0703	.4515	-.3344
252121KP	1.1432	-.1098	.2035	-.2369
252211KP	.9949	-.1277	.4454	-.3126
261111KP	.4862	.0885	-.0598	.4850
261112KP	.4741	.1050	.0302	.3907
261211KP	.2157	.0347	.3799	.3697
261221KP	.2352	-.0135	.3879	.3904
262111KP	.6166	-.0565	.3837	.0562
262121KP	.6637	-.0893	.4390	-.0134
262211KP	.3725	.5957	-.0490	.0809
262212KP	.2801	.6004	.1541	-.0346
271111KP	.5986	-.0452	.5031	-.0564
271211KP	.5651	-.0508	.3694	.1163
271221KP	.8130	-.1515	.0315	.3070
272111KP	.2112	.4702	.0485	.2702
272121KP	.2226	.7838	-.2636	.2572
272211KP	.6931	-.1896	.1670	.3295
272212KP	.3184	-.0346	.7691	-.0528
281111KP	.1828	.7483	-.0866	.1556
281121KP	.2066	.6452	-.1039	.2522
281122KP	.0748	.6835	-.0546	.2963

TABLE 5.—*Loadings for the four factors used in the extended Q-mode model—*
Continued

	Factor 1	Factor 2	Factor 3	Factor 4
Sample	Sample	Sample	Sample	Sample
	252111KP	191111KP	151111KP	142111KP
281211KP	.4772	.1497	.5378	-.1647
282111KP	.2522	.5996	.1546	-.0064
282211KP	.4041	.5025	-.0300	.1234
282221KP	.5327	.4407	-.0469	.0735
291111KP	.7359	-.1072	.3672	.0041
291112KP	.8146	-.1478	.1660	.1671
291121KP	.5563	.0026	.5483	-.1073
291211KP	.2237	-.0815	.8944	-.0366
292111KP	.0820	.6578	.3115	-.0513
292112KP	.2667	.6149	-.0906	.2090
292121KP	.3204	.6799	-.2505	.2502
292211KP	.2070	.7159	-.2264	.3035

TABLE 6.—*Summary statistics for observed data and for data computed by the extended Q-mode factor analysis using samples as end members for each of the four factors*

[All values are in weight percent]

Oxide	Mean		Standard deviation		Proportion of variance explained
	Observed data	Computed data	Observed data	Computed data	
SiO ₂ ---	60.4	60.4	7.80	7.69	0.89
Al ₂ O ₃ --	11.3	11.2	1.64	1.44	.71
Fe ₂ O ₃ --	2.8	2.8	.60	.47	.56
MgO----	2.0	2.0	.87	.66	.58
CaO----	4.3	4.2	3.63	3.63	.89
Na ₂ O---	2.3	2.2	.98	.81	.68
K ₂ O----	3.0	3.0	.53	.38	.47
TiO ₂ ---	.51	.51	.089	.086	.81
Co ₂ ----	13.2	13.4	6.7	6.01	.76
As ₂ O ₃ --	.0010	.0010	.0005	.0003	.35
B ₂ O ₃ ---	.0220	.0220	.0056	.0043	.47
BeO----	.0007	.0007	.0002	.0002	.71
CoO----	.0012	.0012	.0005	.0004	.81
Cr ₂ O ₃ --	.0102	.0103	.0005	.0005	.77
CuO----	.0048	.0048	.0031	.0023	.63
Ga ₂ O ₃ --	.0029	.0029	.0011	.0010	.80
Li ₂ O---	.0087	.0086	.0044	.0032	.58
MnO----	.091	.091	.039	.029	.58
MoO ₃ ---	.0010	.0010	.0005	.0005	.88
NiO----	.0032	.0032	.0013	.0012	.83
PbO----	.0035	.0035	.0015	.0014	.85
Rb ₂ O---	.0127	.0128	.0032	.0023	.45
Sc ₂ O ₃ --	.0012	.0012	.0004	.0004	.83
SrO----	.0383	.0383	.0149	.0136	.79
UO ₃ ----	.0003	.0003	.0001	.0000	.37
V ₂ O ₃ ---	.0095	.0096	.0032	.0028	.73
Y ₂ O ₃ ---	.0022	.0022	.0006	.0005	.45
Yb ₂ O ₃ --	.0003	.0003	.0001	.0001	.69
ZnO----	.0110	.0110	.0024	.0020	.72

In order to determine which elements contributed to which end member, the factor loadings for each sample were treated as composite chemical variables, and correlation coefficients were computed between the loadings and the observed compositional variables (29 element oxides). Results of the correlation analysis are given in table 7.

To illustrate regional groups of soils within the Piceance Creek basin, based on soil chemistry, loadings for each of the four factors are plotted on a map of the basin in figure 8.

