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UNITED STATES DEPARTMENT OF THE INTERIOR

U. S. GEOLOGICAL SURVEY

First annual progress report
work in a broad
study of
bearing
[Reports - Open file series]

Geochemical Survey of the Western Coal Regions

First Annual Progress Report, July, 1974

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GEOCHEMICAL SURVEY OF THE WESTERN COAL REGIONS

July, 1974

First annual progress report describing current work in a broad-scaled reconnaissance geochemical study of landscape materials in the major coal-bearing regions of the western United States

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PROGRAM GOALS AND GUIDELINES

by Jon J. Connor

National energy needs have precipitated an increased interest in the development of a large coal-based electric power industry in the western United States. This anticipated development has, in turn, spawned a great deal of interest in the environmental impact consequent upon the mining and utilization of these coal supplies. Numerous studies directed to assessing this impact are underway or are in the planning stages by agencies of government at all levels as well as by educational institutions and private firms. It is expected that such studies will continue to increase in number in the foreseeable future. Some idea of the diversity of this work is given by Boulding (1974), who surveyed a broad spectrum of people and organizations concerned about the environmental impact of coal development in the Northern Great Plains. This survey included over 50 governmental organizations and over 50 nongovernmental organizations.

Much of the work listed in this tabulation indirectly relates to geochemical aspects of the environment, because the very nature of coal-based energy development results in a large potential for environmental transfer of chemical elements. However, work directed solely or predominantly to geochemical aspects of coal development appears to form only a small part, both in manpower and in funding, of the total effort at assessing overall impact. Generally, such work focuses on three subject areas: 1) the spatial distribution of elements and compounds in nature, 2) the transfer (cycling) of elements and compounds in nature, and 3) the changes in distribution or transfer of elements and compounds consequent upon energy development.

Geochemical survey of western coal regions

Our geochemical work in the western coal regions falls largely under the first subject area (above)--the spatial distribution of elements and compounds in nature or, at least, under the landscape conditions existing at present and, presumably, prior to the time of major impact of energy development. This work was begun on a part-time basis on July 1, 1973, and is patterned after a recently completed reconnaissance geochemical survey of the State of Missouri (Connor and others, 1972). As of this writing, four formally funded projects are involved in this work, one each directed to the geologic, pedologic, hydrologic, and botanic materials of the coal regions environment.

We take as our area of investigation all regions in the Rocky Mountains and Northern Great Plains underlain by coal deposits of Cretaceous and Tertiary age (fig. 1). The emphasis of our work is

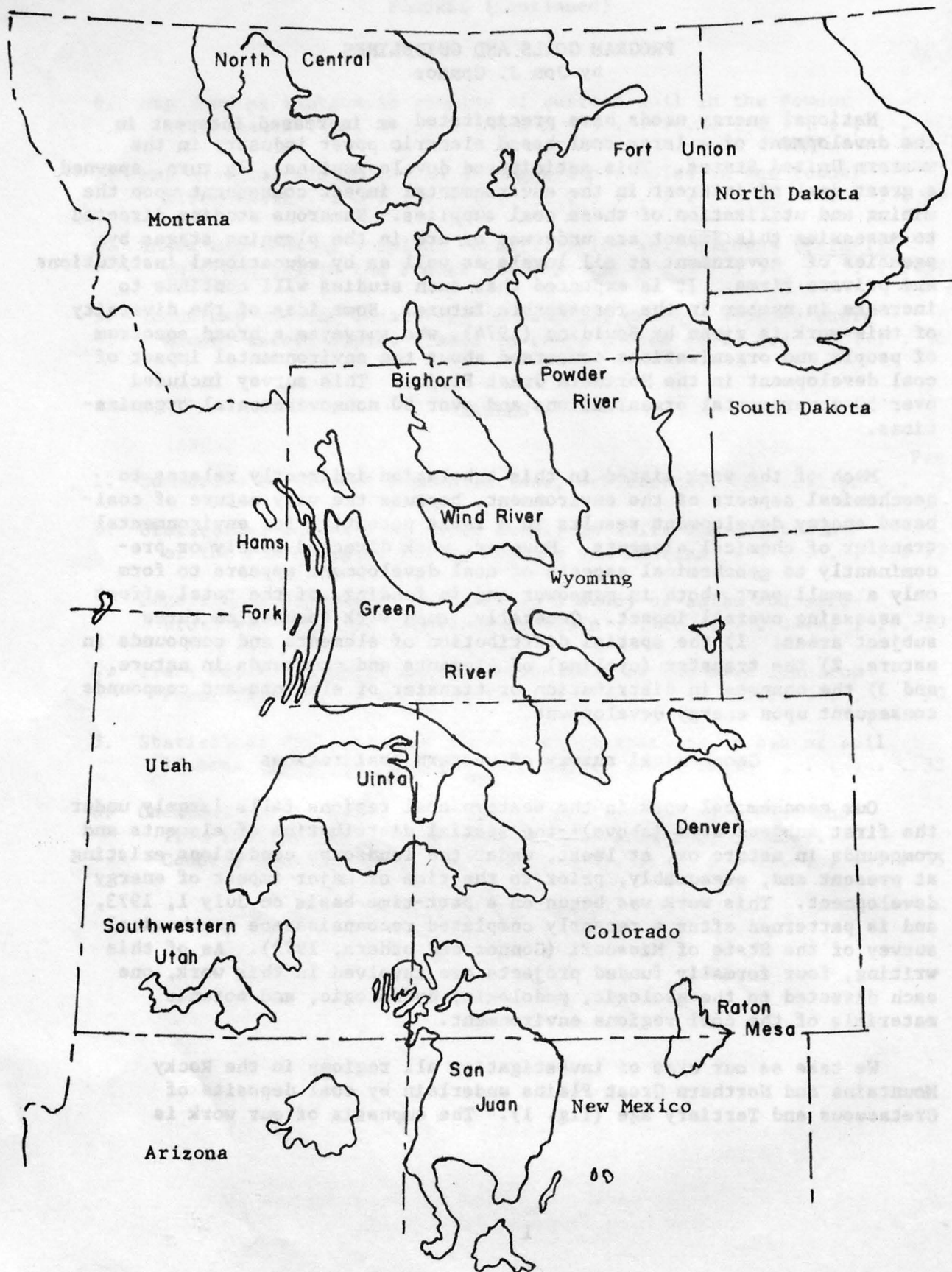


Figure 1. Location of the major coal basins in the western United States (modified from Trumbull, 1960).

directed towards the geochemistry of the environment (landscape materials) of the coal areas and not towards the geochemistry of the coal itself. Preliminary data on coal chemistry may be found in Swanson (1972) and U.S. Geological Survey (1973, 1974). The landscape materials of interest in our work include geologic strata associated with coal, geologic surficial materials, soils, ground and surface waters, and native and cultivated plants.

We intend to examine an aspect of geochemical variation that is particularly difficult to come to grips with--that of demonstrating the magnitude of broad-scale chemical variability of these landscape materials. The purpose of such work is, of course, to determine whether landscapes in the major coal regions, or physiographically distinct parts of them, vary in any important way in their average geochemical properties, particularly their trace metal properties. To the extent that such differences are significant, each such distinct area would require an independent study if the spatial distribution of elements or compounds is to be adequately characterized. In the event that such differences are not deemed significant, a characterization in one area could then be validly applied to other areas. Clearly, an "adequate characterization" would constitute a geochemical baseline against which secular geochemical change could be measured.

There are good reasons, of course, to expect important geochemical differences among the major regions. Areas, or parts of areas, largely underlain by marine or marginal marine Upper Cretaceous rocks should exhibit a rock chemistry distinctly different from areas underlain, or largely underlain, by continental deposits. Soils are expected to exhibit chemical differences reflecting changes in parent material as well as differences reflecting latitudinal or altitudinal changes in climate. A change in dominant vegetation from one region to another will result in differences in plant chemistry due to an apparent "species control" on many trace metals (see Shacklette and others, 1970), and changes in water quality associated with changes in reservoir rocks (ground water) or stream characteristics (surface water) might be paralleled by changes in trace metal content.

Experience demonstrates that important amounts of geochemical variation in landscape materials occur at short-range or "local" scales. For example, trace metal concentrations in soil samples collected close together commonly differ almost as much, on the average, as samples taken 10 or 100 times farther apart. The fundamental problem in surveys of large regions is that of being able to "see through" this local variation and determine the magnitude of the generally weaker regional component. This determination is a prerequisite to any attempts to "map" the regional geochemical picture because it permits both 1) an assessment of the importance of the regional variation--this component may be too small to even worry about--and 2) an assessment of the work or sample load required to produce a stable picture or map. Any assessment of the importance of regional variation and work necessary to describe it is essentially a problem in defining a sampling

interval that can be expected to produce a meaningful geochemical map of the area of interest. A lack of regional variation will force this interval to be so small that the work may become prohibitively expensive.

Hypothetically, a search for the optimum interval may be undertaken as follows: Choose an interval, X km and collect numerous pairs of samples in the area of interest, each pair being separated by X km. The differences in element concentration among these pairs reflect variation arising in nature over a range (scale) of 0 - X km. Repeat the study using a separation of $2X$ km and, again, examine the differences. These differences now reflect variation arising in nature at scales from 0 - $2X$ km, and if this variation is clearly larger than that observed in the first sample set, the difference is attributed to variation arising over the range X - $2X$ km. In this manner, variation over any specified range of geographic scale can be assessed.

Such a procedure would be quite expensive, of course, but there is an experimental design at hand directed to just this kind of problem, the hierarchical case of the analysis of variance where the hierarchy is geographically based. Krumbein and Slack (1956) were the first to apply this procedure to a problem in field geochemistry, Connor and others (1972) touch on its use in Missouri, and our work in the western coal regions will rely heavily on it. The utility of the hierarchical case of the analysis of variance lies in the fact that a number of geographic scales (really, ranges of scale) can be assessed from a single relatively small set of samples.

Once something is known of the scale of geochemical variability, any additional work directed to describing ("mapping") that variation can be based on a sampling interval at which it is known that variation is important. Conversely, a potential sampling interval lying within a range where little or no variation is likely to arise can be rejected as inefficient. The most important benefit, however, is that a knowledge of the scale of variability may well result in a decision to make no map at all, because of a general lack of "mappable" variation at the larger scales of the study area.

Such information is also useful in evaluating a specific type of recurring problem in the use of geochemical "point" data. That is, given a scatter of points for which element concentrations have been measured over an area, how far can an individual value be extrapolated in the geographic sense? If the amount of variation arising from 0 - X km is known, then the element concentration at a point X km away from a known point should be expected to differ from the known concentration to a degree reflecting the amount of variation arising over this scale range.

Summary of first year's work

Geochemical results of the first year's work are described in the four following reports. The first three discuss the elemental composition of soils and plants in the Powder River Basin, and the last lists a few selected analyses of ground waters in the basin. The first report proposes an original definition of the term "geochemical baseline" and gives provisional estimates of such baselines in the Powder River Basin for three soil horizons and a species of sagebrush. The authors define a geochemical baseline as an expected range in concentration rather than as a single concentration value such as an average. They tabulate such ranges for those elements which exhibit no important variation at scales larger than about 10 km. This same report gives a comparison of average elemental concentrations in two species of sagebrush. The marked differences observed indicate the danger of mixing closely related plants in studies aimed at establishing baselines.

The second report is based on work similar in scope and direction to that described in the first, but the focus here is on evaluating the magnitude of four geographic components of trace metal variability in the basin. A discussion on the sampling load required for "mapping" the basin is also given, and these authors conclude, as do those of the first paper, that geochemical variability in soil and sagebrush of the Powder River Basin at scales larger than about 5-10 km is small.

It is gratifying to note that the results of these two studies, undertaken independently, are convincingly close in their assessment of the predominant scale of geographic variation in soil and sagebrush of the Powder River Basin. This indicates that the hierarchical analysis of variance design is a powerful exploratory tool for assessing the magnitude and scale of geochemical variability in nature.

