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COPPER AND ZINC LEVELS AT A MIDDLE TENNESSEE STATE UNIVERSITY VINEYARD SITE

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ABSTRACT—A proposed vineyard and educational field plot was established at Middle Tennessee State University. The vineyard plot contains the Cumberland and Lomond soil series and will be used to test grape varieties and monitor zinc (Zn) and copper (Cu) mobility. Environmentally available soil Zn and Cu levels, cation exchange capacities, and organic matter percentages were measured. Vineyard Zn levels were substantially more variable (0.9–71.4 mg/kg soil) than Cu levels (6.4–51.1 mg/kg soil), with relative standard deviations for Zn up to six times greater than for Cu (*F*-test). Soil Cu levels did not differ between the two soil series, and were consistent throughout the vineyard (mean = 9.2 mg/kg). Plant available Zn levels were as variable as environmentally available Zn levels, and this high variability in Zn levels may lead to differences in vine success throughout the vineyard. These data will serve as the basis for monitoring changes in the field plot soil Zn and Cu levels, and indicate that smaller Zn sampling areas will be needed to reduce variability.

The Departments of Agribusiness and Agriscience, Biology, and Chemistry at Middle Tennessee State University (MTSU) have undertaken a joint project to establish a vineyard field plot. The objective was to establish a well-characterized site for field-testing grape varieties in Tennessee. All three departments will use the plot as a teaching resource, with long-term studies of soil copper (Cu) and zinc (Zn) mobility a major emphasis.

The initial objectives were to establish background information on the soils. Measurements included soil texture, % organic matter, cation exchange capacity, and "environmentally available" Cu and Zn levels (United States Environmental Protection Agency, 1996). Knowledge of background Cu levels is desirable due to the potential application of Cu fungicides. Because Cu tends to adsorb to a variety of soil surfaces, Cu will accumulate in surface soils. Therefore, monitoring for changes in Cu levels in the local environment can be beneficial. Zinc, in contrast, is one of the more mobile heavy metals. Zinc levels were analyzed because Zn is the micronutrient most often deficient in grapevines (Wolf and Poling, 1995).

MATERIALS AND METHODS

Field Site—The site is found on map sheet 25 of the Rutherford County Soil Survey (True et al., 1977), and is located 1.07 km west of the intersection of United States Highways 231 and 268. The United States Department of Agriculture-Natural Resources Conservation Service soil survey showed two soil map units: a Lomond silt loam, 0–2 % slope, and a Cumberland silt loam, 2–5 % slope. The Lomond series is classified as fine-silty, siliceous thermic Mollic Paleudalfs, and the Cumberland series is classified as fine, mixed, thermic Rhodic Paleudalfs (True et al., 1977). Fourteen composite soil samples were collected using standard soil sampling techniques (Petersen and Calvin, 1996).

Soil Sample Preparation—Representative portions of each soil sample were pulverized to a fine powder with an agate mortar and pestle. Processed samples were mixed thoroughly before any part was removed for analysis. Between 25–30 g of soil from each location was prepared in this manner. Since the only sieves on hand were made of brass, sieving steps were omitted due to the risk of contaminating the samples with the analytes of interest, Cu and Zn. Nylon or stainless steel sieves should be used for this process to prevent such problems, but were not available at the time of the analysis. After setting aside a representative portion of soil, one sample was crushed and separated using the available No. 10 (1.0 mm) brass sieve to test for Cu and Zn contamination.

Cation Exchange Capacity (CEC)—The unbuffered salt extraction method was used to determine the CEC (Sumner and Miller, 1996). The final solution was measured for NH_4^+ (Mulvaney, 1996). Eight of the 14 soil samples were analyzed for CEC.

Percentage Organic Matter (%OM)—The loss-on-ignition (LOI) method was used to measure the soil organic matter (Nelson and Sommers, 1996). The organic matter content was assumed to equal the LOI.

Copper and Zinc—EPA Method 3050B was used for Zn and Cu analysis (United States Environmental Protection Agency, 1996). At least three calibration standards were used in all cases in the determination of Cu and Zn. Before the sample digestion procedure, primary standards were used to spike two soil samples for matrix interference checks. Standard aliquots were deposited onto the designated soil samples, which were covered with parafilm, and allowed to stand undisturbed for approximately 12 h.

