Geochemical Anomalies of a Claypit Area, Callaway County, Missouri, and Related Metabolic Imbalance in Beef Cattle

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 807

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

Geochemical Anomalies of a Claypit Area, Callaway County, Missouri, and Related Metabolic Imbalance in Beef Cattle

By RICHARD J. EBENS, JAMES A. ERDMAN, G. L. FEDER,
ARTHUR A. CASE, *and* LLOYD A. SELBY

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A study of the concentrations of chemical elements
and compounds in samples of clays, soils, waters,
and plants, and an interference syndrome in
cattle, where mining activities have altered
the natural geochemical environment

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By Richard J. Ebens, James A. Erdman, G. L. Feder,
Arthur A. Case, and Lloyd A. Selby

ABSTRACT

Geochemical studies of waters, alluvial deposits, and vegetation revealed that aluminum, beryllium, cobalt, copper, molybdenum, and nickel occurred in anomalously high concentrations in an area adjacent to a claypit in Callaway, County, Mo. The principal sources of these and other elements that were found in anomalous amounts are believed to be the clay, shale, limestone, coal, and pyrite that were exposed when the clay was mined. These geologic materials, although they contain normal concentrations of elements, constitute an unusually rich source (compared to typical soils) of certain elements for the plants and waters of the area. Pyrite, especially, affects the mobility of some of these elements because, by weathering, it produces sulfuric acid which increases the solubility of certain compounds.

On the two ranches studied, young beef cattle exposed to anomalous element concentrations in the flood plain below the claypile experienced a severe interference syndrome due to an imbalance of minerals or other nutrients in their feed or water, or both. The disturbance in metabolism of cattle grazing on the pastures effected by the claypile was most similar to chronic molybdenosis. Imbalance of copper and molybdenum, in addition to those of sulfate, cobalt, and other substances, may have contributed to this syndrome.

Anomalous concentrations of elements may exist at many other locations in Missouri and throughout the Midwest where similar materials are brought to the surface by clay and coal strip-mine operations (especially if pyrite is present).

INTRODUCTION

Claypits, with associated mounds of clay and debris distributed about the ground surface, are anomalous features compared to naturally occurring surficial materials. If such materials are suspected of contributing unusual amounts of certain elements to the surroundings, the desirability of making detailed studies of their chemical nature is apparent. One such situation in Callaway County, reported to the Environmental Health Surveillance Center, University of Missouri, was possibly contributing to breeding failures and growth suppression in beef cattle that ranged nearby. The clay deposit and its epidemiological implications were called to the attention of U.S. Geological Survey personnel who currently are engaged in a geochemical survey of Missouri. In this report we describe the results of an exploratory geochemical study of the area and interpret the effects of the clay deposit and mining activities on the health of beef cattle in nearby pastures.

The purpose of this report is to call the situation to the attention of environmental scientists who may wish to compare our findings and interpretations with those resulting from future studies of situations that may be similar. Only through continuing studies of this kind will complete and final interpretation of the health effects be possible.

The western part of the claypit area (fig. 1) is characterized by a flat upland surface (generally above 800 ft in altitude) underlain by interbedded clay, shale, sandstone, and coal of Pennsylvanian age, and largely overlain by a mantle of loess of undetermined thickness. The eastern part of the area (generally below 800 ft in altitude) is moderately well dissected and is underlain by carbonate rocks of Mississippian and Ordovician age. An oak-hickory forest constitutes the predominant native vegetation in both areas. An abandoned claypit several hundred feet wide, about 60 feet deep, and partly filled with water is located at the "break" in the topography near the west edge of the area (fig. 2). The clay, which was mined for use in the ceramic industry, occurred in a sink that had developed in the underlying carbonate rock. McQueen (1943, p. 47) noted that in this part of Missouri, fire clay commonly is mined from deposits in sinks.

A large claypile and a smaller pile immediately north of it are located on a ridge at the east margin of the pit. The large pile consists of clay with abundant fragments of both gray shale and carbonaceous shale, and smaller amounts of pyritic material, gypsum, and carbonate rock, whereas the smaller pile consists almost exclusively of clay. Some surface runoff from the claypiles drains westward into the claypit; the remainder drains northward, eastward, and southward into Rocky Creek.

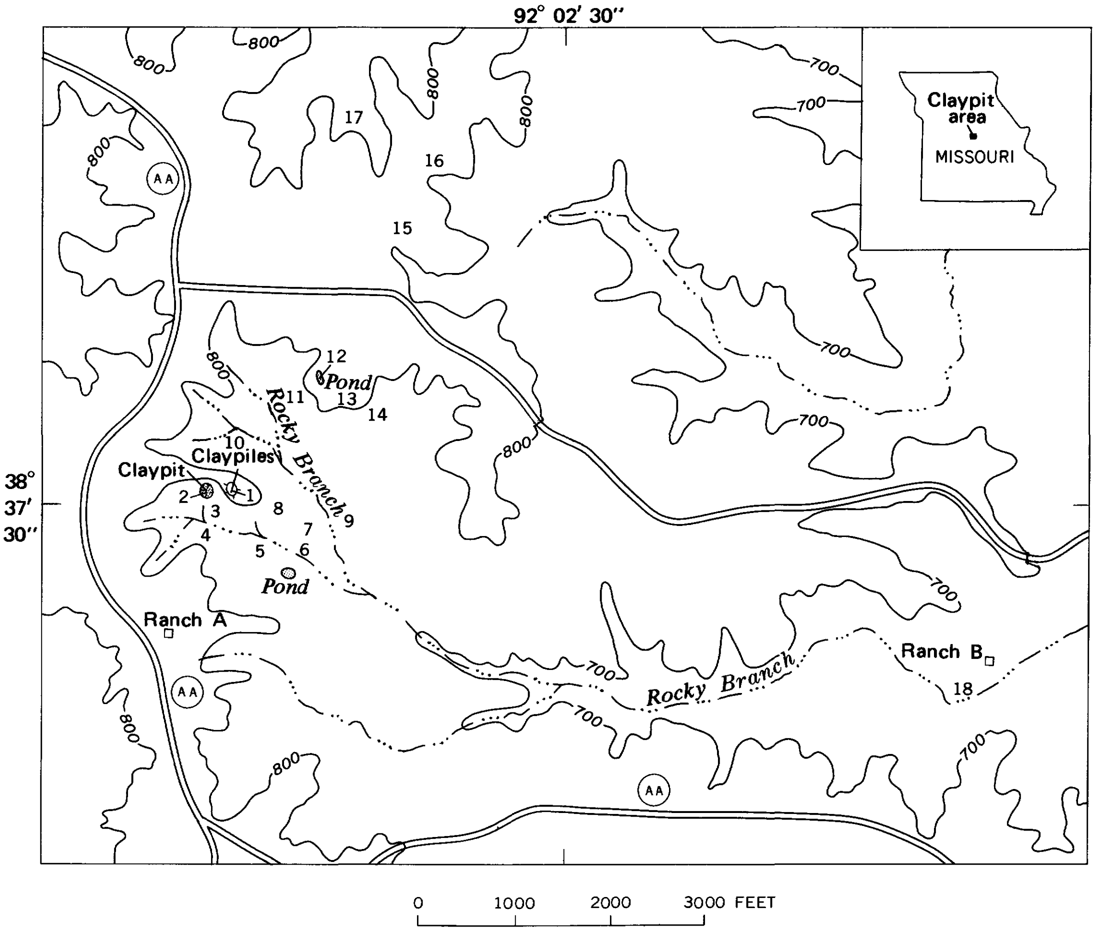

FIGURE 1.—Claypit area, Callaway County, Mo., showing locations of numbered sites where samples were collected. Base from U.S. Geological Survey, New Bloomfield (1969) and Osage City (1967), Mo., 1:24,000.

Only the cattle that were pastured on land with direct access to Rocky Branch were reported to have metabolic disorders.

Ebens (geologist), Erdman (botanist), and Feder (hydrologist) of the U.S. Geological Survey conducted the geochemical studies. Case (clinical veterinarian, toxicologist) of the School of Veterinary Medicine, University of Missouri—Columbia, and Selby (epidemiologist, veterinarian) of the Environmental Health Surveillance Center and the School of Veterinary Medicine, University of Missouri—Columbia, conducted the studies of metabolic imbalances of the beef cattle. Partial support of these studies by Selby was provided by U.S. Public Health Service Grant No. E. S. 00082 to the Environmental Health Surveillance Center.

We express our appreciation to Messrs. Z. S. Altschuler, Hansford T. Shacklette, Richard W. White, and Mrs. Josephine G. Boerngen, all with the U.S. Geological Survey, for their assistance in collecting and preparing samples, and in interpreting the data. We are also indebted to Terrence M. Curtin of the School of Veterinary Medicine, University of Missouri—Columbia, for reviewing the manuscript. Messrs. David P. Hutcheson (nutritionist, School of Veterinary Medicine, University of Missouri—Columbia), Larry Edmonds (Enviromental Health Surveillance Center, University of Missouri—Columbia), and Vincent Raaf (Area Livestock Extension Agent) assisted in gathering and interpreting data. We thank Messrs. Robert Helzer and Byran Hungate (ranchers), and Merrill Townley (veterinarian) for their cooperation in conducting the field studies.

METHODS OF SAMPLING AND ANALYSIS

SAMPLING MEDIA AND TECHNIQUES

Samples were collected to determine which elements were present and in what concentrations in surficial deposits, vegetation, and water in order to characterize the geochemistry of the claypit area. Studies of metabolic imbalances of the beef cattle conducted at the ranches were supplemented by laboratory examinations and analyses of selected materials.

FIGURE 2.—Aerial view of claypit area, Callaway County, Mo. This view, looking south, shows the smaller claypile (left foreground) and the larger claypile (left center) with diversion ditches leading to the water-filled claypit (right center). Before these ditches were constructed, some runoff from both claypiles flowed to the left, and entered a branch of Rocky Branch. Overflow from the claypit enters a branch of Rocky Branch to the right of the wooded area, thence down the valley to low areas of the livestock pasture shown in the left background. Dump truck at lower right indicates scale. Photographed February 1972.

SURFICIAL DEPOSITS

Surficial deposits, as defined in this study, consist of clay and rock collected from the claypiles and the claypit, alluvium collected from two forks of Rocky Branch that drain slopes and small valleys below the claypiles and claypit, and soils collected from plant-sampling sites and from upland fields that are not affected by drainage from the claypiles or pit. A total of 31 samples of surficial materials from 14 sites was collected. The locations of the sampling sites are given in figure 1.

Clay, rock, and some soil samples were collected at depths ranging from a few centimeters to 15 cm by using a mason's hammer or a trowel. The eight samples of loess soils were 1-inch-diameter cores obtained with a stainless steel punch auger from depths of 2–15 cm. Samples of both pyritic material and gypsum were handpicked from the surface of the large claypile. All samples were placed in waterproof paper containers, dried in an oven with circulating air at 50°C, and pulverized in a ceramic mill to approximately minus-100-mesh particle size.

EFFLORESCENT SALTS

Yellowish-brown efflorescent salts a few millimeters thick at water seeps covered several tens of square feet at the southeast side of the large claypile. Two samples of this material were picked by hand from the ground surface and placed in waterproof paper containers. It was not possible to mechanically remove all clay particles from the efflorescent salts. Therefore, in order to obtain a better estimate of the elements present in each component of the samples, the following separation procedure was used: 43 g (grams) of one of the samples (No. 10, table 2) was placed in 1,600 ml (milliliters) of distilled water at about 35°C for 24 hours. This material was then filtered with a ceramic candle that had a maximum pore radius of 0.6 micron, thus removing 16.5 g of insoluble residue from the 43-g sample. The insoluble residue, sample 12, table 2, was dried at 90°C and pulverized in a ceramic mill to a grain size of minus-100 mesh. The filtrate was evaporated at 25°C and the resulting evaporative residue, sample 11, table 2, was air dried and pulverized in a ceramic mill to a grain size of minus-100 mesh.

PLANTS

A total of 36 plant samples, divided into four suites, from 10 sites was collected and analyzed. The sampling localities are indicated by the numbered sites in figure 1.

Two samples of redcedar trees that grew either in native soil or in claypile material were collected on May 7, 1971. One of these samples occurred near the edge of the claypit west of the smaller claypile (fig. 1, site 1). The other sample was collected at site 3 where some dead oak trees stood in clay deposits that resulted from erosion and downslope movement from the larger pile onto the native soil.

A second suite of samples consisted of grasses and forbs (broad-leafed herbs) that were collected on June 17 in conjunction with water sampling, and their localities correspond to the water sampling sites shown in figure 1, as follows: site 2, the south margin of the claypit pond; site 9, streamside about 1,000 feet east-southeast of the claypile; site 12, margin of a farm pond northeast and across the valley from the claypile; and site 18, streamside on Ranch B about 1.5 miles downstream from the claypit.

Woody native plant species sampled June 30 were the same species as those sampled in an earlier study which was made for the purpose of chemically characterizing the vegetation-type areas of Missouri, and for which we had already estimated typical concentrations and ranges of selected elements in the plant species. These samples were collected along the south fork of Rocky Branch along a traverse downslope from the claypile.

The final suite of plant samples, composed mostly of white sweetclover, was collected in late September. This plant species was believed, on the basis of an earlier analysis, to concentrate molybdenum; moreover, these plants showed evidence of having been grazed by cattle. Certain species of plants associated with white sweetclover also were found to contain anomalously high concentrations of molybdenum, and were, therefore, included in this suite of samples.

Plant samples were cut with pruning shears, placed in paper or cardboard containers, and dried in an oven with circulating air at 50°C. Samples of forbs that were used for separate analyses of roots and aboveground parts were pulled from the ground and thoroughly washed in tapwater before being dried. The 6- to 10-inch terminal parts of deciduous tree and shrub stems (branches) without leaves were used for analysis. The redcedar samples were similar, but included both stems and scalelike leaves. Forbs and grasses were sampled by cutting the plants near the ground, and the samples included stems, leaves, and, if present, flowers and seeds. These samples were not washed.

WATER

Water samples were collected from four sites (fig. 1, sites 2, 9, 12, and 18) on June 17. The samples were not filtered, in order to determine the trace elements that were present in the water-sediment mixture that the cattle might drink. Sites 9 and 18 were chosen because adversely affected cattle had access to the water at these sites. Even though cattle did not have direct access to water in the claypit (site 2), during intense rainfall the claypit overflowed and drained into streams that flowed through the pastures. The farm pond at site 12 was chosen as a control because it received no drainage from the claypiles or claypit.