A limited amount of work east of the Dave Johnston Power Plant at the southern edge of the Powder River Basin is also described in the second report. Samples of sagebrush east of the power plant exhibit a statistically significant reduction of selenium, strontium, and vanadium away from the power plant.

The third report describes results of an additional study on the geochemical variability of native plant tissue in the Powder River Basin. A study of elements in soil lichens (Parmelia chlorochroa) demonstrates once again the general lack of basinwide variation in a natural material.

The last report is directed to a brief examination of the gross chemical properties of ground waters associated with coal-bearing rocks in Campbell County, Wyoming.

GEOCHEMICAL BASELINES FOR SAGEBRUSH AND SOIL,

POWDER RIVER BASIN, MONTANA-WYOMING

by Ronald R. Tidball, James A. Erdman,

and Richard J. Ebens

An exploratory study of the Powder River Basin of Montana and Wyoming provides estimates of the element composition of big sagebrush (*Artemisia tridentata*) and associated soils and soil parent materials. For most elements studied, large-scale (regional) variation is negligible compared to the magnitude of the variation at scales less than 10 km (local variation), and we believe that these data can be used as provisional geochemical baselines for the basin as a whole.

Geochemical baselines--a definition

We define a geochemical baseline as the expected range of concentration of an element or chemical compound in a specified sampling medium. We choose as the "expected range" the central 95-percent range, as estimated from the moment properties of the logarithmic frequency distribution of the element. We consider this range to be the most important statistic in assessing geochemically anomalous or unusual samples because it includes consideration not only of the mode of the distribution but also of the variation. We accept the geometric mean (GM) of the observed values as the mode of an element distribution, and we consider it to be the best estimate of the typical or most probable concentration in the area of study. We suggest that the GM, by itself, should not be used to define baseline because it says nothing of the variability that is always present in nature.

The expected ranges in table 1 can be used provisionally as the baseline for any locality within the basin of a size greater than 10 km on a side, because the natural elemental variation is associated predominantly with scales less than about 10 km. In other words, the element concentration of any pair of samples located no more than a few km from each other may differ as much as those located at opposite ends of the basin. The estimate of variability due to analytical error has been removed (see Connor and Shacklette, in press), and so the expected 95-percent range represents only variation arising from nonlaboratory causes.

The elements and soil pH listed in table 1 exhibit no significant regional variation at the 0.05 probability level. Summaries for other elements and pH measurements are not reported for the following reasons:

- 1) Barium, copper, and zirconium in sagebrush ash, aluminum in B-horizon soil, and boron in C-horizon soil or soil parent material exhibit significant regional variation at the 0.05 probability level; the 95-percent expected range based on such data would, therefore, perceptibly overestimate the range in any given locality. Additional sampling is required to establish baselines for these elements.

Table 1.--Summaries of element concentrations^{1/}, ash content, and soil pH

Constituent ^{2/}	Material ^{3/}	Geometric mean	Geometric deviation	Expected range (baseline)	Constituent ^{2/}	Material ^{3/}	Geometric mean	Geometric deviation	Expected range (baseline)	Constituent ^{2/}	Material ^{3/}	Geometric mean	Geometric deviation	Expected range (baseline)
Al, percent	S	3.6	1.57	1.5-8.9	Fe, percent	S	1.0	1.58	0.40-2.5	Pb -----	A	19.0	1.33	11-34
	A	6.1	1.36	3.3-11		A	1.7	1.47	.79-3.7		B	18	1.24	12-28
	C	6.6	1.40	3.4-13		B	1.9	1.35	1.0-3.5		C	17	1.21	12-25
B -----	S	270	1.39	140-530		C	1.7	1.58	.68-4.3	Sc -----	A	7.5	1.47	3.5-16
	A	30	1.52	13-69	Ga -----	A	13	1.25	8.3-20		B	8.6	1.43	4.2-18
	B	30	1.52	13-69		C	15	1.42	7.5-30		C	8.5	1.59	3.4-21
Ba -----	A	670	1.20	470-960	Hg -----	S ^{4/}	.022	1.37	.012-0.041	Se -----	S ^{4/}	.31	2.37	.055-1.7
	B	660	1.20	460-950	K, percent	A	2.9	1.10	2.4-3.5	Sr -----	A	140	1.35	76-260
	C	630	1.34	350-1,100		C	3	1.12	2.4-3.8		B	160	1.60	62-410
Ca, percent	A	.57	2.65	.081-4.0	Mg, percent	S	2.1	1.34	1.2-3.7		C	190	1.78	60-600
	B	.94	3.10	.098-9.0		A	.57	1.74	.19-1.7	Ti, percent	S	.13	1.64	.048-0.35
	C	1.7	3.55	.13-21		B	.74	1.77	.24-2.3	V -----	S	47	1.74	15-140
Cd -----	S	5.9	1.73	2.0-18		C	.94	1.98	.24-3.7		A	65	1.54	28-150
Co -----	S	2.3	1.80	.71-7.5	Mn -----	S	560	1.44	270-1,200		B	78	1.38	41-150
	A	6.8	1.69	2.4-19		A	250	1.76	81-770		C	72	1.71	25-210
	B	7.5	1.61	2.9-19		B	220	1.69	77-630	Zr -----	A	230	1.55	96-550
	C	7.3	1.66	2.6-20		C	190	1.96	49-730		B	200	1.39	100-380
Cr -----	S	30	1.72	10-89	Mo -----	S	7.4	1.53	3.2-17		C	160	1.57	65-400
	A	43	1.66	16-120	Ni -----	S	17	1.36	9.2-31	Ash, percent	S	5.3	1.34	2.9-9.6
	B	46	1.47	21-100		A	15	1.66	5.4-42	pH -----	A	7.2 ^{5/}	.42 ^{5/}	6.4-8.0 ^{5/}
	C	49	1.71	17-140		B	17	1.63	6.4-45					
Cu -----	A	15	2.12	3.3-67		C	17	1.91	4.6-62					
	B	17	1.90	4.7-62	P, percent	S	1.1	1.66	.40-3.0					
	C	17	2.75	2.2-130										

^{1/} Means and deviations based on analyses of 64 samples.^{2/} Values in parts per million except as noted.^{3/} S, sagebrush ash; A, surface horizon soil; B, B-horizon soil; C, C-horizon soil.^{4/} Determined on the dry material.^{5/} Standard units of measurement used; arithmetic mean and standard deviation listed; expected range equals arithmetic mean plus or minus two standard deviations.

2) The analyses for lead in sagebrush, lanthanum, titanium, ytterbium, and yttrium in the surface-horizon soil, gallium, lanthanum, potassium, titanium, ytterbium, and yttrium in B-horizon soil, and lanthanum, titanium, ytterbium, and yttrium in C-horizon soil, and pH determination in B- and C-horizon soil, resulted in an analytical error variance equal to more than 50 percent of the total observed variance, which we view as excessive. Baseline estimates for these constituents should be based on a more precise analytical method.

We consider the listed data as provisional because of the relatively few numbers of samples taken and their limited geographic distribution. We are confident, however, that with few exceptions, the expected 95-percent ranges are relatively stable.

The species effect

A very important aspect of baseline investigations based on vegetative material is that of chemical differences among species (Shacklette and others, 1970). As part of our work in the Powder River Basin, we compared the elemental composition of big sagebrush (Artemisia tridentata) to silver sagebrush (A. cana), based on 11 samples of each. The paired plants generally grew within several metres of each other and no pair was separated by more than 10 m.

Of 21 chemical properties, including percent ash, tested by Student's t, nearly half were found to occur in significantly different concentrations in ash of the two species, as follows:

Property	Geometric mean		Student's <u>t</u>
	<u>A. tridentata</u>	<u>A. cana</u>	
Ash, %	4.6	5.4	-2.28
Al, %	3.1	1.7	2.65
B, ppm	320	620	-5.47
Cr, ppm	25	12	4.59
Fe, ppm	9,200	5,500	2.88
Mg, %	2	5	-5.41
Sr, ppm	1,500	2,100	-2.67
Ti, ppm	1,100	670	2.50
V, ppm	46	16	5.09

The critical value of Student's t at the 0.05 probability level for 20 degrees of freedom is 2.086. These results demonstrate the importance of establishing independent geochemical baselines in plant tissue for each plant species of interest.

Baseline--a standard reference

The anticipated environmental impact of the energy resources development in the Powder River Basin requires the establishment of standards against which we can assess the magnitude of changes in the local geochemical environment due to development. Important aspects of this development are surface mining for coal and uranium, mine-mouth coal-fired electric power generation, coal gasification plants, and petroleum production.

Redistribution of elements in landscape materials, resulting from these and other activities, could be detrimental, depending on the future use of the land. Ebens and others (1973) described an example of detrimental redistribution of trace metals related to a small-scale clay-mining operation in central Missouri. This particular operation has apparently affected the health of cattle ranging nearby, and demonstrates just how vulnerable some environments are to geochemical alteration. Had the problem been foreseen at the time of operation, the impact could probably have been mitigated. The baselines used in that study were previously defined in a broad-scale geochemical survey of the Missouri environment. We stress here that anomalous concentrations of trace elements downstream from the claypit area were identified by comparison to expected 95-percent ranges of concentrations.

Understanding the vagaries of element distributions in the local environment may also help in the rehabilitation of surface-mined or otherwise disturbed land, by identifying those materials that should not be left exposed on the surface. Such materials may either be toxic to plants used to revegetate the surface or may impair their growth. Equally important is an understanding of the potential changes in element concentrations of surface materials in disturbed areas that may affect the health of livestock grazing the area.

Experimental design

We collected both the soil and plant samples in the fall of 1973 according to a nested analysis of variance design (figs. 2 and 3) similar to that described by Krumbein and Slack (1956) and Connor and others (1972). The Powder River Basin extends about 400 km in a north-south direction and about 150 km in an east-west direction. We subdivided the long axis of the basin into about 100-km intervals to establish four nearly equal areas. Within each area we randomly located a barbell cluster with the major axis 10 km in length and with both the midpoint and orientation randomly chosen (fig. 3). The ends of this major axis defined the midpoints of two 1-km axes. In a like manner,

