DISTRIBUTION, SPECIATION, AND BIOAVAILABILITY OF HEAVY METALS IN SOILS OF OKLAHOMA

By

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INTRODUCTION

This thesis consists of two manuscripts that will be submitted for publication in the Journal of Environmental Quality, an American Society of Agronomy publication.

CHAPTER I.

HEAVY METAL DISTRIBUTION OF BENCHMARK SOILS IN OKLAHOMA

ABSTRACT

Total heavy metal content of soil is commonly used to monitor heavy metal accumulation from anthropogenic sources. Background heavy metal levels in soil have been determined on regional and national levels, but information on distribution of heavy metals in geographic regions of Oklahoma is limited. The objectives of this study were to investigate (1) the relationship between total heavy metal content in major soil series and geographical regions in Oklahoma and (2) the distribution of heavy metals within the soil profile. Total amounts of Cd, Co, Cu, Ni, Pb, and Zn were determined by wet digestion in multiple horizons of 28 soil series representing a wide range in soil properties and parent materials. The mean total metal contents of the soils were 0.55 mg kg^{-1} Cd, 14.6 mg kg^{-1} Co, 13.7 mg kg^{-1} Cu, 20.3 mg kg^{-1} Ni, 15.6 mg kg^{-1} Pb, and 58.8 mg kg^{-1} Zn and were within the ranges reported by other studies of heavy metal contents. In general, higher Cd, Ni, Pb, and Zn contents were found in soils from the Ozark Plateau and Ouachita Mountain region. Few differences in heavy metal content were found among soils from the High Plains, Interior Lowlands, and Coastal Plain regions. Most soil profiles (> 68%) showed no significant differences in Cd, Co, Ni, Pb,

and Zn contents among horizons. Those with significant differences, generally showed increased Cd, Ni, and Zn and decreased Co in the lower horizons. Equal numbers of soil profiles showed decreases and increases in Pb content. Copper content varied in most soil profiles (> 50%) had Cu contents that varied, usually exhibiting an increase with depth. Total heavy metal contents showed differences in distribution both within regions and within soil profiles. Heavy metal contents were strongly controlled by parent materials and pedogenic processes that affected metal distribution. Differences in heavy metal content could not be summarized simply by organic matter and clay content relationships in these soils.

INTRODUCTION

Anthropogenic additions of heavy metals to soil is an environmental concern because of their toxicity and persistence in the environment. Excessive contamination with heavy metals has caused Minimata (Hg poisoning) and Itai-itai (Cd poisoning) diseases and focused attention on the environmental impacts of heavy metals in the late 1960's (Adriano, 1986). Since then, the impacts of anthropogenic sources of heavy metals have been evaluated [lime, fertilizers, pesticides, sewage sludge, auto emissions (Pb), and metal smelting industries]. Metal additions to soil may disturb the agroecosystem and introduce large amounts of heavy metal into the food chain. The total heavy metal content of soil is commonly used to monitor heavy metal accumulation (Baker and Chesnin, 1975). The natural levels of heavy metals in soil

originate as trace constituents in igneous rocks and are directly related to soil type (Adriano, 1986; Jenkins and Jones, 1980).

Several studies have provided background heavy metal contents on a local, regional, and national level. Shacklette and Boerngen (1984) reported heavy metal contents of 1,318 sites from the conterminous United States. In their study, soil samples were collected 80 km apart on a grid without regard to soil type. To date, the most extensive sampling of uncontaminated surface soils in the United States has been conducted by Holmgren et al. (1993). Surface samples were collected from 3045 locations representing 307 soil series. It is evident from the variability in heavy metal contents in these studies that natural levels of heavy metal is dependent on the soil type. Many studies have focused on individual states: Ohio (Logan and Miller, 1983), Minnesota (Pierce et al., 1982), Kentucky (Karathanasis and Seta, 1993), and Mississippi (Pettry and Switzer, 1993). Other studies have reported heavy metal contents of Swedish soils (Andersson, 1977), Ontario soils (Whitby et al., 1978), Welsh soils (Davies and Paveley, 1985), and English soils (McGrath, 1986). Although several national studies have provided information on heavy metal content of Oklahoma soils (Holmgren et al., 1993; Shacklette and Boerngen, 1984), the soil series sampled were limited and not representative of many soil series of agronomic importance in Oklahoma. A comprehensive study that includes soil series from major geographical regions of Oklahoma was needed.

Most studies of heavy metal contents have focused on surface soil content. During soil formation, heavy metals are translocated within the profile. Some studies have shown Cd, Cu, Pb, and Zn are concentrated in surface horizons as a result of cycling through vegetation, atmospheric deposition, and adsorption by soil organic matter (Alloway, 1990). However, Sposito and Page (1984) estimated cycling of

metals in grassland soils accounted for only 0.27% of Cd, 0.003% of Co, 0.089% of Cu, 0.016% of Ni, and 0.40% of Zn in the upper 0.05 m of soil. Reviews of other studies report relationships between heavy metal content and soil depth depend on many factors and cannot be easily summarized (Adriano, 1986; Ure and Berrow, 1982) . Most studies have focused on soil surface heavy metal contents and few have investigated the distribution of heavy metals in the soil profile.

The elements observed in this study were Cd, Co, Cu, Ni, Pb, and Zn because of concern over food chain contamination. Cadmium and Pb are both accumulated in animal tissues and are toxic at relatively low concentrations. The other metals are physiologically essential for both plant and animal nutrition; however, several are toxic at relatively low concentrations. Identifying agricultural soils with naturally high or low levels is useful for managing soils and preventing deficiencies or toxicities in both plants and animals. The objectives of this study were: (1) to investigate the relationship among total heavy metal content in major soil series and geographical regions in Oklahoma; and (2) to determine the distribution of heavy metals with depth in the soil profile.

MATERIALS AND METHODS

Sample Collection and Preparation

Samples from soil series were collected by master horizon to a depth of 2 m or bedrock in Oklahoma. The soil series were selected based on agronomic importance and to provide a range of soil properties and parent materials. Each series was

collected in triplicate from a site covering approximately 10 acres. The soils were collected from the following four regions of the state: (1) High Plains, (2) Interior Lowlands, (3) Ozark Plateau and Ouachita Mountains, and (4) Coastal Plain (Fig. 1). The taxonomic classification and parent material of the soil series are summarized in Table 1. Soils were prepared for chemical analysis by air drying and grinding to 2 mm with a stainless steel, flail arm grinder. Soil processing methods were selected to prevent contamination of soil samples with heavy metals (Baker and Amacher, 1982). Approximately 10 g of soil was ground to < 100 mesh using a corundum ball mill for metal analyses. A preliminary study showed the corundum ball mill did not contaminate soil samples with heavy metals (data not shown). The following soil properties were analyzed: soil pH, soil organic carbon (OC), Fe and Mn oxides (Fe_2O_3, MnO), soil texture, and cation exchange capacity (CEC). Soil pH was determined in a 1:2 soil:0.01 M $CaCl_2$ slurry (McLean et al., 1982). Soil organic carbon was analyzed by a modified Mebius method described by Yeomans and Bremner (1988). Iron and Mn oxides were determined by citrate-bicarbonate-dithionite (CBD) extraction developed by Mehra and Jackson (1960). Soil textural analysis was accomplished by the hydrometer method (Gee and Bauder, 1986). Two methods for determining CEC were used for the soils collected. The CEC of acidic and near neutral soils was determined by summation of cations in a barium chloride extract (Hendershot and Duquette, 1986) and the CEC of calcareous soils was determined using the method described by Polemio and Rhodes (1977). The soil property data is summarized by horizon in Table 2.

Sample Analysis

The total amounts of Cd, Co, Cu, Ni, Pb, and Zn were determined by wet digestion of the soil sample with HNO_3, $HClO_4$, and HF acids (Burau, 1982). Severe matrix and interelement spectral interference's prevented direct analysis of the sample digests by atomic absorption spectrophotometry (AA) and inductively coupled plasma atomic emission spectroscopy (ICP). Similar matrix problems with AA (Waughman and Brett, 1980) and ICP (Soltanpour et al., 1982) have been reported for analysis of soil digests with high salt or strong acid contents. Although interelement correction for ICP has been described (Soltanpour et al., 1982), these corrections could not be made by the Jarrell Ash ICP Model 9000 used in this study. Two methods were used to overcome this problem. Cadmium, Co, Ni, Pb, and Zn were removed from the acid sample digest by a solvent extraction procedure and subsequently placed in a matrix suitable for ICP analysis (Øien and Gjerdingen, 1977). The solvent extraction procedure involves removing the Fe interferent with acetylacetone and chloroform and then extracting elements of interest with ammonium pyrrolidine dithiocarbamate (APDC) in chloroform. The chloroform solvent was evaporated and the dithiocarbamate-complexed metals were dissolved in 4 M HNO_3. Since Cu is not quantitatively recovered by the solvent extraction, it was determined by standard additions using three concentrations of spike solutions. The Cu analysis was performed by Atomic Absorption Spectrophotometry (Perkin-Elmer Model 3030B) with deuterium lamp background correction.

Stastical Analysis

Two statistical procedures were used to investigate differences in heavy metal content of soils from different regions. Analysis of variance (ANOVA) was used to find differences in total metal content in soils across regions (Table 5). When differences

were found, a multiple comparison procedure (LSD) was used to investigate regional differences in soil heavy metal content for each horizon (Fig. 2-4). To investigate differences in heavy metal content within the soil profile an analysis of variance and Duncan's Multiple Range Procedure (multiple comparison) was used.

RESULTS AND DISCUSSION

Heavy Metal Content

In general, the relative abundance of the heavy metals was Zn > Ni ≅ Pb > Co ≅ Cu > Cd in the statewide average of heavy metal contents. Total heavy metal content results were summarized for the A, B, and C master horizons and for the composite mean of A, B, and C horizons of the 28 soil series (Table 3). The values in Table 3 were generated from the mean value of the three replicate samples of each soil series. A comparison of total heavy metal contents of surface soils in the present study and previously published values is presented in Table 4. The range in metal contents of the soils in this study were: 0.05 mg kg^{-1} to 2.01 mg kg^{-1} Cd, 6.3 mg kg^{-1} to 63.0 mg kg^{-1} Co, 0.10 mg kg^{-1} to 58.3 mg kg^{-1} Cu, 5.4 mg kg^{-1} to 55.7 mg kg^{-1} Ni, 4.3 mg kg^{-1} to 41.7 mg kg^{-1} Pb, and 18.5 mg kg^{-1} to 222.1 mg kg^{-1} Zn. The heavy metal contents from this study are similar to results reported from previous studies of heavy metal contents but are higher than the results reported by Holmgren et al. (1993) for Oklahoma soils. Cadmium results are the most pronounced with the average reported by Holmgren et al. (1993) as 0.08 mg kg^{-1} and an average of 0.43 mg kg^{-1} for this study.

Several possible explanations exist for the difference in heavy metal content between the two studies of Oklahoma soils. One possibility is that the geographical

regions of Oklahoma sampled by Holmgren et al. (1993) were different than this study. They sampled two series from the High Plains Region, eight series from the Interior Lowlands Region, and two series from the Coastal Plain Region. They did not sample soils from the Ozark Plateau and Ouachita Mountain Region. In general, this region is significantly higher in Cd, Cu, Ni, Pb, and Zn contents than those sampled by Holmgren et al. (1993). A comparison of the four regions is presented later in this section. This study may also be biased by small amounts of anthropogenic heavy metals from fertilizers, lime, and pesticides. Exact management histories were not collected for this study as they were in Holmgren et al. (1993). However, the A horizon does not appear to have large anthropogenic additions because its Cd content is similar to the B and C horizons. Also careful attention was taken to prevent heavy metal contamination during and after sample collection (Baker and Amacher, 1982). The most suspect possibility for the differences in heavy metal contents between the two studies is the wet digestion procedures used. Holmgren et al. (1993) used pressurized wet digestion with HNO_3 to dissolve heavy metals from soil samples. This method does not dissolve heavy metals in primary and secondary minerals (Cuo et al., 1984). In the present study, soil samples were digested by a combination of HNO_3, $HClO_4$ and HF acids. This method dissolves the soil sample and is considered a more complete digestion than HNO_3 alone (Cuo et al., 1984). Even though the digestion procedures were different, heavy metal recoveries from different standard soil reference materials were quantatative in both studies. Many standard soil reference materials contain heavy metal that has been added as metal salts to soils or sediments. Non-occluded, adsorbed, and precipitated heavy metal would be recovered by both digestion procedures. The discrepancy between the heavy metal contents of Oklahoma soils reported in the two studies may be due to a combination of the above factors.

The heavy metal content of Oklahoma soils determined in this study are always within the range reported by Ure and Berrow (1982) for world soils. Ure and Berrow (1982) summarized heavy metal results from studies of uncontaminated soils throughout the world up to 1982. The mean heavy metal contents are reported in Table 4. Cadmium in 1642 soils from studies throughout the world ranged from 0.005 mg kg^{-1} to 8 mg kg^{-1} with a mean of 0.62 mg kg^{-1} Cd. Cobalt ranged from 0.3 mg kg^{-1} to 200 mg kg^{-1} with a mean Co content of 12.0 mg kg^{-1} in 5504 soils collected throughout the world. Copper content in 7819 soils ranged from < 1 mg kg^{-1} to 300 mg kg^{-1} with a mean content of 25.8 mg kg^{-1} Nickel ranged from 0.1 mg kg^{-1} to 1520 mg kg^{-1} with a mean content of 33.7 mg kg^{-1} from 4625 uncontaminated soils. Lead contents in 4970 soils from various heavy metal studies ranged from < 1 mg kg^{-1} to 888 mg kg^{-1} with a mean content of 29.2 mg kg^{-1} Pb. Zinc content of 7402 world soils ranged from 1.5 mg kg^{-1} to 2000 mg kg^{-1} with a mean content of 59.8 mg kg^{-1}. The wide range in heavy metal contents is due to the differences in soil parent materials and geologic soils throughout the world.

Regional Differences

Several studies have shown heavy metal content of soil and parent materials are strongly related (Jenkins and Jones, 1980; Pettry and Switzer, 1993). It is likely that parent materials within geomorphic provinces are more similar with respect to their heavy metal contents than parent materials among different geomorphic provinces. The geographical regions in this study contain materials of various geologic time periods. The High Plains is predominantly composed of Tertiary alluvial deposits formed by ancient rivers draining the Rocky Mountains. The Interior Lowlands contains

mostly Permian sandstones and shales deposited by shallow-marine, deltaic, and alluvial systems. In general, the Ozark Plateau and Ouachita Mountains is dominated by Pennsylvanian and Mississippian deposits exposed by uplift phenomena. The Coastal Plain is composed of sedimentary rocks deposited during the Cretaceous era. Differences in heavy metal composition and the geologic age of the soil parent materials from different regions may result in differences in total heavy metal content of soil.

Regional differences were found for Cd, Ni, Pb, and Zn content in all three horizons and for Cu content in the A horizon (Table 5). No differences were found for Co in any horizon. Cadmium and Pb contents in all horizons, Cu content of the A horizon, and Zn content in the C horizon were greater in soils from the Ozark Plateau and Ouachita Mountain Region than soils from other regions (Fig. 2-4). No differences were found for Cd and Pb between the other three regions. Regional Zn content of the A and B horizons followed the trend Ozark Plateau and Ouachita Mountain Region ≥ High Plains Region ≥ Coastal Plain Region ≥ Interior Lowlands Region. Regional Ni contents in all horizons followed the trend Ozark Plateau and Ouachita Mountain Region ≥ Coastal Plain Region ≥ High Plains Region ≥ Interior Lowlands Region (Fig. 2-4). In summary, regional differences in heavy metal contents existed for all metals of interest except Co. Higher Cd, Ni, Pb, and Zn contents in the Ozark Plateau and Ouachita Mountain Region were found throughout the soil profile and are not consistent with surface contamination from anthropogenic sources. Differences in geologic materials between the regions resulted in the relationships between heavy metal content of soils and geographical regions found in this study.

Soil Profile Differences

Differences in total heavy metal content in individual soil profiles were determined by statistical analysis using Duncan's Multiple Range Procedure (Steel and Torrie, 1980). Results for the individual soil series are listed in the Appendix (Tables A1) and are summarized in Table 6. In general, Cd, Co, Ni, Pb, and Zn did not show differences in total metal content within the soil profiles. The majority of soils showed no change between heavy metal content of soil horizons: 78-89% showed no change between the A and B horizons; 88-100% showed no change between the B and C horizons; and 68-76% showed no change between the A and C horizons. Of the profiles that showed differences in heavy metal contents within the soil profile, the majority increased in Cd, Ni, and Zn and decreased in Co with depth. Equal number of profiles increased as decreased in Pb content within the soil profile. Several studies found Cd and Pb contents tend to be highest at the soil surface (Adriano, 1986; Alloway, 1990; Andersson, 1977; Whitby, 1978). Higher surface contents were attributed to (1) accumulation of metals in vegetation and through other biological processes that predominate in the surface horizon (i.e., bioaccumulation), (2) strong adsorption to organic matter, and (3) contamination from anthropogenic sources. Other studies found Co, Ni, and Zn tend to remain fairly constant with depth (Adriano, 1986; Alloway, 1990). Increased metal contents with depth may be associated with translocation of clay or adsorption of heavy metals by clay in lower horizons (Adriano, 1986; Alloway, 1990; Sposito and Page, 1984; Ure and Berrow, 1982).

In contrast to other metals, total Cu content differed more frequently within the soil profile (Table 6). Comparison of A and B horizons showed 44% of the soils had uniform Cu content, 41% showed increases in the B horizons, and 15% showed

decreases in the C horizon. From the B to C horizon, 58% showed no change, 17% increased, and 25% decreased in total Cu content. The difference in Cu content between the A and C horizons was most pronounced with 40% of the soils showing increased Cu in the C horizon, 24% had decreased Cu in the C horizon, and only 36% of the soils had constant Cu content. Other Cu distribution studies of soil profiles have shown either a decrease in Cu content with depth or uniform Cu contents throughout the profile (Adriano, 1986; Kubota-Pendias and Pendias, 1992). Accumulation of Cu in the surface horizon has been attributed to bioaccumulation and chemical adsorption to organic matter. Copper has a strong affinity for organic matter and forms stable insoluble organic-Cu compounds. In the present study, four soil series showed an accumulation of Cu in the A horizon. Two of these four series also had organic carbon contents > 2%. Most of the soils in this study had low organic C contents (< 2%). Six of the 27 soil series had A horizons with organic C contents > 2%. Only two of these six soil series showed accumulation of Cu in the A horizon. Further investigation showed that accumulation of Cu in the A horizon was not clearly related to the ratio of organic C contents in the A and B horizons. Copper distribution was not solely controlled by organic C contents of the soils studied. Several studies have found that Cu occurs predominantly in primary and secondary mineral clay fractions in soil (Kabata-Pendias and Pendias, 1992); therefore, Cu could be translocated in the profile with the clay fraction. Most of the soils in the present study had argillic horizons, but only 11 of the 27 soils studied showed increases in Cu content from the A to B horizon. Copper distribution was not solely controlled by clay contents of the soils studied.

Several studies have shown relationships between soil properties and heavy metal content (Adriano, 1986; Alloway, 1980; Pettry and Switzer, 1993; Ure and Berrow, 1982). Simple regressions between total metal contents and soil properties

resulted in strong relationships for organic C, clay content, Fe and Mn oxides, and CEC (Table 7). Strong intercorrelations were also found between the following soil properties: (1) clay content and Fe oxide (r = 0.59**), (2) clay content and Mn oxide (r 0.26*), and (3) clay content and CEC (r = 0.70**). The intercorrelation between these soil properties was expected since Fe and Mn oxides occur in the clay fraction and the majority of the CEC in these soils is derived from clay content. Statistical analysis (ANOVA) was conducted to determine differences in soil properties between the soil horizons. Results indicate organic carbon and clay content varied in the soil profile (Table 8). Because many of the soil properties were highly correlated with total metal content, parallel trends were expected between soil properties and heavy metal contents. However, few differences in heavy metal contents within the soil profile were found (Table 8).

Heavy metal distribution within soil is partially controlled by pedogenic processes. Several of these processes such as organic matter accumulation and clay illuviation impact heavy metal distributions. However, because the nature and extent of parent materials and pedogenic processes vary between soils, it is unlikely differences in heavy metal content can be summarized simply by organic matter and clay content relationships.

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Table 1. Taxonomic classification and parent material of the soil series collected in Oklahoma.

Region Soil Series	Taxonomic Classification	Parent Material
High Plains		
Dalhart	Fine-loamy, mixed, mesic Aridic Halpustalf	eolian sand
Mansic	Fine-loamy, mixed, thermic Aridic Calciustoll	alluvium
Richfield	Fine, montmorillonitic, mesic Aridic Argiustoll	loess
Interior Lowlands		
Cobb	Fine-loamy, mixed, thermic Udic Haplustalf	residuum sandstone
Darnell	Loamy, saliceous, thermic, shallow, Udic Ustochrept	residuum sandstone
Dougherty	Loamy, mixed, thermic Arenic Haplustalf	eolian sand
Easpur	Fine-loamy, mixed, thermic Fluventic Haplustolls	alluvium
Grant	Fine-silty, mixed thermic Udic Argiustoll	residuum shale
Kirkland	Fine, mixed, thermic Udertic Paleustoll	alluvium
Lebron	Coarse-loamy, mixed(calcareous), thermic Typic Ustifluvent	alluvium
Pond Creek	Fine-silty, mixed, thermic Pachic Argiustoll	alluvium
Pratt	Sandy, mixed, thermic Psammentic Halpustalf	eolian sand
Renfrow	Fine, mixed, thermic Udertic Paleustoll	residuum shale
Saint Paul	Fine-silty, mixed, thermic Pachic Argiustoll	alluvium / residuum
Tillman	Fine, mixed, thermic Typic Paleustoll	alluvium / residuum
Woodward	Coarse-silty, mixed, thermic Typic Ustochrept	colluvium
Zaneis	Fine-loamy, mixed, thermic Udic Argiustoll	residuum siltstone
Ozark Plateau and Ouachita Mountains		
Carnasaw	Clayey, mixed, thermic Typic Hapludult	residuum shale
Clarksville	Loamy-skeletal, siliceous, mesic Typic Paleudult	residuum limestone
Dennis	Fine, mixed, thermic Aquic Paleudoll	residuum shale
Osage	Fine, smectitic, thermic Vertic Haplaquoll	alluvium
Parsons	Fine, mixed, thermic Mollic Albaqualf	residuum shale
Sallisaw	Fine loamy, siliceous, thermic Typic Paleudalf	alluvium
Stiegler	Fine, mixed, thermic Aquic Paleudalf	residuum shale
Summit	Fine, montmorillonitic, thermic Vertic Argiudoll	residuum shale
Coastal Plain		
Bernow	Fine-loamy, siliceous, thermic Glossic Paleudalf	residuum sandstone
Burleson	Fine, montmorrillonitic, thermic Udic Haplustert	residuum marl
Durant	Fine, montmorrillonitic Vertic Argiustoll	alluvium / residuum

Table 2. Summary of soil properties for the master horizons of the Oklahoma soils studied.

		Soil Properties†					
Horizon	Statistic	pH	Clay	Organic C	Fe Oxide	Mn Oxide	CEC
				%			$cmol_c(½Ba^{2+})\ kg^{-1}$
A	Minimum	3.8	7	0.35	0.19	0.00	1.9
	Maximum	7.7	71	2.95	2.98	0.24	39.1
	Median	5.1	26	1.14	0.71	0.04	12.5
	Mean	5.6	30	1.31	0.95	0.06	16.2
	CV (%)‡	19.9	55.8	56.8	71.5	102.9	72.4
B	Minimum	3.5	11	0.08	0.29	0.00	2.6
	Maximum	7.9	75	1.02	4.56	0.18	48.2
	Median	6.0	47	0.44	1.08	0.03	23.2
	Mean	6.1	44	0.44	1.32	0.04	22.3
	CV (%)	25.0	37.3	48.7	78.6	88.9	56.4
C	Minimum	3.6	5	0.04	0.16	0.00	1.5
	Maximum	8.1	84	0.69	6.32	0.11	51.0
	Median	6.8	44	0.24	0.92	0.03	17.3
	Mean	6.4	42	0.27	1.48	0.03	20.9
	CV (%)	24.9	51.9	63.5	100.8	86.6	67.3
All Horizons§	Minimum	3.5	5	0.04	0.16	0.00	1.5
	Maximum	8.1	84	2.95	6.32	0.24	51.0
	Median	5.8	37	0.47	0.86	0.03	16.2
	Mean	6.0	39	0.69	1.24	0.04	19.8
	CV (%)	23.8	49	93.9	89.4	102.4	65.1

† The soil property data is from one of the replicate samples taken for each series.
‡ The coefficient of variation (CV) is calculated from the variation among all 28 soils.
§ All horizons is a combonation of the A, B, and C horizons.

Table 3. Summary of heavy metal contents for the master horizons of the Oklahoma soils studied.

