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Lithium in Surficial Materials of the Conterminous United States and Partial Data on Cadmium

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ABSTRACT

Concentrations of lithium in 912 samples of soils and other regoliths from sites approximately 50 miles apart throughout the United States are represented on a map by symbols showing five ranges of values. A histogram of the lithium concentrations is also given. The geometric mean lithium concentration is 20.4 ppm (parts per million) for all samples, 17.3 ppm for samples from the Eastern United States, and 23.3 ppm for samples from the Western United States. Cadmium concentrations were less than 1 ppm in all but 11 of the 912 samples. Ten of these 11 samples contained from 1 to 1.5 ppm cadmium; one sample contained 10 ppm cadmium.

INTRODUCTION

The concentrations of 36 elements in samples of soils and other regoliths from sites about 50 miles apart on travel routes throughout the conterminous United States were given in Shacklette, Hamilton, Boerngen, and Bowles (1971) and in Shacklette, Boerngen, and Turner (1971). After these reports were prepared, analytical methods became available for detecting lithium and cadmium in surficial materials in concentrations as low as 5 ppm (parts per million) and 1 ppm, respectively.

The samples were collected and prepared for analysis in the same manner as reported earlier (Shacklette, Hamilton, and others, 1971) and were analyzed in a completely random sequence. Lithium and cadmium concentrations were determined by J. M. Cahill and R. L. Rahill.

Although most samples studied were collected along roads, the specific sampling sites were selected to represent surficial materials that were as close as possible to their natural condition. Some samples, of necessity, were collected in cultivated fields; the degree of contamination of these samples and of a few samples from near roadsides cannot be evaluated from the data at hand. Most surficial materials analyzed were sampled at a depth of 8 inches. We

believe that soils and other regoliths from this depth commonly show few or no effects of any surficial contamination that may have occurred.

Many geologists and other workers of the U.S. Geological Survey assisted in this study by collecting samples along travel routes to their own field-study areas. This assistance, and that of computer specialists, was acknowledged in the earlier reports of this sampling program (Shacklette, Hamilton, and others, 1971; Shacklette, Boerngen, and Turner, 1971).

LITHIUM

ANALYTICAL METHOD

Lithium concentrations in the samples were determined by an atomic-absorption spectrometric method. The samples were digested by use of an HF total-digestion procedure (Huffman, 1968). The final sample solution contained 5 percent HCl; part of this solution was aspirated into the atomic-absorption spectrometer (Perkin-Elmer model 303). An air-acetylene oxidizing flame was used, and the light source was a hollow cathode tube set at 15 milliamperes. The other instrumental parameters included a wavelength setting of 6,708 angstroms and a laminar single-slot burner 10 cm (centimeters) long. The range of standards used for these samples was 0.05 ppm to 2.0 ppm lithium. The lower limit of the determination based on 1 gram of sample in 100 ml (milliliters) volume is 5 ppm lithium.

RESULTS OF ANALYSES

The lithium values were transformed to a logarithmic form because the 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 mean logarithm. The most convenient measure of variation is the geometric deviation, which is the antilogarithm of the standard deviation of the logarithms. Estimates of the arithmetic mean were derived by the use of Sichel's (1952) technique. These methods of statistical evaluation are the same as those used for evaluating other elements in the samples, as reported by Shacklette, Hamilton, Boerngen, and Bowles (1971).

We measured the precision of the analytical method used for lithium by analyzing 48 randomly selected samples in duplicate. The 48 duplicates were randomly interspersed among the other 912 samples and were unknown to the analysts. The precision of the method was estimated by

$$s_a^2 = \frac{\sum_{i=1}^{48} (\log x_i - \log y_i)^2}{96} = 0.00040,$$

where s_a^2 is the precision and x_i and y_i are, respectively, the lithium determinations for the i th sample and the corresponding duplicate. This indicates that the analyses are reproducible within a factor of 1.05 (10^{s_a}) at the 68-percent level of confidence, or within a factor of 1.10 (10^{2s_a}) at the 95-percent level.

The logarithmic variance of lithium concentrations in all 912 samples is 0.0739, indicating that the analytical-error variance contributes less than 1 percent to the total variance in the data.

Statistics for the lithium concentration of all samples, as well as of samples from both east and west of the 97th meridian, are given in table 1. Shown in figure 1 are the distribution of the sample sites throughout the conterminous United States and the lithium concentrations of the samples expressed in terms of five geometric ranges of concentration.