Samples were collected in acid-washed polyethylene bottles by immersing them 1 foot below the surface of the water. Each bottle was filled and drained twice with sample water before collecting the final sample. The trace-element samples were treated with 1.5 ml double redistilled reagent grade concentrated nitric acid. Samples for nitrogen-cycle determinations were collected in 500-ml bottles, treated immediately with 30 mg mercuric chloride, and placed in an ice-filled cooler. The samples in which the various forms of nitrogen were to be determined were shipped in an ice-filled cooler by bus to the U.S. Geological Survey laboratory in Little Rock, Ark., where they were analyzed immediately in order to minimize the effects of changes in the nitrogen cycle components on the analyses. Field determinations of pH, alkalinity, specific conductance, the temperature were made at each sample site.

On July 16 a raw-water sample was collected for microscopic determination of the presence and concentrations of potentially harmful microorganisms in the claypit water. One liter of water was filtered through a 50-mm-diameter 0.45-micron filter. The final 15 ml of unfiltered water and the filter were placed in a petri dish. Within 2 hours of collection, Robert Lipscomb, U.S. Geological Survey, St. Louis, Mo., prepared a wet slide of an aliquot of the water sample which he examined for the presence of microorganisms.

BEEF CATTLE

On two ranches, designated "Ranch A" and "Ranch B" in this report, beef cattle were pastured in fields adjacent to and downstream from the claypile area (fig. 1). Ranch A is immediately adjacent to this area, and cattle on this ranch were more intensively studied than those on Ranch B located farther downstream from the area. A thorough epidemiological workup of the cattle on Ranch A was undertaken, and cattle on both ranches were examined during numerous visits.

On Ranch A, in 1970, the cattle consisted of two distinct herds—one composed of 54 Angus cows 7 years old, the other, 66 Angus cows 4 years old. In 1971 an additional herd of 24 Charolais cows 4 years old was brought to the ranch. Both Angus and Charolais bulls serviced the herds (table 5). Only the herd of 4-year-old Angus cows showed signs of metabolic imbalance. On Ranch B, one yearling and four older Charolais bulls exhibited these signs. The yearling bull was purchased from a ranch in southwest Missouri in April 1970.

Our first visit to observe the cattle was in May 1971. Frequent visits to the ranches were made throughout the summer and autumn of 1971 to examine the cattle, to collect specimens, and to discuss the problem with the ranchers, the local veterinarian, and the Area Livestock Extension Agent. Blood samples of the affected and unaffected cattle were analyzed for selected trace elements, blood serum enzymes, and macrominerals, and the pH of rumen samples was determined. Cattle were isolated from the claypit area and flood plain, and rations were recommended to correct the interference syndrome.

ANALYTICAL METHODS

SURFICIAL DEPOSITS

Concentrations of elements in surficial deposits were determined by analysis of pulverized samples in the laboratories of the U.S. Geological Survey in Denver, Colo. and Washington, D.C. Magnesium, sodium, cadmium, lithium, and zinc contents were determined by atomic absorption methods, arsenic by colorimetric methods, fluorine by the fluorine selective ion electrode method, and mercury by the mercury detector method described by Vaughn (1967). Organic carbon concentrations were determined by making separate analyses for total carbon and carbonate carbon and computing the difference, according to the method described by Tourtelot, Huffman, and Rader (1964). Silicon, aluminum, ferrous iron, calcium, potassium, phosphorus, and selenium contents were determined by X-ray fluorescence methods.

Concentrations of the other elements were determined by semiquantitative spectrographic analysis. The spectrographic method used is virtually that described by Myers, Havens, and Dunton (1961), but the analytical results are given in six, rather than three, steps per order of magnitude. These results were reported in geometric brackets having the boundaries 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, and so forth, percent or parts per million (ppm); the brackets are identified by their respective geometric midpoints, such as 1.0, 0.7, 0.5, 0.3, 0.2, and 0.15. Thus, a reported value of 0.3 ppm, for example, identifies the bracket from 0.26 to 0.38 as the analyst's best estimate of the concentration. The precision of a reported value is approximately plus or minus one bracket at the 68-percent level of confidence, and plus or minus two brackets at the 95-percent level.

The approximate lower limits of analytical detection for surficial deposits are given in table 1. Some combinations of elements in a sample, however, affect these limits. Concentrations somewhat lower than these values may be detected in unusually favorable materials, whereas these limits may not be attained in unfavorable materials.

Surficial materials, except soils, were analyzed by X-ray diffraction to determine their mineral content.

EFFLORESCENT SALTS

Efflorescent salts were analyzed for element concentrations by the same methods that were used for samples of surficial deposits and, in addition, were examined by X-ray diffraction to determine which minerals were present.

PLANTS

The plant samples were oven dried, then pulverized in a Wiley mill. Wet digestion methods were used to prepare the samples for determining the arsenic, mercury, and selenium concentrations. For determining the concentrations of other elements in the samples, the pulverized plants were transferred to ceramic crucibles,

TABLE 1.—*Approximate lower limits of detection for surficial deposits and plant materials*

[Analyses made by semiquantitative spectrographic method, except as indicated. Dry surficial material was used for analyses of all elements. Dry plant material was used for arsenic, mercury, and selenium analyses; plant ash was used for analyses of all other elements. Limits are given in parts per million ...., no data available]

Element	Lower limit of detection (ppm)		Element	Lower limit of detection (ppm)	
	Surficial deposits	Plant materials		Surficial deposits	Plant materials
Al	[1]10,000	20	Li	[2]5	[2]4
As	[3].2	[3].25	Mg	[2]300	50
B	20	50	Mn	1	2
Ba	1.5	3	Mo	3	[3]4
Be	1	2	Na	[2]100	[2]100
C, total	[4]500	....	Nb	10	....
C, in CO_3	[4]100	....	Nd	70	....
C, organic	[4]1,000	....	Ni	5	2
Ca	[1]1,000	[3]150	P	[1]300	[3]40
Cd	[2]1	[2].3	Pb	10	20
Ce	150	....	Pr	100	....
Co	3	[2]1	Se	[1].1	[3].5
Cr	1	2	Sc	5	5
Cu	1	2	Si	[1]10,000	....
Dy	50	....	Sn	....	20
F	[5]40	....	Sr	5	10
Fe in Fe_2O_3	[1]1,000	[6]20	Sm	100	....
Ga	5	5	Ti	2	5
Gd	50	....	V	7	5
Hg	[7].01	[3].025	Y	10	20
K	[1]1,000	[2]50	Yb	1	2
La	30	70	Zn	10	[2]25
			Zr	10	20

[1] Analysis by X-ray fluorescence method.
[2] Analysis by atomic absorption method.
[3] Analysis by colorimetric method.
[4] Analysis by method of Tourtelot, Huffman, and Rader (1964).
[5] Analysis by fluorine selective ion electrode method.
[6] Fe, total.
[7] Analysis by mercury detector method.

weighed, and 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 ash was then weighed to determine the ash yield of the dry plant sample. Colorimetric methods were used to analyze the ash for phosphorus and molybdenum (Reichen and Ward, 1951), and the atomic absorption method was used for cadmium, calcium, cobalt, lithium, potassium, sodium, and zinc determinations.

Concentrations of the remaining elements in ash were determined by the same semiquantitative spectrographic method described under "Surficial Deposits," except that the ash was diluted with an equal weight of matrix composed of sodium silica (10 percent Na).

The lower limits of detection of the analytical methods that were used for plant analyses are given in table 1. Several samples did not contain enough material for these lower limits to be attained; therefore, the detection limits were higher for elements in these samples.

WATER

Because of the possibility of changes occurring rapidly in certain chemical properties of water after sampling, determinations of pH, alkalinity, specific conductance, and temperature were made at the sample sites. Procedures for making these determinations were given by Brown, Skougstad, and Fishman (1970).

All laboratory determinations, except those of nitrogen cycle components, were made in the U.S. Geological Survey laboratories in Denver, Colo., under the supervision of Marvin W. Skougstad. The nitrogen cycle determinations were made in the Survey laboratories in Little Rock, Ark., under the supervision of Charles T. Bryant.

Cadmium, chromium, cobalt, lead, zinc, mercury, arsenic, and nitrogen cycle components were determined by methods given by Brown, Skougstad, and Fishman (1970). All other determinations were made by spectrographic methods described by Barnett and Mallory (1971).

BEEF CATTLE

Whole blood samples from the beef cattle studied were analyzed for trace-element content by the Environmental Trace Substances Center, Research Reactor Facility, Columbia, Mo., under the supervision of Dr. James O. Pierce. Whole blood samples were collected by venipuncture in tubes containing 6 mg EDTA (ethylenediamine tetraacetate) per 5 ml of blood, and were wet ashed with a 5:1 ratio of nitric and perchloric acid. The residue was then dissolved in 1-percent nitric acid and the sample analyzed by atomic absorption spectrophotometry, using recommended methods (Kerber, 1971).

Blood serum analyses, using the methods of Tumbleson(1969), were performed by Dr. David P. Hutcheson, School of Veterinary Medicine, University of Missouri at Columbia, for the determination of the biochemic constituents cholesterol, total bilirubin, glutamic-oxaloacetic transaminase, alkaline phosphatase, lactic dehydrogenase, total protein, creatinine, blood urea nitrogen, calcium, inorganic phosphorus, sodium, potassium, and chloride. The pH of rumen samples was determined by Selby and evaluated by Dr. Hutcheson.

RESULTS AND DISCUSSION

The results of laboratory analyses of surficial materials, efflorescent salts, plants, and water samples are given in tables 2–4. The data and observations pertaining to beef cattle are given in tables 5–7.

ESTABLISHING TYPICAL GEOCHEMICAL VALUES FOR SAMPLING MEDIA AS BASES FOR DEFINING ANOMALOUS VALUES

The substances that occur in anomalous concentrations in various surficial materials must be identified by evaluating the deviations of their concentrations from typical concentrations in comparable materials from other areas. Anomalous values can only be defined as deviations from values that are considered typical for the materials under consideration. Therefore, typical values must first be established for each category of material; then a judgment must be made as to the degree of deviation from the typical value that is required to classify other values as "anomalous." Deviations above the typical values may, for convenience, be designated "positive anomalies," and those below, "negative anomalies."

The selection of criteria that are to be used in distinguishing anomalous from normal concentrations is a matter of judgment that must be made according to the requirements of the study. We have chosen to define normal concentrations as those that are within the central 95-percent range of concentrations found in comparable materials thought not to have been affected by pollution; anomalous concentrations are those that occur outside this range.

The geometric mean is a measure of central tendency of the frequency distribution and, as such, is an estimate of the typical or most common concentration for the element or compound. Approximately 95 percent of the 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 central 95-percent ranges of the distributions of each element and compound were computed on this basis (table 8), and these ranges were used to define anomalous concentrations of the chemical constituents in samples from the claypit area as given in table 10. If the concentration of an element or compound was beyond the normal 95-percent range in one or more samples of a given material (table 10), this element or compound was considered anomalous in that material. For example, the geometric mean alumina content of B-horizon soils from the Oak-Hickory Forest vegetation type area in Missouri is 5.1 percent and the geometric deviation is 1.47 (table 8). Probably 95 percent of the samples have alumina contents in the range $5.1 \div (1.47)^2$ (2.4 percent) to $5.1 \times (1.47)^2$ (11 percent). These two limits define the range against which the alumina analyses of the clay samples from the claypit area were compared; in this example, alumina concentrations in all five of the clay samples were judged to be beyond the normal 95-percent range and are, therefore, anomalous with respect to the B-horizon soils.

Typical values that were used to identify anomalous values in sampling media from the claypit area are given in table 8. This table gives geometric means and geometric deviations for the concentrations of elements and compounds in different categories of surficial deposits and vegetation; they are believed to be the best available data on typical concentrations of elements in the respective materials. The data in table 8 were developed from sampling programs that were entirely unrelated to the claypit study. (See Shacklette, Erdman, and Keith, 1971.) The means and deviations in this table are antilogs of the arithmetic means and standard deviations, respectively, of the logarithms of the analytical values. Where some of the element concentrations were determined to be less than the sensitivity of the analytical method (table 1), the mean and standard deviations of the logarithms were estimated by means of a censored-distribution technique devised by Cohen (1959).

No reliable data were available for use as norms for identifying anomalous concentrations of elements and compounds in water.

SURFICIAL DEPOSITS

The concentrations of selected elements in 31 samples of surficial deposits collected from the claypit area are given in table 2. Sample site numbers, dates samples were collected, and a brief description of the samples are included. The mineralogy, as determined by X-ray diffraction analyses, is shown for all the samples except those of soil.

In order to ascertain the possible effect that the mined clay could have on the local environment, the elemental composition of the clay was compared with that of soils of the area, because both of these materials influence the water in Rocky Branch and the supply of elements available to plants. The elemental compositions of clays from the claypiles and claypit differ markedly from those of soils in the problem area and from most B-horizon soils from the Oak-Hickory Forest, the vegetation type which occurs throughout much of southern Missouri and in which the claypit area is located (table 9). The elements listed in table 9 are those that were found to occur in anomalous concentrations in one or more samples of clay. The four samples of soil (Nos. 32–35, table 2) from the white sweetclover sampling localities were composed mostly of clay on the large claypile or of clay washed from the claypile, and their elemental composition is similar to that of the samples designated as clay.

Except for nickel in sample 21 (table 2), the concentrations of trace elements in a sample of dolomite (No. 19) and in two samples of carbonate residuum (Nos. 20 and 21, table 2) collected from the walls of the claypit are not anomalously high with respect to the soils. A sample of shaly coal (No. 4, table 2) collected from the large claypile contained concentrations of beryllium, lead, lithium, mercury, molybdenum, scandium, vanadium, ytterbium, and zinc that are anomalously high with respect to the soils, although apparently normal for this type of coal.

