
UNIVERSITY OF MISSOURI · COLLEGE OF AGRICULTURE
AGRICULTURAL EXPERIMENT STATION

J. H. LONGWELL, *Director*

TRACE ELEMENTS IN MISSOURI SOILS

E. E. PICKETT AND R. H. DINIUS



(Publication authorized May 7, 1954)

COLUMBIA, MISSOURI

SUMMARY

Ten typical Missouri soils were selected and analyzed for total calcium, magnesium, sodium, potassium, iron, manganese, copper, cobalt, and zinc. These soils also were extracted and the extracts analyzed for these same elements, using four different extracting solutions for one, four, and sixteen hours. The extractants were 0.1 N hydrochloric acid, 2.5 percent acetic acid, normal ammonium acetate and sodium chloride.

Various procedures have been modified and adapted to permit the analyses for all of the above elements on small portions of prepared solutions. Two grams of soil were sufficient for the total analyses. Two extractions, of 20 grams of soil and 400 ml. extractant each, were necessary for the determination of the available nutrient.

Comparison of the value of these soils as agricultural land with results of the analyses for the major elements illustrates the value of chemical analysis in assaying the relative values of soils. There did not appear to be a very close relation between the economic value of the soil and results of the trace element analyses; however, the results for copper, total or extractable by hydrochloric acid, do show some correlation with economic value. The results for the biologically available copper, determined elsewhere (8), compare rather well with those obtained by hydrochloric acid extraction.

This bulletin is a report on Department of Agricultural Chemistry research project number 147, entitled "Mineral Content of Missouri Grown Feeds."

TRACE ELEMENTS IN MISSOURI SOILS

E. E. PICKETT AND R. H. DINIUS

INTRODUCTION

For many years agricultural scientists assumed that only seven elements were essential in a nutrient medium: they were nitrogen, potassium, sulfur, calcium, magnesium, phosphorus, and iron. It had been established for some time that many elements other than those considered to be essential were present in plant material, but their presence was regarded as incidental. It was not until French workers pointed out the importance of such elements as cobalt, manganese, and nickel in biological systems that any great attention was paid to trace elements, those elements which are required by plants and animals in minute amounts. It is now commonly accepted that a rather large number of elements are necessary for the normal growth and reproduction cycle of plants and animals. With the realization of the essentiality of the many elements, the problem of predicting their availability to plants from any particular soil developed. The problem of measuring the nutrient level of a soil had already been approached by the analyses of solutions of various sorts that had been in intimate contact with the soil. It is logical to attempt to determine the availability of trace elements in the same manner.

As the concept of the mechanism of root uptake changed, confidence in the value of soil extraction experiments began to be lost. Chapman and Kelley (4) suggested that the determination of base exchange was not exact and was subject to many interferences. Marshall (10) pointed out the need for new techniques to measure cation activities in the soil. Several workers have considered the significance of ionic reactions in soils and have attempted to treat the soil filtrates from a thermodynamic standpoint. Overstreet (14) has made a rather comprehensive study of ionic reactions and exchange in soil and clay suspensions from the thermodynamic standpoint and, although the work was with rather simplified systems, it could not be said that a true activity was being measured. Davis (5) has made a critical study of base exchange theories and measurements and arrived at the conclusion that the true base exchange capacity is not being measured. It appears to be the opinion of most workers in the field of soil chemistry that the information secured from soil extracts is empirical and not of a fundamental nature.

While soil extracts may not yield information as to the nature of root

uptake or the nature of base exchange in soils, their empirical value in predicting the nutritional value of the soil has not been disregarded. Peech (15), by careful selection of the extracting solution, was able to develop a method of diagnosing magnesium needs in Florida soil to prevent "bronzing" in citrus plants. Terlikowski *et al.* (19) related the assimilation of calcium, magnesium, sodium, and potassium in oats to their presence in soil extracts. Kvas (9) compared the growth of wheat, potatoes, and pasture over a four-year period to the nutrient levels predicted by the Neubauer method and found good correlation. Wohlhier *et al.* (22) found a partial correlation of about 60 percent between the results of yield experiments and Dirk's procedure for potash. There have been numerous attempts to correlate the results of extractions with plant response data. In the majority of these it appears that the main objective has been to establish some fundamental relationship between base exchange measurements and root uptake.

It is difficult to attribute the first use of a particular extractant to any one investigator. The most important property in choosing an extractant is the ion exchange power and the low solubility effects that it might have on the soil minerals. Gedroiz (6) proposed the use of ammonium chloride for estimating base exchange capacity. The replaceable calcium and magnesium were determined by Tjurins (20) using sodium chloride solution. Burd (3) has proposed water for determining fertility values; later he employed 0.1 N barium chloride for replaceable calcium and magnesium. Chapman and Kelley (4) recommended ammonium acetate although it undoubtedly had been used earlier. Reviews in which most of the common extractants are discussed are given by Chapman and Kelley (4) and Puri and Uppal (17). In Table I are listed most of the common extractants together with the cations for which they have been used. It is unfortunate that for most of them no correlation with cropping yields has been attempted.

