TRACE ELEMENTS IN OKLAHOMA SOILS: CONTENT, AVAILABILITY, AND THE EFFECT OF PHOSPHORUS FERTILIZER AND ORGANIC AMENDMENT APPLICATION

By

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INTRODUCTION

Trace elements exist naturally in varying concentrations in soil based upon the soil forming factors of parent material and climate. Also, anthropogenic activities can increase metal content in soil (Adriano, 2001). These trace elements can be both beneficial and potentially toxic. Some of the trace elements are plant essential elements meaning that a plant cannot successfully complete its lifecycle without these elements. These elements are often referred to as micronutrients. However, only a fraction of the total micronutrients in soil are in form that is available to be utilized by plants. Some soil properties that can affect the amount of an element that is plant available are soil pH, organic matter, cation exchange capacity, clay content, aluminum and iron oxide content, and perhaps soil phosphorus levels. Chapter one of this study investigates the effects of long term application of phosphorus fertilizer and organic amendments on micronutrient availability. On the other hand, trace elements can become toxic when accumulated in large concentrations in soil whether naturally or from anthropogenic activities. Therefore it is necessary to determine baseline concentrations of these elements in soil to aid in remediation activities as well as for the determination of whether or not a site has been contaminated. Chapter two of this study documents baseline levels of some of the trace elements for 28 soil series of Oklahoma and determines which soil properties have the strongest relationship with these levels.

CHAPTER I

THE EFFECT OF LONG-TERM APPLICATION OF PHOSPHORUS FERTILIZER AND ORGANIC AMENDMENTS ON MICRONUTRIENT AVAILABILITY

INTRODUCTION

Importance of Micronutrients

Micronutrients are elements essential for plant growth which are absorbed in small (micro) quantities (Sposito, 1989). Commonly recognized micronutrients include boron (B), copper (Cu), chloride (Cl), iron (Fe), manganese (Mn), molybdenum (Mo), and zinc (Zn). Although its importance is sometimes overlooked, micronutrient availability is critical for balanced plant nutrition, thus impacting crop yields. Micronutrients play key roles in many plant processes. Zinc promotes growth hormones, starch formation, seed maturation and production and is involved in a number of metallo-enzymes (Adriano, 2001). Iron is involved in chlorophyll formation while Cu is vital in photosynthesis as well as protein and carbohydrate metabolism and is a constituent of a number of plant enzymes (Adriano, 2001). Manganese plays a role in photosynthesis, nitrogen metabolism and assimilation (Brady and Weil, 1999). Manganese also functions in chlorophyll formation (Adriano, 2001). Although the necessity of B in plant nutrition has been established, its exact role remains somewhat vague (Adriano, 2001). However it is suspected that B functions at the membrane level and is essential for cell division and development. Thus, adequate levels of available micronutrients in soil are essential to achieve maximum yields and efficient use of other nutrients. The importance of micronutrients is magnified by the recent increase in commodity prices as well as increased costs of N, P, and K fertilizers. While micronutrient fertilization may not have been economical for some crops in the past due to low commodity prices, the application of micronutrients when needed to increase crop yields may now be profitable.

Micronutrient Availability and Extraction Methods

Availability describes the forms and quantity of a nutrient that plants are able to take up. The availability of a cationic nutrient is affected by several factors. Organic matter (OM) can affect availability by chelating ions making them more soluble and possibly more available for plant uptake. However, this increase in solubility can also lead to runoff and leaching losses of the chelated nutrients. Wright et al. (2007) found a decrease in DTPA extractable Mn and Cu as well as dissolved organic carbon (DOC) after rainfall events. In their study, they assumed that Mn and Cu complexed by DOC were lost due to either leaching or runoff. Organic matter also acts as a pH buffer. Soil pH affects metal solubility due to protonation and deprotonation of the hydration sphere. Shuman (1986) found that pH has the greatest effect on the exchangeable fraction of micronutrients which is a plant available fraction. Application of ammoniacal fertilizers acidifies soil and lowers soil pH, thus affecting micronutrient availability. Phosphorus fertilizers can affect the availability of micronutrients by changing the pH when the fertilizer dissolves into solution or when phosphate and associated phosphate fertilizer cations react with soil solution components (Shuman, 1988). For example, the dissolution of triple superphosphate releases H^+ into the soil solution and lowers soil pH. Phosphorus can also act as a charge determining ion (CDI) by making the colloid surface more negative through chemisorption, therefore raising soil's cation exchange capacity (CEC). Additionally, phosphate may have an effect on micronutrient availability by forming a precipitate with cationic micronutrients, thus lowering their availability (Shuman, 1988).

Plants take up a fraction of the total micronutrients present in soil. This fraction can be extracted chemically to determine the amount that is available for plant uptake. Plant available forms of micronutrients in soils are labile and dependent on the intensity factor and the capacity factor. The intensity factor refers to those ions specifically or non-specifically adsorbed to the soil surface. The capacity factor refers to the total amount of the element in soil. To estimate availability, a soil test extractant should include these labile forms (Martens and Lindsay, 1990). Over the years, at least four different types of extractants have been developed for micronutrients: neutral salts, inorganic acids, reducing agents, and chelating agents. Neutral salts, such as 1.0 *M* $CaCl_{2,}$ dissociate in soil solution causing the Ca^{2+} cation to compete with other cations for adsorption sites on soil particles. The dissociation of neutral salts forces other exchangeable cations into solution and could produce hydronium ions that displace specifically adsorbed cations (Martens and Lindsay, 1990). The amount of extracted cations is normally lower with neutral salts than with other extractants. "Inorganic acids such as 0.1 M hydrochloric acid (HCl) solubilize cationic micronutrients by dissociating complexes, displacing specifically adsorbed cations, and partially decomposing minerals to release non-labile and occluded cations" (Martens and Lindsay, 1990). However, since non-labile portions of the cations are released, soil pH or titratable alkalinity has to be taken into consideration. Reducing agents were used by Leeper (1934) to reduce amorphous Mn hydrous oxides, releasing Mn into solution. Chelating agents are used to create soluble complexes with free metal ions causing desorption of metal ions from soil surfaces or dissolution of metals in solid phases into soil solution. This is a measure of both the intensity and capacity factors which are important in determining availability (Lindsay and Norvell, 1978). Diethylenetriamine-pentaacetic acid (DTPA) and ethylenediamine-tetraacetic acid (EDTA) are two popular chelating agents for Fe, Zn, Cu, and Mn. Hot water B extraction (Berger and Troug, 1944), pressurized hot water (Webb et al., 2002), and DTPA-sorbitol (Miller et al., 2001) are commonly used B extraction methods. In the hot water B method, precision is difficult to achieve due to method variables (Miller et al., 2001). Rhoades et al. (1970) showed that saccharides chelate B and Vaughn and Howe (1994) demonstrated that sorbitol ($C_6H_{14}O_6$ or (2S,3R,4R,5R)-hexane-1,2,3,4,5,6-hexol) is an effective chelate of B. In a study by Miller et al. (2001), DTPA-sorbitol proved to be more precise than hot water boron while extracting Fe, Cu, Zn, and Mn simultaneously. DTPA-sorbitol has been adopted by many public and private laboratories due to the convenience of quantifying B and other micronutrients using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Miller et al., 2001; Gavlak et al. 2003). While DTPA-sorbitol is a widely accepted method to determine the amount of plant available micronutrients in soils, it is just one piece of the picture. To complete the picture, plant samples must also be analyzed to show correlations between DTPA-extractable micronutrients and plant availability.

Deficiency and Toxicity Levels of Micronutrients

Since only small quantities of micronutrients are needed for plant growth, there is a small margin between deficient, adequate, and toxic levels of available micronutrients. While sensitivity levels differ among crops, soil micronutrient concentration ranges required by most plants have been established. For soil B, adequate concentrations for optimum growth of most plants are between 0.05 and 0.50 mg B kg^{-1} (Adriano, 2001). Boron toxicity may occur above 0.50 mg B kg^{-1} for B-sensitive plants (Adriano, 2001). However, wheat is in the semi-tolerant category along with peanuts and alfalfa. In wheat tissue at the boot stage, concentrations of 8 mg B kg^{-1} in dry matter are considered adequate and > 16 mg B kg^{-1} are toxic (Adriano, 2001). In wheat straw (collected after maturity), concentrations of 17 mg B kg^{-1} are adequate and > 34 mg B kg^{-1} are toxic (Adriano, 2001).

Zinc deficiency is the most common micronutrient problem worldwide (Adriano, 2001). DTPA-extractable Zn levels of 0.5 mg kg^{-1} are considered adequate for most crops, while concentrations less than 0.5 mg kg^{-1} Zn are considered deficient (Adriano, 2001).

Lindsay and Norvell (1978) found the critical level of DTPA-extractable soil Cu is 0.20 mg kg^{-1} and considered soil concentrations below 0.20 mg kg^{-1} Cu as deficient. The toxicity level of Cu in soils varies between 150 and 400 mg kg^{-1} total Cu (Adriano, 2001). In winter wheat tissues, 5 mg Cu kg^{-1} is considered sufficient while concentrations greater than 10 mg Cu kg^{-1} are considered high but not necessarily toxic (Adriano, 2001).

Oklahoma soil test interpretations consider DTPA-extractable Fe levels < 2.0 mg kg^{-1} as deficient for moderately sensitive plants (including wheat), 2.0 to 4.5 mg kg^{-1} as deficient for sensitive crops, and > 4.5 mg kg^{-1} as adequate for all crops (Zhang et al., 2009). DTPA-extractable Mn levels of greater than 1.0 mg kg^{-1} are sufficient and levels less than this are considered deficient (Zhang et al., 2009). However, deficient levels of Mn have not been reported in Oklahoma. Zhang et al. (2009) indicated that soil Mn concentrations above 50 mg kg^{-1} may be toxic. In wheat tissue, Mn concentrations of 75 mg kg^{-1} are considered adequate and concentrations greater than 350 mg kg^{-1} are toxic (Adriano, 2001). Most Mn toxicity is due to acidic soil conditions and can be corrected by liming (Zhang et al., 2009). There are no well established plant sufficiency values for soil Mo because extractable Mo does not always correlate well with plant availability. Another factor is the relatively low levels (mean of 2.5 mg kg^{-1}) of total soil Mo (Adriano, 2001) lead to very low available Mo levels which are difficult to measure. Adriano (2001) described wheat tissue concentrations of 0.09 mg Mo kg^{-1} at the boot stage and wheat grain concentrations of 0.16 mg Mo kg^{-1} as being sufficient. Molybdenum toxicity in plants has not been observed under field conditions (Adriano, 2001). However, forage with levels of 10 to 20 mg Mo kg^{-1} can cause molybdenosis in livestock (Adriano, 2001). Molybdenosis is a Cu induced deficiency in ruminants that occurs when livestock consume forage with a Cu:Mo ratio of less than 2:1 (Mullen et al., 2005).

Fertilization and Micronutrient Availability

Fertilization may alter soil properties and thus affect micronutrient availability. Long term application of P fertilizer can lead to phosphorus (P) levels that are greater than 100% sufficient for a crop. Shuman (1988) showed that P levels can affect the availability of some micronutrients. In Shuman’s study (1988), increasing P increased Cu and Zn in the plant available fraction but had little effect on the plant available fraction of Mn and Fe. Furthermore, studies have been conducted on different P sources and their effect on micronutrient availability. Lehoczky et al. (2005) studied the effects of long-term mineral fertilization on micronutrient availability and found that increasing P fertilizer rates increased plant available Mo but decreased plant available B. In their study, P fertilization levels had no effect on Mn and Zn concentrations. This is somewhat contrary to the findings of Shuman (1988).

Kidd et al. (2007) and Schroder et al. (2008) studied heavy metal availability (including some micronutrients) as affected by long-term biosolids application. Kidd et al. (2007) found that EDTA-extractable Cu, Mn, and Zn were greater in sewage sludge amended soil than in the control. The study by Kidd et al. (2007) also reported acetic acid extractable (CH_3COOH) levels of Mn and Zn were significantly increased. This acetic acid extractable fraction correlates with availability because it extracts the water-soluble, exchangeable, and carbonate bound fractions of the metals (Kidd et al., 2007). Schroder et al. (2008) found that increasing applications of biosolids increased DTPA extractable Cu, Fe, and Zn. Also, high rates of biosolids application increased DTPA-extractable B. Similarly, Soumaré et al. (2007) studied the effects of biosolids application on micronutrient redistribution and availability, and found applications increased availability of Fe and Zn and decreased availability of Cu but did not affect Mn availability. The discrepancy between Schroder et al. (2008) and Soumaré et al. (2007) could be due to the difference in extraction methods. Schroder et al. (2008) used DTPA, whereas Soumaré et al. (2007) used potassium chloride (KCl) and sodium diphosphate ($Na_4P_2O_7$). Herencia et al. (2008) and Li et al. (2007) studied micronutrient availability with long-term application of inorganic fertilizer or compost (from vegetable or crop residues) and reported that DTPA extractable Zn, Fe, and Mn increased with increasing organic matter (OM). Herencia et al. (2008) also found that DTPA-extractable Cu did not increase with increasing OM. Furthermore, Li et al. (2007) found that increased inorganic P levels decreased Cu, Zn, and Mn concentrations in wheat straw tissues and Cu, and Zn concentrations in wheat grain tissues.

Wei et al. (2006) studied long-term applications of inorganic P fertilizer and cattle manure and their effects on micronutrient availability. Both available Zn and Fe were increased in inorganic P plots versus unfertilized treatments. Similarly, fertilization with cattle manure increased available Zn and Fe as compared with the inorganic P treatments.

Although these studies show some similarities, there is a need for research to be conducted comparing the effects of different P treatments and sources on micronutrient availability. The objectives of this project were 1) to study the effects of different sources and rates of P application on DTPA extractable micronutrients and 2) to evaluate the relationship between DTPA-extractable micronutrients and micronutrient concentrations in wheat tissue and grain samples collected from a biosolids amended soil.

MATERIALS AND METHODS

Experimental Sites and Treatments

Long-term Inorganic P Fertilization

Several pre-established long term soil fertility experimental sites located in Stillwater, Altus, and Lahoma Oklahoma were used in this study (Table 1.1). The Stillwater site was established in 1969 on a Kirkland silt loam (fine, mixed, thermic Udertic Paleustoll). The experimental design was a randomized block with four replications. Plot sizes were 6.1 m x 18.3 m with winter wheat being planted annually. Phosphorus application rates ranged from 0 to 44 kg P ha^{-1} yr^{-1} while N and K treatments remained constant at 90 and 37 kg ha^{-1} yr^{-1}, respectively. The Altus site was established in 1972 on a Tillman-Hollister clay loam (fine, mixed, thermic Typic Paleustolls) with cotton being planted annually. Plots were 6.1 m x 18.3 m in a randomized complete block with four replications. In this study, N and K rates were held constant at 134 and 75 kg ha^{-1} yr^{-1}, respectively while P rates ranged from 0 to 59 kg P ha^{-1} yr^{-1}. The Lahoma site was established in the fall of 1970 with wheat being planted annually on a Grant silt loam (fine-silty, mixed, superactive, thermic Udic Argiustoll). Nitrogen and K rates were both held constant at 67 and 56 kg ha^{-1} yr^{-1}, respectively. Annual phosphorus rates ranged from 0 to 39 kg P ha^{-1}. The P source for all of the long term fertility experiments was triple superphosphate.

Long-term Application of Organic Amendments

The long term biosolids site was established in Stillwater, OK at the Agronomy Research Station in the fall of 1993 with winter wheat being planted annually on a Norge loam (fine-silty, mixed, active, thermic Udic Paleustolls). Two N sources (biosolids and ammonium nitrate) were applied at six rates of 0, 45, 90, 180, 269, and 539 kg total N ha^{-1} yr^{-1} from 1993 to 2006 (Table 1.2). Plot sizes were 5 m x 10 m. Biosolids were applied as dry weight based on total N before wheat planting (Schroder et al., 2008). Application rates for all of the organic amendments were based on the amendments N contents. Therefore, the annual P amounts varied slightly from year to year due to amendments compositional difference. During the experiment, annual amounts of P applied ranged from 0 to 948 kg P ha^{-1} yr^{-1}.

The manure application site was located in Guymon, OK. Beef manure, swine effluent, and N fertilizer were applied annually at different N rates (0, 56, 168, and 504 kg ha^{-1}) to plots on a Richfield soil (fine, montmorillonitic, mesic Aridic Argiustoll) with corn being planted annually (Table 1.2). Plot sizes were 4.6 m x 9.1 m. The experimental design was a randomized complete block with three repetitions. The annual application rates were based on crop N requirement, so P levels varied depending on the P contents of the manure and effluent used. Phosphorus applied as beef manure varied from 0 to 691 kg P ha^{-1} yr^{-1}. For the swine effluent treatments, P applied ranged from 0 to 36 kg P ha^{-1} yr^{-1}. The swine effluent was applied by irrigation through a small mobile sprinkler system equipped with nozzles to control application rates. The beef manure was applied as a dry solid.

Soil Sampling and Analysis

Soil samples were collected from the Guymon, Stillwater, Altus and Lahoma long term trials in 2008 using a soil probe. Soil samples from the biosolids experiment were collected in 2009. Ten to fifteen cores per plot were collected from a depth of 0 to 15 cm to form a composite sample.

