Molybdenosis in an Area Underlain by Uranium-bearing Lignites in the Northern Great Plains

LAURA R. STONE, JAMES A. ERDMAN, GERALD L. FEDER, AND HEINRICH D. HOLLAND

Abstract

In the fall of 1975, cattle grazing to the north of an abandoned uranium mine on Flint Butte in Harding County, S. Dak., showed signs of molybdenosis, a disease due to molybdenum-induced copper deficiency. To identify the source of the problem, plant, water, and soil samples were collected on a grid design over a 16 km² (~ 9 miles²) area around Flint Butte. Uranium, molybdenum, and copper concentrations were determined in western wheatgrass *(Agropyron smithii)* and sweetclover *(Mililotus officinalis)*; molybdenum and copper concentrations and pH were determined in pond waters; and the pH of soils was determined. Ratios of copper to molybdenum in the forage were found to be below 2:1, the lowest value considered safe for cattle. Molybdenum concentrations in some surface waters were extremely high. These conditions are related to the outcrop of uranium- and molybdenum-bearing lignites at Flint Butte and in the nearby Flint Hills. Similar lignites are widespread, and it is likely that nutritional problems of the type encountered in the Flint Butte area exist in similar geologic terrain over a broad region of the northern Great Plains.

Several thin beds of uranium-bearing lignite were stripmined at Flint Butte, in the northwestern corner of South Dakota (Fig. 1) during the mid-1960's. These beds represent the Lodgepole facies (Stevenson 1956) in the Tongue River Member of the Fort Union formation. The lignite was taken by truck to an ashing plant in southwestern North Dakota, where it was burned to concentrate the uranium (U). The kilns at the plant operated from July 1963 to May 1967.

In 1968, black angus cattle grazing near the former ashing plant exhibited the following symptoms: excessive weight loss, severe diarrhea, and grayed coats (Christianson and Jacobson 1971). Calves were the most severely affected. Sheep were also affected, but to a lesser degree. The cattle were first treated for possible bacterial infection. When they did not respond to treatment, radiation sickness was suspected. However, the levels of grama radiation in the pastures did not exceed normal background levels. Finally, analyses of soil and fecal samples from the area around the plant revealed abnormally high concentrations of molybdenum (Mo); a sample of the ashed lignite from the partly dismantled plant contained 3,200 ppm Mo. The health problem was diagnosed as molybdenosis, a Mo-induced copper (Cu) deficiency. Molybdenum contamination from the ashing plant was clearly the source of the problem. Molybdenum is strongly associated with the U-bearing lignites in the Cave Hills area of which Flint Butte also is a part (Pipiringos 1966), as well as in the surrounding region (Denson and Gill 1956).

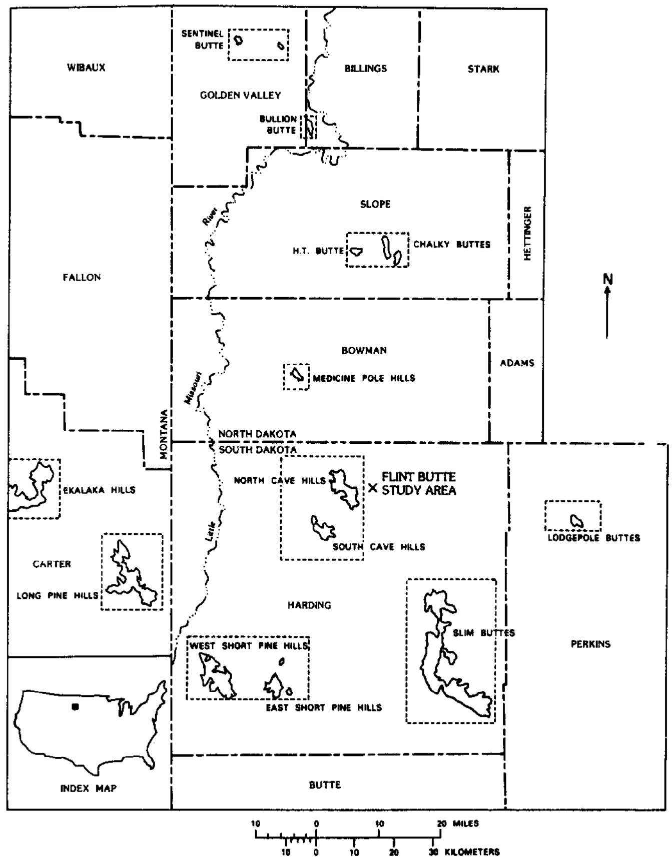

Fig. 1. *Location of the Flint Butte study area, and other areas in eastern Montana and western North and South Dakota underlain by uranium-bearing lignite. (Adapted from Denson and Gill 1956; Pipiringos et al. 1965; Stevenson 1956.)*

In the fall of 1975, cows and calves grazing to the north of the abandoned uranium mine on Flint Butte showed symptoms similar to those of the cattle that had grazed near the ashing plant. The abandoned mine was suspected as the source of the contamination. According to Deutscher et al. (1982), analyses of weathered grass and hay samples revealed relatively low Cu levels (1.5-3.3 ppm), and samples of blood and liver from cattle contained low concentrations of Cu, especially in the liver. Liver Cu levels in 5 mature cows that were slaughtered averaged only 8 ppm, dry-weight basis. In the western parts of the United States these levels are typically 30-100 ppm in the dried tissue (Church et al. 1971, p. 458). Since Mo was normal in both the forage (0.8-4.4 ppm) and cattle tissue, the problem appeared to be due to a Cu deficiency.