The empirical value of soil extractions in estimating fertility levels in soils is fairly well established. The extractions are now in general use in determining fertilizer needs of soils. However, they are not very specific for particular crops. It would be desirable eventually to establish methods to diagnose deficiencies for particular crops, such as was done by Peech in determining magnesium deficiency for citrus crops. The purpose of the present work is to measure the total amounts of iron, calcium, sodium, magnesium, potassium, manganese, copper, cobalt, and zinc in some typical Missouri soils, and to compare these with the amounts of the elements extracted by the four most commonly used extractants in various intervals of time. The percentage of the total amount of each element which is extracted, the relative efficiencies of the different extractants, the influence of time of extraction, and possible correlation of amount extracted with cropping yield or economic value of the soil may thus be evaluated.

TABLE 1 -- COMMON EXTRACTANTS AND THE CATIONS FOR WHICH THEY ARE USED

Extractant Solutions	Cation Exchanged								Exchange Capacity
	Ca	Mg	K	Na	Mn	Fe + Al	Zn + Cu	H ⁺	
NH ₄ OAc	N	N	N	N	N	N	N	N	N
NH ₄ Cl	N	N	N	N					
NaCl	Aqueous								
KCl	Alcohol .02N	N				N	N 0.5N pH 3.2 HAc		
NaOAc		N			N				
AlCl ₃						3%			
H ₂ O	Sat. CO ₂	Sat. CO ₂	Sat. CO ₂	Sat. CO ₂				X	
HOAc	0.5N	0.5N	0.5N	0.5N		0.05N + Non Exchange			
HCl	0.05N	0.05N	0.05N	0.05N	0.05N	0.05N	0.1N		
BaCl ₂									0.1N

NOTE: The N indicates a normal solution.

ANALYTICAL METHODS

Selection and Preparation of Soil Samples: Samples of ten typical Missouri soils of agricultural value were supplied by the Soils Department. Care had been taken in collecting the samples to prevent trace element contamination. The larger lumps were broken up, the sample mixed, quartered, and crushed in an agate mortar. The crushed soil was passed through a fine-mesh nylon cloth and then stored.

Determination of Total Mineral Content: Loss on ignition was measured by the loss in weight of a ten gram sample on heating to 600°C. This material was used for the subsequent total determinations.

Silica, mixed oxides, and calcium were determined after sodium carbonate fusion of one gram of ignited soil. The determinations were performed by conventional chemical methods.

Another portion of ignited soil was brought into solution by means of sulfuric acid and hydrofluoric acid in platinum. (18). Iron, manganese, and magnesium were determined colorimetrically; the first two by A. O. A. C. methods (23) and the last by a modification of the method of Willson (21) involving re-solution in acid of a precipitate of magnesium oxinate and direct measurement of the light absorption of the oxine at 358 millimicrons.

Copper, cobalt, and zinc were determined in a hydrofluoric-sulfuric acid solution of the ignited soil. These metals were extracted by dithizone in carbon tetrachloride after buffering to pH 8.5 with ammonia and ammonium citrate. Organic matter was removed from the extract by evaporation and wet ashing with nitric and perchloric acids; the metal perchlorates were dissolved in water, making a total volume of two milliliters. The metals were determined spectrographically in this solution, after evaporation of small volumes, 0.1 to 0.2 ml., on 5/16 inch graphite electrodes, using spark excitation (7). This procedure has proved to be very helpful and reliable in determining amounts of these metals and zinc in various types of biological materials, soils, and fertilizers.

In all of this work, all reagents must be freed of trace metals and the sample solutions must be handled in such a way that contamination can be avoided.

Analysis of Soil Extracts: One-tenth normal hydrochloric acid and 2.5 percent acetic acid were made by diluting redistilled acids. One normal ammonium acetate and sodium chloride solutions were purified by shaking with dithizone in carbon tetrachloride. Twenty grams of soil were extracted with 400 ml. extractant in rubber-stoppered pyrex glass bottles which were rolled on a jar mill for one, four, or sixteen hours. The suspensions were filtered through Whatman No. 42 filter paper. Two series of extractions were made on each sample; one for determination of iron, manganese, calcium, magnesium, sodium, and potassium, and the other for copper, cobalt, and zinc.

