Reprinted from the *Soil Science Society of America Journal*
Volume 47, no. 3, May–June 1983
677 South Segoe Rd., Madison, WI 53711 USA

The DTPA-Extractable Iron, Manganese, Copper, and Zinc from Neutral and Calcareous Soils Dried Under Different Conditions

G. E. LEGGETT AND D. P. ARGYLE

The DTPA-Extractable Iron, Manganese, Copper, and Zinc from Neutral and Calcareous Soils Dried Under Different Conditions[1]

G. E. LEGGETT AND D. P. ARGYLE[2]

ABSTRACT

DTPA (diethylenetriaminepentaacetic acid)-extractable Fe, Mn, Cu, and Zn were determined on several neutral and calcareous soils dried at various temperatures. Extractable Fe increased linearly over the drying temperature range 22 to 100°C, whereas Mn increased in an irregular manner. Values for Cu and Zn changed only slightly over this temperature range. Extractability of all four elements increased when field-moist samples were air dried; Fe by a factor of 2 to 3, and Mn, Cu, and Zn by a factor of about 1.3 to 1.5. The increases in extractable Fe and Mn appear to result from separate temperature and dehydration effects and are only partially reversible with rehydration and moist incubation. The results of this study indicate that sample handling be standardized for calibration and routine tests before DTPA-extractable Fe and Mn can be used as reliable diagnostic tests for these elements. Close control of drying conditions for Zn and Cu analysis may be desirable but is not as critical as for Fe and Mn.

Additional Index Words: **NH_4HCO_3-DTPA soil test, AB-DTPA soil test.**

Leggett, G. E., and D. P. Argyle. 1983. The DTPA-extractable iron, manganese, copper, and zinc from neutral and calcareous soils dried under different conditions. Soil Sci. Soc. Am. J. 47:518–522.

PRECISE AND ACCURATE soil test values have been the objective of much research. Chemical procedures are continually being developed, improved, and adapted to new and sophisticated laboratory instruments and techniques in order to ensure rapid, reliable results. Some emphasis has been placed on sampling techniques for coping with soil variability and methods for taking soil samples (Peterson and Calvin, 1965) representative of all or parts of fields.

Relatively little emphasis has been placed on sample handling and drying conditions after the samples are taken from the field. Standard works (Black, 1965; Walsh and Beaton, 1973) devote scarcely any space to preparing samples for analysis.

Eik et al. (1975) point out some of the problems associated with sample handling and preparation for analysis. They indicate the use of heat under some conditions of drying for routine samples. Sampling, sample preparation, and analysis are all important factors in any soil testing program.

Bremner (1965) has indicated some of the problems of sample handling and preparation when measuring soil N constituents that may change under different environmental conditions. Special properties of some soils that change soil tests on drying, e.g., release of non-exchangeable K, have also been investigated (Rich, 1968). Laboratory results have shown the effects of soil grinding, suspension shaking and filtering, soil-to-solution ratio (Soltanpour et al., 1976) and air- and oven-drying of samples (Khan and Soltanpour, 1978) on the DTPA-extractable Fe, Mn, Cu, and Zn from Colorado soils. Shuman (1980) has given a thorough review of changes in soil test values for micronutrients as a result of soil drying, and presented data for changes in extractable values brought on by moisture content and drying temperature.

Sample handling and storage are more important aspects of soil analysis than generally recognized. Bartlett and James (1980) present data indicating problems assoicated with drying and storing soil samples and changes that occur under various sample and storage conditions. The objective of this work was to determine the effects of temperature and drying on DTPA-extractable Fe, Mn, Cu, and Zn from neutral and calcareous soils.

METHODS AND MATERIALS

Soils

Samples of several soils from southern Idaho and one from central Washington were obtained for the study. They were selected mainly for convenience and their agricultural importance rather than because of special properties. Some samples had been air-dried initially; others were maintained in their field-moist condition. Water was added to the dried samples to bring them to mid-range field moisture levels, and they were allowed to equilibrate for at least 48 h before use. The undried samples and those rewetted were stored in closed polyethylene bags in a dark chamber controlled at 22°C.

Chemical properties of Sonsen (Xerollic Calciothids), Shano (Xerollic Camborthids), and Portneuf (Durixerollic Calciothids) soils used extensively in the study are given in Table 1. Nine other soils not used in all aspects of the study have properties similar to those given in Table 1.