Authors are respectively, chemist, botanist, and hydrologist, U.S. Geological Survey, Denver, Colorado 80225, and professor, Department of Geological Sciences, Harvard University, Cambridge, Mass. 02138.

L. Stone's current address is Box 299, Strong Memorial Hospital Medical Center, Rochester, N.Y. 14642. Inquiries for reprints should be directed to J. Erdman.

Authors thank R.C. Moul, Harding County Extension agent, for bringing the problem to our attention. He and a neighboring rancher, J. Miller, spent many hours sharing their knowledge of the Flint Butte area. We are also grateful to R.J. Ebens and R.R. Tidball for their help in planning the study; to T. F. Harms, C.S.E. Papp and M.L. Tuttle for their guidance in the laboratory; and to K.C. Stewart and D.M. McKnight for assistance in collecting the samples, often under less than ideal conditions. R.C. Moul, A.A. Case, professor of veterinary toxicology at the University of Missouri, N.M. Denson, and A.T. Miesch of the U.S. Geological Survey reviewed an earlier version of the manuscript.

Manuscript received June 7, 1982.

In September and October of 1978, we interviewed several ranchers in northwestern South Dakota and in southwestern North Dakota. These interviews showed that strikingly similar problems exist in these areas. Some ranchers observed that in years of especially high rainfall the range plants thrive, but that the cattle do poorly in certain pastures. Naturally occurring lime and salts were evident in widespread "seep" areas. In some pastures, calves tend to have chronic diarrhea. They exhibit gaunt, unthrifty frames and do not gain weight. Calves brought in from outside the region had normal liver Cu levels. Copper levels in these calves dropped significantly after 9 months spent in some pastures (Dr. Bart Berg, veterinarian, Hettinger, North Dakota, personal communication 1978). Levels as low as 5 ppm Cu were recorded (Harding County Agricultural Extension Office, 1976). Black cows gave birth to gray calves, and hair loss from the ears and between the rear legs of cattle was noticeable.

Molybdenosis results from the interactions of Cu, Mo, sulfide, and sulfate in the rumen and tissues of ruminants, which make Cu metabolically unavailable. Molybdenosis is a worldwide problem; it has been reported not only in the United States, but also in Canada, Great Britain, New Zealand, and the Soviet Union. The biochemistry of the disease has been discussed by Church et al. (1971) and by Huisingh and Matrone (1976).

In a survey of Mo toxicity in the western United States, Kubota (1975) found that cattle grazing on forage containing 10–20 ppm Mo showed symptoms typical of molybdenosis. Webb and Atkinson (1965) reported that 5 ppm Mo in forage is the approximate upper level tolerated by cattle in Ireland; Alloway (1973) and Thornton (1977) have suggested that values as low as 2 ppm are important in Mo-induced hypocuprosis in cattle. Others believe that it is not high concentrations of Mo alone, but the ratio of Cu to Mo that is the cause of molybdenosis. The recommended Cu:Mo ratio in cattle forage is about 6:1 (Dollahite et al. 1972); Cu:Mo ratios below 2:1 will lead to the development of molybdenosis symptoms (Miltimore and Mason 1971; Dollahite et al. 1972). Dietary Cu can be administered in the form of salt licks that are supplemented with Cu sulfate, or by injections of Cu glycinate (Dye and O'Harra 1959). These methods raise the Cu level in the rumen so that the effective Cu:Mo ratio is higher than 2:1 (Dye and O'Harra 1959).

In October 1978, a study was designed to determine the extent of the molybdenosis problem around Flint Butte. The objective was to determine whether there are specific areas in the vicinity of Flint Butte that are hazardous to cattle, and if the hazard is related to the local geology. If so, it might be possible to identify other areas in the region where similar problems to cattle could be expected. The U, Mo, and Cu concentrations in selected forage plants, the concentrations of Mo, Cu, and pH of water, and soil pH were determined. The availability of Mo to plants increases under conditions of high pH (Alloway 1973), so Mo levels in the forage could be increased by the alkaline conditions that prevail in many soils of the northern Great Plains.

