

REMEDICATION OF ARSENIC CONTAMINATED SOIL AND
TRACE ELEMENT AVAILABILITY TO
WINTER WHEAT IN BIOSOLIDS
AMENDED SOILS

By

ERIC McMASTERS HANKE

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Thesis Approved:

Nicholas I. Basta

Thesis Advisor

Brian J. Carter

Jeffrey A. Hatley

Thomas C. Collins

Dean of the Graduate College

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INTRODUCTION

This document consists of two chapters, each reporting separate studies conducted during my master's program. Both chapters are presented in formats suitable for publication in professional journals.

CHAPTER I

REMEDIATION OF ARSENIC CONTAMINATED SOIL
BY CHEMICAL IMMOBILIZATION

ABSTRACT

Chemical immobilization of arsenic involves treatment of polluted soil to reduce solubility, bioavailability, mobility, and risk to human health from contaminants. The ability of five chemical immobilization treatments to remediate acidic soil (pH 3.6) contaminated with arsenic ($7977 \text{ mg As kg}^{-1}$) from arsenopyrite smelter waste were evaluated. Contaminated soils were incubated with chemical treatments for 4 weeks. Treatments were calcium carbonate (Limed Control), aluminum sulfate (Alum) with CaCO_3 , ferrous sulfate (Fe) with CaCO_3 , manganese sulfate (Mn) with CaCO_3 , and cement kiln dust (CKD) at a 2:1 metal:As treatment rate. Reductions in arsenic solubility, plant As uptake, and As mobility in treated soil were determined by extraction (1M NH_4Cl , Bray #1, and 0.1M PO_4), measuring As in carrot (*Daucus carota L.*) roots and tops, and by leaching soil columns with water and 0.1M PO_4 , respectively. Arsenic solubility (in mg kg^{-1}) for immobilization treatments (in parentheses) ranged from 23.7 (CKD) to 7.7 (Mn) in NH_4Cl , 98.5 (Unlimed Control) to 0.6 (Mn) in Bray #1, and 352 (Unlimed Control) to 154 (Alum) in 0.1M PO_4 . Reduction of extractable

As by the Alum, Fe, and Mn treatments was attributed to chemisorption of As by hydrous oxides formed during soil treatment. The Alum treatment had the most carrot growth while the Mn had the least. Root As concentration ranged from $1.3 \mu\text{g g}^{-1}$ for CKD to $0.23 \mu\text{g g}^{-1}$ for Alum. Treatments increased soil pH and As mobility in water but Alum, Fe, and Mn treatments decreased As mobility in 0.1M PO_4 . Co-application of Alum and Lime promotes plant growth while reducing As solubility, As mobility, and As uptake. Alum treatment may reduce arsenic exposure and risk to human health from groundwater, erosion of denuded soil and incidental ingestion of soil and house dust, and consumption of garden vegetables.

INTRODUCTION

Arsenic is ubiquitous in soil environments and ranges from $0.1\text{-}40 \text{ mg As kg}^{-1}$ with most soils in the lower region of this range (O'Neill, 1990). Arsenic is present in soils as arsenopyrite (FeAsS), enargite (Cu_3AsS_4), orpiment (As_2S_3), and realgar (As_4S_4) minerals, sorbed to hydrous oxides, or co-precipitated with Ca, Mg, Fe, and Al minerals (Huang and Fujii, 1996).

Arsenic production > 30,000 metric tons worldwide (Adriano, 1986) and among its many uses are pesticides, wood preservatives, and growth promoters for poultry and swine (O'Neill, 1990). Arsenic contamination of soil arises from mine tailings and aerial deposition from smelting of As and Cu ores and the use

of inorganic As based pesticides prior to the 1970's (Huang and Fujii, 1996; Lindau, 1977; Nelson, 1977; O'Neill, 1990).

Long-term application of arsenical pesticides to orchards has led to As contamination of soil and As phytotoxicity (Woolson et al., 1971; Hess and Blancher, 1976; Peryea, 1991). Fifty-eight orchard soils nationwide that received arsenical pesticides ranged from 1 to 2553 mg As kg⁻¹ with a mean content of 165 mg As kg⁻¹. Nearby untreated soils ranged from 0 to 96 mg As kg⁻¹ with a mean content of 13 mg As kg⁻¹ (Woolson et al., 1971). Soils contaminated by mining and smelting have resulted in As concentrations greater than 20,000 mg kg⁻¹ (O'Neill, 1990).

Chronic exposure to As can result in human health problems including skin and internal organ cancers, impaired nerve function, kidney and liver damage, and skin lesions (ATSDR, 1991). Humans can be exposed to As from contaminated soils by incidental ingestion of soil and house dust, contaminated groundwater, and movement of As through the food chain (Polissar et al., 1990; Chaney and Ryan, 1994). The soil ingestion pathway has been shown to be the principal exposure pathway for high levels of As in young children (measured as urinary As) living near smelter sites where As contamination of soils is prevalent (Polissar et al., 1990). The use of root vegetable crops such as carrots or radishes, poses a link for As into the food chain (Chaney and Ryan, 1994).

Remediation of smelter-contaminated sites is an expensive problem that often involves excavation and landfilling of contaminated soil. An alternate approach to remediation is chemical immobilization where soil is treated to

reduce solubility, bioavailability, and mobility of contaminants (Logan, 1992). Chemical amendments reduce solubility of soil contaminants by enhancing their sorption, precipitation, or complexation (Logan, 1992). Phosphate fertilizers, organic amendments, and liming materials have been used for chemical immobilization of Pb and Zn in smelter contaminated soils (Anderson and Basta, 1995; Zwonitzer and Pierzynski, 1996; Onken et al., 1996; Chlopecka and Adriano, 1996; Ma et al., 1993; Pierzynski and Schwab, 1993).