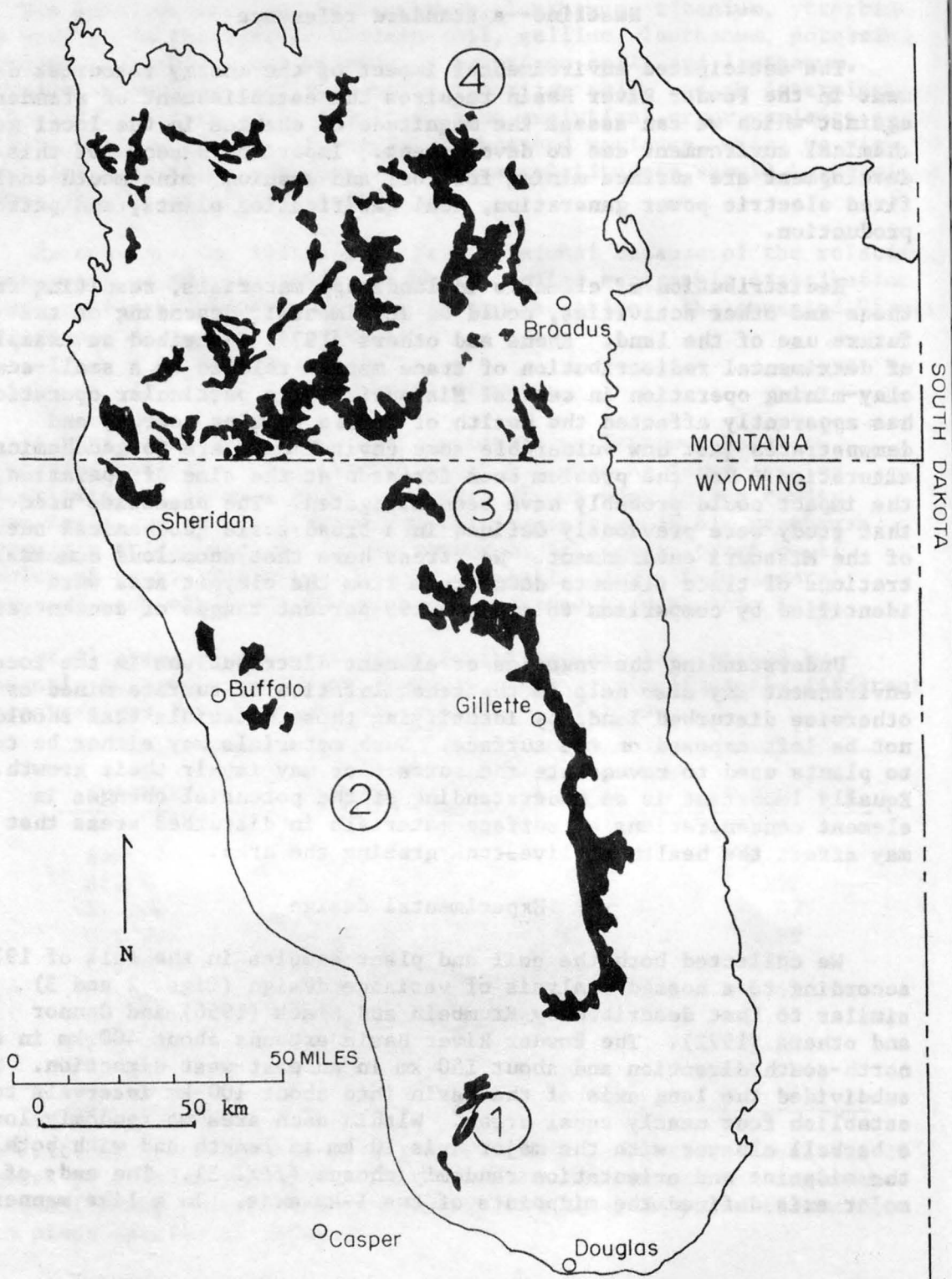


Figure 2. Sampling localities using a barbell-cluster design in the Powder River Basin. Solid patterns indicate known strippable coal reserves. At each numbered locality 16 samples each of big sagebrush (*Artemisia tridentata*), surface soil, B-horizon soil, and C-horizon soil were collected.

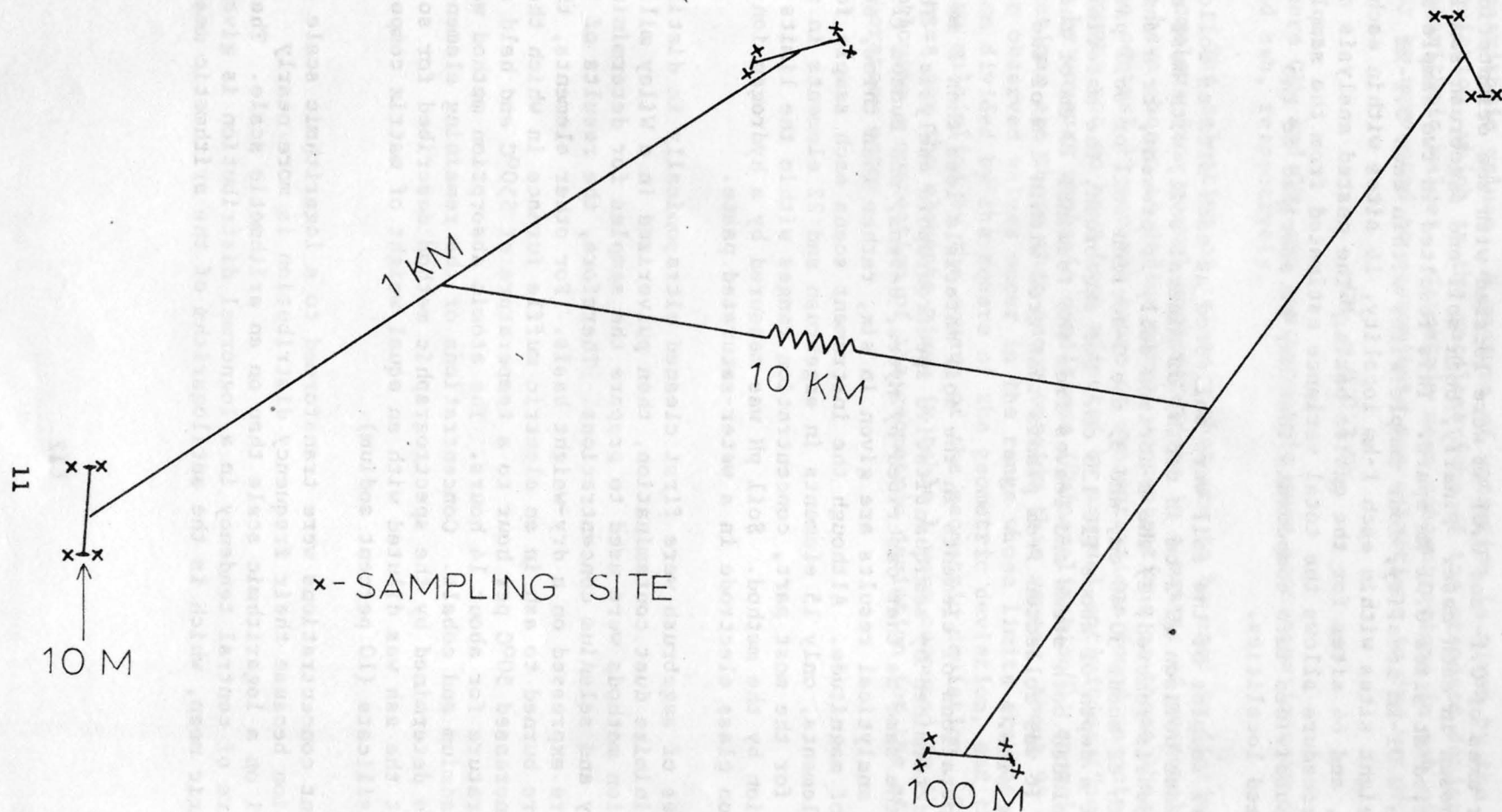


Figure 3. Barbell-cluster design for sampling each locality shown in figure 2.

other minor axes of 0.1- and 0.01-km were located with the orientation randomly chosen in each case. Finally, both soil and sagebrush samples were collected at sites 0.01 km apart. This resulted in two sample sites within each 0.01-km locality, four sample sites within each 0.1-km locality, eight sites within each 1-km locality, 16 sites within each 10-km area, and 64 sites for the entire basin. The nested analysis of variance procedure allows the total variance estimated from the sample set to be subdivided into components that may be ascribed to the various-sized localities.

Channel samples of the soil were collected at each site as follows: 1) the surface horizon (0-2 cm in depth) of mineral soil, with most of the plant debris removed; 2) the B-horizon soil, if present, or a sample from a depth of about 30-40 cm; and 3) the C-horizon soil or soil parent material at a depth of about 110-120 cm. For sagebrush, the material sampled included both stems and leaves from the terminal 10 cm of the branches. It was collected from plants that grew within 1 m of the soil-sample site.

Concentrations of elements in the soil materials less than 2 mm in size were determined by semiquantitative spectrographic analysis. This method is the same as that described by Myers, Havens, and Dunton (1961), except the analytical results are given in six, rather than three, steps per order of magnitude. Although the instrument scans each sample for about 60 elements, only 15 elements in sagebrush and 22 elements in soils exhibited, for the most part, concentration ranges within the limits of determination by the method. Soil pH was measured by a hydrogen ion-specific ion glass electrode in a water-saturated paste.

Samples of sagebrush were first cleaned ultrasonically in distilled water to minimize dust contamination, then pulverized in a Wiley mill. Wet digestion methods were used to prepare the samples for determining the mercury and selenium concentrations. Therefore, the results of these elements are expressed on a dry-weight basis. For other elements, the samples were burned to ash in an electric muffle furnace in which the heat was increased 50°C per hour to a temperature of 550°C and held at this temperature for about 14 hours. The atomic absorption method was used for cadmium and cobalt. Concentrations of the remaining elements in ash were determined by the spectrographic method described for soils, except that the ash was diluted with an equal weight of matrix composed of sodium silicate (10 percent sodium).

Element concentrations were transformed to a logarithmic scale prior to evaluation because their frequency distribution is more nearly symmetrical on a logarithmic scale than on an arithmetic scale. The best measure of central tendency in a lognormal distribution is given by the geometric mean, which is the antilogarithm of the arithmetic mean of

logarithmic values. A measure of variation is given by the geometric deviation, which is the antilogarithm of the standard deviation of the logarithmic values. Geometric mean concentrations in ash of sagebrush may be converted to approximate concentrations in dry weight by:

$$GM_D = 0.053 GM_A \quad (1)$$

where GM_D and GM_A are the geometric mean concentrations in dry material and ash, respectively.

The selection of criteria that are to be used in distinguishing anomalous from normal concentrations is a matter of personal judgment. We have chosen to define normal concentrations as those that are within the central 95-percent range of concentrations found in materials thought not to have been affected by unusual activities ("pollution") or by unusual geologic conditions ("mineralization"); anomalous concentrations are those that occur outside this range. About 95 percent of the observed values occur in the range whose limits are the geometric mean divided by the square of the geometric deviation, and the geometric mean multiplied by the square of the geometric deviation. The expected ranges for the elements given in table 1 were computed on this basis following a correction of the geometric deviation for the effects of laboratory error.

TRACE METAL VARIATION IN THE POWDER RIVER BASIN

by John R. Keith, Barbara M. Anderson, and
Jon J. Connor

This report describes a reconnaissance study of the trace metal chemistry of soil and sagebrush (Artemisia tridentata) in the Powder River Basin. The work on which this report is based is similar in scope and direction to that of Tidball, Erdman, and Ebens (preceding report) but was done independently and is based on a different configuration of sample localities. The study consisted of two parts, the more important part of which is a basinwide assessment of scale-related components of trace metal variation in soil and sagebrush. The second part of this study consists of a preliminary examination of the trace metal content of soil and sagebrush east of the Dave Johnston Power Plant located on the southern edge of the basin.

Geographic variation

The sampling localities used in the basinwide study were placed within 12 nearly square units or cells about 70 km on a side, covering most of the Powder River Basin (fig. 4). Within each cell, we randomly selected two townships (outlined in black) and three sections (solid dots) within those townships. One of the sections in each township (shown by a tick mark) was randomly selected for duplicate sampling. In these sections, two sampling localities about 300 m apart were sampled.

At each of the 48 localities sampled in the basin, three samples were collected: 1) a sample of about 50 g of the terminal stems and leaves from a single sagebrush plant, 2) as near as practical to the sampled plant, a sample of about 200 g of the upper 2½ cm of vegetation-free soil was collected, and 3) at the same point a second sample of soil of about 200 g was collected 15-20 cm below the surface.

The unequal distribution of sagebrush species prevented the collection of a single species throughout the basin. However, at 41 of the 48 localities we sampled Artemisia tridentata, and the trace metal chemistry of these 41 samples is used in this study to assess trace element variability in natural vegetation.

Each material sampled fits into a hierarchical analysis of variance design, described below, of the kind first used in a geochemical field problem by Krumbein and Slack (1956). In such designs the geochemical differences observed among averages computed for the larger units of the design (cells and townships) reflect mostly geologic factors operating at large scales, and differences among averages computed for the smaller units (sections and localities) reflect geologic factors operating over shorter distances.

