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By R. C. SEVERSON

GEOCHEMICAL SURVEY OF THE WESTERN ENERGY REGIONS

GEOLOGICAL SURVEY PROFESSIONAL PAPER 1134-B

*Baseline values for 38 elements characterize
the composition of soils
overlying major geologic units in each Basin*



UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOCHEMICAL SURVEY OF THE WESTERN ENERGY REGIONS

REGIONAL SOIL CHEMISTRY IN THE BIGHORN AND WIND RIVER BASINS, WYOMING AND MONTANA

By R. C. SEVERSON

ABSTRACT

A reconnaissance study of total concentrations of 38 elements in samples of soils (0–40 cm deep, composite) from the Bighorn and Wind River Basins of Montana and Wyoming indicates that the geographic variation for most elements occurs locally (5 km or less). However, in the Bighorn Basin, Zn exhibits significant regional variation (between geologic units); and in the Wind River Basin, Al, Cr, K, Mn, Mo, Ni, U, and V exhibit similar variation. For the remaining elements, the lack of regional variation suggests that a single summary statistic can be used to estimate a baseline value that reflects the range in concentration to be expected in samples of soils in each basin. The concentrations of most of these elements in both basins are not much different from those measured independently in the Powder River Basin of Wyoming or in the Western United States. In addition, data from an analysis of variance provide an estimate of the number of random samples within an area of specified size (10 km square, approximately a township) that are needed to prepare a reliable map of total element concentration in soils for each of the elements in each of the basins.

INTRODUCTION

This reconnaissance study provides data on spatial variation in total element concentrations in soil in the Bighorn and Wind River Basins. The data provide chemical baseline values for the two areas. The baseline values enable the monitoring of any changes that might result from disturbances of the geochemical environment by activities such as energy development. The baseline value for each element accounts for the natural chemical variability of soils and may be defined as the 95-percent range in concentration to be expected in samples of soils in these basins. In addition, differences between cell averages may be used to determine the feasibility of mapping regional variation in concentrations of elements in soils at a mapping interval greater than 10 km.

STUDY AREA

The Bighorn and Wind River Basins are structural basins formed in late Cretaceous and early Tertiary time (Keefer, 1965). During Eocene time, the basins

became progressively filled; by Oligocene time, the bordering mountain ranges were largely buried; and by Pliocene time, only the highest parts of the ranges stood above a broad depositional plain (Love, 1970).

In early Eocene time the basin fill was obtained from erosion of the surrounding mountains made up of Precambrian, Paleozoic, and Mesozoic rocks. The western border of the Bighorn Basin is east of the Absaroka Range at the border of the erosional scarp of the Absaroka volcanic plateau; these volcanic rocks of Eocene and younger ages contributed debris for the later filling of the basin but contributed little to the earlier deposits. The eastern border of the Wind River Basin is the Powder River lineament, a sharply folded belt of Cretaceous and Paleozoic rocks that contributed little debris to the basin fill. The Granite Mountains along the southern margin of the Wind River Basin mark the structural boundary of the basin but are buried by strata of Miocene and Pliocene age; this region is included in this study in order to obtain data on the general composition of these younger rocks, which are markedly different from the lower Eocene rocks that make up the oldest levels of the basin fill. Distribution of rock units is taken from Andrews, Pierce, and Eargle (1947) for the Bighorn Basin and from Whitcomb and Lowry (1968) for the Wind River Basin.

Coal occurs in rocks of Cretaceous and Paleocene age in both basins. Although small amounts of coal have been mined in each basin in the past (Keefer, 1965), it seems unlikely that energy resource development in the Bighorn and Wind River Basins (except for uranium in the Wind River Basin) will be comparable to that foreseen for the Powder River Basin (U.S. Bureau of Land Management, written commun., 1973).

Data on the composition of soils of the two basins are useful for comparison with each other and with data from the Powder River Basin. The data are also used in establishing a chemical background against which any changes can be measured in regions where development has taken place.

SAMPLING DESIGN

Chemical variation between geologic units within basins, and within geologic units across different distances, was estimated from an unbalanced, nested analysis-of-variance design. The analysis-of-variance design used in this study is shown in table 1. Sampling sites were randomly located using a barbell design within each of the primary geologic units within each of the basins (fig. 1).

The major axis of the barbell was 25 km long, and the sequentially smaller axes of each barbell were 10, 5, and 1 km long, respectively. All axes were oriented by selecting a compass direction at random. A barbell design is shown in figure 2. In each of the six barbells, 12 samples were collected for a total of 72 samples. Also, for each set of 12 samples, 4 samples were randomly selected to be split and analyzed twice, yielding a total of 24 samples split and analyzed in duplicate. These sample splits represent the analytical-error level of the sampling design (tables 2 and 3).

Soils on the geologic unit of Paleocene age (Fort Union Formation) were sampled only in the Bighorn Basin, and those on the geologic units of Miocene and Pliocene age (Moonstone and Arikaree Formations, respectively) were sampled only in the Wind River Basin. Soils on the geologic units of Eocene age (Wind River and Indian Meadows Formations in the Wind River Basin and Willwood Formation in the Bighorn Basin)

and on deposits of Quaternary age were sampled in both basins. Soils on the pre-Tertiary geologic unit were not sampled.