Methods

Sampling Design

A grid design with a sample spacing of approximately 500 m (~ 1600 ft) was established in an area of over 16 km² (~ 9 miles²); Flint Butte was near the center of the grid (Fig. 2). Soil samples representing the upper 15 cm (6 in) of the soil profile were collected at each of 81 sites for pH determination. We tried to collect samples of western wheatgrass *(Agropyron smithii)* and sweetclover *(Melilotus officinalis)* at each site, but there were some "holes" in the design due to the absence of one or both species at some sites; only 77 wheatgrass samples and 58 sweetclover samples were obtained. Western wheatgrass was sampled because it was widespread in the area; it also produces high quality hay and provides year-around grazing for livestock (Freeman 1979). Sweetclover was sampled because it is a highly palatable forage plant for cattle and has a high protein content (Miles 1970). Like most legumes, sweetclover is a

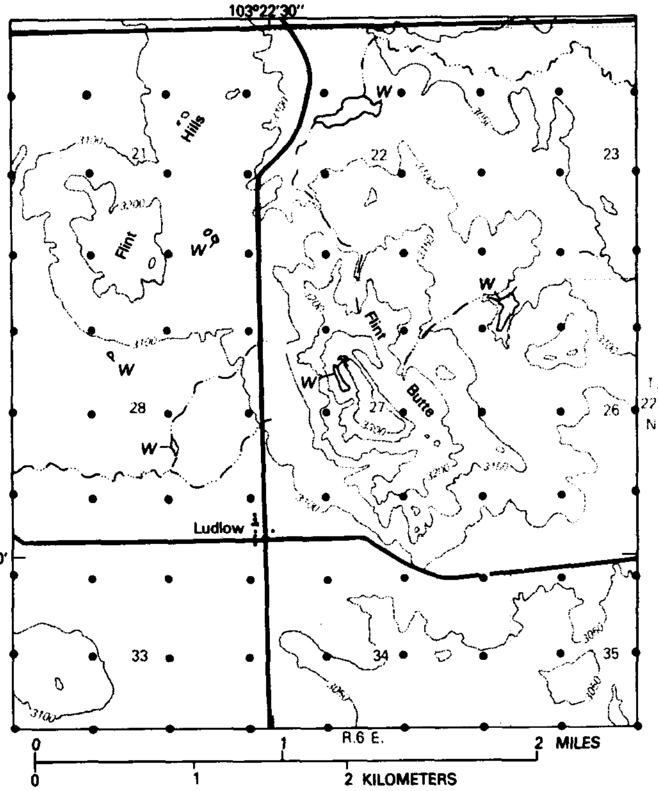

Fig. 2. *Detailed map of Flint Butte and vicinity, showing location of mine, the grid sampling design for plants and soils, and the location of the six pond-water samples (W). Contour intervals are given in feet. (Adapted from U.S. Geological Survey 7.5-minute series topographic maps, Ludlow and Ludlow SE quadrangles.)*

Mo accumulator and therefore, sites with soils that contain anomalous levels of Mo should be more easily detected. Plant samples were composited from several individual plants within a 10-m (~ 30 ft) radius of each sampling site. In a few cases, sampling locations were moved to points where the wheatgrass and sweetclover were present. All of the relocated sampling points were within 100 m (~ 330 ft) of the originally intended site. Vegetation samples were taken in a manner which minimized contamination by soil.

Surface water samples were collected at the 6 ponds indicated in Figure 2. Sediments suspended in most water samples were removed by means of a Millipore[1] pressure syringe apparatus using 0.45 micrometer filters. At two sites the high concentration of sediment made filtering difficult; sediment was removed from these samples by centrifugation in the laboratory prior to filtering. The pH was determined at each site using a Digi-sense pH meter.

Analytical Methods

All methods of analysis used in this study are standard techniques currently in use in the laboratories of the U.S. Geological Survey (USGS) in Denver, Colorado. Plant samples were air dried and ground in a Wiley mill to pass a 1.3-mm sieve. They were not washed since they were meant to be representative of forage as ingested by cattle on the rangeland. Portions of the ground samples were ashed at 500° C in a muffle furnace. The samples were analyzed in randomized order for Cu, Mo, and U. Cu and Mo were determined by the methods outlined by Nakagawa (1975) and Nakagawa et al. (1975). The samples were aspirated in a Perkin Elmer Model 306 atomic absorption unit. Uranium was determined by the method of Huffman and Riley (1970). Fluorescence was measured on a Jarrell Ash Model 26-000 solid state fluorimeter.

Water samples were analyzed for Cu and Mo in the laboratories

[1]Use of trade names is for descriptive purposes only and does not imply endorsement by the U.S.G.S.

of the Water Resources Division, USGS, Denver, Colorado. The samples were aspirated into an Inductively-Coupled Plasma Emission Spectrometer.

The soil samples were dried at room temperature and were sieved to minus 10 mesh (2mm). Soil pH was determined in the laboratory by the method outlined by Peech (1965).

Results

Geochemical Patterns

The concentration of U and Mo in both wheatgrass (Fig. 3a and 3b) and sweetclover (Fig. 3c and 3d) is strongly correlated with the local geology. High concentrations of both metals were found in samples associated with the uraniferous Tongue River member. The U concentrations in the ash ranged from <0.4 ppm (0.4 ppm is the lower limit of detection) to 4.0 ppm in wheatgrass, and <0.4 to 50 ppm in sweetclover. Concentrations of Mo (dry-weight basis) ranged from <1 to 44 ppm in wheatgrass, and from 1 to 203 ppm in sweetclover; the highest values occur in samples taken at the mine.