Table 1—Some chemical properties of some soils used in extraction studies.

Soil	pH	$CaCO_3$ Equiv.	Organic matter
		%	
Shano silt loam			
0–30 cm	7.6	0.4	1.25
Sonsen sandy loam			
0–30 cm	7.8	3.7	1.64
Portneuf silt loam			
0–30 cm	7.7	2.7	1.85
Portneuf silt loam			
38–68 cm	7.6	9.5	--

---

[1] Contribution from the Snake River Conservation Research Center, Agricultural Research Service, USDA, Kimberly, Idaho, and Agricultural Testing and Consultants, Inc., Twin Falls, Idaho. Received 18 May 1982. Approved 11 Jan. 1983.

[2] Soil Scientist, Snake River Conservation Research Center, Kimberly, ID 83341, and Manager, Agricultural Testing and Consultants, Inc., Twin Falls, ID 83301, respectively.

Drying Treatments

Samples were dried on polyethylene sheets or pyrex dishes at specific temperatures in forced-draft ovens or drying chambers. Some samples were freeze-dried at −45°C.

DTPA Extraction

Extractions were carried out according to the procedure of Lindsay and Norvell (1978) at 23 +2°C. All values presented are averages of duplicate determinations, which rarely differed by > 0.1 mg kg^{-1}.

The Fe, Mn, Cu, and Zn concentrations in the filtrate were determined by atomic absorption spectrophotometry using standards made up in the DTPA solution.

For convenience, details of the drying procedures used in each of the various experiments are given along with the results obtained.

RESULTS

The precision of measurement was determined on three field-moist soil samples stored in closed polyethylene bags at 22°C. They were analyzed for DTPA-extractable Fe, Mn, Cu, and Zn seven times over an 8-week period.

The results (Table 2) of these analyses indicate low standard deviations for Fe, Cu, and Zn. The values for Mn, however, fluctuated more than for the other elements, but this was mainly due to high values obtained in the fourth and fifth samplings. The reason for these high values is not known. The same kind of study was not made on dry samples because the dried samples were not stored under controlled conditions and as will be shown later the Fe and Mn values changed with time when dried samples were stored in the laboratory.

Effect of Drying Temperature

The DTPA-extractable Fe, Mn, Cu, and Zn for three contrasting soils dried at various temperatures are shown in Fig. 1. A consistently linear Fe concentration increase with drying over the temperature range 22 to 100°C is evident for all soils tested. The slopes of the lines differ for different soils, e.g., 0.055, 0.113, and 0.170 mg $kg^{-1}deg^{-1}$ for the Sonsen, Shano, and Portneuf (0–30 cm) soils, respectively. Generally, the increase in extractable Fe with increasing drying temperature was greater for soils with higher initial extractable-Fe levels. Similar increases were reported by Khan and Soltanpour (1978) between air- and oven-dried soils.

The Mn values shown in Fig. 1 indicate marked contrasts among the three soils. Values for the Shano soil

Table 2—The ranges, means, and standard deviations for the DTPA-extractable Fe, Mn, Cu, and Zn measured seven times over an 8-week period in moist soils stored at 22°C.

Soil		DTPA-extractable Fe	Mn	Zn	Cu
		mg kg⁻¹			
Shano, 0–30 cm	Range	2.00–2.40	1.40–1.90	0.60–0.70	0.60–0.70
	Mean	2.25	1.59	0.64	0.67
	SD	0.12	0.17	0.05	0.05
Sonsen, 0–30 cm	Range	0.85–1.30	1.75–2.75	0.60–0.70	0.20–0.30
	Mean	1.03	2.00	0.63	0.27
	SD	0.13	0.35	0.05	0.05
Portneuf, 0–30 cm	Range	1.80–2.00	2.85–4.50	0.50–0.60	0.60–0.80
	Mean	1.88	3.36	0.52	0.75
	SD	0.09	0.60	0.04	0.08