SAMPLES AND ANALYSES

The material collected at each sample location consisted of a composite sample of soil, excluding coarse fragments, from 0 to 40 cm in depth. In the laboratory, all samples were dried under forced air at ambient temperature. The samples were disaggregated using a mechanical, ceramic mortar and pestle, and the fraction passing a 10-mesh (2-mm) sieve was saved. The saved fraction was further ground to pass a 100-mesh (150 μ m) sieve; this material was used for all chemical analyses. The 96 total samples (72 samples plus 24 splits) were analyzed in a random sequence, so that any systematic errors in sample preparation and analysis would be effectively converted to random errors and not bias the interpretation of results.

Analyses for some elements present in trace quantities commonly result in censored data, because part of the normal range of concentrations is smaller than the lower limit of determination for the analytical method. Because statistical tests require a complete numeric data set, censored values were replaced by arbitrary concentrations equal to 0.7 times the value that represents a lower limit of determination for the analytical method. This replacement is justified by the fact that

TABLE 1.—Analysis-of-variance design for the Bighorn and Wind River Basins

[Each s_i^2 is an estimate of the variation associated with the sources of variation; for example, s_u^2 is variation between geologic units and s_a^2 is the variation between duplicate analyses; ---, no F-ratio exists]

Source of variation	Degrees of freedom	Mean square estimates	F-ratio	Variance component
Between geologic units	2	$MS_1 = s_u^2 + 1.5s_1^2 + 2.3s_5^2 + 4.1s_{10}^2 + 8.1s_{25}^2 + 16s_u^2$	$\frac{MS_1}{MS_2}$	$s_u^2 = \frac{MS_1 - MS_2}{16} = \sigma_u^2$
10-25 km distance-----	3	$MS_2 = s_u^2 + 1.5s_1^2 + 2.3s_5^2 + 4.0s_{10}^2 + 7.9s_{25}^2$	$\frac{MS_2}{MS_3}$	$s_{25}^2 = \frac{MS_2 - MS_3}{7.9} = \sigma_{25}^2$
5-10 km distance-----	6	$MS_3 = s_u^2 + 1.4s_1^2 + 2.3s_5^2 + 4.0s_{10}^2$	$\frac{MS_3}{MS_4}$	$s_{10}^2 = \frac{MS_3 - MS_4}{4.0} = \sigma_{10}^2$
1-5 km distance-----	12	$MS_4 = s_u^2 + 1.3s_1^2 + 1.7s_5^2$	$\frac{MS_4}{MS_5}$	$s_5^2 = \frac{MS_4 - MS_5}{1.7} = \sigma_5^2$
0-1 km distance-----	12	$MS_5 = s_u^2 + 1.2s_1^2$	$\frac{MS_5}{MS_6}$	$s_1^2 = \frac{MS_5 - MS_6}{1.2} = \sigma_1^2$
Between analyses-----	12	$MS_6 = s_a^2$	---	$s_a^2 = \sigma_a^2$

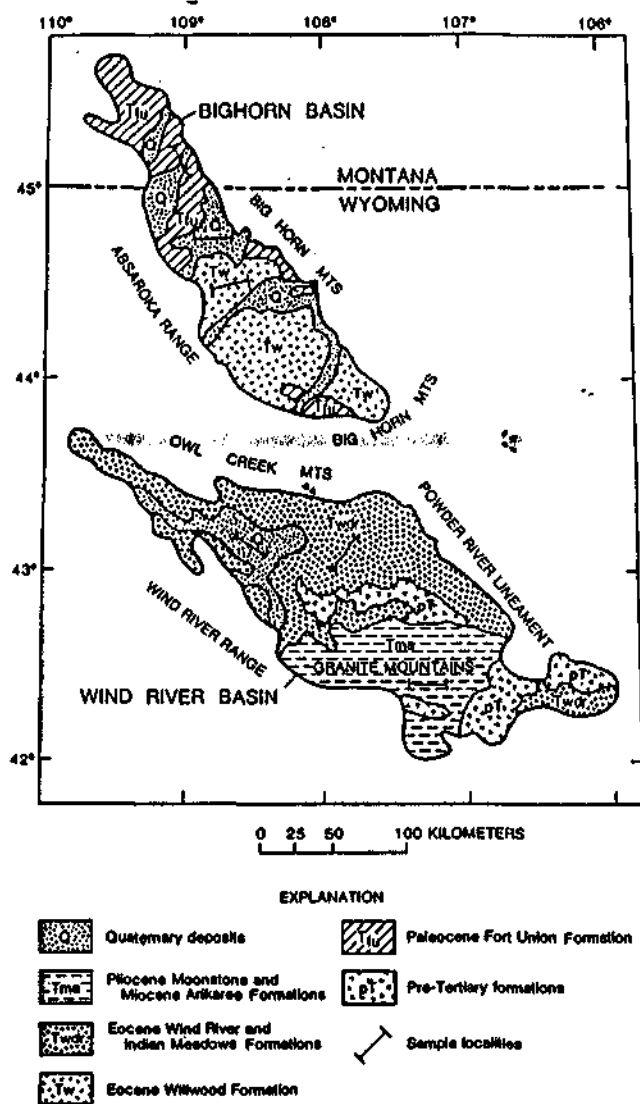


FIGURE 1.—Geologic and sample locality map of the Bighorn and Wind River Basins of Montana and Wyoming. Geology modified from Andrews, Pierce, and Eargle (1947), and Whitcomb and Lowry (1968).

