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Trace Elements and Missouri Soils

I. Copper and Cobalt Contents of Twenty-Six Soil Types

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ABSTRACT

1. The copper and cobalt contents of the soils used in this study varied over a wide range. A number of these soils had contents that were low to the degree where the deficient element might be expected to be a limiting factor in plant and animal growth. Other soils of this group showed a sufficiently high content of both copper and cobalt.
2. No correlation could be established between the levels of copper and those of cobalt in the soils tested. Nor could any correlation be established between the levels of either copper or cobalt and any other soil property commonly considered.
3. From these studies it seems reasonable to believe — and such belief is in agreement with the evidence presented in the literature reviewed — that the copper and cobalt levels of the soil are a function of (1) the parent material from which the soil is derived, (2) the conditions prevailing during the period of soil development, (3) the amount of organic matter present in the soil, (4) the soil texture, and (5) the soil reaction.

Trace Elements and Missouri Soils

I. Copper and Cobalt Contents of Twenty-Six Soil Types[1]

F. R. Johnson and E. R. Graham[2]

For many years botanists and agricultural workers assumed in general that only ten chemical elements were essential for the growth of the higher green plants, namely carbon, hydrogen, oxygen, nitrogen, sulphur, potassium, calcium, magnesium, phosphorus and iron. Of these, only the last seven were commonly considered to be the essential elements of a nutrient medium, whether soil or solution. It was well established that many elements, apart from those regarded as necessary, were present in the plant, but their presence was regarded as incidental, due to their presence in the soil in which the plants grew.

Within the past 25 years it has been universally recognized that there are a number of additional elements that are also essential for plant growth, required only in minor quantity but of major importance. These have been commonly called trace elements. Their prevalence in soils of an area like the state of Missouri may well challenge our consideration as to supplies and availability.

It was the purpose of this study (1) to analyze by various methods for their copper and cobalt contents 26 different Missouri soils, each representing a distinct and separate soil type; (2) to determine whether or not either of these elements possibly could be a limiting factor under Missouri soil conditions in (a) plant and animal nutrition in the case of copper, and (b) animal nutrition in the case of cobalt; and (3) to associate the fertility levels of Missouri soils with the parent materials of their derivation, their organic matter contents, clay contents, and relative soil acidity.

Within the past ten years it has become certain that soils are not always capable of supplying enough of the trace elements to maintain healthy growth of plants. References to deficiencies of trace elements in the soil may not be a question of absolute deficiency in total quantity in the soil but rather a deficiency arising from the insufficient availability of the element to the plant. Much has been written during this

[1]The material of this bulletin was taken from the thesis presented by F. R. Johnson for the degree of M. A., University of Missouri, February, 1950. It is a report on Department of Soils Project Number 51 entitled "Fertility Level of Soils."

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ten-year period of the thousands of cases in many parts of the world where the effects on plant growth, crop failures and plant disease, can be attributed to deficiencies of trace elements. Many nutritional diseases of plants and animals, particularly the ruminants, also can be traced to the inadequacy of the diet, where the vegetation consumed (and that grown on deficient soils) does not supply enough of one or more of the elements that function in minute quantities. The requirements of the plant and of the animal are not necessarily the same, either quantitatively in the case of copper or qualitatively in the case of cobalt.

To date few trace element deficiencies have been reported for the State of Missouri. It has been frequently suggested, however, that such deficiencies of a general nature may exist to the point of becoming a limiting factor in plant and animal growth, particularly on our poorer soils where excessive leaching has occurred. Beeson (6) in reporting on geographical occurrence of mineral nutritional diseases of plants and animals in the United States does not mention Missouri nor does Missouri fall within limits of any area pattern on the maps he has shown. Perhaps this might be due to the lack or inadequacy of information from the Missouri area.

Definitions of Terms Used

Trace Elements. This term has been used to include those elements which are required by the plant and animal in minute amounts. The terms minor and micro-nutrient are often used synonymously.

Pining. A nutritional disease of animals, particularly ruminants, attributed to cobalt deficiency. Other synonymous terms often applied to this and probably those of similar symptoms are: bush sickness, enzootic marasmus, coast disease, nakaturuitis and salt sick.