		Total Metal Content†					
Horizon	Statistic	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1}					
A	Minimum	0.12	6.2	2.4	5.5	5.3	23.0
	Maximum	1.39	63.0	28.5	55.7	32.6	136.5
	Median	0.48	11.8	12.9	13.9	13.5	52.1
	Mean	0.53	15.5	12.4	16.4	15.8	56.1
	GeoMean	0.43	13.2	10.1	14.0	13.9	51.2
	CV (%)‡	63.4	75.1	55.9	65.5	52.0	44.9
B	Minimum	0.08	6.9	1.6	5.4	4.3	20.5
	Maximum	1.89	59.0	30.1	45.3	30.5	112.5
	Median	0.49	11.9	14.4	17.7	13.8	59.9
	Mean	0.58	14.5	14.5	20.8	15.3	57.8
	GeoMean	0.47	12.6	12.2	18.1	13.9	53.3
	CV (%)	62.1	72.5	47.9	53.9	43.3	38.8
C	Minimum	0.05	6.4	1.5	5.7	6.0	19.4
	Maximum	2.01	36.2	58.3	49.3	41.7	222.1
	Median	0.52	11.9	13.3	20.2	12.5	56.1
	Mean	0.57	13.5	14.9	23.9	16.1	64.6
	GeoMean	0.45	12.4	11.2	19.8	13.7	54.7
	CV (%)	70.5	48.3	77.3	61.4	61.6	66.5
All Horizons§	Minimum	0.05	6.3	1.0	5.4	4.3	18.5
	Maximum	2.01	63.0	58.3	55.7	41.7	222.1
	Median	0.49	11.9	13.1	16.6	12.5	54.9
	Mean	0.55	14.6	13.7	20.3	15.6	58.8
	GeoMean	0.44	12.8	10.8	17.1	13.7	52.3
	CV (%)	65.6	66.9	63.1	61.2	52.8	52.8

† The heavy metal data is from an average of the replicate samples taken for each series.
‡ The coefficient of variation (CV) is calculated from the variation among all 28 soils.
§ All horizons is a combonation of the A, B, and C horizons.

Table 4. Comparison of the present study with published data for determination of total metal content of surface soils.

Location	Total Metal Content					
	Cd	Co	Cu	Ni	Pb	Zn
	mg kg^{-1}					
Oklahoma						
Present Study	0.53	15.5	12.4	16.4	15.8	56.1
Present Study†	0.43	13.2	10.1	14.0	13.9	51.2
Holmgren et al. (1993) †	0.08	n.a.	9.7	11.1	6.7	21.0
Ohio (Logan and Miller, 1983)	0.2	n.a.	19	18	19	75
Kentucky (Karathanasis and Seta, 1993)	n.a.	n.a.	21.1	40.6	26.2	42.4
Mississippi (Pettry and Switzer, 1993)	0.5	n.a.	10.4	15.2	20.8	47.8
Minnesota (Pierce et al., 1982)	0.31	n.a.	26	21	25	54
United States						
Holmgren et al. (1993)	0.27	n.a.	29.6	23.9	12.3	56.5
Shacklette and Boerngen (1984)	n.a.	9.1	25	19	19	60
Shacklette and Boerngen (1984) †	n.a.	6.7	17	13	16	48
Sposito and Page (1984)	0.35	8.0	30	50	15	50
English (McGrath, 1986)	0.9	n.a.	18	21	48	85
Welsh (Davies and Paveley, 1985)	0.5	n.a.	16	16	73	79
Sweden (Andersson, 1977)	0.22	4.8	14.6	8.7	15.9	59
World						
Bowen (1979)	0.35	8	30	50	35	90
Ure and Berrow (1982)	0.62	12.0	25.8	33.7	29.2	59.8

† geometric means, all other means are arithmetic means.

Table 5. Analysis of variance results (F values) for total heavy metal contents among regions.

	F Values					
Horizon	Cd	Co	Cu	Ni	Pb	Zn
A	16.65 **	0.83	4.62 **	2.98 *	9.35 **	4.67 **
B	10.97 **	0.62	2.20	8.84 **	12.71 **	6.22 **
C	22.32 **	2.39	1.95	28.07 **	27.49 **	12.23 **

*,** Significant at the 0.05 and 0.01 probability levels, respectively.

Table 6. Percent of soils showing no change, an increase, or a decrease in heavy metal content between horizons.

Observation	Horizons	Cd	Co	Cu	Ni	Pb	Zn
				%			
no change	A to B†	78	89	44	85	86	82
	B to C‡	100	96	58	88	88	89
	A to C§	76	76	36	68	68	68
increase	A to B	18	4	41	15	7	11
	B to C	0	4	17	12	4	13
	A to C	16	12	40	24	12	24
decrease	A to B	4	7	15	0	7	7
	B to C	0	0	25	0	8	0
	A to C	8	12	24	8	20	8

† The number of soils with A and B horizons is 27.
‡ The number of soils with B and C horizons is 24.
§ The number of soils with A and C horizons is 25.

Table 7. Simple regression results (r values) between total metal content and soil properties.

Heavy Metals	Soil Properties					
	pH	Organic C	Clay	Fe Oxide	Mn Oxide	CEC
Cd	-0.05	0.27 *	0.65 **	0.79 **	0.44 **	0.33 **
Co	-0.15	0.01	-0.26 *	-0.01	0.08	-0.20
Cu	0.27 *	0.12	0.63 **	0.40 **	0.30 **	0.46 **
Ni	0.09	0.10	0.74 **	0.65 **	0.36 **	0.53 **
Pb	-0.17	0.30 **	0.66 **	0.66 **	0.46 **	0.30 **
Zn	-0.04	0.17	0.72 **	0.48 **	0.28 **	0.38 **
N	81	81	81	81	81	81

*,** Significant at the 0.05 and 0.01 probability levels, respectively.

Table 8. Analysis of variance results (F values) for soil properties and total heavy metal content within the soil profile.

F values						
Soil Properties						
	pH	Organic C	Clay	Fe Oxide	Mn Oxide	CEC
Horizons	1.5	23.6 **	4.6 **	1.6	2.1	2.1
Heavy metals						
	Cd	Co	Cu	Ni	Pb	Zn
Horizons	1.5	0.5	2.7	3.8 *	1.3	2.2

*,** Significant at the 0.05 and 0.01 probability levels, respectively.

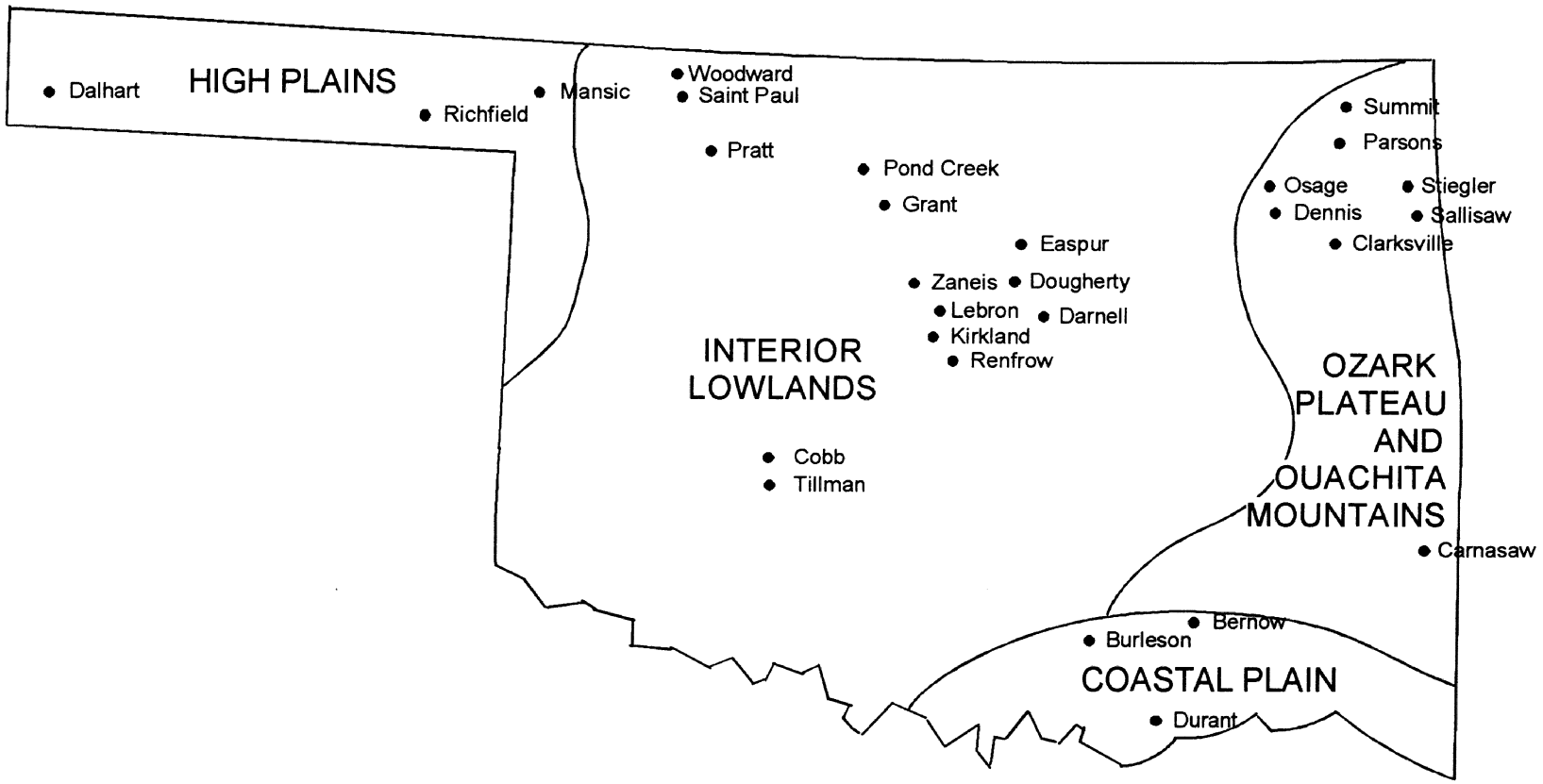
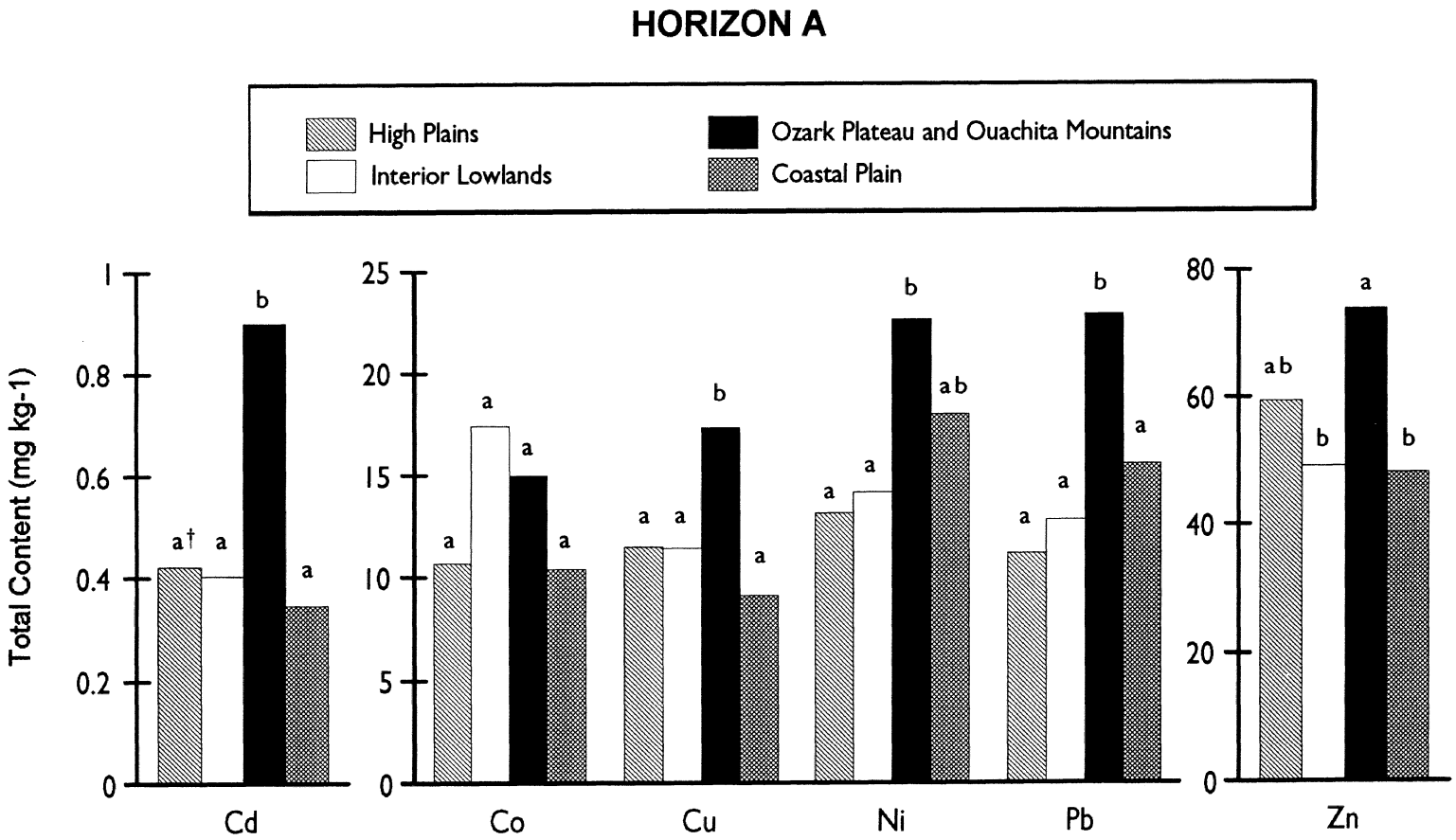
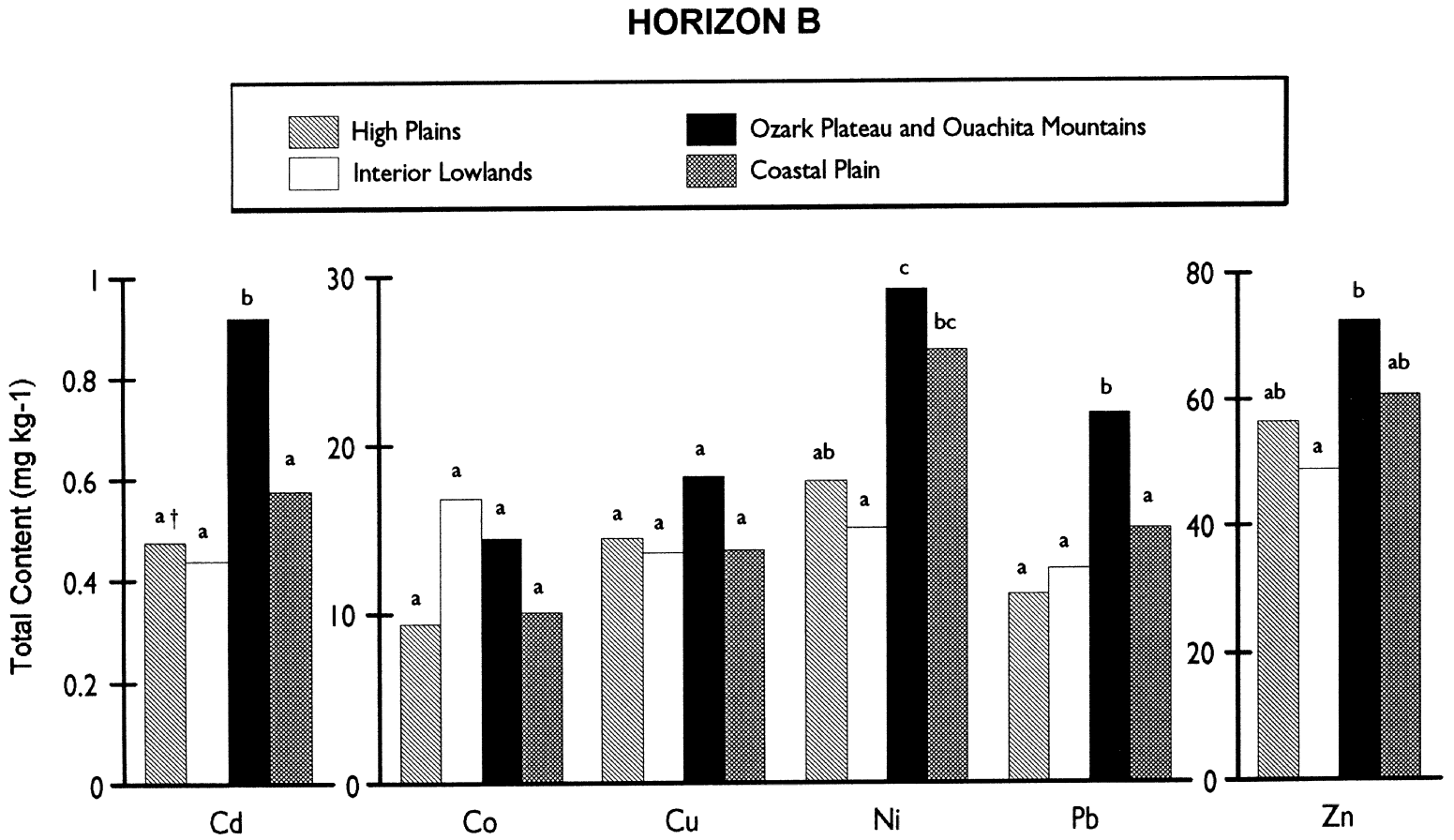


Figure 1. Sample sites and regions in Oklahoma.



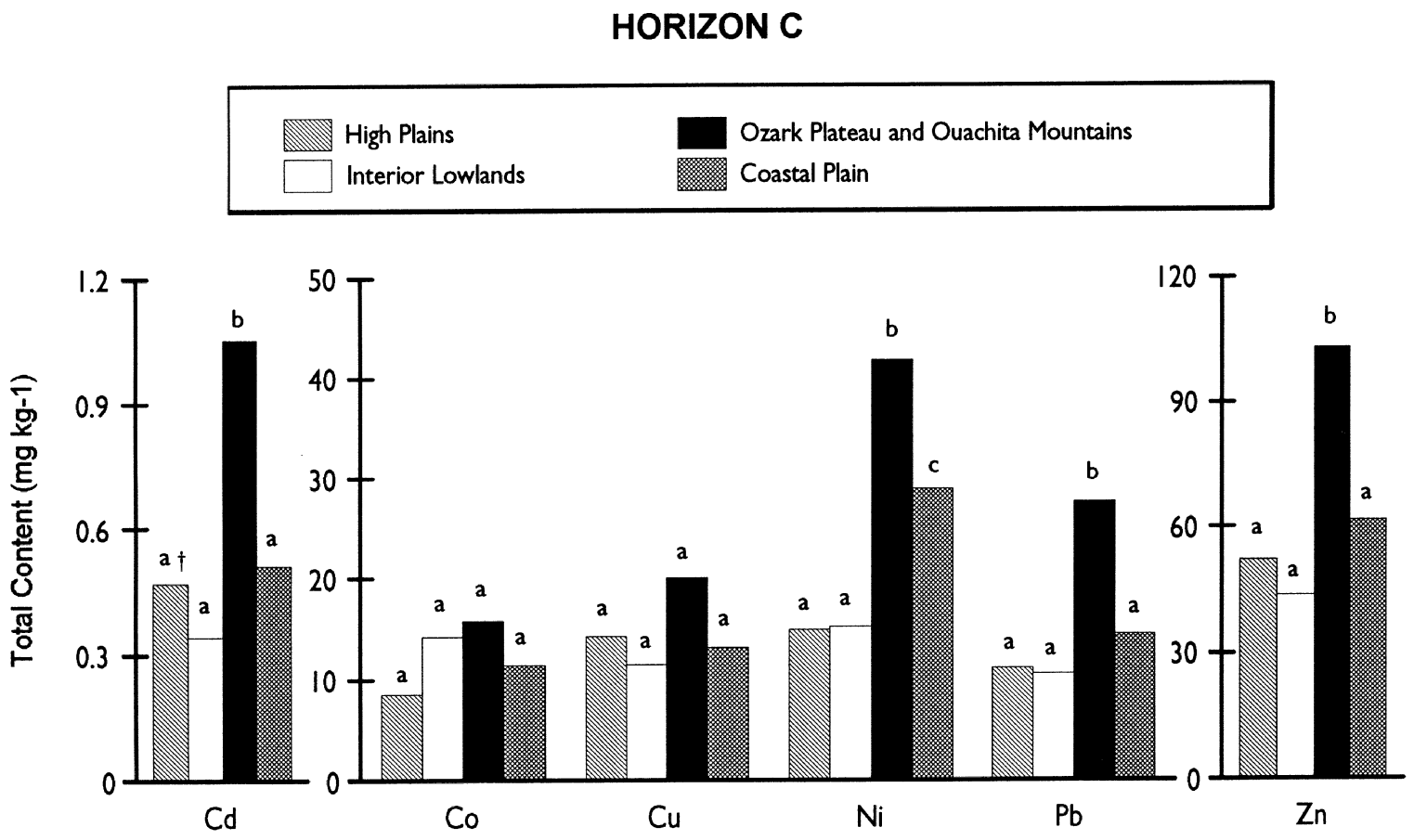
† Means with the same letter are not significantly different for metals within regions ($p < 0.05$).

Figure 2. Comparison of regional heavy metal contents in Horizon A.



† Means with the same letter are not significantly different for metals within regions ($p < 0.05$).

Figure 3. Comparison of state and regional heavy metal contents in Horizon B.



† Means with the same letter are not significantly different for metals within regions ($p < 0.05$).

Figure 4. Comparison of state and regional heavy metal contents in Horizon C.

CHAPTER II.

HEAVY METAL SPECIATION AND BIOAVAILABILITY IN BASELINE, METAL-ENRICHED, AND CONTAMINATED SOILS OF OKLAHOMA

ABSTRACT

Anthropogenic heavy metal additions to soil are an agricultural and environmental concern because of their toxicity and persistence. The objective of this work was to investigate the effect of heavy metal enrichment and contamination on chemical speciation and metal bioavailability in soil. Fifteen Oklahoma soils with heavy metal contents categorized as baseline, enriched, and contaminated and representing a range of soil properties were selected. Heavy metals were sequentially extracted into operationally defined chemical fractions: exchangeable (0.5 M $Ca(NO_3)_2$), carbonate (1M NaOAc, pH 5), oxide (0.04 M $NH_2OH \bullet HCl$), organic (30% H_2O_2, 1M NH_4OAc), and residual (calculated by difference). Heavy metal uptake by lettuce (*Lactuca sativa* L.) was used to indicate bioavailability in soil. Heavy metal additions affected the percentage distribution of chemical species. As total amounts of heavy metal increased from baseline to contaminated levels, the percentage of total metal increased in the exchangeable Cd fraction ($r = 0.69^*$), the organic Cu fraction ($r = 0.74^{**}$), the carbonate Zn fraction ($r = 0.80^{**}$), and the exchangeable Pb fraction ($r = 0.63^*$). The

exchangeable Pb fraction never exceeded 2% of total Pb content, even in severely Pb contaminated soils. The only significant relationships between plant concentration and chemical fractions in baseline and enriched soils were found for exchangeable Zn ($r = 0.70^*$). In contaminated soils, the carbonate and oxide Cd fractions and the organic Zn fraction were strongly correlated with plant metal concentrations. Copper and Pb fractions were not correlated to plant metal concentration. The effect of heavy metal addition on distribution among chemical fractions was strongly dependent on type and chemical properties of heavy metal.

INTRODUCTION

Concern for the addition of metals to soil systems has developed due to anthropogenic additions of heavy metals. Common sources of heavy metals include commercial fertilizers, liming materials, pesticides, sewage sludge, animal wastes, mine tailings, auto emissions, and heavy metal-smelting. Heavy metals exist in soils in many different fractions. These fractions include soil solution, exchange sites, specific adsorption to clay or organic matter, pure or mixed precipitates in secondary minerals, and impurities in primary minerals (McLean and Bledsoe, 1992; Shuman, 1991). The form or 'species' of the metal is thought to affect bioavailability and mobility in soil, with aqueous and exchangeable fractions considered to be the most available and most mobile. Total metal content in soil is used to estimate the degree of contamination by heavy metals but is not a good indicator of bioavailability or mobility since only a small percentage of the total heavy metal content is usually present in bioavailable or mobile

forms. Chemical speciation methods used to determine chemical forms of heavy metals in soil provide more information on bioavailability and mobility than total metal content (Gibson and Farmer, 1986; Gupta and Chen, 1975; Hickey and Kittrick, 1984; Miller et al., 1986; Tessier, 1979).

A widely used chemical speciation procedure for soils developed by Tessier et al. (1979) partitions heavy metals into five chemical fractions: exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter bound, and residual. In this method, a series of progressively stronger extracting solutions are used to sequentially dissolve and extract heavy metals. The exchangeable fraction represents heavy metals that are in solution and on cation exchange sites. The carbonate fraction contains heavy metals that are associated with carbonate minerals or specifically adsorbed. The Fe and Mn oxide fraction represents heavy metals in oxide nodules, concretions, cementing agents, and coatings on soil particles. The organic matter fraction contains heavy metals bound to various forms of soil organic matter. The residual fraction represents heavy metals in primary and secondary minerals. The distribution of heavy metals among fractions depends on the relative binding strengths of the chemical fraction for the heavy metals and the number of binding sites of each component.

Sequential extraction procedures may not be specific for the various chemical fractions because they might partially extract other fractions (Kheboian and Bauer, 1987; Rendell et al., 1980). Therefore, these fractions are operationally defined by the extractants used in the sequential extraction method (Hickey and Kittrick, 1984; Sposito et al., 1982). Sequential extraction procedures have been used to investigate forms of heavy metals in baseline soils (Shuman, 1985; Tessier et al., 1979), sewage sludge-amended soils (Emmerich et al., 1982; Sposito et al., 1982), and heavy metal

contaminated soils (Gibson and Farmer, 1986; Gupta and Chen, 1975; Hickey and Kittrick, 1984; Kuo et al., 1983; Soon and Bates, 1982). Most studies have focused on either baseline soils containing low levels of metal or contaminated soils with very high levels of heavy metals. Few studies have focused on chemical speciation over a wide range of heavy metal contents by studying both baseline and contaminated soils. Chemical speciation of soils that contain a wide range of metal contents and the effect of heavy metal additions to soil on chemical speciation and bioavailability are investigated in this work.