the small number of replaced values (affecting samples with detection ratios of $<1:1$ in tables 4–7) does not significantly alter the results of the statistical tests. However, when one-quarter or more of the analyses for a particular element were censored, the data for that element were discarded and, therefore, not reported in this study. The highly censored elements were Ag, Au, Bi, Br, Cd, Cl, Cs, Dy, Er, F, Gd, Hf, Ho, I, In, Ir, Nd, Os, P, Pd, Pr, Pt, Re, Rh, Ru, S, Se, Sm, Ta, Tb, Te, Tl, Tm, and W.

Elements occurring in trace quantities in natural materials commonly tend to exhibit positively skewed frequency distributions. Therefore, a logarithmic transformation of the data prior to statistical analysis was used to improve the estimate of the most probable concentration of an element in natural materials. The fre-

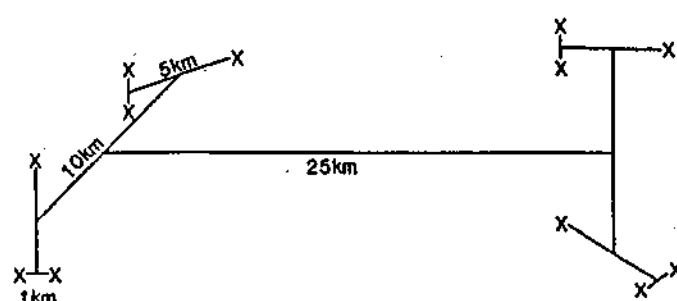


FIGURE 2.—Diagrammatic representation of a barbell design with sample localities shown as 'x's.

TABLE 2.—Variance analysis of total element concentration in soil in the Bighorn Basin

[The sample consisted of a composite of soil from a 0- to 40-cm depth; total variance is computed on logarithmically transformed data; *, variance component is significantly different from zero at the 0.05 probability level; estimates based on analyses of 48 samples]

Element	Total variance	Percent of total variance					Analytical error
		Between geologic units	10-25 km	5-10 km	1-5 km	0-1 km	
Al-----	0.0205	10.2	0	0	51.2*	31.1*	7.5
As-----	.1143	0	14.1*	0	0	26.3	59.6
B-----	.0189	5.9	0	0	21.3	56.8*	16.1
Ba-----	.0335	10.6	2.0	6.3	0	0	81.1
Be-----	.0282	0	5.3	0	51.4*	13.6	29.5
C-----	.0826	0	58.9*	0	24.2*	11.2*	5.6
Ca-----	.0185	0	27.1*	0	27.7	45.1*	0.2
Co-----	.0314	0	27.9*	0	0	17.7	54.4
Co-----	.0183	16.5	0	10.1	34.6	20.8	18.0
Cr-----	.0434	3.4	0	0	77.7*	8.8	8.2
Cu-----	.0610	8.1	0	0	56.1*	16.0	19.8
Fe-----	.0239	23.0	0	8.6	46.3*	17.9*	4.0
Ga-----	.0365	11.7	0	0	42.3	29.7*	16.3
Ca-----	.2257	0	0	6.6	14.7	0	78.7
Hg-----	.0210	5.1	0	17.5	0	57.1*	20.3
K-----	.0081	0	7.7	0	39.0	42.2*	11.1
La-----	.0096	0	0	0	9.2	50.8	40.0
Li-----	.0189	10.5	0	0	49.9*	29.4*	10.3
Mg-----	.0120	10.0	0	32.2	10.4	46.4*	0.8
Mn-----	.0277	0	25.3	0	22.2	44.8*	7.7
Mo-----	.0396	7.6	0	0	43.2	26.9	22.2
Na-----	.0435	42.2	17.4	7.3	0	32.7*	0.3
Nb-----	.0230	2.5	4.2	0	8.3	0	85.0
Ni-----	.0229	12.7	0	0	41.5	34.4*	11.4
Pb-----	.0337	3.6	0	0	0	46.5	49.9
Rb-----	.0223	0	15.2	0	44.0*	0	40.9
Sc-----	.0452	3.6	11.9	0	40.2	31.4*	13.0
Si-----	.0022	10.3	0	31.0	15.3	28.6*	5.8
Sn-----	.1678	0	0	20.9	3.4	0	75.7
Sr-----	.0246	11.1	17.2	14.7	13.9	38.4*	4.8
Tb-----	.0161	0	2.3	0	27.9	51.0*	18.8
Ti-----	.0083	0.7	0	0	26.8	67.6*	5.0
U-----	.0101	0	0	10.6	20.7	65.1*	3.6
V-----	.0253	0	2.2	0	61.6*	30.7*	5.5
Y-----	.0165	0	0	0	50.5*	19.6	21.7
Yb-----	.0187	0	0	3.1	65.1*	20.5	11.3
Zn-----	.0212	13.3*	0	1.5	46.4*	26.6*	10.3
Zr-----	.0253	0	0	32.4	0	17.7	48.1

quency distribution of the log-transformed data more nearly resembles a normal distribution, one of the basic assumptions for the analysis of variance.