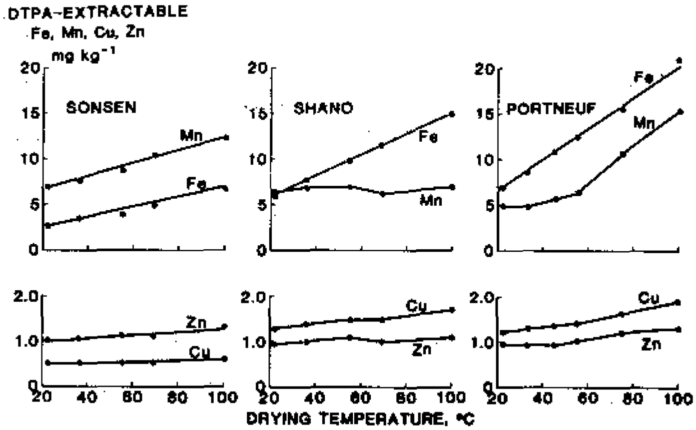

Fig. 1—The effect of drying temperature on the DTPA-extractable Fe, Mn, Cu, and Zn from Sonsen, Shano, and Portneuf (0–30 cm) soils.

were unusual in that they did not change appreciably over the drying range 22 to 100°C. Extractable-Mn values for the Sonsen soil were unusual in that they were larger than their Fe counterparts and that the temperature response was linear over the range studied. The values shown for the Portneuf (0–30 cm) soil, however, indicate the usual temperature response pattern for many calcareous soils of the area, i.e., small increases with increasing drying temperature up to about 55°C, followed by an abrupt increase which is often linear between 55 and 100°C.

The Zn and Cu values presented show only small increases with increasing drying temperature. Over the temperature range 22 to 55°C the Cu increase ranged from 0 to 0.2 mg kg^{-1} and the Zn increase ranged from < 0.1 to 0.15 mg kg^{-1}. These small increases are in contrast to the much larger increases noted for Fe and Mn. Even for a soil fertilized with Zn and Cu (see Portneuf, 36–68 cm, Table 3) the extractable-Zn values increased only from 3.6 to 5.2 mg kg^{-1} and the Cu values from 4.8 to 5.1 mg kg^{-1} over the 22 to 100°C temperature range.

Dehydration and Temperature Effects

Both dehydration and temperature affect the DTPA-extractable Fe, Mn, Cu, and Zn levels of soils used in this study. To separate these effects, wet samples of screened soils were spread in thin layers on large polyethylene-covered trays and dried under forced draft at 22°C until an approximate predetermined weight was reached, thus giving soils with a wide range of water contents without applying heat. Other samples were freeze-dried (−45°C) or oven-dried with heat. The partially dried soil samples were stored for 48 h in closed polyethylene bags at 22°C until analyzed using the conventional DTPA-extraction procedure. The extractable Fe for the partially dried samples (Fig. 2) increased markedly as the soils approached the air-dry state. Values for the Portneuf, 0–30 cm soil increased 260% as the water content decreased from field-moist to air-dry. This increase was greater than for the Sonsen (80%) or Shano (100%) soils. Manganese, Cu, and Zn increased less with air-drying than did Fe (data not given) but the increases were relatively small and ranged from 20 to 60% for the three soils.

Air-dried samples containing very low water content

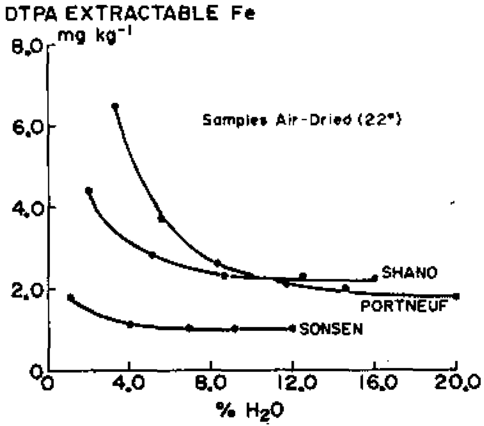

Fig. 2—The DTPA-extractable Fe from Sonsen, Shano, and Portneuf (0–30 cm) soils as influenced by water content.

obtained through prolonged air-drying at 22°C were not prepared in this study. Freeze-drying (−45°C) to remove virtually all water, however, gave larger values for Fe than did air-drying on all four soils and for Mn on three of the soils, but did not affect the Cu and Zn values (Table 3). These data also indicate that all four soils show large increases in Fe and Mn and smaller but constant increases for Cu and Zn, when the soils were oven-dried (100°C) compared to when they were freeze-dried (−45°C).