DISCUSSION

Lithium commonly occurs in small, but measurable, concentrations in both soils and plants. Although this element is not generally considered essential to plant nutrition (Bradford, 1966, p. 218), low concentrations were reported to stimulate plant growth by McMurtrey and Robinson (1938, p. 822) and by Borovik-Romanova (1965, p. 675). High concentrations of lithium, especially the carbonate form, are toxic to plants. However, Bradford (1966, p. 223) stated: "Naturally occurring instances of lithium toxicity to plants are not known, except in the case of citrus." Animals apparently do not have a

TABLE 1.—Concentrations of lithium, in parts per million, in samples of soils and other surficial materials from the conterminous United States

[Number of samples is given in parentheses after area]				
Area	Range	Geometric mean	Geometric deviation	Arithmetic mean ¹
Entire conterminous United States (912).....	5-136	20.37	1.87	24.74
Western United States, west of the 97th meridian (492).....	5-130	23.28	1.62	26.14
Eastern United States, east of the 97th meridian (420).....	5-136	17.31	2.10	22.80

¹ Estimated by method of Sichel (1952).

metabolic requirement for lithium, but recently reported therapeutic uses of lithium compounds have stimulated interest in regional patterns of lithium concentrations in natural materials (Voors, 1970).

The range in the lithium contents of 19 soil samples from throughout the United States was reported by Steinkoenig (1915, p. 426) to be from 0.001 to 0.010 percent lithia (5 to 50 ppm lithium). Vinogradov (1959, p. 184) gave the "average" lithium content of soils as 30 ppm. Hawkes and Webb (1962, p. 368) reported that the lithium content of soils ranges from 5 to 200 ppm, the same range that was reported by Swaine (1955, p. 48) for lithium in ordinary agricultural soils. Bradford (1966, p. 221) stated: "There is no evidence available to indicate that total lithium in soils is in any way related to plant availability. *** Plant content of this element is at present the best guide to the lithium status of the soil."

The difference in geometric mean concentrations of lithium in samples from the Eastern and the Western United States (table 1) is statistically significant at the 99.9-percent confidence level. For soils of the Western United States, higher lithium values parallel higher values of aluminum, barium, magnesium, phosphorus, potassium, sodium, and strontium, as reported by Shacklette (1971, p. 37) and Shacklette, Hamilton, Boerngen, and Bowles (1971).

Some regional patterns in lower concentrations of this element are apparent. The low levels in soils of the Atlantic Coastal Plain region (figs. 1, 2) correspond to low levels of cobalt, gallium, lead, manganese, nickel, scandium, and zinc (Shacklette, 1971, p. 37). Low concentrations of these elements are also noted in the Sand Hills of Nebraska (Great Plains region) and in sandy soils of the lower peninsula of Michigan and northern Wisconsin (Central Stable region).

The medium to high values for lithium in soils from the lower Mississippi River drainage basin are

bounded on the east and west by the typically low to medium values of the Atlantic Coastal Plain region—a pattern characteristic of most metals in soils (Shacklette, Hamilton, and others, 1971, p. D6). Areas having high values are apparent in the Appalachian Highland region, in Nevada, and on east-west routes across the central part of the Cordilleran Mountain region.

Because lithium has many industrial uses, contamination of soils by this element may be expected. Lithium-type greases, for example, are widely used on industrial and agricultural machinery. The United States produced more than 200 million pounds of these greases in 1958 (Kolfenbach and Morway, 1959, p. 22). Bradford (1966, p. 221) listed and discussed practices which may produce lithium toxicity as follows: "Acidification of some neutral or alkaline soils; irrigation with water containing lithium; and contamination of soils or irrigation waters from industrial wastes containing lithium. The production of lithium and its compounds has increased enormously since the development of atomic energy, and consequently these materials are finding many valuable applications in science and industry." He stated further that lithium compounds are used in the rubber, ceramic, and cement industries.

CADMIUM

ANALYTICAL METHOD

The procedure used for cadmium analysis is an adaptation of the method described by Nakagawa and Harms (1968). Transfer a 1-gram dry sample into a 20x200-mm pyrex culture tube. Moisten the sample with water and place a 1-cm teflon magnetic stirring bar in the tube. Add 5 ml HNO₃ and boil and stir the sample for 20 minutes. Wash the tube walls with approximately 10 ml of water and boil the sample for an additional 10 minutes. Remove the tube and cool the sample, then dilute the sample to a

final volume of 20 ml. Measure the cadmium content of the sample solution by aspirating part of the solution into an atomic-absorption spectrometer using a wavelength of 2,288 microns. Other instrumental parameters include an air-hydrogen oxidizing flame and a laminar single-slot burner 10 cm long.