Results from studies using sequential extraction procedures provide useful information and insight on plant availability or mobility of heavy metals in soil. Bioavailable chemical forms of heavy metals in soil have been identified by comparing speciation method results with plant uptake (Iyengar et al., 1981; Sims, 1986; Soon and Bates, 1982). However, only a few metals and soils were investigated in these studies. Little information is available on the relationship between chemical speciation and soil extraction procedures routinely used to assess plant availability (DTPA) or potential mobility (TCLP) of heavy metals.

The relationship between chemical speciation and plant availability of many heavy metals in soils with a wide range of chemical properties and metal contents deserves study. The objectives of this work were (1) to determine the effect of heavy metal enrichment and contamination on the distribution of heavy metal in the chemical fractions and (2) to determine the relationship between bioavailability and chemical speciation.

MATERIALS AND METHODS

Description of Soils

Surface soils (< 20 cm) from 15 locations in Oklahoma (Fig. 1) were selected for study. Soils were collected from "baseline" sites with less than 10% heavy metal enrichment from human activities, agricultural land that had received more than 10 y of sewage sludge application, areas affected by heavy metal mining operations, and areas that received significant atmospheric deposition of heavy metals from smelting of zinc ores. After collection, soil samples were air-dried, and ground to 2 mm with a stainless steel flail arm grinder. The soils collected were categorized into three groups based on anthropogenic contributions of heavy metals. They were (1) baseline soils with less than 10% of the total metal content from anthropogenic sources, (2) enriched soils with 25-90% of total metal content from anthropogenic additions, and (3) contaminated soils with greater than 90% of their total metal content from anthropogenic sources. Heavy metal contributions to soil were estimated from sewage sludge contributions and comparison with the total metal content of "baseline" soils of the surrounding area (Scott, 1994). Based on their heavy metal content , many soils fit into several categories: for example, Soil 13 had baseline levels of Ni, enriched levels of Cu, and contaminated levels of Cd, Pb, and Zn (Table 1).

Soils investigated in this study also had a wide range in soil properties (Table 1) and were characterized using standard methods. Soil pH was determined in a 1:2

soil:0.01 M $CaCl_2$ slurry using a glass electrode (McLean, 1982). Soil organic carbon was determined by a modified Mebius method described by Yeomans and Bremner (1988). Iron and Mn oxides were determined by the citrate-bicarbonate-dithionite (CBD) extraction developed by Mehra and Jackson (1960). Soil texture was determined by the hydrometer method (Gee and Bauder, 1986). Two methods for determining CEC were used for the collected soils. The CEC of acidic and near neutral soils (soil pH < 6.5, 1:2 soil:0.01 M $CaCl_2$ slurry) was determined by barium chloride extraction and summation of extracted Al, Ca, Fe, K, Mg, Mn, and Na (Hendershot and Duquette, 1986). The CEC of calcareous soils was determined using the method described by Polemio and Rhodes (1977). Total Cd, Cu, Ni, Pb, and Zn content was determined by wet digestion of the soil sample using HNO_3, $HClO_4$, and HF (Burau, 1982). The soil digests could not be analyzed directly; therefore, solvent extraction and standard addition methods were used (Scott, 1994).

Chemical Speciation by Sequential Extraction

Chemical speciation of heavy metals in soil was determined by sequential extraction. Trace metal or Ultrex® grade reagents were used when available to make reagents for the sequential extraction. Metals were speciated into (1) exchangeable, (2) carbonate, (3) oxide, (4) organic, and (5) residual fractions by a five step sequential extraction procedure as follows:

Step 1. The exchangeable fraction was determined by extracting 1 g of soil with 20 ml of 0.5 M $Ca(NO_3)_2$ in a 50 ml centrifuge tube. The mixture was placed on a reciprocal shaker and equilibrated for 16 h (180 cycles min^{-1}), centrifuged for 10 min at 2260 X g. The supernatant was then decanted and

saved for heavy metal analysis (Miller et al., 1986). The soil residue remaining in the centrifuge tube was saved for further extraction in Step 2.

Step 2. The carbonate fraction was determined by extracting the residue in the centrifuge tube from Step 1 with 20 ml of 1 M NaOAc (pH 5). The soil was shaken for 5 h, centrifuged for 10 min, and the supernatant decanted and saved for heavy metal determination (Gibson and Farmer, 1986). Shaker and centrifuge speeds were the same as Step 1 throughout the sequential extraction procedure.

Step 3. The oxide fraction was determined by extracting the residue in the centrifuge tube from Step 2 with 20 ml of 0.04 M hydroxylamine hydrochloride ($NH_2OH \bullet HCl$) in 25% HOAc. The soil was shaken for 6 h at 90 ± 2 °C in a hot water bath, centrifuged for 10 min, and the supernatant decanted for heavy metal analysis (Hickey and Kittrick, 1984). The residue was saved for further extraction in Step 4.

Step 4. The organic fraction was determined by shaking the residue from Step 3 with 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 in a hot water bath at 85 ± 2 °C for 2 h. After 2 h, 3 ml of 30% H_2O_2 was added and the soil mixture shaken for 2 h at 85 ± 2 °C. The final volume was then adjusted to 20 ml with 1 M NH_4OAc in 6% HNO_3, shaken for 30 min without heating, centrifuged for 10 min, and the supernatant was decanted and kept for heavy metal analysis (Gupta and Chen, 1975; Tessier et al., 1979).

Step 5. The residual fraction for Cd, Cu, Ni, and Pb was determined by difference between the soil total metal content and the sum of the above four chemical fractions. Total metal content was determined by wet digestion with

HNO_3 /$HClO_4$ / HF, solvent extraction or standard additions, and ICP analysis as described by Scott (1994). The large variability of Zn in all chemical fractions prevented determination of a residual Zn value in this work.

Heavy metals from the sequential procedure sample extracts were determined by inductively coupled plasma atomic emission spectroscopy (ICP). The high salt content of the sequential extracts prevented direct analysis of these solutions by the Jarrell Ash Model 9000 ICAP. Therefore, it was necessary to extract the heavy metals from the sequential extraction sample solutions and place them in a solution matrix compatible with ICP. This was accomplished by passing 20 ml of the sequential procedure solutions through high capacity cation exchange resin (CHELEX® 100, 100-200 mesh, Na form) at less than 2 ml min^{-1}. Because CHELEX® 100 resin preferentially adsorbs heavy metals over the Na^+, Ca^{2+}, and NH_4^+ in the extracting solutions, heavy metals were separated from the high salt sequential extraction solutions. Adsorbed heavy metals were eluted from the resin with 20 ml of 4 M HNO_3 and subsequently analyzed by ICP for Cd, Cu, Ni, Pb, and Zn. Standard solutions that contained heavy metals were used to determine heavy metal recovery of the CHELEX® 100 resin extraction step and to calculate heavy metal concentrations of the initial sequential extraction procedure sample solutions. Heavy metal contributions from reagent grade extracting solutions (e.g. $Ca(NO_3)_2$, NaOAc, $NH_2OH \bullet HCl$, and NH_4OAc) were determined by passing 20 ml of blank extracting solutions through CHELEX® 100 resin, elution with HNO_3, and analysis by ICP. Heavy metal contributions from extracting solutions were subtracted from sample extracts for each chemical fraction.

Extraction of Heavy Metals by DTPA and TCLP

The DTPA bioavailability index (Lindsay and Norvell, 1978) was used to determine potential bioavailability of the heavy metals. The heavy metals in soil were extracted by shaking 10 g of soil with 20 ml of extracting solution (0.005 M diethylene-triaminepentaacetic acid (DTPA), 0.01 M $CaCl_2$, and 0.1 M triethanolamine (TEA) adjusted to pH 7.3) for 2 h. The mixture was filtered through Whatman no. 42 filter paper prior to heavy metal analysis by ICP.

The U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA, 1992) was used to determine the potential mobility of heavy metals in soil. In this procedure 2 g of soil were shaken with 40 ml of extracting solution for 1 h. The extracting solution used in this procedure was dependent on soil pH. Noncalcareous soils were extracted with 0.02 M HOAc (pH 5.0) and calcareous soils were extracted with 0.02 M HOAc (pH not adjusted).

Heavy Metal Bioavailability in Soil

Heavy metal uptake by lettuce (*Lactuca sativa* L. 'Paris cos') was used to determine heavy metal bioavailability in soil. The lettuce was grown for 60 days in plastic pots containing approximately 400 g of soil. Three replicate pots of each soil were planted with six lettuce seeds and thinned to three lettuce plants shortly after emergence. The lettuce was grown in a growth chamber with 16 h of light at 25°C and 8 h of dark at 20°C. All pots received supplemental fertilization to provide adequate N, P, and K nutrition. After maturity (60 days), the vegetative above-ground growth was harvested, dried at 80 °C, and ground with a mortar and pestle. Bioavailability was defined as uptake by above ground lettuce growth and did not include uptake by roots. The plant tissue was digested with concentrated trace metal grade HNO_3 in an

aluminum digestion block at 140°C until clear and analyzed by ICP for Cd, Cu, Ni, Pb, and Zn (Zarcinas et al., 1987).

RESULTS AND DISCUSSION

Distribution of Heavy Metals in Soil Fractions

Although an increase in heavy metal content from baseline to contaminated soil was expected, little information is available on the partitioning of anthropogenic heavy metals in metal-enriched and contaminated soils. The effect of anthropogenic metal additions to soil on percent distribution of heavy metal in each fraction was investigated to determine if metal additions affected metal partitioning and availability in soils.

Cadmium. The distribution and total Cd content of the investigated soils is presented in Fig. 2. The total Cd content ranged from 0.12 mg kg^{-1} in baseline soil to 425 mg kg^{-1} in contaminated soil. The percentage of the total Cd in the exchangeable fraction ranged from 0-8% in baseline soils, 11-30% in enriched soils, and 14-41% in contaminated soils. Cd addition to soil caused an increase in the percent of the total Cd in the exchangeable fraction. In a linear correlation between total Cd content and percentage in the exchangeable fraction the r value was significant (r = 0.69*). The percent of the total Cd in the carbonate fraction ranged from 3-27% in baseline soils, 15-19% in enriched soils, and 14-21% in contaminated soils (Fig. 2). A consistent trend was not evident between percent Cd in the carbonate fraction and total Cd content (r = 0.00). The sum of the percent oxide, organic, and residual fractions

ranged from 73-96% in baseline soils, 50-73% in enriched soils, and 44-68% in contaminated soils. Although there was not a consistent trend between individual oxide, organic, or residual fractions and Cd content, the sum of the oxide, organic, and residual fractions showed a decrease with an increase in Cd content ($r = -0.56$, significant at the 0.10 probability level).

Results from other studies (McLean and Bledsoe, 1992) show Cd contaminated soils tend to have large percentages of total Cd content in the exchangeable fraction. Hickey and Kittrick (1984) investigated chemical partitioning of Cd, Cu, Ni, and Zn in three contaminated soils and one sediment that received massive additions of heavy metals over a six year period. They found 37% of the total Cd in the exchangeable fraction, and 83% of the total Cd in the exchangeable, carbonate, and oxide fractions. Gibson and Farmer (1986) studied chemical speciation of Cd, Cu, Pb, and Zn in 90 Glasgow surface soils. They reported that 32% of the total Cd was in the exchangeable and carbonate fractions of contaminated soils; however, exchangeable Cd did not increase with total Cd content as reported in other studies. The absence of an increase in exchangeable Cd with Cd metal enrichment may be attributed to the small amount of Cd contamination (< 4 mg kg^{-1}) in these soils. Kuo et al. (1983) studied the distribution and forms of Cu, Zn, Cd, Fe, and Mn in 60 surface soils from home gardens surrounding a Cu smelter. They found between 30-60% of the total Cd in the exchangeable fraction of these Cu smelter contaminated soils. Soils enriched with Cd through application of sewage sludge showed < 0.1% (Emmerich et al., 1982) and 1.1 % (Sposito et al., 1982) of the total Cd in the exchangeable fractions. Although sewage sludge application had little effect on exchangeable Cd, increases in carbonate forms of Cd were reported in these studies. Similar results were found in the present study. Increases in exchangeable Cd were associated with contaminated soils

that received much larger quantities of Cd than soils enriched with Cd through sewage sludge application.

Many studies have shown that soil pH and other soil properties affect exchangeable Cd and Cd availability in soils (Adriano, 1986; Alloway, 1990; McLean and Bledsoe, 1992). It is possible that some of the increase in percent exchangeable Cd in enriched and contaminated soils is due to soil properties listed in Table 1. Stepwise multiple regression between percent exchangeable Cd (dependent variable), total Cd content, soil pH, Fe and Mn oxide content, soil organic C content, percent clay content, and soil CEC (independent variables) was used to evaluate the effect of Cd addition and soil properties on the percent of the Cd in the exchangeable fraction. Significant R values were only found between the percent of the total Cd in the exchangeable fraction and the total Cd content (R = 0.69*). Soil properties had little affect on the percent of the total Cd in the exchangeable fraction in these soils that were chosen for their large range in total Cd content and soil properties.

Cadmium and other cationic heavy metals exist as adsorbed and precipitated forms in soils. Cadmium may be bonded tightly to "specific" adsorption sites or held loosely by "non-specific" adsorption sites as exchangeable Cd (Sposito et al., 1982). Soil oxide, organic, and residual fractions contain numerous specific adsorption sites. Specific and non-specific adsorption sites compete for soluble Cd in soil, but specific adsorption sites have a higher affinity than non-specific sites for heavy metals. Metal adsorption studies have shown that small amounts of Cd added in the soil solution are adsorbed tightly by specific adsorption sites with little adsorption by exchange sites; however, high concentrations of dissolved Cd saturate specific adsorption sites and increase Cd adosrption by non-specific sites as weakly held exchangeable Cd (Basta and Tabatabai, 1992; Garcia-Miragaya et al., 1976; Navrot et al., 1978). Most Cd was

specifically adsorbed in the oxide, organic, and residual fraction at the low Cd contents of the baseline soils in this study because only small amounts of exchangeable Cd were found in baseline soils with low Cd content. Increases in exchangeable Cd were associated with Cd additions in enriched and contaminated soils. These increases may be attributed to saturation of specific adsorption sites and filling of non-specific exchangeable sites. Increases in the amount of exchangeable Cd correspond to decreased percentages of specifically adsorbed and precipitated Cd in oxide, organic, and residual fractions. The exchangeable Cd fraction and Cd availability increased dramatically in Cd contaminated soils.

Copper. The distribution and total Cu content of the investigated soils is presented in Fig. 3. The total Cu content ranged from 1.9 mg kg^{-1} in baseline soil to 405 mg kg^{-1} in contaminated soil. Only one of the soils collected had contaminated levels of Cu (> 90% by anthropogenic additions). The percent of the total Cu in the exchangeable fraction ranged from 1-4% in baseline soils (except soil 1 which had 28%), 1-3% in enriched soils, and 0% in the contaminated soil. In general, increasing the total amount of Cu had little effect on the percent of the Cu in the exchangeable fraction ($r = -0.25$). The percentage of the Cu in the carbonate fraction ranged from 0-9% in baseline soils (except soil 1 which had 18%), 4-11% in enriched soils, and 39% in the contaminated soil. The percent of the Cu in the carbonate fraction was strongly related to the total metal content ($r = 0.82^{**}$). However, only the contaminated soil, soil 15, showed an increase in the percent of the Cu in the carbonate fraction and resulted in an exaggerated r value. Excluding soil 15 from the regression resulted in a non-significant r value ($r = -0.12$). The carbonate Cu fraction represents weakly adsorbed and complexed forms of Cu in soil and carbonate minerals (Hickey and Kittrick, 1984).

Soil 15 is not a calcareous soil (pH = 6.2) and does not contain free carbonate. High percentages of carbonate Cu in soil 15 indicates an increase of weakly adsorbed and potentially available forms of Cu in this contaminated soil. The oxide fraction as a percentage of the total Cu ranged from 0-7% in baseline soils, 6-19% in enriched soils, and 9% in the contaminated soil. The percent of the Cu in the oxide fraction was not related to Cu additions (r = 0.28). The percent of the total Cu in the organic fraction ranged from 2-28% in baseline soils, 17-50% in the enriched soils, and 28% in the contaminated soil. There appears to be a relationship between percent Cu in the organic fraction and total Cu content (Fig. 3), but a non-significant r value of 0.33 was found for this relationship. When soil 15 is excluded from the correlation the r value becomes highly significant (r = 0.74**). The percent of the total Cu in the residual fraction ranged from 69-93% in baseline soils (except soil 1 with 14%), 38-67% in enriched soils, and the contaminated soil contained 24%. There appeared to be a decrease in residual Cu with increased Cu content but the relationship was not significant (r = -0.48). In summary, the exchangeable, carbonate, and oxide fractions showed little change and the organic fraction showed a percent increase with increased total Cu content.

Results from other studies (McLean and Bledsoe, 1992) indicate that Cu enriched soils tend to have a large percentage of the total Cu in the organic fraction. Sposito et al. (1982) investigated the fractionation of Ni, Cu, Zn, Cd, and Pb in arid-zone field soils amended with sewage sludge. They found 60% of the total Cu in the organic fraction of the soils investigated. Hickey and Kittrick (1984) studied the chemical partitioning of Cu in three soils and one sediment that were contaminated with Cu and found 28% of the Cu in the organic fraction. They also found 87% of the total Cu in the sum of the oxide, organic, and residual fractions. In contaminated soils

collected from home gardens of Glasgow, Gibson and Farmer (1986) reported 41% of the total Cu in the organic fraction. Results for the present study were similar to these studies.

Many studies have shown that Cu is strongly adsorbed to soil organic matter (Adriano, 1986; Alloway, 1990; McLean and Bledsoe, 1992; Petruzelli et al., 1978; Stevenson and Ardakani, 1972; Stumm and Morgan, 1981). Because of the electronic configuration of the d-orbitals, Cu (d^9) bonds stronger than other heavy metals to organic matter (Irving and Williams, 1948). The strong relationship between total Cu content and organic Cu in the present study may be due to the high organic carbon contents of soils 13 and 14 (> 3.2% organic C), and addition of Cu complexed with sewage sludge in soils 9, 10, and 11 (Table 1). A relationship was found between the percent of the total Cu in the organic fraction and soil organic carbon content ($p = 0.08$) suggesting formation of organic Cu chelates with soil organic matter. Sposito et al. (1982) also found that soil properties other than total metal content did not affect heavy metal distribution in sewage sludge-amended soils. Results from the present study suggest that Cu addition in the enriched soils was preferentially partitioned into the organic fraction.

Nickel. The distribution of the total Ni in the soils investigated is presented in Fig. 4. All of the soils collected contained baseline contents of Ni ranging from 6.2 mg kg^{-1} to 73.9 mg kg^{-1} soil (Fig. 4). None of the soils collected were enriched or contaminated with Ni. The percent of total Ni ranged from 0-16% in the exchangeable fraction, 2-18% in the carbonate fraction, 5-50% in the oxide fraction, 9-21% in the organic fraction, and 9-76% in the residual fraction. In general, the residual fraction contained the largest percent of the total Ni, the organic and oxide fractions contained

intermediate percentages, and the carbonate and exchangeable fractions contained the smallest percentages of the total Ni. The majority, 68-97%, of the total Ni was in the sum of the oxide, organic, and residual fractions. Sposito et al. (1982) also found that in sludge amended soils the residual fraction was the largest fraction. In polluted soils Hickey and Kittrick (1984) found approximately 50% of the Ni in the residual fraction and Soon and Bates (1982) found nearly 50% of the total Ni in the organic fraction of a soil collected near a Ni smelter. Apparently, most Ni remains in the oxide, organic, and residual fractions even in soils that are highly contaminated with Ni.

Lead. The distribution of the total Pb in the investigated soils is presented in Fig. 5. The total Pb content in the soils ranged from 11.3 mg kg^{-1} to 640 mg kg^{-1} soil. The exchangeable fraction accounted for 0% of the baseline and enriched soils, and 0-1.4% in the contaminated soils. As the total amount of Pb in the soils increased the percent in the exchangeable fraction remained very small; however, the percent of the Pb in the exchangeable fraction increased with total Pb content ($r = 0.63^*$). The percent of the total Pb in the carbonate fraction ranged from 8-24% in baseline soils, 15-40% in the enriched soils, and 22-40% in the contaminated soils. Increasing the total amount of Pb caused a slight increase in the percentage of the lead in the carbonate fraction although this increase was not significant ($r = 0.51$). The percent oxide ranged from 17-22% in baseline soils, 24-30% in enriched soils (except soil 10 which had 4%), and 21-29% in contaminated soils. As total Pb content of the soils increased, the percent of the total Pb in the oxide fraction did not show a significant trend ($r = 0.28$). The percent of the total Pb in the organic fraction ranged from 20-34% in baseline soils, 13-20% in enriched soils, and 7-15% in contaminated soils. In general, as the total amount of Pb in the soils increased the percent of the Pb in the

organic fraction decreased (r = -0.66*). The residual percentage ranged from 33-47% in baseline soils, 26-45% in enriched soils, and 30-41% in contaminated soils. No relationship between the total amount of Pb and the percent in the residual fraction was found (r = -0.38).

Results from other studies indicate that Pb is associated with many of the soil fractions. In a study of sludge amended soils, Sposito et al. (1982) found the carbonate fraction was the dominant Pb fraction regardless of the sludge rate. The present study also suggests a trend in which the percentage of the Pb in the carbonate fraction increased with total Pb. In contaminated soils of Glasgow, Gibson and Farmer (1986) found 51% of the total Pb in the oxide fraction and a small increase of Pb in the exchangeable fraction. Sheppard and Thibault (1992) also found that soils treated with Pb had large amount of Pb in the oxide fraction. Other studies show that Pb has a high affinity for organic matter (McLean and Bledsoe, 1992). In Pb-polluted soils of Norway and Wales, the percent of the total Pb in the organic fraction was high (about 62%) as cited by Adriano (1986). However in the present study, percent Pb in the organic fraction decreased with total Pb content. In part, this decrease can be attributed to Pb being preferentially partitioned into the carbonate fraction. Although Pb contamination increased the percent of the total Pb in the exchangeable fraction, these increases were very small.

Zinc. The distribution of the total Zn in the soils is shown in Fig. 6. The total Zn content ranged from 30.2 mg kg^{-1} to 10 400 mg kg^{-1} soil. Inherent variability in Zn determinations for all of the soils resulted in inaccurate residual calculations; therefore, residual fractions are not reported in Fig. 6. Total Zn was calculated from the sum of the exchangeable, carbonate, oxide, and organic fractions. The percent of the total Zn

(sum of fractions 1-4) in the exchangeable fraction ranged from 1-11% in baseline soils, 4-6% in enriched soils, and 14-21% in contaminated soils. There was an increase in the percent in the exchangeable fraction of contaminated soils, but the relationship between exchangeable Zn and total Zn was not significant (r = 0.48). The percent of the total Zn in the carbonate fraction ranged from 2-15% in baseline soils, 15-39% in enriched soils, and 10-60% in contaminated soils. As the total Zn increased the percent of the Zn in the carbonate fraction increased significantly (r = 0.80**). The percent of the total Zn in the sum of the oxide and organic fractions ranged from 74-96% in baseline soils, 55-75% in enriched soils, and 25-76% in contaminated soils. As total Zn increased the percentage in the sum of the oxide and organic fractions decreased (r = -0.80**). As the total amount of Zn increased the exchangeable and carbonate Zn fractions increased and the percent in the sum of the oxide and organic fractions decreased with total Zn.

In uncontaminated soils, Shuman (1979) found small amounts of Zn in the exchangeable fraction. In contaminated soils Kuo et al. (1983) found an average of 8% of the total Zn in the exchangeable fraction and Hickey and Kittrick (1984) had similar results for the percent of the total Zn in the exchangeable fraction (<14%). Results for the percentage of the total Zn in the exchangeable fraction in the present study are similar to these studies. Hickey and Kittrick (1984) found a large percentage of the total Zn (28%) in the carbonate fraction in contaminated soils and Sposito et al. (1982) found the carbonate fraction to have the largest percentage of the total Zn in sludge amended soils. In soils having similar total Zn contents to Hickey and Kittrick (1984), about 25% of the total Zn was found in the carbonate fraction of the present study. Other studies have shown that soils enriched in Zn have relatively large amounts of Zn in the oxide and organic fractions (McLean and Bledsoe, 1992; Hickey and Kittrick,

1984; Gibson and Farmer, 1986; Kuo et al., 1983; Shuman, 1979; Jeng and Singh, 1993; Iyengar et al., 1981). In the present study, the percent of the Zn in the sum of the exchangeable and carbonate fractions increased with total Zn content (r = 0.80**).

The effect of soil contamination on chemical speciation differed between heavy metals. Cd, Zn, and Pb contamination resulted in increased percentages in the exchangeable fraction. Cd showed the largest increase in the percent of the total metal in the exchangeable fraciton and Pb had the smallest increase in the percentage of the Pb in the exchangeable fraction. The exchangeable Pb fraction never accounted for more than 2% of the total Pb. Cu and Zn contamination both caused significant increases in the percent of the total metal in the carbonate fraction.

Relationship Between Plant Concentration and Chemical Extractants

Chemical speciation based on sequential extraction is directly related to the affinity of heavy metals for soil components. Because plant uptake of heavy metals is also related to soil affinity, chemical speciation may provide information on plant availability of these metals. Results from a growth chamber experiment were used to determine the relationship between plant concentration and chemical speciation of heavy metals in soil. The relationship between plant metal concentrations and the following fractions was determined: exchangeable(1); carbonate(2); oxide(3); organic(4); residual (5); Σ 1,2; Σ 1,2,3; Σ 1,2,3,4; and Σ 1,2,3,4,5. The relationship between plant metal concentration, DTPA, and TCLP were also determined. Linear regression results (r values) between plant concentration and chemical extractants are presented in Table 2. The heavy metal contents of the soils studied was poorly distributed. The heavy metal contents in the contaminated soils was much higher than

the baseline and enriched soils. The data appeared to represent two different populations and resulted in artificially high regression r values. Therefore, the data were analyzed in two groups: (1) baseline and enriched, and (2) contaminated soils. To further correct for poor distribution of heavy metal contents, the most highly enriched soils in Cd (Soil 12) and Pb (Soils 10 and 12) were included in the contaminated group when performing regression analysis. Soil 15, the most highly contaminated soil, would not grow lettuce plants and could not be used in the regression analysis.

