MICRONUTRIENTS IN SOILS OF THE TALL-GRASS PRAIRIE OF OKLAHOMA

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Soil from fifteen stands in the tall-grass prairie of Oklahoma was analyzed to determine the pH and EDTA-extractable concentrations of six trace elements: Co, Cu, Fe, Mn, Mo, and Zn. The pH decreased from west to east. The concentrations of Fe, Mn, and Zn in the soil increased from west to east, but no apparent trend was determined for Co or Cu. Molybdenum, required in nitrogen metabolism and cycling, was not detected in soil from six of 10 western and central stands, while soils of all eastern stands had measurable concentrations.

INTRODUCTION

Trace elements, also known as micronutrients or minor elements, are those chemical elements essential in minute amounts for the normal metabolic processes of living organisms. All are important as constituents of prosthetic groups of enzymes or as enzyme activators, except for boron, which appears to be necessary for translocation of sugar in plants and may be necessary for formation of pectins and lignin (1). Cobalt has not been demonstrated to be essential for higher plants but it is required for symbiotic nitrogen fixation, probably because of a vitamin B_{12} requirement of the endophytes and a cobalt-containing coenzyme in the nodules (2, 3).

In spite of the importance of trace elements in plant growth, little research has been done on their concentrations in soils of natural ecosystems in Oklahoma. The one comprehensive project was a quantitative analysis for most of the essential micronutrients in soils of upland forests of Oklahoma by Johnson (4), who used procedures identical to those used in this investigation. There have been several publications on trace elements in relation to agriculture (5, 6, 7) and deficiencies of certain elements were found in some areas. Harper and Reed (5) did a comprehensive study of trace elements in soil and forage plants in the tall-grass prairie area of Oklahoma, but their study included pastures in addition to meadows and the data were combined. They did separate data obtained in plots containing bluestem grasses, "primarily little bluestem" (*Andropogon scoparius* Michx.), from data obtained in plots containing short grasses or introduced grasses.

The present project was undertaken to increase our knowledge of concentrations of trace elements in the soils of one of our important natural ecosystems in Oklahoma, the tall-grass prairie.

MATERIALS AND METHODS

Site Location and Description

This study was done in conjunction with an investigation by Tarr *et al*. (8) involving a broad vegetational analysis of the tall-grass prairie of Oklahoma. Location of stands, climatic conditions, and vegetational descriptions can be found in that paper. Prairie stands were located in 15 counties throughout the range of the tall-grass prairie in Oklahoma (9).

Nine physiographic provinces were represented in this survey (10). The soils of the study area were generally derived from sedimentary rock from the Pennsylvanian Period, although some soils were derived from sedimentary rock from the Permian, Quaternary, and Cretaceous Periods. Soil derived from igneous and metamorphic rock from the Precambian Period was sampled in Comanche County (10).

Soil Analysis

Ten soil samples (0-6 in. level) were collected in a systematic pattern from each of the 15 stands. The soil was air-dried, visible organic matter was removed, and the soil was passed through a stainless steel sieve with 2-mm holes. The samples were combined by pairs to give five samples for each area. The soil pH was determined by the glass electrode method, using a 1:5 ratio of soil to distilled water. A fraction of each soil sample was then weighed, oven-dried for 48 hr at 105 C, cooled in a desiccator, and reweighed to determine the moisture content of the air-dried soil. The samples were then ground in a soil mill to pass a sieve with 0.5-mm holes. A 2-g aliquot of each soil sample was extracted with 1% aqueous disodium ethylenediaminetetraacetate (EDTA) at pH 7.0 and the mixture centrifuged at 12000 × g for 15 min and filtered. All volumes were brought up to 30 m*l* with deionized water. This extraction procedure was used to make comparisons with the upland forest data of Johnson (4) more accurate, and because EDTA extracts only the exchangeable cations plus the relatively water-soluble salts of the metals. Results of micronutrient soil tests based on extraction with chelating agents have been shown by many investigators to correlate well with uptake by plants (11). Several workers have found that the Mo content of plants correlates well with the concentration of water-soluble Mo in soils on which the plants have grown (11), and our procedure extracts this also.

The concentrations of Co, Cu, Fe, Mn, Mo, and Zn in the extract were determined with a Perkin-Elmer Model 303 atomic absorption spectrophotometer, using the procedures outlined in the manual supplied with the instrument (12). Proper precautions were taken to prevent errors due to interfering ions. Air-dried soil was used for all analyses, but all calculations were based on the oven-dry weight.

RESULTS

The pH decreased considerably from west to east in the soil of prairie stands (Table 1). EDTA-extractable concentrations of the trace elements were often quite variable even in a given geographic region, although the concentrations of Co and Fe were relatively consistent in most regions. The ranges of concentration (ppm) of the trace elements for individual stands were Co, 5.1-9.8; Cu, 0.1-9.6; Fe, 23.8-290.2; Mn, 68.6-382.3; Mo, 0.8-10.8; and Zn, 1.9-95.1 (Table 1).