All samples in this study were scanned by use of the HNO₃ atomic-absorption method. A few samples contained large amounts of calcium; these samples were analyzed also by an organic extraction-atomic absorption procedure because high concentrations of calcium are known to interfere with the determination of cadmium. This extraction procedure, developed by Cahill, consists of HNO₃ dissolution and adjustment to pH 8 with NH₄OH. The cadmium is then extracted with 10 ml of *n*-butyl acetate made to contain 2 percent 2-mercapto-benzothiazol (MBT). Measure the cadmium content of the organic phase by atomic absorption, using an air-hydrogen flame and the previously mentioned instrumental parameters. The lower detection limit of this method is 1 ppm.

RESULTS OF ANALYSES

Because of insufficient sensitivity (1 ppm) of the analytical method, cadmium concentrations could be measured in only 11 of the 912 samples analyzed. Cadmium concentrations in the other 901 samples were determined to be less than 1 ppm. The location and description of sample sites where surficial materials contained measurable amounts of cadmium, and the cadmium concentration measured, are given in table 2.

DISCUSSION

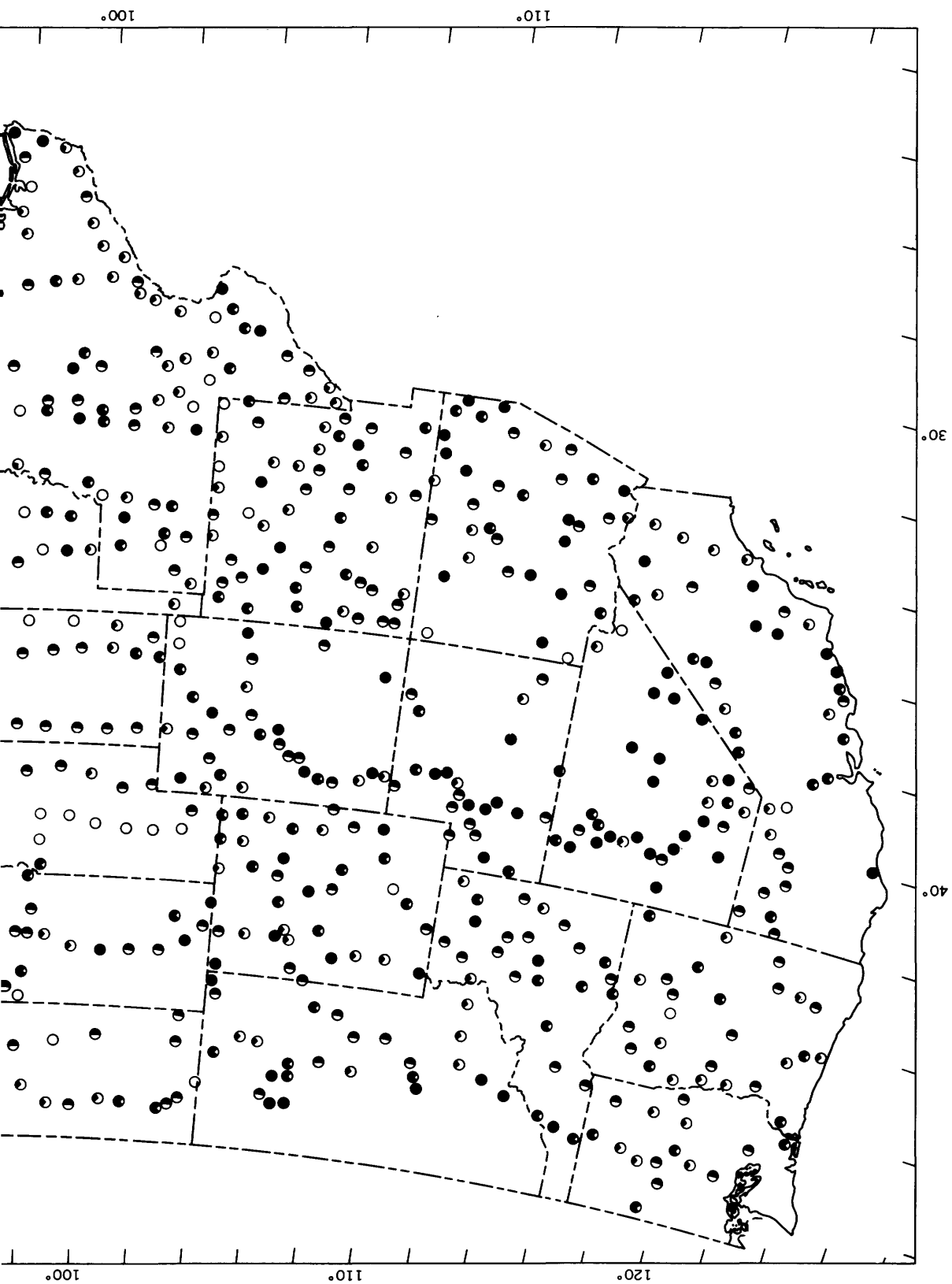
Underwood (1971, p. 276) stated:

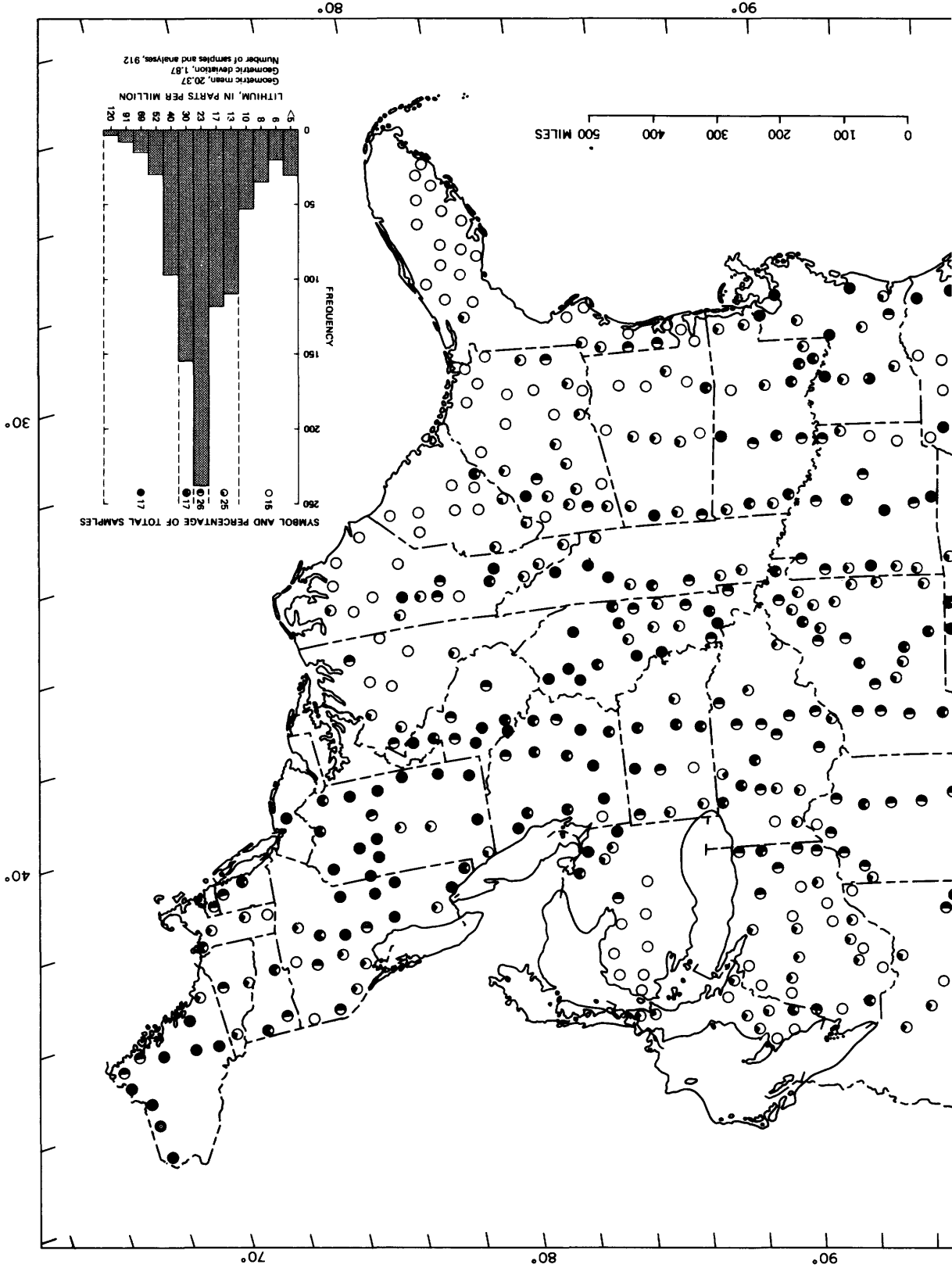
Data on the sources of cadmium to man and domestic animals are exceedingly meager. The factors that affect the magnitude of normal intakes and the movements of cadmium from soils and plants to animals and man have also been little studied. This is a serious gap in knowledge, in view of the geographical differences