Chemical Speciation. Plant concentrations of Cu, Ni, and Pb were not correlated with any of the chemical speciation fractions or sum of fractions for baseline and enriched or contaminated soils. For baseline and enriched soils, plant Cd concentration was not correlated with the extractants; however, plant Cd concentration was correlated with the carbonate and oxide fractions and for all of the sum of fractions for contaminated soils (Table 2). Xian (1989a,b) found that cabbage (*Brassica oleracea* L.) and kidney bean (*Phaseolus vulgaris* L.) Cd concentrations were correlated with exchangeable and carbonate Cd fractions in Cd contaminated soils. In baseline and enriched soils, plant Zn concentration was correlated with exchangeable Zn ($r = 0.70^*$) and several of the sum of fractions (Table 2). Sims (1986) determined that exchangeable Zn was related to wheat (*Triticum aestivum* L.) uptake in baseline soils. In uncontaminated soils, Iyengar et al. (1981) also found the exchangeable Zn fraction was the only fraction that was correlated ($r^2 = 0.62^*$) to Zn uptake by maize (*Zea mays* L.). In sludge enriched soils, LeClaire et al. (1984) found that exchangeable Zn was associated with barley (*Hordeum vulgare* L.) uptake. The organic Zn fraction was the only fraction correlated to plant Zn concentration ($r = 0.99^*$) for contaminated

soils in our study. In eight Zn contaminated soils of Southern Ontario, Soon and Bates (1982) found that maize uptake of Zn was correlated with the exchangeable Zn fraction. Plant Zn concentration and exchangeable Zn appear to be linearly related for (a) baseline and enriched soils and (b) contaminated soils (Fig. 7). However, this relationship is weak and not significant for contaminated soils (Table 2). Perhaps including more contaminated soils in this study might have resulted in a significant relationship between exchangeable Zn fraction and plant Zn concentration.

DTPA and TCLP. Plant metal concentrations were correlated with DTPA extractable metal for Ni ($r = 0.68^*$) and Zn ($r = 0.82^{**}$) in baseline and enriched soils. In contaminated soils, the plant metal concentrations were highly correlated to DTPA extractable metal for Cd ($r = 1.00^{**}$) and Pb ($r = 0.99^*$). Low sample numbers (3 to 4 soils) for the contaminated group resulted in the large r values from the linear correlation analysis. Rappaport et al. (1986) found that corn leaf Zn concentration was correlated to DTPA extractable Zn ($r^2 = 0.64^*$) in sludge amended soils. Pierzynski and Schwab (1993) also found that DTPA extractable Zn was correlated to soybean (*Glycine max* L.) in contaminated soils ($r^2 = 0.49^*$). In general, amounts of metal extracted by TCLP were not related to plant concentration. The only metal extracted by TCLP that was correlated to plant concentration was Cd in contaminated soils ($r = 1.00^{**}$).

The relationship between plant concentrations and the metal extracted by several methods (exchangeable fraction, DTPA, and TCLP) for Cd, Pb, and Zn was studied (Fig. 8). DTPA extracted more heavy metal than methods used to determine exchangeable fraction and TCLP. This finding was consistent with the chemical properties of the extracting solutions used in these methods. DTPA is a strong

chelating agent with a high affinity for heavy metals. Salt or acid solutions (i.e. $Ca(NO_3)_2$, NaOAc, or HOAc) have less ability to dissolve heavy metal in soil. The amounts of Cd, Pb, and Zn extracted from soils followed the trend DTPA > exchangeable > TCLP. Because they are both salt solutions, the extractants used for exchangeable and TCLP methods were expected to dissolve similar amounts of metal. The amounts extracted are proportional to the extraction times for exchangeable (16 h) and TCLP (1 h).

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Table 1. Total metal contents and properties of the soils studied.

Site Type	Soil Number	Total Metal Content					Properties					
		Cd	Cu	Ni	Pb	Zn	pH	MnO	Fe_2O_3	OC	CLAY	CEC
		mg kg^{-1}						%				$cmol_c(½Ba^{2+})$ kg^{-1}
Baseline	1	0.12	2.0	6.2	11.3	30.2	6.8	0.010	0.31	0.27	12	12.5
	2	0.88	23.9	37.7	22.8	127.3	7.5	0.045	1.47	1.94	59	33.0
	3	0.61	13.5	17.1	20.6	65.5	7.7	0.024	0.40	1.45	35	34.0
	4	0.95	20.4	44.6	33.1	132.6	5.3	0.077	2.11	3.06	66	30.0
	5	0.42	15.2	24.1	21.5	54.9	4.3	0.037	0.66	0.89	28	8.5
	6	0.32	11.9	25.3	18.0	53.1	6.4	0.028	0.68	1.08	28	14.0
	7	1.14	27.7	73.9	38.0	83.0	7.0	0.197	3.20	2.49	58	39.5
	8	0.42	12.3	26.2	19.8	66.8	5.2	0.047	1.09	0.68	34	11.0
Sludge Amended	9	1.47 †	27.5 †	11.5	24.2	64.3 †	7.2	0.013	0.44	1.06	6	15.5
	10	1.38	31.5 †	17.6	115 †	89.1 †	6.7	0.018	1.44	1.47	16	11.0
	11	2.32 †	35.4 †	18.7	31.2 †	85.2 †	5.7	0.039	1.25	1.83	14	11.5
Mine Disturbed	12	3.82 †	20.0	29.5	82.5 †	480 ‡	5.6	0.057	2.03	1.52	17	13.5
	13	15.0 ‡	64.2 †	16.1	550 ‡	2150 ‡	6.3	0.042	1.23	3.73	12	18.0
Zn Smelter	14	37.1 ‡	109 †	34.2	586 ‡	2090 ‡	6.0	0.030	2.04	3.29	33	19.5
	15	424 ‡	405 ‡	32.0	640 ‡	10400 ‡	6.2	0.040	0.89	1.46	25	11.5

† Enriched, ‡ Contaminated, soils without † or ‡ are considered baseline soils with respect to each metal.

Table 2. Plant concentration correlation data (r values) for chemical speciation, DTPA, and TCLP.

Extractant	Baseline and Enriched Soils					Contaminated Soils		
	Cd†	Cu	Ni	Pb‡	Zn	Cd†	Pb‡	Zn
Exchangeable (1)	0.33	-0.14	0.38	0.00	0.70*	0.99	0.55	0.82
Carbonate (2)	0.15	0.31	-0.12	-0.44	0.61	1.00**	0.37	0.82
Oxide (3)	0.28	0.12	-0.23	0.19	0.15	1.00**	0.54	0.72
Organic (4)	0.01	0.09	-0.02	0.39	0.37	0.16	0.39	0.99*
Residual (5)	0.18	0.14	0.06	0.36	n.d.	0.97	0.16	n.d.
Σ1,2	0.23	0.24	0.25	-0.44	0.68*	1.00**	0.37	0.82
Σ1,2,3	0.27	0.16	-0.05	-0.06	0.47	1.00**	0.47	0.79
Σ1,2,3,4	0.24	0.11	0.00	0.22	0.68*	1.00**	0.45	0.87
Σ1,2,3,4,5	0.23	0.10	-0.03	0.30	0.72*§	0.99*	0.36	0.86§
DTPA	0.52	0.49	0.68	-0.17	0.82**	1.00**	0.99**	0.92
TCLP	0.00	0.44	0.18	-0.29	0.50	1.00**	0.24	0.68
N	8	13	13	8	9	3	4	3

*,** Significant at the 0.05 and 0.01 probability levels, respectively.

† Soil 12, a severely Cd enriched soil, was included in the Cd contaiminated soils for the simple regression.

‡ Soils 10 and 12, both severely Pb enriched, were included in the Pb contaminated soil for the simple regression.

§ The Zn value for the Σ1,2,3,4,5 is from a single total Zn determination and is not from the sum of all five chemical fractions.

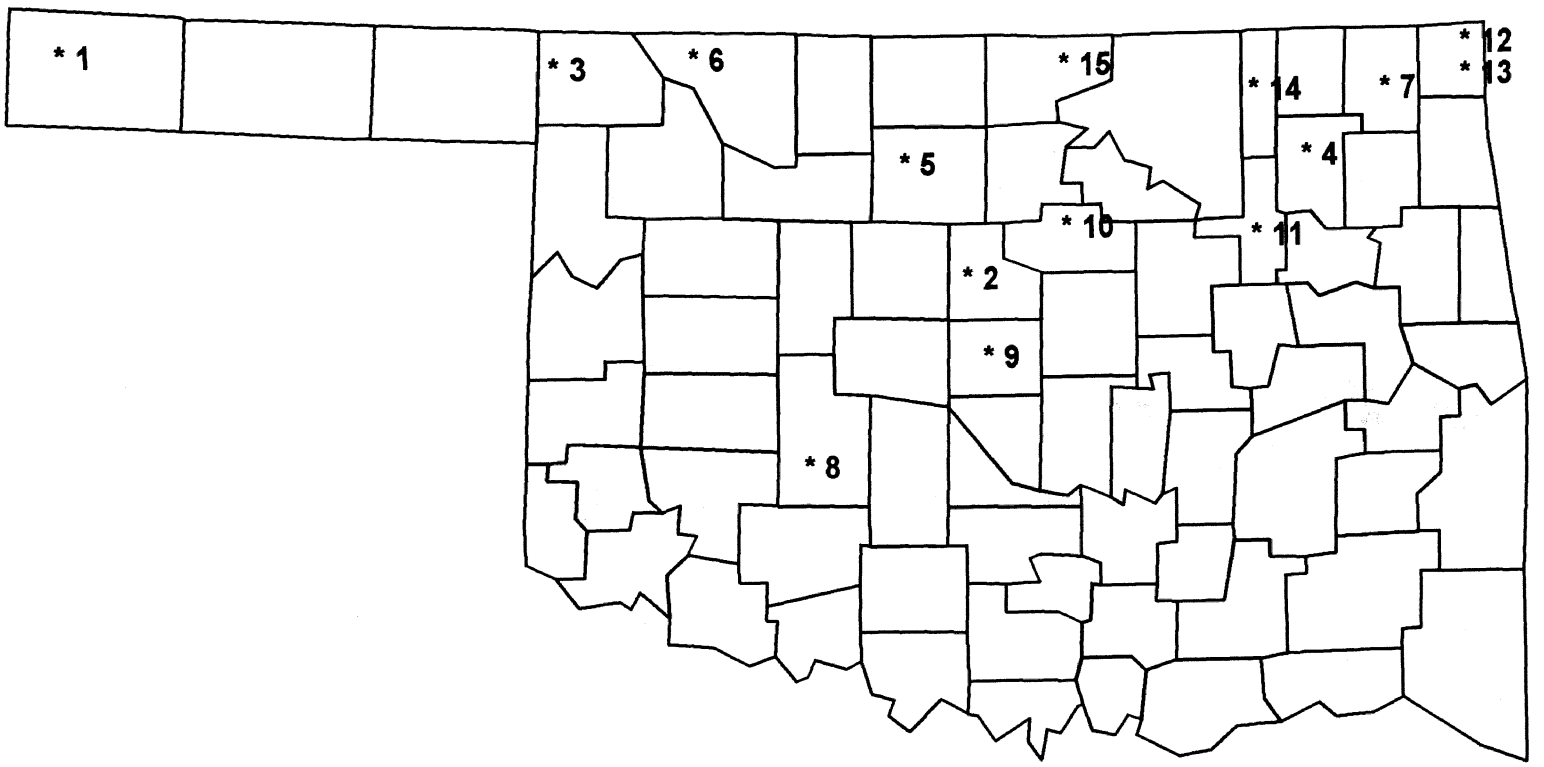

Figure 1. Location of sampling sites in Oklahoma.

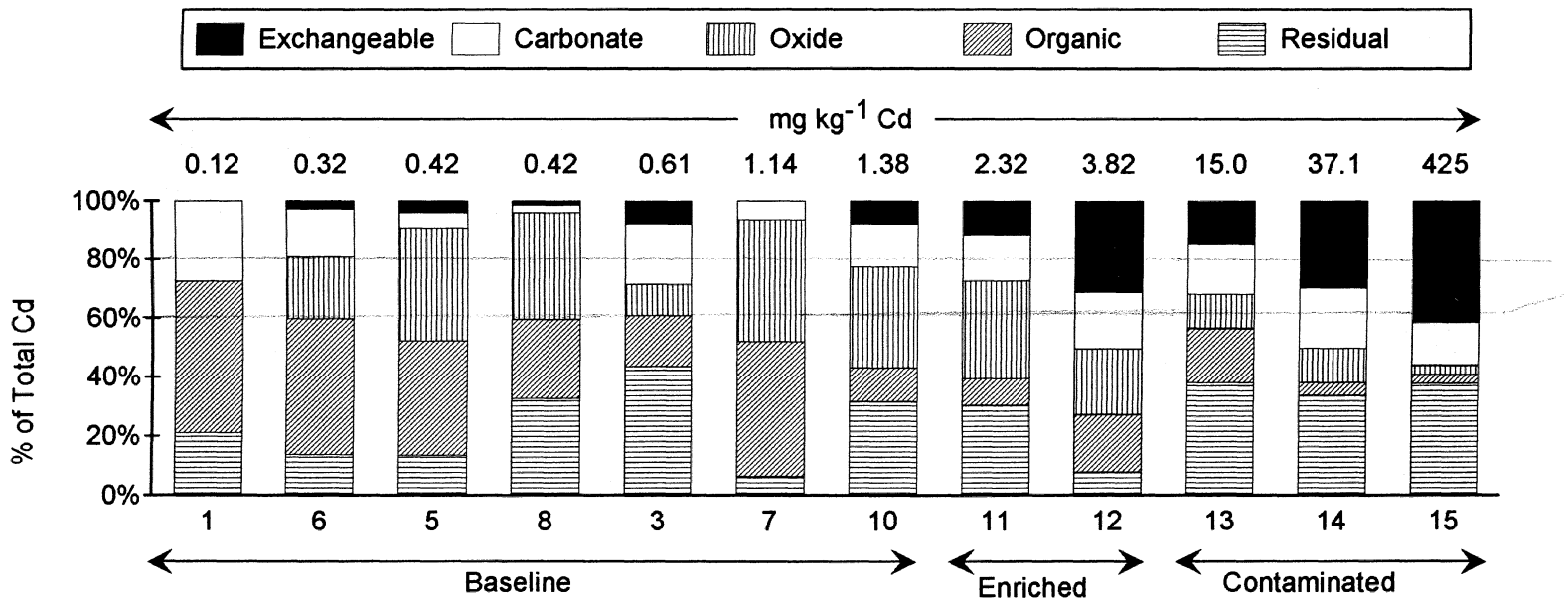

Figure 2. Exchangeable, carbonate, oxide, organic, and residual Cd fractions as a percentage of total Cd in Oklahoma soils.

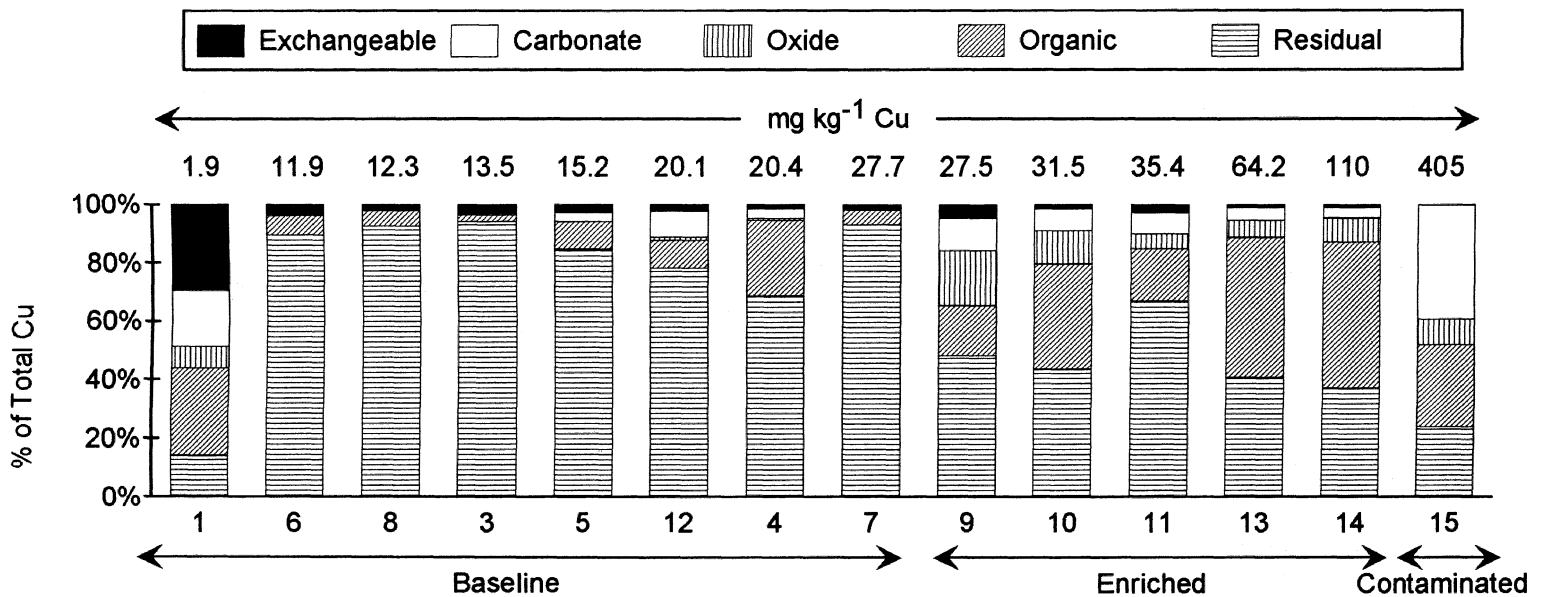

Figure 3. Exchangeable, carbonate, oxide, organic, and residual Cu fractions as a percentage of total Cu in Oklahoma soils.

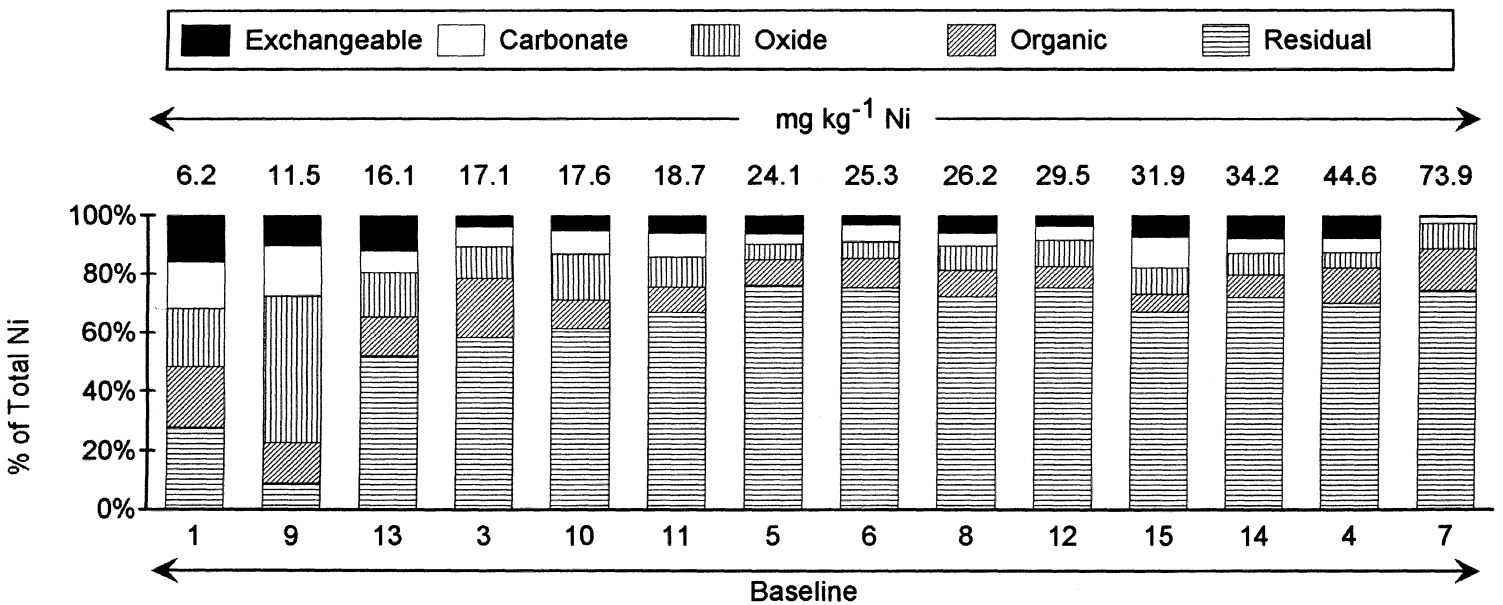

Figure 4. Exchangeable, carbonate, oxide, organic, and residual Ni fractions as a percentage of total Ni in Oklahoma soils.

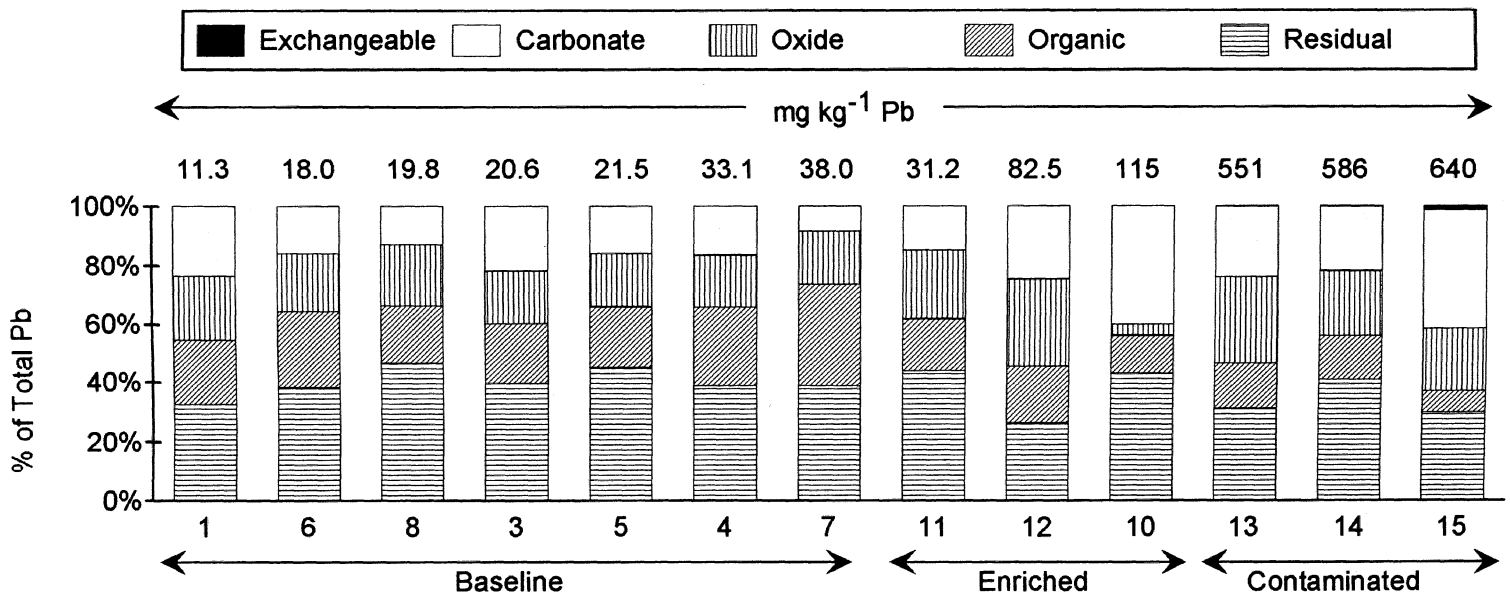

Figure 5. Exchangeable, carbonate, oxide, organic, and residual Pb fractions as a percentage of total Pb in Oklahoma soils.

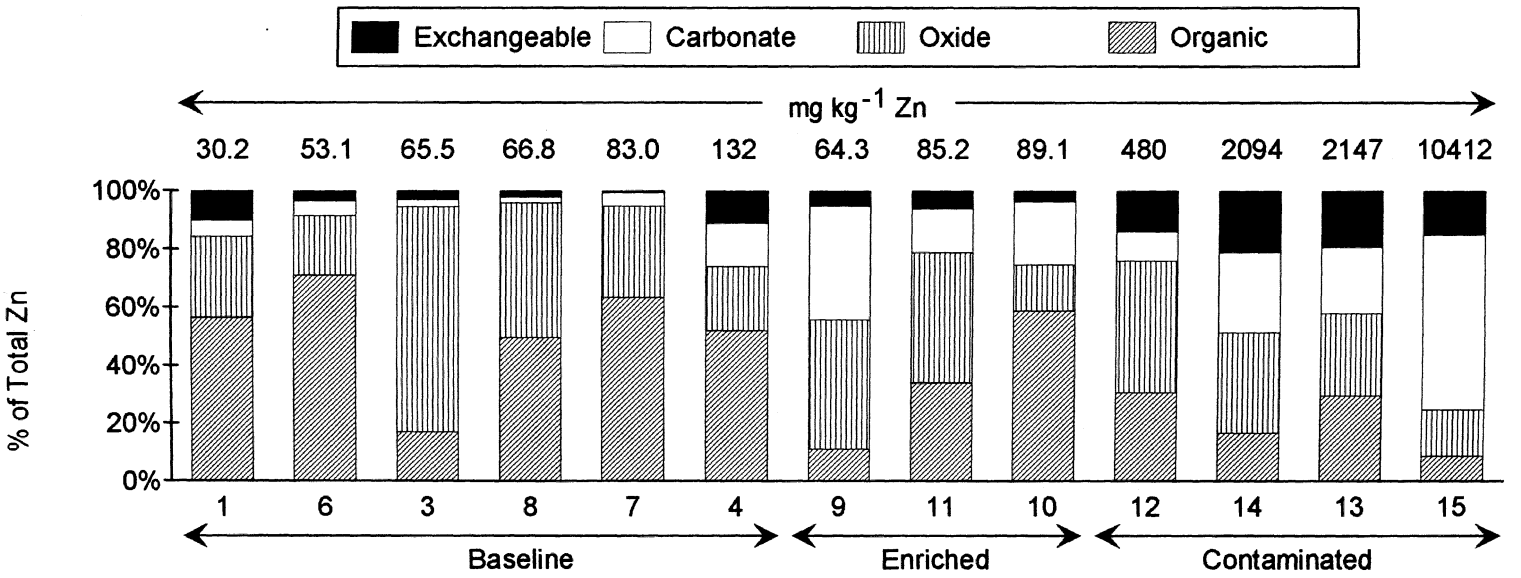

Figure 6. Exchangeable, carbonate, oxide, and organic Zn fractions as a percentage of the sum of exchangeable, carbonate, oxide, and organic Zn in Oklahoma soils.