CONTEMPORARY RESEARCH IN MINOR ELEMENTS

The earliest investigations of trace element essentiality were undertaken by the French workers in the early part of this century. Their work received little attention for a long period of time. The idea still persisted that a plant's indispensable requirements were met by ten chemical elments although often it was considered probable that certain species of plants might have other specific requirements.

Since 1920 conclusive evidence has been accumulating to show that chemical elements in rather large number are essential for the plant in very minute amounts. Extensive evidence presented by McHargue (26)* and others showed that manganese must be regarded as an essential element. Later experiments by Brenchley and Waring-

*Numerals in parentheses refer to Bibliography on pages 15 and 16.

ton (11) and Sommer and Lipman (43) demonstrated the essentiality of boron and zinc for growth of a wide range of plant species. A copper requirement for plant growth was demonstrated by Lipman and MacKinney (24) and Sommer (41) in 1931. More recently, Arnon and Stout (2) have presented strong evidence to show that molybdenum should be added to the list of essential elements. Cobalt and iodine, which have functions in animal metabolism, have not yet been shown to be indispensable to plants.

Copper

Copper is very widely distributed in plants and in considerable quantity. McHargue (27) found that the copper content of various plants and plant parts ranged from a trace to 46 p.p.m. of dry material. According to Beeson (7) the copper content of mature oat plants showing symptoms of copper deficiency was less than 1.0 p.p.m. while the mean copper content of oat plants is 10. p.p.m. Sommer (41) in 1931 found that the addition of small quantities of copper effected a marked increase in growth of sunflowers, flax and tomatoes. In the same year Lipman and MacKinney (24) found that flax and barley grown in water cultures failed to produce seed in complete absence of copper. Bortels (9) found that copper was indispensable to Aspergillus niger, one of the fungi, in the production of black conidia and in its absence there was a decrease in dry weight. Other investigators have found that other microorganisms also show a requirement for copper.

Evidence has been presented by Anderssen (1) and Oserkowsky and Thomas (35) indicating that chlorosis and die-back of the branches of various fruit trees can be cured by proper application of copper salts to the soil. Applications of copper sulphate were also found to cure "reclamation" disease, a pathological condition of cereal grains occurring on peat soils in Holland and elsewhere. This condition, where the tips of the leaves turn yellow or white while seed fails to form, was attributed by Sjollema (40) to be a copper deficiency.

Felix (15) in New York and Harmer (18) in Michigan obtained marked results in increasing the yield and quality of onions and lettuce by the application of copper sulfate to unproductive peat soils. Neal *et al.* (32) found that forage from certain areas of Florida contained a small amount of copper due primarily to the scarcity of this element in the soils in which it grew. Sommer (42) has reported that much more copper is necessary for the correction of copper deficiency in soils of high humus content than in other soils. Also it has been found that increases in yields may be obtained on heavy soils with amounts which would be toxic if applied to lighter soils. This is undoubtedly due to the difference in degree of copper fixation and that amount of copper made available to the plant.

It has been suggested that the chief function of copper, both in the plant and in the soil is that of an oxidizing catalyst. This hypothesis has been affirmed by Willis and Piland (44) who contend that the important function of copper is the regulation of the oxidation-reduction potential in the soil. With the organic matter as the reducing agent and oxygen as the chief oxidizing agent, reduction and oxidation take place only in the presence of activators. Microbial action can activate reduction, with oxidation activated by some inorganic catalyst such as copper. The oxidation-reduction equilibrium in organic soils tends to be on the reducing side unless an oxidizing catalyst is present. The iron in peat soils is organically-bound and does not appear to catalyse oxidation sufficiently to equal the reducing processes. Iron tends to accumulate in the ferrous form under such conditions to the point where it becomes toxic to plant growth. Copper added to these soils may oxidize the soluble ferrous iron, decrease its availability to plants, and thereby reduce its toxicity.