Chemisorption to hydrous oxides and precipitation with Fe, Mn, Al, and Ca limits solubility of arsenate in contaminated soil (Hess and Blancher, 1976). The addition of $\text{Al}_2(\text{SO}_4)_3$, FeSO_4 , or MnSO_4 to contaminated soil can precipitate As or form Al, Fe, or Mn hydrous oxides (Lindsay, 1979) that can adsorb As (McBride, 1994) and may serve as effective chemical immobilization treatments (U.S. EPA, 1984). Ferrous sulfate has been used for chemical immobilization of arsenic as FeAsO_4 in soil contaminated from manufacturing of arsenical pesticides (Artiola et al., 1990), and in soil contaminated with arsenious acid at a chemical manufacturing plant (Liberti and Polemio, 1981). Also, Ca containing amendments (cement kiln dust) precipitate arsenate as $\text{Ca}_3(\text{AsO}_4)_2$ (Sadiq et al., 1983), and may serve as an effective chemical immobilization treatment. To our knowledge, little information is available on the use of Fe, Mn, Al, or Ca-containing treatments for chemical immobilization of As in mining contaminated soil (Hanke and Basta, 1996).

The objectives of this study were to evaluate the ability of five Fe, Mn, Al, or Ca-containing treatments to reduce the solubility, uptake, and mobility of As from soil contaminated with smelter waste.

MATERIALS AND METHODS

Approach

The ability of five chemical treatments to immobilize As by precipitation or adsorption (chemical immobilization) was determined. Arsenic contaminated soil and chemical treatments were mixed and incubated for four weeks at constant temperature and moisture. Soil treatments were evaluated by measuring changes in As solubility, in As uptake and revegetation by carrots, and in As mobility by using packed columns.

Contaminated Soil and Treatments

Surface (0-10 cm) soil samples (Loamy, mixed, mesic Acidic Ustorthent) were collected from an area contaminated with tailings from roasted arsenopyrite ore. Chemical and physical properties, determined on air-dried soil (< 2 mm), were: soil pH 3.6 (1:2 soil:0.01M CaCl₂); electrical conductivity (EC) 2.47 dS m⁻¹ in 1:5 soil:deionized water extract (Rhoades, 1982); soil organic carbon 2.0 g kg⁻¹ (Yeomans and Bremner, 1988); soil texture of fine sandy loam (710 g kg⁻¹ sand, 150 g kg⁻¹ , 140 g kg⁻¹ clay) determined by the hydrometer method of Gee and Bauder (1986); and extractable P of 2.29 mg P kg⁻¹ using Bray #1 extractant (Bray and Kurtz, 1945).

Total soil arsenic of 7977 mg kg⁻¹ was determined by wet digestion with 1:1 HNO₃ and 30% H₂O₂ (U.S. EPA Method 3050B; U.S. EPA, 1996), followed by analysis of digest by direct nebulization inductively-coupled plasma atomic emission spectroscopy (ICP).

Chemical Immobilization Treatments

Chemical treatments were aluminum sulfate [Al₂(SO₄)₃•nH₂O], ferrous sulfate (FeSO₄•7H₂O), manganous sulfate (MnSO₄•H₂O), and cement kiln dust. Metal sulfate salts were reagent grade purity. Calcium carbonate (CaCO₃) was used to adjust the soil pH.

Treatments were applied to soil with three replications in a completely randomized design. Except for the limed control, treatments were added to the contaminated soil on a 2:1 metal:As ratio on a molar basis (Table 1). Calcium carbonate was added to the Limed Control, aluminum sulfate (Alum), ferrous sulfate (Fe), and the manganous sulfate (Mn) treatments to achieve a target soil pH of 7. The amount of CaCO₃ added to these treatments varied according to the acidity produced by the amendments. The Cement Kiln Dust (CKD) treatment did not require supplemental CaCO₃. Comparison of the Limed Control and other treatment results was used to evaluate the effect of pH adjustment on As solubility.

Treatments were added to soil in a sealed container and shaken to achieve thorough mixing. Treated soils were transferred to perforated-lidded clear plastic trays. Deionized water (~ 25% w/w) was added to soils to achieve

moist and unsaturated conditions. Treated soils were incubated at constant temperature (27° C) and water content was adjusted to 25% (w/w) every five days.

Soil pH and phosphate extractable As were measured on subsamples (5 g) of each treatment weekly to determine the extent of CaCO₃ reaction and arsenic sorption. Phosphate extractable As was determined by extracting 2 g of treated soil with 20 mL of a 3:2 solution of 0.1 M Na₂HPO₄ : 0.1 M NaH₂PO₄ on a horizontal shaker for 1 hour. The soil extract was centrifuged at 6000 rpm for 10 min, filtered through 0.45 μm membrane filters and analyzed for As by direct nebulization ICP.