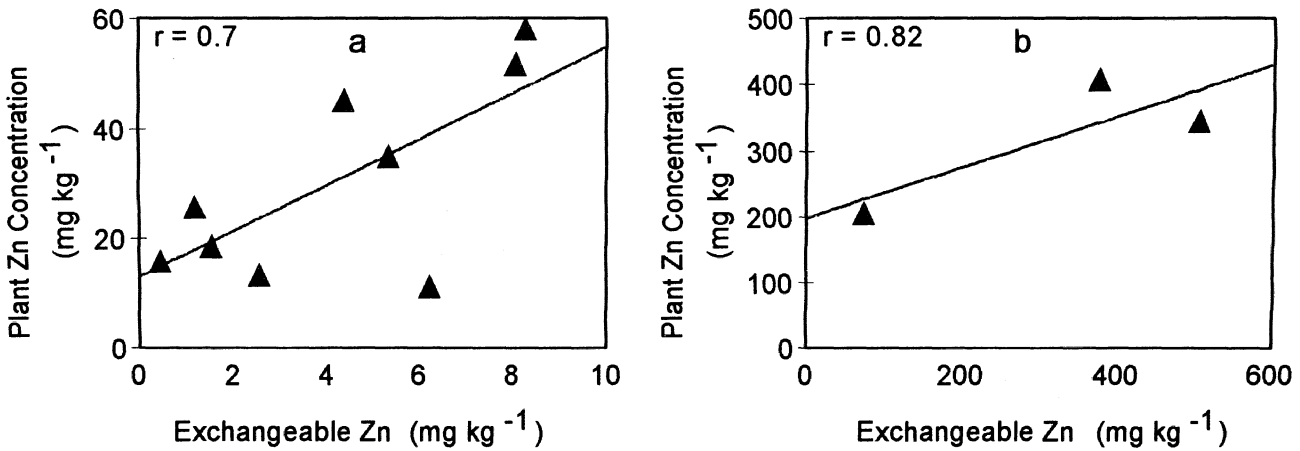

Figure 7. Comparison of plant Zn concentration and exchangeable Zn in (a) baseline and enriched soils and (b) contaminated soils.

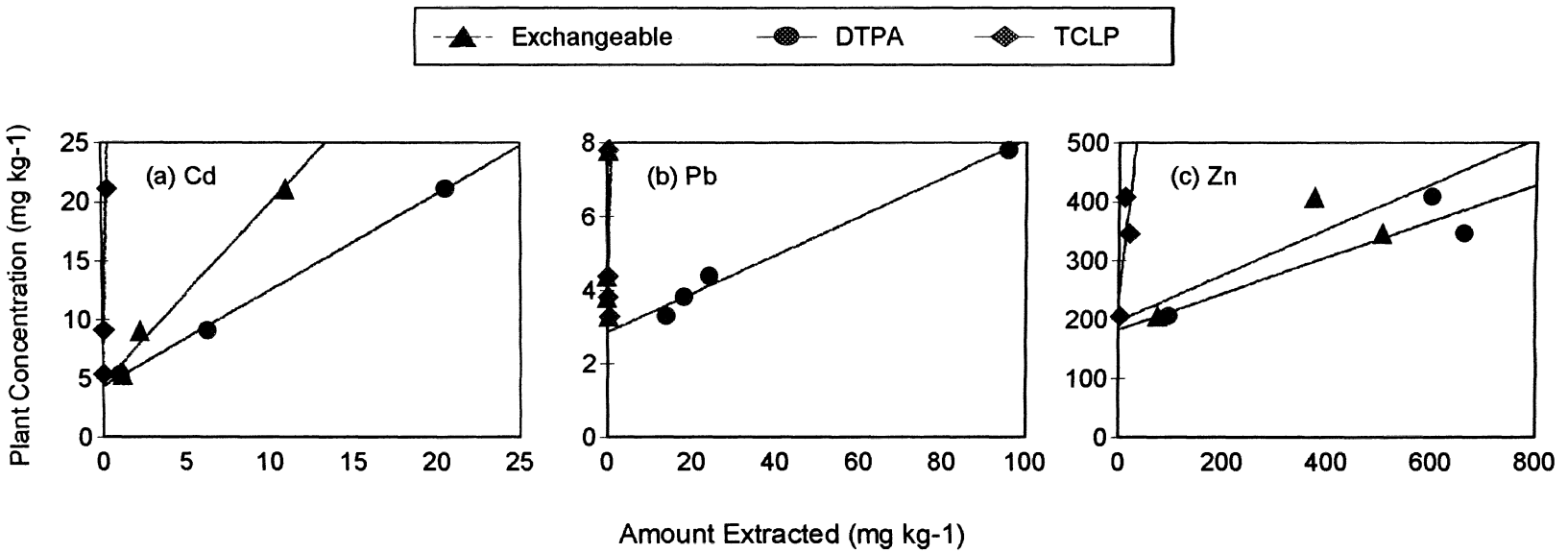

Figure 8. Plant concentration of Cd (a), Pb (b), and Zn (c) vs. metals in exchangeable, DTPA, and TCLP extracts of contaminated soils.

APPENDIX

Table A1. Location of benchmark soils.

Soil	County	Location Sampled
Bernow	Atoka	NE 1/4, SE 1/4, SEC 5, T3S, R11E
Burleson	Johnston	NW 1/4, SW 1/4, SEC 17, T2S, R8E
Carnasaw	LeFlore	SE 1/4, SE 1/4, SEC 31, T4N, R25E
Clarksville	Mayes	NE 1/4, NE 1/4, SEC 36, T21N, R20E
Cobb	Caddo	SW 1/4, SE 1/4, SEC 21, T8N, R12W
Dalhart	Cimarron	SW 1/4, NW 1/4, SEC 20, T3N, R4E
Darnell	Lincoln	SE 1/4, SE 1/4, SEC 17, T16N, R2E
Dennis	Rogers	SW 1/4, SW 1/4, SEC 26, T21N, R17E
Dougherty	Payne	NW 1/4, NE 1/4, SEC 3, T17N, R1E
Durant	Bryan	SW 1/4, SW 1/4, SEC 35, T10E, R7S
Easpur	Payne	SE 1/4, NW 1/4, SEC 16, T19N, 2E
Grant	Garfield	NE 1/4, SE 1/4, SEC 23, T21N, R7W
Kirkland	Logan	SE 1/4, SE 1/4, SEC 36, T16N, R4W
Lebron	Logan	NE 1/4, NE 1/4, SEC 9, T17N, R2W
Mansic	Harper	SW 1/4, SW 1/4, SEC 35, T28N, R25W
Osage	Rogers	SE 1/4, SE 1/4, SEC 35, T22N, R15E
Parsons	Craig	SW 1/4, NE 1/4, SEC 16, T25N, R20E
Pond Creek	Garfield	NE 1/4, NE 1/4, SEC 12, T23N, R8W
Pratt	Woods	NE 1/4, NE 1/4, SEC 34, T25N, R15W
Renfrow	Okalhoma	NE 1/4, NW 1/4, SEC 14, T14N, R4W
Richfield	Beaver	SW 1/4, SW 1/4, SEC 8, T1N, R23E
Saint Paul	Woods	NE 1/4, NE 1/4, SEC 9, T27N, R18W
Sallisaw	Delaware	SE 1/4, SW 1/4, SEC 5, T21N, R25E
Stiegler	Delaware	SE 1/4, N2 1/4, SEC 30, T22N, R25E
Summit	Craig	NW 1/4, SW 1/4, SEC 22, T25N, R21E
Tillman	Caddo	NW 1/4, SE 1/4, SEC 31, T7N, R13W
Woodward	Woods	SE 1/4, SE 1/4, SEC 28, T28N, R18W
Zaneis	Logan	NW 1/4, SW 1/4, SEC 30, T18N, R2W

Table A2. Soil properties of Oklahoma soil series.

Soil	Horizon	Clay	OC	Fe_2O_3	MnO	pH	CEC
		%					$cmol_c\ kg^{-1}$
Benchmark Soils							
Bernow	A	11	1.40	0.27	0.006	3.8	1.9
	B	39	0.20	1.32	0.004	3.8	11.8
	C	33	0.24	0.76	0.003	3.6	11.2
Burleson	A	42	1.13	0.55	0.058	5.1	21.8
	AB	56	0.73	0.57	0.032	5.2	33.3
	AC	58	0.55	0.49	0.041	6.8	37.3
Carnasaw	A	21	2.84	1.93	0.170	5.1	13.4
	B	75	0.23	4.55	0.012	3.8	11.8
	C	45	0.28	3.26	0.013	3.6	17.3
Clarksville	A	26	1.96	0.77	0.241	4.7	8.6
	B	38	0.51	1.27	0.016	3.5	7.7
	C	84	0.20	3.17	0.015	3.8	13.5
Cobb	A	16	0.35	0.54	0.011	4.9	4.5
	B	24	0.20	0.84	0.012	6.3	16.2
	R	18	0.06	0.66	0.010	6.3	13.5
Dalhart	A	12	0.35	0.29	0.010	6.7	12.5
	B	30	0.39	0.60	0.026	7.1	22.2
	C	34	0.19	0.67	0.029	7.8	24.7
Darnell	A	11	0.51	0.57	0.032	4.4	2.1
	B	12	0.45	0.63	0.022	4.6	7.0
	C	24	0.30	1.27	0.015	4.7	2.7
Dennis	A	25	1.58	1.73	0.044	5.0	10.4
	B	50	0.32	2.86	0.098	5.3	14.5
	C	76	0.07	4.64	0.050	6.7	31.7
Dougherty	A	8	0.67	0.19	0.010	4.3	2.5
	E	8	0.15	0.15	0.005	5.2	1.4
	B	20	0.21	0.54	0.004	4.4	6.3
	C	10	0.14	0.16	0.004	5.6	1.5
Durant	A	27	2.47	0.76	0.040	6.4	35.1
	B	53	0.49	1.26	0.017	5.1	44.6
	C	61	0.11	1.86	0.082	7.7	51.0
Easpur	A	22	0.60	1.05	0.040	4.8	7.9
	B	28	0.31	1.52	0.033	4.6	10.0
	C	16	0.10	0.93	0.034	5.2	5.2
Grant	A	26	0.78	0.68	0.031	5.3	9.9
	B	48	0.68	1.04	0.044	7.0	24.1
	C	44	0.38	1.24	0.029	7.8	27.0
Kirkland	A	35	1.08	0.71	0.047	4.8	16.1
	Bt1	51	0.50	0.63	0.046	7.2	40.9
	Bt2	53	0.08	1.10	0.057	7.6	36.2

Table A2. Continued.

Soil	Horizon	Clay	OC	Fe_2O_3	MnO	pH	CEC
		%					$cmol_c\ kg^{-1}$
Lebron	Ap	59	1.97	1.37	0.044	7.4	32.5
	A	71	0.90	1.34	0.047	7.7	36.3
	C3	5	0.04	0.17	0.006	8.1	5.9
Mansic	A	35	1.39	0.37	0.024	7.7	34.0
	B	41	0.30	0.35	0.019	7.8	27.6
	C	35	0.27	0.34	0.024	7.8	24.8
Osage	A	66	2.95	2.02	0.073	5.1	30.2
	B	70	0.80	1.71	0.076	5.7	32.7
	C	72	0.69	1.18	0.061	6.8	38.0
Parsons	A	30	1.40	2.37	0.069	5.8	13.2
	B	50	0.58	4.22	0.059	4.8	11.9
	C	54	0.42	6.32	0.090	4.8	13.5
Pond Creek	A	28	0.98	0.64	0.037	4.4	8.4
	B	46	0.59	0.95	0.046	7.0	26.2
	C	46	0.43	0.92	0.050	7.0	33.6
Pratt	A	7	0.38	0.19	0.008	5.7	6.7
	B	11	0.32	0.29	0.008	5.6	4.6
	C	11	0.22	0.23	0.008	5.8	3.1
Renfrow	A	25	1.35	0.82	0.028	6.3	21.5
	Bt1	49	0.34	1.45	0.059	7.5	35.1
	Bt2	49	0.08	1.77	0.071	7.8	27.9
Richfield	A	45	0.75	0.60	0.038	6.9	33.5
	B	47	0.36	0.67	0.038	7.9	28.8
	C	49	0.22	0.74	0.036	7.8	33.0
Saint Paul	A	28	1.14	0.71	0.029	6.2	14.2
	B1	42	0.57	0.77	0.033	7.7	29.3
	B2	38	0.31	0.92	0.027	7.9	25.5
	C	42	0.12	0.89	0.025	8.0	17.3
Sallisaw	A	22	1.17	0.87	0.142	4.6	5.1
	B	38	0.44	1.30	0.054	4.9	2.6
Stiegler	A	28	2.30	0.68	0.175	4.9	10.6
	B	66	0.66	0.41	0.013	3.7	17.9
	C	56	0.32	0.54	0.013	3.8	16.1
Summit	A	58	2.52	2.98	0.187	7.2	39.1
	B	68	1.02	2.94	0.178	7.7	48.2
	C	70	0.65	2.78	0.108	7.9	48.8
Tillman	A	34	0.74	1.01	0.044	5.4	11.3
	B	62	0.46	1.53	0.045	7.2	34.2
	C	53	0.20	1.58	0.042	8.0	27.0
Woodward	A	20	1.08	0.67	0.022	7.2	21.8
	B	22	0.48	0.72	0.020	7.7	18.5
	C	18	0.35	0.66	0.017	7.8	15.3

Table A2. Continued.

Soil	Horizon	Clay	OC	Fe_2O_3	MnO	pH	CEC
		%					$cmol_c\ kg^{-1}$
Zaneis	A	21	1.21	0.72	0.019	5.1	5.5
	Bt1	35	0.58	1.11	0.010	5.3	10.6
	BC	34	0.25	1.63	0.006	5.6	9.4
Sludge Amended Soils							
Oklahoma City	A	6	1.06	0.44	0.013	7.2	15.5
Stillwater	A	16	1.47	1.44	0.018	6.7	11.0
Tulsa	A	14	1.83	1.25	0.039	5.7	11.5
Mine and Smelter Contaminated Soils							
Bartlesville	A	33	3.29	2.04	0.030	6.0	19.5
Blackwell	A	25	1.50	0.89	0.040	6.2	11.5
Cardin	A	12	3.73	1.23	0.042	6.3	18.0
Picher	A	17	1.51	2.03	0.057	5.6	13.5

Table A3. Total heavy metal concentrations of Oklahoma soils.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Benchmark Soils									
Bernow	1	A	1	0.02	10.6	2.5	3.2	5.0	22.4
			2	0.06	9.5	2.6	4.6	5.2	13.5
		B	1	0.45	6.6	8.4	13.6	11.6	45.7
			2	0.42	6.3	8.6	11.9	10.1	22.5
		C	1	0.36	5.2	6.4	8.0	7.8	21.5
			2	0.21	7.8	7.5	15.4	7.8	23.8
Bernow	2	A	1	0.17	9.3	3.2	16.8	7.2	30.9
			2	0.26	8.5	3.7	11.2	5.2	73.2
		B	1	0.41	6.7	10.9	17.7	5.4	34.4
			2	0.83	8.5	10.0		14.5	30.4
		C	1	0.14	8.3	5.9	12.6	9.0	
			2	0.21	8.3	6.4	13.4	6.8	30.6
Bernow	3	A	1	0.14	14.3	3.9	7.7	8.0	35.1
			2	0.13	13.3	3.5	5.9	10.4	22.7
		B	1	0.30	11.8	8.9	19.0	14.6	37.4
			2	0.35	10.6	9.1	18.9	11.9	33.0
		C	1	0.35	8.1	7.5	17.4	9.6	
			2	0.74	9.6	7.5	17.0	10.0	36.8
Burleson	1	A	1	0.57	10.7	13.7	22.5	20.3	66.1
			2	0.33	11.8	12.9	33.3	17.7	58.0
		AB	1	0.66	8.2	17.0	21.1	11.3	81.3
			2	0.52	9.5	16.7	30.6	17.8	84.9
		AC	1	0.60	12.3	16.3	39.0	20.1	85.6
			2	0.69	12.1	15.8	37.2	19.5	82.5
Burleson	2	A	1	0.66	12.9	16.2	37.0	36.4	80.3
			2	0.55	12.7	15.8	41.8	55.2	78.0
		AB	1	0.58	15.6	18.3	54.8	23.2	94.5
			2	0.72	12.6	19.6	60.9	18.0	85.9
		AC	1	0.49	12.8	17.3	45.1	17.8	73.6
			2	0.74	17.1	17.7	55.8	26.9	111.1
Burleson	3	A	1	0.82	12.4	15.9	33.7	25.8	99.5
			2	0.66	12.8	15.9	42.3	26.4	100.2
		AB	1	1.06	13.5	17.3		22.2	101.2
			2	1.11	13.5	17.4	30.6	26.4	113.6
		AC	1	0.69	15.4	17.4	61.8	26.0	116.7
			2	0.66	14.9	17.9	56.6	25.0	121.9
Carnasaw	1	A	1	1.24	18.3	8.9	18.9	28.3	71.4
			2	1.13	16.1	9.1	12.7	27.6	54.7
		B	1	1.42	5.9	18.7	19.3	24.2	64.2
			2	0.63	6.6	19.6	33.0	18.3	63.0
		C	1	1.04	8.5	30.5	40.5	24.9	102.4
			2	0.71	9.5	28.6	47.9	25.3	99.2

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Carnasaw	2	A	1	0.67	23.6	9.3	26.8	20.8	58.4
			2	0.78	23.9	8.7	20.7	29.3	68.5
		B	1	1.08	6.7	22.6	34.7	21.7	113.6
			2	1.27	7.1	19.5	43.2	25.2	77.8
		C	1	0.68	11.4	22.8	38.7	29.2	122.1
			2	0.71	12.9	23.1	50.0	30.0	125.4
Carnasaw	3	A	1	1.12	17.2	10.1	29.8	31.8	93.2
			2	1.25	20.9	10.3		33.4	85.9
		B	1	1.06	8.6	20.0	43.4	27.4	99.5
			2	0.61	6.8	19.6	31.7	22.0	77.1
		C	1	0.78	13.6	26.3	54.2	26.8	136.2
			2	0.76	12.6	25.0	50.5	14.1	139.2
Clarksville	1	A	1	0.51	17.0	11.5	9.0	12.9	52.6
			2	0.54	19.6	11.5	13.7	19.0	51.2
		B	1	0.48	7.4	7.0	9.3	11.3	58.0
			2	0.45	8.1	6.7	12.0	12.1	56.0
		C	1	1.08	5.9	14.3	29.5	33.3	147.0
			2	1.24	6.2	14.3	35.8	36.1	158.0
Clarksville	2	A	1	1.25	7.4	14.0	36.6	38.2	158.7
			2	0.82	13.6	12.7	20.0	34.0	99.9
		B	1	1.15	6.7	15.5	34.9	36.1	144.5
			2	1.22	13.2	14.4	23.7	29.5	97.9
		C	1	0.38	6.7	17.9	40.9	50.5	246.1
			2	1.07	6.9	18.2	41.7	47.0	337.5
Cobb	1	A	1	0.23	9.3	5.4	7.6	9.8	23.6
			2	0.25	9.7	5.9	8.8	10.8	22.7
		B	1	0.23	8.7	5.1	11.1	11.0	31.3
			2	0.20	11.0	5.3	12.2	10.3	34.8
		R	1	0.10	7.0	6.4	9.5	11.6	33.0
			2	0.14	6.3	6.1	8.9	9.7	25.3
Cobb	2	A	1	0.21	7.5	6.3	10.4	8.0	23.6
			2	0.18	7.0	6.8	14.5	8.2	33.6
		B	1	0.16	8.3	5.4	7.6	7.7	24.0
			2	0.23	9.6	4.9	8.7	10.6	32.8
		R	1	0.15	7.6	7.1	9.8	12.0	33.3
			2	0.27	7.3	7.1	9.6	11.7	26.1
Cobb	3	A	1	0.25	5.5	6.3	9.6	12.0	27.8
			2	0.24	5.6	6.1	9.8	10.7	24.1
		B	1	0.21	6.0	7.2	12.5	11.9	27.1
			2	0.15	5.6	7.0	10.2	10.0	27.1
		R	1	0.17	6.1	9.1	13.4	11.9	27.6
			2	0.22	6.4	10.6	24.1	12.9	

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Dalhart	1	A	1	0.00	12.9	1.9	12.5	9.2	40.3
			2	0.12	14.0	2.1	5.6	9.7	102.7
		B	1	0.20	19.4	8.7	13.3	13.3	109.1
			2	0.34	22.1	9.6	14.1	14.6	41.2
		C	1	0.36	12.4	13.5	22.2	14.7	58.0
			2	0.47	12.2	13.3	17.9	15.1	52.2
Dalhart	2	A	1	0.06	25.6	2.8	11.4	8.2	24.8
			2	0.07	25.5	2.8	8.2	7.8	20.5
		B	1	0.74	11.8	14.6	11.5	11.1	54.9
			2	0.58	11.8	13.2	12.5	10.5	44.0
		C	1	0.42	10.1	16.4	16.4	10.9	54.9
			2	0.49	9.3	16.1	16.6	10.2	47.7
Dalhart	3	A	1	0.23	12.9	2.6	9.3	6.9	50.4
			2	0.12	12.5	2.6	6.9	7.4	56.4
		B	1	0.43	7.9	11.5	5.8	5.8	46.2
			2	0.44	6.6	10.6	6.9	4.1	34.1
		C	1	0.52	5.9	12.8	5.7	6.7	
			2		13.7	12.7	13.6		67.7
Darnell	1	A	1	0.12	132.4	2.3	7.0	5.7	29.4
			2	0.11	143.3	2.0	6.9	6.5	29.5
		B	1	0.10	176.8	1.8	7.4	5.8	21.0
			2	0.12	177.0	1.7	7.6	5.7	17.3
		C	1	0.39	29.7	4.3	12.9	11.3	21.5
			2	0.33	31.6	4.1	12.8	10.5	30.0
Darnell	2	A	1	0.07	31.8	1.8	5.0	3.8	18.4
			2	0.11	36.5	1.8	5.0	3.9	26.3
		B	1	0.10	34.8	1.6	4.9	2.6	11.6
			2	0.07	37.4	1.6	4.9	2.9	20.8
		C	1	0.12	29.5	2.1	5.5	3.8	10.8
			2	0.17	25.6	2.3	5.8	3.5	27.2
Darnell	3	A	1	0.11	15.1	3.4	6.1	4.3	66.8
			2	0.22	19.2	3.2	6.6	7.7	24.6
		B	1	0.12	22.7	1.6	5.6	4.6	38.1
			2	0.14	23.2	1.6	5.6	4.4	14.0
		C	1	0.19	17.5	3.4	9.1	8.0	21.3
			2	0.18	13.4	3.6	7.1	5.1	29.8
Dennis	1	A	1	0.51	9.5	8.9	16.4	13.2	52.3
			2	0.48	4.0	9.4	6.4	8.3	47.8
		B	1	0.77	15.4	11.3	28.9	21.7	52.3
			2	0.64	13.7	12.0	26.6	19.2	51.9
		C	1	1.60	20.6	17.8	54.9	24.8	78.8
			2	1.70	20.8	17.3	62.3	26.1	91.5