TABLE 7.—*Correlation coefficients among composite compositional variables (factor loadings) for each of the four end-member samples used in the extended Q-mode factor model and the observed compositional variables (oxides of elements)*

Oxide	Factor 1 end-member sample 252111KP	Factor 2 end-member sample 191111KP	Factor 3 end-member sample 151111KP	Factor 4 end-member sample 142111KP
SiO ₂ ---	¹ 0.2856	¹ -0.9106	¹ 0.5356	0.0251
Al ₂ O ₃ --	¹ .5627	¹ -.8222	¹ .3438	-.0782
Fe ₂ O ₃ --	¹ .7372	¹ -.6067	¹ .2510	¹ -.3036
MgO----	-.1960	¹ .7269	¹ .3488	-.1204
CaO----	¹ -.5922	¹ .9299	¹ -.5038	.1648
Na ₂ O---	¹ -.3163	¹ -.3484	-.0919	¹ .6234
K ₂ O----	¹ .6643	¹ -.5363	¹ .2819	¹ -.3367
TiO ₂ ---	¹ .7930	¹ -.8026	¹ .4527	¹ -.3769
CO ₂ ----	¹ -.2116	¹ .8209	¹ -.4209	-.1175
As ₂ O---	.1911	¹ .2658	.1771	¹ -.5396
B ₂ O----	¹ .6183	-.1024	¹ -.0591	¹ -.3348
BeO----	¹ .6477	¹ -.6971	.1453	-.0574
CoO----	¹ .5914	¹ -.5541	-.1765	.1760
Cr ₂ O ₃ --	¹ .5169	¹ -.6638	-.0520	.2053
CuO----	¹ .6710	-.1877	-.1273	¹ -.2388
Ga ₂ O ₃ --	¹ .4613	¹ -.5238	¹ -.2571	.3285
Li ₂ O---	¹ .4274	¹ .2839	-.0302	¹ -.5378
MnO----	¹ .3774	-.1267	-.4459	.2432
MoO ₂ ---	¹ .7048	¹ -.5595	-.1340	.0521
NiO----	¹ .6976	¹ -.5646	-.1001	.0292
PbO----	¹ .5513	¹ -.4486	¹ -.3013	¹ .2387
Rb ₂ O---	¹ .6878	¹ -.3717	.1366	¹ -.3518
Sc ₂ O ₃ --	¹ .5870	¹ -.4258	¹ -.3055	.1963
SrO----	¹ -.5091	¹ .6913	¹ -.8001	¹ .5848
VO ₂ ----	¹ .4585	.0395	.1485	¹ -.5296
V ₂ O ₃ ---	¹ .7197	¹ -.3587	-.1311	-.1299
Y ₂ O ₃ --	¹ .5175	¹ -.2238	-.2073	-.0132
Yb ₂ O ₃ ---	¹ .634	¹ -.3757	¹ -.2637	.0630
ZnO----	¹ .7454	-.1092	.2038	¹ -.6800

¹Significant at the 99-percent probability level ($|r| > 0.21$).

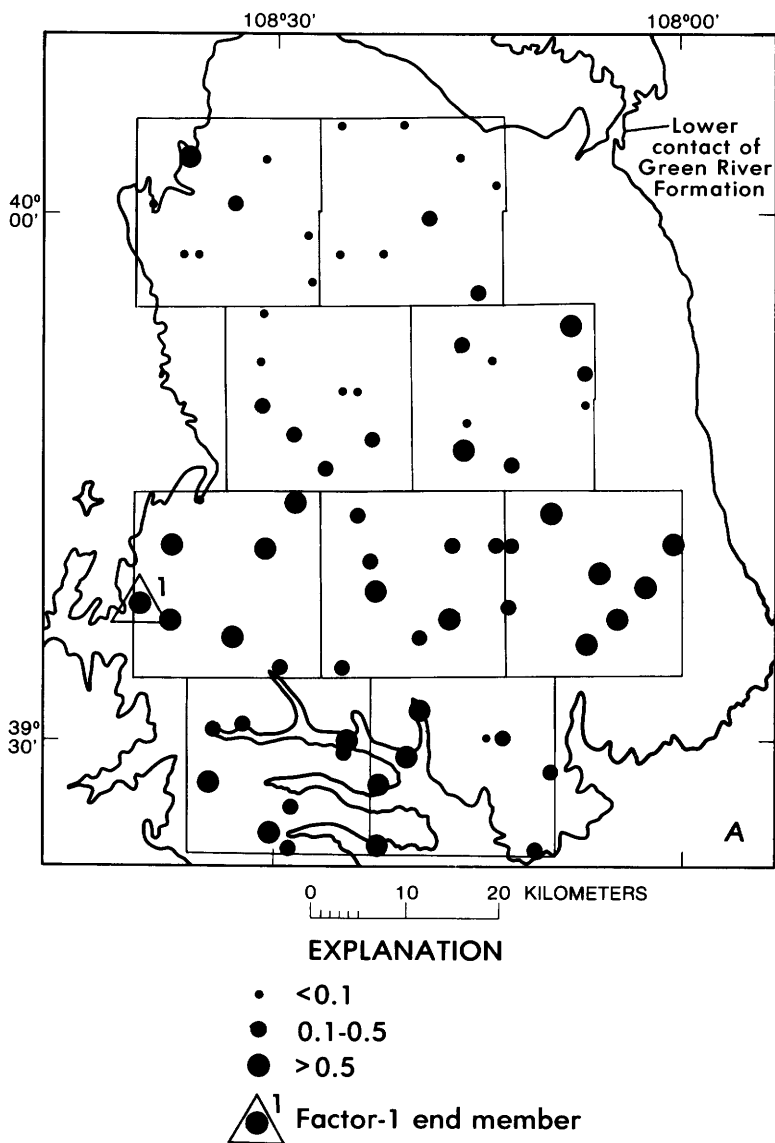


FIGURE 8.—Maps showing *Q*-mode factor loadings (table 5) for A, factor 1; B, factor 2; C, factor 3; and D, factor 4 for soils of the Piceance Creek basin.