The elemental compositions of four samples of alluvium (Nos. 13, 14, 16, and 17, table 2) collected from the beds of creeks that drain away from the claypiles are similar to those of samples of clay from the claypiles. The clay-size fraction and the coarse-grained fraction of the alluvium do not differ significantly in trace-element composition. The amounts of clay and shale particles which are derived from the claypiles and carried by creeks, and the maximum distance that the particles are carried, are not known. However, clay similar to that found in the claypiles has coated rocks in Rocky Branch and occurred as deposits (as much as 10 cm thick at sample site 5) in ephemeral pools in the creekbed as far downstream as Ranch B, the farthest downstream point in the study area. Clay and shale particles similar to those found in the claypiles were observed on parts of the flood plain several hundred feet downstream from sample site 6 (fig. 1), the farthest point downstream that the flood plain was inspected.

Gypsum ($CaSO_4 \cdot H_2O$) was found to be widespread on the surface of the large claypile and probably was produced by the action of sulfuric acid solution on calcium-bearing minerals in the claypile. Sample 8 (table 2), which is composed of gypsum, clay, quartz, apatite, and crandallite(?), had anomalously high concentrations of dysprosium, gadolinium, phosphorus, praseodymium, samarium, and yttrium compared to those found in the clays and the other gypsum sample that were analyzed. In this sample these elements probably occurred in the clay or in the phosphate minerals apatite and crandallite. Barium, chromium, selenium, and strontium were the only trace elements detectable in gypsum sample 7 (table 2) although the concentrations were low; other trace elements, if present, were in concentrations below the detection limits given in table 1.

Pyritic material was widely disseminated throughout the large claypile; the presence of pyrite was verified by X-ray diffraction of samples 5 and 6 (table 2). Sample 5 was contaminated with clay, gypsum, and calcite; hence, the chemical data for this sample reflect the chemical composition of these materials. The concentration of cobalt was high in this sample compared to that found in the clays. Sample 6, which was only slightly contaminated with clay particles, contained no abnormally high concentrations of trace elements compared to the composition of normal soils from the area. The presence of pyrite is important in geochemical systems, however, because the weathering of this material results in the formation of sulfuric acid, which increases the solubility of certain compounds. The mobilities of constituent elements in these compounds, therefore, are generally increased.

EFFLORESCENT SALTS

Chemical properties of the efflorescent salts are given in table 2. X-ray diffraction analyses of sample 11 (table 2), which consisted of residue obtained by evaporating the soluble fraction of the efflorescent salts, and of sample 10 (table 2) indicate that alunogen, a hydrous sulfate of aluminum having the formula $Al_2(SO_4)_3 \cdot nH_2O$, is the dominant crystalline phase of these salts. Palache, Berman, and Frondel (1951, p. 538–539) reported that alunogen occurs principally as an efflorescence or crevice filling in coals, shales, and slates that contain pyrite, and that the mineral is

TABLE 2.—*Compounds and elements in samples of surficial*

[Analysts: Leon A. Bradley, G. T. Burrow, Carroll Burton, J. P. Cahill, W. H. Ficklin, Larry D. Forshey, I. C. Frost, Johnnie Gardner, Roosevelt Moore, M. W. Solt, J. A. Thomas, R. L. Turner, and J. S. Wahlberg. Some elements were looked for in all samples but were not found. These elements, analyzed by the semiquantitative spectrographic method, and their lower detection limits, in parts per million, are as follows: Antimony, 150; bismuth, 10; europium, 100; germanium, 10; gold, 20; hafnium, 100; indium, 10; palladium, 1; platinum, 30; rhenium, 30; silver, 0.5; tantalum, 200; tellurium, 2,000; thallium, 50; thorium, 200; tin, 10; tungsten 100; and uranium, 500. If lanthanum or cerium

Sample No.	Laboratory No.	Site No. (fig. 1)	Date sampled (1971)	Material sampled	Remarks	Compound or element			
						SiO_2 (percent)	Al_2O_3 (percent)	Total Fe as Fe_2O_3 (percent)	MgO (percent)
					Large claypile				
1	D149910	1	May 7	Clay	Kaolinite; lesser amounts of illite and mixed-layer clay	48	30	2.2	0.8
2	D150439	1	June 30	do	do	45	29	2	.64
3	D150448	1	do	do	do	44	31	1.4	.6
4	D149912	1	May 7	Shaly coal		13	8	16	.08
5	D149913	1	do	Pyrite	Contains clay, gypsum, and calcite	8	4	35	.28
6	D150447	1	June 30	do	Slight clay contamination	1	1	65	.1
7	D150433	1	do	Gypsum		.3	.5	<.1	.01
8	D150450	1	do	do	About 50 percent clay; contains quartz, apatite, and crandallite (?)	35	24	2.2	.41
9	D150434	1	do	Efflorescent salts	1–5 mm temporary salt crust (mostly alunogen) on clay at seeps, base of large claypile (south end); contains clay	23	20	6.5	1.04
10	D150435	1	do	do	do	18	17	6.1	1.11
11	D150436	1	do	do	Evaporative residue (1.17 g residue per 100 ml of solution), obtained from sample 10	....	.2	....	.03
12	D150437	1	do	do	Insoluble residue obtained from sample 10	43	24	7.3	.56
13	D154026	5	Sept. 28	Alluvium	Clay, upper 3–10 cm of streambed deposit	52	28	3.9	.97
14	D154027	5	do	do	Sand, silt, and clay collected in creekbed immediately below sample 13	52	27	2.6	.71
					Small claypile				
15	D149911	1	May 7	Clay	Kaolinite; lesser amounts of illite and mixed-layer clay	46	34	1.5	0.55
16	D154024	10	Sept. 28	Alluvium	Clay, upper 3–10 cm of streambed deposit	49	34	1.3	.56
17	D154025	10	do	do	Sand, silt, and clay collected in creekbed immediately below sample 16	51	31	1.7	.54
					Claypit				
18	D150445	2	June 30	Clay	Kaolinite; lesser amounts of illite and mixed-layer clay	41	33	1	0.42
19	D150446	2	do	Silty dolomite	Collected from drainage ditch, southeast part of claypit	5	1	2	16
20	D150442	2	do	Carbonate residuum	Collected from north wall of claypit	79	8	2.8	.45
21	D150449	2	do	do	do	71	11	5.7	.64
					Soils from vicinity of claypit				
22	D149914	8	May 7	Loess soils		75	9	2.8	0.52
23	D149915	7	do	do		75	9	2.5	.48
24	D149916	11	do	do		70	11	4.7	.86
25	D149917	13	do	do		70	11	4.4	.78
26	D149918	14	do	do		82	7	2	.36
27	D149919	15	do	do		75	8	3.8	.47
28	D149920	16	do	do		77	8	3	.48
29	D149921	17	do	do		82	7	1.7	.29
30	D150440	6	June 30	Soils	Associated with white oak and buckbrush sampling localities	77	8	2.9	.38
31	D150441	4	do	do	do	78	7	2.1	.33
32	D154028	1	Sept. 26	do	Associated with white sweetclover sampling localities	47	32	1.4	.56
83	D154029	1	do	do	do	59	25	2.8	.89
84	D154030	2	do	do	do	50	30	1.7	.58
35	D154031	4	do	do	do	54	29	2.6	.90

formed by the action of sulfate solutions resulting from the oxidation of the pyrite on aluminous minerals.

Analysis of the efflorescent salts served to identify some of the elements that move in solution in the immediate vicinity of the claypile. Samples 9 and 10 (table 2) reflect, in part, the chemical composition of the clay from the large claypile because it was not possible to remove all clay particles from the salts. The chemical composition of the residue sample (No. 11) derived from the evaporated soluble material in sample 10 reveals soluble elements in the efflorescent salts, plus those that were released from the clay by the acid solution.

Aluminum, cobalt, copper, and nickel have the highest concentrations in sample 11, and barium, beryllium, chromium, gallium, lithium, manganese, scandium, ytterbium, yttrium, and zinc are present in lower concentrations. Other trace elements analyzed for, if present, were in concentrations below the detection limits given in table 1. The complete distance that these elements are moved in solution or in suspended solids by runoff from the claypile is not known. However, the crust of efflorescent salts that was sampled on June 30 was not observed during a visit to the claypit area on September 28. A 3-inch rainfall on September 22 is thought to have washed the efflorescent salts from this area, and conditions conducive to the formation of new crusts of salts were not in evidence.

PLANTS

Chemical analyses of the 36 plant samples from the claypit area are given in table 3. Where several samples of a species were collected and analyzed, the samples that are considered to be more directly affected by the chemical composition of the claypile generally are listed first in the table in order to facilitate examina-

deposits and efflorescent salts from the claypit area

were found in a sample, praseodymium with a lower detection limit of 1 ppm was looked for in the same sample but was not found. If yttrium concentration in a sample exceeded 50 ppm, the following elements, with their stated lower detection limits, were looked for in the same sample, but were not found: Erbium, 50; holmium, 20; lutetium, 30; terbium 300; and thulium, 20. Asterisk, analysis by a semiquantitative spectrographic method. Results are reported as geometric midpoints of geometric classes, in the series 1, 1.5, 2, 3, 5, 7, 10, 15, and so forth. --------------, no data available]

Compound or element														
CaO (percent)	Na_2O (percent)	K_2O (percent)	P_2O_5 (percent)	Total C (percent)	Carbonate C (percent)	Organic C (percent)	As (ppm)	B* (ppm)	Ba* (ppm)	Be* (ppm)	Cd (ppm)	Ce* (ppm)	Co* (ppm)	Cr* (ppm)
Large claypile														
0.3	0.13	3.6	0.5	0.6	0.06	0.5	....	70	500	3	<1	300	7	300
.1	.14	2.9	.3	.88	.01	.9	8.6	50	200	3	<1	150	3	150
.3	.09	2.9	.3	.6	.01	.6	6.4	50	150	2	<1	150	3	300
<.1	.02	.4	.1	37.8	.06	37.7	....	<20	30	3	.5	<150	3	70
16	.02	.5	.1	3.3	3.3	<.1	....	<20	30	1.5	.5	<150	30	30
.4	.01	<.1	.3	7.24	.2	7.2	.3	<20	30	<1	<1	<150	<3	7
32	<.01	<.1	<.05	....	....	....	<1	<20	10	<1	<1	<150	<3	2
5.9	.13	2.1	5.9	.51	<.01	.5	6.8	50	500	3	<1	300	<3	150
.6	.04	1	.3	....	....	....	6.7	20	70	5	<1	<150	50	70
.6	.03	.9	.2	....	....	....	13.4	20	100	7	<1	<150	70	50
....	.0001	....	....	....	....	....	....	<20	1.5	15	<1	<150	200	15
.2	.09	2.1	.5	....	....	....	12.9	50	300	3	<1	150	15	150
.2	.16	4.3	.2	2.34	<.01	2.3	8.0	70	300	3	<1	300	10	200
.5	.11	2.7	.3	1.02	.13	.9	9.1	70	300	3	<1	300	15	200
Small claypile														
<0.1	0.36	2.5	0.2	0.71	0.09	0.6	....	70	200	2	<1	300	5	300
.2	.10	2.9	.2	.44	.01	.4	2.1	70	200	3	<1	300	7	300
.2	.14	2.7	.2	2.99	<.01	3.0	5.6	70	200	3	<1	300	15	200
Claypit														
0.2	0.08	1.3	0.1	0.32	<0.01	0.3	5.4	30	30	2	<1	<150	15	200
29	.02	.3	<.05	11.8	11.3	.5	2.4	<20	30	<1	<1	<150	5	7
.4	.63	1.4	.05	.83	<.01	.8	6.5	30	500	<1	<1	<150	7	30
.6	.75	1.6	.1	.37	<.01	.4	12.5	20	700	1.5	<1	<150	7	70
Soils from vicinity of claypit														
0.4	1.05	2	0.1	1.91	0.1	1.8	....	30	1,000	<1	<1	150	15	70
.5	1.08	1.8	.2	2.6	.11	2.5	....	50	700	1.5	<1	150	15	70
.5	.94	1.9	.2	1.88	.11	1.8	....	30	700	1	<1	150	15	70
.4	1.03	1.8	.2	1.25	.07	1.4	....	30	700	1	<1	150	15	70
.2	.94	2.1	.1	1.17	.08	1.1	....	50	700	<1	<1	150	15	70
.6	1.06	1.6	.2	1.82	.06	1.8	....	30	700	<1	<1	150	15	70
.5	1.01	1.8	.1	1.32	.12	1.2	....	50	700	1	<1	150	15	70
.2	.88	1.8	.1	2.05	.08	2	....	50	700	<1	<1	150	5	70
.5	.81	1.7	.1	1.48	.01	1.5	7.9	30	500	<1	<1	<150	15	50
.3	.9	1.9	.3	1.16	<.01	1.2	5.5	30	700	<1	<1	<150	10	50
.3	.09	2.9	.3	.33	<.01	.3	1.2	70	300	3	<1	300	7	300
.4	.06	4.7	.07	3.41	.02	3.4	1.4	70	300	2	<1	150	7	300
.3	.08	2	.2	.46	<.01	.5	6.9	70	200	3	<1	700	30	200
.8	.11	4	.3	.53	.06	.5	2.7	70	300	3	<1	300	10	200

TABLE 2.—*Compounds and elements in samples of surficial*

Sample No.	Laboratory No.	Compound or element									
		Cu[2] (ppm)	Dy[2] (ppm)	F (percent)	Ga* (ppm)	Gd* (ppm)	Hg (ppm)	La* (ppm)	Li (ppm)	Mn* (ppm)	Mo* (ppm)
				Large claypile							
1	D149910	70	....	....	50	....	0.08	150	153	30	< 3
2	D150439	100	<50	.03	30	....	.17	70	242	20	3
3	D150448	50	....	.11	50	....	.12	100	258	7	15
4	D149912	50	....	....	7	....	1.3	30	78	3	7
5	D149913	70	<50	....	<5	<50	.75	30	22	50	<3
6	D150447	15	....	<.001	15	....	.48	<30	10	5	3
7	D150433	<1	....	<.001	<5	....	.15	<30	<5	<1	<3
8	D150450	30	50	.084	50	50	<.01	150	195	3	<3
9	D150434	700	<50	.11	20	<50	.34	30	180	30	<3
10	D150435	700	<50	.17	20	<50	.27	30	156	50	<3
11	D150436	2,000	<50	....	50	<50	....	<30	1.6	100	<3
12	D150437	300	<50	.096	50	<50	.25	100	210	15	5
13	D154026	100	<50	.12	70	<50	.06	150	150	100	3
14	D154027	150	<50	.1	70	<50	.06	150	242	700	3
				Small claypile							
15	D149911	30	<50	....	50	<50	0.11	150	320	7	7
16	D154024	50	....	.098	70	....	.03	70	284	30	3
17	D154025	50	....	.084	70	....	.02	70	280	300	3
				Claypit							
18	D150445	150	....	0.084	50	....	0.06	70	338	50	7
19	D150446	10	....	.034	<5	....	<.01	<30	<5	150	<3
20	D150442	10	....	.022	10	....	.07	30	22	500	<3
21	D150449	20	....	.052	20	....	.04	30	27	150	<3
				Soils from vicinity of claypit							
22	D149914	15	....	....	15	....	0.04	50	24	1,000	<3
23	D149915	15	....	....	15	....	.07	70	24	1,500	<3
24	D149916	20	....	....	20	....	.06	70	25	500	<3
25	D149917	20	....	....	20	....	.05	50	24	700	<3
26	D149918	7	....	....	10	....	.04	50	21	500	<3
27	D149919	10	....	....	15	....	.05	70	20	1,000	<3
28	D149920	10	....	....	15	....	.05	50	23	1,500	<3
29	D149921	7	....	....	15	....	.07	30	20	200	<3
30	D150440	10	....	.006	10	....	.09	50	22	1,500	<3
31	D150441	15	....	.014	10	....	.08	70	22	1,000	<3
32	D154028	100	<50	.09	70	<50	.02	150	246	15	3
33	D154029	70	....	.12	70	....	.02	70	41	20	3
34	D154030	50	....	.082	50	....	.05	300	148	70	7
35	D154031	30	....	.12	50	....	.02	150	144	70	3

tion of the table for anomalous element concentrations in plants.