Arsenic Solubility

Ammonium chloride (1M) was used to measure water soluble and anion exchange As. Soil (1 g) was extracted with 20 mL of 1M NH₄Cl on a horizontal shaker for 30 min. Bray #1 solution (0.025 M HCl and 0.03 M NH₄F; Bray and Kurtz, 1945) was used to extract water soluble As, weakly adsorbed As, and easily dissolved As precipitates. Soil (2 g) was extracted with 14 mL of Bray #1 on a horizontal shaker for 5 minutes. Phosphate solution (3:2 0.1 M Na₂HPO₄ : 0.1 M NaH₂PO₄, pH 7.0) (Yamamoto, 1975) was used to extract the water soluble, weakly adsorbed, and strongly adsorbed As fractions. Treated soil (2 g) was extracted with 20 mL of the phosphate solution on a horizontal shaker for 1 hour. All soil extracts were filtered through 0.45μm membrane filters and arsenic in the filtered extracts was determined by ICP.

Revegetation Ability and Plant Uptake of Arsenic

The ability of treated soils to support vegetation and the amount of As accumulated in vegetation was determined by growing carrots (*Daucus carota* L.) for 73 days. Treated soil (500 g) and 25 % (v/v) vermiculite were placed in 600 cm³ cups with holes drilled in the bottom for drainage. Approximately 15 carrot seeds were planted in each pot. Nutrient solution, 40 mL of 0.5 g L⁻¹ Miracle Grow®, was added every 3 days. Three weeks after emergence, the pots were thinned to 5 carrot plants per pot. The carrots were grown in 18 hours of light under Gro-Lux® fluorescent bulbs (Sylvania Inc., Danvers MA). The temperature was 22°C during light and 17°C during darkness. The relative humidity was kept at approximately 70%.

After maturity (73 days), the carrots were removed and carefully washed with deionized water to remove soil. Carrots were dried at 80°C for 24 hours. Carrot tops and roots were separated and ground (40 mesh).

Ground carrot tops and roots were prepared by the wet digestion of Zarcinas et al. (1987) modified for ICP analysis by Hydride Generation. In this method, carrot tops or roots were placed overnight in 10 mL of trace metal grade HNO₃ and subsequent digestion at 90°C for 45 minutes in an aluminum digestion block. The temperature was then raised to 150°C and heated until approximately 1 mL of solution was left in the tube. The tubes were allowed to cool and then 3 mL of trace metal grade concentrated HCl was added and heated at 120°C for 30 minutes. The solution was cooled and the volume was raised to 12.5 mL and then filtered through 0.45 µm membrane filters. The root

digests were diluted 1:50 and the top digests were diluted 1:10 with 3 M HCl and analyzed by Hydride Generation ICP.

Reduction in Arsenic Mobility

Mobility of As in treated soils was determined by pumping deionized water or phosphate solution mobile phases through columns packed with treated soils.

Arsenic mobilized by water was determined by packing 50 g of treated soil into a 2.5 cm X 10 cm Kontes Flex-Column™ with a 2.5 cm flow adapter (Kontes Glass Co.). Pore volume was determined for each treatment from measured bulk density of soil in each packed column. Deionized water was pumped through the column at 1.0 mL min^{-1} and a fraction collector was used to collect each pore volume for a total of 50 pore volumes. Pore volumes analyzed for As were 1-10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 50. Arsenic in column leachates was measured by Hydride Generation ICP.

Arsenic mobilized by phosphate solution (3:2 0.1 M Na_2HPO_4 : 0.1 M NaH_2PO_4 , pH 7.0) from treated soils was determined by using the same procedure as previously described for collection of water leachate. Dissolved As in phosphate leachate was measured by direct nebulization ICP.

Arsenic Analysis

The type of As analysis by ICP (Hydride Generation or Direct Nebulization) used depended on As concentration in sample extract, digest, or leachate. Hydride Generation was used for low level As analysis ($< 1 \text{ mg L}^{-1}$ in

solution). Sample pretreatment included acidification of sample to 3 M HCl by adding 2.5 mL of trace metal grade hydrochloric acid to 7.5 mL of filtered extract. Following sample acidification, 3 mL of a 10% (w/v) KI and 1% (w/v) ascorbic acid solution was added to 10 mL of acidified sample to reduce As(V) to As(III) for Hydride Generation. Arsenic was then measured using a Hydride Generator connected to a Fison's Maxim, Inductively Coupled Plasma - Atomic Emission Spectrophotometer (ICP). The conditions for the Hydride generator and the ICP are shown in Table 2.

Direct Nebulization ICP was used for $>1 \text{ mg As L}^{-1}$. The ICP conditions were as follows: Forward Power at 1100 W, plasma flow at 1.05 L min^{-1} , carrier flow at 0.5 L min^{-1} , sample pump speed at 2.2 mL min^{-1} , and analytical wavelength of 193.761 nm.

RESULTS AND DISCUSSION

Soil pH and EC

Soil pH or phosphate extractable As did not change after four weeks of incubation indicating rapid chemical reactions were complete. Calcium carbonate, added to raise the soil pH to allow revegetation, resulted in soil pH values of 6.8 to 7.6 in treated soils (Table 3). Slight but significant ($P < 0.05$) increases in soil EC were found between treatments (Table 3). Soil EC $> 1.0 \text{ dS m}^{-1}$ will decrease carrot growth by $>10\%$ (Rhodes and Miyamoto, 1990) but most differences in EC between treatments were small and should not result in differences in carrot growth due to treatment.