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Dennis	2	A	1	0.51	12.4	15.7	17.6	14.5	63.4
			2	0.79	11.4	14.1	10.8	16.2	67.8
		B	1	1.02	17.2	25.5	39.3	20.2	63.6
			2	1.04	18.0	18.9	42.2	21.2	62.7
		C	1	1.02	18.7	27.4	35.7	19.7	98.6
			2	1.03	19.8	25.9	36.8	20.1	98.6
Dennis	3	A	1	1.02	8.4	13.9	17.4	18.2	55.3
		A	2	1.05	8.9	14.8	17.5	19.1	63.5
		B	1	0.67	11.7	18.3	41.8	17.7	71.2
		B	2	0.52	11.0	17.8	39.7	16.1	68.1
		C	1	0.96	15.3	20.0	48.0	20.5	81.5
		C	2	0.79	16.5	19.9	54.8	21.4	88.1
Dougherty	1	A	1	0.13	47.9	3.2	5.5	13.8	22.5
			2	0.12	49.5	2.9		13.3	23.1
		E	1	0.62	32.2	1.0	48.3	6.7	38.6
			2	0.00	31.6	1.1	47.9	7.0	16.5
		B	1	0.10	12.3	2.4	9.7	7.9	24.8
			2	0.12	15.6	2.4	7.4	9.6	20.2
		C	1	0.00	24.2	0.9	16.0	7.8	14.9
			2	0.01	11.3	0.9	2.6	6.9	10.9
Dougherty	2	A	1	0.23	19.7	2.7	4.3	8.7	29.6
			2	0.05	18.5	2.7	11.0	7.1	21.9
		E	1	0.04	20.5	1.0	4.7	5.0	12.6
			2	0.00	23.4	0.9	14.2	7.0	15.0
		B	1	0.15	12.0	2.7	15.6	5.6	26.4
			2	0.01	13.2	2.9	31.5	7.7	17.4
		C	1	0.10	9.5	2.3	7.2	5.9	15.9
			2	0.02	10.0	2.5	19.9	6.0	22.4
Dougherty	3	A	1	0.20	21.3	2.4	6.7	7.7	18.5
			2	0.04	21.2	2.2	13.2	6.9	22.0
		E	1	0.01	14.7	1.0	11.8	4.3	12.8
			2	0.00	16.0	1.2	17.1	5.2	15.8
		B	1	0.11	13.2	2.9	15.5	8.8	20.8
			2	0.00	12.4	2.6	28.2	6.8	24.4
		C	1	0.05	13.6	1.3	7.5	5.1	36.7
			2	0.09	11.4	1.2	6.5	4.4	15.5
Durant	1	A	1	0.28	7.6	9.1	12.2	15.1	31.4
			2	0.19	8.3	9.1	13.0	16.4	37.0
		B	1	0.20	12.9	14.6	47.5	20.9	69.3
			2	0.60	10.6	13.8	23.9	19.3	53.1
		C	1	0.56	15.3	22.9	45.2	19.4	73.6
			2	0.68	15.3	17.1	40.5	19.6	75.0

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Durant	2	A	1	0.25	6.9	9.3	9.9	7.8	28.0
			2	0.40	6.5	8.8	12.2	7.8	38.1
		B	1	0.48	7.5	16.2	20.1	7.1	52.6
			2	0.45	8.0	12.5	16.1	9.0	41.4
		C	1	0.45	9.6	13.9	12.0	5.6	46.5
			2	0.73	10.9	13.1	13.6	9.6	48.0
Durant	3	A	1	0.41	10.6	9.1	9.1	6.4	28.8
			2	0.32	9.5	9.3	7.8	4.0	24.7
		B	1	0.43	10.1	14.3	16.4	12.2	69.4
			2	0.79	9.7	13.2	10.4	14.2	42.6
		C	1	0.36	11.0	13.9	15.0	9.0	45.4
			2	0.55	12.1	13.9	16.4	12.2	49.6
Easpur	1	A	1	0.39	16.3	8.3	16.2	18.4	46.4
			2	0.50	16.2	8.7	16.7	18.6	46.7
		B	1	0.23	13.6	10.0	15.3	1.7	43.2
			2	0.55	11.1	10.0	12.2	11.5	40.8
		C	1	0.31	14.7	6.1	8.9	5.6	32.3
			2	0.14	12.5	6.8	4.2	0.5	28.5
Easpur	2	A	1	0.45	12.8	7.0	14.3	16.7	179.2
			2	0.49	11.6	7.0	17.7	16.6	86.3
		B	1	0.41	13.5	11.9	23.1	15.9	41.4
			2	0.61	11.4	8.6	7.4	16.1	44.0
		C	1	0.42	11.2	10.5	7.4	15.9	38.0
			2	0.27	13.4	11.5	15.9	11.6	37.9
Easpur	3	A	1	0.79	10.8	11.3	7.0	24.5	56.0
			2	0.77	11.2	11.8	7.5	24.5	62.8
		B	1	0.03	10.7	12.6	23.4	3.8	145.5
			2	0.17	11.1	11.8	24.6	8.7	45.8
		C	1	0.05	11.8	9.7	18.3	2.1	38.4
			2	0.55	9.2	8.7	9.6	13.9	93.1
Grant	1	A	1	0.35	9.9	9.3	17.1	15.5	45.6
			2	0.21	9.7	13.6	25.4	14.8	51.4
		B	1	0.34	15.0	14.3	27.4	18.0	66.2
			2	0.52	15.0	14.0	28.6	18.9	68.1
		C	1	0.46	12.8	11.3	26.4	16.0	52.8
			2	0.38	11.5	11.5	25.2	14.7	55.1
Grant	2	A	1	0.43	10.6	10.2	15.1	13.8	48.1
			2	0.41	13.4	27.6	28.4	32.0	66.9
		B	1		14.3	14.7		24.1	63.8
			2	0.30	10.1	14.2	9.4	4.3	125.3
		C	1	0.72	10.6	14.9	30.1	7.8	188.1
			2	0.60	8.6	11.8	15.0	6.5	66.9

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Grant	3	A	1	0.49	10.2	11.2	6.7	10.3	51.0
			2	0.47	11.0	10.9	7.1	16.5	51.7
		B	1	0.56	10.6	15.3	24.1	20.5	72.8
			2	0.55	10.5	13.8	24.4	17.7	65.7
		C	1	0.52	9.3	13.7	14.8	17.5	69.5
			2	0.44	9.7	12.9	26.4	19.9	86.3
Kirkland	1	A	1	0.52	11.8	13.7	15.7	20.0	53.5
			2	0.52	11.5	14.7	15.4	19.7	42.2
		Bt1	1	0.62	12.2	15.1	24.7	19.3	58.3
			2	0.55	11.4	15.8	26.1	17.0	69.9
		Bt2	1	1.06	9.4	18.6	23.2	21.8	60.1
			2	0.88	10.8	18.3	13.7	19.2	66.4
Kirkland	2	A	1	0.60	10.5	13.4	10.1	16.6	35.1
			2	0.36	8.5	13.7	7.6	13.2	39.2
		Bt1	1	0.59	8.7	20.5	17.6	15.7	54.0
			2	0.66	10.3	16.3	17.3	19.7	64.2
		Bt2	1	0.39	11.3	16.0	17.7	15.6	51.1
			2	0.48	11.0	18.3	24.9	15.2	52.2
Kirkland	3	A	1	0.48	10.4	13.9	12.2	16.7	38.2
			2	0.37	8.8	14.2	11.4	14.0	30.7
		Bt1	1	1.04	11.1	15.3	0.1	20.3	55.1
			2	1.04	11.4	15.6	0.1	20.8	60.9
		Bt2	1	1.04	12.0	18.8	0.1	19.7	69.3
			2	1.12	12.4	19.6	0.1	20.2	70.7
Lebron	1	Ap	1	0.80	13.5	24.1	38.3	22.3	112.9
			2	0.96	14.5	23.7	37.0	23.3	110.1
		A	1	0.81	16.1	24.4	37.0	21.9	96.8
			2	1.07	15.9	23.9	36.7	23.1	97.1
		C3	1	0.00	16.9	1.0	3.1	7.1	27.1
			2	0.04	18.0	1.0	3.3	9.6	27.9
Lebron	2	Ap	1	0.90	10.4	24.9	24.0	14.5	74.3
			2	0.60	9.5	48.4	22.4	10.6	73.1
		A	1	0.91	9.4	22.9	20.4	13.3	76.0
			2	0.68	8.5	22.3	12.6	9.6	58.0
		C3	1	0.21	7.7	2.5	6.5	6.0	32.4
			2	0.20	8.2	2.9	6.4	5.3	38.5
Lebron	3	Ap	1	0.94	9.8	31.6	21.4	13.5	74.7
			2	0.86	9.5	23.8	17.0	13.0	75.8
		A	1	0.59	8.1	17.6	11.9	9.8	55.6
			2	0.59	8.7	17.6	18.2	10.2	115.4
		C3	1	0.19	5.2	2.0	7.3	5.6	21.5
			2	0.17	5.0	2.1	7.2	5.7	43.7

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Mansic	1	A	1	0.52	6.4	13.6	13.6	15.9	76.8
			2	0.69	8.8	13.4	17.6	16.4	60.1
		B	1	0.38	9.5	11.5	23.7	14.5	58.4
			2	0.54	9.4	12.3	21.0	14.9	47.7
		C	1	0.45	8.2	11.5	17.9	15.2	50.3
			2	0.48	8.3	11.5	15.4	15.4	47.3
Mansic	2	A	1	0.33	5.6	13.6	9.5	6.3	43.8
			2	0.36	4.4	13.4	8.0	6.8	40.3
		B	1	0.44	5.3	12.5	10.1	8.3	41.5
			2	0.51	5.5	12.5	11.9	10.3	52.8
		C	1	0.45	6.6	9.2	9.7	10.0	40.0
			2	0.34	6.0	8.9	8.8	6.4	29.0
Mansic	3	A	1	0.87	6.2	17.7	20.6	10.8	62.5
			2	0.42	6.2	11.6	10.2	6.5	40.4
		B	1	0.26	6.2	10.8	7.6	5.7	33.7
			2	0.05	6.2	12.0	9.6	1.7	32.1
		C	1	0.37	7.0	10.9	8.7	7.3	34.5
			2	0.24	6.6	10.2	8.9	6.9	34.6
Osage	1	A	1	0.96	13.9	20.8	8.7		127.1
			2	1.29	15.9	19.9	42.5	31.2	125.9
		B	1	1.05	17.5	32.1	52.4	25.5	106.0
		C	1	1.21	16.1	24.5	46.6	25.5	128.5
			2	0.84	16.8	24.7	64.9	25.2	109.0
Osage	2	A	1	1.91	20.6	21.6	39.8	38.2	153.2
			2	1.26	16.8	19.7	40.3	28.2	120.7
		B	1	0.68	17.4	29.5	46.5	26.4	112.9
			2	0.59	15.9	30.4	38.6	22.4	101.3
		C	1	0.76	16.1	25.2	41.3	24.1	101.7
			2	0.65	14.8	25.8	43.1	20.2	79.8
Osage	3	A	1	1.32	14.2	19.1	34.4	29.6	142.3
			2	1.12	17.2	19.9	46.1	35.9	150.0
		B	1	0.63	17.7	29.4	43.9	29.1	116.2
			2	0.89	18.2	29.0	43.5	29.5	126.2
		C	1	0.87	17.1	25.0	50.9	30.9	129.9
			2	0.81	15.7	23.4	49.1	28.1	122.8
Parsons	1	A	1	1.43	12.2	18.2	18.5	17.9	90.2
			2	2.16	9.3	19.1	19.4	21.0	82.5
		B	1	3.33	15.7	22.9	27.6	26.3	72.2
			2	1.95	16.1	24.1	10.1	16.1	68.3
		C	1	1.62	15.5	22.9			81.7
			2	3.43	20.5	23.4	52.7	41.1	79.6

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Parsons	2	A	1	1.42	15.3	14.4	21.5	33.5	57.2
			2	1.59	13.2	14.5	18.4	33.5	57.0
		B	1	1.96	21.5	26.3	36.0	33.4	67.5
			2	1.67	22.6	25.4	35.7	29.3	65.7
		C	1	2.01	26.3	25.1	58.9	46.3	84.0
			2	1.69	23.6	26.2	49.4	32.3	77.5
Parsons	3	A	1	0.71	9.0	13.9	16.0	28.8	50.0
			2	1.01	7.8	15.0	10.7	28.6	53.7
		B	1	1.17	7.7	23.3	27.3	38.7	63.5
			2	1.26	7.5	24.1	26.6	39.4	67.4
		C	1	1.45	11.4	22.0	31.2	39.8	60.1
			2	1.85	12.8	22.3	35.8	45.8	66.8
PondCreek	1	A	1	0.32	10.5	11.1	4.4		51.2
			2	0.51	12.0	19.3	15.6	17.1	47.6
		B	1	0.84	20.1	18.8	24.3	21.5	65.3
			2	0.79	19.6	18.8	24.3	21.5	63.2
		C	1	0.73	13.4	18.1	24.2	20.5	65.3
			2	0.74	12.4	19.3	22.8	19.2	65.4
PondCreek	2	A	1	0.56	18.0	12.4	17.4	20.8	51.8
			2	0.51	19.5	12.5	23.4	21.3	62.3
		B	1	0.42	11.2	25.9	22.9	18.2	78.4
			2	0.51	12.8	15.3	23.3	23.0	66.0
		C	1	0.55	13.6	18.2	25.5	25.9	74.8
			2	0.48	13.3	30.0	32.2	24.3	75.2
PondCreek	3	A	1	0.59	10.9	11.1	17.2	21.5	53.4
			2	0.38	11.7	12.0	44.3	21.3	91.5
		B	1	0.46	11.2	16.9	24.3	20.6	67.9
			2	0.64	11.7	16.6	29.1	23.8	74.4
		C	1	0.47	9.7	16.2	33.7	22.5	
			2	0.58	9.8	19.5	24.7	22.1	81.7
Pratt	1	A	1	0.02	33.7	3.5	5.9	18.5	
			2		26.9	2.7	2.9	12.2	29.4
		B	1	0.15	32.6	2.9	3.8	12.2	45.0
			2	0.11	43.3	2.6	7.8	9.4	41.2
		C	1		50.9	3.6	5.5	10.4	
			2	0.70	50.1	2.9	6.7	13.3	7.2
Pratt	2	A	1	0.00	40.7	2.4	5.3	1.4	20.0
			2	0.27	41.9	3.4	6.4	2.9	29.8
		B	1	0.05	26.2	2.8	3.9	1.2	15.5
			2	0.10	39.8	2.2	5.0	6.9	15.6
		C	1	0.34	34.6	2.9	7.8	6.6	22.6
			2	0.29	38.7	3.9	7.1	5.7	46.9

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Pratt	3	A	1	0.48	36.4	2.5	5.3	5.4	21.1
			2	0.25	24.5	3.3	8.5	5.2	29.6
		B	1		24.6	2.9	6.2	7.7	23.3
			2	0.05	21.1	3.1	5.8	0.9	46.6
		C	1	0.33	19.5	4.4	6.2	4.7	17.1
			2	0.93	23.6	3.6	6.9	6.8	63.4
Renfrow	1	A	1	0.45	9.9	10.6	11.4	17.2	36.3
			2	0.38	11.0	10.3	9.9	15.2	38.6
		B	1	0.72	9.8	16.1	10.9	17.1	48.9
			2	0.21	11.0	16.1	19.5		69.2
		B	1		18.8	20.4	21.8	21.7	90.5
			2	0.36	15.5	20.8	25.0	15.8	57.7
Renfrow	2	A	1	0.53	20.1	23.4	14.9	14.9	48.3
			2	0.28	12.0	21.1	7.5		32.7
		B	1	0.90	9.6	18.9	10.8	10.7	40.7
			2	0.90	9.8	17.8	10.6	12.2	43.0
		B	1	0.38	11.6	21.1	19.1	6.5	40.3
			2	0.37	12.3	20.9	5.8	2.6	65.6
Renfrow	3	A	1	0.40	9.6	10.1	9.3	3.0	38.7
			2	0.33	9.1	10.8	6.6	3.0	27.9
		B	1	0.55	10.2	16.2	14.3	11.1	
			2	0.53	9.0	15.2	10.1	8.4	36.3
		B	1	0.84	12.9	15.3	10.9	14.4	44.1
			2	0.51	9.1	17.4	12.3	7.8	37.4
Richfield	1	A	1	0.83	10.4	17.4	20.1	20.8	69.2
			2	0.42	10.5	17.7	21.5	20.2	75.7
		B	1	0.46	9.3	17.8	22.3	18.0	73.3
			2		10.1	29.7	96.1	20.2	122.7
		C	1	0.47	8.9	17.3	21.9	18.5	65.6
			2	0.48	8.7	17.0	20.7	16.2	60.0
Richfield	2	A	1	0.54	7.4	19.7	14.5	10.8	49.8
			2	0.56	7.8	19.4	22.4	11.3	106.8
		B	1	0.63	7.1	18.6	14.0	10.6	51.7
			2	0.67	7.8	18.9	16.3	12.3	56.4
		C	1	0.56	8.7	21.9	22.9	10.2	62.7
			2	0.79	9.0	23.5	18.5	13.0	80.0
Richfield	3	A	1	0.72	7.4	17.1	9.7	11.8	60.0
			2	0.76	8.2	18.0	14.8	14.6	87.6
		B	1	0.78	7.1	18.6	9.7	12.5	58.7
			2	0.66	7.1	17.5	14.4	11.6	59.1
		C	1	0.42	6.3	14.6	12.8	8.1	45.1
			2	0.63	5.6	16.2	11.5	9.0	46.1

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
SaintPaul	1	A	1	0.22	10.9	12.0	37.1	13.5	53.6
			2	0.43	11.4	11.9	13.7	16.4	45.2
		Bt1	1	0.69	10.8	14.6	18.0	18.6	62.4
			2	0.51	9.6	15.1	15.1	14.1	55.4
		Bt2	1	0.48	10.4	14.2	17.3	15.6	47.7
			2	0.50	12.2	14.1	18.1	16.0	45.5
		C	1	0.27	8.6	15.4	22.3	11.7	47.5
			2		6.8	15.6	13.4	12.4	44.0
SaintPaul	2	A	1	0.55	3.0	12.7	4.8	6.0	35.8
			2	0.54	2.5	13.2	3.4	5.3	36.4
		Bt1	1	0.32	5.2	16.0	2.6	2.2	41.1
			2	0.35	7.7	16.1	10.5	4.7	36.1
		Bt2	1	0.56	9.4	16.2	15.3	10.1	43.2
			2	0.35	7.2	17.6	10.3	6.8	56.8
SaintPaul	3	A	1	0.32	7.6	13.8	10.4	6.7	31.3
			2	0.37	12.8	13.3	11.1	7.5	34.5
		Bt1	1	0.59	7.6	15.8	9.6	9.6	45.6
			2	0.42	8.8	15.1	13.7	8.2	41.2
		Bt2	1	0.46	9.6	28.5	13.5	8.7	63.0
			2	0.61	7.0	28.2	6.3	7.0	40.3
		C	1	0.48	10.0	103.5	23.0	7.1	51.1
			2		12.8	98.7	32.5	10.3	80.0
Sallisaw	1	A	1	0.47	7.4	12.5	6.6	12.2	45.8
			2	0.32	12.0	13.0	6.5	3.0	45.9
		B	1	0.43	11.1	11.3	6.0	3.6	41.9
			2	0.32	15.0	11.7	14.3	7.7	41.6
Sallisaw	2	A	1	0.37	12.8	12.5	7.0	17.2	42.6
			2	0.32	13.9	12.2	12.8	16.1	43.1
		B	1	0.60	13.8	10.8	12.6	17.0	36.4
			2	0.33	16.2	10.3	18.3	19.7	41.4
Sallisaw	3	A	1	0.64	13.3	14.4	11.7	12.0	61.6
			2	0.51	10.1	14.1	8.2	9.5	71.9
		B	1		14.5	11.8	14.1	12.3	42.3
			2	0.37	12.4	12.5	9.9	14.9	49.2
Stiegler	1	A	1	0.50	6.3	29.4	2.4	17.0	45.4
			2	0.54	6.3	29.2	5.6	11.1	51.1
		B	1	0.55	6.4	21.7	7.1	8.4	77.3
			2	0.86	7.1	20.9	11.4	18.0	71.6
		C	1	0.53	9.6	17.1	14.6	18.4	62.2
			2	0.50	8.8	17.6	16.6	20.4	63.9

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Stiegler	2	A	1	0.27	5.6	24.3	7.7	6.2	34.2
			2	0.25	5.9	22.9	6.6	11.9	30.0
		B	1	0.41	6.7	13.8	14.3	14.9	34.3
			2	0.70	7.7	13.3	10.3	20.6	45.5
		C	1	0.85	25.4	9.2	11.8	28.8	33.3
			2	0.72	30.1	9.4	15.4	31.2	35.5
Stiegler	3	A	1	0.80	6.8	33.2	3.4	15.0	58.6
			2	0.93	12.0	32.2	7.1	11.5	59.4
		B	1	1.09	13.9	14.3	9.7	25.7	
			2	1.21	14.9	14.0	1.2	25.8	70.6
Summit	1	A	1	1.38	37.5	25.6	65.6	35.5	75.3
			2	1.11	38.8	28.5	75.7	34.4	79.4
		B	1	1.27	37.6	12.2	61.4	28.7	68.9
			2	1.05	37.1	11.7	40.6	12.9	74.3
		C	1	0.99	20.2	11.1	43.1	15.6	71.3
			2	1.19	20.8	11.5	47.5	17.9	71.6
Summit	2	A	1	1.07	29.6	23.0	39.4	27.6	59.2
			2	0.38	28.9	23.9	48.3	25.8	56.0
		B	1	0.52	24.5	13.5	41.3	22.6	65.1
			2	0.80	23.7	11.0	41.0	22.1	61.1
		C	1	0.34	19.8	11.3	45.5	19.0	66.5
			2	0.89	20.2	11.5	36.6	22.9	78.6
Summit	3	A	1	0.84	23.9	24.4	45.3	34.0	86.0
			2	0.86	23.1	24.6	59.9	31.6	95.6
		B	1	0.53	22.7	12.0	57.0	27.0	78.2
			2	0.72	22.2	12.0	30.7	15.6	70.2
		C	1	0.75	15.4	11.7	31.8	14.9	82.9
			2	0.51	19.1	12.7	29.5	12.2	80.3
Tillman	1	A	1	0.48	12.2	11.9	20.6	18.0	50.3
			2	0.37	13.7	12.6	26.2	14.0	100.6
		B	1	0.64	12.5	18.8	31.6	20.7	74.8
			2	0.99	12.7	19.3	29.1	19.5	77.9
		C	1	0.66	12.2	18.8	24.7	18.0	72.0
			2	0.67	11.8	18.5	25.8	18.0	76.7
Tillman	2	A	1	0.48	7.5	14.0	15.7	15.0	53.3
			2	0.54	8.1	13.6	17.0	17.5	100.6
		B	1	0.83	11.4	18.7	27.3	25.3	88.5
			2	0.60	8.0	19.0	18.2	16.6	68.0
		C	1	0.54	8.6	17.9	17.3	14.1	55.4
			2	0.58	9.7	17.4	17.3	13.4	56.6

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Tillman	3	A	1	0.57	7.4	13.3	8.2	14.1	72.6
			2	0.41	8.1	13.1	12.0	14.6	45.8
		B	1	0.58	9.5	43.2	19.1	23.2	70.3
			2	0.64	9.1	45.8	20.7	22.9	63.2
		C	1	0.39	10.6	22.0	18.2	12.8	61.6
			2	0.42	10.7	21.7	18.0	12.7	56.8
Woodward	1	A	1	0.36	23.9	9.4	15.3	14.6	34.9
			2	0.16	25.0	10.4	41.1	13.8	55.0
		B	1		21.8			15.7	
			2	0.35	21.5	13.0	18.4	13.3	43.2
		C	1	0.35	13.1	8.5	18.8	12.1	64.3
			2		13.5	9.0	18.1	10.9	34.4
Woodward	2	A	1	0.31	10.1	10.9	10.3	8.8	40.7
			2	0.35	8.6	10.4	6.2	9.8	31.7
		B	1	0.47	7.9	16.8	7.0	9.4	39.6
			2	0.37	11.8	17.6	18.0	15.8	46.7
		C	1	0.27	10.2	11.4	14.1	7.9	31.4
			2	0.30	10.1	11.4	11.2	9.2	32.1
Woodward	3	A	1	0.49	11.0	10.4	12.7	10.6	33.1
			2	0.53	9.0	9.9	12.1	8.5	48.2
		B	1	0.30	9.1	16.8	15.6	9.7	34.3
			2	0.54	10.2	16.7	16.6	10.6	36.9
		C	1	0.31	10.7	10.9	19.6	9.1	38.6
			2	0.45	11.9	10.9	21.6	10.4	35.0
Zaneis	1	A	1	0.26	13.6	5.8	9.7	8.1	30.2
			2	0.19	15.8	5.8	12.9	11.2	28.3
		B	1	0.63	16.2	13.3	12.5	11.7	49.2
			2	0.27	15.2	13.6	27.4	11.9	42.5
		C	1	0.16	14.8	5.6	20.3	10.5	41.4
			2	0.21	15.1	5.5	26.6	9.9	35.8
Zaneis	2	A	1	0.30	11.8	6.6	8.2	3.4	33.4
			2	0.37	13.3	6.4	8.8	7.6	33.6
		B	1	0.49	9.7	11.1	21.8	8.6	37.8
			2	0.54	10.2	10.5	13.1	9.1	33.5
		C	1	0.41	10.1	5.6	16.7	8.0	33.6
			2	0.55	11.1	7.3	29.1	8.5	51.8
Zaneis	3	A	1		12.8	9.5	38.3	9.4	48.7
			2	0.20	14.4	6.4	13.4	9.8	69.5
		B	1	0.32	9.9	10.8	11.1	6.6	28.7
			2	0.34	10.2	11.1	12.5	6.0	35.3
		C	1	0.32	10.0	6.1	15.6	5.1	25.6
			2	0.25	10.4	5.6	14.1	5.5	24.3

Table A3. Continued.

Soil	Rep	Hor	Obs	Cd	Co	Cu	Ni	Pb	Zn
				mg kg^{-1} soil					
Sludge Amended Soils									
Oklahoma City	1	A	1	1.40	3.6	33.0	17.7	117.1	112.2
			2	1.46	3.9	30.0	18.2	121.0	80.3
			3	1.28	6.4		17.0	107.6	74.9
Stillwater	1	A	1	1.30	6.3	30.6	9.5	21.9	53.5
			2	1.49	6.5	24.5	12.0	26.3	76.6
			3	1.62	5.9		12.9	24.4	62.7
Tulsa	1	A	1	2.62	10.1	35.6	21.5	34.0	95.0
			2	2.33	8.3	35.3	18.9	32.0	86.2
			3	2.00	7.1		15.6	27.5	74.4
Mine and Smelter Contaminated Soils									
Bartlesville	1	A	1	38.4	12.1	111	35.3	625	2820
			2	36.8	12.2	108	34.8	594	2810
			3	36.2	11.4		35.0	610	2812
Blackwell	1	A	1	443	21.0	412	30.6	663	10700
			2	435	16.5	399	38.1	606	10400
			3	396	16.0		34.4	634	10600
Cardin	1	A	1	15.7	6.7	66.2	16.7	544	2200
			2	15.8	7.1	16.7		590	2250
			3	13.5	6.1				
Picher	1	A	1	3.90	18.6	20.7	27.8	83.2	469
			2	3.84	21.7	19.4	33.2	83.5	486
			3	3.73	21.0				

Table A4. Mean and standard deviation (SD) of heavy metal contents in 28 benchmark soil series of Oklahoma.