Additional data for the dehydration effect are given in Table 4. These samples represent different field samples than those used elsewhere in the study and thus, the DTPA-extractable Fe, Mn, Cu, and Zn are different. The results indicate the same trends as shown before with the oven-dried values being larger than their freeze-dried counterparts. The data also show that heating freeze-dried samples, containing 0% water, at 100°C for 6 h increased the DTPA-extractable values to near those obtained from oven-dried moist samples. The differences in values obtained between freeze-dried and oven-dried samples is attributed to temperature, whereas the differences obtained between field-moist and freeze-dried samples is attributed to dehydration.

Table 3—The DTPA-extractable Fe, Mn, Cu, and Zn from soils as affected by drying conditions and water content.

Soil	Moisture cond.		DTPA-extractable Fe	Mn	Cu	Zn
		%	mg kg⁻¹			
Sonsen, 0–30 cm	FM†	12.0	1.0	2.3	0.3	0.6
	AD	1.1	1.8	3.4	0.4	0.8
	OD	0	6.7	12.2	0.6	1.3
	FD	0	2.4	4.7	0.4	1.0
Shano, 0–30 cm	FM	16.0	2.2	1.6	0.7	0.6
	AD	1.9	4.4	1.9	1.0	0.8
	OD	0	14.9	7.0	1.7	1.1
	FD	0	5.8	2.3	1.0	1.0
Portneuf, 0–30 cm	FM	20.0	1.8	2.9	0.8	0.5
	AD	3.3	6.5	4.2	1.2	0.8
	OD	0	20.9	15.2	1.9	1.3
	FD	0	7.8	5.8	1.2	0.9
Portneuf, 38–68 cm	FM	20.0	1.4	4.7	3.9	2.8
	AD	1.4	2.5	6.1	4.8	3.6
	OD	0	5.7	6.5	5.1	5.2
	FD	0	2.8	5.9	4.8	3.8

† FM = Field moist. AD = air-dried (22°C). FD = freeze dried (−45°C). OD = oven dried (100°C).

Wet Incubation of Previously Dried Samples

To determine if the increases noted on drying were reversible, samples of Shano and Sonsen soils that had been previously dried at various temperatures were weighed (12.5 g) into extraction bottles. Water (22.5 mL) was added at selected times so that samples had been wet 0, 2, and 24 h before adding 2.5 mL of DTPA solution that was 10 times the normal extraction concentration. The results for Fe extraction on Shano and Sonsen soils (Fig. 3) indicate that the enhanced values brought on by drying were only partially overcome by wet incubation of the samples before analysis. Even adding the water 24 h before the DTPA does not return the extraction values to the low values shown for the continuously moist samples. It is striking that the values for the 2- and 24-h series decrease proportionately and that linear relationships are maintained.

The Mn extracted from both soils (data not given) after being wet for 2 h decreased slightly from that extracted from the dry samples; values for the Shano samples wet 24 h changed very little from those wet 2 h. For the Sonsen soil, however, being wet for 24 h increased DTPA-extractable Mn markedly. The increases were erratic but generally were 2 to 3 times greater than values for their dry counterparts.

The values for Cu and Zn (data not given) tended to decrease as a result of wetting before adding DTPA. The differences, however, were small in comparison to those encountered for Fe and Mn.

Effect of Dry Storage

A serious problem encountered with the DTPA extraction method is that Fe and Mn change with time after the soil is dried. Samples were dried at various temperatures, ground, and stored in closed plastic bags in the laboratory. They were extracted with DTPA soon after drying and again approximately 3 and 8 months later. The 22°C-dried samples contained < 2.0% water after drying; those dried with heat contained < 1.0%. After 8 months the water contents of all samples ranged between 1.0 and 2.0%

The DTPA-extractable Fe and Mn for the Portneuf, 0–30 cm, after 0 and 8 months are shown in Fig. 4. The Zn and Cu values did not change measurably and thus are not shown. After 8 months' storage the Fe values increased for the 22-, 33-, and 45°C-dried samples but those for the 100°C-dried samples decreased. These

Table 4—The DTPA-extractable Fe, Mn, Cu, and Zn from soils as influenced by temperature.