Copper concentrations in forage showed no consistent relationship to the local geology. However, the concentrations of Cu in wheatgrass ranged from only 0.2 to 1.6 ppm on a dry-weight basis; these values are well below the levels judged optimal for cattle nutrition. Concentrations of Cu in sweetclover were generally nutritionally adequate and ranged from 4.6 to 10.7 ppm. The pattern of the Cu:Mo ratio was found to be similar to the Mo patterns shown in Figures 3b and 3d; the lowest ratios were associated with the areas of highest Mo concentrations. In wheatgrass, the Cu:Mo ratios ranged from 0.01 to 1.1, well below the critical threshold value of 2:1. The ratios for sweetclover ranged from 0.03 to 5.9; 41 of the 58 values fell below the critical Cu:Mo ratio.

The soil pH showed no clear relationship to topography or to geology (Fig. 4), and has been discounted as a factor in controlling the Mo levels in the plants of this area. The correlations between the soil pH and Mo content of both plant species were not significant at the 95% confidence level.

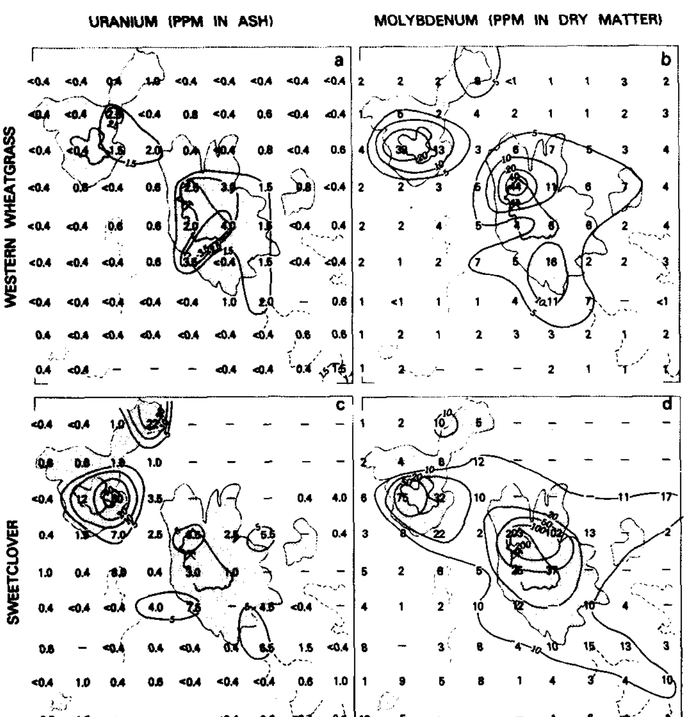

Fig. 3. Uranium and molybdenum concentrations in western wheatgrass (a and b) and in sweetclover (c and d). Dashes indicate that samples were unavailable at the site. Cross-hatched areas are underlain by the Tongue River Member of the Fort Union Formation, and the bold contour indicates the outcrop of the Lodgepole facies which contains the uranium-bearing lignites. Areas not cross-hatched are underlain by the Ludlow Member of the Fort Union; dotted lines indicate outcrops of non-uraniferous lignites. (Geology adapted from Stevenson 1956).

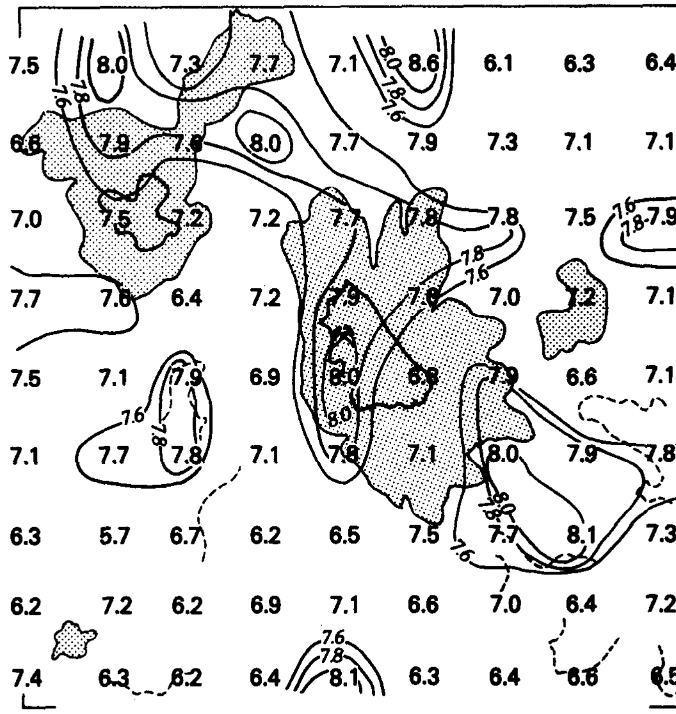

Fig. 4. *The pH of surface soils. (Geologic detail explained in Figure 4.)*

The Mo concentrations in the water samples are shown in Figure 5. Molybdenum concentrations ranged from 11 to 910 $\mu g/L$, which are well above the concentration of 1 $\mu g/L$ that is considered normal for surface waters in the region (Feder and Saindon 1976). There was no apparent relationship between the pH and Mo concentration in the water samples. All of the Cu concentrations were in a range which is close to the normal value of about 10 $\mu g/L$.