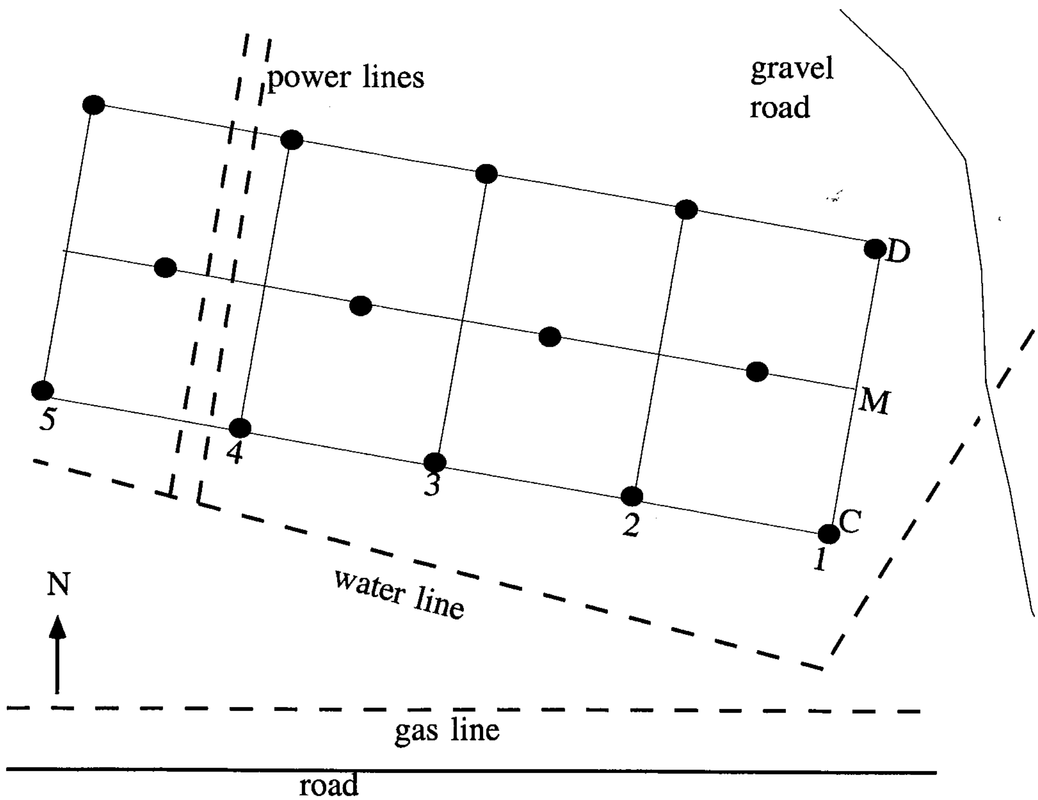

FIG. 1. Sampling grid for a Middle Tennessee State University vineyard plot. The black circles represent the 14 composite sampling points. The map scale is 80,000 ft^2 broken into eight 100 ft by 100 ft grids.

Spiked samples were treated in the same manner as untreated samples during the subsequent digestion and analytical procedures. The Cu and Zn concentrations in the filtrate were determined by Atomic Absorption Spectrophotometry (Perkin-Elmer Analyst 300 equipped with a flame atomizer, Perkin-Elmer, Shelton, Connecticut).

In addition to the Zn analysis described above, plant available Zn levels were measured in some of the soils by the University of Tennessee Institute of Agriculture.

TABLE 1. Cation exchange capacities (CEC) and organic matter percentages (%OM) of soil samples (Depths 0–8″).