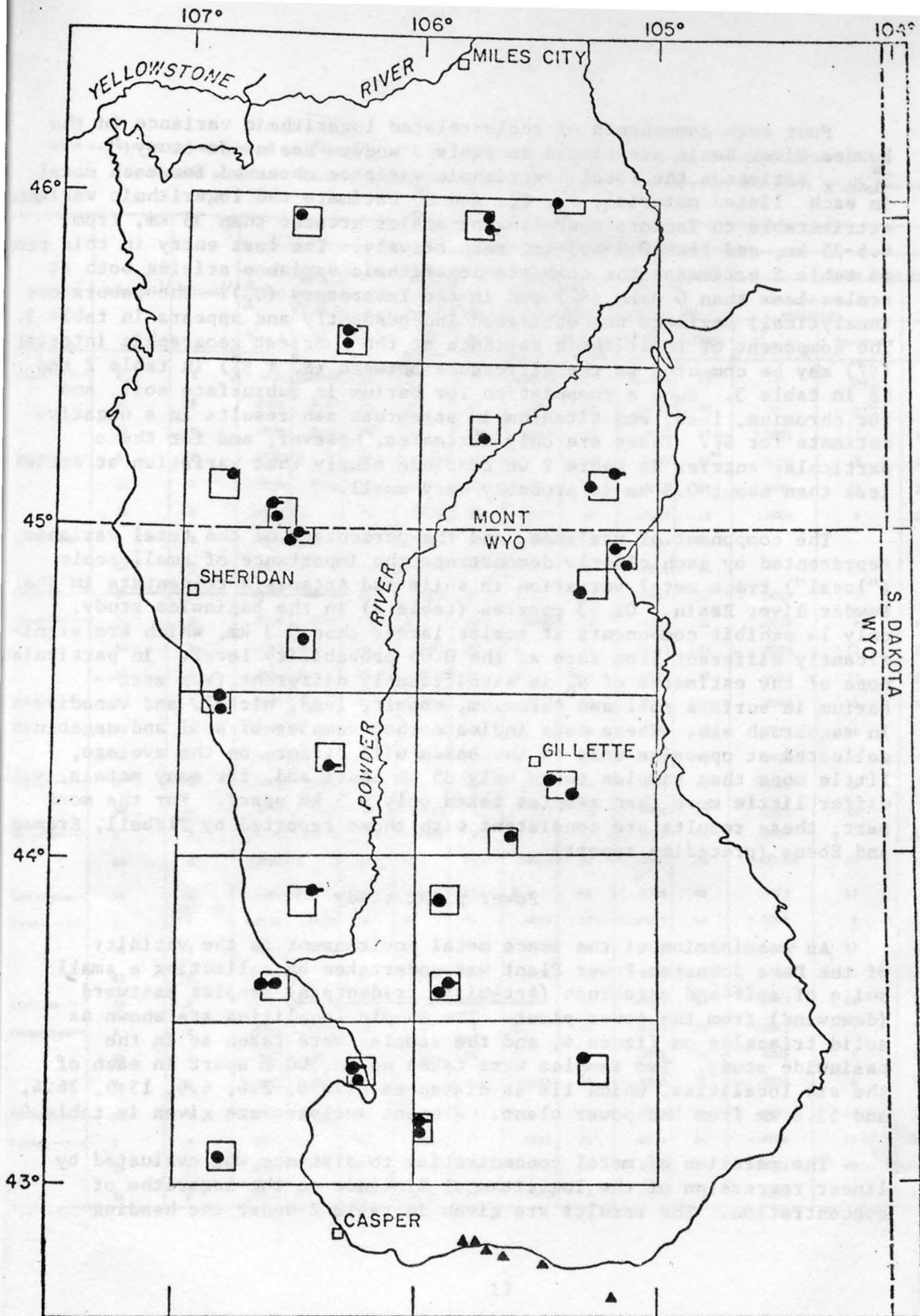


Figure 4. Sampling localities using a nested-cell design in the Powder River Basin. Solid dots are sampling localities used in the basinwide study; solid triangles are localities used in the Dave Johnston Power Plant study.

Four such components of scale-related logarithmic variance in the Powder River Basin are listed in table 2 under "Basinwide study." $S_{\text{Log } x}^2$ estimates the total logarithmic variance observed for each metal in each listed material, S_B^2 , S_T^2 , and S_S^2 estimate the logarithmic variance attributable to factors operating at scales greater than 35 km, from 4.5-35 km, and from 0.3-4.5 km, respectively. The last entry in this part of table 2 estimates the combined logarithmic variance arising both at scales less than 0.3 km (S_L^2) and in the laboratory (S_E^2). The laboratory (analytical) variance was estimated independently and appears in table 3. The component of logarithmic variance at the shortest geographic interval (S_L^2) may be computed as the difference between ($S_L^2 + S_E^2$) in table 2 and S_E^2 in table 3. Such a computation for barium in subsurface soil, and for chromium, lead, and titanium in sagebrush ash results in a negative estimate for S_L^2 . These are only estimates, however, and for these particular entries in table 2 we conclude simply that variation at scales less than about 0.3 km is probably very small.

The component of variance, and the percentage of the total variance represented by each clearly demonstrate the importance of small-scale ("local") trace metal variation in soils and Artemisia tridentata in the Powder River Basin. Of 53 entries (table 2) in the basinwide study, only 14 exhibit components at scales larger than 0.3 km, which are significantly different from zero at the 0.05 probability level. In particular, none of the estimates of S_B^2 is significantly different from zero--barium in surface soil and chromium, cobalt, lead, nickel, and vanadium in sagebrush ash. These data indicate that samples of soil and sagebrush collected at opposite ends of the basin will differ, on the average, little more than samples taken only 35 km apart and, for many metals, will differ little more than samples taken only 4.5 km apart. For the most part, these results are consistent with those reported by Tidball, Erdman, and Ebens (preceding report).

Power plant study

An examination of the trace metal environment in the vicinity of the Dave Johnston Power Plant was undertaken by collecting a small suite of soil and sagebrush (Artemisia tridentata) samples eastward (downwind) from the power plant. The sample localities are shown as solid triangles on figure 4, and the samples were taken as in the basinwide study. Two samples were taken up to 300 m apart in each of the six localities, which lie at distances of 0.8, 2.6, 6.6, 13.5, 26.4, and 53.8 km from the power plant. Element analyses are given in table 4.

The relation of metal concentration to distance was evaluated by linear regression of the logarithm of distance on the logarithm of concentration. The results are given in table 2 under the heading

Table 2.--Statistical analyses of trace metals in soils and sagebrush of the Powder River Basin, Wyoming and Montana

[* , component of variance tested to be significantly different from zero at the 0.05 probability level; --, no data available.]

Metal	Material ^{1/}	Method ^{2/}	Analysis of logarithmic variance												
			Total	Basinwide study						Power plant study					
				Between supertownships (>35 km)		Between townships (35-4.5 km)		Between sections (4.5-0.3 km)		Between samples ^{3/} (0.3-0 km)		Distance-related variance		Regression ^{4/} parameters	
				S ² _{Log X}	S ² _B	Percent	S ² _T	Percent	S ² _S	Percent	S ² _L +S ² _E	Percent	S ² _{Log D}	Percent	\hat{a}
Boron-----	S	E	0.0473	0.0080	17	0	<1	0.0268*	57	0.0125	27	--	--	--	--
	SS	E	.0372	.0067	18	0	<1	.0084	22	.0221	60	--	--	--	--
	SA	E	.0225	.0026	11	0	<1	.0049	22	.0150	67	0.0001	7	2.48	-0.02
Barium-----	S	E	.0288	0	<1	.0099*	34	0	<1	.0189	66	.0004	7	2.84	.04
	SS	E	.0210	.0025	12	0	<1	.0125*	59	.0060	28	.0023	23	2.85	.09
	SA	E	.0563	0	<1	.0213	38	.0233	41	.0117	21	.0004	2	2.88	.04
Beryllium--	S	E	.0159	0	<1	.0052	33	.0002	1	.0104	66	--	--	--	--
	SS	E	.0322	0	<1	.0051	16	0	<1	.0271	84	--	--	--	--
Cadmium----	SA	A	.1073	.0255	24	.0212	20	0	<1	.0607	57	.0007	3	.68	-.05
Chromium----	S	E	.0376	.0050	13	0	<1	.0209*	56	.0117	31	.0010	6	1.51	-.06
	SS	E	.0265	0	<1	.0072	27	0	<1	.0193	73	.0023	12	1.44	.09
	SA	E	.0865	0	<1	.0605*	70	0	<1	.0260	30	.0063	17	1.58	-.15
Cobalt-----	S	E	.0265	0	<1	.0025	9	.0156*	59	.0084	32	.0007	5	.65	.05
	SS	E	.0360	0	<1	.0102	28	0	<1	.0258	72	.0034	14	.57	.11
	SA	A	.1335	0	<1	.0535*	40	0	<1	.0800	60	.0055	28	.61	-.14
Copper-----	S	E	.0597	.0064	11	0	<1	.0262	44	.0271	45	.0001	<1	.84	.02
	SS	E	.0499	.0047	9	.0023	5	.0013	3	.0416	83	.0071	14	.68	.16
Gallium----	S	E	.0136	.0004	3	.0009	6	0	<1	.0123	91	.0004	7	1.07	.04
	SS	E	.0124	0	<1	0	<1	.0053	42	.0071	58	.0040*	40	1.02	.12
Lanthanum--	SS	E	.0394	0	<1	.0058	15	0	<1	.0336	85	.0023	13	1.41	.09
Lead-----	S	E	.0114	.0018	16	0	<1	.0019	17	.0077	67	<.0001	6	1.28	.01
	SS	E	.0447	.0060	13	0	<1	.0273*	61	.0114	26	.0040*	57	1.08	.12
	SA	E	.0391	0	<1	.0231*	59	.0030	8	.0130	33	.0018	6	1.92	.08
Lithium----	SA	A	.0786	0	<1	.0285	36	0	<1	.0501	64	.0047	25	1.31	-.13
Manganese--	S	E	.0826	.0073	9	.0047	6	0	<1	.0705	85	.0023	7	2.29	.09
	SS	E	.0421	.0055	13	.0119	28	0	<1	.0246	59	.0001	1	2.29	.02
	SA	E	.0453	.0095	21	0	<1	.0216	48	.0143	31	.0010	6	2.72	.06
Molybdenum	SA	E	.0317	.0042	13	.0009	3	0	<1	.0266	84	.0023	13	1.05	-.09
Nickel-----	S	E	.0371	0	<1	.0043	11	.0093	25	.0236	64	.0034	11	1.03	-.11
	SS	E	.0396	0	<1	.0041	10	0	<1	.0356	90	<.0001	<1	.94	.01
	SA	E	.0315	0	<1	.0187*	59	.0005	2	.0123	39	.0010	8	1.24	-.06

Table 2.--Statistical analyses of trace metals in soils and sagebrush of the Powder River Basin, Wyoming and Montana -- Continued

* , component of variance tested to be significantly different from zero at the 0.05 probability level; --, no data available¹