Arsenic Solubility

Except for Mn, treatments increased NH_4Cl extractable As (Fig. 1A). Because As solubility increases with soil pH, CaCO_3 addition may have contributed to increases in NH_4Cl extractable As by simply raising soil pH. Soluble As was $\text{CKD} > \text{Fe} > \text{Alum}$ even though these treatments had similar soil pH. Solubility diagrams of Al-, Ca-, Fe-, and Mn- arsenates, based on K_{sp} values given by Sadiq et al. (1983) suggests treatments should have followed the trend $\text{Fe} > \text{Al} > \text{Ca}, \text{Mn}$ at pH 7 if precipitation was the only immobilization mechanism (Fig. 2). The addition of metal salts of Al, Fe, and Mn, along with the addition of lime to raise the pH, forms additional hydrous oxides in the Alum, Fe, and Mn treatments (Lindsay, 1979). Hydrous oxides are able to strongly adsorb As (McBride, 1994) or precipitate As (Hess and Blancher, 1976). Therefore both adsorption and precipitation mechanisms reduce soluble As in the Alum, Fe, and Mn treatments. However, only precipitation of CaAsO_4 could have occurred in the Limed Control and CKD treatments. Soluble arsenate trend of $\text{CKD} > \text{Alum}, \text{Fe}, \text{Mn}$ (Fig. 1A) is consistent with adsorption of arsenate by hydrous oxides formed during treatment with metal salts. Artiola et al. (1990) treated As-contaminated soil with ferrous sulfate and reduced water soluble As from 2.5 g L^{-1} to 0.017 g L^{-1} . They attributed the reduction in water soluble As to adsorption and precipitation of As onto Fe oxides formed by addition of ferrous sulfate. Similarly, Liberti and Polemio (1981) used FeSO_4 additions to form highly insoluble arsenates in soil contaminated with arsenite.

Because arsenate and phosphate chemistry are similar in soil, dilute acid fluoride extractants including Bray #1 was used to measure labile As in soil (Jacobs et al., 1970). The Bray #1 extractable As from each treatment was Unlimed Control > Limed Control > CKD > Alum, Fe, Mn (Fig. 1B). In addition to soluble P, Bray extractant dissolves limited amounts of inorganic Ca-P, Al-P, and Fe-P in soil (Fixen and Grove, 1990) and should dissolve analogous forms of arsenates. Sesquioxides and free Fe_2O_3 increase As retention and reduce the amount of As extracted by Bray #1 (Jacobs et al., 1970). The additional hydrous oxides created in the metal treatments and the precipitation of the metal arsenates explains the greater reduction in the Bray #1 extractable As compared to the Limed control.

Phosphate extractant (3:2 0.1M $\text{Na}_2\text{HPO}_4:\text{NaH}_2\text{PO}_4$) has been used to desorb arsenate from soils (Yamamoto, 1975). Because phosphate has very similar chemistry to arsenate, phosphate is able to desorb arsenate from soil (Woolson et al., 1973; Peryea, 1991; Creger and Peryea, 1994; Roy et al., 1986). Arsenic extracted by phosphate solution was Unlimed Control, Limed Control, CKD > Fe > Mn, Alum (Fig. 1C). Phosphate fertilizer addition to contaminated soil could desorb arsenate (Peryea,1991), increase plant uptake of As (Creger and Peryea,1994; Woolson et al.,1973), and potentially increase mobility of As in soil. The greater reduction of extractable As by the Alum, Fe, and Mn treatments compared to the other treatments is most likely due to strong adsorption of As by hydrous oxides (Fig. 1C). Hydrous oxides strongly adsorb As, and some adsorbed forms are not desorbed by phosphate (Woolson et al.,

1973). The Alum and Mn treatments were able to reduce the extractable As by more than 50 percent of the controls and should reduce environmental impacts associated with As solubility from phosphate fertilization.

Revegetation Ability and Plant Uptake of Arsenic

Accumulation of As in garden vegetables in suburban areas adjacent to contaminated sites is a concern (Chaney and Ryan, 1994). To determine if treated soils could support plant growth and reduce As uptake, carrots (*Daucus carota L.*), a root crop known to accumulate As (Woolson, 1983), were grown.

The average dry weights obtained from each treatment in both roots and shoots are shown in Figure 3A. The Unlimed Control was unable to produce any growth due to its low pH (3.6). Limed Control, Alum, and Fe treatments produced more top growth than the CKD and Mn treatments (Figs. 3A,B). Because soil pH and EC of CKD treatment was similar to other treatments (Table 3), the reduced growth obtained with CKD may be due to larger amounts of NH_4Cl extractable As compared to other treatments (Fig. 1A). The reduced growth in the Mn treatment compared to Fe and Alum can not be explained by As solubility but may be attributed to manganese toxicity.

The As concentrations in the roots and the shoots of the carrots are shown in Figure 3C. Greater concentrations of As in the roots than shoots is commonly found for root crops (Merry et al., 1986; Woolson, 1983). The CKD treatment had the highest root As concentration ($1.3 \mu\text{g g}^{-1}$) and the Alum treatment had the lowest root As concentration ($0.23 \mu\text{g g}^{-1}$) of all the treatments.

Apparently, NH_4Cl extractable As (Fig. 1A) is a better indicator of As uptake than Bray #1 (Fig. 1B) extractable As.

Reduction in Arsenic Mobility

The mobility of arsenic through a packed soil column was determined for each treatment (Fig. 4). Arsenic removed in each pore volume of leachate after pumping deionized water through the soil column showed As mobility followed the trend $\text{CKD} > \text{Fe, Alum} \geq \text{Limed Control} > \text{Mn, Unlimed Control}$ (Fig. 4A). Increased pH associated with the chemical treatments increased As mobility (Fig. 4A). The trends in As concentrations in column leachates parallels trends in NH_4Cl extractable As discussed previously (Fig. 1A).