Soil†	Drying conditions	DTPA-extractable Fe	Mn	Cu	Zn
		mg kg⁻¹			
Sonsen, 0–30 cm	FM‡	2.4	1.4	0.2	0.5
	FM-FD	5.5	3.0	0.4	0.8
	FM-OD	10.3	9.7	0.5	1.1
	FM-FD-OD	10.3	9.7	0.5	1.1
Portneuf, 0–30 cm	FM	2.2	2.6	0.7	0.3
	FM-FD	9.2	4.4	1.1	0.5
	FM-OD	22.3	14.3	1.7	0.9
	FM-FD-OD	18.2	12.2	1.5	0.8

† These samples of Sonsen and Portneuf soils are different field samples than those reported elsewhere in this paper.
‡ FM = Field moist. FD = freeze dried. OD = oven dried.

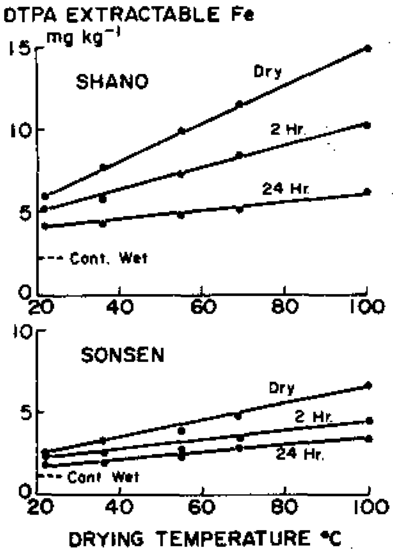

Fig. 3—The DTPA-extractable Fe from two soils as influenced by drying temperature and time of wet incubation before extraction.

changes resulted in a new linear relationship being formed having a different slope than that of the original analysis.

The Mn values increased to a greater extend than did Fe, in all samples except one after 8 months' dry storage.

The reasons for these changes in dried soil samples are not known and indeed are unusual. Over the 8-month storage the Fe values for the 22°C-dried soil increased from 6.8 to 10.5 mg kg^{-1} (54%) whereas the Mn values increased from 4.7 to 13.1 mg kg^{-1} (178%) for the Portneuf (0–30 cm) soil. At least part of the increases may have resulted from laboratory temperatures during the storage that were as high as 29°C for at least parts of some days.

The results for Portneuf (0–30 cm) soil are not unique with respect to change of DTPA-extractable Fe and Mn. Nine other soils stored dry under the same laboratory conditions for 3 months showed similar changes. Also, as with the Portneuf soil, the Zn and Cu values were not measurably changed as a result of dry storage. All of these air-dried soils contained < 2.5% water during the storage period.

Comparison of Standard Test with AB-DTPA Test

Because of the large drying temperature effects observed with the standard DTPA soil test, variously dried Shano and Sonsen soils were also extracted using the modified ammonium bicarbonate DTPA test (Soltanpour and Workman, 1979). The two tests give similar results; Fe increased linearly with drying temperature although at a slightly different slope for the Shano soil. Manganese values were essentially parallel for the two tests on both soils, and showed little change with temperature on the Shano soil, and Cu and Zn changed little over the range of drying. The modified method gave higher values for Fe, Cu, and Zn, but lower values for Mn than did the standard DTPA test. Soltanpour and Workman (1979) reported similar results on soils from Colorado.

DISCUSSION

Drying moist soils by any means used in this study increased the DTPA–extractable Fe, Mn, Cu, and Zn.

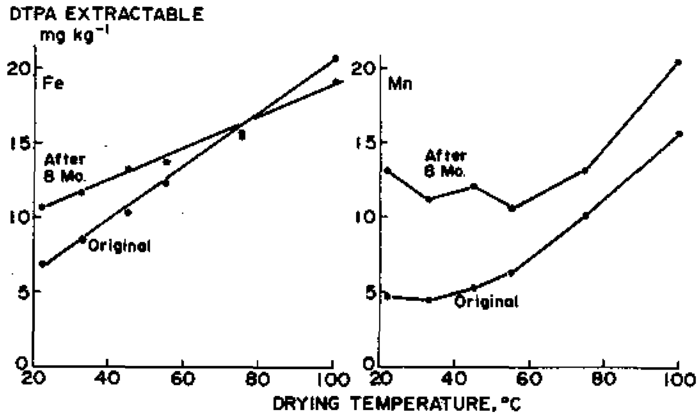

Fig. 4—The DTPA-extractable Fe and Mn from Portneuf (0–30 cm) soil as affected by drying temperature and time of storage in the laboratory.