TABLE 2.—Location and description of sample sites where surficial materials contained measurable amounts of cadmium and the cadmium concentration measured, in parts per million

Sample No.	State	County	Locality and description of sample	Cadmium, in dry material
GC 0422 ..	Ohio	Auglaize	U.S. Highway 33, 1 mile northwest of Lakeview; brown silty loam, cultivated	1.0
0560 ..	Wisconsin	Polk	State Route 35, 2 miles south of Luck; yellow sandy loam	1
0602 ..	California	Kern	Junction of State Route 33 and unnumbered road, 10 miles northwest of Button Willow; B horizon soil	1
1521 ..	Texas	Harris	U.S. Highway 90, 2 miles east of Addicks; dark alluvial clay	1
1558 ..	Kansas	Bourbon	U.S. Highway 54, 10 miles west of Fort Scott; dark prairie soil over limestone	1.5
1854 ..	Colorado	Moffat	U.S. Highway 40, 8 miles east of Massadona; brown clayey silt	1
1913 ..	New Mexico	Chaves	U.S. Highway 70, 18 miles southwest of Roswell; very dry tan soil with many chert fragments	1.5
2427 ..	California	Nevada	Junction of U.S. Highway 40 and State Route 20, near Cisco; B horizon soil	1
2431 ..	California	Santa Clara	U.S. Highway 101 at State Route 152 exit, Gilroy; B horizon soil	10
2674 ..	South Dakota ..	Brown	State Route 37, 1 mile south of Groton; gray-mottled B horizon lacustrine clay, in grassland	1
2706 ..	California	Shasta	In Lassen Volcanic National Park, 3 miles southeast of Manzanita Lake; B horizon soil	1