Site	CEC (cmol/kg)	%OM	Soil series
c-1	4.4	3.5	Cumberland
c-2	—	4.8	Cumberland
c-3	5.0	3.2	Cumberland
c-4	—	3.4	Lomond
c-5	4.7	3.4	Lomond
m-1	—	3.0	Cumberland
m-2	5.6	4.0	Cumberland
m-3	—	4.7	Cumberland
m-4	6.3	3.4	Lomond
d-1	7.4	4.9	Cumberland
d-2	—	3.1	Cumberland
d-3	5.2	4.0	Cumberland
d-4	—	3.6	Lomond
d-5	4.6	3.9	Lomond

RESULTS AND DISCUSSION

Soil Samples—The sampling grid for the vineyard is shown in Fig. 1. The plot is 80,000 ft^2 broken into eight 10,000 ft^2 grids. The M grid points were sampled halfway between the corresponding grid numbers. For example, m-1 was sampled at the M grid line halfway between grid lines one and two.

The topsoil depth ranged from 7.5 cm to greater than 25 cm and had a silt loam texture. The Lomond has a mollic epipedon (Ap and AB horizons) with A horizon hues from 10YR to 5YR (reddish brown, brown, yellowish brown). The Cumberland has an ochric epipedon with Ap horizon hues from 5YR to 2.5YR. Based on the observed topsoil properties, grid points containing 1, 2, or 3 are Cumberland and 4 or 5 are Lomond. Both of these soils are classified as medium acidic (5.6–6.0) in the Ap horizon (True et al., 1977). Actual pH measurements will be made at planting time.

CEC and %OM—The importance of CEC and %OM in controlling the availability of trace metals like Zn cannot be overemphasized. The CEC can be a function of pH and %OM. As the CEC decreases, less Zn would be available on exchange sites for the plants to utilize. Organic matter is an excellent complexing agent of metal ions, and higher levels will mean less available metal ions for plant usage. The results for CEC and %OM are summarized in Table 1. A direct comparison of means for the Cumberland and Lomond soils cannot be made since each soil sample is a discrete sample and not a true replicate. However,

TABLE 2. Environmentally available soil Cu and Zn levels measured from all sample locations (Depths 0–8″).

Site	Cu (mg/kg)	Zn (mg/kg)	Soil series
c-1	6.4	15.1	Cumberland
c-2	8.8	17.4	Cumberland
c-3	12.4	25.2	Cumberland
c-4	10.3	12.5	Lomond
c-5	9.3	9.1	Lomond
m-1	9.1	17.2	Cumberland
m-1 (sieve)	51.1	25.0	Cumberland
m-2	10.8	19.1	Cumberland
m-3	8.7	7.2	Cumberland
m-4	9.4	9.3	Lomond
d-1	10.2	71.4	Cumberland
d-2	9.2	15.3	Cumberland
d-3	9.4	15.4	Cumberland
d-4	7.2	0.9	Lomond
d-5	7.5	8.5	Lomond

there appear to be no differences in the CEC values between soil series. The %OM may be slightly higher in the Cumberland soil, but this cannot be substantiated. Monitoring changes in CEC and %OM over the course of the vineyard life may prove valuable in addressing potential problems, such as Zn deficiencies.

Copper and Zinc—EPA Method 3050B was chosen because the field plot will be used as an educational resource for students to study Cu and Zn mobility in soils. This method is not a total digestion technique, but will dissolve most of the Zn and Cu that could become "environmentally available" (United States Environmental Protection Agency, 1996).

The results for percent elemental Cu and Zn were calculated using the following equation:

{[Final Digestate Sample Volume (ml)] [AAS Read (mg/l)] [Dilution Factor][100%]} ÷ {[Soil Sample Weight (mg)] [1000 ml/l]}

The elemental percentages were then converted to mg/kg. Results are shown in Table 2 as mg of analyte/kg of dry soil (mg/kg).

The sieved sample, m-1, showed approximately 42 mg/kg Cu and 8 mg/kg Zn above that determined in the unsieved sample. This is from contamination via use of the No. 10 brass sieve, which should not be used for sieving samples for trace metal measurements. Either a stainless steel or nylon sieve should be used for this purpose.