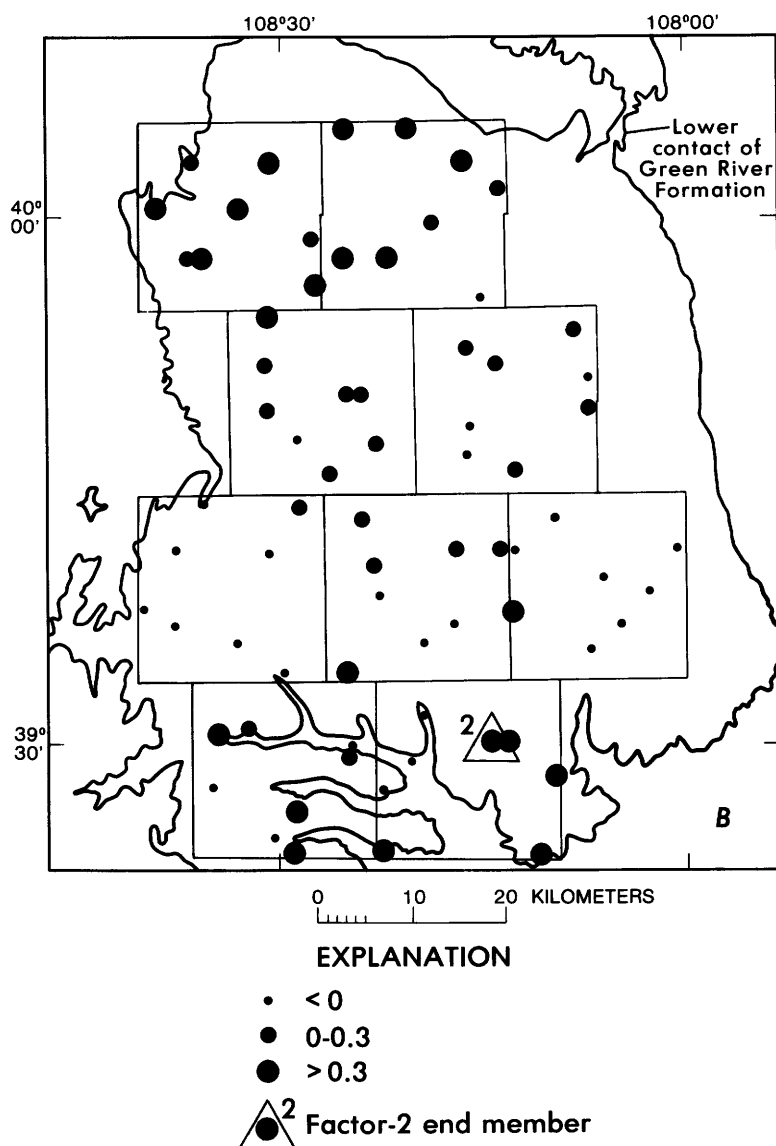


FIGURE 8.—Continued.

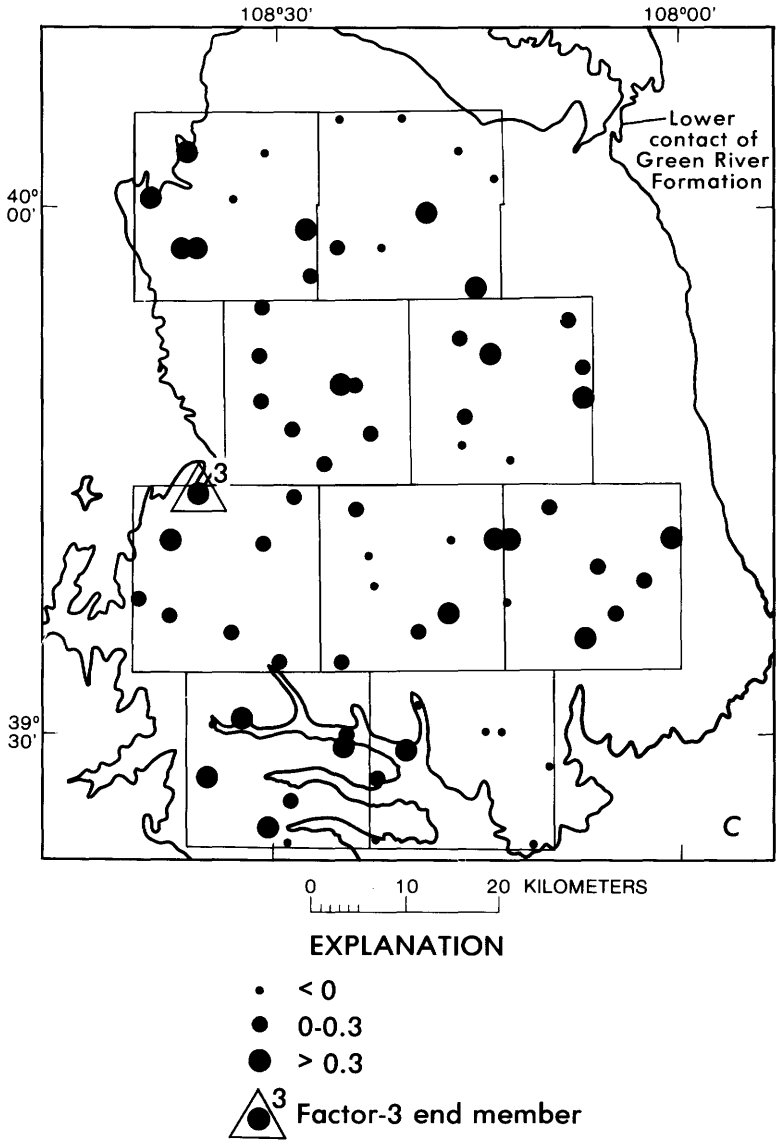


FIGURE 8.—Continued.