Figure 1.—Lithium concentrations in surficial





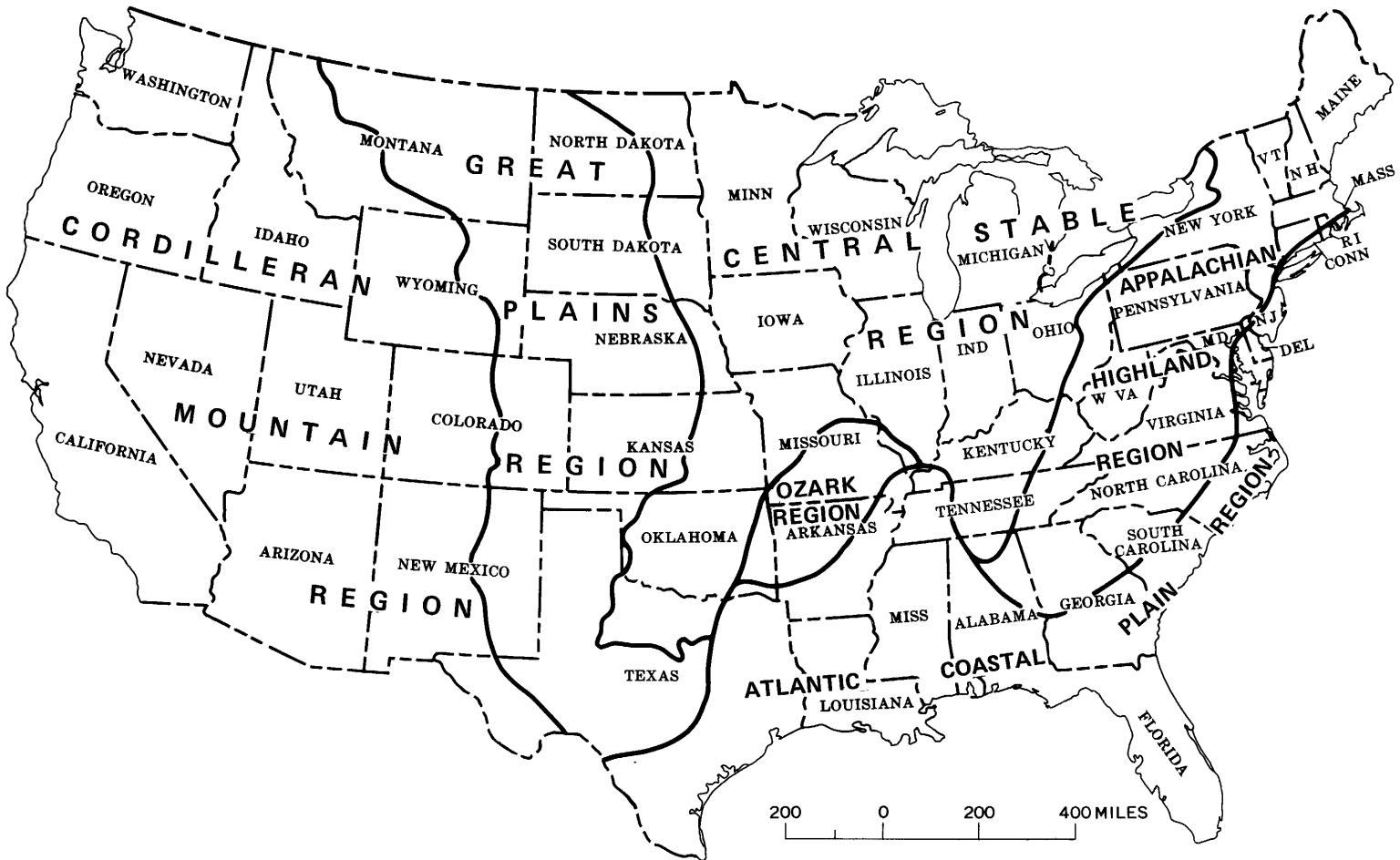


FIGURE 2.—Physiographic regions of the conterminous United States.

in human renal cadmium levels and their increase with age, the toxicity of this element, and the possible association of cadmium with human hypertension. The interactions of cadmium with zinc, copper, iron, and selenium also indicate the need for more information on sources of cadmium to man and animals.

Cadmium concentrations in various plants, including food plants, were given by Shacklette (1972). Analyses of cadmium concentrations in soils have been hampered because of insufficient sensitivity of available analytical methods. The concentrations commonly found in ordinary soils are at or below the detection limit of the methods that are used. Swaine (1955, p. 20) wrote: "It is unlikely that normal soils would contain more than c.[circa] 1 ppm Cd." Vinogradov (1959) gave 0.5 ppm as the "average" concentration of this element in soils; the same value was given as a "suggested" average by Warren, Delavault, and Fletcher (1971, p. 2).

Miesch and Huffman (1972, p. 76-77) reported cadmium concentrations in upper and lower soil horizons from the Helena Valley area, Montana, where pollution from smelters is widespread. In regard to soils just outside the immediate Helena Valley area they stated: "The mean is estimated to be approximately 0.8 ppm, and the range is from less than 0.5 to 2 ppm." Within the Helena Valley area they observed that:

The highest cadmium content was found in soils collected near the smelter stack; approximately 150 ppm cadmium was found in samples collected from the upper 4-inch soil layer 0.67 mile northwest of the stack along traverse C. The cadmium content of the upper 4-inch soil layer, like the lead and zinc content, decreases systematically with distance from the stack, but no soils taken beyond a distance of about 5 miles from the stack were found to contain more cadmium than those soils sampled outside the Helena Valley. This does not necessarily mean that cadmium contained in smelter stack emissions is less widely dispersed than lead or zinc; cadmium is more difficult to assess because it is less abundant. The cadmium content of soils collected at a depth of 6 to 10 inches is one-fifth to one-tenth of that in soils of the upper 4-inch layer, indicating that the chemical mobility of cadmium in the soils is somewhat greater than that of lead, but less than that of zinc. This is in accord with the observed general behavior of cadmium in soils as reported from studies in geochemical prospecting.

In the present study, regional trends in cadmium concentrations in soils cannot be demonstrated by the very few reported cadmium values. Likewise, the "average" soil cadmium value of 0.5 ppm, as given by Vinogradov (1959) and by Warren, Delavault, and Fletcher (1971), cannot be evaluated by using our data because of the limitation in sensitivity of the analytical method that was used for samples in this study. The depth at which these samples were collected (about 8 in.) most likely precludes airborne industrial contamination of most samples, if judged

by the results of Miesch and Huffman (1972), who reported greatly reduced cadmium levels with increasing depth of soil sampling. Nonetheless, the high value of 10 ppm cadmium in the Santa Clara County, Calif., sample probably represents contamination from some unidentified source.

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