TABLE 2 -- TOTAL MAJOR ELEMENTS OF THE SOILS

Soil	SiO ₂	R ₂ O	Ca	Mg	Na	K	Loss on Ignition
Marshall	79.16	15.66	0.55	0.42	0.95	1.85	8.11
Wabash	78.31	15.31	0.69	0.53	1.15	2.08	7.47
Shelby	74.40	13.94	0.44	0.40	0.85	1.21	8.40
Putnam	82.55	13.18	0.37	0.27	0.96	1.17	5.20
Campbell	86.55	10.69	0.31	0.21	1.17	1.85	5.16
Gerald	89.36	8.28	0.29	0.15	0.49	1.04	4.30
Winfield	84.00	11.80	0.31	0.23	0.78	1.23	4.10
Union	84.45	12.23	0.08	0.27	0.63	1.26	3.30
Lebanon	84.25	12.58	0.10	0.24	0.69	1.23	5.46
Hanceville	87.80	9.74	0.12	0.23	0.39	1.08	3.52

NOTE: The values of the total elements are expressed as percent of ignited soil. The Loss of Ignition is expressed as percent of the air dried soil.

TABLE 3 -- TOTAL MINOR ELEMENTS AND WATER SOLUBLE BORON

Soil	Fe	Mn	Cu	Co	Zn	B
Marshall	2.05	0.08	19.4	5.9	68.1	0.9
Wabash	2.01	0.05	20.2	7.3	50.5	1.4
Shelby	1.98	0.05	21.4	6.76	40.4	1.3
Putnam	1.51	0.06	15.2	3.2	50.1	1.6
Campbell	1.05	0.04	10.3	4.4	16.1	0.5
Gerald	1.07	0.03	15.8	5.2	17.9	0.6
Winfield	1.29	0.09	13.1	7.0	25.3	0.5
Union	1.50	0.06	15.6	9.2	31.1	0.7
Lebanon	1.03	0.10	15.8	9.5	20.3	0.4
Hanceville	1.10	0.05	12.7	6.8	18.2	0.6

NOTE: The values for iron and magnesium are expressed as percent of ignited soil. The values of copper, cobalt and zinc are expressed as ppm of ignited soil. The water soluble boron is parts per million of air dried soil.

The extracts were evaporated, wet ashed, and made up to 25 ml. Of this, 4 ml. aliquot is used for calcium and magnesium. Manganese and iron required 4 ml. from the acetic acid and ammonium acetate extracts. One ml. of the hydrochloric acid extract was used to determine manganese and 1 ml. of a tenfold dilution of another portion of the extract was used for the iron determination. The remainder of the solution was centrifuged and used for determination of sodium and potassium with the flame photometer. Final determination steps were done in the same way as the total mineral content analyses above. Copper, cobalt, and zinc were determined in duplicate extracts just as was done for total analyses of soils. The authors will furnish details of this dithizone extraction and spectrographic determination procedure for copper, cobalt, and zinc upon request.

RESULTS

Results of the total analyses are presented in Tables 2 and 3. The results are averages of duplicate analyses which agreed to within about three parts per thousand for the gravimetric work, consisting of the determinations of silica, mixed oxides, and loss on ignition, and five parts per thousand for the volumetric calcium determination. The colorimetric determinations gave results that were within four and five parts per thousand for iron and manganese and six parts for magnesium. The flame photometer gave results for sodium and potassium that agreed to within twenty-five parts per thousand or thirteen parts per thousand on the average.

The results of the extraction experiments are recorded in Tables 4 through 10. These are the results of single extractions; however, duplicate extractions were made on two soils using hydrochloric and acetic acid extractants to check the precision of the extraction step itself. In these duplicate extractions calcium varied by 0.7 percent; magnesium, iron, and manganese varied in the range of 0.9 to 1.2 percent, all based on the amount present.

The dithizone extraction-graphite spark spectrographic method for copper, cobalt, and zinc has an accuracy of about 8 percent, plus or minus, as determined by Hankins (7). The relative mean deviations had an average value for duplicate determinations of 5 percent.