All soil samples were oven dried at 70 °C for 15-24 h, ground by ceramic mortar and pestle, and passed through a 2 mm sieve. Soil pH was measured in a 1:1 soil to de-ionized water suspension (Thomas, 1996). For total micronutrients and P, samples were digested in duplicate by U.S.EPA Method 3050B (U.S.EPA, 1996) and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). EPA Method 3050B involves digesting one gram of soil by the addition of trace metal grade HNO_3, H_2O_2, and HCl. While EPA Method 3050B technically is not a true total digestion, it was used in this study because it is a good measure of metals that could potentially become environmentally available while excluding silicate bound metals that are basically immobile. Blanks and certified biosolids-treated reference soil (CRM 005-050, RTC Corporation, Laramie, WY USA) were analyzed with each digestion for quality control. One certified reference soil and one blank was included for every ten samples. Acceptable recoveries for the certified reference soil were ±10% of certified values. Acceptable blank concentrations of individual micronutrients were below the established method detection limits. Lab triplicates of each field rep and treatment were analyzed.

For plant available micronutrients, samples were extracted using DTPA-sorbitol (diethylenetriamine-pentaacetic acid and sorbitol) (Gavlak et al., 2003). For each sample, 20 mL of DTPA-sorbitol was added to 10.0 g of soil, shaken for two h on an orbital shaker, gravity filtered through SAP 1F Laboratory Filtration Group filter paper, and analyzed by ICP-AES. One blank and one reference soil sample from the North American Proficiency Testing Program (NAPT, 2007-116 Hermiston) were analyzed for every ten samples for quality control. Acceptable concentrations for the reference samples were within ±10% of the certified values for each element. Acceptable blank concentrations were below the method detection limits. Lab triplicates of all samples were analyzed.

Soil organic matter (SOM) was determined by loss on ignition (Gavlak et al., 2003) for the calcareous soils located in Guymon, Oklahoma. Soil samples were weighed and then placed in an oven at 425 °C for two h. After two h the samples were removed and weighed again. A reagent grade calcium carbonate sample was included to evaluate losses of inorganic carbon. If the calcium carbonate sample showed >0.05% losses the oven temperature was checked and the samples were analyzed again. For all the other sites, SOM was determined by dry combustion using a LECO TruSpec Carbon and Nitrogen Analyzer.

Plant Sampling, Processing, and Analysis

Plant samples were collected from the biosolids plots to establish the relationship between soil DTPA-sorbitol extractable micronutrients and micronutrients in plant tissues. The biosolids plots were chosen for this because the treatments showed the best correlation between biosolids added and DTPA-extractable micronutrients. Wheat forage samples were collected from the biosolids plots in March 2009 at Feeke's growth stage 6. Samples were hand clipped from one-meter long segments of one row within each treatment. The entire aboveground part of the plant was collected. Plant samples were washed with deionized water, dried at 70 °C for 48 h, and ground using a stainless steel mechanical grinder. For digestion, 10 mL of trace metal grade HNO_3 was added to 0.5 g of plant sample and allowed to pre-digest for one h followed by heating at 115°C for two h (Jones and Case, 1990). Subsequent analysis of micronutrients and P was performed by ICP-AES. Quality control samples (NIST SRM 1515, apple leaves) were analyzed for every ten plant samples. Acceptable recoveries were within ±10% of certified values. Additionally, one blank per every ten samples was included in the digestion and analysis of micronutrients. Acceptable blank concentrations of individual micronutrients were below the established method detection limits.

Wheat Grain Sample Collection and Analysis

Wheat was harvested by hand from the biosolids plots to determine grain yield as well as to analyze grain samples for Fe, Cu, Zn, Mn, B, Mo, and P. The wheat grain samples were dried at 70 °C for 96 h, weighed, ground, digested and analyzed using the same method as for the plant samples.

Statistical Analysis

Statistical analysis was performed using SAS 9.2. Analysis of variance was conducted with Proc GLM. Planned comparisons were evaluated with an LSMEANS statement to determine if treatment differences existed. Simple correlation analyses were used as well as reverse stepwise multiple regression analysis to show relationships between the soil characteristics and DTPA-extractable micronutrients.

RESULTS AND DISCUSSION

Impact of Inorganic Phosphorus Application on Micronutrient Availability

The long-term application of inorganic P had varying effects on DTPA-sorbitol extractable micronutrients (DTPA-micronutrient) (Table 1.3). Overall, at the Altus site, DTPA-B was significantly decreased while DTPA-Fe and DTPA-Zn were significantly increased ($p<0.05$) at the largest P application level as compared to the control. Concentrations of DTPA-Cu, DTPA-Mn, and DTPA- Mo were not affected by long-term inorganic P application. The decrease in DTPA-B was not seen in any of the other sites and can probably be attributed to large variability among field replications. The significant decrease in B and increase in Fe and Zn were only seen at the highest P treatment level. Concentrations of DTPA-Fe ranged from 7.34 mg kg^{-1} in the control treatment to 10.9 mg kg^{-1} with the largest treatment of 59 kg P ha^{-1}. The concentrations of DTPA-Zn ranged from 0.20 to 0.28 mg kg^{-1}. While Zn availability increased, it was still below the sufficiency level of 0.3 mg kg^{-1} established by Zhang et al. (2009). All other micronutrients were at levels considered to be sufficient. With the exception of Cu, DTPA-extractable micronutrients were not correlated with total micronutrients (Table 1.4) and no significant treatment differences existed among total soil micronutrients (Table 1.5). However, DTPA-B, DTPA-Fe, and DTPA-Zn were significantly correlated with total soil P ($p<0.05$) while DTPA-B and DTPA-Fe were significantly correlated with soil pH ($p<0.01$) (Table 1.4).

Somewhat similar results were seen at the Lahoma site. DTPA-Cu and DTPA-Fe concentrations of the highest P treatment level were significantly increased ($p<0.05$) compared to the control (Table 1.3) and were correlated with total soil P ($p<0.05$ and $p<0.001$ respectively) and soil pH ($p<0.01$) (Table 1.4). Concentrations of DTPA-Fe ranged from 26.3 to 43.9 mg kg^{-1} while concentrations of DTPA-Cu ranged from 1.04 to 1.21 mg kg^{-1}. Concentrations of DTPA-B, DTPA-Mn, DTPA-Mo, and DTPA-Zn were not affected by long-term application of inorganic P fertilizer ($p<0.05$) (Table 1.4). Unlike the Altus site, DTPA-Cu was not correlated with total soil Cu, but DTPA-Fe was correlated with total soil Fe ($p<0.01$) (Table 1.4). All the DTPA-micronutrient concentrations were considered sufficient in Oklahoma.

Unlike the Altus and Lahoma sites, the Stillwater site showed no significant differences in DTPA-extractable micronutrients due to long-term application of inorganic P fertilizer (Table 1.3). All the DTPA-micronutrient concentrations were at levels considered to be adequate.

Inorganic P fertilizers may contain some micronutrients as impurities. In order to quantify the micronutrient additions from P fertilizer, six TSP samples were digested using EPA Method 3050B. The average concentrations of B, Cu, Fe, Mn, Mo, and Zn in TSP were 174, 12.7, 12037, 376, 9.88, and 94.1 mg kg^{-1}, respectively. These results were then utilized to calculate the micronutrient additions based on application rate and years of application until sampling (Table 1.6). These results indicate that relatively small additions of micronutrients were added over the long period of these experiments, thus explaining why treatment differences did not exist for total micronutrients in soil.

Micronutrients As Affected by Organic Amendments

The long-term application of organic amendments increased the majority of the DTPA-extractable micronutrients as compared to controls (Table 1.7). The long-term application of biosolids increased DTPA-Cu, DTPA-Fe, DTPA-Mo, and DTPA-Zn ($p<0.05$) as compared to the control plot that did not receive biosolids (Table 1.7). Concentrations of DTPA-Cu increased from 1.37 mg kg^{-1} in the control to 11.5 mg kg^{-1} in the highest biosolids treatment level. These levels are all considered adequate and are below toxicity levels (Lindsay and Norvell, 1978). Concentrations ranged from 20.2-78.6 mg kg^{-1} and 0.00-0.14 mg kg^{-1} for DTPA-Fe and DTPA-Mo, respectively. These DTPA-Fe levels are considered adequate for all crops. Concentrations of DTPA-Zn ranged from 0.81-12.4 mg Zn kg^{-1}, and are sufficient for all crops (Zhang et al., 2009) while not being toxic (Adriano, 2001). Somewhat contrary to the inorganic P treatments, DTPA-Cu, DTPA-Mo, and DTPA-Zn were all highly correlated ($p<0.001$) with total soil Cu, Mo, and Zn, respectively (Table 1.8). Significant positive correlations for the biosolids treatments were found between DTPA-Cu, DTPA-Fe, DTPA-Mo, and DTPA-Zn and total soil P as well as SOM. Total soil micronutrients, total soil P, and SOM increased as the amount of biosolids added to the plot increased. In order to further quantify this relationship, the annual amounts of Cu, Mo, and Zn applied in biosolids were summed to obtain cumulative values for each treatment level. The relationship between DTPA-Cu and cumulative Cu applied from biosolids was highly significant ($p<0.001$, $r^2=0.87$) (Figure 1.1A). Similarly, significant relationships existed between DTPA-Mo and cumulative Mo applied from biosolids ($p<0.001$, $r^2=0.91$) (Figure 1.1B) and between DTPA-Zn and cumulative Zn applied from biosolids ($p<0.001$, $r^2=0.86$) (Figure 1.1C).

Therefore, the increase in plant available micronutrients was probably due to the addition of micronutrients through the application of biosolids. This is further supported by the fact that there was an increase in Total Cu, Mo and Zn when compared to the control ($p<0.05$) (Table 1.9). DTPA-Cu, DTPA-Fe, and DTPA-Zn were correlated with soil pH while DTPA-Mo was not.

Similarly, the long-term application of beef manure showed a significant increase in all DTPA-extractable micronutrients as compared to the control ($p<0.05$) (Table 1.7). Concentrations ranges of DTPA-extractable micronutrients were B (1.63 to 2.26 mg kg^{-1}), Cu (1.50 to 2.16 mg kg^{-1}), Fe (3.56 to 6.57 mg kg^{-1}), Mn (21.0 to 37.9 mg kg^{-1}), Mo (0.02 to 0.07 mg kg^{-1}), and Zn (0.82 to 9.14 mg kg^{-1}). These concentrations are considered adequate for most crops. All DTPA-extractable elements were highly correlated ($p<0.01$) with total soil micronutrients except for DTPA-B (Table 1.8). Similar to the biosolids site, the Cu, Fe, Mn, and Zn content of the annual beef manure applications were summed in order to compare plant available micronutrients to cumulative micronutrients added from beef manure. Once again, these relationships were all found to be highly significant ($p<0.001$, $r^2>0.87$) for Cu, Fe, and Zn and significant ($p<0.01$, $r^2=0.59$) for Mn (Figure 1.2). Also similar to the biosolids plots, there was a significant ($p<0.05$) increase in total soil Cu, Mo, and Zn only at the largest application rates when compared to the control (Table 1.9). These significant relationships imply the increase in plant available micronutrients was due to the addition of micronutrients through the organic amendment (beef manure). All DTPA-extractable micronutrients were also highly correlated ($p<0.001$) with total soil P as well as soil pH ($p<0.01$) (Table

1.8). However, significant correlations were not observed between any of the micronutrients and SOM.

The swine effluent site in Guymon, OK showed an increase in DTPA-B, DTPA-Cu, and DTPA-Zn at the two higher application rates as compared to the control (Table 1.7). Concentrations of DTPA-B ranged from 1.62-2.16 mg kg^{-1}, while DTPA-Cu and DTPA-Zn levels ranged from 1.41-1.97 mg kg^{-1} and 0.74-6.95 mg kg^{-1}, respectively. The levels of all micronutrients were 100% sufficient. Significant correlations ($p<0.05$) occurred between DTPA-Cu and DTPA-Zn and total soil micronutrients, total soil P, and pH (Table 1.8). As in the other organic amendment sites, the cumulative application of Cu and Zn was quantified in order to determine their relationships with plant available Cu and Zn. The relationship between DTPA-Cu and cumulative Cu applied from swine effluent was significant ($p<0.01$, $r^2=0.61$) (Figure 1.3A). Similarly, the relationship between DTPA-Zn and cumulative Zn applied was highly significant ($p<0.001$, $r^2=0.80$) (Figure 1.3B). There was also a significant ($p<0.05$) increase in total soil Cu and Zn at the two largest application rates when compared to the control (Table 1.9). The increase in plant available micronutrients was probably due to the addition of micronutrients through swine effluent application. Significant correlations between DTPA-B and total soil B did not exist. For both the swine effluent and beef manure sites, DTPA-Mo concentrations were hovering around the detection limits. This caused high variability and could explain why correlations were not present between DTPA-Mo and soil properties in the swine effluent treatments.

Multiple Regression Analysis

Reverse stepwise multiple regression analysis was performed in order to further separate the effects of soil properties on DTPA-extractable micronutrients. This analysis was only performed on the elements that significantly changed for each site. At the Altus site, pH and soil total B were found to explain most of the variability of DTPA-B while the inclusion of total soil P did not improve the regression model (Table 1.10). In the DTPA-Fe regression model, total soil P, pH, and total soil Fe together explained 88% of the variation. However, with the exclusion of total soil Fe from the model, 87% of the variability is explained by soil pH and total soil P. For DTPA-Zn, total soil P explained the majority of the variation (R^2=0.76), while the inclusion of soil pH and total soil Zn did not improve the model. These results mostly agree with the simple correlation results.

For the Lahoma site, DTPA-Cu was affected by pH but the inclusion of total soil P and Cu did not improve the regression model (Table 1.10). This contrasts somewhat with the simple regression in which total soil P was correlated with DTPA-Cu at the 0.05 level. This suggests that while a relationship between DTPA-Cu and total soil P and Cu exists, the decrease in soil pH had the greatest effect on increasing DTPA-Cu. The reverse stepwise regression for DTPA-Fe at the Lahoma site showed that the inclusion of total soil P, total soil Fe, and soil pH explained 91% of the variability. All of these variables explained a significant amount of variability and could not be removed from the model. This agrees with the simple correlation procedure.

For the most part, the DTPA-extractable micronutrients in the long-term inorganic P sites showed no relationship with total soil micronutrients. Increases in DTPA-micronutrients were most often correlated with total soil phosphorus and a decrease in pH. However, these increases were often small and associated only with the highest P treatment level.

The reverse stepwise multiple regression analyses for the organic amended sites (Table 1.11-1.13) showed some differences from the inorganic P sites. For the site receiving long-term application of biosolids, DTPA-Cu had the strongest relationship with SOM and total soil copper (R^2=0.96) (Table 1.11). The inclusion of total soil P did not improve the model. This differs from the simple correlation results in which there was a significant relationship ($p<0.001$) between DTPA-Cu and total soil P. The difference between the simple correlation and the reverse stepwise multiple regression probably exists because total soil P and DTPA-Cu both increase with increased biosolids application, but total soil P does not significantly affect DTPA-Cu. For DTPA-Fe, 88% of the variability was explained by pH, total soil P, and SOM. The inclusion of total soil Fe did not improve the regression model. This agrees with the simple correlation analysis. All the other DTPA-extractable elements in the biosolids plots were found to be correlated to their corresponding total soil element except for Fe. This could be due to the large concentrations of total soil Fe present in the soil. Although Fe was added through the application of biosolids (Table 1.9), it was not a large enough quantity to significantly increase the total Fe content of the soil. In the DTPA-Mo regression model, soil pH and total soil Mo explained a 98% of the variability and the inclusion of SOM and total soil P did not improve the regression model. Once again, this is different from the simple correlation procedure in that, total soil P was not found to be significant in the reverse stepwise multiple regression while it was significant in the simple correlation procedure. This is probably because they both have a relationship with the amount of biosolids applied, but total soil P does not directly affect Mo availability. Similarly, the increase in DTPA-Zn was found to best be explained by total soil Zn and pH (R^2=0.97). Once again, total soil P did not improve the model and was removed by the reverse stepwise multiple regression.

The beef manure site in Guymon, OK showed somewhat similar results (Table 1.12). Once again, the best models for DTPA-Cu, DTPA-Mo, and DTPA-Zn included the variables of total soil Cu, total soil Mo, and total soil Zn, respectively. This would again seem to mean that the increase in plant available micronutrients is coming from the addition of micronutrients through the addition of manure. Iron and Mn did not display this same relationship. This is probably due to the same reason that DTPA-Fe was not correlated with total soil Fe at the biosolids site. However, in the DTPA-Fe regression pH and total soil P explained the majority of the variation (R^2=0.85). Somewhat similarly, the DTPA-Mn model was best explained by total soil P alone (R^2=0.77). Similarly, for DTPA-B, total soil P alone explained 74% of the variability and was the only significant factor ($p<0.10$).

The reverse stepwise multiple regression analysis for the site receiving long-term application of swine effluent showed slightly different relationships (Table 1.13). As discussed earlier, DTPA-B significantly increased at the swine site. However, neither simple correlation nor reverse stepwise multiple regression analysis showed significant relationships between DTPA-B and the soil properties investigated in this study. The same is true for DTPA-Mo. This could be due to high B variability among field replicates and the analytical difficulty associated with measuring Mo at very low concentrations as discussed earlier. Similar to the beef manure and biosolids sites, DTPA-Cu was best explained by total soil Cu (R^2=0.88). Zinc at the swine effluent site showed somewhat similar trends to the other organic amendment sites. The best model was found by the inclusion of soil pH, total soil P, SOM and total soil Zn. All were found to be significant ($p<0.001$) and explained 98% of the variability. However, in the biosolids and beef manure sites, total soil P and SOM were excluded from the models because they did not explain a significant amount of the variability. This difference could be due to the fact that DTPA-Zn did not increase as much for the swine effluent site as it did for the beef manure and biosolids sites (Table 1.7).