Chemical analyses were done in the U.S. Geological Survey analytical laboratories in Denver, Colorado.

TABLE 3.—Variance analysis of total element concentration in soil in the Wind River Basin

[The sample consisted of a composite of soil from a 0- to 40-cm depth; total variance is computed on logarithmically transformed data; *, variance component is significantly different from zero at the 0.05 probability level; estimates based on analyses of 48 samples]

Element	Total variance	Percent of total variance					Analytical error
		Between geologic units	10-25 km	5-10 km	1-5 km	0-1 km	
Al	0.0069	33.1*	0	2.6	5.9	43.2*	15.0
As	.1012	3.2	0.4	0	62.7*	13.1	20.6
B	.0272	14.0	0	0	27.1	44.7*	14.2
Ba	.0082	0	0	4.9	17.9	0	77.2
Be	.0184	11.4	0	24.4	21.7	0	42.5
C	.0494	5.4	0	20.8	13.7	50.9*	9.2
Ca	.0987	11.8	0	21.6	37.6*	28.8*	0.3
Ce	.1290	1.0	1.3	0.2	0	0	97.5
Co	.0333	15.2	0	8.4	34.9	28.9*	12.6
Cr	.0566	65.4*	0	0	5.9	25.2*	3.5
Cu	.0731	11.7	0	0	22.6	38.5*	27.2
Fe	.0228	7.9	0	29.4	0	59.2*	3.5
Ga	.0229	12.4	6.2	0	51.0*	9.7	20.7
Ge	.1575	0	0	5.4	15.9	14.0	64.7
Hg	.0267	0	23.6	0	10.2	23.4	42.8
K	.0042	12.0*	0	0	67.6*	5.7	14.7
La	.1116	0.6	1.4	4.8	0	0	93.2
Li	.0359	3.4	0	14.7	21.8	57.6*	3.1
Mg	.0528	37.1	0	15.1	0	46.9*	1.0
Mn	.0305	26.3*	0	0	34.9	26.2*	12.6
Mo	.0441	22.1*	0	0	16.9	42.4*	18.6
Na	.0115	0	0	16.4	69.8*	12.8*	1.0
Nb	.0340	0.2	0	0	33.9	0	65.9
Ni	.0492	47.9*	0	0	14.9	29.2*	8.1
Pb	.0395	0	0	0	8.2	0	91.8
Rb	.0240	15.6*	0	6.8	0	14.0	63.6
Sc	.0342	16.6	0	22.3	14.3	22.3	24.5
Si	.0011	0	2.3	9.5	33.7*	14.0	20.6
Sr	.2108	0	0	0	13.0	16.7	70.3
Ta	.0258	2.5	32.6	31.4*	7.5	14.7	11.4
Tb	.0238	32.8	12.2	0	30.1*	16.0*	7.9
Ti	.0098	12.6	0	25.9	13.3	40.4*	7.8
U	.0097	15.6*	0	0	0.6	79.7*	4.2
V	.0195	10.4*	0	0	18.9	59.5*	11.0
Y	.0410	0	4.4	0	11.8	0	83.9
Yb	.0639	0	5.1	0	11.7	0	83.2
Zn	.0163	24.0	0	2.8	10.4	55.2*	7.5
Zr	.0247	9.4	0	0	0	0	90.6

TABLE 4.—Statistical summary for elements that lack regional variation in soils of the Bighorn Basin

[Detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed; *, elements measured in percent; other elements measured in parts per million]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline value ¹	Detection ratio
Al*	4.0	1.32	1.09	2.4 - 4.8	36:36
B	50	1.33	1.14	30 - 83	36:36
Be	2.0	1.40	1.23	1.2 - 3.4	36:36
C*	1.5	1.72	1.17	0.53 - 4.2	36:36
Ca*	3.0	1.78	1.03	0.95 - 9.5	36:36
Co	6.3	1.33	1.14	3.8 - 10	36:36
Cr	59	1.55	1.15	26 - 135	36:36
Cu	20	1.65	1.29	8.4 - 47	36:36
Fe*	1.8	1.38	1.07	0.96 - 3.4	36:36
Ga	.11	1.47	1.19	5.5 - 22	36:36
Hg	0.026	1.33	1.16	0.016 - 0.042	36:36
K*	1.5	1.19	1.07	1.1 - 2.1	36:36
La	36	1.20	1.15	20 - 45	36:36
Li	18	1.31	1.11	11 - 30	36:36
Mg*	0.86	1.41	1.04	0.4 - 1.7	36:36
Mn	400	1.38	1.11	220 - 740	36:36
Mo	4.8	1.47	1.24	2.5 - 9.1	35:36
Na*	0.53	1.53	1.03	0.23 - 1.2	36:36
Ni	22	1.37	1.13	12 - 39	36:36
Pb	8.6	1.44	1.35	5.7 - 13	36:36
Rb	55	1.32	1.25	40 - 77	36:36
Sc	5.9	1.59	1.19	2.5 - 14	32:36
Si*	32	1.10	1.03	27 - 38	36:36
Sr	230	1.39	1.08	120 - 440	36:36
Th	8.5	1.27	1.13	5.6 - 13	36:36
Ti*	0.26	1.22	1.05	0.18 - 0.38	36:36
U	2.7	1.25	1.05	1.7 - 4.2	36:36
V	68	1.34	1.09	39 - 120	36:36
Y	20	1.28	1.15	13 - 30	36:36
Yb	2.7	1.33	1.11	1.6 - 4.6	36:36
Zr	320	1.35	1.29	230 - 440	36:36

¹ Expected 95-percent range.