TABLE 4 -- HYDROCHLORIC ACID EXTRACT OF THE MAJOR ELEMENTS

Soils	Time in Hours	Ca	Mg	Na	K
Marshall	1	2963	502	34.6	179
	4	2935	503	34.6	182.6
	16	3020	515	41.3	196.6
Wabash	1	2842	75.1	33.5	262
	4	2875	157.5	39.2	291.5
	16	3200	208.3	52.1	321.1
Shelby	1	1470	61.3	45.9	159.7
	4	1514	63.8	48.7	171.2
	16	1535	68.7	53.3	173.2
Putnam	1	2455	39.0	43.1	134.9
	4	2591	45.8	56.1	142.8
	16	2628	55.1	60.3	145.0
Campbell	1	400	29.6	19.6	91.6
	4	406	25.8	20.6	88.0
	16	406	25.8	46.6	105.8
Gerald	1	1970	58.0	50.6	64.9
	4	2053	76.2	53.3	62.5
	16	2053	124.2	56.3	70.8
Winfield	1	371	21.8	21.0	94.3
	4	388	22.9	23.0	103.5
	16	395	31.6	35.5	103.6
Union	1	363	40.3	20.1	103.3
	4	402	44.9	23.1	111.0
	16	440	47.8	26.6	115.7
Lebanon	1	686	85.1	59.9	68.6
	4	709	127.2	61.0	72.1
	16	989	131.7	79.6	76.6
Hanceville	1	487	72.0	20.0	78.4
	4	507	68.0	18.6	78.4
	16	511	81.6	25.6	87.5

NOTE: The values of the major elements are expressed as ppm of the air dried soil.

TABLE 5 -- HYDROCHLORIC ACID EXTRACT OF THE TRACE ELEMENTS

Soils	Time in Hours	Fe	Mn	Cu	Co	Zn
Marshall	1	183.6	55.9	1.97	0.56	8.85
	4	297.0	107.8	2.76	1.08	10.50
	16	784.0	261.5	2.82	----	18.7
Wabash	1	48.3	222	2.60	0.39	5.84
	4	80.0	388.5	2.53	0.57	16.6
	16	134	388.5	2.62	----	12.2
Shelby	1	163.3	73.8	3.93	0.75	6.1
	4	391.1	118	4.07	1.24	4.2
	16	571.5	145.5	3.35	----	21.8
Putnam	1	83.3	112.5	2.51	0.34	11.2
	4	183.3	155.5	4.51	0.48	8.9
	16	574.2	208.5	4.02	0.76	22.1
Campbell	1	83.4	48.7	1.35	0.23	1.8
	4	133.2	55.4	1.37	0.37	1.1
	16	334.5	93.3	1.12	0.67	1.74
Gerald	1	250	73.7	1.87	0.46	1.6
	4	516	183.4	1.81	0.69	2.0
	16	1069	217.7	1.76	----	2.16
Winfield	1	76.6	92.9	1.73	0.46	2.6
	4	130.0	119.6	1.44	0.53	19.2
	16	299	151.3	1.87	----	19.4
Union	1	50	62.3	1.48	0.84	1.4
	4	91.6	95.0	1.68	1.14	0.9
	16	146.5	123.8	1.69	----	18.6
Lebanon	1	90	558	1.86	0.27	1.5
	4	193	628	2.54	0.57	1.5
	16	471	791	1.75	0.70	2.6
Hanceville	1	91.7	89.5	1.06	0.61	1.3
	4	138.5	112	1.69	1.14	2.2
	16	316.5	118.7	1.10	----	1.9

NOTE: The values of the trace elements are expressed as ppm of the air dried soil.

TABLE 6 -- ACETIC ACID EXTRACT OF MAJOR ELEMENTS

Soil	Time in Hours	Ca	Mg	Na	K
Marshall	1	1770	95.6	10.3	55.8
	4	1870	190.5	22.0	129.1
	16	2000	188.7	41.8	207.3
Wabash	1	1928	87.9	29.8	177.0
	4	2036	108.0	33.6	186.2
	16	2148	127.3	41.8	207.3
Shelby	1	970	33.5	42.3	88.7
	4	1336	46.0	41.6	103.5
	16	1336	47.4	41.3	122.4
Putnam	1	1910	29.1	38.1	92.4
	4	2098	45.5	39.5	92.4
	16	2146	47.4	41.3	122.4
Campbell	1	331	3.9	7.8	72.1
	4	352	4.6	13.2	75.5
	16	414	6.8	30.3	79.3
Gerald	1	1595	48.0	41.8	48.6
	4	1678	47.7	44.2	69.9
	16	1769	49.8	69.1	68.5
Winfield	1	316	18.3	27.9	61.2
	4	364	26.0	33.3	71.9
	16	389	25.4	32.5	94.0
Union	1	334	19.7	24.6	66.4
	4	385	37.3	25.0	75.0
	16	398	39.6	31.8	90.8
Lebanon	1	594	32.1	38.6	42.5
	4	598	76.8	38.3	44.1
	16	653	101.6	52.9	48.3
Hanceville	1	440	26.6	10.3	55.8
	4	441	41.4	9.8	56.3
	16	492	52.3	11.6	64.9

NOTE: The values of the major elements are expressed as ppm of air dried soil.