For long-term organic amended sites, DTPA-Cu and DTPA-Zn always showed the strongest relationship with total soil Cu and total soil Zn, respectively. This supports the idea that the addition of metals through the addition of organic amendments was responsible for the increase in DTPA-micronutrients. Molybdenum followed this same trend; however, relationships were difficult to determine due to the small concentrations of Mo being analyzed. On the other hand, DTPA-B appeared to be most significantly affected by total phosphorus. For DTPA-Fe, the most significant relationships were found with soil pH and total soil P.

Micronutrient Concentrations in Wheat Tissue and Grain As Affected By Biosolids Amendment

Wheat tissue samples were collected in March 2009 from the biosolids site and digested in order to determine micronutrient concentrations (Table 1.14). Wheat tissue B concentrations ranged from 3.89-8.53 mg kg^{-1}. However, no significant treatment differences existed due to high variability among treatments. Two of the treatments were in the deficient range for wheat (i.e. < 5.0 mg B kg^{-1}) (Adriano, 2001). None of the tissue samples showed toxic levels of B. On the other hand, wheat tissue Cu concentrations ranged from 10.1-14.5 mg kg^{-1} and were at levels considered sufficient (Adriano, 2001). No significant differences in wheat tissue Cu concentrations existed among biosolids application rates. Wheat tissue Fe and Mn concentrations ranged from 105-148 mg kg^{-1} and 29.7-51.8 mg kg^{-1}, respectively. There were no significant differences in wheat tissue Fe concentrations among treatments. Significant differences existed among some treatments for wheat tissue Mn; however no real trend existed in these differences. The largest wheat tissue Mn concentration was found in the 45 kg N ha^{-1} treatment. Perhaps this is due to the increasing amount of SOM. The SOM could have complexed the Mn at the higher treatment levels, thus decreasing availability. This is somewhat similar to the results found by Wright et al. (2007) which found decreases in DTPA-Mn after rainfall events due to the runoff of organically complexed Mn. The wheat tissue Mn concentrations are above levels considered deficient (Adriano, 2001). Wheat tissue Mo concentrations ranged from 0.00-0.54 mg kg^{-1}. The control and the 45 kg N ha^{-1} treatments were deficient while all the other treatments were at levels considered adequate for Mo (Adriano, 2001). Wheat tissue Mo concentrations for the higher treatment levels were significantly different from the control. Ratios of Cu:Mo were found to be much greater than 2:1. Thus, there is no threat of molybdenosis in ruminants for the biosolids treated plots (Mullen et al. 2005). Wheat tissue Zn concentrations ranged from 15.2-45.5 mg kg^{-1}. Wheat tissue Zn concentrations for the higher treatment levels (i.e. ≥ 180 kg N ha-1) were significantly different from the control. For the lower applications of 0, 45, and 90 kg N ha^{-1}, wheat tissue Zn levels were below the critical value of 20 mg kg^{-1} (Adriano, 2001), suggesting possible zinc deficiencies existed. This does not agree with the DTPA-extractable Zn data, which indicated adequate Zn in the soil.

The wheat tissue micronutrient concentrations were regressed against the DTPA-extractable soil micronutrient concentrations. Significant relationships did not exist ($p>0.05$) between wheat tissue B, Cu and Fe and DTPA-B, DTPA-Cu and DTPA-Fe, respectively (data not shown). However, wheat tissue Fe was highly correlated with soil pH and total soil Fe ($p<0.01$) as shown in the following equation:

$$\text{Tissue Fe} = -175 - 1.26(\text{DTPA-Fe}) - 50.8(\text{pH}) + 0.04(\text{Total Fe}),\ r^2 = 0.62.$$

Including soil pH and total soil Fe greatly improved the ability to predict plant available Fe from the DTPA soil test. Likewise, a significant relationship ($p<0.05$, $r^2=0.30$) existed between DTPA-Mn and wheat tissue manganese (Figure 1.4). However this relationship was greatly improved by the addition of total soil Mn into the regression ($p<0.01$, $r^2=0.55$). A significant relationship ($p<0.05$, $r^2=0.55$) was found between DTPA-Mo and wheat tissue Mo. Similarly, wheat tissue Zn was found to be highly correlated ($p<0.001$, $r^2=0.87$) with DTPA-zinc.

Micronutrient concentrations from the wheat grain samples were determined in order to assess their relationship with plant available micronutrients in the soil (Table 1.14). All wheat grain B concentrations were below the detection limits of the ICP-AES. Wheat grain Cu concentrations ranged from 3.45-5.84 mg kg^{-1} and significantly decreased with increasing biosolids application rate. No significant differences existed in wheat tissue Fe concentrations among treatment levels. Similar to the wheat tissue samples, significant differences in wheat grain Mn concentrations existed among treatments with the highest concentration found at the 45 kg N ha^{-1} treatment. Wheat grain Mo concentrations ranged from 0.23-0.70 mg kg^{-1} and were significantly different from the control at the higher treatment levels. These concentrations are considered sufficient. Wheat grain zinc levels ranged from 37.6-57.7 mg Zn kg^{-1}. The higher treatment levels increased wheat grain Zn as compared to the control.

The relationship between DTPA-B and wheat grain B could not be determined due to the fact that wheat grain B was below the detection limit (0.01 ppm). There was a significant ($p<0.01$, $r^2=0.35$) inverse relationship between wheat grain Cu and DTPA-Cu (Figure 1.5). This could be partly due to increasing SOM making the Cu less plant available, but still extractable by the DTPA soil test. Similar to Fe in the wheat tissue samples, a significant relationship was not found between DTPA-Fe and wheat grain Fe concentrations. However, unlike the wheat tissue samples, the inclusion of pH and total Fe did not improve the relationship. Unlike the wheat tissue samples, no significant relationship was found between wheat grain Mn and DTPA-Mn. Wheat grain Mo, and Zn agreed with the wheat tissue data. Significant relationships existed between wheat grain Mo and DTPA-Mo ($p<0.01$, $r^2=0.41$) and between wheat grain Zn and DTPA-Zn ($p<0.01$, $r^2=0.67$).

CONCLUSIONS:

Long-term inorganic P fertilization did not contribute significantly to soil total micronutrients. Increased soil P had little effect on micronutrient availability. At some of the sites, an increase in DTPA-extractable micronutrients existed at the highest P treatment level. However, these increases were mostly minor and probably due to a decrease in soil pH. Micronutrient additions through impurities in inorganic P fertilizer were small relative to total soil micronutrient concentrations.

On the other hand, long-term application of organic amendments increased some of the soil total micronutrient contents and most DTPA-extractable micronutrients. These increases occurred even in a high pH soil which had received beef manure applications. Our results indicate organic amendments make an ideal fertilizer source for areas with micronutrient deficiencies.

The micronutrient concentrations in the wheat tissue and wheat grain samples showed that the DTPA-sorbitol soil test adequately predicts plant available Mn, Mo, and Zn. However, it did not accurately predict B and Cu concentrations in wheat tissue or wheat grain samples. The DTPA soil test alone did not correlate with wheat tissue or wheat grain Fe concentrations. However, when the DTPA soil test was used in conjunction with the total soil Fe concentration and soil pH, a significant relationship existed with wheat tissue Fe concentrations. These relationships are only based on one year of data, so additional research needs to be conducted to determine if the DTPA-sorbitol soil test correlates with plant uptake of micronutrients.

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TABLES

Table 1.1. Locations, treatments, and other information of the long-term inorganic phosphorus (P) trials used for the present study.

Location	**Year Established**	**P Rates** (kg P ha^{-1} yr^{-1})	**Cumulative P Applied *** (kg P ha^{-1})	**N Rate** (kg N ha^{-1} yr^{-1})	**K Rate** (kg K ha^{-1} yr^{-1})	**Plot Size** (m)	**Crop**
Altus	1972	0, 20, 39, and 59	0, 703, 1406, and 2110	134	75	6.1 x 18.3	Cotton
Lahoma	1970	0, 10, 20, 29 and 39	0, 371, 742, 1114, and 1484	67	56	4.9 x 18.3	Continuous Winter Wheat
Stillwater	1969	0, 15, 29, and 44	0, 571, 1143, and 1714	90	37	6.1 x 18.3	Continuous Winter Wheat

*Total amount of P applied from the year of establishment to 2008

Table 1.2. Locations, treatments, and other information of the long-term organic amendment trials used for the present study.

Location	**Year Established**	**Organic Amendment**	**Average Annual P Rates** (kg P ha^{-1} yr^{-1})	**Cumulative P Applied*** (kg P ha^{-1})	**N Rate** (kg N ha^{-1} yr^{-1})	**Crop**
EFAW (Stillwater)	1993	Biosolids	0, 78, 158, 316, 473 and 948	0, 1009, 2057, 4111,6150, 12319	0, 45, 90, 180, 269, and 539	Continuous Winter Wheat
Guymon	1995	Beef	0, 77, 232, and 691	0, 767, 2317, 6908	0, 56, 168, and 504	Continuous Corn
Guymon	1995	Swine	0, 5, 12, and 36	0, 50, 119, 357	0, 56, 168, and 504	Continuous Corn

*Total amount of P applied from the year of establishment to 2007 for beef manure and swine effluent and 2005 for biosolids

Table 1.3. The effect of annual inorganic P rates on mean DTPA-extractable micronutrients.

Site	P Rate	DTPA-B	DTPA-Cu	DTPA-Fe	DTPA-Mn	DTPA-Mo	DTPA-Zn
	kg P ha^{-1}	mg kg^{-1}					
Altus	0	1.42a*	0.86a	7.34a	14.9a	BDL**	0.20a
	20	1.37a	0.92a	7.73a	14.8a	BDL	0.22a
	39	1.34ab	0.89a	9.17ab	14.5a	BDL	0.23a
	59	1.12b	0.82a	10.9b	15.8a	BDL	0.28b
Lahoma	0	0.20a	1.04a	26.3a	38.6a	BDL	0.42a
	10	0.20a	1.16ab	35.7ab	40.5a	BDL	0.44a
	20	0.20a	1.11ab	38.5ab	35.8a	BDL	0.45a
	29	0.19a	1.14ab	42.6b	41.1a	BDL	0.46a
	39	0.20a	1.21b	43.9b	39.0a	BDL	0.46a
Stillwater	0	0.17a	1.37a	46.6a	69.2a	BDL	0.84a
	15	0.21a	1.51a	83.8a	97.1a	BDL	0.83a
	29	0.22a	1.51a	82.5a	93.4a	BDL	0.81a
	44	0.23a	1.50a	91.2a	88.8a	BDL	0.82a

* The same letter in the same column for each site denotes no statistical difference ($p>0.05$).

**BDL: below detection limit (0.01 mg kg^{-1})

Table 1.4. P values for the relationships between DTPA-extractable micronutrients and soil total micronutrients and properties for the long-term application of inorganic phosphorus.

Altus								
	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn	Total Soil P	pH
DTPA-B	0.079						0.020	0.011
DTPA-Cu		0.001					0.352	0.370
DTPA-Fe			0.139				<0.001	0.005
DTPA-Mn				0.459			0.124	0.003
DTPA-Mo					---		---	---
DTPA-Zn						0.493	<0.001	0.168
Lahoma								
	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn	Total Soil P	pH
DTPA-B	0.408						0.232	0.028
DTPA-Cu		0.770					0.040	0.002
DTPA-Fe			0.003				<0.001	<0.001
DTPA-Mn				0.512			0.468	0.002
DTPA-Mo					---		---	---
DTPA-Zn						<0.001	0.002	0.002
Stillwater								
	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn	Total Soil P	pH
DTPA-B	0.142						0.102	0.339
DTPA-Cu		0.031					0.373	0.135
DTPA-Fe			0.251				0.170	0.118
DTPA-Mn				0.980			0.852	0.007
DTPA-Mo					---		0.152	0.140
DTPA-Zn						0.477	0.229	0.110

Table 1.5. The effect of annual inorganic P rates on mean total soil micronutrients.

Site	P Rate	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn
		------mg kg^{-1}------		g kg^{-1}	------------mg kg^{-1}------------		
Altus	0	56.2a*	10.4a	17.1a	330a	BDL	53.8a
	29	67.8a	9.69a	17.1a	336a	BDL	52.8a
	39	68.2a	10.5a	16.3a	367a	BDL	56.1a
	59	65.9a	9.49a	16.0a	346a	BDL	53.1a
Lahoma	0	59.5a	6.91a	14.3a	305a	BDL	55.5a
	10	58.2a	6.59a	14.1a	313a	BDL	54.1a
	20	53.0b	9.22b	15.0b	331a	BDL	53.7a
	29	55.5ab	6.29a	13.8a	305a	BDL	53.9a
	39	55.8ab	6.81a	14.3a	326a	BDL	55.3a
Stillwater	0	76.5a	10.2a	18.4ab	510ab	BDL	57.4a
	20	74.0a	9.96a	18.2a	543ab	BDL	57.9a
	29	75.7a	10.7a	18.6b	570b	BDL	58.9a
	44	46.4b	10.4a	17.8c	474a	BDL	52.7b

* The same letter in the same column for each site denotes no statistical difference ($p>0.05$)

Table 1.6. Total micronutrient additions from triple super phosphate fertilizer over the entire experiment period.

P Rate kg ha^{-1}	TSP Rate kg ha^{-1}	Total B g ha^{-1}	Total Cu g ha^{-1}	Total Fe kg ha^{-1}	Total Mn g ha^{-1}	Total Mo g ha^{-1}	Total Zn g ha^{-1}
				Altus			
0	0	0.00	0.0	0.0	0	0.0	0.0
45	98	17.1	1.2	1.2	37	1.0	9.2
90	196	34.1	2.5	2.4	74	1.9	18.4
134	291	50.8	3.7	3.5	110	2.9	27.4
				Lahoma			
0	0	0.0	0.0	0.0	0.0	0.0	0.0
10	21	3.7	0.3	0.3	8.0	0.2	2.0
20	43	7.6	0.6	0.5	16.3	0.4	4.1
29	63	11.0	0.8	0.8	23.7	0.6	5.9
39	85	14.8	1.1	1.0	31.9	0.8	8.0
				Stillwater			
0	0	0.0	0.0	0.0	0.0	0.0	0.0
15	33	5.7	0.4	0.4	12.3	0.3	3.1
29	63	11.0	0.8	0.8	23.7	0.6	5.9
44	96	16.7	1.2	1.2	36.0	0.9	9.0

Table 1.7. The effect of organic amendment rates on mean concentrations of DTPA-extractable micronutrients.

Site	Organic Amendment	N Rate	DTPA-B	DTPA-Cu	DTPA-Fe	DTPA-Mn	DTPA-Mo	DTPA-Zn
		kg ha^{-1}				mg kg^{-1}		
Efaw	Biosolids	0	0.34a*	1.37a	20.2a	21.0a	0.00a	0.81a
		45	0.24a	2.66a	39.1a	26.9a	0.01a	1.78a
		90	0.34a	3.79ab	40.3ab	30.0a	0.03a	3.03ab
		180	0.27a	6.25bc	55.8bc	33.5a	0.07b	6.03bc
		269	0.32a	7.46c	66.9c	33.0a	0.09b	7.30c
		539	0.42a	11.5d	78.6bc	25.1a	0.14c	12.41d
Guymon	Beef	0	1.63a	1.50a	3.56a	21.0a	0.04a	0.82a
		56	1.64a	1.50a	3.77a	20.0a	0.02a	1.42ab
		168	1.85a	1.68a	4.55b	28.5ab	0.04a	4.39b
		504	2.26b	2.16b	6.57c	37.9b	0.07b	9.14c
Guymon	Swine	0	1.62a	1.41a	3.42a	19.4a	0.04a	0.74a
		56	1.76ab	1.53a	3.43a	22.3a	0.04ab	2.10ab
		168	2.02bc	1.78b	3.44a	22.5a	0.05ab	3.54b
		504	2.16c	1.97b	3.77a	21.4a	0.05b	6.95c

* The same letter in the same column for each site denotes no statistical difference ($p>0.05$).

Table 1.8. P values for the relationships between DTPA-extractable micronutrients and soil total micronutrients, total phosphorus, soil pH, and soil organic matter content (SOM) for the long-term application of organic amendments.

Biosolids

	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn	Total P	pH	SOM
DTPA-B	0.852						0.624	0.002	0.456
DTPA-Cu		<0.001					<0.001	0.039	<0.001
DTPA-Fe			0.232				<0.001	0.004	<0.001
DTPA-Mn				<0.001			0.621	0.081	0.179
DTPA-Mo					<0.001		<0.001	0.088	<0.001
DTPA-Zn						<0.001	<0.001	0.046	<0.001

Beef Manure

	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn	Total P	pH	SOM
DTPA-B	0.429						<0.001	0.004	0.333
DTPA-Cu		<0.001					<0.001	0.001	0.310
DTPA-Fe			0.001				<0.001	<0.001	0.441
DTPA-Mn				0.003			<0.001	0.002	0.663
DTPA-Mo					<0.001		0.001	<0.001	0.976
DTPA-Zn						<0.001	<0.001	<0.001	0.153

Swine Effluent

	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn	Total P	pH	SOM
DTPA-B	0.889						0.153	0.601	0.927
DTPA-Cu		<0.001					0.005	0.046	0.487
DTPA-Fe			0.5903				0.001	<0.001	0.099
DTPA-Mn				0.3542			0.061	0.014	0.247
DTPA-Mo					0.148		0.082	0.309	0.596
DTPA-Zn						<0.001	0.001	0.023	0.369

Table 1.9. The effect of organic amendment rates on mean concentrations of total micronutrients.