Within the plant, copper is often reported to function as the prosthetic group of some oxidative enzymes. Another frequently suggested function of copper in plant metabolism is that of chlorophyll formation. Reports of increased chlorophyll content after applications of copper are numerous. Outstanding is the report of Orth *et al.* (34), wherein they state that the chlorophyll content of leaves of orange trees is 4.6 times greater after fertilization with copper sulfate than the leaves of untreated trees.

The investigation of trace elements in animals has not progressed as rapidly as with plants but there are nevertheless a few trace elements which are well established as essential for certain groups of animals. Of these perhaps copper is one of the more emphasized. McHargue *et al.* (28) and Hart *et al.* (19) showed that copper is required for the utilization of iron in hemoglobin formation. As a result, a deficiency of copper in animals may result in anemia and the cure may be effected by supplementing the ration with copper sulfate.

The occurrence of a "licking sickness" of cattle in Holland where reclamation disease of cereals also occurs led Sjollema (40) to connect the two, and attribute both to a copper deficiency. Moving the affected animals to land where reclamation disease does not occur resulted in the rapid improvement of the anmials. Analyses show that hays from farms on which the reclamation disease occurs have an abnormally low copper content of 1-3 p.p.m. while hay from normal farms contains 6-12 p.p.m.

According to Neal *et al.* (32) the disease of cattle in Florida known as "salt sick" is a nutritional anemia resulting from an inadequate supply of copper and iron in the diet. That the disease occurs on certain sandy soils where the iron and copper contents are below normal is reported by Bryan and Becker (12). They found that cattle became salt sick on soils containing 0.036% of iron and 3.85 p.p.m. of copper. The similarity of this disease and licking sickness in Holland suggests that the two diseases are the same.

A disease known as swayback affects lambs in widely separated parts of the world and is commonly considered to result from a shortage of copper. The disease known by several different names is characterized by lack of coordination of movement and sometimes blindness due undoubtedly to the degeneration of the brain and spinal cord which postmortem examination reveals. Although a large-scale experiment has been carried out to test the theory that swayback is a nutritional disease, by feeding gestating ewes a mineral supplement with copper, no evidence is offered that the vegetation on which the ewes normally feed in swayback areas is necessarily deficient in copper. Dunlop and Wells (14) point out that the presence of an excess of lead or other minerals may render the copper unavailable and it may not be utilized by the animal.

Ritchie (38) reports that "steely" wool lacking the characteristic crimp and exhibiting a "straight, glittering fibre" has been linked up with a copper deficiency. He also reports low lambing percentages as a result of this copper deficiency. Corrective measures have been taken in the form of an application of 7 pounds of copper sulfate to the acre.

Holmes (20) states that the composition of the parent material has a varying influence on the copper content of the resulting soil, which depends materially on the conditions existing during soil development. In the analyses of a number of different soils he found that many soils with a low copper content are acid and highly pervious. He related this to the probable rapid removal of copper from the parent material as it weathered. The soils of higher copper contents are not so highly leached and, with few exceptions, are nearly neutral or alkaline.

Peech (36) reported that copper was fixed even in light sandy soils at comparatively low pH values. Whereas 40% of the copper applied to a soil as a sulfate was recovered at a pH of 3.0, only <20% and <10% were recovered at pH values of 4.0 and 5.0, respectively. Piper (37), investigating soil reaction and copper uptake, presented evidence to show also that there is a greater availability in more acid soils (pH 4.0 to 4.7) and that if there is a toxic effect of copper it is more apparent at a low pH value. Jamison (21) states that the fixation of copper in acid soils must be due to the formation of slowly soluble organic copper compounds. When the pH is 6.0 or above copper fixation can be partly due to the precipitation of basic copper compounds.

Cobalt

To date, no evidence has been presented to show a requirement of cobalt by higher plants. It does not appear to be essential for plant growth but if it is required it can be said that it is in an amount not greater than that present as an unavoidable impurity in culture solutions.

Cobalt is now regarded as nutritionally essential for sheep and cattle, for with a deficiency of this element in the diet, serious nutritional diseases may develop which often prove fatal. An early indication of the essential nature of cobalt in the nutrition of sheep resulted from the work of Lines (23) in South Australia. More recently, other reports have been made by Neal and Ahmann (33) of similar beneficial results by supplementing the animal diet with cobalt. The symptoms of cobalt deficiency in sheep are progressive debility: retarded growth, stunted and unthrifty lambs, broken wool, increasing emaciation, and weakness. However, the precise role of cobalt in animal nutrition is not yet established.