TABLE 7 -- ACETIC ACID EXTRACT OF TRACE ELEMENTS

Soils	Time in Hours	Fe	Mn	Cu	Co	Zn
Marshall	1	1.7	55.0	0.58	0.16	4.6
	4	2.5	69.6	0.76	0.28	5.3
	16	2.35	96.3	0.59	0.55	4.6
Wabash	1	2.6	27.3	0.31	0.15	2.2
	4	3.1	36.0	0.54	0.27	1.4
	16	3.4	54.2	0.91	0.31	9.8
Shelby	1	2.3	13.7	0.61	0.31	1.4
	4	4.5	22.9	0.55	0.35	1.2
	16	6.0	41.7	0.54	0.73	9.5
Putnam	1	2.3	6.7	0.37	0.04	5.2
	4	3.5	13.8	0.48	0.46	4.0
	16	6.0	41.7	0.70	0.11	4.1
Campbell	1	1.1	33.3	0.36	0.12	0.7
	4	2.3	38.7	0.69	0.15	1.2
	16	5.3	50	0.87	0.38	1.6
Gerald	1	2.7	38.3	0.36	0.11	0.8
	4	2.3	72.5	0.43	0.19	0.7
	16	6.8	173.5	0.62	0.49	0.8
Winfield	1	4.7	30.0	0.35	0.14	0.9
	4	5.8	41.7	0.67	0.16	1.3
	16	7.3	56.1	0.80	0.25	1.8
Union	1	4.7	21.3	0.35	0.34	0.5
	4	5.3	27.9	0.39	0.39	0.7
	16	7.4	39.2	1.79	1.41	2.3
Lebanon	1	4.1	99.9	0.44	0.15	0.9
	4	5.1	109.6	0.69	0.20	0.8
	16	7.9	134.0	0.78	0.37	1.1
Hanceville	1	1.7	55.0	0.54	0.49	0.7
	4	3.3	66.7	0.96	0.78	0.8
	16	4.64	106.8	0.93	----	1.3

NOTE: The values of the trace elements are expressed as ppm of the air dried soil.

TABLE 8 -- AMMONIUM ACETATE EXTRACT OF THE MAJOR ELEMENTS

Soil	Time in Hours	Ca	Mg	Na	K
Marshall	1	2690	17.4	27.6	191.0
	4	2700	114.0	28.5	219.0
	16	2763	157.0	53.3	219.0
Wabash	1	2422	54.9	22.6	275.8
	4	2497	67.8	24.5	298.8
	16	2535	151.8	27.5	327.2
Shelby	1	846	35.0	42.6	90.5
	4	1092	40.3	43.9	166.3
	16	1422	39.1	49.6	174.8
Putnam	1	1765	13.2	36.6	90.7
	4	1894	18.2	42.9	115.3
	16	2210	18.5	47.1	122.1
Campbell	1	362	7.3	10.6	81.6
	4	361	11.9	13.5	82.6
	16	367	11.7	24.3	87.9
Gerald	1	1810	4.6	41.7	72.8
	4	1924	5.5	48.2	71.6
	16	1910	73.0	66.6	71.3
Winfield	1	286	7.4	25.5	68.7
	4	333	8.0	31.1	91.2
	16	376	9.5	34.3	90.8
Union	1	299	9.1	20.0	68.9
	4	359	11.9	29.8	91.2
	16	387	11.4	34.6	90.6
Lebanon	1	704	42.1	34.8	75.4
	4	787	66.8	35.8	76.9
	16	972	110.7	39.1	77.4
Hanceville	1	460	9.8	13.1	76.6
	4	491	11.0	15.2	79.4
	16	488	82.6	29.1	77.6

NOTE: The values of the major elements are expressed as ppm of air dried soil.

TABLE 9 -- AMMONIUM ACETATE EXTRACT OF THE TRACE ELEMENTS

Soils	Time in Hours	Fe	Mn	Cu	Co	Zn
Marshall	1	0.50	46.3	0.73	0.04	2.9
	4	0.8	45.8	0.62	0.07	3.3
	16	1.34	54.2	0.62	0.07	11.4
Wabash	1	1.37	15.4	0.49	0.03	0.7
	4	1.58	21.2	0.61	0.06	1.5
	16	2.29	24.3	0.38	0.05	0.9
Shelby	1	1.2	23.3	0.42	0.05	0.7
	4	1.1	24.2	0.34	0.06	0.9
	16	2.0	62.1	0.36	0.05	7.7
Putnam	1	1.43	16.8	0.36	0.01	0.6
	4	1.5	24.2	0.65	0.01	1.6
	16	2.1	70.4	1.01	----	11.2
Campbell	1	0.6	29.2	0.75	0.05	0.7
	4	0.6	30.0	0.50	0.08	0.7
	16	0.8	31.0	0.69	0.8	9.9
Gerald	1	0.6	14.6	0.31	0.01	0.3
	4	0.8	16.4	0.55	0.01	----
	16	1.06	25.6	0.57	0.02	10.4
Winfield	1	4.2	42.5	0.29	0.06	0.6
	4	4.4	44.6	0.63	0.05	0.9
	16	4.6	85.4	0.50	0.04	0.8
Union	1	2.2	32.1	0.50	0.16	0.5
	4	2.6	31.7	1.42	0.25	0.8
	16	4.2	58.7	0.30	0.11	9.3
Lebanon	1	1.67	90.7	0.39	0.06	0.4
	4	2.0	89.9	0.22	0.07	0.2
	16	3.4	99.1	0.55	0.08	9.1
Hanceville	1	0.5	58.8	0.55	0.01	0.5
	4	0.7	60.5	0.12	0.23	0.8
	16	1.7	64.5	0.60	0.19	9.4