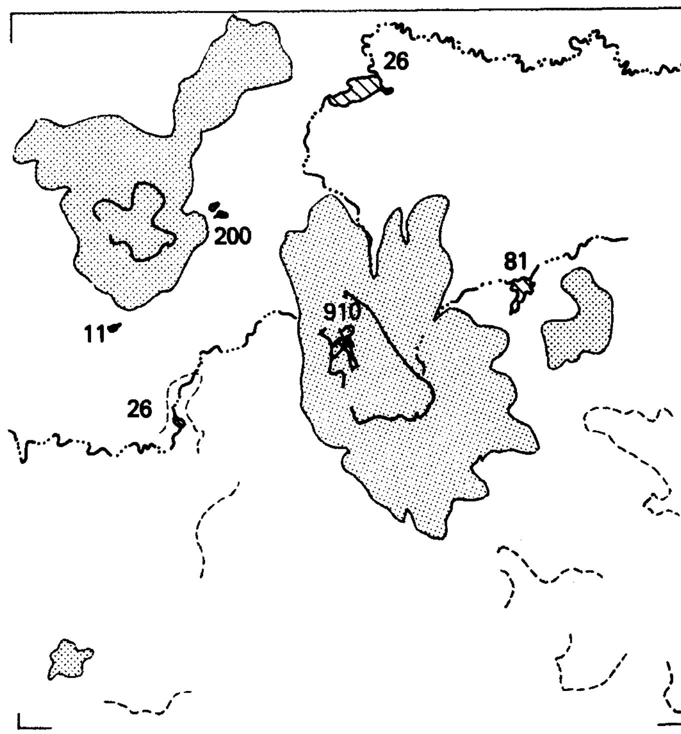

Fig. 5. *Molybdenum (ug/L) in pond waters. (Geologic detail explained in Figure 4.)*

The geochemical anomalies are clearly stratigraphically controlled. The highest U and Mo concentrations and the lowest Cu:Mo ratios in forage plants generally occur near outcrops of the Tongue River Member of the Fort Union Formation. Major anomalies occur not only in the mined area of Flint Butte, but also to the northwest in the undisturbed area on the Flint Hills (Fig. 2).

Seasonal Variation

In 1976, the Agricultural Extension Service in Harding County conducted a study of the seasonal effects on Cu and Mo levels in forage. Deutscher et al. (1982) reported that Cu concentrations decreased from an average of 4.3 ppm in samples collected in June, to 2.7 ppm in samples collected in the September-October period. Concentrations of Mo in the same forage samples remained constant throughout the season.

We conducted a somewhat similiar study in the Flint Butte area. Vegetation at 8 of the grid-point sites sampled in October 1978 were resampled in August 1979. The results (Fig. 6) are similar to those reported by Deutscher et al. (1982). The Cu levels, on dry weight basis, in the 8 samples of wheatgrass collected in August 1979 ranged from 3.5 to 10 ppm, whereas the 8 samples collected at the same sites in October 1978 ranged from 0.2 to 1.5 ppm. On the other hand, the Mo concentrations in wheatgrass from these grid points remained fairly constant. The same relationship is evident for sweetclover: Cu levels in sweetclover were lower in the October samples than in August samples, and the Mo concentrations were again fairly constant. Although the Cu levels were lower in the October samples, sweetcover sampled at that time was not nutritionally deficient. The Cu:Mo ratios were, however, critically low in both species during both seasons.

It appears, then, that as the season progresses the Cu concentrations in forage decrease while Mo concentrations remain fairly constant. This may cause some areas to become Cu deficient, and Mo anomalies in some localities may aggravate the deficiency.

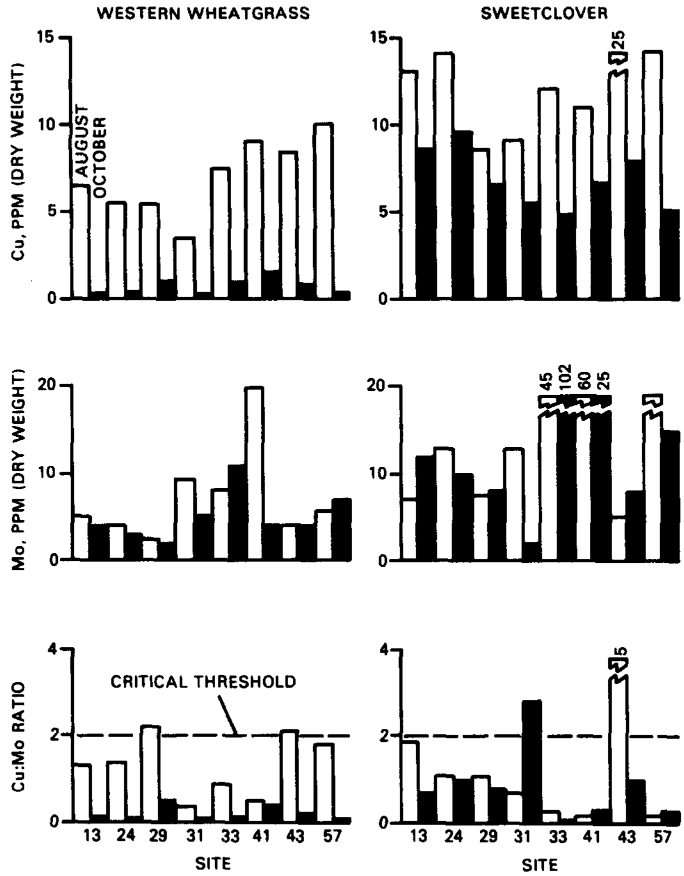

Fig. 6. *Copper and molybdenum concentrations in western wheatgrass and sweetcover from 8 sites that were sampled first in October 1978 (bargraph) and later in August 1979 (open bargraph).*