Mitchell (29) has reported that herbage contents of above 0.08 p.p.m. cobalt are necessary to insure complete animal health. Below 0.04 p.p.m. it is unlikely that a healthy permanent sheep stock can be carried.

By feeding cobalt salts, the cure of some serious nutritional diseases can readily be effected. Askew (3) suggested that the occurrence of cobalt pining in affected areas can be prevented by top-dressing with a cobalt salt thoroughly mixed with a phosphatic fertilizer at about the rate of 2 pounds of cobalt salt per acre.

Becker *et al.* (5), in Florida, have related some sandy soils and their low cobalt and copper contents to the occurrence of nutritional anemia in cattle. They believe that it may be possible to predict whether or not local areas may be deficient by observing the soil type. Predictions may be later verified by an analysis of the soil in question.

Conditions of emaciation in cattle and sheep in Michigan have been reported by Baltzer *et al.* (4). These conditions have been an annual occurrence during the winter and spring months for many years. In the event of survival the condition was usually alleviated when the animals were put on succulent spring pasture. This condition was attributed to a cobalt deficiency and was eventually corrected by feeding cobalt. Geyer *et al.* (16) have reported a similar situation in Northeastern Wisconsin. Beeson (8) has designated other areas in Eastern United States where cobalt deficiencies are also known to occur.

Mitchell (29) states that a cobalt content of 20 to 100 p.p.m. is to be expected in soils derived from basic igneous rocks or argillaceous sediments, whereas contents below 20 p.p.m. cobalt are normal in soils from sandstones, limestones and acid igneous rocks. He suggests that these generalizations are of use when dealing with residual soils or those derived from glacial drifts in areas of uniform geology. Soils derived from a till of mixed origin would complicate any such description as to their probable cobalt content. The bulk of the cobalt content in soils is bound up in the crystal lattice of minerals and is not readily available to plants. Comparisons of total cobalt in the soil with plant uptake have shown little correlation.

Kidson (22) suggests that the cobalt contents of soil are in general related to the magnesium contents of their parent rock. She states that serpentine rich in magnesium gives rise to soils of high cobalt content while granite produces soils low in cobalt.

Lyford *et al.* (25) have reported that there exists a strong relationship between a cobalt deficiency of New Hampshire soils and the parent soil materials from which derived. This deficiency is relatively more prevalent on soils developed principally from a granitic till or outwash than on those soils developed largely on till derived from granite, mica schists, or both. Also, the deficiencies appear to prevail on lighter textured soils rather than on heavier soils.

PLAN AND METHODS OF INVESTIGATION

Soils Investigated

Twenty-six different Missouri soils were selected for this study of their copper and cobalt contents. All are surface soils and, for the most part, each is representative of a distinct soil type. The group as a whole represents a variety of parent materials found throughout the state. These soils chosen at random were obtained from several sources, principally from those previously collected samples that have been authentically classified.

Methods of Analysis

Spectrographic. Soil samples were prepared for analysis by grinding in an agate mortar until all would pass through a 100 mesh nylon screen. A one-gram aliquot was then ignited at 450°C. overnight. The cobalt and copper contents were then determined by the emission spectrographic method using a Jarrell-Ash grating spectrograph.

Chemical Methods for Copper. A soil extract was obtained by following the procedure outlined by Sherman and McHargue (39) according to which 0.5 gram of soil was dissolved using a mixture of perchloric and hydrofluoric acids. A modified colorimetric method depending on dithizone to develop a dithizone-copper complex as suggested by Morrison and Paige (30) was used to complete the determination. It was found necessary to modify the Morrision and Paige method somewhat by substituting 125 ml. separatory funnels for the Majonnier extraction flasks.