There was no west-east gradient in mean concentrations of Co or Cu, but mean concentrations of Fe, Mn, and Zn increased from west to east (Table 2). Most of the trace elements increase in solubility as the pH decreases, and the pH was lowest in the eastern region also. Mean concentrations of Mo did not have a west-east gradient, but concentrations showed less variability in eastern stands. Concentrations were generally either relatively high or not measurable in the western and central stands, most of the stands having concentrations which were not detectable by the procedure employed. On the other hand, all eastern stands had measurable concentrations of Mo.

DISCUSSION

Johnson (4) reported that the concentration of Cu ranged from 2.4-10.0 ppm in upland forest soils of Oklahoma, which was slightly higher than the range in the tall-grass prairie. Harper and Reed (5) in their study of trace elements in soils of pastures and meadows in the tall-grass prairie area of Oklahoma reported a range for Cu of 1.3-38.6 ppm. Calculations from their data revealed no appreciable differences in mean Cu concentrations in the geographic regions. This agreed with our findings, but their values were slightly higher. This could have resulted in part from different analytical procedures, and in part from their inclusion of data from pastures. Iron concentrations in upland forest ecosystems were much higher generally than in the tall-grass prairie, ranging from 110-1066 ppm (4). The lowest concentration noted in the prairie was 23.8 ppm. Concentrations of Fe above 4.5 ppm are rated as adequate in agriculture (7).

The range of concentrations reported for Mn in soils of forest ecosystems was 56-685 ppm (4), which was also higher than the range we found in the tall-grass prairie. The lowest concentration in both vegetation types was above 50 ppm, which is noteworthy since the Oklahoma Agricultural Extension Service (7) reported that Mn toxicity should be suspected in agricultural soils with concentrations above 50 ppm. Harper and Reed (5) reported a range of concentrations of Mn in soils of pastures and meadows of 6-572 ppm. Calculations from their data revealed the same trend we found of increases in Mn concentrations from west to east, but their mean values in the three geographic regions were lower. Only soils with Mn con-

TABLE 1. *Range of pH and average concentration of trace elements (ppm ± SD) in prairie stands.*

Prairie Stand (counties)	pH Range	Co	Cu	Fe	Mn	Mo	Zn
Northwest							
Alfalfa	7.6 — 8.3	6.7 ± 0.4	3.9 ± 6.2	47.9 ± 29.8	151.8 ± 98.0	ND[a]	3.4 ± 2.4
Custer	6.9 — 7.0	7.1 ± 0.4	3.0 ± 0.5	59.9 ± 30.3	148.0 ± 21.6	10.8 ± 2.9	22.9 ± 27.4
Dewey	8.6 — 8.9	6.2 ± 0.0	0.9 ± 0.3	64.1 ± 30.1	68.6 ± 27.4	ND	2.0 ± 1.0
Southwest							
Comanche	6.3 — 6.5	5.6 ± 0.4	1.0 ± 1.2	207.4 ± 26.6	104.2 ± 22.7	ND	11.2 ± 9.3
Tillman	8.6 — 8.8	5.1 ± 0.3	2.8 ± 2.0	23.8 ± 4.8	114.8 ± 66.8	3.6 ± 2.2	12.2 ± 6.2
North Central							
Payne	5.8 — 6.2	5.8 ± 0.8	2.7 ± 0.2	234.7 ± 44.7	86.1 ± 16.8	ND	19.6 ± 33.3
South Central							
Hughes	5.6 — 6.0	7.6 ± 0.6	2.8 ± 0.5	290.2 ± 29.0	278.7 ± 44.4	0.8 ± 1.8	15.4 ± 3.5
Jefferson	6.1 — 6.4	7.3 ± 0.3	9.6 ± 6.8	111.4 ± 25.9	278.7 ± 48.9	ND	1.9 ± 0.7
McClain	6.5 — 8.3	5.9 ± 0.4	0.1 ± 0.2	57.2 ± 28.3	195.6 ± 92.7	ND	2.1 ± 0.8
Marshall	7.5 — 7.9	8.8 ± 1.1	4.9 ± 0.6	198.0 ± 27.9	382.3 ± 105.0	6.3 ± 1.5	11.1 ± 7.8
Northeast							
Craig	5.3 — 5.5	6.2 ± 0.1	3.4 ± 0.4	292.9 ± 28.5	193.9 ± 19.4	0.8 ± 1.8	58.7 ± 34.4
Muskogee	5.5 — 5.6	5.7 ± 0.2	3.0 ± 0.4	321.6 ± 38.3	175.2 ± 23.7	1.6 ± 2.2	12.2 ± 4.3
Ottawa	5.3 — 5.5	5.8 ± 0.9	2.8 ± 0.5	300.9 ± 48.0	230.7 ± 36.5	3.1 ± 2.9	95.1 ± 60.5
Washington	6.1 — 6.9	9.8 ± 0.5	2.1 ± 1.4	287.6 ± 58.9	305.8 ± 34.4	1.8 ± 2.5	18.3 ± 6.3
Southeast							
Haskell	5.9 — 6.4	6.3 ± 0.3	2.2 ± 0.2	317.8 ± 52.0	310.0 ± 31.7	3.5 ± 3.3	52.7 ± 33.5

[a]ND = Not detectable with analytical procedure employed.