Site	Manure	N Rate	Total B	Total Cu	Total Fe	Total Mn	Total Mo	Total Zn
		kg ha^{-1}	mg kg^{-1}		g kg^{-1}		mg kg^{-1}	
Efaw	Biosolids	0	69.6a*	11.6a	16.8a	398a	0.20a	49.5a
		45	71.2a	16.6a	16.8a	648a	0.38a	53.2a
		90	69.0a	19.7a	17.4a	523a	0.55ab	61.4a
		180	72.0a	29.3b	17.1a	544a	1.02bc	77.5b
		269	69.3a	28.0b	17.1a	423a	1.22c	78.1b
		539	68.0a	39.2c	17.4a	490a	1.84d	103c
Guymon	Beef	0	56.3a	12.0a	14.8a	396a	0.26a	63.9a
		56	54.9a	12.2a	14.5a	398a	0.25a	64.9a
		168	55.7a	12.9a	14.2ab	385a	0.27a	73.1a
		504	54.9a	14.7b	13.4b	380a	0.31b	85.1b
Guymon	Swine	0	55.7a	11.9a	15.5a	398a	0.26a	65.9a
		56	54.6a	12.4ab	15.1a	399a	0.24a	70.8ab
		168	55.5a	13.3bc	15.1a	404a	0.28a	77.1bc
		504	56.1a	13.9c	14.9a	400a	0.28a	83.8c

* The same letter in the same column for each site denotes no statistical difference ($p>0.05$).

Table 1.10. Reverse stepwise multiple regression between plant available micronutrients (DTPA-extractable) and other soil properties for the inorganic P sites with significant changes in micronutrient concentrations.

Site	Response	Independent variables	Equation	Statistics (n=16)
Altus	DTPA-B	pH, Total B, Total P	$y = -1.85 + 0.57(\text{pH}) - 0.01(\text{Total B}) - 0.0008(\text{Total P})$	$R^2=0.59$ $p=0.010$
		pH, Total B	$y = -3.06 + 0.72(\text{pH}) - 0.01(\text{Total B})$	$R^2=0.52$ $p=0.010$
	DTPA-Fe	pH, Total Fe, Total P	$y= 20.3 - 2.60(\text{pH}) + 0.0002(\text{Total Fe}) + 0.01(\text{Total P})$	$R^2=0.88$ $p<0.001$
		pH, Total P	$y= 23.0 - 2.59(\text{pH}) + 0.01(\text{Total P})$	$R^2=0.87$ $p<0.001$
	DTPA-Zn	pH, Total Zn, Total P	$y= 0.14 + 0.01(\text{pH}) + 0.0002(\text{Total P}) - 0.0007(\text{Total Zn})$	$R^2=0.76$ $p<0.001$
		Total P, Total Zn	$y= 0.18 + 0.0002(\text{Total P}) - 0.0006(\text{Total Zn})$	$R^2=0.76$ $p<0.001$
		Total P	$y= 0.14 + 0.0002(\text{Total P})$	$R^2=0.76$ $p<0.001$
Lahoma	DTPA-Cu	pH, Total Cu, Total P	$y= 2.72 - 0.28(\text{pH}) + 0.01(\text{Total Cu}) + 0.00002(\text{Total P})$	$R^2=0.46$ $p=0.018$
		pH, Total Cu	$y= 2.76 - 0.29(\text{pH}) + 0.01(\text{Total Cu})$	$R^2=0.46$ $p=0.006$
		pH	$y= 2.71 - 0.26(\text{pH})$	$R^2=0.43$ $p=0.002$
	DTPA-Fe	pH, Total Fe, Total P	$y=190 - 21.9(\text{pH}) - 0.003(\text{Total Fe}) + 0.08(\text{Total P})$	$R^2=0.91$ $p<0.001$

Table 1.11. Reverse stepwise multiple regression between plant available micronutrients (DTPA-extractable) and other soil properties for the micronutrients with significant changes at the biosolids site.

Amendment	Response	Equation	Statistics (n=18)
Biosolids	DTPA-Cu	$y = -2.30 - 0.41(\text{pH}) + 1.97(\text{OM}) + 0.27(\text{Total Cu}) + 0.0002(\text{Total P})$	R^2=0.96 $p<0.001$
		$y = -2.42 - 0.41(\text{pH}) + 2.01(\text{OM}) + 0.28(\text{Total Cu})$	R^2=0.96 $p<0.001$
		$y = -5.09 + 2.03(\text{OM}) + 0.29(\text{Total Cu})$	R^2=0.96 $p<0.001$
	DTPA-Fe	$y = 60.3 – 16.0(\text{pH}) + 22.9(\text{OM}) + 0.002(\text{Total Fe}) + 0.02(\text{Total P})$	R^2=0.88 $p<0.001$
		$y = 85.70 – 15.6(\text{pH}) + 24.0(\text{OM}) + 0.02(\text{Total P})$	R^2=0.88 $p<0.001$
	DTPA-Mo	$y = -0.08 + 0.01(\text{pH}) – 0.0003(\text{OM}) + 0.08(\text{Total Mo}) + 0.00001(\text{Total P})$	R^2=0.99 $p<0.001$
		$y = -0.08 + 0.01(\text{pH}) + 0.08(\text{Total Mo}) + 0.00001(\text{Total P})$	R^2=0.99 $p<0.001$
		$y = -0.09 + 0.01(\text{pH}) + 0.09(\text{Total Mo})$	R^2=0.98 $p<0.001$
	DTPA-Zn	$y = -3.07 – 1.04(\text{pH}) + 0.38(\text{OM}) + 0.19(\text{Total Zn}) + 0.0003(\text{Total P})$	R^2=0.97 $p<0.001$
		$y = -3.16 – 1.07(\text{pH}) + 0.38(\text{OM}) + 0.20(\text{Total Zn})$	R^2=0.97 $p<0.001$
		$y = -2.82 – 1.09(\text{pH}) + 0.21(\text{Total Zn})$	R^2=0.97 $p<0.001$

Table 1.12. Reverse stepwise multiple regression between plant available micronutrients (DTPA-extractable) and other soil properties for the micronutrients with significant changes at the beef manure site.

Manure	Response	Equation	Statistics (n=12)
Beef	DTPA-B	$y = -0.64 + 0.05(\text{pH}) + 0.01(\text{OM}) + 0.03(\text{Total B}) + 0.0007(\text{Total P})$	$R^2=0.77$ $p=0.020$
		$y = -0.07 + 0.01(\text{OM}) + 0.02(\text{Total B}) + 0.0007(\text{Total P})$	$R^2=0.77$ $p=0.006$
		$y = -0.03 + 0.02(\text{Total B}) + 0.0007(\text{Total P})$	$R^2=0.77$ $p<0.001$
		$y = 1.36 + 0.0006(\text{Total P})$	$R^2=0.74$ $p=0.013$
	DTPA-Cu	$y = 4.36 - 0.65(\text{pH}) + 0.02(\text{OM}) + 0.21(\text{Total Cu}) - 0.0003(\text{Total P})$	$R^2=0.89$ $p=0.002$
		$y = 4.41 - 0.64(\text{pH}) + 0.20(\text{Total Cu}) - 0.0002(\text{Total P})$	$R^2=0.89$ $p<0.001$
		$y = 4.40 - 0.57(\text{pH}) + 0.15(\text{Total Cu})$	$R^2=0.88$ $p<0.001$
		$y = -0.86 + 0.20(\text{Total Cu})$	$R^2=0.84$ $p<0.001$
	DTPA-Fe	$y = 40.0 - 3.63(\text{pH}) - 0.10(\text{OM}) - 0.0005(\text{Total Fe}) + 0.001(\text{Total P})$	$R^2=0.87$ $p=0.004$
		$y = 38.7 - 3.86(\text{pH}) - 0.0003(\text{Total Fe}) + 0.001(\text{Total P})$	$R^2=0.86$ $p=0.001$
		$y = 36.5 - 4.11(\text{pH}) + 0.002(\text{Total P})$	$R^2=0.85$ $p<0.001$
	DTPA-Mn	$y = 249 - 17.6(\text{pH}) - 1.05(\text{OM}) - 0.22(\text{Total Mn}) + 0.01(\text{Total P})$	$R^2=0.87$ $p=0.004$
		$y = 263 - 18.2(\text{pH}) - 0.25(\text{Total Mn}) + 0.01(\text{Total P})$	$R^2=0.85$ $p<0.001$
		$y = 162 - 18.2(\text{pH}) + 0.02(\text{Total P})$	$R^2=0.81$ $p<0.001$
		$y = 10.7 + 0.02(\text{Total P})$	$R^2=0.77$ $p<0.001$
	DTPA-Mo	$y = 0.48 - 0.06(\text{pH}) - 0.004(\text{OM}) + 0.27(\text{Total Mo}) + 0.00001(\text{Total P})$	$R^2=0.90$ $p=0.002$
		$y = 0.47 - 0.06(\text{pH}) - 0.004(\text{OM}) + 0.38(\text{Total Mo})$	$R^2=0.89$ $p<0.001$
	DTPA-Zn	$y = -0.08 - 2.38(\text{pH}) + 0.08(\text{OM}) + 0.31(\text{Total Zn}) + 0.0007(\text{Total P})$	$R^2=0.99$ $p<0.001$
		$y = -5.20 - 1.83(\text{pH}) + 0.33(\text{Total Zn}) + 0.0007(\text{Total P})$	$R^2=0.99$ $p<0.001$
		$y = -21.9 + 0.35(\text{Total Zn}) + 0.0007(\text{Total P})$	$R^2=0.99$ $p<0.001$
		$y = -23.2 + 0.38(\text{Total Zn})$	$R^2=0.99$ $p<0.001$

Table 1.13. Reverse stepwise multiple regression between plant available micronutrients (DTPA-extractable) and other soil properties for the micronutrients with significant changes at the swine effluent site.

Manure	Response	Equation	Statistics (n=12)
Swine	DTPA-B	y = -20.6 + 2.20(pH) - 0.03(OM) - 0.004(Total B) + 0.01(Total P)	R^2=0.44 p=0.33
		y = -21.3 + 2.26(pH) - 0.03(OM) + 0.01(Total P)	R^2=0.44 p=0.18
		y = -18.4 + 1.94(pH) + 0.01(Total P)	R^2=0.41 p=0.09
		y = 0.42 + 0.004(Total P)	R^2=0.19 p=0.15
	DTPA-Cu	y = -3.29 + 0.16(pH) - 0.02(OM) + 0.25(Total Cu) + 0.001(Total P)	R^2=0.90 p=0.002
		y = -1.75 - 0.02(OM) + 0.26(Total Cu) + 0.0004(Total P)	R^2=0.89 p<0.001
		y = -1.71 - 0.02(OM) + 0.27(Total Cu)	R^2=0.89 p<0.001
		y = -1.83 + 0.27(Total Cu)	R^2=0.88 p<0.001
	DTPA-Mo	y = -0.37 + 0.04(pH) - 0.001(OM) + 0.07(Total Mo) + 0.0002(Total P)	R^2=0.55 p=0.18
		y = -0.26 + 0.03(pH) + 0.06(Total Mo) + 0.0001(Total P)	R^2=0.46 p=0.15
		y = -0.23 + 0.0002(Total P)	R^2=0.36 p=0.13
		y = 0.01 + 0.00007(Total P)	R^2=0.27 p=0.08
	DTPA-Zn	y = -78.7 + 5.88(pH) - 0.37(OM) + 0.24(Total Zn) + 0.04(Total P)	R^2=0.98 p<0.001

Table 1.14. Micronutrient concentrations in wheat tissue (sampled at Feeke's growth stage 6.0) and grain samples harvested at maturity from the biosolids site.

Wheat Tissue						
N Rate	B	Cu	Fe	Mn	Mo	Zn
kg N ha^{-1}			mg kg^{-1}			
0	4.14a*	14.5a	133a	29.7a	0.00a	16.8a
45	5.34a	10.4a	146a	51.8b	0.10a	15.2a
90	8.53a	10.1a	148a	35.3ab	0.38bc	17.7a
180	3.89a	10.1a	107a	37.5ab	0.30b	33.9b
269	7.10a	11.6a	113a	41.7ab	0.45bc	40.4b
539	5.32a	11.8a	105a	32.5a	0.54c	45.5b

Wheat Grain						
N Rate	B	Cu	Fe	Mn	Mo	Zn
kg N ha^{-1}			mg kg^{-1}			
0	BDL	5.84a	28.5a	42.6ab	0.23a	39.4a
45	BDL	5.16ab	26.8a	56.0b	0.29a	37.7a
90	BDL	4.62b	26.4a	37.9a	0.43ab	37.6a
180	BDL	3.45c	26.0a	36.0a	0.70b	50.8ab
269	BDL	3.61c	28.5a	43.8ab	0.55ab	57.7b
539	BDL	4.20bc	28.2a	39.2a	0.68b	56.4b

* The same letter in the same column for each site denotes no statistical difference ($p>0.05$).

FIGURES

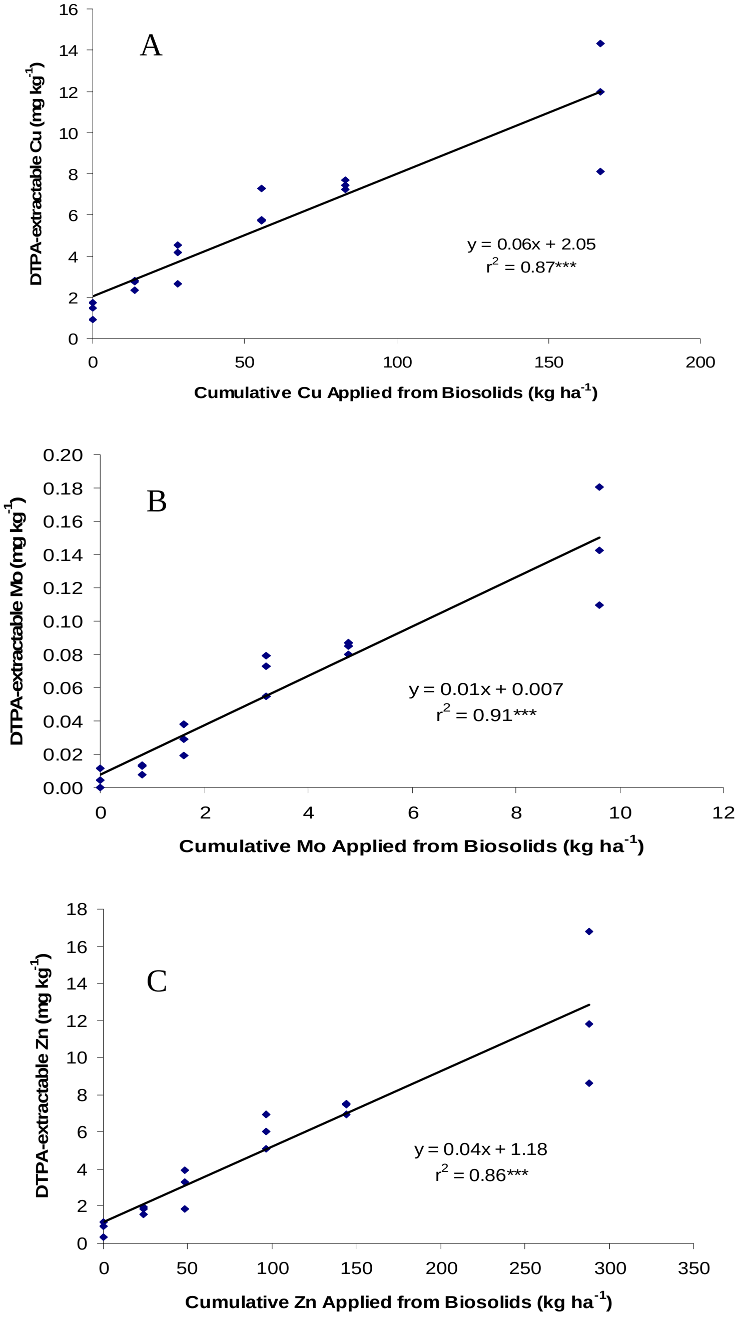

Figure 1.1. The relationship between DTPA-extractable micronutrients and corresponding amount of that nutrient applied from biosolids (A:Cu, B:Mo, C:Zn)
*** Denotes $p<0.001$