NOTE: The values of the trace elements are expressed as ppm of the air dried soil.

TABLE 10 -- SODIUM CHLORIDE EXTRACT OF THE TRACE ELEMENTS

Soils	Time in Hours	Cu	Co	Zn
Marshall	1	0.34	0.02	0.5
	4	0.41	----	0.4
	16	0.39	0.13	1.1
Wabash	1	0.39	0.01	0.3
	4	0.26	0.01	0.3
	16	0.79	0.02	0.6
Shelby	1	0.56	0.02	1.0
	4	0.31	0.01	0.3
	16	0.85	0.04	0.5
Putnam	1	0.38	----	0.7
	4	0.33	0.01	0.8
	16	0.71	0.01	0.3
Campbell	1	0.60	0.1	0.4
	4	0.45	0.02	0.4
	16	0.42	0.02	0.5
Gerald	1	0.37	----	0.2
	4	0.68	0.01	0.2
	16	1.02	0.01	0.4
Winfield	1	0.46	0.03	0.2
	4	0.31	0.01	0.3
	16	0.47	0.02	0.6
Union	1	0.51	0.05	0.3
	4	0.48	0.04	0.4
	16	0.78	0.05	0.5
Lebanon	1	0.58	0.06	0.3
	4	0.42	0.03	0.03
	16	0.77	0.04	1.1
Hanceville	1	0.51	0.06	0.2
	4	0.39	0.06	0.2
	16	0.31	0.08	0.5

NOTE: The values of the trace elements are expressed as ppm of the air dried soil.

DISCUSSION

Soils included in this study were of a wide variety of types and their monetary value as agricultural land ranged from very high to very low. In Table 11 the soils are arranged in the order of their relative economic value. This value was determined as part of a survey made by Miller and Krusekopf (13) immediately prior to the depression of 1929. Also included in the table is the parent material from which each soil was formed.

The range of values for the various total determinations are indicative of the parent materials from which the soils were formed. The data reported here compare well with the analyses of similar soil types (12) except for the value given for potassium by Miller and Krusekopf which is almost twice as great as that found here. No explanation can be offered for this

TABLE 11 -- SOILS STUDIED, ARRANGED ACCORDING TO DECREASING MONETARY VALUE

Series Name	Parent Material
Marshall Silt Loam	Loess
Wabash Clay Loam	Alluvial (N. Missouri)
Shelby Clay Loam	Kansan Glacial Till
Putnam Silt Loam	Loess over Glacial Till
Campbell Sandy Loam	Old Alluvial (S. E. Missouri)
Gerald Silt Loam	Shale
Winfield Clay Loam	Loess
Union Silt Loam	Jefferson City Dolomite Limestone
Lebanon Silt Loam	Gasconade & Roubidoux Limestone
Hanceville Sandy Loam	Lamotte Sandstone

discrepancy. The totals for the trace elements agree well for copper and cobalt given by Johnson (8), within the relatively large error of the semi-quantitative spectrographic analyses reported by him. Values reported by Johnson for a Marshall silt loam are 20 ppm. copper and 8.7 ppm. cobalt; the quantitative determinations reported here give 19.4 ppm. copper and 5.9 ppm. cobalt.

In Tables 2 and 3 the percentages of each of the total elements are tabulated, with the soils arranged according to decreasing value. It is apparent that the total values for the major elements fall into the same relative groupings and that the values for the trace elements copper, iron, and zinc show a similar trend.

Results of the extraction experiments were of considerably more interest. The amounts of the major elements extracted either remained constant or increased with time as was anticipated. Again, with the soils arranged according to decreasing monetary value as shown (Tables 4, 6, and 8), it is found that the values for the major elements extracted fall into the same relative economic groups. This provides some additional verification of the usefulness of extraction analyses. The amounts of iron, manganese, and cobalt extracted usually increased with time but the amounts of copper and zinc often showed no increase with time (Tables 5, 7, 9, and 10).