ANALYTICAL ERROR VARIANCE

The distributions of variance components for 38 elements in soils from the two basins are shown in tables 2 and 3. For 6 elements in the Bighorn Basin and 11 elements in the Wind River Basin, the variance due to analytical error accounts for more than 50 percent of the total observed variation. This error is judged to be excessive and, therefore, any interpretation of the data for these elements must be made with extreme caution.

Excessive analytical errors result in duplicate samples being reported as having widely different concentrations. The analytical procedure, rather than splitting errors or particle effect, is probably the best explanation for this excessive error. If splitting errors or particle effect were responsible, then a larger number of elements would exhibit excessive error. Concentrations of all elements, except Rb, that exhibit excessive analytical error were determined by multi-element emission spectrography or X-ray fluorescence. Atomic ab-

Sample preparation and analyses were performed by James S. Baker, A. J. Bartel, E. L. Brandt, J. G. Crock, I. C. Frost, Johnnie M. Gardner, Patricia Gayle Guest, Raymond G. Havens, J. P. Hemming, Kathryn E. Horan, Claude Huffman, Jr., J. O. Johnson, R. J. Knight, R. M. Lemert, R. E. McGregor, Violet M. Merritt, H. T. Millard, Jr., Wayne Mountjoy, G. O. Riddle, V. E. Shaw, M. W. Solt, J. A. Thomas, Michele L. Tuttle, R. E. Van Loenen, R. J. Vinnola, J. S. Wahlberg, and R. J. White. The analytical methods are described in a previously published report (U.S. Geological Survey, 1975).

All computations were done on a Honeywell-MULTICS computer using statistical programs in the U.S. Geological Survey's STATPAC Library (Van Trump and Miesch, 1977).

TABLE 5.—Statistical summary for elements that lack regional variation in soils of the Wind River Basin.

[Detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed; *, elements measured in percent; other elements measured in parts per million]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline value ¹	Detection ratio
-----	3.6	1.90	1.39	1.2 - 10.8	36:36
-----	28	1.38	1.15	16 - 50	36:36
-----	2.4	1.29	1.23	1.8 - 3.2	36:36
-----	0.85	1.62	1.17	0.34 - 2.1	36:36
-----	2.2	1.93	1.04	0.59 - 8.2	36:36
-----	5.5	1.49	1.16	2.6 - 12	36:36
-----	15	1.70	1.38	6.5 - 35	36:36
-----	1.5	1.36	1.07	0.82 - 2.7	36:36
-----	15	1.32	1.17	9.5 - 24	36:36
-----	0.020	1.45	1.28	0.011 - 0.035	35:36
-----	15	1.49	1.08	6.9 - 33	36:36
-----	0.63	1.54	1.05	0.27 - 1.5	36:36
-----	1.3	1.26	1.03	0.8 - 2.1	36:36
-----	5.3	1.47	1.23	2.8 - 10	34:36
-----	31	1.07	1.03	28 - 35	36:36
-----	340	1.42	1.13	180 - 660	36:36
-----	12	1.43	1.10	6.0 - 24	36:36
-----	0.22	1.22	1.07	0.15 - 0.32	36:36
-----	43	1.31	1.08	26 - 72	36:36

Expected 95-percent range.

TABLE 6.—Statistical summary for the element having regional variation in soils that overlie the three major geologic units in the Bighorn Basin.

[Detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed; *, elements measured in percent; other elements measured in parts per million]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline value ¹	Detection ratio
Willwood Formation					
Zn-----	51	1.32	1.11	30-85	12:12
Fort Union Formation					
Zn-----	66	1.36	1.11	37-118	12:12
Quaternary deposits					
Zn-----	55	1.26	1.11	36-83	12:12

¹Expected 95-percent range.

sorption was used for the determination of Rb concentration.

BASELINE VALUES

A total of 31 elements in soils from the Bighorn Basin (table 2) and 19 elements in soils from the Wind River Basin (table 3) do not exhibit statistically significant

TABLE 7.—Statistical summary for elements having regional variation in soils that overlie the three major geologic units in the Wind River Basin.

[Detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed; *, elements measured in percent; other elements measured in parts per million]

Element	Geometric mean	Geometric deviation	Geometric error	Baseline value ¹	Detection ratio
Moonstone and Arikaree Formations					
Al*-----	4.4	1.18	1.08	3.3- 5.9	12:12
Cr-----	27	1.45	1.11	13 - 55	12:12
K*-----	2.1	1.13	1.06	1.7- 2.6	12:12
Mo-----	3.7	1.64	1.23	1.5- 9.1	11:12
Mn-----	270	1.50	1.15	130 - 580	12:12
Ni-----	12	1.56	1.16	5 - 28	12:12
U-----	2.6	1.15	1.05	2.0- 3.4	12:12
V-----	43	1.44	1.11	21 - 86	12:12
Wind River and Indian Meadows Formations					
Al*-----	5.0	1.16	1.08	3.9- 6.4	12:12
Cr-----	52	1.36	1.11	29 - 93	12:12
K*-----	2.0	1.09	1.06	1.8- 2.3	12:12
Mo-----	5.0	1.43	1.23	2.8- 9.0	12:12
Mn-----	320	1.29	1.15	210 - 490	12:12
Ni-----	21	1.39	1.16	12 - 38	12:12
U-----	2.9	1.27	1.05	1.8- 4.6	12:12
V-----	48	1.22	1.11	34 - 67	12:12
Quaternary deposits					
Al*-----	5.5	1.17	1.08	4.2- 7.2	12:12
Cr-----	61	1.24	1.11	42 - 89	12:12
K*-----	1.9	1.12	1.06	1.6- 2.3	12:12
Mo-----	5.8	1.43	1.23	3.2- 10.0	12:12
Mn-----	420	1.32	1.15	260 - 680	12:12
Ni-----	23	1.25	1.16	16 - 32	12:12
U-----	2.8	1.14	1.05	2.2- 3.6	12:12
V-----	53	1.26	1.11	35 - 80	12:12

¹Expected 95-percent range.

(0.05 probability level) variability between geologic units and do not exhibit excessive analytical error. Thus, a single baseline value is the optimum estimate to describe the total concentrations of these elements in soils from each of these basins (tables 4 and 5). The results of analysis of variance (tables 2 and 3) suggest that the composition of soil samples taken from within different geologic units within a basin are expected to vary little more than the composition of soil samples taken at distances of 5 km or less apart. The baseline value is defined by Tidball and Ebens (1976) as the expected 95-percent range in concentration in samples of soils in these basins. The expected range is estimated from the residual variation after analytical error has been removed. This residual variation is the natural chemical variation measured between samples and excludes variation due to sample preparation and analysis.

Rocks of Paleocene age in the Bighorn Basin consist of thin-bedded, light-colored sandstone and conglomerate with drab to olive-brown shale and some red shale in the upper part (Andrews and others, 1947). The rocks of Eocene age in the Wind River Basin are made up of varicolored claystone and siltstone interbedded with white to gray, fine- to medium-grained arkosic sandstone (Keefer, 1965); about half the soils sampled on the Wind River Formation lay on a drab-colored sandstone and shale sequence and the other half, on varicolored mudstone. In the Bighorn Basin, the rocks of Eocene age are typically a variegated shale with abundant beds of white and yellow sandstone composed of unsorted grains whose mineralogy represents crystalline rather than sedimentary rocks as source material (Van Houten, 1944). The Miocene and Pliocene rocks in the Wind River Basin consist of medium- to coarse-grained, gray to buff, massive to coarsely crossbedded sandstone with common limestone beds, algal reefs, and pumicite beds, and also consist of stratified gray arkosic conglomerate containing boulders of granite and Paleozoic rock (Love, 1970). These rocks of Miocene and Pliocene age are different in composition from strata of Eocene age in the Wind River Basin. The deposits of Quaternary age are highly variable; the soils at the sampling localities on the western end of the barbell in the Wind River Basin are mostly developed in fine-grained alluvium (Thompson, 1954) in the nearly undrained part of the Wind River Basin in which Ocean Lake was formed when irrigation began. Two of the localities at the southeastern end of the same barbell are on low terrace deposits along the Wind River north of the city of Riverton, and four are on erosional remnants of coarse-grained, bouldery, high-terrace deposits (Thompson, 1954). On Quaternary deposits in the Bighorn Basin, three sampling localities are on the Powell terrace 50 to 80 m above present stream level; five are on high, dissected gravelly pediment surfaces older than the Powell terrace; and four are on gravelly pediment surfaces younger than the Powell terrace (Andrews and others, 1947).

The rock types described for the various geologic units differ from one another in ways that suggest they should differ also in chemical composition. The nonsignificant variability between the soils on the geologic units for most elements in both basins suggests that the soils on strata of different ages are not chemically distinct from one another. This implies that either the soils are not genetically related to the rock units which they overlie or, if the soils represent the compositions of the rock units, that the rock units are not chemically distinct from one another. Possibly, the soils are not genetically related to the geologic units because soil composition reflects surficial geology and geomorphology of

Holocene age rather than rock-stratigraphic units of Tertiary age. However, for the Wind River Basin, several elements exhibit significant variability between soils on the various map units.

Zinc is the only element that exhibits a significant variability in soil between map units from the Bighorn Basin (table 2). The soils sampled on the Fort Union Formation had the highest average Zn concentration, and those on the Willwood Formation and deposits of Quaternary age were about equal. However, in the Wind River Basin, eight elements (Al, Cr, K, Mn, Mo, Ni, U, and V) exhibit variability between geologic units that is significant at the 0.05 probability level; Rb was eliminated because of excessive analytical error. All these elements, except K, were highest in average concentration in soils on deposits of Quaternary age and lowest in average concentration on those soils developed in the Miocene Moonstone and Pliocene Arikaree Formations. For K, the trend was reversed. Concentrations of these elements are best described by individual estimates of a baseline for each mapping unit, because the differences between mapping units are greater than the differences between samples within the mapping units. Statistical summaries and baseline values for these elements are given in tables 6 and 7.