Plant species have inherent abilities to concentrate certain elements in their tissues. This ability varies among different species in such a manner that normal levels of certain elements in one species may be highly anomalous in another. Superimposed on this inherent ability of species is their tendency to increase their absorption of some of the elements that are unusually abundant in the soil on which they grow. Both of these characteristics of species must be taken into account when seeking to identify anomalous element concentrations in plant tissues that may be related to anomalous levels of the same elements in the soil.

Ideally, data on the typical concentrations of elements in plants that are to be used for identifying anomalous concentrations should be established for each species, on the basis of analyses of plants that grew in an environment that was typical for the species. Because of the large number of plant species that may be of interest in the geochemical study of a suspected anomalous area, completely satisfactory data of this sort are not commonly available. Therefore, the best available data must be used, with the result that the typical values that are established for each species or group may range from highly reliable to doubtfully applicable as bases for identifying anomalies. This variation in reliability of typical values was found in our study of the plant species that grew in the claypit area. The data that were used for establishing typical values (table 8), arranged in order of most reliable to least reliable, are discussed in the paragraphs that follow.

In earlier biogeochemical studies in Missouri, we established estimates of typical element concentrations in three species of woody plants that are widespread in the State, and that grow in the claypit area. These species (white oak, buckbrush, and smooth sumac) are common in the Oak-Hickory Forest, a vegetation type mapped by Küchler (1964) in which the Callaway County claypit area is located. Typical ranges of element concentrations for the three species are presented in table 8.

Redcedar is another species which grows in the claypit area and for which we have estimates of typical element concentrations. These estimates (table 8) are based on analyses of 10 samples from the Oak-Hickory Forest area.

In certain species for which we do not have adequate data, the normal element concentrations can be estimated by using the analyses of closely related species; this procedure is based on the assumption that the element-concentrating ability among species is related to their degree of taxonomic affinity, which may be generally, but not invariably, true. For example, data are *deposits and efflorescent salts from the claypit area*—Continued

Compound or element														
Nb* (ppm)	Nd* (ppm)	Ni* (ppm)	Pb* (ppm)	Pr* (ppm)	Sc* (ppm)	Se (ppm)	Sm* (ppm)	Sr* (ppm)	Ti* (percent)	V* (ppm)	Y* (ppm)	Yb* (ppm)	Zn (ppm)	Zr* (ppm)
Large claypile														
15	150	100	30	....	30	4	<100	2,000	1	300	50	5	35	150
10	100	50	30	<100	30	3.2	<100	700	.3	300	70	7	31	150
10	100	30	50	<100	30	1.7	<100	700	.5	700	50	5	27	150
<10	<70	20	70	....	15	....	<100	70	.15	500	50	7	132	30
<10	<70	150	15	....	10	....	<100	70	.15	50	70	....	17	30
<10	....	15	<10	....	<5	....	....	30	.02	10	15	....	12	10
<10	....	<5	<10	....	<5	.5	....	70	.002	<7	<10	<1	<5	<10
<10	200	30	30	100	30	.6	100	2,000	.5	200	150	7	20	100
<10	<70	300	15	<100	15	3.6	<100	150	.2	70	70	7	33	70
<10	<70	500	15	<100	15	4.8	<100	150	.15	70	100	7	31	70
<10	<70	1,500	<10	....	10	....	....	<5	<.0002	<7	150	15	1.7	<10
10	100	100	30	<100	20	6.7	<100	1,500	.3	200	70	7	48	100
15	150	100	50	<100	30	2.3	<100	1,000	.7	300	70	7	47	150
15	150	100	70	<100	30	2.3	<100	1,000	.5	300	70	7	32	150
Small claypile														
15	150	70	50	....	50	3	<100	700	1	700	70	7	26	150
20	70	100	30	<100	30	1.6	<100	700	.7	500	50	5	30	150
20	100	100	50	<100	30	1.8	<100	700	.7	300	50	7	30	150
Claypit														
10	70	100	20	....	30	0.4	<100	150	0.5	500	20	3	31	150
<10	....	20	<10	....	<5	1	....	150	.01	15	<10	<1	8	<10
10	<70	7	15	....	7	.2	<100	100	.3	50	30	3	39	300
<10	<70	50	15	<100	10	.2	<100	150	.2	100	30	3	77	200
Soils from vicinity of claypit														
10	70	15	15	....	10	0.3	<100	200	0.3	100	30	3	49	300
10	70	20	20	....	7	.6	<100	150	.3	70	30	5	52	300
10	70	15	30	....	15	.6	<100	200	.5	150	30	3	67	300
10	70	15	30	....	15	.7	<100	200	.5	150	50	7	56	200
10	70	15	15	....	7	.2	<100	150	.5	70	30	3	34	300
10	70	15	30	....	7	.4	<100	150	.5	70	30	3	44	300
10	70	15	20	....	7	.2	<100	150	.5	100	30	3	43	300
10	70	15	15	....	7	.3	<100	150	.5	70	30	3	39	300
10	<70	15	20	....	7	.6	<100	150	.3	70	50	5	47	300
10	70	7	15	....	7	.5	<100	150	.5	50	50	5	29	500
20	200	70	70	<100	30	.7	<100	700	.7	700	70	7	31	150
20	70	70	30	<100	20	.9	<100	500	.7	150	50	5	36	200
20	300	50	30	<100	30	2.8	<100	1,000	.7	300	50	7	24	150
50	150	70	30	<100	30	1.2	<100	1,000	.7	300	50	5	38	150

not available in our files or in the available literature on which to establish typical element concentrations in white sweetclover; however, we do have data on the element content of 10 samples of yellow sweetclover, a closely related species, from other parts of the United States. In the absence of better estimates of the normal values, these data are given in table 8 for use in evaluating the element content of white sweetclover samples from the claypit area.

Certain element-concentrating capabilities are characteristic of many species within a plant family, and somewhat predictable differences in these abilities may occur among families. We have seven samples of grasses from the claypit area, but have no highly reliable means of estimating a corresponding norm for use in identifying anomalous values. If we assume that members of the Grass Family tend to concentrate elements similarly, analytical data obtained for 18 samples of meadow fescue from locations throughout Missouri, as given in table 8, may be used for judging anomalies in the claypit grass samples.

If corresponding analytical data for certain species sampled in the claypit area are unavailable, there may be no reliable basis for judging anomalous element concentrations in these species. Nevertheless, we do have estimates of typical element values, and ranges in values, for plants in general; these estimates are based on about 1,100 plant samples, including many different species, from throughout the conterminous United States. These samples were collected in a nationwide study of soils, described by Shacklette, Hamilton, Boerngen, and Bowles (1971). The values, given in table 8, may be used for identifying extremely high or extremely low concentrations of elements in plant samples from the claypit area if no better means for such identifications are available.

Anomalies in the elemental compositions of the plants growing in the claypit area are recognized by comparing their analyses as given in table 3 to the typical values (central 95-percent range) listed in table 8. The following discussion of these anomalies is organized by species or plant type, and the sample numbers refer to those in table 3.

Five white oak trees were sampled on a traverse extending from the margin of the larger claypile to the wall of the claypit and down the drainage system to the area in which cattle had been pastured. Cadmium was unusually highly concentrated in all the samples except No. 3, and sodium was abnormally low in all the samples (table 3). Elemental compositions of the samples from the trees most closely associated with the claypile (Nos. 1 and 2) were the most divergent from typical values. In general, these samples had positive anomalies in concentrations of aluminum, cadmium, cobalt, copper, potassium, lanthanum, molybdenum, nickel, ytterbium, and zinc. Negative anomalies were apparent for barium, calcium, and sodium. Several anomalies, unique to samples of white oak, were the low calcium levels in the samples from site 1 near the claypile, the only lanthanum anomaly (sample 1), and the abnormally high zinc values in samples 1 and 4, collected from the pasture site. The most extreme positive anomalies were reflected in the cobalt, copper, molybdenum, and nickel concentrations in these samples.

Both samples of redcedar from near the claypiles contained unusually high levels of aluminum, beryllium, cobalt, and nickel, and unusually low levels of barium and sodium. Sample 6, collected at site 3 where the surficial deposits from the larger claypile were thick, had additional positive anomalies in chromium, copper, gallium, scandium, titanium, vanadium, and ytterbium. The scandium anomaly in this sample is unique; no other sample collected from the area contained detectable amounts of this element.

Of all the plants sampled, only redcedar contained detectable beryllium. This element was found in samples of the claypile, and analyses of water samples and efflorescent salts showed that it was moving from this source. Beryllium is not commonly detected in plant samples. Of about 900 samples of various plant species from throughout Missouri, only eight contained 2 ppm or more beryllium, and of these eight samples, all were of shagbark hickory *(Carya ovata)* trees except one which was of smooth sumac. No beryllium

TABLE 3.—*Ash yield and elemental composition*

[Analysts: Harriet G. Neiman, Thelma F. Harms, and Clara S. E. Papp. ...., no data available. Ash, As, Hg, and Se reported as percent or ppm in dry following equation: element (ppm) in dry material = element (ppm) in ash × $\frac{\text{ash content (percent)}}{100}$. Some elements were looked for in all samples but follows: Antimony, 300; bismuth, 20; cerium, 300; europium, 200; germanium, 20; gold, 50; hafnium, 200; indium, 20; niobium, 20; palladium, 2; platinum, sample, the following elements, with their stated lower detection limits, were looked for in the same sample, but were not found: Neodymium, 150; geometric classes, in the series 1, 1.5, 2, 3, 5, 7, 10, 15, and so forth]

Sample No.	Laboratory No.	Site No. (fig. 1)	Date sampled (1971)	Species	Plant part sampled	Ash or element					
						Ash (percent)	Al* (percent)	As (ppm)	B* (ppm)	Ba* (ppm)	Be* (ppm)
Trees											
1	D415622	1	June 30	White oak *(Quercus alba)*	Branches, terminal 8–10 in.	2	0.7	<0.25	300	500	<2
2	D415623	1	do	do	do	3	.7	<.25	200	1,000	<2
3	D415627	4	do	do	do	3.8	.3	<.25	200	3,000	<2
4	D415625	6	do	do	do	3.2	.2	<.25	200	3,000	<2
5	D415630	2	do	do	do	3.5	.15	.25	150	2,000	<2
6	D415578	3	May 7	Redcedar *(Juniperus virginiana)*	Branches, with leaves	3.7	7	<.25	200	500	3
7	D415579	1	do	do	do	4.5	1.5	<.25	200	150	2
Shrubs											
8	D415621	1	June 30	Buckbrush *(Symphoricarpos orbiculatus)*	Stems, without leaves	2.4	1.5	<0.25	200	5,000	<2
9	D415626	4	do	do	do	2.3	1.5	<.25	150	2,000	<2
10	D415624	6	do	do	do	2.2	.7	<.25	100	2,000	<2
11	D415629	2	do	do	do	2.5	1.5	<.25	150	3,000	<2
12	D415692	10	Sept. 28	do	do	2.2	3	<.25	200	3,000	<2
13	D415620	1	June 30	Smooth sumac *(Rhus glabra)*	Stems, terminal 8–10 in.	3	.2	<.25	200	7,000	<2
14	D415628	2	do	do	do	3.2	.5	<.25	200	3,000	<2
Grasses and sedges											
15	D415641	2	June 17	Wood reed grass *(Cinna arundinacea)*	Above-ground parts	10	0.5	<0.25	50	200	<2
16	D415643	9	do	Fowl meadow grass *(Glyceria striata)*	do	7.4	.5	<.25	50	200	<2
17	D415642	9	do	Common bullrush *(Scirpus atrovirens)*	do	7.4	.5	<.25	100	300	<2
18	D415648	18	do	Meadow fescue *(Festuca elatior)*	do	8.4	.7	<.25	70	200	<2
19	D415649	18	do	Timothy *(Phleum pratense)* and Japanese chess *(Bromus japonicus)*	do	16	5	.5	100	700	<2
20	D415651	18	do	Bluegrass *(Poa pratensis)* and meadow fescue	do	9.7	1	<.25	70	500	<2
21	D415647	18	do	Timothy, meadow fescue, and redtop *(Agrostis alba)*	do	11	.7	<.25	50	1,000	<2
Forbs											
22	D415639	2	June 17	Goldenrod *(Solidago* sp.*)*	Above-ground parts	11	1	<0.25	150	150	<2
23	D415644	9	do	Common plantain *(Plantago major)*	do	14	.5	<.25	150	2,000	<2
24	D415650	18	do	do	do	13	1	.25	150	700	<2
25	D415646	12	do	White snakeroot *(Eupatorium rugosum)*	do	18	1.5	<.25	100	1,500	<2
26	D415640	2	do	White sweetclover *(Melilotus alba)*	2d-yr. green stems and leaves	10	.1	<.25	150	1,000	<2
27	D415684	1	Sept. 26	do	2d-yr. dead stems and seeds	2.9	1	.25	300	1,000	<2
28	D415685	1	do	do	do	2.3	1	<.25	700	300	<2
29	D415686	2	do	do	do	2.1	1.5	<.25	300	500	<2
30	D415687	4	do	do	1st-yr. green stems and leaves	7.2	.7	<.25	300	70	<2
31	D415688	5	Sept. 28	do	do	8	3	.25	300	200	<2
32	D415689	5	do	do	1st-yr. roots	3.8	5	<.5	150	150	<2
33	D415690	4	do	do	1st-yr. green stems and leaves	7.2	3	....	300	150	<2
34	D415691	4	do	Japanese clover *(Lespedeza striata)*	Above-ground parts	5.2	2	<.25	200	500	<2
Aquatic plants											
35	D415638	2	June 17	Cattail *(Typha latifolia)*	Leaves	6.7	0.1	<0.25	70	70	<2
36	D415645	12	do	do	do	10	.1	<.25	70	3,000	<2

was found, however, in any of the 110 samples of redcedar collected from throughout Missouri in an earlier study. If this plant is, in fact, a beryllium accumulator, high soil concentrations of this element appear necessary for the accumulation to occur.