Chemical Methods for Cobalt. The procedure followed for the determination of cobalt was that devised by Davidson and Mitchell (13) where cobalt forms an intensely colored soluble compound with nitroso-R-salt. This is an extremely sensitive colorimetric method for the determination of small amounts of cobalt.

Biological Methods for Copper. The Mulder (31) method for the biological determination of copper was used. This method involves the use of one of the fungi, *Aspergillus niger* (M strain), as an indicator since it is sensitive to the variable concentration of copper, which it requires for acid-, pigment- and spore-production.

Other Determinations

Organic Matter. The organic matter content of the soils studied was determined by the use of the photo-electric colorimeter as outlined by Graham (17).

Clay Content. The clay content of the soils studied was determined by the use of the hydrometer method as developed by Bouyoucos (10).

Soil Acidity. The pH was determined by use of the Limemeter and a 1:1 ratio of soil and water.

RESULTS

The inventory of the resources of copper and cobalt in 26 soils, widely distributed in Missouri, as determined by means of spectrographic, chemical and biological methods of analysis, reveals variations over a wide range. That there might be soils too low for the needs of some plants can readily be pictured. The data for copper are assembled in Table 1 and for cobalt in Table 2. Other soil properties such as reaction, organic matter content and clay content have also been measured and considered in conjunction with the contents of these elements. Data for these are presented in Table 3.

Copper

The results of the analyses of the soils by the different methods are shown under the appropriate column headings. The soil types are listed in column one in descending order of their contents of copper as determined by the chemical method. This method involved the use of dithizone (diphenylthiocarbazone) to develop a dithizone-copper complex at a pH of 2.3. The optical density was then determined from the resulting solution using a suitable photometer. The corresponding concentration of copper was interpreted from a calibration curve previously prepared from standard solutions similarly manipulated. These results are shown in column two, Table 1.

TABLE 1. -- COPPER CONTENTS OF SOME MISSOURI SOILS

Soil Type (Col. 1)	Copper (p.p.m.)		
	Chemical (Total) (Col. 2)	Spectrographic (Total) (Col. 3)	Biological (Available) (Col. 4)
High Group			
Ashe silt loam	82.0	50.0	2.5
Bates silt loam	62.0	30.0	2.5
Huntington silt loam	60.0	30.0	2.5
Cherokee silt loam	52.0	30.0	1.3
Sharkey clay	52.0	20.0	1.8
Crawford silt loam	46.0	20.0	1.6
Grundy silt loam	44.0	20.0	1.6
Osage silt loam	44.0	30.0	2.0
Newtonia silt loam	44.0	10.0	1.6
Mean	54.0		
Medium Group			
Shelby clay loam	39.0	30.0	1.6
Sarpy f. sandy loam	36.0	30.0	1.0
Wabash clay loam	32.0	20.0	1.3
Marshall silt loam	32.0	20.0	1.3
Tilsit silt loam	32.0	10.0	1.6
Lindley silt loam	32.0	20.0	1.5
Summit clay loam	30.0	20.0	1.3
Mean	33.0		
Low Group			
Oswego silt loam	27.0	10.0	1.3
Waverly silt loam	27.0	10.0	1.3
Putnam silt loam	26.0	20.0	1.0
Memphis silt loam	26.0	20.0	2.0
Hagerstown silt loam	22.0	10.0	2.0
Knox silt loam	19.0	5.0	1.0
Union silt loam	17.0	5.0	.8
Lintonia f. sandy loam	15.0	10.0	.8
Clarksville grav. loam	15.0	10.0	.6
Lebanon silt loam	15.0	10.0	.5
Mean	21.0		

The results of the spectrographic analyses of this group of soils for copper are recorded in column three, Table 1. This semi-quantitative method provided a rapid means for the study of these trace constituents of the soil.

The amounts of available copper in these soils were determined by comparing the extent of pigmentation of the spores of *Aspergillus niger* grown on the soil cultures with that resulting when grown on corresponding standard solution cultures. These values for available copper were determined by assuming that the amounts of copper added to the standard solution cultures are completely used by the *Aspergillus niger* for acid-, spore-, and pigment-production. Where the extent of pigmentation in the soil culture was essentially the same as that in the standard culture, the amount of available copper was taken to be the same. These determinations are recorded in column four, Table 1.