An *F*-test was performed to assess differences between the two soil series. The sieved sample was not included in any statistical calculations. Copper showed no statistically significant difference (*F*-ratio < *F*-critical) between the Cumberland and Lomond soils at a 95% confidence level. Zinc showed a significant difference (*F*-ratio > *F*-critical) at the same confidence level. This suggests the variation in Cu concentration within a soil series is not significantly different from the variation between soil series, and the average Cu level for the entire field (9.2 mg/kg) may be a fairly good approximation of the Cu level at any point in the field. However, the Zn results suggest there is considerably more variation, with possible local regions of excessively high and low levels when compared to the entire field plot average level. Previous studies also have shown that Zn levels typically vary more than Cu levels (Förstner, 1995; Krauskopf, 1972). Förstner (1995) reported Cu levels in uncontaminated soils range from <1–390 mg/kg, while Zn ranges from 1.5–2000 mg/kg.

The standard deviations (*SD*) of the Cu measurements cannot be compared directly to the Zn measurements because of the differences in the mean ($\bar{x}$) levels, which might indicate differences in the mineralogy of the Lomond and Cumberland soils. One way to normalize the data for comparison is to express *SD* as a percentage of the mean value ($100 \times SD/\bar{x}$), called the relative standard deviation (*RSD;* Harris, 1999). This comparison is summarized in Table 3.

These results indicate that in our soil samples Zn levels are much more variable than are Cu levels. The *RSD* for Zn ranged from 3.5–6 times the *RSD* for Cu, depending on whether one considers the overall *RSD* or the *RSD* for the individual soil series. Furthermore, sampling groups C and D were independently analyzed for plant available Zn by The University of Tennessee Institute of Agriculture (Table 4). Although they cannot be compared directly because our analyses were for environmentally available Zn, we can compare the *RSDs*. The *RSDs* were 28.0% and 99.0% (plant available Zn) and 38.4% and 79.4% (environmentally available Zn) for sampling groups C and D respectively. This further supports the conclusion that Zn levels vary to a great extent across the field plot, and much of the variation in Zn levels may be attributed to the two soil series.

Although we would not expect any direct correlations between plant available Zn and environmentally available Zn, due to sample heterogeneity, demonstrated variations in Zn levels, and different soil series, one would expect higher concentrations of environmentally available Zn due to the more rigorous diges-

TABLE 3. Middle Tennessee State University vineyard soil mean ($\bar{x}$), standard deviation (*SD*), and relative standard deviation (*RSD*)[1] values for environmentally available Cu and Zn.

Element	Overall[2]			Cumberland			Lomond		
	$\bar{x}$	*SD*	*RSD*	$\bar{x}$	*SD*	*RSD*	$\bar{x}$	*SD*	*RSD*
Cu	9.2	1.5	16.3	9.4	1.6	17.0	8.7	1.3	14.9
Zn	17.4	16.7	96.0	22.6	18.9	83.6	8.1	4.3	53.1

[1] $RSD = (100 \times SD/\bar{x})$.
[2] Overall: $\bar{x}$ and *SD* for the entire 14-sample data set excluding sieved sample.

TABLE 4. Plant available soil zinc levels determined by The University of Tennessee Institute of Agriculture (Depths 0–8″).

Site	Zn (pounds/acre)	Soil series
c-1	4.4	Cumberland
c-2	5.0	Cumberland
c-3	3.1	Cumberland
c-4	6.8	Lomond
c-5	5.7	Lomond
d-1	22.5	Cumberland
d-2	6.1	Cumberland
d-3	4.1	Cumberland
d-4	5.5	Lomond
d-5	2.7	Lomond

tion. If one assumes an acre of soil to a depth of normal plowing (15 cm) contains 2×10^6 pounds of soil, a conversion from pounds/acre to mg/kg is possible (Brady, 1984). In all samples except one (d-4), the plant available Zn was less than the environmentally available Zn (Tables 2 and 4) due to the more rigorous EPA digestion method.

Background data on Zn and Cu levels have been established at an MTSU vineyard field plot. These data will serve as baseline information for students monitoring the potential accumulation and mobility of Cu and Zn. This information also will help assess the success of grapevines since Zn is the micronutrient most often deficient in these plants. The sampling area used was sufficient for Cu characterization in the Cumberland and Lomond soil series. However, the Zn sample areas will have to be smaller in order to reduce variability in Zn determinations.

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