Buckbrush samples, collected at the white oak sampling sites, generally contained positively anomalous concentrations of molybdenum and nickel, and negatively anomalous amounts of sodium. Cadmium occurred in unusually high concentrations in the two samples (Nos. 8 and 9) from nearest the larger claypile. Abnormally high concentrations of aluminum, copper, gallium, tin, and vanadium were found in the single sample that was collected in September (No. 12). Anomalous concentrations of iron, potassium, manganese, lead, and titanium occurred in other samples of this species.

Smooth sumac, as indicated by the analyses on table 3, is much less sensitive to the element content of the underlying soils than is white oak, an observation consistent with the conclusions of Shacklette, Sauer, and Miesch (1970, p. C25). In the two sumac samples, only cadmium and cobalt occurred in unusually high concentrations, and sodium occurred as a negative anomaly. Molybdenum was abnormally high in sample 13 collected at the edge of the claypile, and magnesium was anomalous in sample 14 collected from the wall of the claypit.

Of the six samples of grasses that were collected in the claypit area, only sample 19, from Ranch B, con-

of plant samples from the claypit area

material. Other elements reported as ppm or percent in ash; these values in ash can be converted to approximate values in dry material by using the
were not found. These elements, analyzed by the semiquantitative spectrographic method, and their lower detection limits, in parts per million, are as
70; rhenium, 70; silver, 1; tantalum, 500; tellurium, 5,000; thallium, 100; thorium, 500; tungsten, 200; and uranium, 1,000. If lanthanum was found in a
praseodymium, 200; and samarium, 200. Asterisk, analysis by a semiquantitative spectrographic method. Results are reported as geometric midpoints of

Ash or element															
Ca (percent)	Cd (ppm)	Co (ppm)	Cr* (ppm)	Cu* (ppm)	Fe* (percent)	Ga* (ppm)	Hg (ppm)	K (percent)	La* (ppm)	Li (ppm)	Mg* (percent)	Mn* (ppm)	Mo (ppm)	Na (percent)	Ni* (ppm)
Trees															
22	10	60	7	500	0.3	<5	<0.025	13	70	20	3	30,000	10	0.04	200
26	11	60	3	200	.2	<5	<.025	9.8	<70	16	2	30,000	10	.04	200
30	6.2	4	5	150	.3	<5	<.025	6.4	<70	4	3	20,000	4	.04	70
31	7.4	4	2	150	.15	<5	<.025	7.4	<70	<4	3	10,000	4	.04	30
32	8.4	7	2	100	.1	<5	<.025	8	<70	4	1.5	20,000	<4	.03	50
22	9	20	50	200	1	7	.025	11	<70	40	2	15,000	<5	.07	300
23	5.4	25	20	70	.5	<5	.025	9.2	<70	18	3	15,000	<5	.08	300
Shrubs															
16	45	6	15	300	0.7	<5	<0.025	17	<70	8	3	20,000	10	0.06	50
15	35	8	20	150	.5	<5	<.025	22	<70	16	2	15,000	10	.06	50
12	10	2	10	150	.2	<5	<.025	25	<70	<4	3	3,000	10	.06	7
12	28	8	30	100	1	<5	<.025	18	<70	12	5	20,000	<4	.11	50
15	14	5	50	1,000	.7	10	.025	17	<70	22	3	7,000	20	.22	30
23	5.2	9	5	150	.1	<5	<.025	15	<70	4	2	1,500	10	.03	30
21	4.8	5	5	50	.2	<5	<0.25	17	<70	<4	5	1,500	4	.02	20
Grasses and sedges															
3.4	0.4	2	7	50	0.15	<5	<0.025	17	<70	220	0.7	1,500	10	0.02	20
3.6	.3	1	7	30	.15	<5	.025	20	<70	4	3	700	10	.03	5
4.6	.9	1	7	50	.1	<5	<.025	24	<70	4	2	1,500	4	.03	7
3.2	.3	3	7	30	.3	<5	.025	26	<70	4	3	1,000	10	.12	7
6	.3	7	50	50	2	7	....	14	<70	12	5	1,500	10	.09	7
4.4	1.2	2	7	50	.3	<5	.025	26	<70	<4	3	1,000	4	.07	10
2.4	.5	1	5	50	.3	<5	.05	28	<70	14	2	1,000	<4	.12	20
Forbs															
8.6	2	14	15	150	0.3	<5	<0.025	26	<70	12	2	2,000	10	0.03	50
15	1	2	3	100	.15	<5	.025	22	<70	<4	5	500	<4	.03	7
....	.9	9	20	50	.5	<5	....	....	<70	<4	7	1,500	......	.04	10
4.2	1.2	15	15	100	.5	<5	.05	29	<70	<4	1.5	7,000	4	.06	15
22	.8	4	2	50	.1	<5	<.025	17	<70	<4	5	300	60	.05	30
16	9.2	28	10	150	.2	<5	<.025	19	<70	22	3	500	10	.17	100
29	3.2	17	15	200	.3	<5	<.025	6.6	<70	6	3	500	60	.18	50
25	3.3	14	30	1,500	.5	<5	<.025	8.4	<70	12	5	500	750	.27	70
16	1.0	3.5	15	300	.15	<5	.025	21	<70	10	3	300	180	.13	50
14	.8	8	50	1,000	.5	<5	.025	17	<70	16	3	700	40	.19	30
4.3	......	15	70	200	.7	10	....	27	<70	28	5	500	250	1.8	70
11	......	10	50	200	.7	<5	<.05	20	<70	8	5	700	50	.26	70
17	......	<5	30	700	.7	<5	.025	12	<70	16	5	7,000	50	.15	150
Aquatic plants															
10	0.3	8	3	100	0.1	<5	<0.025	29	<70	4	2	15,000	10	0.88	30
6.8	.4	20	<2	50	.2	<5	.025	30	<70	<4	3	20,000	10	.6	15

TABLE 3.—*Ash yield and elemental composition of plant samples from the claypit area*—Continued

Sample No.	Laboratory No.	Ash or element P (ppm)	Pb* (ppm)	Sc* (ppm)	Se (ppm)	Sn* (ppm)	Sr* (ppm)	Ti* (percent)	V* (ppm)	Y* (ppm)	Yb* (ppm)	Zn (ppm)	Zr* (ppm)
						Trees							
1	D415622	24,000	300	<5	<0.5	<20	1,000	0.03	<5	<20	2	1,060	<20
2	D415623	24,000	200	<5	<.5	<20	1,000	.02	<5	<20	2	380	<20
3	D415627	18,000	150	<5	<.5	<20	1,000	.02	<5	<20	<2	360	<20
4	D415625	12,000	150	<5	<.5	<20	2,000	.015	<5	<20	<2	680	<20
5	D415630	12,000	70	<5	<.5	<20	2,000	.01	<5	<20	<2	400	<20
6	D415578	12,000	300	7	<.5	<20	1,000	.20	70	<20	5	440	50
7	D415579	24,000	100	<5	<.5	<20	500	.07	30	<20	<2	440	30
						Shrubs							
8	D415621	18,000	500	<5	<0.5	<20	3,000	0.10	20	<20	<2	1,600	70
9	D415626	18,000	200	<5	<.5	<20	1,500	.10	30	<20	2	1,000	50
10	D415624	24,000	30	<5	<.5	<20	2,000	.05	10	<20	<2	1,500	20
11	D415629	24,000	300	<5	<.5	<20	2,000	.20	50	<20	2	2,100	70
12	D415692	24,000	500	<5	....	70	2,000	.10	50	20	<2	1,550	70
13	D415620	18,000	50	<5	<.5	<20	5,000	.02	<5	<20	<2	1,000	<20
14	D415628	24,000	50	<5	<.5	<20	3,000	.03	<5	<20	<2	680	30
						Grasses and sedges							
15	D415641	6,000	<20	<5	0.5	<20	200	0.02	10	<20	<2	240	50
16	D415643	24,000	<20	<5	<.5	<20	200	.02	10	<20	<2	240	<20
17	D415642	18,000	<20	<5	<.5	<20	300	.02	10	<20	<2	260	<20
18	D415648	18,000	<20	<5	<.5	<20	200	.02	10	<20	<2	160	20
19	D415649	12,000	20	<5	.5	<20	200	.20	70	<20	2	260	150
20	D415651	24,000	<20	<5	<.5	<20	200	.05	10	<20	<2	470	30
21	D415647	24,000	<20	<5	<.5	<20	300	.03	10	<20	<2	340	20
						Forbs							
22	D415639	12,000	<20	<5	<0.5	<20	500	0.05	20	<20	<2	380	<20
23	D415644	18,000	<20	<5	.5	<20	1,500	.05	<5	<20	<2	360	50
24	D415650	24,000	<20	<5	<1	<20	700	.05	20	<20	<2	280	50
25	D415646	18,000	<20	<5	<1	<20	1,000	.07	20	<20	<2	300	70
26	D415640	12,000	<20	<5	<.5	<20	1,000	.007	<5	<20	<2	220	<20
27	D415684	18,000	70	<5	....	<20	1,500	.03	<5	<20	<2	270	20
28	D415685	12,000	150	<5	....	<20	1,000	.05	<5	<20	<2	240	20
29	D415686	24,000	300	<5	....	70	1,500	.05	20	<20	<2	420	20
30	D415687	18,000	100	<5	....	20	700	.015	<5	<20	<2	290	<20
31	D415688	24,000	200	<5	....	70	700	.1	50	<20	<2	410	70
32	D415689	48,000	20	<5	....	<20	1,000	.3	100	20	2	520	50
33	D415690	18,000	20	<5	....	<20	700	.1	50	20	2	280	50
34	D415691	45,000	200	<5	....	50	500	.1	30	20	2	700	50
						Aquatic plants							
35	D415638	12,000	<20	<5	<0.5	<20	700	0.005	<5	<20	<2	220	<20
36	D415645	24,000	<20	<5	<.5	<20	2,000	.01	<5	<20	<2	220	<20

tained anomalous concentrations of elements, all of which were positive. These anomalies were in aluminum, boron, cobalt, chromium, iron, gallium, titanium, and ytterbium. Inasmuch as the mixture of grasses in this sample did not include meadow fescue (the grass species used to establish typical values), these unusually high concentrations may be due more to species differences in absorption capability than to contamination of the soil.

White sweetclover is of special interest because it is a known molybdenum accumulator, and because molybdenum was found in anomalous concentrations (3–15 ppm) in samples of clay, shale, and alluvium from the claypit area. In parts of the Western United States where soils contain high levels of molybdenum (1.5 ppm or more), severe illness has occurred in cattle that grazed this plant (Barshad, 1948). In white sweetclover sample 26 (table 3), collected in June, 60 ppm molybdenum was found in the ash (6 ppm in dry matter), and although this concentration is not considered anomalous if judged by the central 95-percent range of values for a closely related species (yellow sweetclover, table 8), it exceeds the tolerance level of 5 ppm in dry matter for cattle that was given by Webb and Atkinson (1965). Molybdenum levels in another sample of white sweetclover (No. 29, table 3) from the claypit area, collected in September, exceeded this tolerance level by a factor of three. In addition, samples of white sweetclover contained anomalous concentrations of aluminum, boron, chromium, cobalt, copper, gallium, lead, manganese, nickel, tin, and titanium.

Japanese clover (sample 34, table 3) was the only other forb (broad-leaved forage herb) sampled that reflected the anomalous copper and nickel levels in substrates of the claypit area. This species, like white sweetclover, is a palatable forage plant and its element content, therefore, is important in searching for causes of the metabolic disorders of cattle at this site.

WATER

Chemical analyses of the four samples of water from the claypit area are given in table 4. The chemical compositions of surface waters, as were sampled at the claypit study area, are greatly influenced by meteorological conditions at a location both before and at the time of sampling. Water samples from this area were collected June 17, about 1 week after a mild thunderstorm had occurred. During the previous few months, however, very little rain had fallen; therefore, the properties of the samples were more representative of water

TABLE 4.—*Physical properties and chemical composition of surface water samples from the claypit study area*

[Analysts: P. R. Barnett, O. J. Feist, Jr., Darwin Golden, R. L. James, E. C. Mallory, Jr., and R. D. McKibben. All samples collected June 17, 1971]

Origin of sample..	Farm pond	Claypit	Small pool in Rocky Branch	Rocky Branch on Ranch B
Site No. (fig. 1)....	12	2	9	18
Physical properties, at time of collection				
Appearance	Medium brown, muddy	Bluish green, with murky cast	Light tan, milky	Slightly turbid
Temperature °C....	33.5	29.0	26.9	28.4
Specific conductance (μmhos/cm at 25°).	165	830	295	800
pH	7.50	4.27	7.73	8.22
Chemical composition (μg/l, except as indicated)				
Al	110,000	13,000	59,000	630
As	4	<1	<1	<1
B	250	19	110	14
Ba	1,600	90	300	190
Be	<4	10	<1	<2
Bi	<16	<5	<5	<5
Cd	1	2	1	<1
Co	17	120	4	<1
Cr	5	7	3	2
Cu	170	1,400	76	2
Fe	83,000	300	8,000	440
Ga	38	<5	17	<5
Ge	<33	<11	<10	<11
Li	48	60	52	2
Mn	4,900	1,900	1,700	100
Mo	<8	<3	<2	<3
Ni	130	470	78	<11
Pb	72	8	46	4
Rb	260	2	33	<.8
Sr	260	220	360	170
Ti	1,700	6	1,700	27
V	230	2	130	3
Zn	60	210	10	20
Zr	880	<11	120	<11
Organic N (mg/l) as N	3.5	.07	1.2	.34
NO_2 (mg/l)	.17	0	.01	0
NH_3 (mg/l) as N	.7	.02	.01	0
NO_3 (mg/l)	2.3	.3	1.3	.2

as it occurs during dry, rather than wet, periods. During wet periods the stream waters carry abundant suspended material and, consequently, higher concentrations of the elements that occur in the clay.