Summary data on the average composition of soils of the Bighorn and Wind River Basins, of soils and surficial materials of the Powder River Basin, and of surficial materials of the Western United States are presented in table 8. The data show that, for most elements, the average composition of the soil differs little between the Bighorn Basin, the Wind River Basin, the Powder River Basin, and the Western United States. Concentrations of Na in soil in the Wind River Basin; B, C, and Ca in the Bighorn Basin; and Ba, Be, Mo, and Sr in both basins are 50 to 100 percent higher than in soils in either the Powder River Basin or the Western United States. Li is the only element in the Wind River and Bighorn Basins that is about 50 percent lower in concentration than in either the Powder River Basin or the Western United States. However, concentrations that differ by a factor of one to two are generally within a 95-percent expected range and should not be considered as anomalous values that warrant special consideration.

MAPPING REQUIREMENTS

This geochemical survey is preliminary in character; it is conducted mainly to measure chemical variability and to estimate the magnitude of the sampling effort that will be required to assess the present, natural geochemical status of the soils in each basin. Data from the analysis of variance are useful for estimating the

TABLE 8.—Average concentrations (geometric means) of elements in soils and surficial materials in the Bighorn, Wind River, and Powder River Basins and in the Western United States

[All elements in Bighorn and Wind River Basins are included regardless of the magnitude of analytical error; *, element measured in percent; other elements measured in parts per million; ---, no data available]

Element	Bighorn Basin	Wind River Basin	Powder River Basin		Western United States ³
			Subsurface ¹	B horizon ²	
Al*----	4.0	5.0	---	5.6	5.4
As-----	4.7	3.6	---	---	6.1
B-----	50	28	26	30	22
Ba-----	1300	1500	720	660	560
Be-----	2.0	2.4	.99	---	.6
C-----	1.5	.85	---	.88	---
Ca*-----	3.0	2.2	---	.87	1.8
Ce-----	57	54	---	---	74
Co-----	6.3	5.5	6.3	7.6	8
Cr-----	59	52	49	46	88
Cu-----	20	15	16	17	21
Fe*-----	1.8	1.5	---	2.2	2.0
Ga-----	11	15	13	---	18
Ge-----	.87	.88	---	---	---
Hg-----	.25	.020	.023	.022	.055
K*-----	1.5	2.0	---	2.0	1.7
La-----	36	33	28	---	35
Li-----	18	15	24	27	23
Mg*-----	.86	.63	---	.67	.78
Mn-----	400	320	230	270	389
Mo-----	4.8	5.0	<3	---	---
Na*-----	.53	1.3	---	4.45	1.0
Nb-----	8.9	6.9	6.2	---	11
Ni-----	22	21	15	17	16
Pb-----	8.6	13	17	18	18
Rb-----	55	63	---	---	---
Sb-----	.16	.23	---	---	---
Sc-----	5.9	5.3	7.8	8.6	9
Si*-----	32	31	---	34	---
Sn-----	.71	.87	---	---	---
Sr-----	230	340	160	160	210
Th-----	8.5	12	9.6	---	---
Ti*-----	.26	.22	---	5.29	.21
U-----	2.7	2.9	3.0	---	---
V-----	68	48	87	78	66
Y-----	20	18	17	---	25
Yb-----	2.7	2.6	1.8	---	3
Zn-----	57	43	61	56	51
Zr-----	320	230	140	200	170

¹Connor, Keith, and Anderson (1976).²Tidball and Ebens (1976).³Surficial material, from Shacklette and others (1971a, b, 1973, 1974).⁴Arithmetic mean of four geometric means.⁵Arithmetic mean.

number of samples that would be required within an area of specified size to prepare a reliable map of total element concentration.

Sampling cells 10 km on a side were arbitrarily chosen to illustrate the concepts used in interpreting the analysis of variance and applying it to the preparation

of maps of regional variation. Such variation may easily be mapped as differences between cell averages, if an adequate number of random samples are taken within each cell to produce a stable average. The methods for estimating the minimum number of random samples (n_r) required in each cell, based on the concept of a variance ratio (v), were developed by Miesch (1976). The variance ratio is a ratio of the variance measured *between* increments of distance (in this case 10 km) to the variance measured *within* increments of distance. The minimum number of random samples that need to be collected in each 10-km cell is determined from the following equation:

$$F = 1 + n_r v \quad (1)$$

where n_r is adjusted so that the sum, $(1 + n_r v)$, exceeds the critical F-statistic (F) at the 80 percent confidence interval with 1 and $2n_r - 2$ degrees of freedom.