Cobalt

A colorimetric method was used for the chemical determination of cobalt in which the cobalt combines with nitroso-R-salt (sodium salt of 1-nitroso, 2-naphthol, 3:6 disulphonic acid) and forms an intensely colored soluble compound. After the formation of the cobalt complex the photometer was used to determine the transmittance of the solution. The concentration of cobalt was then calculated by using a curve previously prepared and calibrated by means of standard solutions of cobalt. These results are shown in column two, Table 2, where the soil

TABLE 2. -- COBALT CONTENTS OF SOME MISSOURI SOILS

Soil Type (Col. 1)	Cobalt (p.p.m.) Chemical (Total) (Col. 2)	Cobalt (p.p.m.) Spectrographic (Total) (Col. 3)
Ashe silt loam	37.0	50.0
Crawford silt loam	13.8	20.0
Tilsit silt loam	12.1	20.0
Hagerstown silt loam	9.4	10.0
Wabash clay loam	9.3	10.0
Grundy silt loam	9.1	2.0
Lebanon silt loam	8.9	5.0
Marshall silt loam	8.7	5.0
Shelby clay loam	8.4	5.0
Union silt loam	8.3	10.0
Huntington silt loam	8.2	10.0
Bates silt loam	8.1	5.0
Newtonia silt loam	7.9	10.0
Cherokee silt loam	7.4	5.0
Sharkey clay	7.3	10.0
Lintonia f. sandy loam	6.9	5.0
Sarpy f. sandy loam	6.8	5.0
Osage silt loam	6.2	5.0
Lindley silt loam	5.8	5.0
Summit clay loam	5.8	---
Putnam silt loam	5.7	5.0
Knox silt loam	5.7	3.0
Memphis silt loam	5.3	3.0
Waverly silt loam	5.1	---
Oswego silt loam	4.4	3.0
Clarksville grav. loam	4.2	3.0

types are listed in column one in descending order according to their contents of cobalt as determined by this method. This colorimetric method is extremely sensitive and permits the determination of small amounts of cobalt.

The results of the spectrographic analyses for cobalt are recorded in column three, Table 2. The method employed was the same as that used for the determination of copper.

DISCUSSION OF RESULTS

The soils used in this study were formed from a variety of parent materials and for the most part were developed under varying conditions of weathering.

Chemical Analyses

With respect to copper, these soils may be divided into three groups; namely, low, medium and high. The low group includes the Lebanon, Clarksville, Oswego, Lintonia, Memphis, Knox, Putnam, Waverly, Union and Hagerstown soils, in which the copper content ranges from 15 to 27 p.p.m. The mean is 21 p.p.m.* The medium group includes the Tilsit, Wabash, Marshall, Shelby, Lindley, Summit and Sarpy soils in which the copper ranges from 30 to 39 p.p.m. The mean is 33 p.p.m. The high group includes the Ashe, Crawford, Grundy, Huntington, Bates, Newtonia, Cherokee, Osage, and Sharkey soils in which the copper

TABLE 3. -- THE PARENT MATERIALS AND SOME PROPERTIES OF THE MISSOURI SOILS ANALYZED FOR THEIR CONTENTS OF COPPER AND COBALT