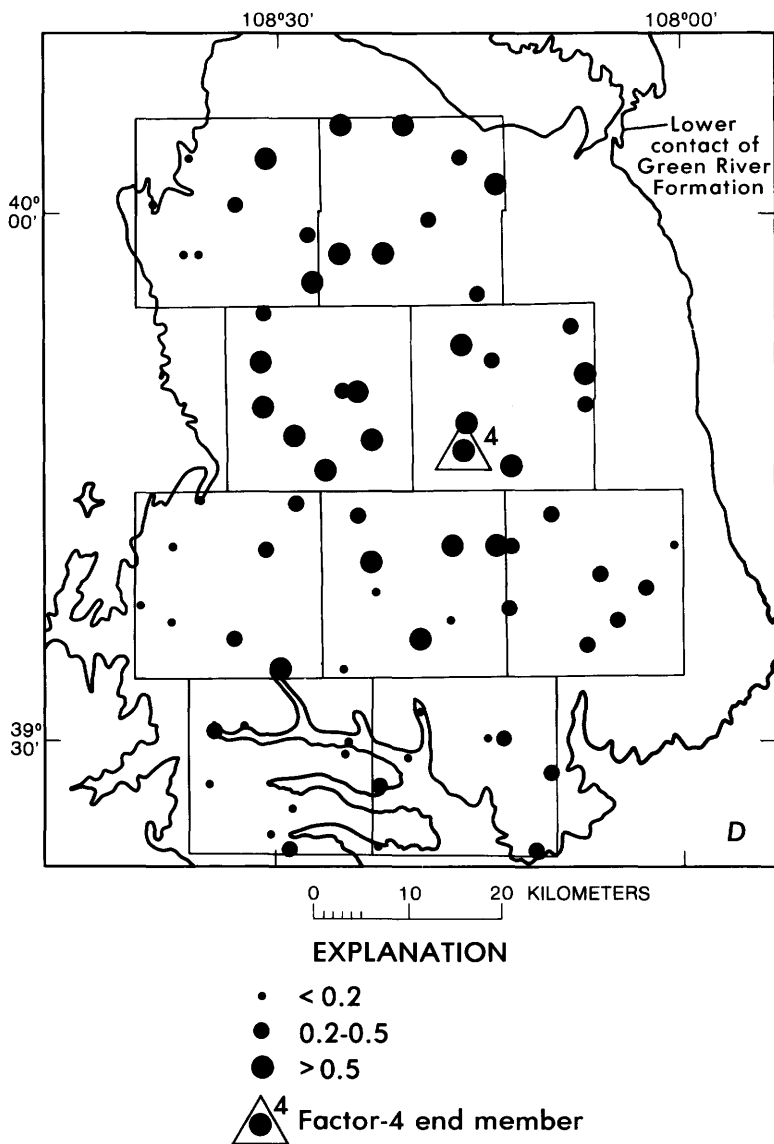


FIGURE 8.—Continued.

RESULTS

Table 7 indicates that the elements having the greatest influence in grouping samples having high loadings for factor 1 (those samples most similar to sample 252111KP) are titanium, zinc, iron, vanadium, molybdenum, nickel, rubidium, copper, potassium, ytterbium, beryllium, cobalt, scandium, aluminum, lead, yttrium, and chromium in approximately that order of importance. A glance at table 4 shows that the factor-1 end member does indeed contain higher concentrations of these elements than the other three end members. Samples that load high on factor 1 tend to be the most trace-element rich of all samples in this study. Samples having highest loadings for factor 1 are from the southern part of the basin (fig. 8A).

Soil samples that load high on factor 2 tend to contain high concentrations of the carbonate-related elements calcium, total carbon, magnesium, and strontium, and lower concentrations of the resistate elements silicon, aluminum, titanium, and beryllium (tables 4 and 7). Samples having high loadings for factor 2 are from both the northern and southern parts of the basin (fig. 8B); samples having lowest loadings for factor 2 occur over most of the central part of the basin. The inverse relationship between the carbonate and resistate variables can also be seen by comparing the map of factor-2 loadings (fig. 8B) and maps of element concentrations based on supertownship means (fig. 5).

Soil samples having high loadings for factor 3 are from scattered areas throughout the basin (fig. 8C), have relatively high concentrations of silicon and titanium, and tend to have low concentrations of strontium, calcium, total carbon, and manganese (tables 4 and 7).

Soil samples having high loadings for factor 4 tend to be from the northern and central parts of the basin (fig. 8D). These samples tend to have relatively high concentrations of sodium and strontium and relatively low concentrations of zinc, arsenic, lithium, and vanadium (tables 4 and 7).