Table 9 summarizes the number of mappable elements in each basin for increasing n_r values. Maps showing regional distribution of C and Na concentration in soil in the Bighorn Basin and Cr in the Wind River Basin would require a minimum sampling intensity of two random samples per 10-km cell to describe more than half of the natural variation. At the other extreme, it would not be feasible to attempt a mapping program based on 10-km cells for several elements in each basin (elements labeled "n.d." in table 9). For these

TABLE 9.—Minimum number of random samples needed (n_r) in a 10-km square to map total element concentrations in soils of the Bighorn and Wind River Basins at the 80 percent confidence level[---, no element can be mapped in a basin using this n_r value; n.d., not determined because n_r is infinitely large]

n_r	Mappable elements	
	Bighorn Basin	Wind River Basin
2	C, Na	Cr
3	---	Al, Mg, Ni, Sr, Th
4	Ca, Ce, Fe, Mn, Sr	Hg, Mn, Mo, Zn
5	Co, Si	Ga
6	As, Ni, Rb, Sc, Zn	B, Co, Rb, Sc, Ti, U
7	Ba, Ga	Be, Ca, Cu, K
8	Al, Li, Mg	V, Zr
9	Cu	---
10	K, Mo	Fe
12	Nb	C
13	B, Be, Cr, Hg	---
14	---	Yb
17	---	Li, Y
20	Pb	---
25	---	As
n.d.	Ce, La, Sn, Th, Ti, U, V, Y, Yb, Zr	Ba, Ce, Co, La, Na, Nb, Pb, Si, Sn

elements, variation estimated at distances of 10 km or greater was very small or nonexistent, so a minimum sampling intensity could not be calculated. The sampling intensity necessary to map the regional distribution of single elements differs between the Bighorn and Wind River Basins. For example, if there is interest in mapping the regional distribution of Mo in the Bighorn Basin, it would require a minimum of 10 random samples per 10-km cell. To map the regional distribution of Mo in the Wind River Basin would require a minimum of four random samples per cell. The geographic variability of element concentration is unique for any single element in the sampling area.

The previous paragraphs have illustrated the methods for determining minimum sampling intensity for mapping variation in element concentration between 10-km cells. Similar tables of minimum sampling intensities can be constructed for each element in each basin for 5- or 1-km cells by using the analysis-of-variance data in tables 2 or 3 to compute the variance ratios and by using Equation 1 to compute n_r values. The analysis-of-variance data can also be used to estimate the portion of the total variation explained by the size of the geographic unit selected for mapping regional distribution. The proportion of the total variation explained for mapping at a 10-km cell size is determined by summing the analysis-of-variance values for "Between Map Units" and "10-25 km" (tables 2 or 3). For example, mapping Mo at a 10-km interval with a sampling intensity of 10 samples per cell in the Bighorn Basin and 4 samples per cell in the Wind River Basin would describe only about 8 percent of the natural variation of this element in the Bighorn Basin (table 2) and only about 22 percent of the natural variation in the Wind River Basin (table 3). To describe more than half of the natural variation of an element concentration, add together the percent of total variance at each level of the sampling design, starting with the "Between Map Unit" level (tables 2 or 3), until a value of 50 percent is exceeded. To describe more than half of the natural variation of Mo, it would be necessary to sample at a 1-km interval in the Bighorn Basin and at an interval of <1 km in the Wind River Basin. At either of these intervals, the sampling load and costs would be very high.

Because of the dominant local variation for most elements, the baseline value is more practical than a map of regional variation. For most elements, maps prepared at an interval requiring a reasonable sample load would explain a very small portion of the total natural variation, whereas, at the other extreme, maps that explain a reasonable portion of the total natural variation would require such a large sample load as to be impractical at present.

CONCLUSIONS

This reconnaissance study of spatial variation in total concentration of elements in soils in the Bighorn and Wind River Basins suggests the following:

1. Geographic variation in total concentration of elements in soil occurs mainly at distance intervals of less than 5 km.
2. Because of the large local variation, *individual* measurements of total element concentration in soil cannot be extrapolated over great distances.
3. The summary data for a *group* of samples, however, expressed as a baseline value, may be extrapolated over great distances (geologic units or whole basins) depending on the magnitude of the regional variation.
4. The lack of significant variation between geologic units for most elements suggests that soils mask the presumed variation between rock differences that make up the mapping units and possibly indicates that the soil materials are not genetically related to the geologic mapping units. This lack of significant relations between soil composition and geologic units seems reasonable, because soil composition probably reflects differences in surficial geology and geomorphology of Holocene age rather than rock-stratigraphic units of Tertiary age.
5. The average concentration for most elements in soil is not greatly different between the Bighorn, Wind River, and Powder River basins or the Western United States. The geometric means for Ba, Be, Mo, and Sr in soil, however, in both the Bighorn and Wind River Basins are 50 to 100 percent greater than in the Powder River Basin or the Western United States. Concentrations of Na in soil in the Wind River Basin and B, C, and Ca in soil in the Bighorn Basin are also slightly higher than in the other areas. Lithium in soil in the Bighorn and Wind River Basins has an average concentration that is about half that in the Powder River Basin or the Western United States; however, these values generally lie within an expected 95-percent range in concentration and should not be considered anomalous values.
6. The analysis of variance indicates that it is possible to map regional variation in element concentration in soil as differences among 10-km cell averages for C and Na in the Bighorn Basin and for Cr in the Wind River Basin; with only two random samples per cell, a large portion of the natural variation would be described. At the other extreme, it is not feasible to even attempt to map regional variation for several elements, because analysis of variance indicates that little or no variation is expected to exist at 10-km or greater distances. Therefore, for most elements in

soil in both basins, a mapping program designed to describe more than half of the natural variation in element concentration is impractical.

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