Metal	Material ^{1/}	Method ^{2/}	Analysis of logarithmic variance											Regression parameter	
			Basinwide study									Power plant study			
			Total $S^2_{\text{Log } X}$	Between supertownships (>35 km)		Between townships ($35-4.5$ km)		Between sections ($4.5-0.3$ km)		Between samples ^{3/} ($0.3-0$ km)		Distance-related variance			
				S^2_B	Percent	S^2_T	Percent	S^2_S	Percent	$S^2_L+S^2_E$	Percent	$S^2_{\text{Log } D}$	Percent		
Niobium----	S	E	--	--	--	--	--	--	--	--	--	.0007	20	.94	
Scandium----	S	E	.0465	0	<1	.0078	17	.0138	30	.0249	54	<.0001	<1	.70	
	SS	E	.0338	0	<1	.0067	20	.0002	1	.0268	79	.0018	12	.66	
Selenium----	SA ^{5/}	D	.2751	.0041	2	.0646	23	0	<1	.2064	75	.0564*	82	-.04	
Strontium----	S	E	.0383	0	<1	.0156	41	0	<1	.0226	59	.0003	2	2.29	
	SS	E	.0298	.0067	23	.0021	7	.0022	8	.0188	63	.0023	9	2.25	
	SA	E	.1020	.0036	4	0	<1	.0610*	60	.0374	37	.0234*	53	3.16	
Thorium----	S	N	.0143	0	<1	0	<1	.0063	44	.0080	56	.0055	30	.93	
	SS	N	.0138	.0008	6	0	<1	0	<1	.0130	94	.0071*	38	.91	
Titanium----	SA	E	.0379	0	<1	.0186	49	0	<1	.0193	51	.0071	32	3.33	
Uranium----	S	N	.0161	0	<1	.0057	36	.0025	15	.0079	49	.0007	13	.40	
	SS	N	.0155	0	<1	.0051	33	.0021	14	.0083	53	.0014	18	.37	
Vanadium----	S	E	.0230	0	<1	.0100	44	.0063	27	.0067	29	.0018	11	1.79	
	SS	E	.0273	0	<1	.0043	16	0	<1	.0230	84	<.0001	1	1.78	
	SA	E	.0968	0	<1	.0575*	59	.0096	10	.0297	31	.0147*	49	2.00	
Ytterbium----	S	E	.0198	.0017	9	0	<1	0	<1	.0180	91	.0007	15	.16	
	SS	E	.0188	.0007	3	0	<1	.0030	16	.0152	81	.0010	8	.14	
Yttrium----	S	E	.0183	.0020	11	0	<1	.0110*	60	.0052	28	.0007	6	1.11	
	SS	E	.0169	.0003	2	.0019	11	0	<1	.0147	87	.0028	28	1.04	
Zinc-----	SA	A	.0182	0	<1	.0027	15	.0074	41	.0080	44	.0028	31	2.71	
Zirconium----	S	E	.0260	0	<1	.0035	13	.0078	30	.0147	57	.0001	1	2.18	
	SS	E	.0279	.0043	15	0	<1	.0135*	48	.0101	36	.0047	21	2.31	
	SA	E	.0403	.0044	11	.0015	4	.0055	14	.0289	72	.0028	14	1.91	

1/ S, surface soil 0-2.5 cm depth; SS, subsurface soil 15-20 cm depth; SA, ash of sagebrush (*Artemisia tridentata*).

2/ E, semi-quantitative emission spectrography; A, atomic absorption; N, neutron activation; D, 2-3 diamionaphthalene extraction, fluorimetry.

3/ Includes laboratory variance.

4/ Coefficients of prediction equation, $\text{Log } X = \hat{a} + b \text{ Log } D$.

5/ Determined in dry weight.

Table 3.--Logarithmic laboratory variance in a study of soils and sagebrush ash from the Powder River Basin

[----, no data]

Metal	Material	
	Soil	Sagebrush
Boron -----	0.0083	0.0053
Barium -----	.0122	.0104
Beryllium -----	.0042	-----
Cadmium -----	-----	.0044
Chromium -----	.0117	.0312
Cobalt -----	.0014	.0266
Copper -----	.0039	-----
Gallium -----	.0029	-----
Lanthanum -----	.0158	-----
Lead -----	.0056	.0264
Lithium -----	-----	.0053
Manganese -----	< .0001	.0054
Molybdenum -----	-----	.0084
Nickel -----	.0084	.0049
Niobium -----	.0046	-----
Scandium -----	.0050	-----
Selenium -----	-----	.0028 ^{1/}
Strontium -----	.0080	.0063
Thorium -----	.0016	-----
Titanium -----	-----	.0205
Uranium -----	.0002	-----
Vanadium -----	.0067	.0203
Ytterbium -----	.0120	-----
Yttrium -----	.0052	-----
Zinc -----	-----	.0013
Zirconium -----	.0065	.0108

^{1/} Determined on dry weight.

Table 4.--Trace metals in soils and sagebrush ash east of the Dave Johnston Power Plant

[Analysts: P. J. Aruscavage, Ardith Bartel, T. F. Harms, H. T. Mallard, Jr., H. G. Neiman, C. S. E. Papp, and R. A. Zielinski.]

Laboratory No.	Aluminum	Boron	Barium	Beryllium	Cadmium	Chromium	Cobalt	Copper	Gallium	Lanthanum	Lead	Lithium	Manganese	Molybdenum	Nickel	Niobium	Scandium	Selenium	Strontium	Thorium	Titanium	Uranium	Vanadium	Ytterbium	Yttrium	Zinc	Zirconium
Surface soil																											
D161965	0.8	20	700	< 1	---	50	5	10	15	50	20	---	200	< 3	15	10	7	---	200	7.9	1,500	2.6	70	1.5	15	---	150
D161893	.8	20	700	1	---	30	5	7	10	50	20	---	150	< 3	10	10	5	---	150	7.1	1,500	2.7	70	1.5	15	---	150
D161968	2.6	< 20	700	< 1	---	20	5	5	10	30	20	---	200	< 3	5	< 10	< 3	---	200	10.3	1,500	2.2	50	1.5	15	---	200
D161895	2.6	< 20	700	< 1	---	20	< 3	2	10	< 30	15	---	100	< 3	5	< 10	< 3	---	150	6.8	1,000	1.8	30	1	< 10	---	100
D161986	6.6	30	700	1	---	30	5	15	15	30	20	---	300	< 3	15	10	7	---	300	11.2	2,000	3.2	70	1.5	15	---	150
D161955	6.6	20	1,000	1.5	---	30	7	10	15	50	20	---	500	< 3	15	< 10	7	---	500	21.3	2,000	3.5	70	2	15	---	100
D161917	13.5	< 20	700	1	---	70	7	10	15	30	20	---	500	< 3	10	< 10	10	---	200	15.6	2,000	3.4	70	2	15	---	200
D161850	13.5	30	500	1	---	30	5	10	15	50	20	---	300	< 3	15	< 10	5	---	200	16.2	1,500	3.6	70	2	20	---	200
D161861	26.4	20	700	< 1	---	20	5	7	10	< 30	20	---	200	< 3	7	10	5	---	150	11	2,000	2.8	30	1.5	15	---	200
D161918	26.4	< 20	1,000	< 1	---	20	5	7	10	30	20	---	200	< 3	5	< 10	< 5	---	150	8.3	1,500	2.5	30	1.5	10	---	150
D161902	53.8	< 20	700	1	---	20	5	5	15	50	20	---	150	< 3	5	< 10	5	---	200	15.6	1,500	2.9	50	2	20	---	70
D161957	53.8	< 20	1,000	1	---	30	5	7	15	30	20	---	300	< 3	7	< 10	5	---	300	12.6	2,000	2.8	50	1.5	15	---	150
Subsurface soil																											
D161943	0.8	20	700	< 1	---	30	5	5	10	30	10	---	200	< 3	10	< 10	5	---	150	8.6	2,000	2.4	70	1.5	15	---	200
D161921	.8	20	700	< 1	---	30	5	3	10	30	10	---	150	< 3	7	15	5	---	100	7.6	2,000	2.4	70	1.5	10	---	200
D162001	2.6	< 20	1,000	< 1	---	20	< 3	5	10	< 30	20	---	200	< 3	7	< 10	< 3	---	300	8.7	1,500	2	50	1	10	---	200
D161949	2.6	< 20	700	< 1	---	20	< 3	2	10	< 30	15	---	100	< 3	5	< 10	< 3	---	200	5.8	1,000	1.6	30	1	< 10	---	150
D161947	6.6	50	700	1	---	50	7	20	15	50	15	---	300	< 3	15	10	10	---	300	17.6	3,000	3.2	70	2	15	---	200
D161938	6.6	30	1,000	1	---	30	5	15	20	< 30	15	---	700	< 3	10	< 10	7	---	500	14.4	1,500	3.4	70	1.5	15	---	100
D161846	13.5	20	500	1	---	50	5	10	15	50	15	---	200	< 3	15	10	7	---	200	14.5	1,500	3.4	70	2	15	---	200
D161907	13.5	< 20	1,000	1	---	50	7	10	15	30	15	---	200	< 3	15	10	7	---	200	15.9	2,000	3.5	70	3	20	---	200
D161919	26.4	< 20	1,500	< 1	---	50	5	7	10	< 30	15	---	200	< 3	7	< 10	5	---	100	9.1	2,000	2.9	50	1.5	15	---	300
D161900	26.4	< 20	1,000	1	---	30	7	7	15	50	20	---	200	< 3	7	< 10	5	---	200	9.6	2,000	3.2	70	1.5	15	---	100
D161935	53.8	< 20	1,000	1.5	---	20	5	5	20	50	20	---	150	< 3	7	< 10	5	---	300	17	1,500	2.4	50	1.5	15	---	70
D161987	53.8	< 20	1,000	1	---	50	5	7	15	30	20	---	200	< 3	7	< 10	7	---	300	16	1,500	2.6	50	1.5	15	---	100
Sagebrush ash 1/																											
D416136	0.8	300	700	< 1	3.0	30	3	150	15	---	150	16	500	10	20	---	15	0.9	2,000	----	2,000	---	100	< 2	< 20	540	70
D416187	.8	300	500	< 1	5.9	15	5	150	10	---	70	12	1,000	15	10	---	< 10	1.6	700	----	1,500	---	70	< 2	< 20	500	70
D416135	2.6	300	700	< 1	8.3	50	3	150	15	---	50	35	300	7	20	---	10	.7	1,500	----	2,000	---	100	< 2	< 20	550	70
D416132	2.6	300	1,000	< 1	6.8	70	6	200	20	---	50	24	500	15	30	---	15	.55	1,000	----	3,000	---	150	< 2	30	530	100
D416156	6.6	300	1,000	< 1	3.1	50	4	150	15	---	150	22	500	7	15	---	15	.45	700	----	2,000	---	100	2	20	320	100
D416128	6.6	300	1,000	< 1	1.9	30	2	200	15	---	70	16	500	15	15	---	< 10	.2	1,500	----	1,500	---	70	< 2	< 20	400	70
D416130	13.5	300	700	< 1	3	30	3	150	10	---	150	16	700	7	10	---	< 10	.25	700	----	1,500	---	70	< 2	< 20	270	70
D416172	13.5	300	1,000	< 1	6.8	30	3	150	15	---	200	16	1,000	7	15	---	< 10	.25	1,000	----	1,500	---	70	< 2	< 20	410	70
D416202	26.4	300	1,500	< 1	5.6	15	2	150	< 10	---	100	12	500	7	15	---	< 10	.15	700	----	700	---	30	< 2	< 20	540	30
D416140	26.4	200	1,500	< 1	4.8	30	4	150	15	---	150	14	500	7	20	---	< 10	.25	700	----	2,000	---	70	< 2	< 20	380	70
D416145	53.8	300	500	< 1	3	15	---	150	< 10	---	70	8	700	7	10	---	< 10	.2	300	----	700	---	30	< 2	< 20	420	30
D416179	53.8	300	500	< 1	4	15	2	150	< 10	---	100	12	1,000	15	15	---	< 10	.2	300	----	1,500	---	50	< 2	< 20	280	100

1/ Selenium determined on dry material.

"Power Plant study" and pertain to prediction equations of the form:

$$\text{Log } X = \hat{a} + \hat{b}\text{Log } D \quad (2)$$

$\hat{\text{Log}} X$ is the estimate of the logarithmic concentration, \hat{b} is the slope of the linear trend, and \hat{a} is the expected logarithmic concentration at 1 km. The regression is based on a least-squares criterion, and the estimate of logarithmic variance attributable to the trend is given as $S^2_{\text{Log } D}$ (table 2).

It seems reasonable to require that effects due to the power plant should show up as a decrease in concentration away from the plant; that is, \hat{b} should be negative. Twenty such entries in table 2 are negative but only three of these exhibit variance components significantly different from zero at the 0.05 probability level. They are selenium, strontium, and vanadium, all in sagebrush, and they have been graphed in figure 5. These metals, thus, appear to be prime suspects insofar as potential metal pollution is concerned. However, four other entries may also be considered suspect. Cobalt, lithium, titanium, and zinc in sagebrush exhibit more than 20 percent of their variation as a linear decrease from the power plant, and the associated components of variance are statistically significant at the 0.10 probability level.