The copper content of the hydrochloric acid extracts shows fair correlation with economic value. The hot water extractable boron shows good correlation with economic value. The other extracted trace elements show no such correlation.

Table 12 tabulates the biologically available copper for six of the soil types studied, as determined by Johnson (8), using the *aspergillus niger* assay method, together with the values determined here with the various extractants and time periods used. It is seen that none of the extracting solutions used gives very good correlation with the biologically available copper; however, there is fair correlation between the hydrochloric acid extracted copper and the biologically available copper. This comparison is not fully justifiable because, unfortunately, the soils compared from Johnson's work are different samples and the fields from which they were taken

TABLE 12 -- BIOLOGICALLY AVAILABLE COPPER AND EXTRACTED COPPER (ppm.)

Soils	Biologically Available	Extracted Available			
		HCl	HAc	NH ₄ Ac	NaCl
Marshall	1.3	1.9	0.6	0.7	0.3
		2.7	0.8	0.6	0.4
		2.8	0.6	0.6	0.4
Wabash	1.3	2.6	0.3	0.5	0.4
		2.5	0.5	0.6	0.3
		2.6	0.9	0.4	0.8
Shelby	1.6	3.9	0.6	0.4	0.6
		4.1	0.5	0.3	0.3
		3.3	0.5	0.4	0.8
Putnam	1.0	2.5	0.4	0.4	0.4
		4.5	0.5	0.6	0.3
		4.0	0.7	1.0	0.7
Union	0.8	1.5	0.4	0.5	0.5
		1.7	0.4	1.4	0.5
		1.7	1.8	0.3	0.8
Lebanon	0.5	1.9	0.4	0.4	0.6
		2.5	0.7	0.2	0.4
		1.7	0.8	0.5	0.8

may have been treated differently. It is felt, however, that due to the excellent agreement between the two sets of total analyses of the soils, it is worth while comparing the results of the two widely differing techniques for measuring the available copper.

As borne out in the introduction, it is not the purpose of this study to make any theoretical consideration of the accumulated data. However, it is interesting to speculate about the meaning of the trends shown in the data. The constancy or the increase with time of the major elements in the extracts may be explained according to the older ideas of base exchange measurements of soils. Base exchange is considered to be a rapid process and perhaps the value for the four-hour extraction may be considered as the amount of replaceable cation in the soil. The increase in the value with time is then interpreted as due to the solubility of the various mineral compounds. The considerable fluctuation in the amounts of the extracted trace elements with time is more difficult to explain. It has been suggested that the fluctuations are caused by heterogeneity in the samples and that the fluctuations are more evident in the case of the trace elements. This is because of the statistically poorer chance of obtaining a sub-sample which is representative of the trace element content of the large sample. Should this be the case, then more uniformity in the results for zinc and less for cobalt would be expected because there is more zinc extracted than cobalt. However, on the contrary, better uniformity appears in the trend with time of extraction for cobalt than for zinc.

An alternative explanation is that there are several different reactions taking place at different rates and competing for the same elements. As the time varies, different reactions predominate and govern the concentration of the trace elements.

Nevertheless, in most cases, the amount of trace element extracted increases fairly regularly with time. The occasional departures from this trend can also be explained, in part, by assuming in those cases that most of the available trace element is extracted in the one-hour period and that the fluctuations thereafter are merely caused by the errors in the rather inexact analytical methods. Highly accurate data on trace elements require averaging results of many runs on a sample, using the greatest care and the best methods available. Such accuracy is seldom desired or obtained in trace element work.

In comparing with each other the fractions of the total element content of the soils which were extractable in four hours time, the hydrochloric acid extractant gave a very wide range for calcium, from 10 percent to 69 percent. Magnesium showed an average of 2 percent with an upper extreme of 12 percent. Copper and zinc averaged 10 percent, with little deviation. Cobalt averaged about 14 percent extracted. The acetic acid extracted somewhat smaller percentages of major elements, but the percentages varied considerably from one sample to another, while copper, zinc, and cobalt dropped to about 4 percent with little deviation. The ammonium acetate gave results which were quite similar to those found with acetic acid.

Concerning the relative efficiencies of the different extractants for calcium and magnesium, hydrochloric and acetic acids and ammonium acetate give generally similar results with the hydrochloric acid results being somewhat higher in every case. For extraction of potassium, the acids give very similar results, ammonium acetate gives somewhat lower but parallel values. For extraction of sodium, all three give roughly similar results. For extraction of iron, the hydrochloric acid naturally gives much higher results than the others, with one exception, but no other correlations are evident among them. For extraction of manganese, hydrochloric acid gives much higher values; the other extractants show no similarities. For extraction of copper, the hydrochloric acid gives higher values than the other two, and they give results which are similar. The same is approximately true for cobalt and zinc.