Revegetation of this soil will require significant P fertilizer (Bray #1 extractable P = 2.29 mg kg^{-1}) and may increase As mobility. We determined the mobility of As by using 0.1M PO_4 to simulate potential increase of As mobility in treated soils (Fig. 4B). Arsenic in column leachates and As mobility was $\text{CKD, Limed Control} > \text{Unlimed Control} > \text{Fe, Mn, Alum}$. The calcium treatments increased As mobility while the Alum, Fe, and Mn treatments decreased As mobility compared to the Unlimed Control. These results suggest P fertilizer application may increase As mobility in Limed and CKD treatments. Another column study (Woolson et al., 1973) found 77% of total As was removed by passing $0.05\text{M KH}_2\text{PO}_4$ through a soil contaminated by As (625 ppm) from pesticide use.

CONCLUSION

Only co-application of Alum and Lime promotes plant growth while reducing As solubility, As mobility, and As uptake. This treatment may reduce arsenic exposure and risk to human health from groundwater, erosion of denuded soil and incidental ingestion of soil and house dust, and consumption of garden vegetables. Co-application of ferrous sulfate and lime promoted plant growth and reduced As solubility but did not decrease uptake of As by carrots. The Fe treatment may be an acceptable remediation method when consumption of root crops does not constitute a significant risk or plants that do not accumulate As are grown. Co-application of manganous sulfate and lime reduced As solubility and mobility but stunted carrot growth. The Mn treatment should reduce As transport and risk to groundwater from As contaminated soil providing surface erosion is reduced by using tolerant cover crops or artificial surface. The CKD treatment did not reduce As solubility, uptake, or mobility and should not be used for remediation of As contaminated soil.

Phosphorus fertilizer and lime, required to revegetate the contaminated soil, will increase As solubility and mobility and may threaten water resources. However, addition of metal ions that form amorphous hydrous oxides (Fe, Al, Mn) will reduce solubility and mobility of As in phosphate rich soil environments. These treatments may serve as an alternate remediation technology to expensive currently used techniques such as excavation.

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Table 1. Amendment and CaCO₃ addition rates for chemical treatments

Treatment	Chemical Formula	Soil (g)	Amendment (g)	CaCO ₃ (g)
Limed Control	CaCO ₃	700	0.0	7.0
Alum	Al ₂ (SO ₄) ₃ •nH ₂ O	700	43.15	71.7
CKD	CaO †	700	29.23	0.0
Fe	FeSO ₄ •7H ₂ O	700	41.63	69.3
Mn	MnSO ₄ •H ₂ O	700	24.72	44.1

† contains 2.0 g Ca kg⁻¹, CCE 87%

Table 2. ICP conditions for As analysis by Hydride Generation.

Hydride Generation Conditions		ICP Conditions	
Reductant	1% NaBH ₄ in 0.1 M NaOH @ 3 ml min ⁻¹	Forward Power	1150 W
Blank Acid	3 M HCl @ 8 ml min ⁻¹	Plasma Flow	1.05 L min ⁻¹
Sample	make 3 M HCl @ 8 ml min ⁻¹	Carrier Flow	0.8 L min ⁻¹
KI	add 3 ml of 10%KI, 1% ascorbic acid solution per 10 ml sample	As wavelength	193.761 nm

Table 3. Soil pH and soil EC of treated soils.

Treatments	Soil pH	Soil EC (dS m⁻¹)
Unlimed Control	3.6	2.47
Limed Control	7.4	2.23
Alum	7.4	2.20
CKD	7.5	2.32
Fe	7.6	2.23
Mn	6.8	2.97
LSD $\alpha=0.05$	0.5	0.08