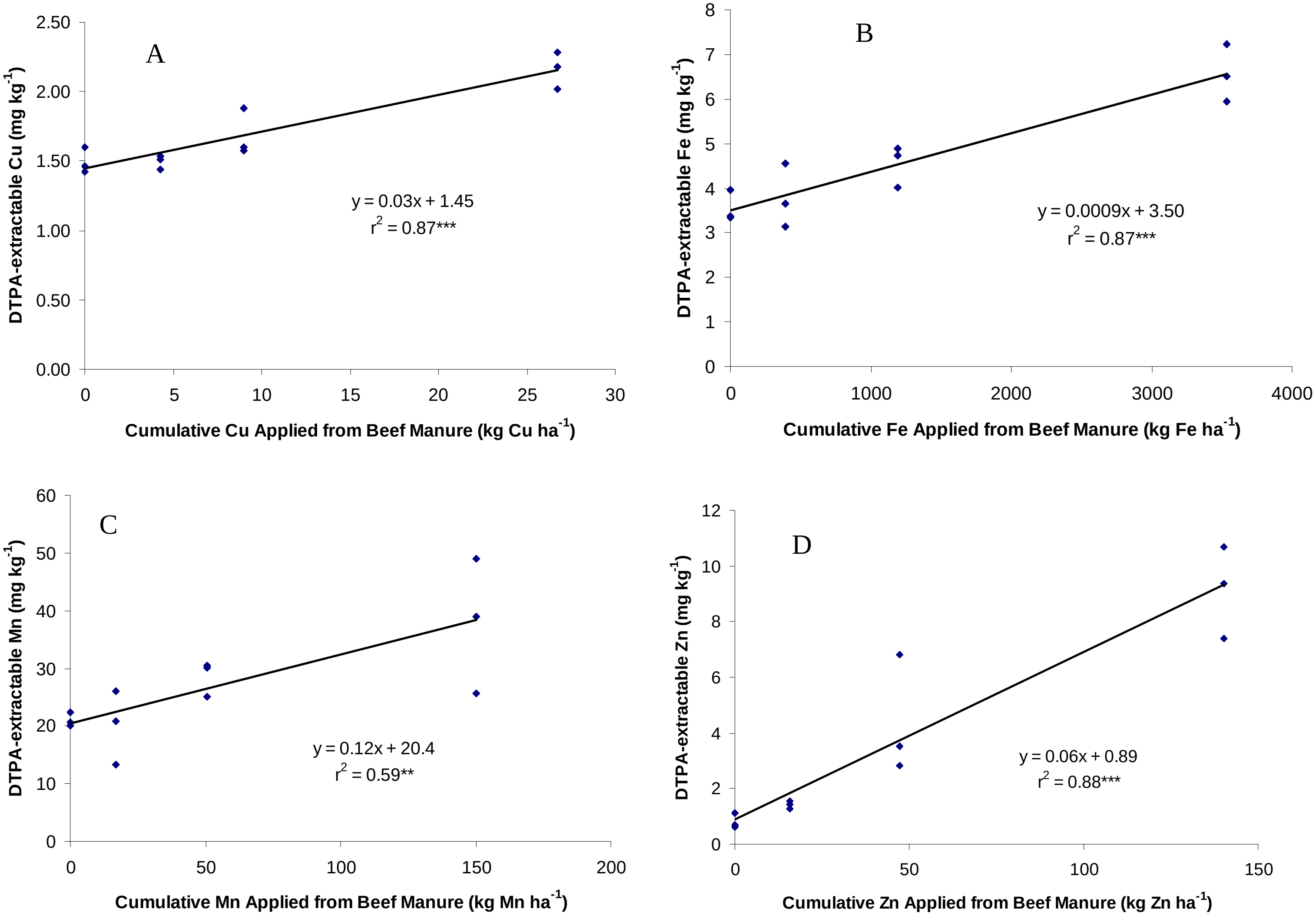

Figure 1.2. The relationship between DTPA-extractable micronutrients and corresponding amount of that nutrient applied from beef manure (A:Cu, B:Fe, C:Mn, D:Zn)
*** Denotes $p<0.001$
**Denotes $p<0.01$

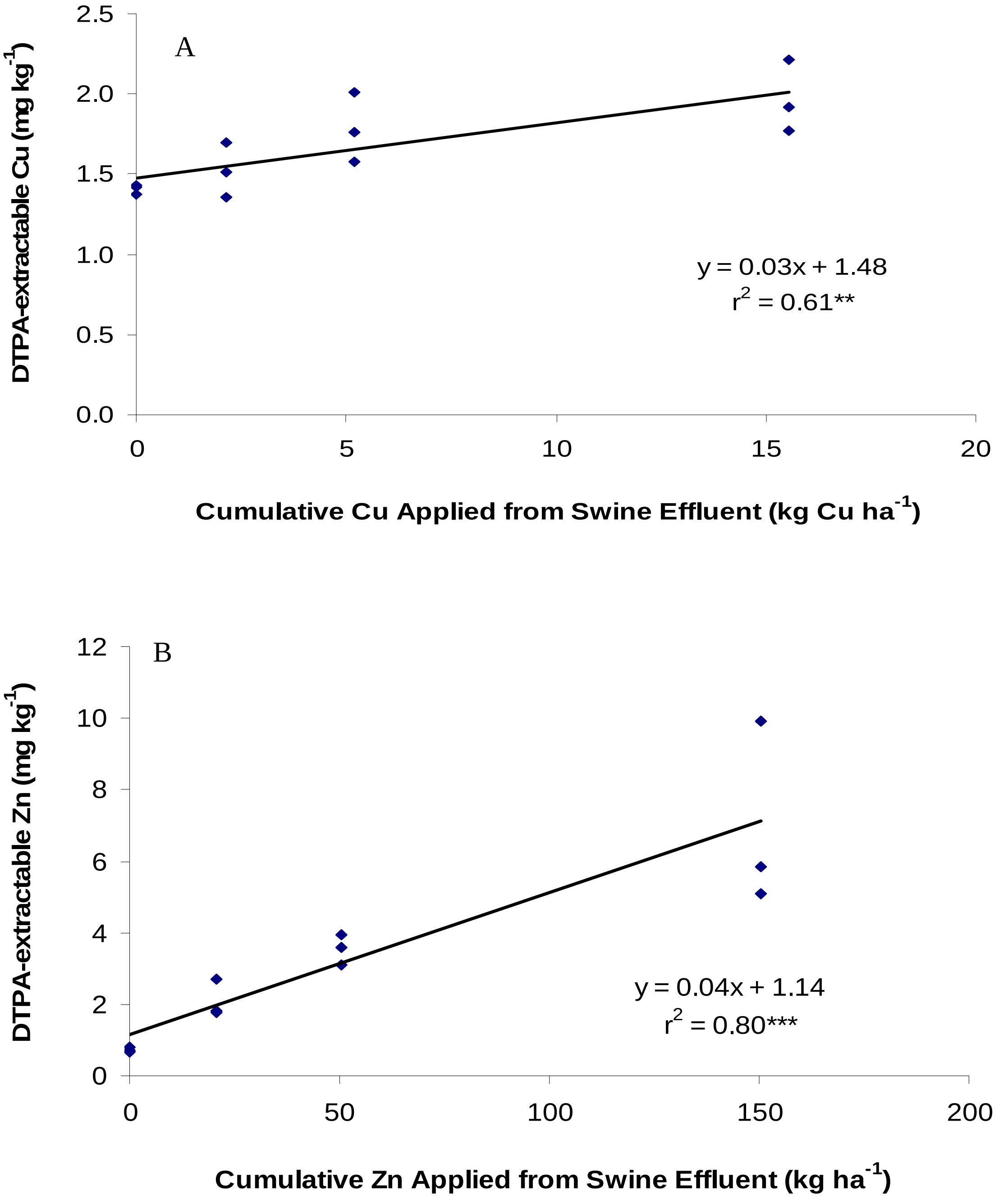

Figure 1.3 The relationship between DTPA-extractable micronutrients and corresponding amount of that nutrient applied from beef manure (A:Cu, B:Zn)

*** Denotes $p<0.001$

**Denotes $p<0.01$

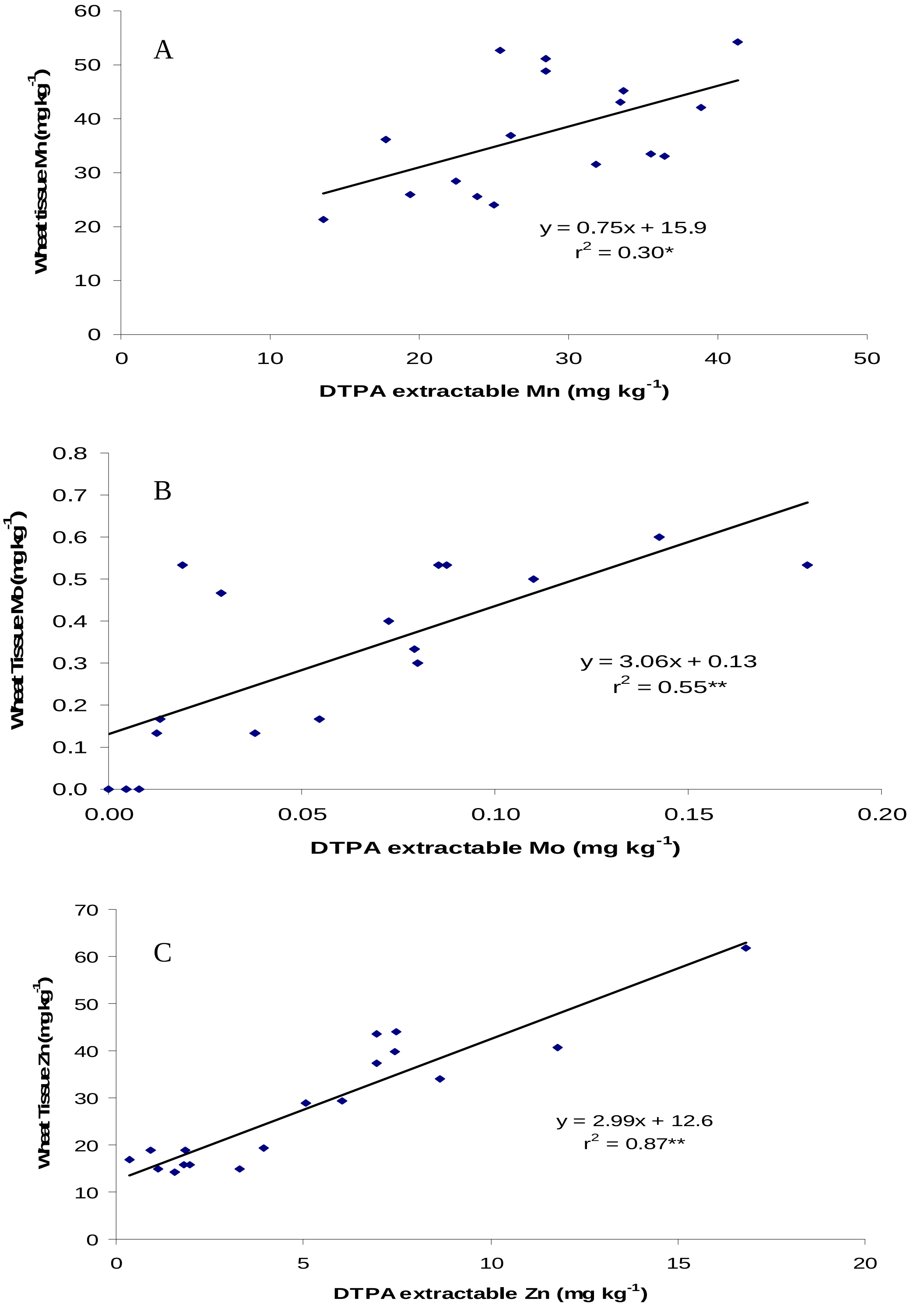

Figure 1.4. The relationship between wheat tissue micronutrient concentrations and DTPA-extractable micronutrients for soil samples collected from the biosolids site (A:Mn, B:Mo, C:Zn)

* $p<0.05$

**$p<0.01$

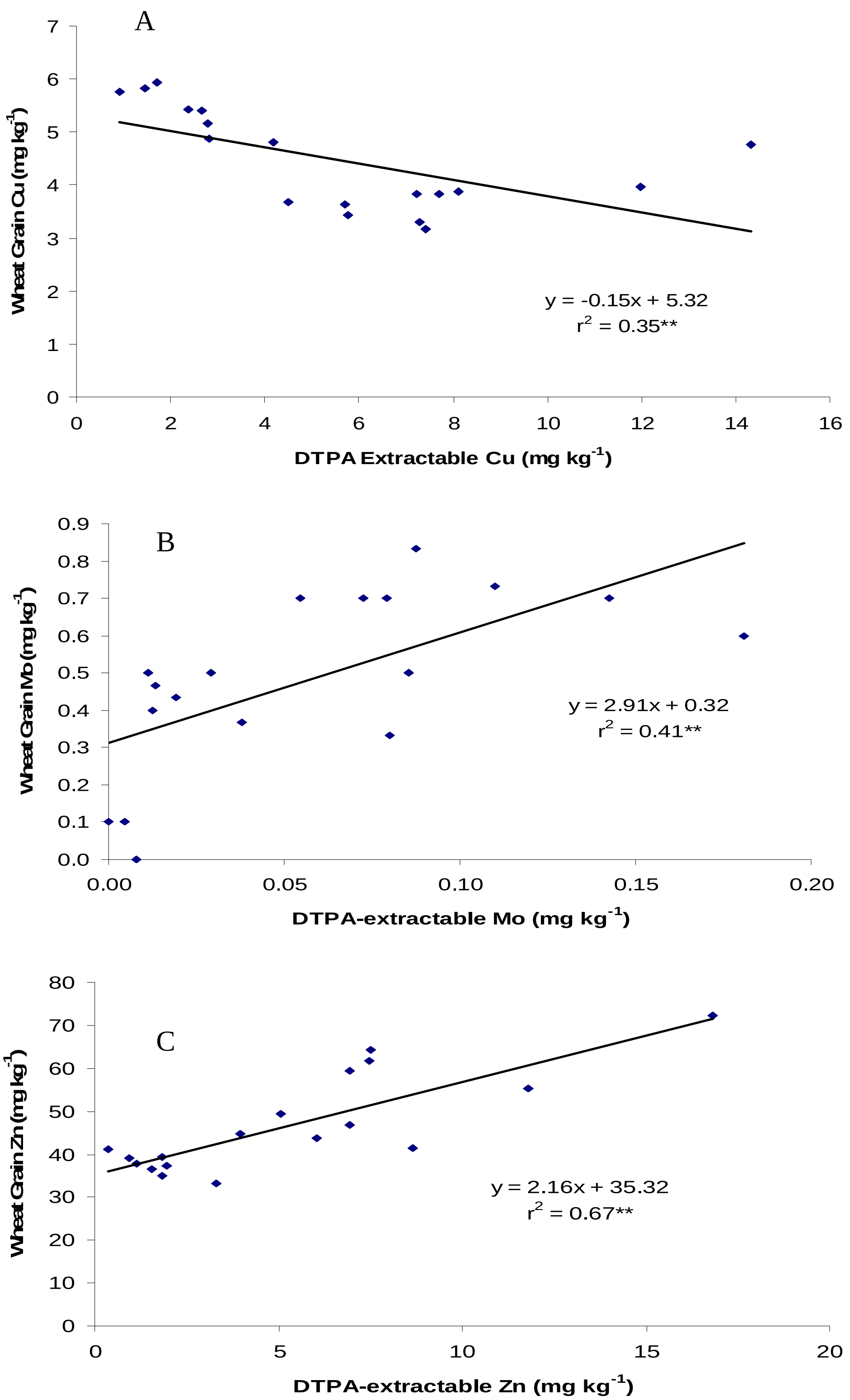

Figure 1.5. The relationship between wheat grain micronutrient concentrations and DTPA-extractable micronutrients for soil samples collected from the biosolids site (A:Cu, B:Mo, :C:Zn)
** $p<0.01$

CHAPTER II

TOTAL ELEMENTS IN THE BENCHMARK SOILS OF OKLAHOMA

INTRODUCTION

Trace elements naturally occur in varying concentrations in surface soils. These concentrations are dependent on the mineralogical composition and chemical characteristics of the parent material (Adriano, 2001). However, trace elements may become an environmental problem when present at elevated concentrations due to their persistence, potential to bioaccumulate, and their mobility in the environment. Thus, some trace elements are often listed as contaminants of potential concern on Superfund sites by the U.S. EPA (U.S. EPA, 2003). In order to accurately evaluate the possible effects of trace elements on the environment and whether anthropogenic activities altered trace element concentrations, a natural background concentration in soil must be determined (Chen et al. 1999).

Numerous studies have been conducted to document baseline soil metal concentrations in the United States and worldwide. However, these studies are normally broad and regional in scope. Chen et al. (1999) documented baseline levels of Silver (Ag), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd,) chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), and zinc (Zn) in Florida using 448 soils. Total iron (Fe) and aluminum (Al) as well as organic carbon (OC) and clay content were found to have strong correlations with total soil trace elements (Chen et al., 1999). Shacklett and Boerngen (1984) documented levels of 30 elements in soils across the United States using 863 sample sites. Tack et al. (1997) documented As, Cd, cobalt (Co), Cr, Cu, Hg, Ni, Pb and Zn levels in soils of Flanders, Belgium. Strong correlations were found between soil trace elements and clay content. While these regional studies are very useful, soil remediation often requires site-specific baseline concentrations. While this is impossible considering that contamination has already taken place; it is possible to provide soil series specific background concentrations to aid in remediation activities.

Few soil series-specific studies documenting background trace element concentrations have been conducted and even fewer still in Oklahoma. Lee et al. (1997) used x-ray fluorescence to document levels of Cu, Co, Fe, Ni, and Pb throughout the profiles of six Oklahoma soil series. The concentrations of the metals studied were found to be dependent on the clay content of the soils (Lee et al., 1997).

In order to determine baseline trace element concentrations, uncontaminated soils must be used. Also, to make these concentrations relevant, benchmark soils should be used. Benchmark soils are defined as being prevalent over one or more major land resource areas, having a large amount of data, holding special importance to one or more land uses, or being ecologically important (USDA NRCS, 2009). Benchmark soils are important because their data can be extrapolated to other similar soils (USDA NRCS, 2009). This data is useful for many applications including soil fertility, soil remediation, and land use planning. If these benchmark soils are collected from areas that have had minimal exposure to anthropogenic activities, the soils can be used to determine normal background levels in a particular area. The objectives of this study were 1) to quantify the background total trace element concentrations including cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), and zinc (Zn) in 28 Oklahoma benchmark soils and 2) to determine the relationship between soil properties and these concentrations.