DISCUSSION

The map patterns of factor loadings shown in figure 8 and the map patterns of element concentration shown in figure 5 can be explained in general terms of regional geology, physiography, and hydrology of the Piceance Creek basin. Parent material for most of the soils from the northern and central parts of the basin is sandstone of the Uinta Formation that overlies the Green River Formation (fig. 2). However, in the southern part of the basin, most soils are derived from finer grained dolomitic marlstone of the Green River Formation. A few samples used in this investigation are from soils derived from sandstone of the Wasatch Formation that underlies the Green River For-

mation (fig. 2). In general, the Green River Formation contains higher concentrations of most trace and minor elements than does sandstone of early Eocene age in the same area (table 8). Therefore, soils derived from the Green River Formation would be expected to contain higher concentrations of most trace elements than do soils derived from sandstone of either the underlying Wasatch Formation or the overlying Uinta Formation.

Additional evidence for contributions of higher trace-element concentrations from the Green River Formation was provided by Candito (1977) and McNeal, Feder, Ringrose, and Klusman (1976). Candito examined concentrations of boron, molybdenum, zinc, lithium, arsenic, mercury, and organic carbon in soils developed on the Uinta Formation and on the Parachute Creek Member of the Green River Formation on lease site C-a. He found significant differences in concentrations of lithium, boron, molybdenum and organic carbon between soils developed on the two formations, the concentrations of all four elements being higher in the soils developed on the Parachute Creek. McNeal, Feder, Ringrose, and Klusman (1976) measured concentrations of 32 elements in sediments from four streams, two each from the Piceance Creek and Uinta basins. They found significant between-stream variability for 19 of these elements, including the carbonate-related elements calcium, magnesium, strontium, lithium, carbonate carbon, sodium, boron, and barium. They interpreted these differences as being due to variable contributions from the carbonate strata of the Green River Formation.

In a general way, the map-distribution pattern of factor-1 loadings (fig. 8A) is the inverse of the map-distribution pattern of factor-4 loadings (fig. 8D); samples having highest loadings for factor 1 are in the southern part of the basin, and those having highest loadings for factor 4 are in the central and northern parts of the basin. Analysis-of-variance results have shown that several trace elements having regional components of variance have concentration gradients in soils across the basin that increase from northeast to southwest. The northeast-to-southwest gradient is particularly evident in maps of concentrations of zinc, lithium, and copper (figs. 5A-C). It is not surprising, therefore, that samples having high loadings for factor 1 (that is, samples high in trace elements) should come from the southern part of the basin, because soils there are derived more from the Green River Formation than are soils in the north. The distribution of samples having high loadings for factor 4 reflects the inverse relationship between factor-4 loadings and zinc and lithium; factor-4 loadings are highest in the central and northern parts of the basin where concentrations of these two elements are lowest. Factor-4 samples also tend to be rich in silicon (table 4), reflecting the fact that most of these soils are derived from sandstone.

TABLE 8.—Average composition (geometric means) of Green River Formation oil shale and lower Eocene sandstones of the Rocky Mountain region

[Leaders(---), not determined or not reported]

Oxide	Oil shale, Green River Formation ¹	Mahogany zone, Green River Formation ²	Wasatch Formation, Piceance Creek basin ³	Lower Eocene sandstones, Rocky Mountain region ⁴
Al ₂ O ₃	⁵ 7.0	-----	6.0	6.6
CaO	⁵ 1.0	-----	2.0	2.4
Fe ₂ O ₃	2.9	-----	.77	1.2
MgO	3.7	-----	.53	.55
K ₂ O	2.6	-----	1.3	1.4
SiO ₂	⁵ 31	-----	81	73
Na ₂ O	2.1	-----	.68	.51
TiO ₂	.22	-----	.27	.20
CO ₂	-----	-----	1.3	.71
As ₂ O ₃	.0046	0.0038	-----	-----
B ₂ O ₃	.0230	.0240	.0052	.0042
BeO	-----	.0005	-----	-----
CoO	.0013	.0012	.0004	.0006
Cr ₂ O ₃	.0051	.0700	.0012	.0019
CuO	.0050	.0061	.0008	.0010
Ga ₂ O ₃	.0013	.0013	.0010	.0012
Li ₂ O ₃	.0210	.0030	-----	-----
MnO	.0320	.0320	.0150	.0190
MoO ₃	.0015	.0026	-----	-----
NiO	.0032	.0420	.0008	.0011
PbO	.0022	.0003	.0008	.0008
Rb ₂ O	-----	.0013	-----	-----
Sc ₂ O ₃	.0012	.0011	-----	-----
SrO	.0350	.1100	.0110	.0160
V ₂ O ₃	.0150	.0160	.0034	.0035
Y ₂ O ₃	-----	.0034	.0010	.0012
ZnO	.0093	.0022	-----	-----
UO ₂	-----	.0005	.0002	.0003

¹From U.S. Geological Survey (1976); includes Mahogany zone.²12 composite samples from the Mahogany zone, Poulson and others (1977).³12 samples of the Wasatch Formation, Piceance Creek basin, Vine and Tourtelot (1973).⁴216 samples of lower Eocene (including the 12 Wasatch samples) from the Rocky Mountain region, Vine and Tourtelot (1973).⁵USGS Green River oil-shale standard, SGR-1, Flanagan (1976).

The highest loadings for factor 2 are for soils in the northern and southern parts of the basin (fig. 8B). Samples having high loadings for factor 2 are characterized by relatively high concentrations of the carbonate-related elements calcium, magnesium, strontium, and lithium (tables 4 and 7), and low concentrations of the resistate elements silicon, aluminum, titanium, and beryllium. This pattern of high-carbonate soils in the northern and southern parts of the basin and low-carbonate soils in the central part of the basin is also reflected in the distributions of magnesium, calcium, and strontium (figs. 5D-F), which have highest concentrations in the northern and southern parts of the basin. Three of the resistate elements (iron, titanium, and beryllium) have significant regional components of variance and have map distributions opposite those for calcium, magnesium, and strontium, with a ridge of higher concentrations running east-west across the central part of the basin (figs. 5G, 5I, and 5J).