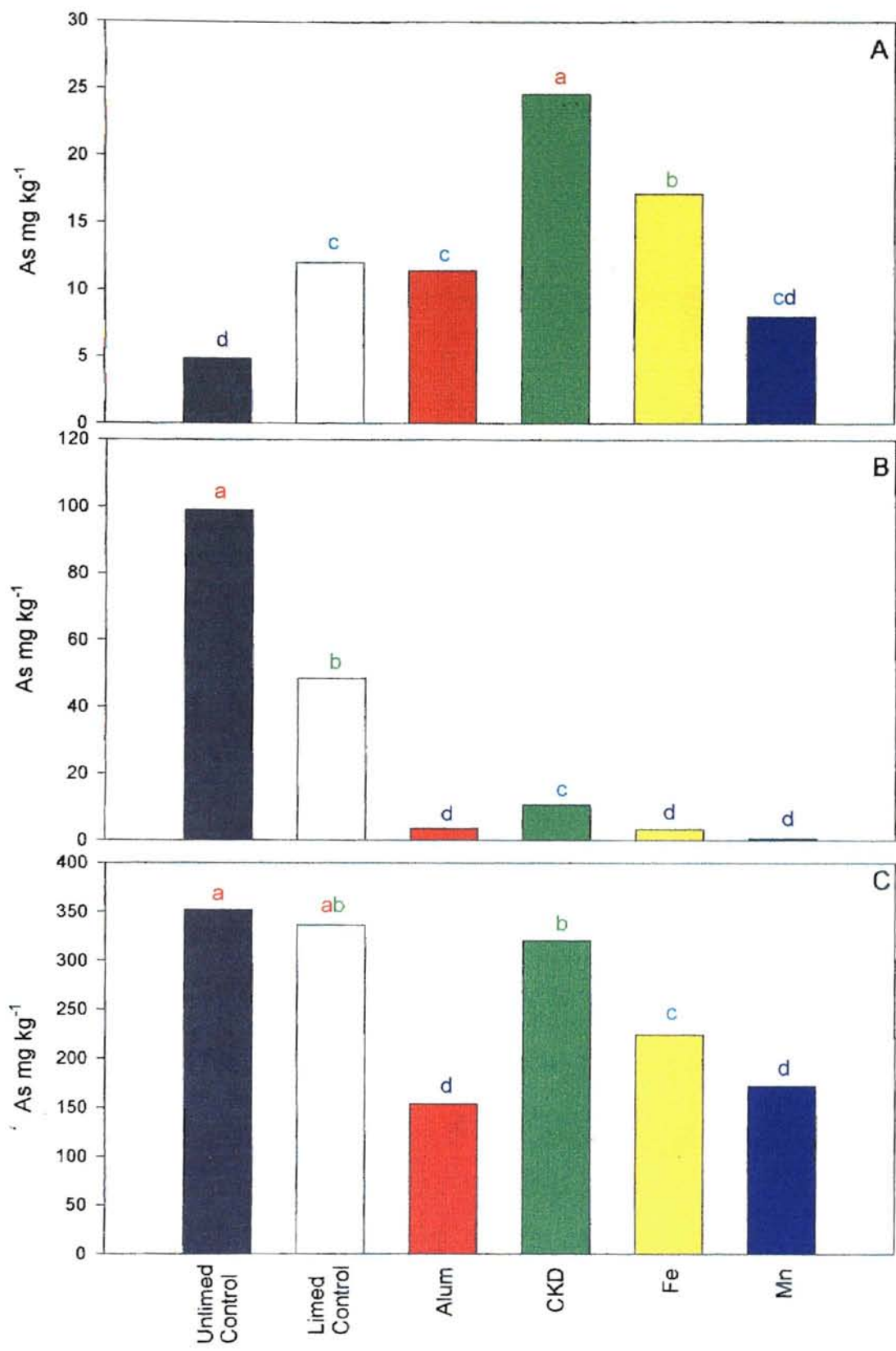


Figure 1. Arsenic solubility of treated soils determined with (A) NH₄Cl, (B) Bray #1, and (C) 0.1M phosphate. Letters represent Duncan's LSD at $\alpha=0.05$

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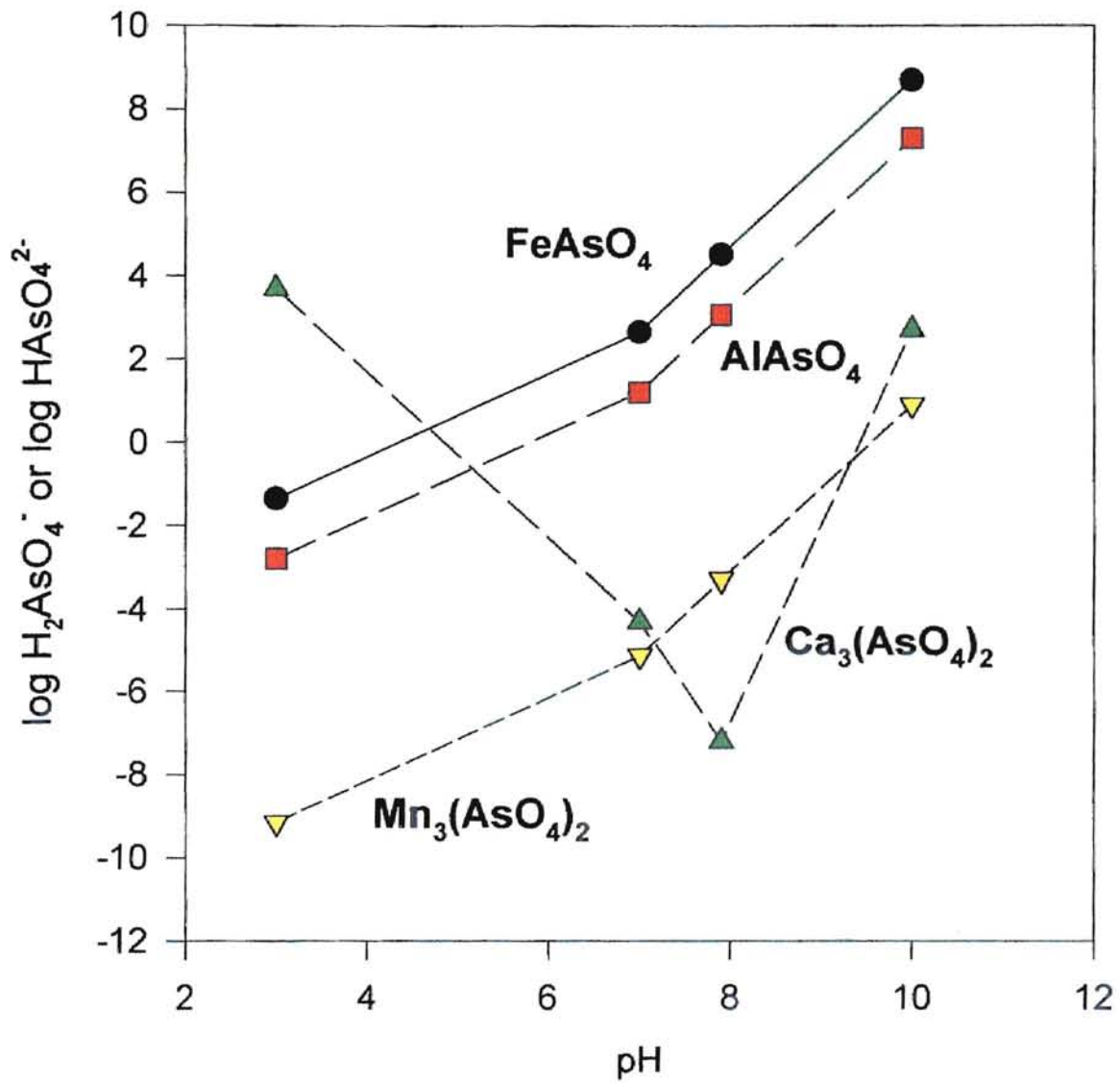


Figure 2. Solubility diagram of Al-, Ca-, Fe-, and Mn-arsenate derived from mineral equilibria of Sadiq et al. (1983).