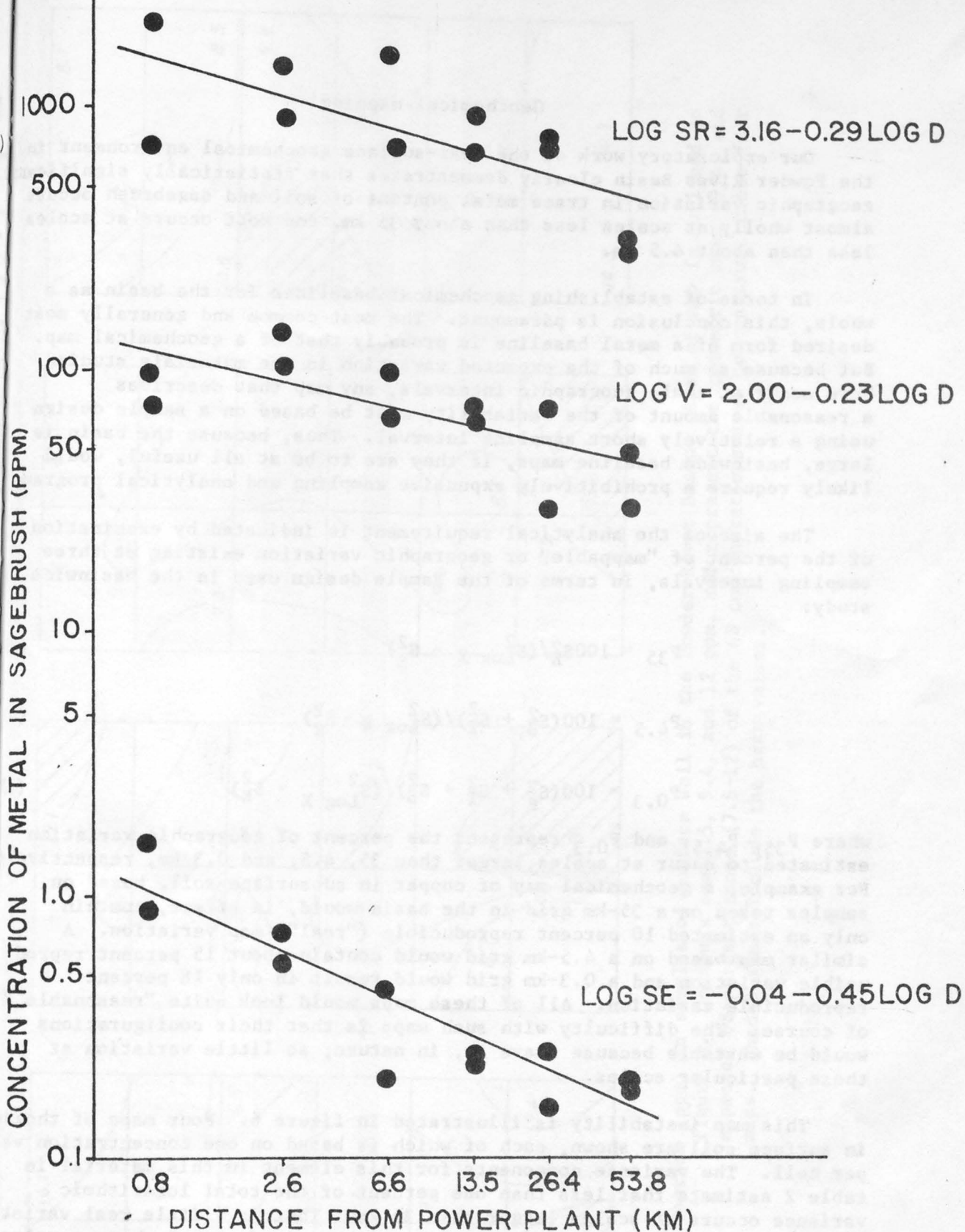


Figure 5. Trend lines relating metal concentration in sagebrush to distance from the Dave Johnston Power Plant.

Our exploratory work on the near-surface geochemical environment in the Powder River Basin clearly demonstrates that statistically significant geographic variation in trace metal content of soil and sagebrush occurs almost wholly at scales less than about 35 km, and most occurs at scales less than about 4.5 km.

In terms of establishing geochemical baselines for the basin as a whole, this conclusion is paramount. The most common and generally most desired form of a metal baseline is probably that of a geochemical map. But because so much of the expected variation in the materials studied here occur at small geographic intervals, any map that describes a reasonable amount of the variability must be based on a sample design using a relatively short sampling interval. Thus, because the basin is large, basinwide baseline maps, if they are to be at all useful, would likely require a prohibitively expensive sampling and analytical program.

The size of the analytical requirement is indicated by examination of the percent of "mappable" or geographic variation existing at three sampling intervals, in terms of the sample design used in the basinwide study:

$$P_{35} = 100S_B^2 / (S_{\text{Log } X}^2 - S_E^2) \quad (3)$$

$$P_{4.5} = 100(S_B^2 + S_T^2) / (S_{\text{Log } X}^2 - S_E^2) \quad (4)$$

$$P_{0.3} = 100(S_B^2 + S_T^2 + S_S^2) / (S_{\text{Log } X}^2 - S_E^2) \quad (5)$$

where P_{35} , $P_{4.5}$, and $P_{0.3}$ represent the percent of geographic variation estimated to occur at scales larger than 35, 4.5, and 0.3 km, respectively. For example, a geochemical map of copper in subsurface soil, based on samples taken on a 35-km grid in the basin would, in effect, contain only an estimated 10 percent reproducible ("real") map variation. A similar map based on a 4.5-km grid would contain about 15 percent reproducible variation and a 0.3-km grid would result in only 18 percent reproducible variation. All of these maps would look quite "reasonable," of course. The difficulty with such maps is that their configurations would be unstable because there is, in nature, so little variation at these particular scales.

This map instability is illustrated in figure 6. Four maps of thorium in surface soil are shown, each of which is based on one concentration value per cell. The variance components for this element in this material in table 2 estimate that less than one percent of the total logarithmic variance occurs at scales larger than 35 km. That is, little real variation exists that can be shown on a map such as those in figure 6 where samples are spaced at an average interval greater than 35 km. As judged by the

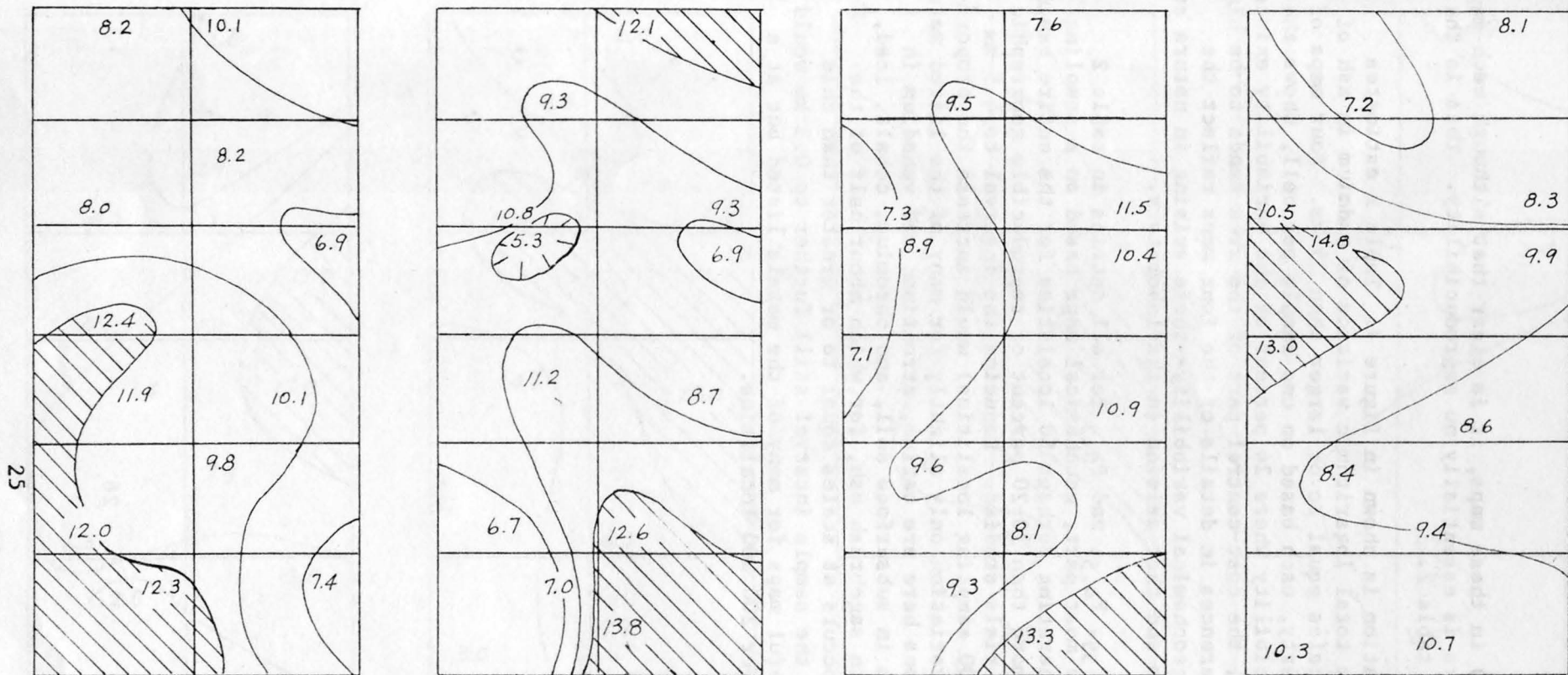


Figure 6. Thorium (ppm) in samples of surface soil in the Powder River Basin. Area of map is outlined in figure 4. Contours are 7.5, 9.4, and 12 ppm, and represent the geometric mean (9.4) and expected 68-percent range (7.5-12) of the 48 concentrations used to construct these four maps. Shaded areas include the high values.

"highs" (shaded areas) in these maps, it is clear that although each map looks reasonable, there is essentially no reproducibility. This is the meaning of results in table 2.

A different situation is shown in figure 7. Table 2 estimates that 24 percent of the total logarithmic variance of cadmium in ash of sagebrush occurs at scales equal to or larger than 35 km. Four maps of this geochemical property, each based on one sample per cell, shows the degree of map reproducibility where 24 percent of the variability exists among cells. Clearly, the east-central part of the area tends to be high in cadmium. The differences in details of the four maps reflect the remaining sources of geochemical variability--those arising in nature at scales less than 35 km and that arising in the laboratory.

Computations of P_{35} , $P_{4.5}$, and $P_{0.3}$ for all entries in table 2 indicate that, for the most part, geochemical maps based on a sampling interval of 35 km (generating perhaps 50 localities for the entire basin) would rarely contain more than 10-20 percent of reproducible geographic variation for the materials studied. Reducing the interval to 4.5 km (generating about 2,600 sampling localities) would increase the proportion of reproducible variation only slightly for many of the listed metals. The important exceptions here are barium, strontium, and vanadium in surface soil, chromium in subsurface soil, and chromium, cobalt, lead, nickel, and vanadium in sagebrush ash, for which about half of the geographic variation occurs at scales equal to or greater than this interval. Decreasing the sample interval still further to 0.3 km would probably result in useful maps for many of the metals listed but at a cost of sampling in over 200,000 localities.