The occurrence of more carbonate-rich soils in the southern part of the basin is probably related to the fact that most soils there are derived from carbonate-rich strata of the Green River Formation. The carbonate-rich soils in the northern part of the basin (fig. 8B) cannot be accounted for by the occurrence of the Green River Formation because most soils in this area are derived from sandstone of the Uinta Formation (fig. 2). Relatively high concentrations of the carbonate-related elements calcium, magnesium, strontium, and sodium in soils in the northern part of the basin may be related to climate, ground-water conditions, compositional variability within the Uinta Formation, or a combination of the three. At least some of the carbonate is derived from ground water. Springs are common in the northern part of the basin and form white coatings, travertine mounds, and flowstone of calcium carbonate. Many of the springs are associated with a fracture system that trends approximately N. 70° W. across the northern part of the basin (George J. Saulnier, Jr., U.S. Geological Survey, oral commun., 1977). This fracture system apparently acts as a conduit for ground water from a lower aquifer consisting of fractured marlstone below the Mahogany zone in the Parachute Creek Member of the Green River Formation. The water in the lower aquifer in the northern part of the basin is characterized by very high concentrations of sodium and bicarbonate (several thousands of milligrams per liter, or mg/L, each) resulting from the dissolution of nahcolite from the lower part of the Parachute Creek Member (Weeks and others, 1974).

Above the Mahogany zone is a second aquifer in fractured marlstone of the Parachute Creek Member and fractured sandstone of the lower part of the overlying Uinta Formation. Water in the upper aquifer also contains high concentrations of sodium and bicar-

bonate, but concentrations are about an order of magnitude less than concentrations in the lower aquifer (hundreds rather than thousands of milligrams per liter). The upper aquifer also contains about 50 mg/L each of magnesium and calcium, about an order of magnitude higher than concentrations of these two ions in the lower aquifer (Weeks and others, 1974). Water from either or both of these two aquifers, introduced into soils by springs, would result in precipitation of CaCO_3 and possibly Na_2CO_3 . Strontium and magnesium would be coprecipitated with calcium, resulting in high concentrations of calcium, magnesium, strontium, and sodium in soils in the northern part of the basin, as reflected in the distributions of high loadings for factors 2 and 4 (tables 4 and 7; figs. 8B and 8D).

Introduction of CaCO_3 from ground water might be expected to be more prevalent in soils in valley walls and bottoms, producing a significant difference in composition between ridgetop and valley-bottom soils. That carbonate precipitation in ridgetop soils does occur is indicated by the common occurrence of CaCO_3 coatings on rock fragments in soils on the ridges. Precipitation of carbonate minerals in soils in the northern part of the basin, even on ridgetops, may be aided by the fact that this part of the basin is lower in elevation, receives less rain and snow than most of the rest of the basin, and has a higher rate of evapotranspiration. Figure 9 shows that most of the northern part of the basin is at elevations less than 2,286 m, and much of the area is less than 1,981 m. Wymore (1974) has shown that there are marked differences in precipitation-evapotranspiration balances related to elevation differences within the Piceance Creek and Yellow Creek watershed. At elevations between 2,134 and 2,430 m, precipitation is about 4.6 cm per year, and evapotranspiration is about 10 cm per year. Below 1,829 m, precipitation is less than 3 cm per year, and evapotranspiration is greater than 12 cm per year. Temperatures also show marked differences with elevation, decreasing by almost 1°C on an annual basis for each 100-m rise in elevation. These marked climatic differences suggest that the higher carbonate content of soils in the northern part of the basin (relative to the central part of the basin) may be related to lower precipitation, lower elevation, and higher temperature.

Evidence for climatic control on soil composition was also reported by Candito (1977). He found that concentrations of several trace elements in soils developed on the Uinta Formation on lease tract C-a are strongly controlled by organic carbon and pH, which, in turn, are controlled by climatic differences manifested in differences in available moisture and vegetation cover.