MATERIALS AND METHODS

Twenty-eight Oklahoma benchmark soils originally classified by Gray and Roozitalab (1976) were selected for this study. Study soils represent the diversity of soils in Oklahoma as well as the major land resource areas (Figure 2.1) (Zhang et al. 2005). The soils were originally collected by Scott (1994). One sample per soil type was chosen for this study. The soils had no known history of biosolids application and had not received manure or commercial fertilizers within three yr of collection. Soils were collected from areas at least 5 km from any industrial stack emitter, at least 500 m from U.S. and state highways, and 25 m from field boundaries. The soils were sampled from the surface horizon (A horizon) then air-died and ground to pass a 2.0 mm sieve. Because exact management histories are impossible to determine, small amounts of anthropogenic metals from fertilizers, lime, manures, and pesticides could have been introduced to these soils. Oklahoma has a diverse paleoclimate and geology with soils that represent six of the twelve soil orders. The samples selected contained all six soil orders (Table 2.1).

Soil samples were digested in duplicate by U.S.EPA Method 3050B (U.S.EPA, 1996) and analyzed for total Cd, Cr, Cu, Mn, Mo, Ni, Pb, and Zn using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). EPA Method 3050B involves digesting a one gram soil sample by the addition of trace metal grade HNO_3, H_2O_2, and HCl. While EPA Method 3050B technically is not technically a true total digestion, it was used in this study because it is a good measure of metals that could potentially become environmentally available. Blanks and certified biosolids-treated reference soil (CRM 005-050, RTC Corporation, Laramie, WY USA) were analyzed with each digestion for quality control. One certified reference soil and one blank was included for every ten samples. Acceptable recoveries for the certified reference soil were ±10% of certified values. Acceptable blank concentrations of individual trace elements were below the established method detection limits. Lab duplicates of each benchmark soil were analyzed.

The soil properties of organic carbon (OC), pH, acidified ammonium oxalate-extractable Al (Al_{ox}) and Fe (Fe_{ox}), cation exchange capacity (CEC), and clay content analyzed by Scott (1994) were utilized for this study. Soil OC was determined by acid dichromate as described by Heanes (1984). Soil pH was determined from a 1:2 soil/0.01 CaCl2 solution (McLean, 1982). Iron and aluminum oxides were determined by shaking 1.5-g samples of soil with 30mL of 0.5M (COONH4) 2·H2O at pH 3.0 in 50-mL centrifuge tubes (Schoumans, 2000) for 2h, in the dark, on an end-to-end shaker at 150 opm and centrifuged for 10 min at 5211••X g (Davis et al. 2005). Supernatants were analyzed for Al, and Fe using ICP–AES. Clay content was determined by the hydrometer method described by Gee and Bauder (1986).

Statistical Analysis

Statistical analyses were conducted using PC SAS Version 9.1 (SAS Institute, Cary, NC). Backward stepwise regression analysis and path analysis were used to evaluate the effect of soil properties on trace element content in soil. Backward stepwise regression analysis was utilized to derive empirical models capable of predicting trace element content based on soil properties. Soil properties that were not statistically significant ($p > 0.05$) were eliminated from the multiple regression equation.

Path analysis partitions simple correlation coefficients between dependent variables (trace element content) and independent variables (soil properties), thus distinguishing between correlation and causation (Afifi and Clark, 1984; Basta et al., 1993). Path analysis is capable of indicating the relative strength of causal relationships by providing a arithmetical value for direct and indirect effects (Loehlin, 1987). Path coefficients represent direct effects and are standardized partial regression coefficients (Basta et al., 1993).

A path analysis model similar to those utilized by Basta et al. (1993) and Zhang et al. (2005) was also used to evaluate the relationships between trace element content and soil properties (Figure 2.2). Single-headed arrows represent direct effects of soil properties on trace element content whereas coefficients of intercorrelations between soil properties are displayed with double-headed arrows. The product of one double-headed arrow and one single-headed arrow determine the effects of indirect effects of soil properties on trace element content. The independent variables of the model were soil pH, OC content, clay content, CEC, Al_{ox}, and Fe_{ox}. For the path analysis model, direct and indirect effects were obtained using multiple regression of soil properties on trace element content and simple correlations between soil properties (SAS Institute, 2004). The uncorrelated residue was calculated using the following equation:

$$U = \sqrt{1 - R^2} \qquad [1]$$

where R^2 is the coefficient of determination. Path analysis results were calculated from the following equations (Williams et al., 1990):

$$r_{17} = P_{17} + r_{12}P_{27} + r_{13}P_{37} + r_{14}P_{47} + r_{15}P_{57} + r_{16}P_{67} \qquad [2]$$

$$r_{27} = r_{12}P_{17} + P_{27} + r_{23}P_{37} + r_{24}P_{47} + r_{25}P_{57} + r_{26}P_{67} \qquad [3]$$

$$r_{37} = r_{13}P_{17} + r_{23}P_{27} + P_{37} + r_{34}P_{47} + r_{35}P_{57} + r_{36}P_{67} \qquad [4]$$

$$r_{47} = r_{14}P_{17} + r_{24}P_{27} + r_{34}P_{37} + P_{47} + r_{45}P_{57} + r_{46}P_{67} \qquad [5]$$

$$r_{57} = r_{15}P_{17} + r_{25}P_{27} + r_{35}P_{37} + r_{45}P_{47} + P_{57} + r_{56}P_{67} \qquad [6]$$

$$r_{67} = r_{16}P_{17} + r_{26}P_{27} + r_{36}P_{37} + r_{46}P_{47} + r_{56}P_{57} + P_{67} \qquad [7]$$

where r_{ij} is the simple correlation coefficient between soil property and trace element content, P_{ij} are path coefficients (direct effects) and $r_{ij}P_{ij}$ are the indirect effects of soil property on trace element content. Subscript designations are: (1) pH, (2) OC content, (3) clay content, (4) CEC (5) Al_{ox} and (6) Fe_{ox} (Figure 2.2).

Williams et al. (1990) conveniently summarized path analysis results in a concise table consisting of a matrix with the main diagonal representing direct effects and off-diagonal elements representing indirect effects. The position of each element in the matrix corresponds to its position in the normal equations presented above.

In order to satisfy the assumption of normality for statistical analysis, the total trace metal data was either log transformed (Cu, Mn, Mo, and Zn) or square root transformed (Cd, Cr, Ni, and Pb) (Tack et al. 1997, Chen et al. 1999).

RESULTS AND DISCUSSION

Soil Properties

The 28-benchmark soils of Oklahoma had a wide range of physical and chemical properties (Table 2.2). The range of soil properties describes the diverse parent materials and climates of the different regions of Oklahoma. Soil pH ranged from acidic to basic (4.3-8.1). This wide range of soil pH indicates that a wide range of metal species exists, from unavailable to readily available for plant uptake. Soil organic carbon and clay content ranged from 4.0-30 and 70.0-660 g kg^{-1}, respectively. This wide range of OC improves the ability to determine which metals have a strong affinity for OC. The cation exchange capacity (CEC) varied from 1.9-39 cmol kg^{-1}. This range in CEC is much narrower than that found for Florida soils by Chen et al. (1999). Concentrations of Al_{ox} and Fe_{ox} concentrations ranged from 140-2000 and 120-9600 mg kg^{-1}, respectively. These wide ranges in soil physical and chemical properties are conducive to the identification of the factors that control trace element concentrations in soil.

Baseline Trace Element Concentrations

Concentrations of the trace elements Cd, Cr, Cu, Mn, Mo, Ni, Pb, and Zn varied among soil series (Table 2.3). The levels of Cd ranged from BDL to 0.80 mg kg^{-1}. Values for Cd were at the upper end of the range found for Florida soils by Chen et al. (1999). The maximum concentration for Cd occurred in the Osage soil.

Concentrations of Cr and Cu ranged from 4.30 to 69.7 mg kg^{-1} and 1.94 to 32.7 mg kg^{-1}, respectively (Table 2.3). Chromium concentrations in the benchmark soils of Oklahoma were within the same range as those in Florida soils (Chen et al., 1999). However, when compared to soils of the U.S. the Cr concentrations in the Oklahoma soils tended to be toward the lower end of the range documented by Shacklette and Boerngen (1984). Copper concentrations were generally larger in the benchmark soils of Oklahoma than those found in Florida soils (Chen et al., 1999). However, Cu concentrations in soils across the U.S. were generally larger than those in Oklahoma soils (Shacklette and Boerngen, 1984). Copper concentrations in the present study agreed well with those found by Lee et al. (1997), which utilized six of the benchmark soils of Oklahoma. The discrepancies can most likely be attributed to the fact that X-ray fluorescence was used by their study, while the present study used EPA Method 3050B digestion and ICP-AES.

Total soil Mn and Mo levels ranged from 27.4 to 2165 mg kg^{-1} and 0.10 to 1.06 mg kg^{-1}, respectively (Table 2.3). Mn concentrations in Oklahoma soils were higher than those found in Florida soils (Chen et al., 1999) and within the range found in soils of the U.S. (Shacklette and Boerngen, 1984). Molybdenum levels in Oklahoma soils were generally low, but were within the ranges set forth by both Chen et al. (1999) and Shacklette and Boerngen (1984).

Maximum Ni and Pb concentrations were found in the Summit soil at 57.3 mg kg^{-1} and 31.7 mg kg^{-1}, respectively. Nickel concentrations in Oklahoma soils were somewhat higher than those in Florida soils (Chen et al., 1999), but agreed well with the range found in U.S. soils (Shacklette and Boerngen, 1984). Lead concentrations were within the range found by Chen et al. (1999) for Florida soils and were toward the low end of the range of U.S. soils (Shacklette and Boerngen, 1984). The Ni concentrations in this study were generally higher than those found in the study by Lee et al. (1997). On the other hand, Pb concentrations in this study were slightly lower than those found by Lee et al.

(1997) with the exception of the Carnasaw soil in which the concentrations were identical. These discrepancies are probably due to the different methods employed by the two studies.

Minimum and maximum values for Zn were 15.3 and 142 mg kg^{-1}. Oklahoma soil Zn concentrations were generally higher than those found in Florida soils (Chen et al., 1999), but were within the same range found in U.S. soils (Shacklette and Boerngen, 1984).

Simple Regression Analysis

Regression analysis was conducted between total trace elements and soil properties (Table 2.4). Total soil Cu and Ni were significantly correlated ($p<0.05$) with soil pH (Table 2.4). No other trace elements were correlated with soil pH. While at first this may seem surprising, soil pH controls the amount of metal in solution and does not affect the total amount of metal present in the soil. However, these results agree with those found by Chen et al. (1999) with the exception of total soil Cu and Ni. In the study by Chen et. al (1999), no significant correlation existed between soil pH and any of the trace elements analyzed. The trace elements studied were significantly correlated ($p<0.05$) with soil OC with the exception of total soil Mo (Table 2.4). This disagrees with Chen et al. (1999) because in their study only significant correlations occurred between total soil Mn and Ni and soil OC. In the present study, significant correlations between total soil Mo and soil physical and chemical factors were not present. This could be due to the relatively small amount of total Mo present in soil and the difficulties associated with measuring these low concentrations. However, it would be expected that Mo would be correlated with soil OC, because this trace element mainly exists as an oxyanion and should be associated with soil factors that would contribute to variable charge (i.e. OC, Al_{ox}, and Fe_{ox}). This could be explained by the relatively low concentration of this element in vegetation from which the OC would have been created in these benchmark soils of Oklahoma. Total soil Cd, Cr, Cu, Mn, Ni, Pb, and Zn were all correlated with clay content ($p<0.05$) with partial correlation coefficients ranging from 0.57 to 0.88 (Table 2.4). This agrees with Lee et al. (1997) who reported that total soil metals were highly correlated with clay content. The total soil trace elements (with the exception of Mo) were also significantly correlated with soil CEC. This is probably due to the relationship between CEC and clay content. As the Clay content increases, CEC should theoretically increase as well. All of the total soil trace elements, excluding Mo, were also correlated ($p<0.05$) with Al_{ox} and Fe_{ox} (Table 2.4).

Multiple Regression Analysis

Reverse stepwise multiple regression analysis was used to determine which soil physical and chemical characteristics determine total trace element levels (Table 2.5). The best multiple regression model for total soil Cd was found with the soil factors OC and clay content ($R^2=0.71$, $p<0.001$). These findings somewhat agree with Lee et al. (1997) in that Cd was highly correlated with clay content. The reverse stepwise multiple regression model revealed that total soil Cr was most effected by clay content as well as Al_{ox} ($R^2=0.73$, $p<0.001$). The Cr could be associated with clay through surface attraction (CEC) in some cases or by chemisorption onto the clay particles. For total soil Cu, clay content explained the majority of the variation ($R^2=0.67$) and was highly significant ($p<0.001$). Inclusion of other soil chemical and physical properties did not improve the model. It is no surprise that the Cu would be correlated with clay content, but it would be expected that Cu would also be closely associated with OC. This could be explained by the historically low (relative to other regions) OC content of Oklahoma soils due to the hot climate.

The variability for total soil Mn was best explained by the soil factor Al_{ox} ($R^2=0.65$, $p<0.001$) (Table 2.5). The addition of other soil properties did not significantly improve the regression model. This could be due to the coating of Al_{ox} particles with Mn through chemisorption. A reverse stepwise multiple regression was not conducted on total soil Mo because significant correlations did not exist between total soil Mo and any individual soil property examined in this study (Table 2.4). For total soil Ni, the soil properties of clay content and Al_{ox} explained a significant amount of the variability ($R^2=0.83$, $p<0.001$). Results for total soil Pb were similar to those of total soil Cd in that the soil properties OC and Clay content explained a significant amount of variation ($R^2=0.69$, $p<0.001$). The addition of other soil properties did not significantly improve the regression model. A significant amount of the variation in total soil Zn was explained by clay content ($R^2=0.70$, $p<0.001$). The addition of the other soil properties did not significantly improve the model.

Path Analysis

Path analysis was also conducted in order to separate indirect effects from direct effects on total soil trace elements (Table 2.6).

Significant correlations ($p < 0.001$) were found between OC ($r = 0.63$), clay content ($r = 0.81$), CEC ($r = 0.61$), Al_{ox} ($r = 0.72$), and Fe_{ox} ($r = 0.53$) and total soil Cd (Table 2.6). Path analysis found significant ($p < 0.05$) direct effects for OC ($r = 0.56$) and clay ($r = 0.99$) and found the direct effects for pH, CEC, Al_{ox}, and Fe_{ox} were not significant ($p > 0.05$). Path analysis indicated the indirect effect of clay ($r = 0.55$) was an important contributor to the correlation between total Cd in soil and OC. Likewise the indirect effect of OC ($r = 0.31$) contributed greatly to the correlation between clay and total Cd in soil. The indirect effects of OC ($r = 0.42$) and clay ($r = 0.78$) were important contributors to the correlation between Al_{ox} and total soil Cd. Similarly, the indirect effects of OC ($r = 0.40$) and clay ($r = 0.62$) contributed greatly to the correlation between Fe_{ox} and total Cd. The stepwise multiple regression for Cd agreed well with path analysis. Stepwise multiple regression identified the best model was a combination of OC and clay that explained 71% of the variation in total soil Cd.

Significant correlations ($p < 0.001$) were found between OC ($r = 0.63$), clay content ($r = 0.81$), CEC ($r = 0.65$), Al_{ox} ($r = 0.81$), and Fe_{ox} ($r = 0.55$) and total soil Cr (Table 2.6). Path analysis found significant direct effects ($p < 0.05$) for clay ($r = 0.63$) and found the direct effects for pH, OC, CEC, Al_{ox}, and Fe_{ox} were not significant ($p > 0.05$). Path analysis indicated the indirect effect of clay ($r = 0.35$) was an important contributor to the correlation between OC and total Cr in soil. The indirect effect of clay ($r = 0.49$) contributed greatly to the correlation between CEC and total soil Cr. This would be expected due to the relationship between clay content and CEC. As Clay content increases there is normally an increase in CEC. Similarly, the indirect effect of clay ($r = 0.50$) was an important contributor to the correlation between Al_{ox} and total soil Cr. The indirect effect of clay content on Al_{ox} likely exists due to the fact that the amorphous Al_{ox} normally exists in the clay sized fraction of soil. Likewise, the indirect effects of OC ($r = 0.18$) and clay ($r = 0.40$) contributed greatly to the correlation between

Fe_{ox} and total Cr. The relationship between OC and Fe_{ox} could be due to organic matter coating the Fe_{ox} particles. The stepwise multiple regression for Cr agreed well with path analysis. Stepwise multiple regression identified the best model was a combination of Al_{ox} and clay that explained 73% of the variation in total soil Cd.

Significant correlations ($p < 0.001$) were found between OC ($r = 0.53$) clay ($r = 0.82$), CEC ($r = 0.61$), Al_{ox} ($r = 0.75$), and Fe_{ox} ($r = 0.53$) and total soil Cu (Table 2.6). A significant direct effect ($p < 0.05$) was found between clay ($r = 0.76$) and total Cu in soil. Path analysis found no significant ($p > 0.05$) direct effects between pH, OC, CEC, Al_{ox}, and Fe_{ox} and total soil Cu. The indirect effect of clay ($r = 0.59$) contributed greatly to several correlations between soil properties and total soil Cu including the OC, CEC, Al_{ox} and Fe_{ox} correlations with r values ranging from 0.42 to 0.60. These indirect effects could be due to coating of the clay particles by organic matter, the direct relationship between clay and CEC, and the existence of Al_{ox} and Fe_{ox} in the clay sized fraction of the soil. The path analysis model agreed well with the reverse stepwise multiple regression analysis. In the reverse stepwise multiple regression analysis, clay explained 67% of the variability in total soil Cu.