Regional Implications

Denson and Gill (1956) compiled a generalized section of geologic formations, most of which are uraniferous, that are exposed in southeastern Montana and adjacent areas in North Dakota and South Dakota (Table 1). Many of these exposures occur as hills or buttes that are underlain by uranium-bearing strata. The locations of some of these hills and buttes are shown in Figure 1. Sedimentary rocks of Late Cretaceous through Eocene age generally have a dip of ~ 2-7 m per km (10-40 ft per mi) to the northeast into the Williston Basin of North Dakota. The lignite-bearing beds comprise a sequence that is ~ 600 m (2000 ft) thick (Denson and Gill 1956).

The overlying younger volcanic tuffs found in the Arikaree Formation and White River Group are mildly radioactive. It is thought that U and Mo in the lignite were probably leached from the overlying tuffs by oxidizing groundwater and deposited in the reducing environment of the lignites; field evidence supports this theory. The lignites that dip into the Williston Basin and lie unconformably below the Oligocene and Miocene tuffs contain the highest concentrations of U and Mo (Denson and Gill 1956). These high concentrations occur in the upper parts of the stratigraphically higher beds regardless of age (Fig. 7).

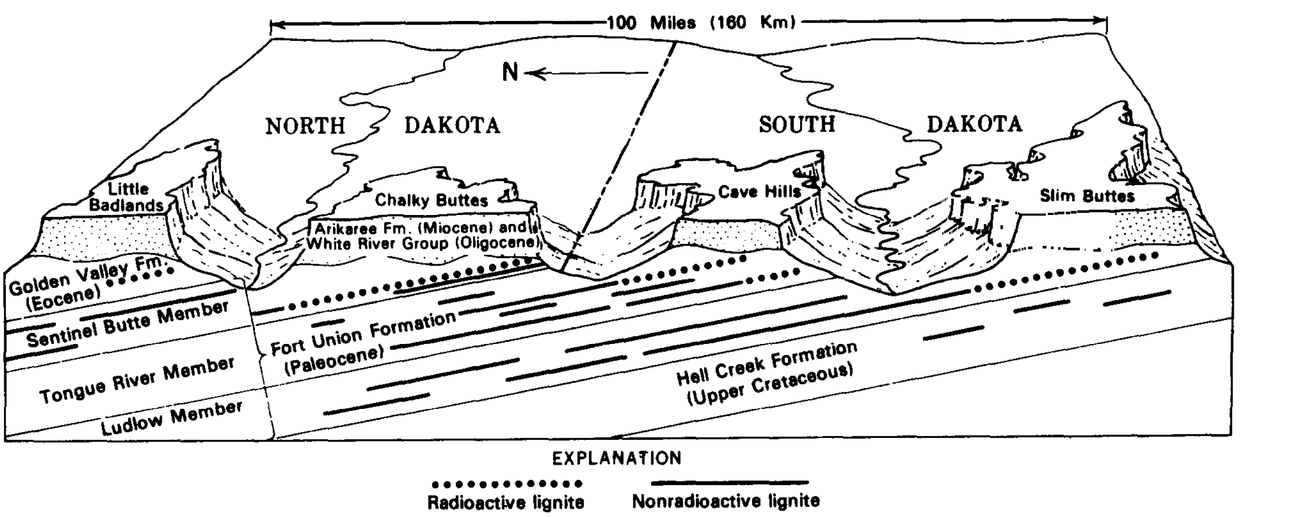

Fig. 7. *Diagrammatic section across northwestern South Dakota and southwestern North Dakota showing stratigraphic distribution of uranium-bearing lignite. (From Denson and Gill 1956.)*

In the vicinity of Flint Butte, the lignites in the Lodgepole facies of the Tongue River Member of the Fort Union Formation are stratigraphically higher and closer to the unconformity below the radioactive tuffs (which have since been completely eroded) than those of the Ludlow Member of the Fort Union Formation. Uranium and Mo were therefore concentrated in the Tongue River strata. Subsequent weathering of the Tongue River strata has remobilized the U and Mo into the area immediately surrounding the butte.

We propose that the conditions that are causing Cu-Mo imbalances in cattle at Flint Butte probably occur in geologically similar areas elsewhere in the region. An incidence of Mo-induced Cu deficiency in cattle from western Manitoba has been described by Doyle and Fletcher (1977).

Table 1. Generalized section of formations exposed in southeastern Montana and adjacent parts of North and South Dakota (from Denson and Gill 1956).