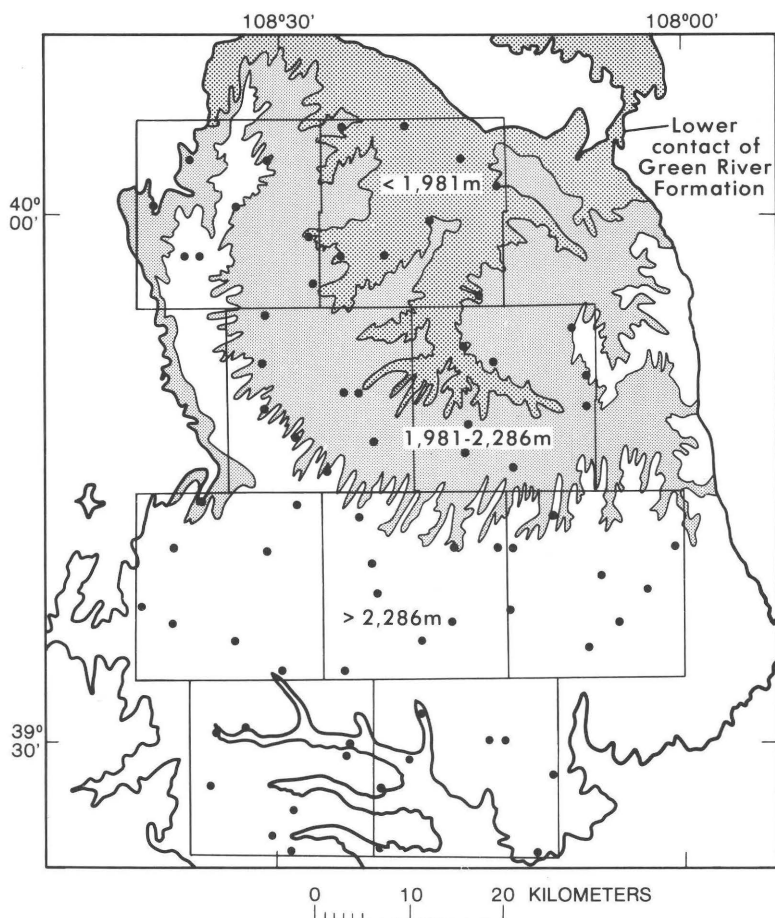


FIGURE 9.—Subdivision of the Piceance Creek basin into three elevation zones.

Samples having high loadings for factor 3 are scattered throughout the basin and show no regional trends (fig. 8C). The end-member sample for factor 3 is a soil developed on sandstone of the Wasatch Formation underlying the Green River Formation. Tables 4 and 7 indicate that factor-3 soils tend to be among the most silica rich in the basin. The scattered map distribution of these samples (fig. 8C) suggests that they represent a residuum of high-silicon soils that differ from factor-4 soils probably because of low concentrations of sodium and strontium. As discussed above, the high concentrations of sodium and strontium in factor-4 soils are probably the result of additions from ground water.

COMPARISON OF TRACE ELEMENTS IN OIL SHALE AND SOILS OF THE PICEANCE CREEK BASIN

As indicated in table 8, dolomitic marlstone of the Green River Formation contains higher concentrations of most trace elements than sandstone of the underlying Wasatch Formation. Although no analyses are available, we would expect the sandstone of the overlying Uinta Formation also to contain lower concentrations of most trace elements relative to the Green River Formation. Therefore, oil-shale development resulting in land fill containing either untreated or spent oil shale has the potential of producing higher trace-element concentrations in surficial materials. The volumes of material would be considerably less in an in situ or modified in situ mining process than in either surface or subsurface mining processes. A comparison of trace-element concentration in soils from the Piceance Creek basin (table 1) with concentration in oil shale is shown in figure 10. Oil shale tends to contain substantially (5 to 10 times) higher concentrations of arsenic, mercury, and selenium, and slightly higher concentrations of fluorine, lithium, vanadium, and molybdenum.

Arsenic, antimony, mercury, selenium, cadmium, fluorine, and boron have been specified by the U.S. Geological Survey as being of particular environmental concern because they occur in relatively high concentrations in oil shale. The lessees of the prototype oil-shale tracts are required to establish baselines for these seven elements in oil shale, soil, stream sediment, and water on the lease sites.

In view of the risk of molybdenosis in cattle grazing on forage grown on coal-mine spoils (Erdman and others, 1978), we also include molybdenum in the list of trace elements that should be of particular environmental concern. Molybdenosis is a nutritional disease caused when high concentrations of molybdenum depress the physiological availability of copper. Molybdenosis in cattle is of particular concern when the ratio of copper to molybdenum in forage is less than 2.0 (Erdman and others, 1978; it is usually due to high levels of molybdenum rather than low levels of copper). Results of analyses of barley grown on spent oil shale and on soils from the Piceance Creek basin, reported by Harbert and Berg (1974), indicate that plants grown on spent shale have ratios of copper to molybdenum below the critical limit of 2.0 (1.2 to 1.8). However, plants grown on the soils have ratios of copper to molybdenum considerably above the critical limit, increasing from about 5.5 in soils from the northern part of the basin to about 6.6 in soils from the southern part of the basin. The north-to-south regional difference in the ratio of copper to molybdenum in plants reflects the regional north-to-south increase in copper in soils in the Piceance Creek basin (fig. 5C). These data suggest that any land reclamation in the Piceance Creek basin using oil shale could induce an increase in several of the better known noxious trace elements.