Path analysis showed significant correlations between OC ($r = 0.61$, $p < 0.001$), clay ($r = 0.58$, $p < 0.01$), and Al_{ox} ($r = 0.80$, $p < 0.001$) and total soil Mn (Table 2.6). Soil Al_{ox} levels had a significant ($p < 0.01$, $r = 0.81$) direct effect on total Mn. No significant direct effects on total soil Mn existed from pH, OC, Clay, CEC, and Fe_{ox}. The indirect effect of Al_{ox} contributed greatly to the correlation between OC and total soil Mn ($r = 0.61$) as well as the correlation between total soil Mn and clay ($r = 0.64$). Similarly, the indirect effect of Al_{ox} contributed to the correlation between total soil Mn and CEC ($r =$

0.49). The path analysis model strongly agrees with the reverse stepwise multiple regression model in which 65% of the variation in total soil Mn was explained by Al_{ox} (Table 2.5). The relationship between total soil Mn and Al_{ox} may be explained from Mn sorption onto the surface of the Al_{ox} thus creating a Mn coating.

Significant correlations ($p < 0.001$) were found between OC ($r = 0.58$), clay ($r = 0.88$), CEC ($r = 0.67$), and Al_{ox} ($r = 0.85$) and total Ni in soil (Table 2.6). Path analysis found a significant direct effect by clay alone ($p < 0.01$, $r = 0.75$). No other soil properties had a significant direct effect. However, the indirect effect of Al_{ox} contributed to the correlations between OC ($r = 0.24$) and CEC ($r = 0.19$) and total soil Mn. The indirect effect of clay made large contributions to the correlations between OC ($r = 0.41$), CEC ($r = 0.58$), and Al_{ox} ($r = 0.59$) and total Ni. The path analysis model somewhat agreed with the reverse stepwise multiple regression model. The stepwise multiple regression model found that the soil properties clay and Al_{ox} explained 83% of the variation in total soil Ni (Table 2.5). While the path model did not find Al_{ox} to have a significant direct effect; path analysis did show that the indirect effect of Al_{ox} contributed to the correlations between other soil properties and total soil Ni.

The path analysis model found significant correlations ($p < 0.001$) between OC ($r = 0.73$), clay ($r = 0.72$), Al_{ox} ($r = 0.77$), and Fe_{ox} ($r = 0.60$) and total soil Pb (Table 2.6). Path analysis found significant direct effects ($p < 0.05$) for OC ($r = 0.53$) and clay ($r = 0.61$), while the direct effects of pH, CEC, Al_{ox}, and Fe_{ox} were not significant. The indirect effects of clay ($r = 0.48$) and OC ($r = 0.40$) contributed to the correlation between Al_{ox} and total Pb. Similarly, the indirect effects of clay ($r = 0.38$) and OC ($r = 0.38$) contributed greatly to the correlation between Fe_{ox} and total Pb. Likewise, the indirect effect of clay ($r = 0.34$) contributed to the correlation between OC and Pb. The path model for total Pb agrees well with the reverse stepwise multiple regression model. Clay and OC were the soil properties that had the greatest effect on total soil Pb. In the reverse stepwise multiple regression model, clay and OC explained 69% of the variation in total Pb (Table 2.5).

The path analysis model found highly significant ($p < 0.001$) correlations between clay ($r = 0.84$), CEC ($r = 0.60$), Al_{ox} ($r = 0.71$), and Fe_{ox} ($r = 0.60$) and total soil Zn (Table 2.6). Path analysis also identified a significant ($p < 0.01$) direct effect for clay ($r = 0.88$). The direct effects of pH, OC, CEC, Al_{ox} and Fe_{ox} were not significant ($p > 0.05$). Not surprisingly, the indirect effect of clay greatly contributed to the correlations between CEC, Al_{ox}, and Fe_{ox} and total soil Zn. Once again, the path analysis and reverse stepwise multiple regression models agreed. Path analysis identified a direct effect from clay on total soil Zn, and the stepwise regression model found that clay content explained 70% of the variation in total Zn.

CONCLUSION

Total trace element concentrations varied greatly among soil series in Oklahoma. The ranges of concentrations were in agreement with those found elsewhere in the U.S. The low concentrations and high variability made it difficult to determine which soil properties controlled total soil Mo concentrations. Total soil Cd, Cr, Cu, Ni, Pb, and Zn concentrations were dependent largely on clay content. Organic carbon content also significantly affected total soil Cd and Pb concentrations, while total soil Mn concentrations were dependent upon Al_{ox} levels. Path analysis separated direct effects from indirect effects and proved to be an asset when determining which soil properties controlled total soil trace element concentrations.

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TABLES

Table 2.1. Taxonomic classifications of the 28 benchmark soil series analyzed.

Soil Series	Taxonomic Classification†
Bernow	Fine-loamy, siliceous, thermic Glossic Paleudalf
Burleson	Fine, montmorrillonitic, thermic Udic Haplustert
Carnasaw	Clayey, mixed, thermic Typic Hapludult
Clarksville	Loamy-skeletal, siliceous, mesic Typic Paleudult
Cobb	Fine-loamy, mixed, thermic Udic Haplustalf
Dalhart	Fine-loamy, mixed, mesic Aridic Halpustalf
Darnell	Loamy, saliceous, thermic, shallow, Udic Ustochrept
Dennis	Fine, mixed, thermic Aquic Paleudoll
Dougherty	Loamy, mixed, thermic Arenic Haplustalf
Durant	Fine, montmorrillonitic Vertic Argiustoll
Easpur	Fine-loamy, mixed, thermic Fluventic Haplustolls
Grant	Fine-silty, mixed, superactive, thermic Udic Argiustoll
Kirkland	Fine, mixed, thermic Udertic Paleustoll
Lebron	Coarse-loamy, mixed(calcareous), thermic Typic Ustifluvent
Mansic	Fine-loamy, mixed, thermic Aridic Calciustoll
Osage	Fine, smectitic, thermic Vertic Haplaquoll
Parsons	Fine, mixed, thermic Mollic Albaqualf
Pond Creek	Fine-silty, mixed, thermic Pachic Argiustoll
Pratt	Sandy, mixed, thermic Psammentic Haplustalf
Renfrow	Fine, mixed, thermic Udertic Paleustoll
Richfield	Fine, montmorillonitic, mesic Aridic Argiustoll
St. Paul	Fine-silty, mixed, thermic Pachic Argiustoll
Sallisaw	Fine-loamy, siliceous, thermic Typic Paleudalf
Stiegler	Fine, mixed, thermic Aquic Paleudalf
Summit	Fine, montmorillonitic, thermic Vertic Argiudoll
Tillman	Fine, mixed, thermic Typic Paleustoll
Woodward	Coarse-silty, mixed, thermic Udic Argiustoll
Zaneis	Fine-loamy, mixed, thermic Udic Argiustoll

†USDA-NRCS, 2001

Table 2.2. Soil chemical and physical properties of the 28 benchmark soils of Oklahoma*

Soil	pH	OC	Clay	CEC	Alox	Feox
		g kg^{-1}	g kg^{-1}	cmol kg^{-1}	mg kg^{-1}	mg kg^{-1}
Bernow	4.3	14	110	1.9	290	670
Burleson	5.9	11	420	22	1100	1600
Carnasaw	5.7	28	210	13	1200	1600
Clarksville	5.5	20	260	8.6	1200	1200
Cobb	5.5	4.0	160	4.5	510	360
Dalhart	7.3	4.0	120	13	260	150
Darnell	5.4	5.0	110	2.1	270	240
Dennis	5.7	16	250	10	900	2200
Dougherty	5.2	7.0	80	2.5	190	280
Durant	6.7	25	270	35	800	2300
Easpur	5.9	6.0	220	7.9	420	580
Grant	6.0	8.0	260	9.9	620	640
Kirkland	5.7	11	350	16	860	1300
Lebron	7.9	20	590	33	1100	1100
Mansic	8.1	14	350	34	780	230
Osage	5.6	30	660	30	1600	9600
Parsons	6.5	14	300	13	770	2700
Pond Creek	5.2	10	280	8.4	730	800
Pratt	6.3	4.0	70	6.7	140	120
Renfrow	6.4	14	250	22	640	860
Richfield	7.4	8.0	460	34	1100	670
St. Paul	6.9	11	280	14	890	470
Sallisaw	5.5	12	220	5.1	1200	1300
Stiegler	5.6	23	280	11	1200	4000
Summit	7.6	25	580	39	2000	3400
Tillman	6.4	7.0	340	11	720	820
Woodward	7.7	11	200	22	950	220
Zaneis	5.7	12	210	5.5	800	890
Mean	6.2	13.4	280	15.5	830	1439
Max	8.1	30	660	39	2000	9600
Min	4.3	4.0	70.0	1.9	140	120

*Adopted from Scott (1994)

Table 2.3. Trace element concentrations in the 28 benchmark soils of Oklahoma.

Soil	Cd	Cr	Cu	Mn	Mo	Ni	Pb	Zn
				mg kg^{-1}				
Bernow	BDL	4.83	2.13	27.4	0.26	2.41	5.45	15.3
Burleson	0.36	53.7	14.3	580	0.89	21.6	19.1	67.6
Carnasaw	0.66	51.0	8.43	1690	1.06	25.1	29.0	63.2
Clarksville	0.30	16.7	11.9	2165	0.44	15.3	19.3	59.1
Cobb	BDL	10.7	5.78	106	0.16	7.46	6.04	26.4
Dalhart	BDL	7.14	3.78	98.0	0.18	5.46	4.23	26.5
Darnell	BDL	6.95	3.39	236	0.19	4.91	6.46	24.6
Dennis	0.34	32.8	10.7	515	0.75	19.3	12.9	53.0
Dougherty	BDL	4.63	2.76	133	0.31	2.85	7.81	40.8
Durant	BDL	25.7	10.7	508	0.40	10.9	17.1	45.2
Easpur	0.28	22.6	10.0	388	0.20	15.2	19.9	57.3
Grant	0.25	20.1	9.36	383	0.18	14.3	11.9	47.2
Kirkland	0.29	27.2	14.5	523	0.21	17.5	16.4	61.2
Lebron	0.75	51.0	31.9	658	0.10	37.2	22.6	106
Mansic	0.40	22.4	16.0	332	0.23	15.5	12.3	61.4
Osage	0.80	54.1	31.2	725	0.26	38.0	27.6	142
Parsons	0.73	57.0	20.1	853	0.59	29.4	28.8	94.2
Pond Creek	0.25	19.6	11.5	409	0.18	13.9	12.0	50.6
Pratt	BDL	4.30	1.94	52.6	0.10	3.00	2.60	20.9
Renfrow	BDL	19.9	10.9	292	0.15	12.3	13.7	41.7
Richfield	0.39	29.4	19.4	469	0.34	20.1	15.1	79.5
St. Paul	BDL	19.9	12.1	314	0.15	14.2	10.2	47.8
Sallisaw	BDL	19.7	11.3	1475	0.91	12.3	14.3	51.7
Stiegler	BDL	19.4	32.7	1601	0.39	10.7	20.2	56.7
Summit	0.76	69.7	15.6	2119	0.16	57.3	31.7	72.1
Tillman	BDL	26.4	13.6	506	0.19	19.7	13.3	56.7
Woodward	BDL	19.9	10.4	293	0.13	16.2	7.49	41.5
Zaneis	BDL	16.8	6.43	166	0.24	9.91	9.41	35.0
Mean	0.28	26.2	12.6	629	0.33	16.9	14.9	55.2
Min	BDL	4.30	1.94	27.4	0.10	2.41	2.60	15.3
Max	0.80	69.7	32.7	2165	1.06	57.3	31.7	142
Stdev	0.25	17.8	8.33	607	0.26	12.1	7.90	26.7

Below detection Limits of 0.25 mg kg^{-1}

Table 2.4. Multiple and partial correlation coefficients for trace element concentrations and soil physical and chemical properties of the benchmark soils of Oklahoma

	Partial correlation coefficient (r)						Multiple Correlation Coefficient	
Trace element	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	R^2	F-test
Cd	NS	0.63***	0.81***	0.61***	0.72***	0.53**	0.74	***
Cr	NS	0.63***	0.81***	0.65***	0.81***	0.55**	0.74	***
Cu	0.38*	0.53**	0.82***	0.61***	0.75***	0.53**	0.72	***
Mn	NS	0.61***	0.58**	0.37*	0.80***	0.45*	0.70	***
Mo	NS	NS	NS	NS	NS	NS	0.38	NS
Ni	0.44*	0.58***	0.88***	0.67***	0.85***	0.54**	0.86	***
Pb	NS	0.73***	0.72***	0.51**	0.77***	0.60***	0.73	***
Zn	NS	0.54**	0.84***	0.60***	0.71***	0.60***	0.74	***

NS $p > 0.05$
* $p < 0.05$
** $p < 0.01$
*** $p < 0.001$

Table 2.5. Reverse stepwise multiple regression between total trace element concentrations and soil physical and chemical properties of the benchmark soils of Oklahoma.

Response	Equation	Statistics
Total Cd	$y = -0.25 + 0.04(pH) + 0.02(OC) + 0.002(Clay) - 0.01(CEC) - 0.00(A_{lox}) - 0.00(Fe_{ox})$	$R^2=0.74$ n=14 $p<0.001$
	$y = -0.21 + 0.03(pH) + 0.02(OC) + 0.001(Clay) - 0.01(CEC) - 0.00(Fe_{ox})$	$R^2=0.74$ n=14 $p<0.001$
	$y = -0.03 + 0.01(OC) + 0.001(Clay) - 0.004(CEC) - 0.00(Fe_{ox})$	$R^2=0.73$ n=14 $p<0.001$
	$y = -0.003 + 0.01(OC) + 0.001(Clay) - 0.00(Fe_{ox})$	$R^2=0.72$ n=14 $p<0.001$
	$y = 0.03 + 0.01(OC) + 0.001(Clay)$	$R^2=0.71$ n=14 $p<0.001$
Total Cr	$y = 0.23 + 0.25(pH) + 0.06(OC) + 0.01(Clay) - 0.03(CEC) + 0.001(A_{lox}) - 0.00(Fe_{ox})$	$R^2=0.74$ n=28 $p<0.001$
	$y = 0.08 + 0.30(pH) + 0.05(OC) + 0.01(Clay) - 0.03(CEC) + 0.001(A_{lox})$	$R^2=0.74$ n=28 $p<0.001$
	$y = 1.18 + 0.11(pH) + 0.03(OC) + 0.01(Clay) + 0.001(A_{lox})$	$R^2=0.74$ n=28 $p<0.001$
	$y = 1.79 + 0.03(OC) + 0.01(Clay) + 0.001(A_{lox})$	$R^2=0.73$ n=28 $p<0.001$
	$y = 1.86 + 0.01(Clay) + 0.001(A_{lox})$	$R^2=0.73$ n=28 $p<0.001$
Total Cu	$y = -0.18 + 0.11(pH) + 0.007(OC) + 0.002(Clay) - 0.01(CEC) + 0.0001(Al_{ox}) + 0.00(Fe_{ox})$	$R^2=0.72$ n=28 $p<0.001$
	$y = -0.17 + 0.11(pH) + 0.007(OC) + 0.002(Clay) - 0.01(CEC) + 0.0001(Al_{ox})$	$R^2=0.72$ n=28 $p<0.001$
	$y = -0.25 + 0.12(pH) + 0.01(OC) + 0.002(Clay) - 0.01(CEC)$	$R^2=0.72$ n=28 $p<0.001$
	$y = 0.31 + 0.03(pH) + 0.006(OC) + 0.002(Clay)$	$R^2=0.68$ n=28 $p<0.001$
	$y = 0.47 + 0.005(OC) + 0.002(Clay)$	$R^2=0.68$ n=28 $p<0.001$

	$y = 0.50 + 0.002(Clay)$	$R^2=0.67$ n=28 $p<0.001$
Total Mn	$y = 1.30 + 0.09(pH) + 0.02(OC) + 0.0005(Clay) - 0.02(CEC) + 0.001(A_{lox}) - 0.00004(Fe_{ox})$	$R^2=0.70$ n=28 $p<0.001$
	$y = 1.40 + 0.08(pH) + 0.01(OC) - 0.01(CEC) + 0.001(A_{lox}) - 0.00003(Fe_{ox})$	$R^2=0.69$ n=28 $p<0.001$
	$y = 1.83 + 0.01(OC) - 0.008(CEC) + 0.001(A_{lox}) - 0.00004(Fe_{ox})$	$R^2=0.69$ n=28 $p<0.001$
	$y = 1.87 - 0.007(CEC) + 0.001(A_{lox}) - 0.00003(Fe_{ox})$	$R^2=0.68$ n=28 $p<0.001$
	$y = 1.89 - 0.007(CEC) + 0.001(A_{lox})$	$R^2=0.67$ n=28 $p<0.001$
	$y = 1.88 + 0.001(A_{lox})$	$R^2=0.65$ n=28 $p<0.001$
Total Ni	$y = - 1.60 + 0.49(pH) + 0.03(OC) + 0.01(Clay) - 0.05(CEC) + 0.001(A_{lox}) - 0.0001(Fe_{ox})$	$R^2=0.86$ n=28 $p<0.001$
	$y = - 1.70 + 0.53(pH) + 0.03(OC) + 0.01(Clay) - 0.05(CEC) + 0.001(A_{lox})$	$R^2=0.86$ n=28 $p<0.001$
	$y = - 0.90 + 0.40(pH) + 0.01(Clay) - 0.03(CEC) + 0.001(A_{lox})$	$R^2=0.85$ n=28 $p<0.001$
	$y = 0.32 + 0.18(pH) + 0.005(Clay) + 0.001(A_{lox})$	$R^2=0.84$ n=28 $p<0.001$
	$y = 1.34 + 0.005(Clay) + 0.001(A_{lox})$	$R^2=0.83$ n=28 $p<0.001$
Total Pb	$y = 1.63 + 0.01(pH) + 0.07(OC) + 0.004(Clay) - 0.03(CEC) + 0.0004(A_{lox}) - 0.0001(Fe_{ox})$	$R^2=0.73$ n=28 $p<0.001$
	$y = 1.70 + 0.07(OC) + 0.004(Clay) - 0.03(CEC) + 0.0004(A_{lox}) - 0.0001(Fe_{ox})$	$R^2=0.73$ n=28 $p<0.001$
	$y = 1.70 + 0.09(OC) + 0.005(Clay) - 0.03(CEC) - 0.0001(Fe_{ox})$	$R^2=0.72$ n=28 $p<0.001$
	$y = 1.87 + 0.07(OC) + 0.004(Clay) - 0.02(CEC)$	$R^2=0.71$ n=28 $p<0.001$
	$y = 1.91 + 0.07(OC) + 0.003(Clay)$	$R^2=0.69$ n=28

		$p<0.001$
Total Zn	$y = 0.97 + 0.06(pH) + 0.005(OC) + 0.001(Clay) - 0.008(CEC) + 0.00(A_{lox}) + 0.00(Fe_{ox})$	$R^2=0.74$ n=28 $p<0.001$
	$y = 0.96 + 0.07(pH) + 0.006(OC) + 0.001(Clay) - 0.009(CEC) + 0.00(Fe_{ox})$	$R^2=0.74$ n=28 $p<0.001$
	$y = 0.98 + 0.06(pH) + 0.007(OC) + 0.001(Clay) - 0.009(CEC)$	$R^2=0.74$ n=28 $p<0.001$
	$y = 1.34 + 0.004(OC) + 0.001(Clay) - 0.003(CEC)$	$R^2=0.72$ n=28 $p<0.001$
	$y = 1.34 + 0.003(OC) + 0.001(Clay)$	$R^2=0.71$ n=28 $p<0.001$
	$y = 1.36 + 0.001(Clay$	$R^2=0.70$ n=28 $p<0.001$

Table 2.6. Path analysis between total trace element concentrations and soil physical and chemical properties of the benchmark soils of Oklahoma.