Soil Series	Master Horizon	Cd		Co		Cu		Ni		Pb		Zn	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
		mg kg^{-1}											
Bernow	A	0.13 a†	0.09	10.9 a	2.5	9.3 a	0.6	8.2 a	5.2	6.8 a	2.1	33.0 a	17.4
	B	0.46 a	0.15	8.4 a,b	2.5	6.9 b	1.0	16.4 b	3.3	11.4 b	1.7	33.9 a	1.4
	C	0.34 a	0.19	7.9 b	1.2	3.2 c	0.7	14.0 a,b	2.9	8.5 c	1.1	30.0 a	7.1
Burleson	A	0.60 a	0.15	12.2 a	0.8	15.0 a	1.5	35.1 a	6.3	30.3 a	13.8	80.3 a	18.9
	AB	0.77 a	0.27	12.1 a	2.9	17.7 b	1.1	38.1 a	17.3	19.8 a	4.9	93.6 b	12.5
	AC	0.65 a	0.03	14.1 a	1.7	17.1 b	0.9	49.3 a	10.6	22.5 a	2.8	98.6 b	18.4
Carnasaw	A	1.03 a	0.26	20.0 a	3.4	9.4 a	0.7	23.1 a	7.0	28.5 a	3.8	72.0 a	15.2
	B	1.01 a	0.17	6.9 b	0.7	20.0 b	1.0	34.2 b	7.0	23.1 a	1.7	82.5 a	16.8
	C	0.78 a	0.09	11.4 c	2.1	26.0 c	3.3	47.0 c	4.7	25.0 a	4.6	120.7 b	18.6
Clarksville	A	0.78 a	0.36	14.4 a	5.5	12.4 a	1.3	19.8 a	12.0	26.0 a	14.3	90.5 a	54.8
	B	0.82 a	0.51	8.8 a	1.6	10.9 a	5.7	20.0 a	13.2	22.2 a	14.9	89.1 a	45.4
	C	0.94 a	0.31	6.4 a	0.5	16.2 a	2.7	37.0 b	6.1	41.7 b	9.9	222.1 b	98.5
Cobb	A	0.23 a	0.03	7.5 a	2.0	6.1 a	0.5	10.1 a	2.2	9.9 a	1.7	25.9 a	2.7
	B	0.20 a	0.02	8.2 a	2.1	5.8 a	1.1	10.4 a	1.9	10.2 a	1.0	29.5 a	3.1
	R	0.17 a	0.05	6.8 a	0.6	7.7 a	1.9	12.5 a	5.4	11.6 a	0.9	28.8 a	1.1
Dalhart	A	0.10 b	0.06	17.2 a	7.2	2.5 a	0.4	9.0 a	0.9	8.2 a	1.2	49.2 a	24.7
	B	0.45 a	0.20	13.3 a	6.9	11.3 b	2.4	10.7 a,b	3.8	9.9 a	4.5	54.9 a	18.1
	C	0.47 a	0.05	10.6 a	1.5	14.1 c	1.9	15.4 b	5.3	10.7 a	4.1	58.0 a	8.6
Darnell	A	0.12 a	0.04	63.0 a	65.3	2.4 a,b	0.8	6.1 a	1.0	5.3 a	1.3	32.5 a	12.0
	B	0.11 a	0.02	78.6 a	85.3	1.6 b	0.1	6.0 a	1.3	4.3 a	1.5	20.5 b	5.1
	C	0.23 a	0.12	24.5 a	8.0	3.3 c	1.0	8.9 a	3.7	7.0 a	6.7	23.4 a,b	3.8
Dennis	A	0.73 a	0.23	9.1 a	2.6	12.8 a	3.2	14.3 a	3.0	14.9 a	4.0	58.3 a	7.8
	B	0.78 a	0.23	14.5 b	3.1	17.3 b	5.3	36.4 b	7.5	19.3 a	2.1	61.6 a	8.9
	C	1.19 a	0.41	18.6 b	2.5	21.4 c	4.7	48.8 b	11.4	22.1 a	2.9	89.5 b	7.9

Table A4. Continued.

Soil Series	Master Horizon	Cd		Co		Cu		Ni		Pb		Zn	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
		mg kg^{-1}											
Dougherty	A	0.13 a	0.01	29.7 a	16.5	2.7 a	0.4	7.7 a	2.3	9.6 a	3.4	23.0 a	2.8
	E	0.11 a	0.17	23.0 a,b	8.3	1.0 b	0.1	24.0 a	21.0	5.9 b	1.1	18.5 a	7.8
	B	0.08 a	0.03	13.1 b	0.8	2.7 a	0.2	18.0 a	8.2	7.7 a,b	1.0	22.3 a	0.4
	C	0.05 a	0.04	13.3 b	4.1	1.5 b	0.8	9.9 a	3.3	6.0 b	1.3	19.4 a	6.6
Durant	A	0.31 a	0.07	8.2 a	1.7	9.1 a	0.1	10.7 a	2.1	9.6 a	5.5	31.3 a	4.0
	B	0.49 a,b	0.11	9.8 a,b	2.0	14.1 b	0.3	22.4 a	11.8	13.8 a	6.0	54.7 b	7.2
	C	0.56 b	0.09	12.4 b	2.6	15.8 b	3.6	23.8 a	16.6	12.6 a	6.2	56.4 b	15.6
Easpur	A	0.57 a	0.19	13.1 a	2.7	9.0 a	2.3	13.2 a	5.2	19.9 a	4.1	79.6 a	46.5
	B	0.33 a	0.21	11.9 a	0.9	10.8 a	1.2	17.7 a	5.7	9.6 a,b	5.5	60.1 a	30.8
	C	0.29 a	0.06	12.1 a	1.5	8.9 a	2.3	10.7 a	3.4	8.3 b	5.4	44.7 a	18.6
Grant	A	0.39 a	0.10	10.8 a	1.1	13.8 a	4.4	16.6 a	8.4	17.2 a	5.1	52.4 a	4.6
	B	0.43 a	0.13	12.6 a	2.3	14.4 a	0.2	20.6 a	9.8	17.3 a	2.7	77.0 a	15.2
	C	0.52 a	0.12	10.4 a	1.5	12.7 a	1.1	23.0 a	2.6	13.7 a	6.0	86.5 a	37.5
Kirkland	A	0.48 a	0.05	10.2 a	1.2	13.9 a	0.3	12.1 a	3.3	16.7 a	2.7	39.8 a	7.1
	Bt	0.79 a	0.27	11.0 a	1.0	17.3 b	1.6	13.8 a	11.0	18.7 a	2.0	61.0 b	6.3
Lebron	A	0.81 a	0.13	11.2 a	3.3	25.4 a	6.4	24.7 a	10.1	15.4 a	5.7	85.0 a	16.7
	C	0.14 b	0.10	10.2 a	6.5	1.9 b	0.9	5.7 b	2.1	6.6 b	1.6	31.9 b	4.0
Mansic	A	0.53 a	0.16	6.3 a	1.3	13.9 a	0.7	13.3 a	3.9	10.4 a	5.0	54.0 a	13.4
	B	0.37 a	0.18	7.0 a	2.1	11.9 a,b	0.5	14.0 a	7.3	9.2 a	5.5	44.4 a	10.3
	C	0.39 a	0.08	7.1 a	1.0	10.4 b	1.2	11.6 a	4.4	10.2 a	4.5	39.3 a	8.2
Osage	A	1.31 a	0.25	16.4 a	2.0	20.2 a	0.6	35.3 a	8.4	32.4 a	1.1	136.5 a	9.8
	B	0.81 a	0.21	17.4 a	0.7	30.4 b	1.5	46.2 a	5.4	26.4 b	2.6	111.4 b	8.4
	C	0.86 a	0.16	16.1 a	0.6	24.8 c	0.7	49.3 a	6.8	25.7 b	3.7	111.9 b	18.7
Parsons	A	1.39 a	0.47	11.1 a	2.9	15.8 a	2.4	17.4 a	3.5	27.2 a	7.1	65.1 a	18.6
	B	1.89 b	0.72	15.2 a,b	7.2	24.3 b	1.3	27.2 a	8.5	30.5 a,b	8.9	67.4 a	2.5
	C	2.01 b	0.46	18.4 b	6.4	23.7 b	1.8	46.8 b	11.5	41.0 b	1.8	47.9 a	9.9

Table A4. Continued.

Soil Series	Master Horizon	Cd		Co		Cu		Ni		Pb		Zn	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
		mg kg^{-1}											
Pond Creek	A	0.48 a	0.06	13.7 a	4.3	13.0 a	1.9	20.4 a	10.4	19.8 a	2.4	59.6 a	11.8
	B	0.61 a	0.18	14.4 a	4.7	18.7 b	1.9	24.7 a	1.9	21.4 a	0.8	69.2 a,b	4.3
	C	0.59 a	0.12	12.0 a	2.0	20.2 b	3.4	27.2 a	3.2	22.4 a	2.7	74.0 b	8.2
Pratt	A	0.17 a	0.18	34.0 a	6.3	3.0 a	0.1	5.7 a	1.3	7.6 a	6.9	26.5 a	2.5
	B	0.84 a	0.04	31.3 a	7.7	2.7 a	0.3	5.4 a	0.8	6.4 a	3.8	31.2 a	14.2
	C	0.55 b	0.20	36.2 a	14.5	3.6 b	0.4	6.7 a	0.7	7.9 a	3.4	27.4 a	17.7
Renfrow	A	0.40 a	0.03	11.9 a	3.4	14.4 a	6.8	9.9 a	1.7	11.3 a	7.3	37.1 a	3.6
	Bt	0.55 a	0.21	11.6 a	2.9	18.0 a	2.4	14.2 a	4.7	12.1 a	5.1	50.8 a	14.2
Richfield	A	0.64 a	0.10	8.6 a	1.6	18.2 a	1.1	17.2 a	4.4	14.9 a	5.0	74.8 a	3.1
	B	0.61 a	0.13	8.1 a	1.4	20.2 a	3.1	28.8 a	26.4	14.2 a	4.3	70.3 a	24.1
	C	0.56 a	0.10	7.9 a	1.7	18.4 a	3.8	18.1 a	5.1	12.5 a	4.5	59.9 a	13.1
Saint Paul	A	0.40 a	0.12	8.0 a	4.6	12.8 a	0.8	13.4 a	10.9	9.2 a	5.0	39.5 a	8.7
	Bt	0.49 a	0.09	8.8 a	1.7	17.6 a,b	5.3	12.5 a	4.2	10.1 a	5.0	48.2 a	7.0
	C	0.38 a	0.15	9.5 a	2.6	58.3 b	60.5	22.8 a	7.0	10.4 a	2.4	55.7 a	14.0
Sallisaw	A	0.44 a	0.12	11.6 a	1.8	13.1 a	1.0	8.8 a	2.0	11.7 a	4.6	51.8 a	13.0
	B	0.40 a	0.05	13.8 a	1.1	11.4 b	0.8	12.5 a	2.7	12.5 a	6.4	42.1 a	3.4
Stiegler	A	0.55 a	0.30	7.2 a	2.0	28.5 a	4.6	5.5 a	1.6	12.1 a	2.7	46.4 a	13.6
	B	0.80 a	0.31	9.5 a	4.3	16.3 b	4.3	9.0 a,b	3.4	18.9 a	6.3	61.7 a	19.0
	C	0.65 a	0.19	18.5 a	13.1	13.3 b	5.7	14.6 b	1.4	24.7 a	7.5	48.7 a	20.2
Summit	A	0.94 a	0.27	30.3 a	7.4	25.1 a	1.8	55.7 a	13.7	31.5 a	4.3	75.3 a	16.7
	B	0.81 b	0.30	28.0 a,b	8.2	12.1 b	0.1	45.3 a,b	5.1	21.5 b	0.8	69.6 a	5.8
	C	0.78 b	0.27	19.2 b	1.7	11.6 b	0.5	39.0 b	7.5	17.1 b	3.7	75.2 a	5.6
Tillman	A	0.48 a	0.05	9.5 a	3.0	13.1 a	0.8	16.6 a	6.6	15.5 a	1.0	70.5 a	9.8
	B	0.71 b	0.10	10.5 a	1.8	27.5 a	14.8	24.3 b	5.4	21.4 b	1.5	73.8 a	6.2
	C	0.54 a,b	0.13	10.6 a	1.4	19.4 a	2.2	20.2 a,b	4.4	14.8 a	2.8	63.2 a	9.8

Table A4. Continued.

Soil Series	Master Horizon	Cd		Co		Cu		Ni		Pb		Zn	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
		mg kg^{-1}											
Woodward	A	0.37 a	0.13	14.6 a	8.5	10.2 a	0.4	16.3 a	10.5	11.0 a	2.8	40.6 a	4.3
	B	0.39 a	0.04	13.7 a	6.9	15.6 b	2.3	15.7 a	3.0	12.4 a	2.2	40.7 a	4.4
	C	0.34 a	0.05	11.6 a	1.6	10.3 a	1.4	17.2 a	4.1	9.9 a	1.5	39.3 a	9.1
Zaneis	A	0.25 a	0.07	13.6 a	1.1	6.7 a	1.1	15.2 a	9.3	8.2 a	2.4	40.6 a	16.1
	Bt	0.43 b	0.09	11.9 a	3.2	11.7 b	1.5	16.4 a	4.2	9.0 a	2.8	37.8 a	7.2
	BC	0.32 a,b	0.15	11.9 a	2.6	5.9 a	0.5	20.4 a	4.8	7.9 a	2.5	35.4 a	9.3

† Means with the same letter are not significantly different within a soil using Duncan's Multiple Range Procedure ($p < 0.05$).

Table A5. Plant concentrations of heavy metals.

Soil	Dupe	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1}					
		Benchmark Soils					
Dalhart	1	0.93	0.15	3.43	1.59	2.83	3.9
	2	0.50	0.02	2.71	1.01	3.10	14.9
	3	0.84	0.17	3.29	1.72	3.05	15.1
Lebron	1	0.83	0.17	3.64	1.09	2.53	16.8
	2	0.95	0.17	3.50	1.00	2.36	13.4
	3	0.79	0.12	3.87	0.79	2.07	10.9
Mansic	1	0.71	0.25	4.04	1.09	3.59	12.3
	2	0.62	0.14	4.19	1.09	2.08	14.9
	3	0.44	0.24	5.63	0.97	3.09	13.0
Osage	1	4.74	0.19	7.08	3.56	3.10	63.5
	2	3.58	0.18	5.20	2.49	3.14	49.3
	3	2.73	0.18	5.56	2.07	2.86	42.5
Pond Creek	1	2.47	0.27	4.04	2.86	2.56	17.5
	2	4.22	0.45	6.69	3.56	4.81	47.9
Saint Paul	1	0.82	0.32	3.67	2.15	3.69	21.5
	2	0.88	0.15	2.66	1.96	1.88	12.1
	3	0.90	0.16	3.18	2.39	2.80	22.3
Summit	1	0.82	0.26	3.02	1.30	3.91	12.8
	2	1.06	0.24	3.99	1.32	4.25	19.1
Tillman	1	1.13	0.24	3.77	2.36	3.39	22.1
	2	1.52	0.35	4.10	2.34	4.80	29.5
		Sludge Amended Soils					
OKC	1	2.04	0.17	4.67	1.32	3.19	40.2
	2	1.40	0.24	4.92	1.97	3.77	40.7
	3	0.88	0.23	4.18	2.07	3.50	24.3
Stillwater	1	0.73	0.19	6.14	1.42	4.25	45.0
	2	0.88	0.24	6.21	1.14	4.31	48.7
	3	0.49	0.31	8.08	1.59	4.61	41.9
Tulsa	1	3.03	0.26	5.26	1.25	3.35	67.2
	2	2.19	0.15	4.24	0.86	2.76	55.2
	3	2.17	0.17	3.84	1.17	2.83	52.2
		Mine and Smelter Contaminated Soils					
Bartlesville	1	23.4	0.20	4.22	0.96	3.70	362
	2	14.5	0.14	4.06	0.71	2.88	280
	3	25.4	0.24	4.71	1.01	3.47	397
Cardin	1	10.3	0.19	7.07	1.07	4.74	433
	2	8.62	0.28	7.91	2.08	10.87	472
	3	7.19	0.10	6.47	1.10	3.40	321
Picher	1+2	5.34	0.19	6.03	1.12	3.82	206

Table A6. DTPA extractable heavy metal concentrations of Oklahoma soils.

SOIL	Horizon	Obs	Cd	Co	Cu	Ni	Pb	Zn
			mg kg^{-1} soil					
Benchmark Soils								
Bernow	A	1	0.094	0.16	0.22	0.20	2.29	0.98
		2	0.095	0.16	0.22	0.21	2.41	0.99
		3	0.166	0.20	0.23	0.25	2.41	1.02
		4	0.163	0.21	0.24	0.24	2.47	1.14
	B	1	0.000	0.12	0.06	0.21	0.46	0.08
		2	0.000	0.12	0.06	0.21	0.44	0.08
	C	1	0.000	0.31	0.13	0.35	0.59	0.15
		2	0.000	0.31	0.13	0.36	0.62	0.14
Burleson	A	1	0.125	0.49	1.96	2.44	2.26	0.93
		2	0.133	0.50	2.08	2.62	2.38	0.99
		3	0.154	0.55	2.03	2.61	2.45	1.17
		4	0.154	0.56	1.99	2.57	2.37	1.06
	AB	1	0.036	0.35	2.30	1.88	2.24	2.78
		2	0.034	0.37	2.37	1.94	2.26	0.30
	AC	1	0.030	0.13	1.35	1.03	1.57	0.18
		2	0.026	0.13	1.35	1.02	1.53	0.19
Carnasaw	A	1	0.091	0.38	0.49	0.79	2.32	1.54
		2	0.094	0.35	0.50	0.80	2.37	1.60
		3	0.115	0.29	0.50	0.72	2.05	1.54
		4	0.135	0.30	0.47	0.73	2.13	1.43
	B	1	0.000	0.09	0.04	0.23	0.50	0.17
		2	0.000	0.09	0.05	0.23	0.52	0.17
	C	1	0.000	0.79	0.90	1.91	0.79	1.98
		2	0.000	0.79	0.88	1.91	0.83	1.94
Clarksville	A	1	0.201	0.39	1.54	2.17	2.57	6.46
		2	0.194	0.37	1.46	2.11	2.43	6.23
		3	0.211	0.33	1.15	1.88	2.33	5.99
		4	0.221	0.34	1.40	1.93	2.44	6.10
	B	1	0.000	0.09	0.14	0.09	0.41	0.20
		2	0.000	0.09	0.15	0.10	0.40	0.20
	C	1	0.000	0.05	0.02	0.10	0.41	0.11
		2	0.000	0.04	0.02	0.09	0.32	0.10
Cobb	A	1	0.023	0.20	0.71	0.23	0.83	0.26
		2	0.027	0.21	0.75	0.23	0.84	0.28
		3	0.040	0.27	0.74	0.28	1.20	0.38
		4	0.037	0.28	0.75	0.28	1.23	0.35
	B	1	0.004	0.09	0.16	0.05	0.54	0.07
		2	0.008	0.09	0.17	0.05	0.53	0.08
	R	1	0.005	0.09	0.37	0.08	0.50	0.09
		2	0.010	0.07	0.35	0.08	0.51	0.08

Table A6. Continued.

SOIL	Horizon	Obs	Cd	Co	Cu	Ni	Pb	Zn
			mg kg^{-1} soil					
Dalhart	A	1	0.030	0.11	0.32	0.32	0.37	0.12
		2	0.026	0.11	0.33	0.30	0.32	0.14
		3	0.043	0.15	0.33	0.35	0.67	0.16
		4	0.040	0.18	0.34	0.36	0.68	0.17
	B	1	0.027	0.10	0.92	0.31	0.86	0.23
		2	0.028	0.11	0.91	0.32	0.82	0.14
	C	1	0.010	0.07	1.13	0.22	1.26	0.21
		2	0.011	0.07	1.11	0.19	1.23	0.14
Darnell	A	1	0.055	0.15	0.28	0.47	0.65	0.67
		2	0.054	0.16	0.26	0.47	0.74	0.61
		3	0.069	0.19	0.26	0.48	0.93	0.70
		4	0.066	0.23	0.28	0.49	0.88	0.67
	B	1	0.030	0.21	0.23	0.36	0.47	0.33
		2	0.027	0.22	0.23	0.36	0.47	0.35
	C	1	0.023	0.28	0.32	0.15	0.68	0.18
		2	0.016	0.28	0.32	0.16	0.69	0.18
Dennis	A	1	0.092	0.22	1.26	1.21	1.94	0.86
		2	0.090	0.22	1.27	1.20	1.88	0.87
		3	0.121	0.28	1.19	1.16	2.01	0.91
		4	0.114	0.26	1.20	1.18	2.05	0.88
	B	1	0.000	0.00	0.00	0.00	0.00	0.00
		2	0.009	0.22	0.21	0.15	1.27	0.08
	C	1	0.003	0.19	0.24	0.14	1.14	0.32
		2	0.006	0.17	0.26	0.14	1.13	0.22
Dougherty	A	1	0.073	0.10	0.41	0.12	3.38	2.71
		2	0.073	0.09	0.41	0.12	2.32	2.59
		3	0.085	0.13	0.36	0.14	2.08	2.53
		4	0.082	0.12	0.35	0.14	1.76	2.56
	B	1	0.015	0.08	0.30	0.20	1.11	0.21
		2	0.016	0.08	0.28	0.20	1.04	0.25
	C	1	0.020	0.10	0.20	0.16	0.86	0.37
		2	0.018	0.09	0.19	0.13	0.64	0.31
	E	1	0.018	0.02	0.14	0.07	0.14	1.67
		2	0.017	0.02	0.15	0.07	0.16	1.73
Durant	A	1	0.051	0.15	1.34	0.46	1.88	0.70
		2	0.053	0.15	1.33	0.47	1.91	0.70
		3	0.096	0.21	1.30	0.55	2.05	0.80
		4	0.090	0.20	1.30	0.49	2.05	0.87
	B	1	0.014	0.31	1.29	0.26	2.04	0.24
		2	0.012	0.29	1.31	0.25	1.95	0.23
	C	1	0.017	0.06	0.87	0.19	1.25	0.22
		2	0.018	0.07	0.90	0.18	1.28	0.22

Table A6. Continued.

SOIL	Horizon	Obs	Cd	Co	Cu	Ni	Pb	Zn
			mg kg^{-1} soil					
Easpur	A	1	0.074	0.28	1.36	1.05	3.28	5.48
		2	0.084	0.30	1.41	1.10	3.36	5.59
		3	0.098	0.35	1.40	1.11	3.28	5.75
		4	0.105	0.36	1.38	1.14	2.83	5.43
	B	1	0.028	0.34	1.21	0.70	1.63	0.38
		2	0.024	0.34	1.21	0.70	1.57	0.33
	C	1	0.011	0.17	0.53	0.24	0.68	0.13
		2	0.016	0.17	0.49	0.25	0.71	0.13
Grant	A	1	0.093	0.32	1.00	1.33	1.19	0.61
		2	0.095	0.32	1.00	1.31	1.15	0.57
		3	0.119	0.43	1.06	1.41	1.43	0.74
		4	0.113	0.42	1.04	1.42	1.41	0.74
	B	1	0.026	0.16	0.86	0.41	1.18	0.11
		2	0.024	0.15	0.88	0.40	1.20	0.15
	C	1	0.009	0.05	0.37	0.13	0.94	0.09
		2	0.007	0.06	0.38	0.14	0.92	0.09
Kirkland	A	1	0.114	0.53	1.99	2.16	1.94	0.74
		2	0.112	0.53	1.98	2.12	1.88	0.74
		3	0.146	0.62	2.00	2.28	2.17	0.95
		4	0.180	0.60	1.96	2.28	2.17	0.93
	Bt1	1	0.030	0.15	1.12	0.69	1.45	0.15
		2	0.029	0.13	1.10	0.67	1.40	0.13
	Bt2	1	0.010	0.05	0.49	0.13	1.09	0.10
		2	0.010	0.05	0.51	0.12	1.13	0.11
Lebron	Ap	1	0.111	0.08	3.66	0.72	2.91	2.25
		2	0.113	0.08	3.65	0.71	2.95	2.33
		3	0.145	0.16	3.34	0.78	2.83	2.21
		4	0.142	0.14	3.34	0.75	2.83	2.19
	A	1	0.089	0.08	3.38	0.46	2.46	0.78
		2	0.095	0.09	3.22	0.46	2.41	0.74
		3	0.123	0.14	3.08	0.54	2.63	0.93
		4	0.120	0.18	3.18	0.54	2.66	0.98
	C3	1	0.025	0.02	0.16	0.03	0.18	0.34
		2	0.012	0.02	0.17	0.03	0.16	0.33
Mansic	A	1	0.093	0.14	0.65	0.43	1.53	0.47
		2	0.073	0.13	0.67	0.42	1.53	0.42
		3	0.100	0.19	0.73	0.50	1.49	0.55
		4	0.100	0.20	0.73	0.49	1.62	0.56
	B	1	0.015	0.10	0.92	0.30	0.81	0.21
		2	0.017	0.11	0.92	0.30	0.82	0.20
	C	1	0.013	0.07	0.87	0.21	0.90	0.18
		2	0.016	0.06	0.89	0.22	0.89	0.17

Table A6. Continued.