System	Series	Group, formation, member	Thickness in feet	Lithologic characteristics (italics added)
Quaternary---	Holocene and--- Pleistocene.	------------------------	0-100	Silt, sand and gravel in dunes, terraces, and alluvial fans along main stream channels
	Miocene-----	Arikaree Formation-----	260	Massive greenish-white to ash-gray tuffaceous sandstone and siltstone with a few thin beds of quartzite and volcanic ash. Dominantly of aeolian origin. *Contains local occurrences of carnotite*[1] *in calcareous siltstone in the Short Pine Hills.* Caps most of the high buttes of eastern Montana and North and South Dakota.
	— Unconformity			
		Brule Formation----	0-240	Massive buff to pinkish-tan tuffacerous siltstone and claystone. Contains abundant vertebrate remains. Well exposed in Chalky Buttes and Little Badlands of North Dakota. Preserved only in pre-Arikaree landslide blocks in Slim Buttes and Short Pine Hills of South Dakota. Not present in southeastern Montana.
	Oligocene	White River Group		
		Chadron Formation--	0-160	Dark-gray bentonite and light-gray tuffaceous claystone, siltstone and sandstone. Basal unit consists of coarse-grained conglomeratic sandstone. Lower part at many places weather golden yellow. *Carnotite occurs in upper part of formation in the Slim Buttes.*
	— Unconformity			
Tertiary-----	Eocene------	Golden Valley Formation--	0-175	Gray to yellow sandstone, siltstone, and purplish-gray to white kaolinitic clay. Contains a few thin lenticular beds of lignite and carbonaceous shale. *In the Little Badlands where closely overlain by Oligocene and Miocene rocks, carbonaceous beds are radioactive.*
		Sentinel Butte Member	0-660	Dark-gray bentonitic claystone and shale, buff to brown sandstone with *numerous beds of lignite which are radioactive in HT, Sentinel, Bullion,* and *Chalky Buttes. Contains carnotite-bearing sandstone at Whetstone Butte.*
	Fort Paleocene---- Union Formation	Tongue River Member- Paleocene----Union	600+	Massive gray to tan sandstone, siltstone, and shale. Contains many lenticular beds of quartzite and thick persistent beds of lignite. *Formation has large deposits of uranium bearing lignite in Medicine Pole and Cave Hills areas, and at Lodgepole Butte.*
		Cannonball Member--	0-300	Marine dark-gray and brown sandstone and shale with large limey concretions. Intertongues and thins to the west with the Ludlow Member of the Fort Union Formation.
		Ludlow Member------	350	Gray to light-yellow-tan sandstone, gray shale, and thick lenticular beds of lignite. *Contains radioactive lignite deposits in the Slim Buttes and Cave, Long Pine and Ekalaka Hills. Local deposits of uranophane*[1]*-bearing sandstone in the Slim Buttes.*
		Hell Creek Formation------	425	Dark-gray bentonitic claystone and gray-brown lenticular sandstone. Many concretions and thin lenses of iron carbonate. Contains thin lenses of lignite in upper part. *Local occurrence of carnotite in sandstone in the Long Pine Hills.*
Cretaceous---	Upper Cretaceous---	Fox Hills Sandstone---------	25-75	Marine grayish-white to brown sandstone.
		Pierre Shale----------------	500± exposed	Marine dark-gray to brownish-black bentonitic claystone and shale containing large limestone concretions and thin beds of bentonite.

[1]Uranium-bearing minerals of secondary origin.

Summary

High concentrations of Mo in forage and water appear to have caused molybdenosis—a Mo-induced Cu deficiency—in cattle grazing in the vicinity of Flint Butte in northwest South Dakota. The high concentrations of Mo are clearly related to high concentrations of this element in lignites of the Tongue River Member of the Fort Union Formation. The lowest Cu:Mo ratios and the highest Mo concentrations occur in plants growing on soils derived from this stratigraphic unit. Grasses were found to be Cu deficient, and the concentrations of Mo in all forage samples ranged from less than 1 to 203 ppm. All surface water samples from the study area contained more than 10 μg/L Mo, well above the normal value of 1 μg/L.

Uranium and Mo were probably deposited epigenetically in the Lodgepole facies of the Tongue River member by the same processes that enriched lignites of Upper Cretaceous through Eocene strata in these elements over a wide region in the northern Great Plains. Oxidized ground water probably leached U and Mo from Oligocene and Miocene tuffs and redeposited the metals in the reducing environment of the lignites in the underlying strata. The lignites closest to the unconformable contact below the tuffs, contain the highest concentrations of U and Mo regardless of age.

Uranium- and Mo-rich lignites are now exposed at the surface in large parts of the northern Great Plains. Molybdenum is mobile under wet, oxidizing conditions; exposure of the lignites to air, shallow oxygenated groundwater, and surface waters therefore releases Mo to the environment. Molybdenum in solution is readily available to plants. When forage and water containing high concentrations of Mo are ingested by cattle, copper becomes metabolically unavailable to the rumen. If these conditions persist, tissue Cu begins to be depleted, and molybdenosis results.

The Cu-Mo imbalance in cattle in the Flint Butte area is due to conditions that probably affect areas over a broad region of the northern Great Plains. The high conceentrations of Mo in the Flint Butte area are associated with high concentrations of U; other U-rich areas may also contain levels of Mo that are unhealthy for cattle.