Total Cd

Response	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	r	R^2	U
pH	0.15	0.03	0.41	-0.28	-0.04	0.03	0.30	0.74^{***}	0.51
OC	0.01	0.56^{*}	0.55	-0.21	-0.11	-0.17	0.63		
Clay	0.06	0.31	0.99^{**}	-0.29	-0.11	-0.15	0.81		
CEC	0.11	0.29	0.77	-0.38	-0.09	-0.09	0.61		
Al_{ox}	0.04	0.42	0.78	-0.23	-0.14	-0.15	0.72		
Fe_{ox}	-0.02	0.40	0.62	-0.14	-0.09	-0.24	0.53		

Total Cr

Response	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	r	R^2	U
pH	0.13	0.01	0.26	-0.14	0.06	0.01	0.33	0.74^{***}	0.51
OC	0.01	0.25	0.35	-0.10	0.18	-0.06	0.63		
Clay	0.06	0.14	0.63^{*}	-0.15	0.19	-0.06	0.81		
CEC	0.10	0.13	0.49	-0.19	0.15	-0.03	0.65		
Al_{ox}	0.04	0.19	0.50	-0.11	0.25	-0.06	0.81		
Fe_{ox}	-0.02	0.18	0.40	-0.07	0.15	-0.09	0.55		

Total Cu

Response	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	r	R^2	U
pH	0.31	0.01	0.32	-0.31	0.05	0.00	0.38	0.72^{***}	0.53
OC	0.02	0.17	0.42	-0.23	0.14	0.01	0.53		
Clay	0.13	0.09	0.76^{*}	-0.32	0.15	0.01	0.82		
CEC	0.23	0.09	0.59	-0.42	0.12	0.00	0.61		
Al_{ox}	0.08	0.12	0.60	-0.25	0.19	0.01	0.75		
Fe_{ox}	-0.04	0.12	0.47	-0.15	0.12	0.01	0.53		

Total Mn

Response	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	r	R^2	U
pH	0.18	0.01	0.07	-0.33	0.21	0.02	0.16	0.70^{***}	0.55
OC	0.01	0.27	0.09	-0.24	0.61	-0.13	0.61		
Clay	0.08	0.15	0.16	-0.34	0.64	-0.11	0.58		
CEC	0.13	0.14	0.12	-0.44	0.49	-0.07	0.37		
Al_{ox}	0.05	0.20	0.12	-0.27	0.81^{**}	-0.11	0.80		
Fe_{ox}	-0.02	0.20	0.10	-0.16	0.51	-0.18	0.45		

Total Ni

Response	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	r	R^2	U
pH	0.34	0.01	0.31	-0.31	0.08	0.01	0.44	0.86^{***}	0.37
OC	0.02	0.19	0.41	-0.23	0.24	-0.05	0.58		
Clay	0.14	0.10	0.75^{**}	-0.32	0.25	-0.04	0.88		
CEC	0.25	0.10	0.58	-0.42	0.19	-0.03	0.67		
Al_{ox}	0.09	0.14	0.59	-0.25	0.32	-0.04	0.85		
Fe_{ox}	-0.04	0.13	0.47	-0.15	0.20	-0.07	0.54		

Total Pb

Response	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	r	R^2	U
pH	0.01	0.03	0.26	-0.22	0.04	0.02	0.14	0.73^{***}	0.52

OC	0.00	$\underline{0.53}^{*}$	0.34	-0.16	0.13	-0.11	0.73		
Clay	0.00	0.30	$\underline{0.61}^{*}$	-0.23	0.14	-0.10	0.72		
CEC	0.01	0.27	0.48	$\underline{-0.29}$	0.10	-0.06	0.51		
Al_{ox}	0.00	0.40	0.48	-0.18	$\underline{0.17}$	-0.10	0.77		
Fe_{ox}	0.00	0.38	0.38	-0.11	0.11	$\underline{-0.16}$	0.60		
Total Zn									
Response	pH	OC	Clay	CEC	Al_{ox}	Fe_{ox}	r	R^2	U
pH	$\underline{0.28}$	0.01	0.37	-0.33	0.01	-0.01	0.33	0.74^{***}	0.51
OC	0.02	$\underline{0.19}$	0.49	-0.24	0.03	0.05	0.54		
Clay	0.12	0.11	$\underline{0.88}^{**}$	-0.34	0.03	0.04	0.84		
CEC	0.21	0.10	0.68	$\underline{-0.44}$	0.03	0.02	0.60		
Al_{ox}	0.07	0.14	0.69	-0.27	$\underline{0.04}$	0.04	0.71		
Fe_{ox}	-0.03	0.14	0.55	-0.16	0.03	$\underline{0.07}$	0.60		

§ Direct effects are underlined

* $p<0.05$

** $p<0.01$

*** $p<0.001$

FIGURES

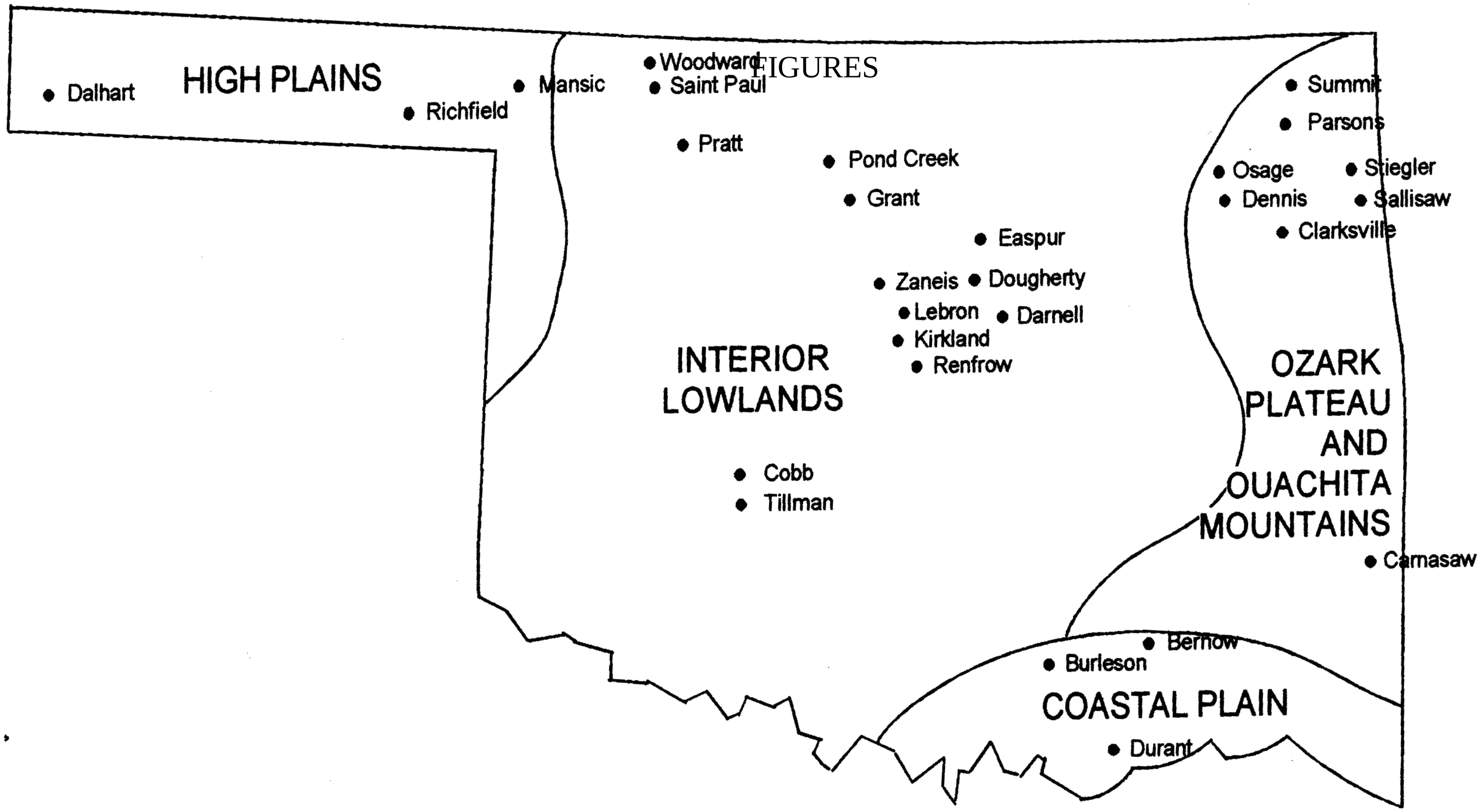

Figure 2.1 Benchmark soils sample sites and regions in Oklahoma (Scott, 1994)

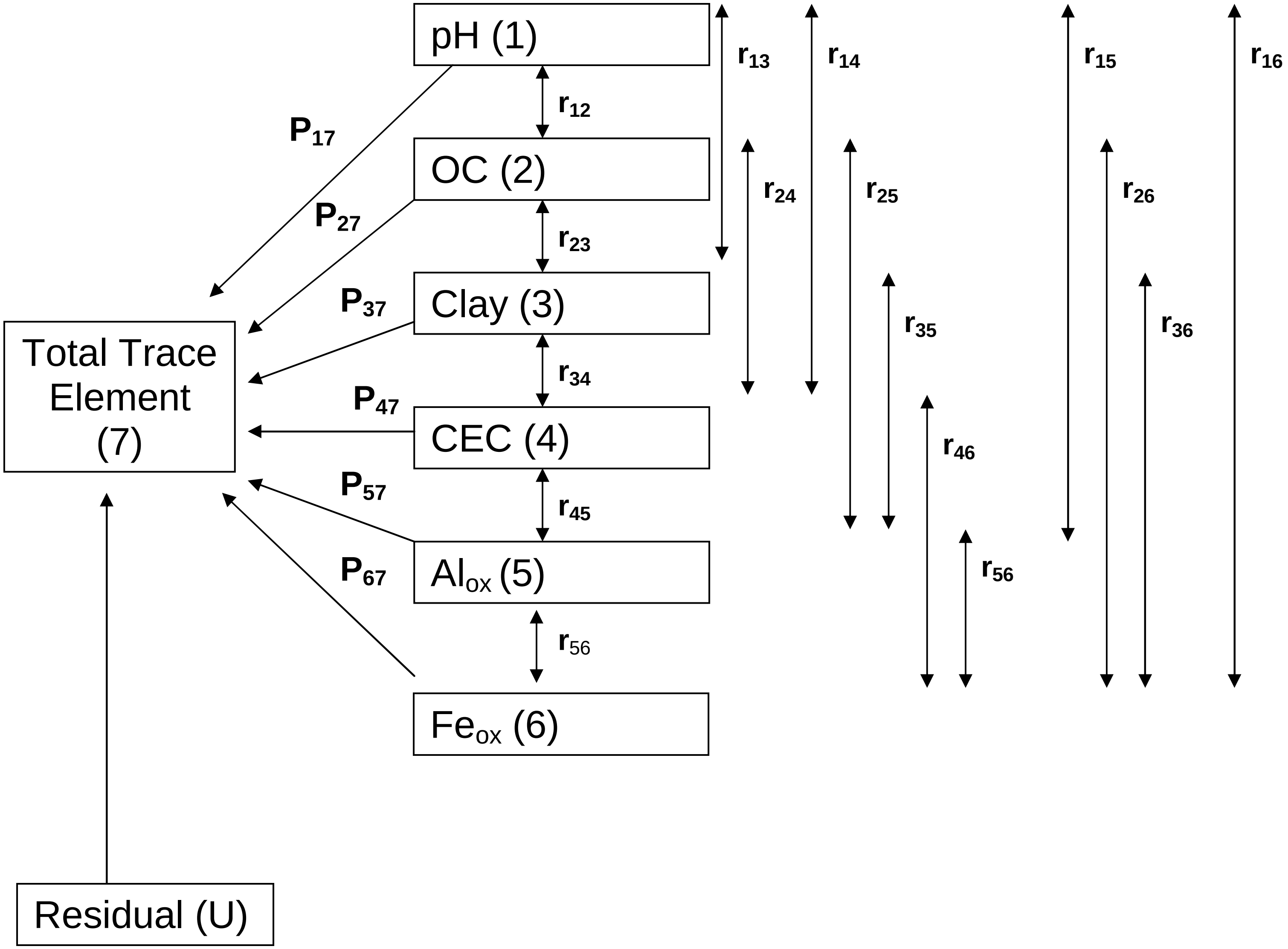

Figure 2.2. Path analysis diagram for the benchmark soils of Oklahoma with six independent variables and one dependent variable.

VITA

Jaben R. Richards

Candidate for the Degree of

Master of Science

Thesis: TRACE ELEMENTS IN OKLAHOMA SOILS: CONTENT, AVAILABILITY, AND THE EFFECT OF PHOSPHORUS FERTILIZER AND ORGANIC AMENDMENT APPLICATION

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Title of Study: TRACE ELEMENTS IN OKLAHOMA SOILS: CONTENT, AVAILABILITY, AND THE EFFECT OF PHOSPHORUS FERTILIZER AND ORGANIC AMENDMENT APPLICATION

Pages in Study: 82 Candidate for the Degree of Master of Science

Major Field: Soil Science

Scope and Method of Study:
Trace elements in soil are important both for the necessity of some for life and for their potential toxicity when present in elevated levels. Micronutrient availability is important to crop production and can be affected by long-term application of phosphorus (P) fertilizer and other amendments. This study was conducted to determine the effects of the long term application of inorganic and variably sourced organic amendments on micronutrient availability. Extractable (DTPA-sorbitol) and total micronutrients were determined from sites that had long-term application of beef manure, swine effluent, biosolids, or commercial fertilizer across Oklahoma. Three continuous inorganic P experiments that have been conducted for 36 to 39 years and two organic amendment experiments that have been conducted for 11-12 years were evaluated. Soil properties including organic matter, pH, and total soil P were also determined. In the case of micronutrient toxicity, baseline levels need to be established in order to determine the extent of anthropogenic influences to a site. Total trace element levels were determined for 28 benchmark soils of Oklahoma and path analysis was used to determine relationships between these trace element levels and the soil properties pH, OC, clay content, CEC, Al_{ox} and Fe_{ox}.

Findings and Conclusions:
Different relationships were observed between DTPA-extractable micronutrients and total P for different P sources. Significant relationships ($p < 0.01$) were found between DTPA-extractable Cu, Zn, Fe, and Mo and total P applied in the biosolids amended plots. For the beef manure plots, significant relationships existed between DTPA-extractable B, Fe, Zn, Cu, and Mn and total P applied. Significant relationships were also found between extractable B, Zn, and Cu and total P applied for the swine effluent plots. However, significant relationships were not found between the vast majority of inorganic commercial P fertilizer treatments and DTPA-extractable micronutrients. Long-term application of organic amendments increased micronutrient availability, but long-term application of inorganic P had no effect on micronutrient availability. Trace element concentrations varied in Oklahoma soils. The trace elements Cd, Cr, Cu, Ni, Pb, and Zn were significantly correlated with clay content while Mn was correlated with Al_{ox}.

ADVISER'S APPROVAL: Hailin Zhang