Iron and Mn also increased markedly with increasing drying temperature, whereas Cu and Zn increased only slightly under the same conditions. Attempts were made to find a common factor among soils to correct for differences of values resulting from different drying temperatures. For example, a factor to correct values obtained from 55°C-dried soil to 22°C would be extremely useful because many soil testing laboratories dry soil samples near 55°C. Moreover, the soil samples used in calibrating the tests were air-dried (Lindsay and Norvell, 1978; de Boer and Reisenauer, 1973). The results for 12 soils used in this study indicate that obtaining a usable factor is not likely. The ratios of values from 55°C-dried samples to 22°C-dried samples ranged from 1.1 to 1.9 for Fe, 1.0 to 1.6 for Mn, and 1.0 to 1.4 for Cu and Zn. These ranges are too wide to be useful on different soils and quite likely the ranges would become greater for additional soils. Also, different factors would be required for different elements on the same soil.

A more simple approach to the problem is that the correlation samples be analyzed after drying at different temperatures. Then routine samples dried at a selected temperature could be analyzed and the results applied to the proper calibrations. Of course, this scheme would work only if the calibrations for all of the drying temperatures were good indicators of nutrient availability. It would not apply to samples obtained and dried years ago and stored under usual conditions, because the extractable values for Fe and Mn likely would have changed since drying. The fact that DTPA-extractable Fe and Mn change drastically after drying is a serious shortcoming of the method. The effect is not unique to this method, however, since Fujimoto and Sherman (1945) and Bartlett and James (1980) showed similar effects on Mn using NH_4OAc extracting solutions.

REFERENCES

1. Bartlett, Richmond, and Bruce James. 1980. Studying dried, stored soil samples—some pitfalls. Soil Sci. Soc. Am. J. 44:721–724.
2. Black, et al. C.A. 1965. Methods of soil analysis, parts 1 and 2. Agronomy 9:1–1572. Am. Soc. of Agron., Madison, Wis.
3. Bremner, J.M. 1965. Inorganic forms of nitrogen. *In* C.A. Black et al. (ed.) Soil analysis, part 2. Agronomy 9:1179–1237. Am. Soc. of Agron., Madison, Wis.
4. de Boer, G.J., and H.M. Reisenauer. 1973. DTPA as an extractant of available soil iron. Commun. Soil Sci. Plan Anal. 4:121–128.
5. Eik, K., E.L. Hood, and J.J. Hanway. 1975. Soil sample prepa-

ration p. 2–3. *In* N.C. Regional Publ no. 221. North Dakota Agric. Exp. Station Bull. no. 499, Fargo.
6. Fujimoto, C.K., and G.D. Sherman. 1945. The effect of drying, heating, and wetting on the level of exchangeable manganese in Hawaiian soils. Soil Sci. Soc. Am. Proc. 10:107–112.
7. Khan, A., and P.N. Soltanpour. 1978. Effect of wetting and drying on DTPA-extractable Fe, Zn, Mn and Cu in soils. Commun. Soil Sci. Plant Anal. 9:193–202.
8. Lindsay, W.L., and W.A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42:421–428.
9. Petersen, R.G., and L.D. Calvin. 1965. Sampling. *In* C.A. Black et al. (ed.). Soil analysis, part 1. Agronomy 9:54–72. Am. Soc. of Agron., Madison, Wis.
10. Rich, C.I. 1968. Mineralogy of soil potassium. p. 79–108. *In* V.J. Kilmer et al. (ed.) The role of potassium in agriculture. American Society of Agronomy, Madison, Wis.
11. Soltanpour, P.N., A. Khan, and W.L. Lindsay. 1976. Factors affecting DTPA-extractable Zn, Fe, Mn, and Cu from soils. Commun. Soil Sci. Plant Anal. 7:797–821.
12. Soltanpour, P.N., and S. Workman. 1979. Modification of the NH_4HCO_3-DTPA soil test to omit carbon black. Commun. Soil Sci. Plant Anal. 10:1411–1420.
13. Shuman, L.M. 1980. Effects of soil temperature, moisture and air-drying on extractable manganese, iron, copper, and zinc. Soil Sci. 130:336–343.
14. Walsh, Leo M., and James D. Beaton (ed.) 1973. Soil testing and plant analysis. Soil Sci. Soc. Am., Madison, Wis.