Soil Type	Parent Material	pH	O.M. (%)	Clay (%)
Cherokee silt loam	Cherokee shale	4.8	2.3	15
Sarpy f. sandy loam	Aluvial (S.E. Missouri)	6.0	1.2	12
Ashe silt loam	Pre-Cambrian granite & rhyolite	6.0	2.9	14
Lebanon silt loam	Gasconade & Roubidoux limestone	5.4	1.3	18
Sharkey clay	Alluvial (S.E. Missouri)	5.7	2.9	39
Crawford silt loam	Burlington limestone	6.4	1.8	19
Newtonia silt loam	Burlington limestone	6.8	2.3	18
Putnam silt loam	Loess over glacial till	5.7	1.9	19
Clarksville grav. loam	Gasconade & Roubidoux limestone	5.8	1.9	16
Grundy silt loam	Loess	5.4	1.7	19
Bates silt loam	Cherokee sandstone	5.4	1.5	17
Wabash clay loam	Alluvial (N. Missouri)	6.2	2.0	24
Shelby clay loam	Kansan glacial till	5.0	2.7	17
Marshall silt loam	Loess	5.5	2.4	19
Huntington silt loam	Alluvial (Ozark)	5.8	2.3	18
Summit clay loam	Cherokee calcareous shale	5.4	1.8	19
Osage silt loam	Alluvial (S.W. Missouri)	5.0	1.9	15
Lindley silt loam	Kansan glacial till	4.4	0.5	18
Union silt loam	Jefferson City dolomitic limestone	5.6	1.2	19
Oswego silt loam	Cherokee shale	6.0	1.7	15
Waverly silt loam	Alluvial (S.E. Missouri)	4.6	1.4	19
Tilsit silt loam	LaMotte sandstone	6.0	1.4	16
Knox silt loam	Loess	5.8	2.4	18
Lintonia f. sandy loam	Old alluvial (S.E. Missouri)	5.4	0.6	8
Memphis silt loam	Loess	5.9	0.8	12
Hagerstown silt loam	Boone Terre limestone	7.2	1.6	18

*This mean figure may be expressed as 42 pounds per acre or per two million pounds equivalent of plowed surface soil per acre.

ranges from 44 to 82 p.p.m. The mean is 54 p.p.m. Grouping these soils according to their copper content thus resulted in three groups of low, medium and high with means of 21, 33 and 54 p.p.m., respectively.

The cobalt contents of these same twenty-six soils varied from 4.2 to 37.0 p.p.m. with a mean of 8.5 If the Ashe silt loam figure for cobalt, the highest in the group, were omitted from the calculation the mean would be reduced to 7.5 p.p.m. These variations in cobalt contents do not parallel those of copper.

Davidson and Mitchell (13) observed that livestock suffering from nutritional disease are sometimes found in soil regions containing less than 5.0 p.p.m. of cobalt. If this is considered the critical level of cobalt, then the Oswego and Clarksville soils fall in this dangerous group, with the Waverly and Memphis soils barely outside of it. Not too far removed from this group are the Knox, Putnam, Summit and Lindley soils. All of the aforementioned soils have contents of cobalt less than 6.0 p.p.m. and should probably be considered types in which areas may be deficient or slightly deficient in this element. The other soils have a cobalt content ranging from 37.0 to 6.2 p.p.m. and may be considered to have sufficient cobalt, according to the above standard.

Spectrographic Analyses

The data from the spectrographic analyses parallel those of the chemical analyses but vary in some instances of the copper determinations by as much as a factor of 2. No obvious explanation for such wide differences can be presented. The data from the spectrographic and chemical analyses of cobalt compare favorably and are within the range of experimental error.

Biological Determination

The biological determinations of available copper parallel, with some exceptions, both the chemical and spectrographic results. The Mulder (31) method for estimating the available copper in soils was used and the results obtained were easily reproducible. Using this method, the soils were again divided into three groups; low, medium and high. The low group included the Lebanon, Clarksville, Lintonia, Union, Knox, Putnam and Sarpy soils, in which the available copper ranged from 0.5 to 1.0 p.p.m. These soils may be considered as deficient in available copper. The medium group included the Waverly, Oswego, Summit, Marshall, Wabash, Cherokee and Lindley soils in which the contents of available copper ranged from 1.0 to 1.5 p.p.m. These soils may be considered to be slightly deficient in available copper. The high group included the Tilsit, Shelby, Newtonia, Grundy, Crawford, Sharkey, Hagerstown, Memphis, Osage, Huntington, Bates and Ashe soils in each of which the content of available copper was 1.6 p.p.m. or more.

These soils may be considered to have a sufficient amount of available copper. The ratios of total to available copper varied from 11 to 40. This variance was undoubtedly due to those factors concerned with availability; that is, the form in which the copper was present, the amount and kind of organic matter and the percentage of clay.

The conclusions which the authors have drawn from this investigation will be found on page 2 under the heading, Abstract.

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