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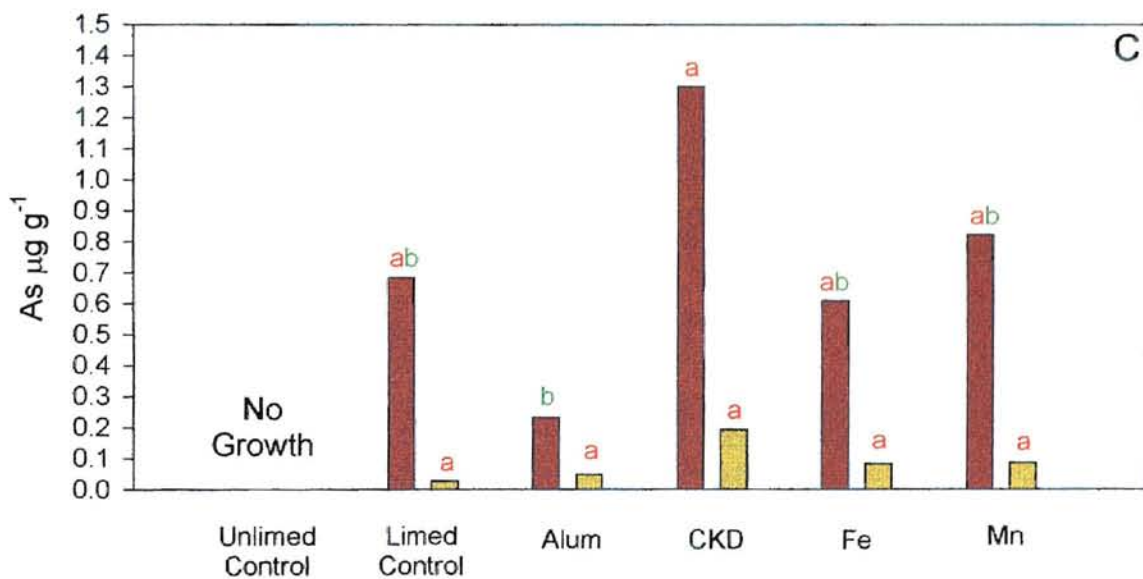
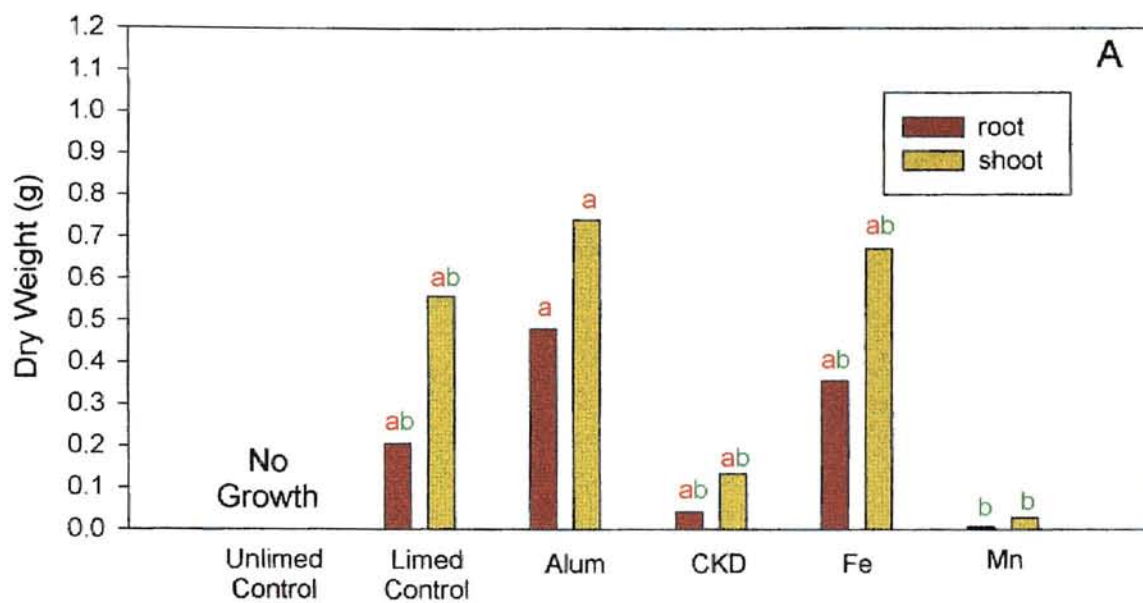


Figure 3. The average (A) weight, (B) picture of, and (C) average As concentration of carrots grown on treated soils. Letters represent Duncan's LSD at $\alpha=0.05$.