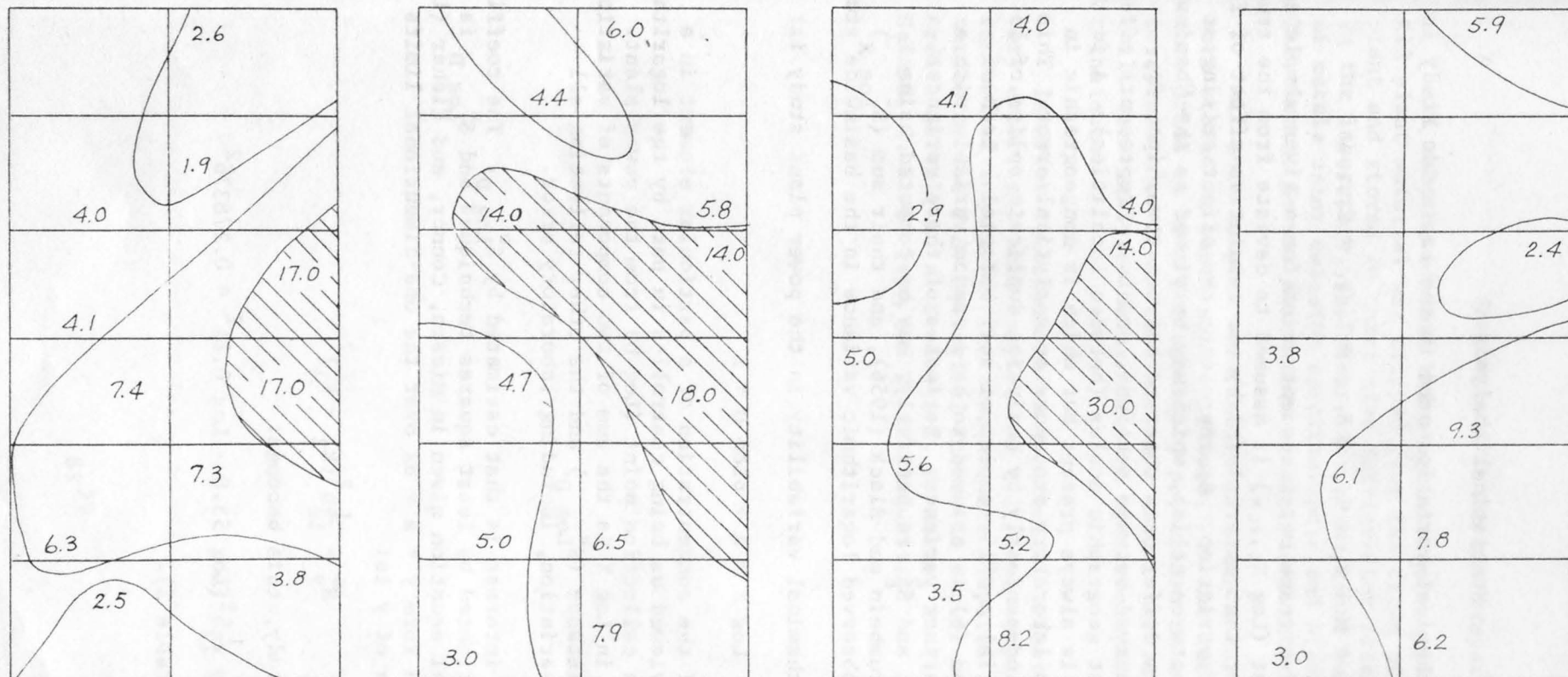


Figure 7. Cadmium (ppm) in ash of sagebrush samples in the Powder River Basin. Area of map is outlined in figure 4. Contours are 2.9, 5.5, and 11 ppm, and represent the geometric mean (5.5) and expected 68-percent range (2.9-11) of the 41 concentrations used to construct these four maps. Shaded areas include the high values.

Statistical analysis

The model of geochemical variation used in the basinwide study is written as:

$$\text{Log } X_{ijklm} = M + B_i + T_{ij} + S_{ijk} + L_{ijkl} + E_{ijklm} \quad (6)$$

where the logarithm of a trace metal concentration for a given sample as reported by the analyst ($\text{Log } X_{ijklm}$) is assumed to deviate from the true logarithmic average for that material (M) by the cumulative effect of five independent sources of variation. B_i represents the effect arising at the broadest scales (between cells), which may be viewed as the "basinwide" effect. T_{ij} represents differences observed between townships, S_{ijk} represents effects observed between sections, and L_{ijkl} represents effects arising at the smallest geographic scales (between localities). A fifth effect, E_{ijklm} , which is always present but which is nongeographic in nature, is that due to laboratory procedure or analytical error. This effect was evaluated independently by analyzing duplicate splits of 15 samples of plant material and 15 samples of soil material. Each of the effects in equation (6) is assumed to be a random variable with a mean of zero and a distinct variance. Estimates of these variances, denoted as S_B^2 , S_T^2 , S_S^2 , and S_E^2 , respectively, may be computed using procedures given in Krumbein and Slack (1956), and their sum ($S_{\text{Log } X}^2$) represents the total observed logarithmic variance in the basinwide study.

The model of geochemical variability in the power plant study is:

$$\text{Log } X = a + b \text{Log } D + R \quad (7)$$

where the logarithm of the concentration of a particular element in a particular sample is viewed as being controlled in part by the logarithm of the distance of the collection point ($\text{Log } D$) from the power plant. Geochemical variation in $\text{Log } X$ is the sum of two components of variation, one associated with distance ($S_{\text{Log } D}^2$) and the other reflecting all remaining sources of variation, including laboratory error.

The variation of interest is that estimated by $S_{\text{Log } D}^2$. The coefficients a and b are estimated by least squares techniques and $S_{\text{Log } D}^2$ is computed by an integral equation given in Miesch, Connor, and Eicher (1964). For an equation of the form $y = a + bx$ over the one-dimensional limits $k_1 \rightarrow k_2$, the variance of y is:

$$S_y^2 = \frac{1}{12} b^2 (k_2 - k_1)^2 \quad (8)$$

For the power plant study, this becomes:

$$S_{\hat{\text{Log } X}}^2 = S_{\text{Log } D}^2 = \frac{1}{12} \hat{b}^2 (\text{Log } 53.8 - \text{Log } 0.8)^2 = 0.27837 \hat{b}^2 \quad (9)$$

where \hat{b} estimates b (table 2).

Sample collection and preparation

All samples of soil and sagebrush were collected in May, 1973. All plant material was clipped from the crown of a living sagebrush plant and stored in quart-size refrigerator freezer boxes for shipment. In the laboratory, the plant tissue was ashed and analyzed for a variety of metals using emission spectrographic and atomic absorption techniques. The element Se was determined on dry plant material.

All soil samples were collected using a chrome-plated trowel and were stored in paper soil envelopes. In the laboratory, these samples were dried at 45°C for one week, pulverized in a ceramic mill, and sieved to obtain the -2 mm fraction. All larger particles were discarded. The soils were analyzed using emission spectrographic and neutron activation techniques.

In order to circumvent any potential effects of systematic laboratory error, all soil samples and all plant samples were analyzed in a randomized sequence. The samples were prepared and analyzed in laboratories of the U.S. Geological Survey in Denver by P. J. Aruscavage, Ardith Bartel, L. A. Bradley, T. F. Harms, H. T. Millard, Jr., H. G. Neiman, C. S. E. Papp, and R. A. Zielinski.

TRACE METAL VARIATION IN SOIL LICHENS, POWDER RIVER BASIN
by James A. Erdman

Concurrently with the soil and sagebrush sampling described by Tidball, Erdman, and Ebens (first report), an attempt was made to collect native vegetation other than sagebrush. A sample suite of soil lichen (Parmelia chlorochroa) and blue grama grass (Bouteloua gracilis) were taken along with big sagebrush.

Certain metals, particularly zinc, tend to be readily absorbed by lichens (Lounamaa, 1956). Lichens were used by Sloover and LeBlanc (1968) to map urban and industrial airborne pollution, and Jaakkola, Takahashi, and Miettinen (1971) analyzed samples of the lichen Cladonia alpestris to measure the airborne cadmium released by a recently-constructed zinc refinery in Finland. The soil lichens that we sampled, therefore, may prove to be especially useful in environmental monitoring in the Powder River Basin.

This study of the chemical variability of soil lichens is based on 19 samples collected at three localities in the Powder River Basin (fig. 8). The sample design used in this study was a nested barbell type similar to that used by Tidball, Erdman, and Ebens (first report). The absence of lichens at some sites has resulted in an "unbalanced" design with unequal numbers at the various levels. Each sample consists of a composite of lichen material collected over an area of about 100 m². The analyses were performed by T. F. Harms, C. S. E. Papp, and H. G. Neiman in the Denver laboratories of the U.S. Geological Survey.

When sampling soil lichens, soil contamination is an obvious problem; particles of clay and sand are easily caught in the rootlike rhizines and curled-up thalli of the samples. To minimize this effect, all samples were cleaned in distilled water with an ultrasonic probe.

Results of the element analyses are given in table 5. All evaluation was done using logarithms of concentration in order to counter the skewness commonly found in geochemical properties in nature. The geometric mean is the antilog of the mean logarithmic concentration. The geometric mean on a dry weight basis (GM_D) may be estimated from the relation:

$$GM_D = 0.14 \text{ GM} \quad (10)$$

where GM is the geometric mean observed on an ash basis (table 5). The geometric deviation is the antilog of the standard deviation of the logarithmic concentrations; the standard deviation, in turn, is computed as the square root of the sum of the logarithmic variance components. All entries in table 5, except laboratory error, are based on 19 samples.

The percent of regional variance observed gives insight to the importance of variation at scales greater than 10 km in the basin.

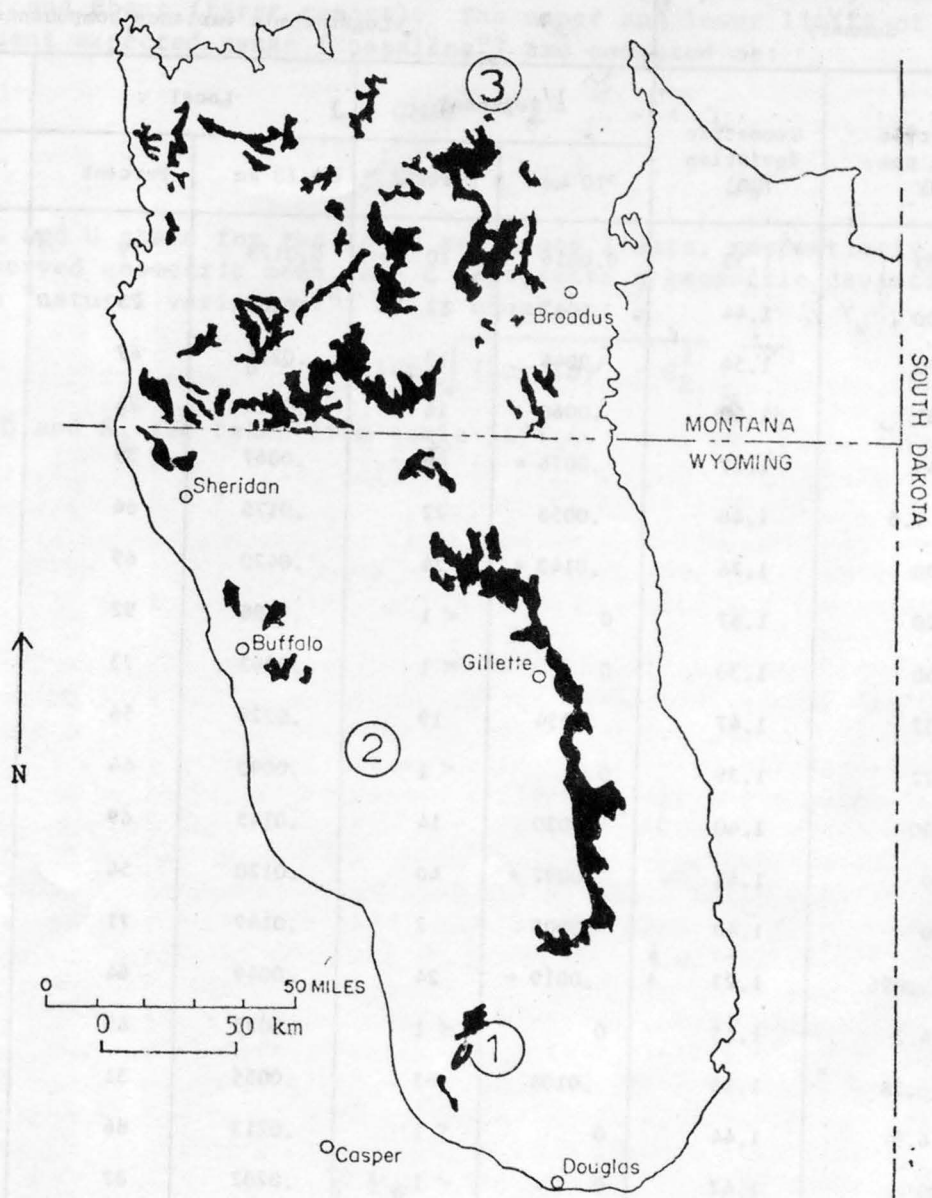


Figure 8. Sampling localities for soil lichens (*Parmelia chlorochroa*) in the Powder River Basin. Samples were collected as follows: Area 1, 8 samples; area 2, 5 samples; and area 3, 6 samples.