Disruption of rock and soil during mining can mobilize enough Mo to cause pronounced molybdenosis in cattle. Elsewhere in the region, naturally occurring release of Mo into the environment from U-bearing lignites may also cause molybdenosis.

Literature Cited

Alloway, B.J. 1973. Copper and molybdenum in swayback pastures. J. Agr. Sci. 80:521-524.

Christianson, G.A., and G.A. Jacobson. 1971. Report on molybdenosis in farm animals and its relation to a uraniferous lignite ashing plant. Unpublished report, available from North Dakota State Department of Health, Environmental Health and Engineering Service, Bismarck, N. Dak.

Church, D.C., G.E. Smith, J.P. Fontenot, and A.T. Ralston. 1971. Digestive physiology and nutrition of ruminants, vol. 2—Nutrition. Oregon State Univ.

Denson, N.M., and J.R. Gill. 1956. Uranium-bearing lignite and its relation to volanic tuffs in eastern Montana and North and South Dakota. *In:* Contributions to the Geology of Uranium and Thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland 1955. U.S. Geol. Survey Prof. Pap. 300:413-418.

Deutscher, G.H., J.R. Johnson, R.J. Emerick, R.E. Moul, and D.L. Whittington. 1982. Copper injections and supplementation for range and beef cows and calves. Amer. Soc. Anim. Sci., Western Section, Proc. 33:235-238.

Dollahite, J.W., L.D. Rowe, L.M. Cook, D. Hightower, E.M. Bailey, and J.R. Kyzar. 1972. Copper deficiency and molybdenosis intoxication associated with grazing near a uranium mine. Southwestern Vet. 9:47-50.

Doyle, P.J., and K. Fletcher. 1977. Molybdenum content of bedrock, soils, and vegetation and the incidence of copper deficiency in cattle in western Manitoba. *In:* W.R. Chappell and K. Petersen (Eds.) Proc. Symp. on Molybdenum in the Environment, Vol. 2. Marcel Dekker, Inc., New York.

Dye, W.B., and J.L. O'Harra. 1959. Molybdenosis. Nevada Agr. Exp. Sta. Bull. 208.

Feder, G.L., and L.G. Saindon. 1976. Geochemistry of ground waters in the Fort Union Coal Region. *In:* Geochemical survey of the western energy regions, 3rd annual progr. rep. (July, 1976). U.S. Geol. Survey Open-File Rep. 76-279. 86-93.

Freeman, D. 1979. State grasses. Rangelands 1:223-225.

Huffman, C., Jr., and L.B. Riley. 1970. The fluorometric method—its use and precision for determination of uranium in the ash of plants. U.S. Geol. Survey Prof. Paper 700-B: B181-B183.

Huisingh, J., and G. Matrone. 1976. Interactions of molybdenum in animal nutrition. *In:* W.R. Chappell and K. Peterson (Eds.) Proc. Symp. on Molybdenum in the Environment, Vol. 1. Marcel Dekker, Inc. New York.

Kubota, J. 1975. Areas of molybdenum toxicity to grazing animals in the western United States. J. Range Manage. 28:252-256.

Miles, A.D. 1970. Sweetcover as a range legume. J. Range Manage. 23:220-222.

Miltimore, J.E., and J.L. Mason. 1971. Copper to molybdenum ratio and molybdenum and copper concentrations in ruminant feeds. Can. J. Anim. Sci. 51:193-200.

Nakagawa, H.M. 1975. Atomic absorption determination of silver, bismuth, cadmium, cobalt, copper, nickel, lead, and zinc in calcium and iron-rich geologic material. *In:* F.N. Ward (Ed.) New and Refined Methods of Trace Analysis Useful in Geochemical Exploration. U.S. Geol. Survey Bull. 1408:85-96.

Nakagawa, H.M., J.R. Watterson, and F.N. Ward. 1975. Atomic absorption of molybdenum in plant ash. *In:* F.N. Ward (Ed.) New and Refined Methods of Trace Analysis Useful in Geochemical Exploration. U.S. Geol. Survey Bull. 1408:29-35.

Peech, M. 1965. Hydrogen ion activity. *In:* C.A. Black et al. (Eds.) Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, Agron. Series No. 9, Amer. Soc. Agron., Madison, Wis., p. 914-926.

Pipiringos, G.N. 1966. Origin of elements associated with uranium in the Cave Hills area, Harding County, South Dakota. U.S. Geol. Survey Prof. Pap. 476-B:B1-B75.

Pipiringos, G.N., W.A. Chisholm, and R.C., Kepferle. 1965. Geology and uranium deposits in the Cave Hills areas, Harding County, South Dakota. U.S. Geol. Survey Prof. Pap. 476-A:A1-A64.

Stevenson, R.E. 1956. Areal geology of the Ludlow Quadrangle. South Dakota Geol. Survey (map with text).

Thornton, I. 1977. Biogeochemical studies on molybdenum in the United Kingdom. *In:* W.R. Chappell and K. Petersen (Eds.) Proc. Symp. on Molybdenum in the Environment, Vol. 2. Marcel Dekker, Inc., New York.

Webb, J.S., and W.J. Atkinson. 1965. Regional geochemical reconnaissance applied to some agricultural problems in Co. Limerick, Eire. Nature. 208:1056-1059.