SOIL	Horizon	Obs	Cd	Co	Cu	Ni	Pb	Zn
			mg kg^{-1} soil					
Osage	A	1	0.340	0.88	4.29	2.94	2.47	5.18
		2	0.224	0.62	2.83	1.94	1.87	3.58
		3	0.114	0.33	0.96	0.77	1.10	1.36
		4	0.442	1.02	4.64	3.18	3.00	5.87
	B	1	0.060	0.25	2.81	1.52	2.91	0.60
		2	0.063	0.25	2.91	1.53	2.97	0.61
	C	1	0.047	0.10	2.33	0.60	2.73	0.62
		2	0.044	0.10	2.11	0.56	2.56	0.56
Parsons	A	1	0.112	0.31	1.37	1.12	2.10	4.55
		2	0.115	0.33	1.42	1.18	2.20	4.75
		3	0.142	0.35	1.41	1.15	2.05	4.77
		4	0.142	0.31	1.42	1.19	2.08	4.70
	B	1	0.008	0.47	0.45	0.44	1.82	0.26
		2	0.013	0.51	0.46	0.45	1.89	0.22
	C	1	0.009	0.87	0.48	0.66	1.03	0.42
		2	0.006	0.81	0.50	0.68	1.07	0.44
Pond Creek	A	1	0.148	0.42	1.56	1.61	1.76	0.55
		2	0.155	0.44	1.60	1.65	1.78	0.57
		3	0.185	0.51	1.66	1.71	1.77	0.74
		4	0.188	0.54	1.68	1.75	1.99	0.78
	B	1	0.026	0.13	1.08	0.26	1.05	0.11
		2	0.025	0.13	1.09	0.26	1.09	0.11
	C	1	0.033	0.09	1.15	0.41	1.03	0.15
		2	0.033	0.09	1.15	0.40	1.04	0.15
Pratt	A	1	0.031	0.09	0.29	0.17	0.30	0.38
		2	0.031	0.08	0.39	0.17	0.33	0.60
		3	0.041	0.15	0.28	0.21	0.63	0.42
		4	0.038	0.18	0.26	0.18	0.42	0.39
	B	1	0.010	0.06	0.31	0.13	0.30	0.29
		2	0.013	0.07	0.31	0.13	0.29	0.37
	C	1	0.014	0.05	0.26	0.08	0.29	0.25
		2	0.012	0.06	0.25	0.09	0.34	0.23
Renfrow	A	1	0.063	0.25	1.73	0.75	1.78	0.94
		2	0.063	0.27	1.85	0.76	1.81	0.97
		3	0.080	0.31	1.68	0.85	1.91	1.08
		4	0.087	0.32	1.75	0.84	1.80	1.11
	Bt1	1	0.013	0.13	1.11	0.20	1.26	0.18
		2	0.014	0.12	1.12	0.20	1.21	0.18
	Bt2	1	0.008	0.06	0.40	0.09	0.97	0.20
		2	0.009	0.06	0.40	0.10	1.04	0.09

Table A6. Continued.

SOIL	Horizon	Obs	Cd	Co	Cu	Ni	Pb	Zn
			mg kg^{-1} soil					
Richfield	A	1	0.097	0.15	1.32	1.08	1.51	0.29
		2	0.110	0.16	1.37	1.13	1.55	0.32
		3	0.127	0.22	1.43	1.29	1.74	0.39
		4	0.127	0.24	1.44	1.30	1.63	0.43
	B	1	0.043	0.08	1.27	0.39	1.32	0.17
		2	0.034	0.08	1.28	0.38	1.26	0.19
	C	1	0.024	0.06	1.31	0.24	1.12	0.17
		2	0.022	0.09	1.33	0.25	1.14	0.16
Saint Paul	A	1	0.038	0.29	1.30	1.09	1.14	0.33
		2	0.039	0.27	1.32	1.06	1.10	0.34
		3	0.060	0.30	1.33	1.20	1.42	0.52
		4	0.063	0.30	1.34	1.22	1.36	0.42
	Bt1	1	0.030	0.11	1.12	0.40	1.29	0.14
		2	0.030	0.11	1.12	0.40	1.33	0.16
	Bt2	1	0.008	0.08	0.88	0.18	1.35	0.15
		2	0.010	0.07	0.88	0.17	1.36	0.14
	C	1	0.012	0.06	0.91	0.13	0.91	0.23
		2	0.011	0.06	0.89	0.14	0.93	0.35
Sallisaw	A	1	0.086	0.29	2.73	0.69	1.50	7.89
		2	0.086	0.31	2.86	0.72	1.59	8.19
		3	0.108	0.30	2.58	0.66	1.48	7.61
		4	0.112	0.28	2.47	0.66	1.45	7.89
	B	1	0.009	0.52	0.48	0.07	1.17	0.20
		2	0.012	0.50	0.50	0.07	1.16	0.19
Stiegler	A	1	0.159	0.26	9.43	1.77	3.11	7.91
		2	0.155	0.25	9.22	1.73	3.02	7.75
		3	0.192	0.24	8.15	1.68	2.77	7.55
		4	0.196	0.24	7.97	1.63	2.72	7.25
	B	1	0.002	0.32	0.27	0.86	0.53	0.18
		2	0.001	0.33	0.27	0.86	0.52	0.18
	C	1	0.021	0.64	0.67	1.24	0.87	0.37
		2	0.020	0.62	0.63	1.24	0.91	0.35
Summit	A	1	0.090	0.29	1.23	0.81	1.60	1.11
		2	0.099	0.30	1.26	0.83	1.63	1.15
		3	0.117	0.29	1.16	0.86	1.49	1.15
		4	0.117	0.31	1.09	0.85	1.49	1.12
	B	1	0.037	0.13	1.02	0.34	1.37	0.29
		2	0.037	0.14	1.02	0.35	1.47	0.33
	C	1	0.022	0.11	0.72	0.26	1.35	0.27
		2	0.021	0.11	0.67	0.26	1.37	0.25

Table A6. Continued.

SOIL	Horizon	Obs	Cd	Co	Cu	Ni	Pb	Zn
			mg kg^{-1} soil					
Tillman	A	1	0.071	0.29	1.06	1.48	1.09	0.53
		2	0.071	0.30	1.09	1.48	1.09	0.58
		3	0.100	0.28	1.07	1.68	1.28	0.68
		4	0.097	0.31	1.07	1.71	1.30	0.72
	B	1	0.032	0.13	0.92	0.45	1.01	0.20
		2	0.027	0.14	0.93	0.45	1.06	0.20
	C	1	0.013	0.06	0.45	0.16	0.80	0.13
		2	0.012	0.07	0.48	0.16	0.74	0.14
Woodward	A	1	0.034	0.10	0.53	0.41	0.62	0.29
		2	0.033	0.10	0.56	0.41	0.64	0.30
		3	0.059	0.17	0.60	0.51	1.00	0.37
		4	0.052	0.15	0.57	0.51	0.93	0.35
	B	1	0.015	0.04	0.71	0.18	0.94	0.41
		2	0.015	0.04	0.72	0.18	0.95	1.09
	C	1	0.008	0.03	0.27	0.07	0.39	0.23
		2	0.015	0.03	0.28	0.08	0.33	0.23
Zaneis	A	1	0.069	0.34	0.86	0.48	1.80	1.04
		2	0.076	0.33	0.86	0.48	1.73	1.07
		3	0.096	0.39	0.83	0.51	1.81	1.12
		4	0.093	0.38	0.83	0.49	1.76	1.11
	Bt1	1	0.012	0.15	1.12	0.14	1.15	0.17
		2	0.010	0.15	1.12	0.14	1.13	0.14
	BC	1	0.005	0.08	0.48	0.08	0.82	0.14
		2	0.007	0.08	0.46	0.08	0.80	0.14
Sludge Amended Soils								
Oklahoma City	A	1	0.267	0.12	4.41	0.60	2.45	10.0
		2	0.267	0.12	4.44	0.57	2.38	10.0
		3	0.289	0.21	3.91	0.73	3.17	10.5
		4	0.297	0.19	4.14	0.73	3.16	10.9
Stillwater	A	1	0.206	0.14	7.99	0.41	24.7	14.8
		2	0.199	0.15	7.76	0.39	23.7	14.2
		3	0.208	0.22	7.10	0.53	26.0	14.6
		4	0.217	0.22	7.00	0.51	25.3	14.7
Tulsa	A	1	0.709	0.32	4.34	1.21	3.81	16.6
		2	0.743	0.32	4.64	0.14	3.95	17.4
		3	0.643	0.36	3.73	1.29	4.31	16.1
		4	0.686	0.34	3.83	1.30	4.41	16.4

Table A6. Continued.

SOIL	Horizon	Obs	Cd	Co	Cu	Ni	Pb	Zn
			mg kg^{-1} soil					
Mine and Smelter Contaminated Soils								
Bartlesville	A	1	22.1	0.20	10.1	1.34	14.5	719
		2	22.1	0.19	9.9	1.38	14.5	711
		3	16.5	0.26	5.2	1.30	10.1	623
		4	15.8	0.25	5.3	1.27	10.9	622
Blackwell	A	1	114	1.24	18.1	0.64	3.69	1530
		2	116	1.28	17.8	0.64	3.60	1550
		3	93.6	1.07	12.0	0.72	3.30	1330
		4	93.1	1.07	11.2	0.74	3.30	1310
Cardin	A	1	6.89	0.19	8.5	0.86	99	645
		2	6.84	0.18	8.4	0.87	100	646
		3	6.05	0.25	5.9	0.98	73.0	576
		4	5.77	0.23	6.2	0.93	77.7	573
Picher	A	1	1.05	0.27	1.2	0.48	19.0	103
		2	1.03	0.33	1.2	0.46	18.9	101
		3	0.90	0.31	1.0	0.55	16.0	92
		4	0.87	0.30	1.0	0.55	15.7	90

Table A7. TCLP extractable heavy metal concentrations of Oklahoma soils.

Soil	Obs	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1} soil					
Benchmark Soils - A Horizons							
Bernow	1	0.000	0.059	0.155	0.618	0.832	0.000
	2	0.000	0.093	0.208	0.684	0.587	1.087
	3	0.000	0.128	0.232	0.213	0.387	0.802
Burleson	1	0.000	0.356	0.314	0.000	1.810	0.000
	2	0.000	0.217	0.000	0.000	0.000	0.000
	3	0.000	0.158	0.274	0.683	0.927	0.628
	4	0.000	0.237	0.260	0.632	0.828	0.727
Carnasaw	1	0.000	0.112	0.260	0.520	0.221	0.924
	2	0.000	0.198	0.279	0.553	1.076	1.420
	3	0.000	0.150	0.260	0.265	0.633	0.802
Clarksville	1	0.000	0.182	0.604	1.249	1.810	0.000
	2	0.000	0.122	0.260	0.525	0.681	1.765
Cobb	1	0.000	0.251	0.507	0.769	1.198	0.000
	2	0.000	0.217	0.824	0.553	0.710	0.000
	3	0.000	0.058	0.322	0.301	0.633	0.579
Dalhart	1	0.000	0.043	0.000	0.438	0.711	0.493
	2	0.000	0.164	0.366	0.000	0.833	0.000
	3	0.000	0.050	0.356	0.186	0.387	0.654
	3	0.000	0.072	0.300	0.330	0.290	0.357
Darnell	1	0.000	0.409	0.358	1.333	0.710	0.000
	2	0.000	0.303	0.225	1.464	0.098	1.551
	3	0.000	0.050	0.232	0.432	0.387	0.666
Dennis	1	0.000	0.251	0.182	0.503	0.098	0.591
	2	0.000	0.165	0.316	1.022	1.328	0.000
	3	0.000	0.072	0.280	0.380	0.878	0.444
	4	0.000	0.000	0.294	0.330	1.172	0.506
Dougherty	1	0.000	0.182	0.200	0.569	0.710	2.281
	2	0.000	0.093	0.165	0.519	0.220	5.196
	3	0.000	0.000	0.294	0.221	0.534	5.336
Durant	1	0.000	0.513	0.428	1.463	0.952	2.247
	2	0.000	0.356	0.322	0.386	1.199	1.587
	3	0.000	0.044	0.350	0.120	0.927	0.529
Easpur	1	0.000	0.198	0.287	0.901	0.587	3.940
	2	0.000	0.146	0.260	0.749	1.074	3.899
	3	0.000	0.128	0.322	0.582	0.975	2.791
Grant	1	0.000	0.233	0.366	0.835	0.710	0.000
	2	0.000	0.198	0.244	0.751	1.566	0.000
	3	0.000	0.158	0.322	0.495	0.584	0.555
Kirkland	1	0.000	0.251	0.296	1.000	0.954	0.000
	2	0.000	0.269	0.287	1.050	0.587	1.122
	3	0.000	0.094	0.300	0.560	0.828	0.555

Table A7. Continued.

Soil	Obs	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1} soil					
Lebron A	1	0.000	0.164	0.497	0.771	3.230	0.727
	2	0.000	0.193	0.579	0.517	3.230	0.616
	3	0.000	0.251	0.878	0.935	3.404	0.000
	4	0.000	0.269	0.428	0.935	4.261	1.553
Lebron Ap	1	0.000	0.146	0.331	0.968	1.566	0.393
	2	0.000	0.000	0.631	1.184	0.000	0.000
	3	0.000	0.086	0.399	0.654	0.927	0.889
	4	0.000	0.000	0.419	0.582	1.710	1.038
Mansic	1	0.000	0.529	0.658	0.951	5.238	0.000
	2	0.000	0.599	0.595	1.479	3.886	1.716
	3	0.000	0.313	0.511	0.499	3.222	0.601
Osage	1	0.000	0.461	0.306	1.134	1.200	2.916
	2	0.000	0.617	0.366	1.218	1.200	2.815
	3	0.000	0.265	0.393	0.834	0.878	1.963
Parsons	1	0.000	0.285	0.603	0.733	0.463	2.179
	2	0.000	0.217	0.323	0.752	1.447	2.784
	3	0.000	0.086	0.447	0.380	0.828	1.259
Pond Creek	1	0.000	0.408	0.349	1.331	0.709	0.000
	2	0.000	0.303	0.217	0.901	0.832	0.000
	3	0.000	0.172	0.314	0.662	0.878	0.567
Pratt	1	0.000	0.199	0.323	1.317	0.000	0.000
	2	0.000	0.077	0.306	0.835	0.832	0.000
	3	0.000	0.000	0.274	0.251	0.731	0.480
Renfrow	1	0.000	0.112	0.296	0.769	0.710	
	2	0.000	0.077	0.225	1.184	0.464	0.393
	3	0.000	0.080	0.314	0.293	0.681	0.431
	4	0.000	0.108	0.314	0.257	0.878	0.468
Richfield	1	0.000	0.199	0.562	0.000	1.078	0.000
	2	0.000	0.094	0.000	0.000	1.325	0.000
	3	0.000	0.000	0.260	0.632	0.927	0.456
	4	0.000	0.072	0.274	0.662	1.122	0.444
Saint Paul	1	0.000	0.568	0.226	0.638	1.081	1.560
	2	0.000	0.303	0.225	0.867	0.709	1.022
	3	0.000	0.080	0.308	0.344	1.172	0.518
Sallisaw	1	0.000	0.043	0.358	0.553	0.587	4.305
	2	0.000	0.043	0.385	1.350	0.221	0.000
	3	0.000	0.064	0.399	0.489	0.828	3.655
Stiegler	1	0.000	0.215	0.531	0.473	0.927	2.420
	2	0.000	0.146	0.799	1.481	0.833	3.210
	3	0.000	0.286	0.605	1.817	0.711	5.109
Summit	1	0.000	0.216	0.200	0.884	0.953	0.000
	2	0.000	0.356	0.190	0.967	0.709	1.851
	3	0.000	0.193	0.274	0.539	1.074	0.678

Table A7. Continued.

Soil	Obs	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1} soil					
Tillman	1	0.000	0.164	0.209	0.000	1.812	0.000
	2	0.000	0.000	0.155	0.653	0.834	0.692
	3	0.000	0.114	0.314	0.481	0.878	0.579
	4	0.000	0.108	0.286	0.511	1.074	0.506
Woodward	1	0.000	0.000	0.288	1.235	0.098	0.000
	2	0.000	0.000	0.147	0.455	0.836	0.000
	3	0.000	0.265	0.274	0.410	0.534	0.456
Zaneis	1	0.000	0.251	0.260	0.470	0.832	0.000
	2	0.000	0.182	0.366	0.885	1.077	0.000
	3	0.000	0.094	0.328	0.330	0.731	0.605
Sludge Amended Soils							
Oklahoma City	1	0.000	0.112	0.745	1.250	0.710	0.000
	2	0.000	0.093	0.807	1.300	0.833	16.106
	3	0.000	0.114	0.866	0.790	0.633	15.275
Stillwater	1	0.000	0.564	1.168	0.000	3.890	28.930
	2	0.000	0.599	1.404	0.000	3.886	32.810
	3	0.000	0.744	1.471	0.691	4.307	20.760
Tulsa	1	0.000	0.146	0.341	1.033	0.953	7.220
	2	0.000	0.093	0.385	0.852	1.688	7.255
	3	0.000	0.257	0.497	0.670	1.122	7.090
Mine and Smelter Contaminated Soils							
Bartlesville	1	6.24	0.000	0.98	0.000	8.30	394
	2	6.12	0.182	0.96	0.901	8.29	389
	3	6.53	0.144	1.09	0.675	7.84	359
Blackwell	1	227	2.482	36.9	0.000	92.9	5680
	2	225	2.486	38.5	2.117	95.6	5650
	3	214	2.455	31.2	1.917	81.8	5199
Cardin	1	1.42	0.164	0.000	61.3	7.69	251
	2	0.98	0.217	0.000	22.0	6.09	218
	3	0.67	0.209	0.802	0.4	4.90	171
Picher	1	0.000	0.000	0.217	0.000	1.57	41.1
	2	0.000	0.146	0.287	0.718	0.00	46.0
	3	0.000	0.179	0.364	0.388	0.93	36.1

Table A8. Mehlich III extractable heavy metal concentrations of Oklahoma soils.

Soil	Obs	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1} soil					
Benchmark Soils - A Horizon							
Bernow	1	0.09	0.13	0.11	0.15	0.77	0.81
	2	0.11	0.15	0.12	0.31	0.97	1.81
	3	0.16	0.18	0.21	0.54	1.02	1.70
Burleson	1	0.12	0.45	1.13	1.79	1.77	0.80
	2	0.18	0.57	1.28	4.45	1.84	2.94
	3	0.19	0.59	1.04	2.49	3.53	1.57
Carnasaw	1	0.10	0.49	0.44	0.59	2.44	1.45
	2	0.16	0.78	0.39	0.96	2.28	3.32
	3	0.17	0.76	0.39	0.86	2.15	2.54
Clarksville	1	0.17	0.30	1.07	1.10	1.72	4.64
	2	0.18	0.39	0.81	1.26	1.59	6.05
	3	0.20	0.46	1.20	1.74	2.19	7.55
Cobb	1	0.07	0.25	0.55	0.23	1.62	0.33
	2	0.37	0.31	0.71	1.71	1.58	3.07
	3	0.13	0.31	0.59	0.49	1.65	3.20
Dalhart	1	0.06	0.52	0.54	0.53	1.32	0.22
	2	0.11	0.53	0.50	0.64	1.11	2.04
	3	0.25	0.61	1.21	2.48	1.69	4.52
Darnell	1	0.09	0.35	0.32	0.60	1.46	0.83
	2	0.66	0.45	0.64	3.27	1.68	4.01
	3	0.14	0.41	0.36	0.85	1.70	2.30
Dennis	1	0.09	0.20	0.94	0.81	1.96	0.81
	2	0.13	0.31	0.82	1.27	1.83	1.98
	3	0.17	0.29	0.79	1.12	1.86	2.32
Dougherty	1	0.10	0.09	0.39	0.14	2.88	2.97
	2	0.12	0.15	0.29	0.21	2.56	4.57
	3	0.13	0.15	0.31	0.33	2.59	5.39
Durant	1	0.09	0.22	1.07	0.40	2.38	0.79
	2	0.12	0.39	1.03	0.66	2.16	1.89
	3	0.17	0.38	1.15	0.68	2.74	4.21
Easpur	1	0.09	0.41	1.22	1.00	3.25	5.22
	2	0.34	1.72	1.86	2.00	7.49	19.17
	3	0.34	1.80	1.85	1.85	5.50	14.61
Grant	1	0.12	0.46	0.76	1.13	1.77	0.69
	2	0.17	0.60	0.73	1.60	1.93	1.73
	3	0.20	0.61	0.77	1.70	1.82	3.30
Kirkland	1	0.13	0.48	1.30	1.59	1.81	0.77
	2	0.17	0.59	1.03	1.83	1.78	1.56
	3	0.14	0.53	0.94	1.76	1.66	2.56
Lebron Ap	1	0.17	0.18	1.38	0.68	2.19	5.49
	2	0.12	0.16	1.22	0.39	1.99	2.23
	3	0.15	0.22	2.74	0.52	3.97	2.32

Table A8. Continued.

Soil	Obs	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1} soil					
Lebron A	1	0.15	0.18	2.15	0.42	3.10	0.89
	2	0.21	0.28	2.35	0.68	3.37	3.83
	3	0.21	0.28	2.23	0.63	3.24	2.98
Mansic	1	0.16	0.31	0.83	0.37	2.61	0.58
	2	0.18	0.38	0.68	0.52	2.25	1.27
	3	0.20	0.37	0.77	0.48	2.77	2.08
Osage	1	0.15	0.60	0.81	1.37	1.27	3.10
	2	0.13	0.42	0.46	1.11	1.11	3.81
	3	0.14	0.44	0.53	1.13	1.10	3.56
Parsons	1	0.12	0.48	1.12	0.95	2.24	4.32
	2	0.13	0.63	0.91	1.13	1.94	4.93
	3	0.14	0.70	1.03	1.17	2.11	6.53
Pond Creek	1	0.14	0.38	0.99	1.27	1.64	0.61
	2	0.20	0.46	0.96	1.55	1.85	3.89
	3	0.18	0.43	0.86	1.52	1.76	2.74
Pratt	1	0.05	0.17	0.30	0.22	0.79	0.44
	2	0.09	0.26	0.29	0.38	1.07	1.40
	3	0.09	0.31	0.32	0.29	1.10	1.13
Renfrow	1	0.09	0.43	1.30	0.63	2.28	1.02
	2	0.18	0.66	1.87	1.26	2.27	2.49
	3	0.12	0.59	1.19	1.07	2.14	1.90
Richfield	1	0.15	0.78	1.39	1.18	2.56	0.43
	2	0.19	1.17	1.32	1.55	2.28	2.13
	3	0.20	1.27	1.66	1.89	2.47	1.96
Saint Paul	1	0.13	0.69	1.23	1.04	1.93	0.43
	2	0.15	0.90	1.15	1.23	3.79	2.10
	3	0.18	1.02	1.52	1.62	2.17	3.86
Sallisaw	1	0.09	0.33	1.88	0.54	1.53	6.85
	2	0.17	0.44	1.88	0.88	1.78	9.30
	3	0.84	0.44	2.00	0.84	1.80	23.04
Stiegler	1	0.11	0.15	5.02	0.86	1.87	6.34
	2	0.13	0.24	4.21	1.10	1.24	6.29
	3	0.16	0.24	4.52	1.16	1.61	7.49
Summit	1	0.09	0.79	1.04	0.91	1.99	1.08
	2	0.15	1.24	0.99	1.28	2.05	2.26
	3	0.15	1.21	0.91	1.32	2.01	2.72
Tillman	1	0.09	0.48	0.94	1.37	1.69	0.68
	2	0.55	0.71	1.09	1.68	1.91	18.95
	3	0.13	0.65	0.82	1.68	1.69	1.25
Woodward	1	0.09	0.60	0.83	0.63	1.84	0.47
	2	0.12	0.76	0.76	0.90	1.80	2.26
	3	0.16	0.89	1.09	1.26	2.07	4.09
Zaneis	1	0.09	0.40	0.67	0.43	2.16	1.02
	2	0.19	0.51	0.84	1.01	2.14	5.72
	3	0.16	0.51	0.72	0.86	2.16	2.29

Table A8. Continued.

Soil	Obs	Cd	Co	Cu	Ni	Pb	Zn
		mg kg^{-1} soil					
Sludge Amended Soils							
Oklahoma City	1	0.36	0.16	5.59	0.62	4.4	18.2
	2	1.49	0.95	10.76	8.25	10.0	41.1
	3	0.66	0.75	6.53	1.89	10.4	24.9
Stillwater	1	0.24	0.25	8.71	0.45	34.3	21.0
	2	0.59	1.27	11.95	2.52	57.5	35.4
	3	0.66	1.18	10.73	1.26	51.8	40.9
Tulsa	1	0.48	0.24	2.81	0.80	3.0	15.6
	2	1.01	1.03	4.54	2.38	8.1	40.6
	3	1.01	1.08	4.66	2.39	8.5	33.7
Mine and Smelter Contaminated Soils							
Bartlesville	1	15.9	0.19	18.59	1.24	88.1	995
	2	17.0	0.49	17.07	6.11	82.8	1200
	3	14.3	0.44	13.80	1.50	72.9	1050
Blackwell	1	270	3.76	146.64	3.17	86.4	10300
	2	286	4.22	127.21	4.05	80.5	14900
	3	270	4.18	126.46	3.89	81.1	14000
Cardin	1	4.49	0.16	11.28	0.76	106.3	617
	2	4.95	0.41	10.58	1.65	99.1	787
	3	5.59	0.45	15.43	3.53	99.6	810
Picher	1	1.24	1.30	2.21	0.62	26.8	121
	2	1.36	1.82	1.87	1.82	24.4	136
	3	1.34	1.70	1.75	1.74	23.3	126

VITA

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Candidate for the Degree of

Master of Science

Thesis: DISTRIBUTION, SPECIATION, AND BIOAVAILABILITY OF HEAVY METALS IN SOILS OF OKLAHOMA

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