Table 5.--Statistical evaluation of element concentrations in ash of soil

lichens (Parmelia chlorochroa), Powder River Basin

Element	Summary		Logarithmic variance components				
	Geometric mean, ppm (GM)	Geometric deviation (GD)	<u>1</u> /Regional		Local		<u>2</u> /Laboratory
			>10 km	Percent	0-10 km	Percent	(S _E ²)
Mg	6,400	1.33	0.0016	10	0.0123	79	0.0017
Ti	1,600	1.44	.0042	17	.0188	75	.0022
Ba	370	1.54	.0044	13	.0234	67	.0070
Cr	31	1.60	.0068	16	.0315	76	.0035
Cu	65	1.37	.0076 *	40	.0067	35	.0048
Ni	9.5	1.46	.0058	22	.0175	66	.0034
Pb	100	1.76	.0143 *	24	.0420	69	.0044
Sr	320	1.87	0	< 1	.0688	92	.0057
V	58	1.30	0	< 1	.0093	73	.0035
Y	32	1.47	.0054	19	.0228	56	.0070
Zr	77	1.39	0	< 1	.0090	44	.0116
Al	37,000	1.40	.0030	14	.0145	69	.0035
<u>3</u> /F	29	1.41	.0092 *	40	.0120	54	.0014
<u>3</u> /S	720	1.40	.0005	2	.0149	71	.0057
<u>3</u> /Hg	.096	1.23	.0019 *	24	.0049	64	.0009
<u>3</u> /I	4.3	1.15	0	< 1	.0025	65	.0013
<u>3</u> /Se	.38	1.35	.0108	63	.0055	31	.0010
Li	6.3	1.44	0	< 1	.0213	86	.0033
Na	400	1.42	0	< 1	.0202	87	.0030
Cd	3.5	1.64	.0090	20	.0358	78	.0011
Co	3.3	1.48	.0067	23	.0145	50	.0078

1 / *, significantly different from zero at the 0.05 probability level.2 / Based on duplicate analysis of seven samples.3 / Determined on dry weight.

Only four of the elements--copper, lead, fluorine, and mercury--are expected to vary significantly at these scales. For the remaining elements excluding selenium, which appears to have an important though nonsignificant component, the summary data may form the basis for establishing provisional geochemical baselines as defined by Tidball, Erdman, and Ebens (first report). The upper and lower limits of the 95-percent expected range ("baseline") are computed as:

$$L = GM/d^2 \quad (11)$$

$$U = GM \cdot d^2 \quad (12)$$

where L and U stand for the lower and upper limits, respectively, GM is the observed geometric mean, and d represents a geometric deviation based only on "natural variation." It is equal to:

$$d = \text{Antilog} \sqrt{(\text{Log GD})^2 - S_E^2} \quad (13)$$

where GD and S_E^2 are taken from table 5.

HYDROCHEMISTRY OF MINE WATER, CAMPBELL COUNTY, WYOMING
by Gerald L. Feder

The two parts of the natural geochemical environment likely to be most affected by coal-based energy development in the western United States are the atmosphere and the hydrosphere. The impact upon ground and surface waters is expected to result in redistribution of water as well as changes in chemical composition. One aspect of concern is the effect of surface mining on aquifers within and adjacent to coal beds, and the possible effects of mine discharge on surface waters. The purpose of this report is to make available a chemical analysis (table 6) of drainage water from the working face of the Amax Strip Mine in Campbell County, Wyoming (Powder River Basin), and to compare it to a limited number of chemical analyses of water from the same aquifer system in the Fort Union Formation (fig. 9).

The sample was collected during a reconnaissance field trip to both the Northern Great Plains and the Rocky Mountain Coal Provinces. This trip pointed up the dual problems faced by environmentally oriented hydrochemists--that of the lack of surface water and the scarcity of wells in these areas. These constraints on hydrologic work can partly be remedied by sampling large perennial streams and making use of extensive drilling programs for ground water, undertaken by both industry and government for purposes of sampling and/or monitoring.

Ground-water quality data on file with the Wyoming district, U.S. Geological Survey, indicate that ground water in the Fort Union Formation in Campbell County, Wyoming, both in the vicinity of coal mining operations and outside of actively mined areas, is highly variable both in type of water and dissolved-solids concentrations. These wells (table 6) range in depth from 53 to 187 m. The sample of mine drainage water was collected from water flowing out of a fracture in the working face of a coal seam being mined in the Fort Union Formation. A comparison of this water with the well waters shows that the mine-drainage water is not too dissimilar to ground water in the same formation in unmined areas. Sodium appears to be slightly low and potassium and chlorine slightly high in the mine water, but only sulfate, which appears to be extremely low, is markedly different from the waters listed in table 6. Although no trace-element data are available for the Fort Union ground-water samples, concentrations in the mine-drainage water are generally low for constituents; none exceeds U.S. Public Health Service (1962) mandatory or recommended limits.

Further systematic sampling of surface waters and ground waters in the western coal regions will provide data on the natural variation in the hydrochemical environment, particularly trace-element quality, against which changes induced by mining and associated operations may be accurately assessed.

Table 6.--Chemical constituents (in mg/l, except as noted) in ground water from one coal mine and five shallow wells in the Fort Union Formation, Campbell County, Wyoming. Well data from Hodson (1971)

Constituent	Water from coal mine	Water from Fort Union wells ^{1/}					Geometric mean (wells)
		(63)	(53)	(177)	(187)	(122)	
SiO ₂ ----	9.5	6.9	7.6	8.7	9.6	7.1	7.9
Ca -----	34	28	379	2.9	2.3	444	88
Mg -----	11	3.9	102	.7	.9	319	10
Na -----	220	450	431	300	254	890	420
K -----	7.5	4.9	17	1.5	1.1	21	5
HCO ₃ ----	631	576	1,350	514	468	729	671
SO ₄ ----	63	530	1,120	206	129	3,560	562
Cl -----	13	1.5	9.3	6.1	5	10	5.3
F -----	.7	2.8	.7	.7	2.3	.2	.9
B -----	.03	.10	.03	.19	.13	.33	.12
^{2/} TDS ----	669	1,340	2,740	792	661	5,620	1,610
^{3/} pH ----	8	8.7	7.5	8.5	8.8	8.3	8.4
(no data on remaining elements)							
Al -----	.13						
Ba -----	.21						
Be -----	< .005						
Bi -----	< .015						
Cd -----	< .001						
Cr -----	< .007						
Cu -----	< .004						
Co -----	< .015						
Ga -----	< .007						
Ge -----	< .015						
Fe -----	< .015						
Pb -----	< .015						
Li -----	.05						
Mn -----	< .01						
Mo -----	< .007						
Ni -----	< .015						
Ag -----	< .003						
Sr -----	.7						
Sn -----	< .015						
Ti -----	< .01						
V -----	.01						
Zn -----	.01						
Zr -----	< .025						
As -----	.004						
Se -----	.005						
Hg -----	> .0001						
Br -----	.2						
I -----	> .1						
^{4/} Gross alpha	.012						
^{5/} Gross beta	14						

1/ Depth of well in parentheses (in metres).

2/ Total dissolved solids.

3/ In standard units.

4/ As U-nat.

5/ As Cs-137 (in Pic/l).

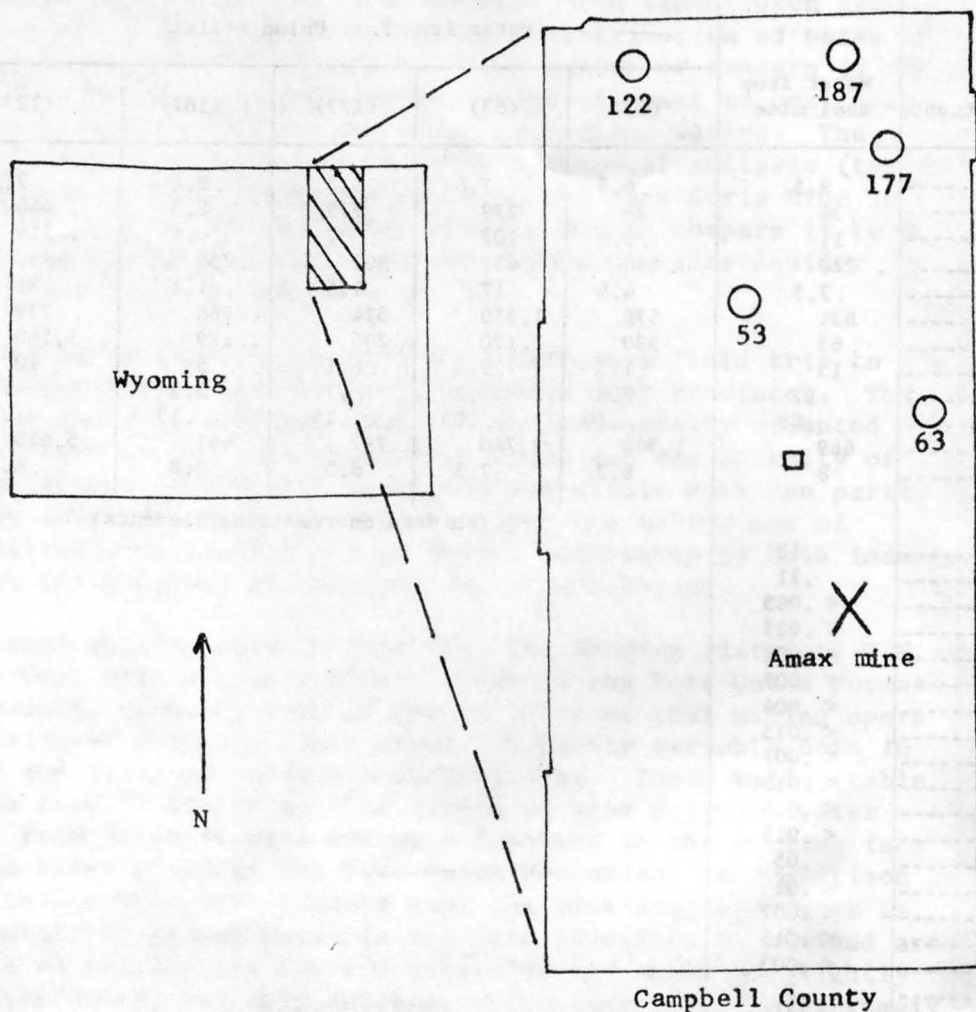


Figure 9. Localities in Campbell County, Wyoming where ground-water samples listed in table 6 were collected. Open circles indicate wells, with well depth listed in metres.

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