TABLE 2. *Average concentrations of trace elements (ppm ± SD) by geographic region.*

Region	Co	Cu	Fe	Mn	Mo	Zn
Western	6.1 ± 0.8	2.3 ± 1.3	80.6 ± 72.6	117.5 ± 34.2[a]	2.9 ± 4.7	10.3 ± 8.4
Central	7.1 ± 1.2	4.0 ± 3.6	178.3 ± 93.8[b]	244.3 ± 110.5	1.4 ± 2.8	10.0 ± 7.9[b]
Eastern	6.7 ± 1.7	2.7 ± 0.6	304.2 ± 15.0[c]	243.1 ± 62.4[c]	2.2 ± 1.1	47.4 ± 33.6[c]

a. Difference between west and central means significant at .05 level or better.
b. Difference between central and east means significant at .05 level or better.
c. Difference between west and east means significant at .05 level or better.

centrations below 1.0 ppm are classified as deficient for crop plants (7).

The concentrations of Zn in soils of forest ecosystems in Oklahoma ranged from 1.9-9.4 ppm (4), which was much lower than the range in soils of the tall-grass prairie. Harper and Reed (5) reported concentrations of Zn from 3.6-193 ppm in soils of pastures and meadows in the tall-grass prairie area of Oklahoma. They found the highest mean concentration in the eastern section, just as we did. Concentrations of Zn of 2 ppm or above are considered adequate for all crops (7).

Harper and Reed (5) found that Co concentrations in soils of pastures and meadows in the tall-grass prairie area ranged from 0.1-4.9 ppm. This range was considerably lower than the range we found in soils of climax prairie stands. This element is apparently required only in very small amounts, if at all, by higher plants as indicated by the fact it has not definitely been shown to be essential for their growth (13). Only very small amounts are required by nitrogen-fixing microorganisms. Ahmed and Evans (14) found that 1.0 ppb of Co was sufficient for maximum growth of *Glycine max* (L.) Merr. in purified nutrient solution lacking combined nitrogen. Delwiche, Johnson, and Reisenauer (15) reported that a concentration of $CoSO_4$ of $2 \times 10^{-8} M$ in the culture solution was effective for nitrogen fixation in *Medicago sativa* L. Kliewer and Evans (2) found that maximum growth of *Rhizobium meliloti* occurred in a medium containing 1.0 ppb of Co, and of *R. japonicum* in a medium containing 0.01 ppb. They reported that *Azotobacter vinelandii* had normal growth in a medium containing 0.001 ppb of Co. Thus, the concentrations of Co in soils appear to be completely adequate for nitrogen fixation in the tall-grass prairie of Oklahoma, because values ranged from 5.1-9-8 ppm.

Harper and Reed (5) reported a range of concentrations of Mo in soils of pastures and meadows of 0.04-1.1 ppm. We found a somewhat higher range of Mo concentrations in soils of tall-grass prairie stands. Nevertheless, concentrations of Mo were so low in central and western regions that none was detected in six of 10 stands sampled. Our failure to detect Mo was not related to interference of Ca in extraction since soils of three of the six stands were in the pH range of 5.8-6.5. Most of the soil samples taken in another stand in which no Mo was detected, had pH values below 7.0 also. Additionally, a stand with one of the highest pH ranges (Tillman County — 8.6 to 8.8) had a relatively high mean concentration of Mo, 3.6 ppm. The low Mo concentrations in the soil have interesting implications in the nitrogen economy of these regions of our tall-grass prairie. Nitrate reductase is very low in plants growing in Mo-deficient soils, since it is an adaptive enzyme produced only when nitrate is present (1). Plants growing in such soils apparently use ammonium-N as the chief source of nitrogen. It is noteworthy that Rice and Pancholy (16) found that the climax tall-grass prairie vegetation inhibits nitrification so that most of the available nitrogen stays in the ammonium form. Richardson (17, 18) found in grassland soils at Rothamsted Experiment Station that the level of ammonium nitrogen was several times as great as the level of nitrate nitrogen. He reported also that prairie plants absorb the ammonium nitrogen as readily as nitrate and that much of the nitrogen is taken up as ammonia.

Molybdenum is essential for nitrogen fixation by both free-living and symbiotic microorganisms (1, 13). The rate of nitrogen fixation may be reduced, therefore, in areas with extremely low levels of Mo. Rice (19) found that addition of 1 ppm of Mo to prairie soil at Norman, Oklahoma significantly increased the number of nodules produced on inoculated legumes. Our results suggest the need for additional investigations on the Mo nutrition of legumes grown on soils formed originally under tall-grass prairie in the central and western regions of Oklahoma.

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