TABLE 6.—*Selected trace elements in whole blood samples from beef cattle having interference syndrome and from those that were unaffected*

[Concentrations given as mg/100 g. Blood samples were drawn on the ranches in the forenoon of June 17, 1971, and submitted immediately for analysis]

Laboratory No.	Cattle having interference syndrome				Unaffected cattle (controls)		
	Angus cows, Ranch A			Charolais bull, Ranch B	Angus cows, Ranch A		Charolais bull, Ranch B
	C1–821	C2–875	C3–851	C7–038	C4–422	C5–456	C6–11068
Element							
Al	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Co	<.05	<.05	<.05	<.05	<.05	<.05	<.05
Cu	.088	.080	.070	.067	.067	.071	.071
Fe	1.83	1.74	1.84	2.04	2.04	2.04	2.04
Mn	.010	.010	.010	.010	.010	.010	.010
Mo	.050	.050	.050	.050	.050	.050	.050
Zn	1.11	.97	1.22	.95	.95	2.04	.95

The part of Rocky Branch that drains the claypiles (fig. 1) was not flowing at the time of sampling, and the only water in the creekbed occurred in isolated pools. Therefore, water from the claypit pond and the claypiles was not reaching Ranch B. However, during periods of intense rainfall water from the claypit area does flow through this ranch, as indicated by the clay coatings on many rocks in the streambed. Rocky Branch is springfed at Ranch B, and at the time of sampling was flowing at an aproximate rate of 1 cubic foot per second.

The only basis available for judging any possible abnormalities in the compositions of surface waters collected from the claypit area is an analysis (table 4) of a sample from the farm pond at site 12 (fig. 1). The sample collected and analyzed contained a large quantity of suspended silt and clay and, therefore, represents stock water about as impure as it occurs under normal conditions. The pond, however, received no drainage from the claypit or the claypiles adjacent to it.

The acid water in the claypit, as is evident from the data in table 4, contains unusually high concentrations of several elements, including beryllium, cobalt, copper,

TABLE 5.—*Breeding and calving history of three distinct beef cattle herds on Ranch A for the 1970 and 1971 breeding and calving seasons*

[All cows were pasture bred; bulls remained in the pasture from June to September, therefore most cows calved during March and April of the following year. Numbers in parentheses are percentages. Herd No. 2 ranged on pasture affected by the claypile; herds 1 and 3 were kept on unaffected pastures. The breed of Herds 1 and 2, designated "Angus" in 1970, was changed to "Angus-Charolais" in 1971 because the sires were changed from Angus to Charolais]

Herd		Sires			Dams		Cows		Calves		Comments
No.	Breed	Breed	Number	Age (yrs)	Breed	Age (yrs)	Bred	Calved	Born alive	Stillborn	
						1970					
1	Angus	Angus	3	7	Angus	7	54	54 (100)	54 (100)	0 (0)	Brought to ranch in 1966.
2	......do......	......do......	1	2	......do......	4	66	36 (54.5)	31 (86.1)	5 (13.9)	Brought to ranch Oct. 1969 already bred; 7–8 cows rebred.
						1971					
1	Angus-Charolais	Charolais	1	9	Angus	8	54	54 (100)	54 (100)	0 (0)	One calf died soon after birth.
2	......do......	......do......	1	5	......do......	5	66	24 (36.5)	23 (95.8)	1 (4.2)	Undersized dam of stillborn calf died soon after calving.
3	Charolais	......do......	1	4	Charolais	4	24	24 (100)	24 (100)	0 (0)	Two cows had difficulty calving, but recovered. Artificial insemination, in addition to pasture breeding, was used.

TABLE 7.—*Concentrations of biochemic constituents in blood serum from beef cattle having interference syndroms and from those that were unaffected*

[Blood samples were drawn on the ranches in the forenoon of June 17, 1971, and submitted immediately for analysis. mg/100 ml=milligrams per 100 milliliters; mEq/l=milliequivalents per liter; g/100 ml=grams per 100 milliliters]

Constituents of serum and reporting units	Cattle having interference syndrome				Unaffected cattle (controls)		
	Angus cows, Ranch A			Charolais bull, Ranch B	Angus cows, Ranch A		Charolais bull, Ranch B
	C1–821	C2–875	C3–851	C7–038	C4–422	C5–456	C6–11068
Cholesterol, mg/100 ml	154	128	126	95	170	128	87
Calcium, mg/100 ml	9.8	9.4	9.3	9.6	9.2	9.3	9.7
Chloride, mEq/l	97	96	98	97	99	98	96
Total bilirubin, g/100 ml	.4	.3	.3	.5	.4	.4	.5
Creatinine, g/100 ml	1.0	1.0	1.0	.7	.3	.4	.9
Total protein, g/100 ml	7.4	6.6	7.4	7.0	7.6	7.7	6.7
Inorganic phosphorus, mg/100 ml	7.2	5.9	6.2	7.9	5.9	5.5	7.0
Blood urea nitrogen, mg/100 ml	25	21	18	14	24	26	18
Lactic dehydrogenase, Wacker Units[1]	572	530	576	511	547	455	403
Alkaline phosphatase, King-Armstrong Units[1]	19	18	17	28	20	16	27
Glutamic-oxaloacetic transaminase, King Units[1]	124	140	116	127	116	112	106
Sodium, mEq/l	149	143	150	152	146	149	147
Potassium, mEq/l	6.3	4.8	5.6	4.9	4.6	5.2	5.6

[1] Tumbleson (1969).

nickel, and zinc. Samples collected downstream from the claypit, however, contained no concentrations of elements that were notably high with respect to the water in the farm pond at site 12.

Because samples of whole water were collected and analyzed, it is not known whether the elements present are in solution or in suspended particles. However, the low pH (4.3) of the claypit water may cause many elements in the suspended particles to occur in soluble form.

The question as to whether elements occur in soluble form or within suspended materials may be important

TABLE 8.—*Mean chemical compositions, with central 95-percent range,*

[These data were used for establishing ranges in typical chemical compositions of certain sampling media. GM, geometric mean; GD, geometric deviation; ratio, per million,

Element or compound	B-horizon soils from Oak-Hickory Forest vegetation type				White oak stems			
	GM	GD	Central 95-percent range	Ratio	GM	GD	Central 95-percent range	Ratio
Al, or Al_2O_3, percent[1]	5.1	1.47	2.4–11	50:50	0.19	1.62	0.072–0.50	50:50
B	39	1.41	20–78	49:50	190	1.47	88–410	50:50
Ba	390	1.78	120–1,200	50:50	4,200	1.58	1,700–10,000	50:50
Be	.77	1.42	.38–1.5	20:50	<2	....	....	0:50
C, total, percent	1.1	1.72	.37–3.3	50:50	....	....	....	....
C, carbonate, percent	.054	4.14	.0032–.93	44:50	....	....	....	....
C, organic, percent	.96	1.69	.34–2.7	50:50	....	....	....	....
Ca, or CaO, percent[1]	.21	2.80	.027–1.6	46:50	33	1.11	27–41	17:17
Cd	<1	....	....	0:50	3.7	1.33	2.1–6.5	17:17
Ce	78	1.45	37–160	6:50	<300	....	....	0:17
Co	10	1.71	3.4–29	49:50	2.2	2.33	.41–12	15:17
Cr	43	1.45	20–90	50:50	3.5	1.85	1.0–12	46:50
Cu	13	1.99	3.2–51	50:50	130	1.51	57–300	50:50
Fe, or total Fe as Fe_2O_3, percent[1]	2.7	1.43	1.3–5.5	50:50	.14	1.88	.040–.50	50:50
Ga	8.4	1.54	3.5–20	48:50	<5	....	....	0:50
Hg	.055	1.91	.015–.20	50:50	....	....	....	....
K, or K_2O, percent[1]	1.3	1.61	.50–3.4	50:50	5.5	1.35	3.0–10	17:17
La	35	1.37	19–66	46:50	<70	....	....	0:50
Li	18	1.33	10–32	50:50	....	....	....	....
Mg, or MgO, percent[1]	.30	2.25	.059–1.5	50:50	1.8	1.86	.51–6.2	50:50
Mn	730	2.16	160–3,400	50:50	12,000	1.74	4,000–36,000	50:50
Mo	<3	....	....	2:50	<5	....	....	0:50
Na, or Na_2O, percent[1]	.38	2.01	.094–1.5	50:50	.15	1.31	.087–.26	17:17
Nb	8.0	1.38	4.2–15	22:50	<20	....	....	0:50
Nd	47	1.35	26–86	12:50	....	....	....	....
Ni	12	1.82	3.6–40	47:50	21	1.80	6.5–68	50:50
P, or P_2O_5, percent[1]	.076	1.88	.022–.27	40:50	1.3	1.52	.56–3.0	17:17
Pb	23	1.50	10–52	50:50	100	1.85	29–340	50:50
Sc	5.4	1.49	2.4–12	37:50	<5	....	....	0:50
Se	.31	1.90	.086–1.1	48:50	....	....	....	....
Si, or SiO_2, percent[1]	[2]83	[3]7.43	[4]68–97	50:50	....	....	....	....
Sr	66	1.66	24–180	50:50	1,800	1.59	710–4,600	50:50
Ti, percent	.35	1.44	.17–.73	50:50	.016	1.68	.0057–.045	50:50
V	53	1.48	24–120	50:50	<5	....	....	2:50
Y	27	1.50	12–61	50:50	<20	....	....	1:50
Yb	2.8	1.44	1.4–5.8	50:50	<2	....	....	0:50
Zn	36	1.59	14–91	50:50	310	1.21	210–450	17:17
Zr	300	1.63	110–800	50:50	<20	....	....	12:50

See footnotes at end of table.

because it bears on the availability of the elements to plants and animals. In other words, the environmental significance of an occurrence of a trace element in water cannot be ascertained from the magnitude of its concentration alone. The lead concentration in the sample from the control farm pond, for example, is greater than that in the other samples; yet the lead that is present may be in a form that is not available to animal metabolism, whereas the lead of lesser concentrations in the other waters may be readily available. Moreover, many elements that were not present in high concentrations in the waters from the claypit area at the time of sampling may occur in high concentrations during periods of heavy surface runoff. The elements found in the precipitate at the base of the claypiles could be expected to occur in solution or as particulate matter in waters running off the claypiles during and immediately after periods of intense rainfall.

High concentrations of certain microorganisms that may occur in water produce toxins to levels that can be harmful or fatal to cattle. Some species of blue-green algae are especially toxic. The concentration of microorganisms was found to be low in an aliquot of water from the claypit; only a few objects that appeared to be unicellular green algae were found by microscopic examination (Robert Lipscomb, oral commun., 1971).

BEEF CATTLE

The extent of the interference syndrome in the breeding and calving history for the three herds on Ranch A is given in table 5. Analyses for trace elements in whole blood specimens from herds on both Ranch A and Ranch B are given in table 6; analyses for biochemic constituents in blood serum are given in table 7.

We first observed the affected cattle on Ranch A and Ranch B in May 1971, although the ranchers had noticed interferences with growth, nutrition, and reproduction nearly a year earlier. We advised the ranchers to exclude the cattle from the claypit area and the flood plain below it by fencing; this was done on Ranch A only. At the time of this visit we thought these cattle were showing a favorable response to the better ration that had been provided and to the spring grass. On later visits, however, the cattle were noticed to be unthrifty and to be losing weight as the grass became short under the influence of a drought in July and August, despite supplemental rations that were provided.

of media that are comparable to those sampled in the claypit area

number of samples in which detected : total number of samples; central 95-percent range is calculated as GM÷GD² to GM×GD². Means are given in parts except as indicated]