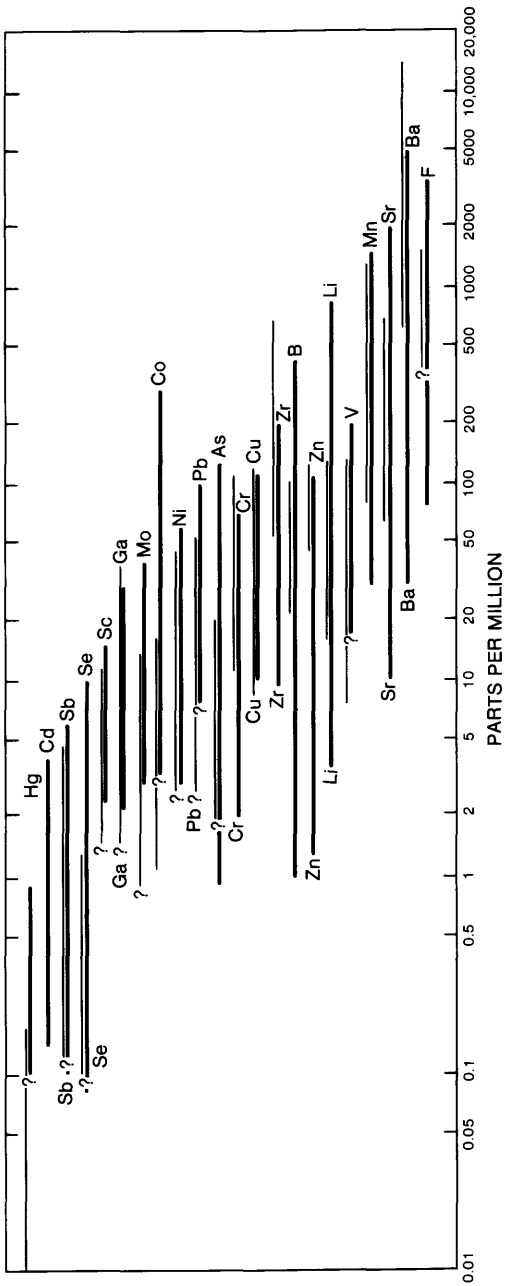


FIGURE 10.—Comparison of concentrations of trace elements in oil shale from the Green River Formation (Heavy lines) and soils from the Piceance Creek basin (light lines). Data for mercury are from Donnell and Shaw (1977). Data for all other elements in oil shale are compiled in U.S. Geological Survey (1976). Data for soils are from table 1.

CONCLUSIONS

1. Most of the variation in elemental abundance in soils from the Piceance Creek basin occurs between sections within townships; that is, over distances of about 3 to 10 km. Of the 39 elements discussed in this report, 28 show significant variance between sections. Only seven elements (calcium, sodium, mercury, strontium, total carbon, uranium, and thorium) have significant variance between townships within supertownships (distances of 10 to 19 km), and only 11 elements (aluminum, potassium, silicon, sodium, titanium, total carbon, fluorine, lithium, nickel, zinc, and uranium) have significant variance between samples (100 m). None of the elements show significant variability between samples collected on ridgetops and those collected in valley bottoms.
2. Fourteen elements (calcium, iron, magnesium, silicon, titanium, boron, beryllium, chromium, copper, gallium, lithium, yttrium, ytterbium, and zinc) show significant variation between supertownships (distances greater than 19 km) at the 95-percent probability level. The distribution of strontium is close to significant at this level and it has been included with these 14 elements because of its close association with carbonate-related variables. Of these 15 elements, 10 (calcium, iron, magnesium, silicon, titanium, beryllium, copper, lithium, zinc, and strontium) have variance-mean ratios (v_m) greater than or equal to 1.0 at the supertownship level, indicating that supertownship means are sufficiently stable (reproducible) to use in constructing geochemical maps. The geochemical maps for these 10 elements show three different types of regional trends. Concentrations of zinc, lithium, and copper have a regional gradient across the Piceance Creek basin, increasing from northeast to southwest. Iron, beryllium, silicon, and titanium are most concentrated in soils in the central part of the basin, and least concentrated in soils in the northern and southern parts of the basin. Concentrations of calcium, magnesium, and strontium show the opposite map pattern; that is, their concentrations are greatest in the north and south and least in the center of the basin. Of the remaining five elements that have significant variance components at the supertownship level (namely boron, chromium, gallium, yttrium, and ytterbium) but do not have supertownship mean values sufficiently stable to construct geochemical maps, most show regional trends similar to those of iron, beryllium, silicon, and titanium, with highest values in the central part of the basin. However, the observed trends for these five elements are not judged to be reliable in themselves because the supertownship means are not sufficiently reproducible.

3. Soil samples having similar chemical composition were examined by Q-mode factor analysis. Based on the Q-mode analysis, several regional trends are apparent that substantiate the regional trends determined by examination of maps of super-township means for individual elements. Soils in the southern part of the basin are mostly derived from fine-grained dolomitic marlstone of the Green River Formation and therefore contain relatively high concentrations of the carbonate-related elements calcium, magnesium, strontium, lithium, and total carbon, and low concentrations of the resistate elements silicon, aluminum, titanium, and beryllium. These soils also tend to be enriched in most trace elements because Green River marlstone contains higher trace-element concentrations than do underlying and overlying sandstones of the Wasatch and Uinta Formations. Soils in the central part of the basin are mostly derived from sandstone of the Uinta Formation and therefore tend to contain relatively high concentrations of silicon and low concentrations of carbonate-related elements and most trace elements. Soils in the northern part of the basin are also derived from sandstone of the Uinta Formation but are distinguished from soils in the central part of the basin by higher concentrations of calcium, magnesium, strontium, and sodium. The higher concentrations of these four carbonate-related elements in the northern part of the basin may be due to additions of dissolved salts from ground water and/or greater aridity as indicated by lower precipitation, greater evapotranspiration, and higher temperature.
4. Relative to soils in the Piceance Creek basin, oil shale of the Green River Formation is enriched in four of seven trace elements (arsenic, mercury, selenium, and fluorine) that are considered to be environmentally sensitive in areas being considered for oil-shale development. In addition, oil shale contains elevated levels of molybdenum that could result in molybdenosis in certain ruminants grazing on forage grown on oil-shale spoils. This enrichment suggests that land reclamation in the Piceance Creek basin using oil shale as fill could produce an increase in several trace elements of environmental concern.

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