In general, 2.5 percent acetic acid probably is to be preferred for extraction of calcium, magnesium, sodium, potassium, iron, and manganese, and 0.1 N hydrochloric acid is to be preferred for extraction of copper, cobalt, and zinc. These conclusions follow from the relative ease of analytical manipulation of the extracts and also from the more significant correlations which the results afford. The single most useful extractant is probably 0.1 N hydrochloric acid, although it gives useless results for iron. The 2.5 percent acetic acid is almost as useful; the smaller amounts of trace elements

obtained with it make their determination somewhat more difficult. Sodium chloride solution gives extracts which are more difficult to handle and the results obtained with it show little significance.

The data presented here represent the ranges of mineral element content, total and extractable, which one may expect to encounter in examining Missouri soils. Of the elements included in this study, the major element contents, the amounts of calcium, magnesium, and potassium, total or extractable, seem to reflect the economic value of Missouri soils more reliably than the trace elements.

BIBLIOGRAPHY

1. Bear, F. E., and H. B. Kitchen, *Diagnostic Techniques for Soils and Crops*, Amer. Potash Inst., 1948.
2. Berger, K. C., and E. Truog, "Boron Tests and Determinations for Soils and Plants," *Soil Sci.*, 57:1, 1944.
3. Burd, J. S., "Water Extractions of Soils as Criteria of Their Crop Producing Power," *Calif. Agr. Expt. Sta. and Agr. Res.*, 12:297-305, 1918.
4. Chapman, H. D., and W. P. Kelley, "The Determination of Replaceable Base and the Base Exchange Capacity of Soils," *Soil Sci.*, 59:391-406, 1930.
5. Davis, L. E., "Theories of Base Exchange Equilibriums," *Soil Sci.*, 59:379-395, 1945.
6. Gedroiz, "Contribution to the Method of Determining Zeolite Bases in the Soil," *Zhur. Opyth. Agron.*, 19:224-226.
7. Hankins, B., "Determination of Copper, Cobalt, and Zinc by the Graphite Spark," Master's Thesis, University of Missouri, 1950.
8. Johnson, "Trace Elements of Missouri Soils," Master's Thesis, University of Missouri, 1950.
9. Kyas, O., "Comparison of Neubauer Method with the Results of Growing Tests Carried Out in Moravia in 1926-1931," *Chimie und Industrie*, Special No. 1217-41, 5, 1931.
10. Marshall, C. E., "Cationic Activity, Exchangeable Bases, and Root Uptake by Plants," *Soil Sci. Society Am. Proc.*, 8:175-8, 1943.
11. Piper, C. S., *Soil and Plant Analysis*, Interscience, New York, 1944, p. 323.
12. Mathews, *Chemical Studies of Soil Formation in the Grundy Silt Loam*. Master's Thesis, University of Missouri, 1948.
13. Miller, M. F., and H. H. Krusekopf, "Soils of Missouri," Univ. of Mo. Agr. Expt. Sta. Bul., 264, 1929.
14. Overstreet, R., "Ionic Reactions in Soils and Clay Suspensions," *Soil Sci.*, 59:265-70, 1945.
15. Peech, M., "Determination of Exchangeable Magnesium in Soils by Titan Yellow with Reference to Magnesium Deficiencies in Citrus," *Soil Sci. Soc. Am. Proc.*, 4:189-195, 1939.
16. Peech, M., "Determination of Exchange Cations and Exchange Capacity of Soils," *Soil Sci.*, 59:25-38, 1945.
17. Puri, A. N., and M. L. Uppal, "Base Exchange in Soils," *Soil Sci.*, 47: 245-53, 1939.
18. Shapiro, L., and W. W. Brannock, "Rapid Analysis of Silicate Rocks," U. S. Geol. Survey Circ. 165, 1952.

19. Terlikowski, F., S. Sozauki, and M. Kwinichidze, "The Assimilation of Calcium, Magnesium, Sodium, and Potassium by Plants from the Sorption Complex of Soils," *Polish Agron. Forest Ann.*, 37:31-34.
20. Tjurins, I. W., "Method of Determination of Exchangeable Calcium and Magnesium in Soils Containing Alkaline Earth Carbonates," *La Pedologic*, 22:5-24.
21. Willson, A. E., *Analytical Chemistry*, 23:754-7, 1951.
22. Wohlhier and Schulze, "Laboratory Methods of Soil Investigation Compared with Field Experiments," *Z. Pflanzener. Dung. Bodenk.*, 12B: 460-8, 1933.
23. *Official Methods of Analysis*, Assoc. Off. Agr. Chem., 7th ed. 1950.