Buckbrush stems				Smooth sumac stems				Redcedar stems and leaves				Fescue grass, aboveground parts			
GM	GD	Central 95-percent range	Ratio	GM	GD	Central 95-percent range	Ratio	GM	GD	Central 95-percent range	Ratio	GM	GD	Central 95-percent range	Ratio
1.2	1.33	0.68–2.1	49:49	0.12	2.11	0.026–0.53	50:50	0.47	1.61	0.18–1.2	10:10	0.56	2.53	0.087–3.6	18:18
180	1.35	99–330	49:49	200	1.26	130–320	50:50	210	1.30	120–350	10:10	48	1.24	31–74	14:18
3,800	1.63	1,400–10,000	49:49	3,400	2.33	630–18,000	50:50	3,800	2.04	920–16,000	10:10	340	1.72	110–1,000	18:18
<2	....	....	0:49	<2	....	....	0:50	<2	....	....	0:10	<2	....	....	0:18
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
15	1.21	10–22	22:22	24	1.24	16–37	15:15	28	1.13	22–36	10:10	....	....	....	....
11	1.68	3.9–31	22:22	2.5	1.32	1.4–4.4	15:15	2.6	2.64	.37–18	10:10	....	....		
<300	....	....	0:22	<300	....	....	0:15	<300	....	....	0:10	<300	....	....	0:18
5.2	1.64	1.9–14	22:22	1.3	1.54	.55–3.1	13:15	<5	....	....	2:10	<5	....	....	0:18
21	1.57	8.5–52	49:49	2.7	1.95	.71–10	40:50	9.8	1.81	3.0–32	10:10	8.6	2.28	1.7–45	18:18
180	1.45	86–380	49:49	89	1.43	44–180	50:50	66	1.71	23–190	10:10	59	1.56	24–140	18:18
.69	1.58	.28–1.7	49:49	.11	1.89	.031–.39	50:50	.35	1.72	.12–1.0	10:10	.30	2.19	.063–1.4	18:18
<5	....	....	8:49	<5	....	....	0:50	<5	....	....	0:10	<5	....	....	1:18
....	....	....	....	....	....	....	....	<.5	....	....	0:10	....	....	....	....
15	1.24	9.8–23	22:22	14	1.15	11–19	15:15	9.8	1.32	5.6–17	10:10	....	....	....	....
<70	....	....	5:49	<70	....	....	0:50	<70	....	....	0:10	<70	....	....	0:18
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
3.6	1.65	1.3–9.8	49:49	2.0	1.43	.98–4.1	50:50	4.8	1.42	2.4–9.7	10:10	2.9	1.41	1.5–5.8	18:18
10,000	1.62	3,800–26,000	49:49	700	1.60	270–1,800	50:50	5,700	1.92	1,500-21,000	10:10	820	1.62	310–2,200	18:18
1.4	2.49	.23–8.7	7:49	<5	....	....	3:50	2.3	2.80	.29–18	3:10	4.8	2.47	.79–29	10:18
.24	1.21	.16–.35	22:22	.11	1.56	.045–.27	15:15	.27	1.65	.099–.74	10:10	....	....	....	....
<20	....	....	0:49	<20	....	....	0:50	< 20	....	....	0:10	<20	....	....	0:18
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
11	1.49	5.0–24	49:49	4.0	2.82	.50–32	36:50	37	2.03	9.0–150	10:10	7.1	2.56	1.1–47	12:18
2.2	1.31	1.3–3.8	22:22	1.7	1.30	1.0–2.9	15:15	1.9	1.32	1.1–3.3	10:10	1.3	1.45	.62–2.7	18:18
260	1.88	74–920	49:49	30	2.36	5.4–170	37:50	120	3.25	11–1,300	10:10	43	1.59	17–110	18:18
<5	....	....	0:49	<5	....	....	0:50	<5	....	....	0:10	<5	....	....	0:18
....	....	....	....	....	....	....	....	<1	....	....	0:10	....	....	....	....
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
1,500	1.96	390–5,800	49:49	2,700	2.19	560–13,000	50:50	2,300	2.01	570–9,300	10:10	280	1.56	120–680	18:18
.12	1.73	.040–.36	49:49	.013	2.15	.0028–.060	50:50	.030	2.00	.0075–.12	10:10	.037	2.23	.0074–.18	18:18
19	1.50	8.4–43	49:49	<5	....	....	3:50	4.6	3.10	.48–44	5:10	2.0	5.99	.056–72	6:18
15	1.45	7.1–32	16:49	<20	....	....	0:50	<20	....	....	0:10	<20	....	....	0:18
1.4	1.42	.69–2.8	13:49	<2	....	....	0:50	<2	....	....	0:10	<2	....	....	0:18
1,300	1.40	660–2,500	22:22	610	1.33	340–1,100	15:15	480	1.67	170–1,300	10:10	....	....	....	....
79	2.16	17–350	49:49	11	1.85	3.2–38	11:50	29	1.89	8.1–100	8:10	44	2.42	7.5–260	15:18

See footnotes at end of table.

TABLE 8.—*Mean chemical compositions, with central 95-percent range, of media that are comparable to those sampled in the claypit area*—Continued

Element or compound	Yellow sweetclover, total plant				Parts of various species from throughout the conterminous United States			
	GM	GD	Central 95-percent range	Ratio	GM	GD	Central 95-percent range	Ratio
Al, or Al_2O_3, percent[1]	0.26	4.26	0.014–4.7	10:10	0.65	3.52	0.052–8.1	1,109:1,117
B	160	1.56	66–390	10:10	240	2.10	54–1,100	1,133:1,150
Ba	270	2.03	66–1,100	10:10	390	3.75	28–5,500	1,151:1,151
Be	<2	......	......	0:10	<2	......	......	8:1,153
C, total, percent	......	......	......	......	......	......	......	......
C, carbonate, percent	......	......	......	......	......	......	......	......
C, organic, percent	......	......	......	......	......	......	......	......
Ca, or CaO, percent[1]	......	......	......	......	12	2.69	1.7–87	988:988
Cd	......	......	......	......	......	......	......	......
Ce	<300	......	......	0:10	<300	......	......	2:1,117
Co	<5	......	......	1:10	.94	5.83	.028–32	232:1,119
Cr	4.6	2.40	.80–26	9:10	9.6	2.85	1.2–78	1,096:1,139
Cu	100	1.63	38–270	10:10	100	1.98	26–390	1,153:1,153
Fe, or total Fe as Fe_2O_3, percent[1]	.21	2.70	.029–1.5	10:10	.36	2.51	.057–2.3	1,153:1,153
Ga	<5	......	......	1:10	.20	9.83	.0021–19	150:1,105
Hg	......	......	......	......	......	......	......	......
K, or K_2O, percent[1]	......	......	......	......	13	1.82	3.9–43	1,006:1,006
La	<70	......	......	1:10	<70	......	......	46:1,123
Li	......	......	......	......	......	......	......	......
Mg, or MgO, percent[1]	2.7	1.93	.72–10	10:10	3.0	2.05	.71–13	1,120:1,153
Mn	250	1.50	110–560	10:10	1,000	4.38	57–21,000	1,153:1,153
Mo	20	3.40	1.7–230	8:10	4.2	3.94	.27–65	453:1,124
Na, or Na_2O, percent[1]	......	......	......	......	.46	4.00	.029–7.4	277:277
Nb	<20	......	......	0:10	......	......	......	......
Nd	......	......	......	......	32	6.21	.83–1,200	11:47
Ni	12	1.63	4.5–32	10:10	16	2.84	2.0–130	1,028:1,135
P, or P_2O_5, percent[1]	.94	2.83	.12–7.5	7:10	2.0	2.27	.39–10	991:991
Pb	34	2.22	6.9–170	8:10	86	6.17	2.3–3,300	980:1,142
Sc	<5	......	......	1:10	<5	......	......	39:1,153
Se	......	......	......	......	......	......	......	......
Si, or SiO_2, percent[1]	......	......	......	......	......	......	......	......
Sr	880	1.89	250–3,100	10:10	880	3.78	62–13,000	1,145:1,152
Ti, percent	.0091	2.39	.0016–.052	10:10	.026	3.49	.0021–.32	1,122:1,148
V	.82	29.0	.00098–690	3:10	11	4.15	.64–190	694:1,123
Y	<20	......	......	1:10	<20	......	......	158:1,128
Yb	<2	......	......	1:10	<2	......	......	101:1,108
Zn	......	......	......	......	450	2.73	60–3,400	642:643
Zr	1.8	16.7	.0065–500	2:10	13	3.44	1.1–150	470:1,152

[1] Means given for plants are percentages of the element; means for soils are percentages of the compound.

[2] Arithemtic mean.

[3] Standard deviation.

[4] Central 95-percent range is calculated as arithmetic mean minus two standard deviations to arithmetic mean plus two standard deviations.

One herd, composed of 54 older Angus cows on Ranch A, did not have access to the claypit area and in both 1970 and 1971 it produced 54 live calves (table 5). A herd composed of 66 younger Angus cows that were pastured adjacent to the claypit area produced 31 live and five stillborn calves in 1970, and 23 live calves and one stillborn calf in 1971. A third herd, consisting of 24 Charolais cows 4 years old, was kept on pastures unaffected by the claypit area, and in 1971 it produced 24 live calves.

On Ranch B one yearling and four older Charolais bulls that had access to a pasture affected by runoff from the claypile developed the interference syndrome. These bulls were unthrifty, grew slowly, and gained weight at a very low rate, although they were on adequate rations for normal development. After being removed from the part of the pasture that was affected by runoff, the bulls slowly improved in condition, and finally recovered without obvious signs of permanent injury.

The yearling Charolais bull weighed approximately 1,100 pounds (500 kg) when purchased in April 1970. During the following year he gained only 100 pounds (45.4 kg). On being returned to the southwestern Missouri ranch from which he came, he gained even more than the normal expected daily weight gain of 2–3 pounds (0.9–1.4 kg). Using this latter rate of gain, it is estimated that a yearling Charolais bull could gain 730—1,095 pounds (331.1—497.7 kg) in 365 days.

Herds 1 and 3 on Ranch A (table 5), which were not exposed to the pasture affected by runoff from the claypile, produced excellent calf crops, and the calves were normal and healthy. The breeding and calving record of Herd 2 which grazed on the affected pasture (table 5) indicates that the interference syndrome greatly reduced the reproductive capability of the herd. In addition, the condition and growth rate of the cows were affected; in 1971 these cows averaged about 600 pounds (270 kg) in weight, whereas normal Angus cows of the same age should weigh about 1,100 pounds (500 kg). After the 1971 calving season, all but 21 cows of this herd were disposed of, as it was apparent that they were not likely to reach the full size and weight usual for mature Angus cows. The calves produced by the 21 remaining cows were smaller and less growthy than is usual for Angus-Charolais calves.

Interference syndromes are slow to develop, and corrective response to a change in environment is likely

TABLE 9.—*Concentrations of selected elements and compounds in anomalous amounts in one or more samples of clay from the claypit area, the average of these elements and compounds in soils in vicinity of the claypit, and the average for the Oak-Hickory Forest soil*

[Values are in parts per million, except as indicated]

Element or compound	Sample No. D149910[1]	Sample No. D150439[1]	Sample No. D150448[1]	Sample No. D149911[2]	Sample No. D150445[3]	Average in soils in vicinity of claypit[4]	Average, Oak-Hickory Forest soils in Missouri[5]
Al_2O_3, percent	30	29	31	34	33	8.4	5.1
Ba	500	200	150	200	30	700	390
Be	3	3	2	2	2	<1	.77
Ce	300	300	150	300	<150	<150	78
Co	7	3	3	5	15	13	10
Cr	300	150	300	300	200	65	43
Cu	70	100	50	30	150	12	13
Total Fe, as Fe_2O_3, percent	2.2	2	1.4	1.5	1	2.8	2.7
Ga	50	30	50	50	50	14	8.4
K_2O, percent	3.6	2.9	2.9	2.5	1.3	1.8	1.3
La	50	70	100	150	70	54	35
Li	153	242	258	320	338	22	18
Mn	30	20	7	7	50	810	730
Mo	<3	3	15	7	7	<3	<3
Nd	150	100	100	150	70	<70	47
Ni	100	50	30	100	100	14	12
P_2O_5, percent	.5	.5	.3	.2	.1	.14	.076
Sc	30	30	30	50	30	8.4	5.4
Se	4	3.2	1.7	3	.4	.4	.31
SiO_2, percent	48	45	44	46	41	76	83
Sr	2,000	700	700	700	150	160	66
Ti, percent	1	.3	.5	1	.5	.43	.35
V	300	300	700	700	500	85	53
Y	50	70	50	70	20	35	27
Yb	5	7	5	7	3	3.8	2.8

[1] Samples of clay from large pile east of claypit. Sample did not contain visible amounts of coal or sulfide minerals.

[2] Sample of clay from smaller pile immediately north of large pile.

[3] Sample of clay from southwest wall of claypit about 5 ft above water level.

[4] Geometric means of 10 samples of soil (Nos. 22–31 of table 2) from the vicinity of the claypit. The samples were collected at depths of 2–15 cm and were not visibly contaminated with clay from the claypit.

[5] Geometric means of 50 B-horizon soil samples from Oak-Hickory Forest areas in southern Missouri (Shacklette, Erdman, and Keith, 1971).

to be slow. The syndromes represented by the two groups of young cattle discussed in this report are not instances of calculated and controlled experimental procedures with known or predetermined factors. Although the cows in Herd 2 had free access to rations that were more than adequate for young beef cattle during their first gestation, their health steadily deteriorated, with malnutrition, loss of weight, signs of avitaminosis-A, and other evidence of starvation becoming apparent. Yet these interference phenomena were not fully appreciated for many months. Infectious diseases and other possible causes for the deterioration of the herd were ruled out insofar as was possible under the circumstances.

Although the history of the animals, and their condition as determined by observations, are of major importance in the establishment of a diagnosis, analyses from laboratory examinations provide very important supportive evidence and often reveal hidden interrelationships. The blood samples reported in tables 6 and 7 were taken 8 months after the cattle had been removed from the affected pasture, and their analyses indicate a trend toward recovery of the animals. The trace element content of whole blood and the macromineral and enzyme values of the blood serum are within the normal range for beef cattle, although the ratios of concentrations of some elements may be abnormal.

The effects of trace elements on human and animal health have recently been discussed by Selby, Marienfeld, and Pierce (1970). Deficiencies, as well as excesses, of certain elements may result in imbalances which disturb the normal nutrition and health of plants and animals (Mills, 1970; Church, 1971). The disturbance in animals may be so subtle as to suggest a minor ration deficiency, or so pronounced that an obvious toxicity is observed. We have worked with such interference phenomena before, and are of the opinion that the syndrome shown by the young cattle on both ranches discussed in this report is most likely a complex imbalance of molybdenum, cobalt, sulfate, and copper. Poole (1970) emphasized the fact that cytochrome oxidase activity is depressed by copper deficiency in the presence of interference by molybdenum or other trace substances. The copper values in blood shown in table 6 may be within low normal ranges, and are difficult to evaluate.

The severe depression of nutrition, growth, and reproduction in Herd 2 best fits a diagnosis of chronic molybdenosis as reported by Fleming, McCormick, and Dye (1961) from Nevada, and by Barshad (1948) from California. The changes in color and condition of the hair coat and the abnormal thickening of the skin also fit cases of unthrifty animals seen at our veterinary clinics during the last 20 years, and resemble those described by Muir (1941). Other workers have described similar metabolic disturbances from many places. (See Britton and Goss, 1946; Kretschmer and Beardsley, 1956; Underwood, 1970, 1971; Dye and O'Harra, 1959; Clarke and Clarke, 1967; Radeleff, 1970; and Mills, 1970.)

Our diagnosis of the problem as an interference syndrome is supported by the studies of the element content of the vegetation and other materials from the area affected by drainage from the claypile, as given in tables 2, 3, 4, 9, and 10 of this report. Data in these tables suggest that in plants from the affected area, certain elements other than those linked to molybdenosis occur in concentrations greatly in excess of nutritional requirements of cattle, as well as above the usual ranges for such elements in Missouri plants (Pickett, 1955; Church, 1971).

There could be many interrelations and imbalances of major and minor elements in addition to those mentioned. Several workers have reported imbalances in which phosphorus, calcium, or vital metabolic enzymes were adversely affected by anomalously high or low amounts of other substances ingested by cattle (Thompson and others, 1971; Britton and Goss, 1946;

Davis, 1950; and Muir, 1941). Nickel may contribute to interactions with other trace substances when present in excessive amounts, and may reach interference levels that correspond to the levels reported in tables 2 and 3 (especially the levels in sweetclover and lespedeza). O'Dell and Miller (1971) discussed various aspects of nickel as it affects ruminant rations. Muir (1941) described the natural soil, pH, and related conditions which promote mineral imbalances such as anomalous concentrations of trace elements (especially molybdenum), and he cited the work of pioneers such as J. S. Watson who suspected the nature of the copper-molybdenum-sulfate and other trace element interrelationships early in the present century.

We are of the opinion that the young Charolais bulls on Ranch B farther down the valley were affected by the same trace element imbalances that caused the interference syndrome in Herd 2 of Ranch A. These bulls were not as near the sources of the environmental contamination as were the cows of Herd 2, and received less exposure to the water and vegetation that contained the anomalous concentrations of elements nearer the claypit. These bulls made better recovery of health than did the cows of Herd 2, when both were moved from the affected pastures.

The toxic plants native to the flood-plain pasture could make the imbalance of the trace elements worse, but has, in our opinion, made only minor contribution to the interference syndrome on Ranch A. The bulls on Ranch B were confined to lots where they did not have access to toxic plants, but grazed in a small pasture that was flooded by Rocky Branch, and they depended on a spring in the creek for their water supply. In our opinion, white snakeroot *(Eupatorium rugosum)* is the most dangerous of the toxic plants growing on either farm. Plants of the Nightshade Family, some of which are of known toxicity, are also present in the flood-plain pasture. We believe that the principal contribution of plants to the interference syndrome was not the organic poisons of certain plants, but the concentration of elements that were found in certain plants, especially sweetclover and lespedeza, that grew in the pastures. Buckbrush also is browsed by cattle, and it contained anomalous amounts of certain elements where it grew in the contaminated area. Direct ingestion of the clay and associated materials, or of water that carried these materials, may also have affected the metabolism of these animals.

SUMMARY AND CONCLUSIONS

Anomalous concentrations of elements in the claypit area were due, in a large measure, to the chemical composition of the materials that have been exposed by the mining operation. These materials include clay, shale, coal, limestone, and pyrite. Pyrite is of special importance in effecting the release of certain elements into the natural environment because, by weathering, it produces sulfuric acid which is strongly reactive with other materials in the claypiles.

Water that drained from the claypiles into the claypit was highly acid and supported few aquatic organisms. We believe that the principal importance of the water in the local geochemical environment was its downstream transport of elements in solution and in particulate matter, and the subsequent deposition of these materials in the flood-plain alluvium and in the beds of the streams.

Plants that grow on the claypiles or in the alluvium that was carried from the claypiles may concentrate certain elements in their tissues as controlled by the inherent characteristics of the different species; and the concentrations present in the soil on which they grow. Some of these elements probably produce no important alteration of the natural environment, whereas others, if concentrated, are known to be toxic to most organisms.

In this summary, as in the report, element concentrations in the clay and in other materials brought to the surface by mining are regarded as anomalous wherever they differ from the range of concentrations to be expected in soils of the area.

Elements and compounds that are judged to occur in anomalous amounts in sampling materials from the claypit area are listed in table 10. Examination of this table reveals that the elements and compounds may be arranged in five groups, as follows:

1. Those that occur in anomalous amounts in the clay or alluvium, or both, and that also were found in anomalous amounts in many of the plant samples—aluminum, copper, gallium, molybdenum, nickel, sodium, and ytterbium. Special mention should be made of cobalt, which is negatively anomalous in the clay but positively anomalous in five kinds of plant samples.
2. Those which occur in anomalous amounts in the clay and alluvium, but which were found in anomalous concentrations in none, or only a few, of the plant samples—barium, beryllium, cerium, chromium, lanthanum, niobium, phosphorus, potassium, scandium, titanium, vanadium, and yttrium.
3. Those that occur in typical, or lower, concentrations in the clay and alluvium but, nevertheless, are absorbed in anomalous amounts by some plants—boron, cadmium, calcium, and zinc.
4. Those which are anomalous in the clay or alluvium, but for which we have no means of evaluating their concentrations in plants—carbon, lithium, neodymium, selenium, and silicon. Carbon is a major constit-

TABLE 10.—*Elements and compounds that occur in anomalous concentrations in one or more samples of materials from the claypit area.*

[+, anomalously high; o, typical; –, anomalously low; ...., no data available]

Element or compound	Materials sampled Clay from claypiles and claypit	Stream alluvium	White oak stems	Buckbrush stems	Smooth sumac stems	Redcedar stems and leaves	Grasses and sedge, above-ground parts[1]	White sweet-clover, total plant	Other forbs, above-ground parts[2]
Al, or Al_2O_3	+	+	+	+	o	+	+	+	o
B	o	o	o	o	o	o	+	+	o
Ba	–	o	–	o	o	–	o	o	o
Be	+	+	o	o	o	+	o	o	o
C, total	–	o	....	....	....	....	....	....	....
C, organic	o	+	....	....	....	....	....	....	....
Ca, or CaO	o	o	–	o	o	o	....	....	o
Cd	o	o	+	+	+	o	....	....	....
Ce	+	+	o	o	o	o	o	o	o
Co	–	o	+	o	+	+	+	+	o
Cr	+	+	o	o	o	+	+	+	o
Cu	+	+	+	+	o	+	o	+	+
Fe, or total Fe as Fe_2O_3	–	o	o	–	o	o	+	o	o
Ga	+	+	o	+	o	+	+	+	o
K, or K_2O	+	+	+	+	o	o	....	....	o
La	+	+	+	o	o	o	o	o	o
Li	+	+	....	....	....	....	....	....	....
Mg, or MgO	o	o	o	o	+	–	o	o	o
Mn	–	–	o	–	o	o	o	+	o
Mo	+	+	+	+	+	o	o	+	o
Na, or Na_2O	–	o	–	–	–	–	....	....	o
Nb	o	+	o	o	o	o	o	o	o
Nd	+	+	....	....	....	....	....	....	....
Ni	+	+	+	+	o	+	o	+	+
P, or P_2O_5	+	+	o	o	o	o	o	o	o
Pb	o	+	o	–	o	o	o	+	o
Sc	+	+	o	o	o	+	o	o	o
Se	+	+	....	....	....	....	....	....	....
Si, or SiO_2	–	–	....	....	....	....	....	....	....
Sr	+	+	o	o	o	–	o	o	o
Ti	+	o	o	o	o	+	+	+	o
V	+	+	o	+	o	+	o	o	o
Y	+	+	o	o	o	o	o	o	o
Yb	+	+	+	o	o	+	+	o	+
Zn	o	o	+	o	o	o	....	....	o

[1] Bluegrass, common bullrush, fowl meadow grass, Japanese chess, meadow fescue, redtop, timothy, and wood reed grass.

[2] Cattail, common plantain, goldenrod, Japanese clover, and white snakeroot.

uent of plants; the other elements are nonessential to plant metabolism.

5. Those whose tendencies in concentrations and movements through the local environment cannot be readily categorized with the data that are now available—iron, lead, magnesum, manganese, and strontium.

Elements in groups 1 and 3 potentially can influence the metabolism of grazing animals because of their concentrations in plants, or their presence in deposits of the clay on the plant surfaces. Elements in groups 1 and 2 can affect these animals if the clay or alluvium is ingested directly, or if water is drunk in which these elements are in solution or suspension, even if the vegetation is not grazed.

Plants that concentrate certain elements in high amounts may be particularly important in contributing to nutritional disorders of animals, especially (as in sweetclover and Japanese clover) if the plants are very palatable and therefore preferentially grazed. The importance to the geochemical environment of certain less palatable accumulator plants, such as the trees and shrubs sampled in this study, may lie principally in their ability to concentrate certain elements in the upper soil horizons where they are readily available to other plants.

In evaluating the total geochemical environment of the claypit area, four elements (beryllium, copper, molybdenum, and nickel) are seen to be conspicuously anomalous in the clay, alluvium, and plant samples. Moreover, the mobilities of certain elements (aluminum, beryllium, cobalt, copper, and nickel, among others) are demonstrated by their high concentrations in efflorescent salts and in the claypit water. Cobalt, although not anomalous in the clay and alluvium samples, is a common anomaly in the plant samples. Of these elements, cobalt, copper, and molybdenum are known to be metabolically significant; in trace amounts they are essential to animals, but in high concentrations may be toxic. Aluminum occurs in anomalously high concentrations in all sampling media, and in an acid environment such as may be provided by the oxidation of pyrite it is readily mobile. However, high concentrations of aluminum were found in plants only in samples that were on or near the claypiles. If highly concentrated, aluminum is thought to be toxic to animals.

The interpretation of the movements of elements and compounds through the local environment from their principal source to grazing animals is summarized in figure 3.

The interference with normal growth, nutrition, and reproduction in the cattle was caused by the severe imbalance of several elements that occur in anomalous concentrations in both the drainage from the claypit area, and in the vegetation contaminated by this drainage The most likely imbalance is in the complex relationship between copper and molybdenum, which is possibly influenced by other elements that are present in anomalous concentrations and that can, in themselves, influence metabolism of cattle. Similar interference syndromes (or toxicities) in which young cattle are most seriously affected are known to occur in the States of California, Florida, and Nevada, and in Canada, Europe, Australia, and other places.

In field situations, some variables of the animals' actual feed intake are not measurable—the amount of any one plant that the animals eat, whether all animals eat the same plants, the season of plant growth, and the individual consumption of feed supplements. Unlike laboratory experiments, the natural environment cannot be treated as a rigorously controlled system. Therefore, diagnosis of metabolic disorders must employ plausible inferences that are supported by observations of the animals, study of the laboratory results, and evaluation of the total environment to which the animals were subjected.

The clay and associated materials that were exposed by the clay mining operation contain concentrations of certain elements that can be considered anomalous in the natural geochemical environment of plants and animals. Runoff from the claypiles transports these elements, either in solution or in suspended sediment, to other parts of the area. These elements generally can be absorbed by plants, and some of them may be concentrated to high levels. Of the elements studied, aluminum, beryllium, cobalt, copper, molybdenum, and nickel generally were found to have the greatest mobil-

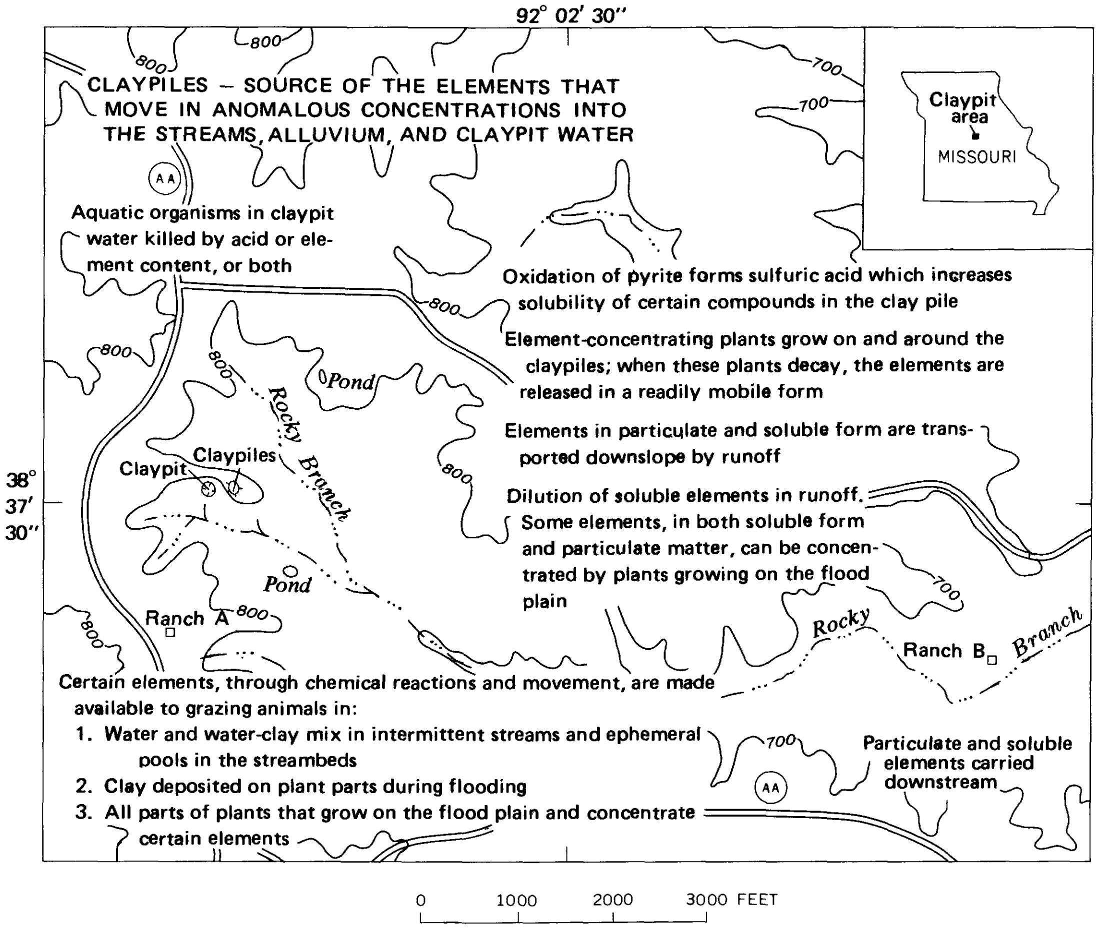

FIGURE 3.—Movement of elements through the geochemical system, claypit area, Callaway County, Mo.

ity in the local environment and to occur most commonly in anomalous concentrations through the area.

Young beef cattle exposed to anomalous element concentrations in the flood plain below the claypile experienced a severe interference syndrome due to an imbalance of minerals or other nutrients in their feed or water, or both. The disturbance in metabolism of cattle grazing on pastures affected by the claypile was most similar to chronic molybdenosis. Imbalances of copper and molybdenum, in addition to those of sulfate, nickel, cobalt, and other substances, may have contributed to this syndrome.

Anomalous concentrations of elements that present a hazard to livestock may exist at many other locations in Missouri and throughout the Midwest where similar materials are brought to the surface by clay and coal mining, especially if the chemical mobility of elements is increased under the acid conditions that may result from the presence of pyrite.

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