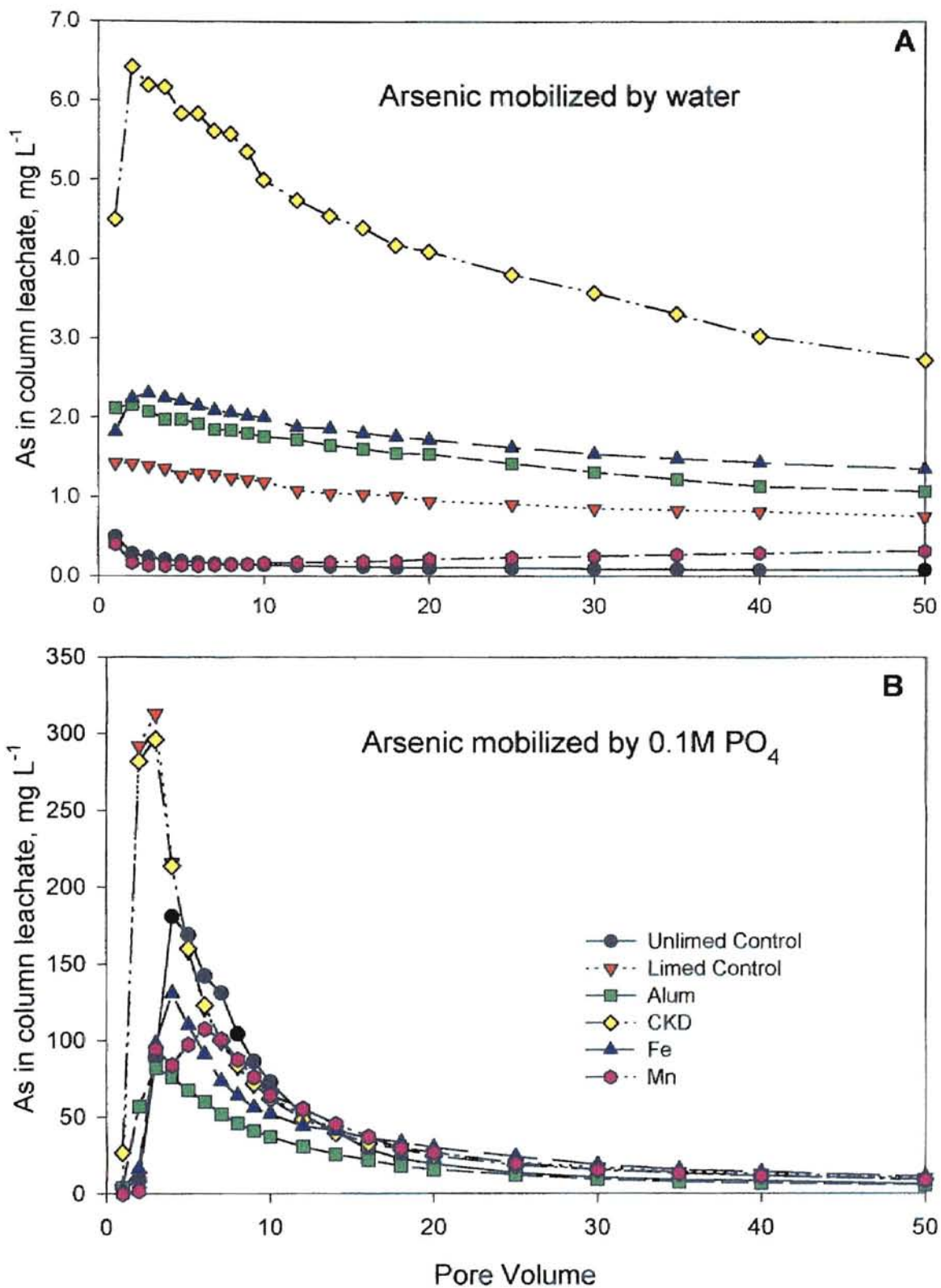


Figure 4. The arsenic removed in each pore volume from soil columns by (A) deionized water and (B) 3:2 mixture of 0.1M Na₂HPO₄:0.1M NaH₂PO₄

CHAPTER II

TRACE ELEMENT AVAILABILITY TO WINTER WHEAT IN BIOSOLIDS AMENDED SOIL

ABSTRACT

A new rule promulgated by U.S. EPA limits land application of biosolids based on As, Mo, and Se. More information is needed to document uptake of oxyanions (As, Mo, Se) by crops to evaluate their risk to human and animal health and strengthen federal guidelines. The objective of this study was to determine the uptake of As, Mo, Se to wheat in biosolid-amended soils under field conditions. Biosolids were added at 5 rates ranging from 45 to 540 kg ha⁻¹ of plant available N to plots and winter wheat was grown for 2 consecutive years. In addition, 3 treatments were used to determine liming effect on trace element uptake. These treatments included lime addition to a 540 kg N ha⁻¹ biosolids treatment, and ammonium nitrate treatments at 540 kg N ha⁻¹, with and without lime. Trace element content of soil and wheat grain (*Triticum aestivum* L.) was determined by acid digestion analysis by inductively coupled plasma atomic emission spectroscopy.

Application of biosolids increased soil content of Cd, Mo, and Zn but not As and Se. Biosolids application increased grain Mo from 0.4 mg kg⁻¹ to 0.8 mg kg⁻¹ but did not increase grain As, Cd, Se, and Zn.

The addition of lime, to soils receiving the high sludge rate, increased grain Mo from 0.76 mg kg⁻¹ to 1.13 mg kg⁻¹. Increases in grain Mo is consistent with greater solubility and availability of Mo from increases in soil pH. Lime treatment increased soil pH and grain Mo from 0.26-0.69 mg kg⁻¹ on control plots that did not receive any biosolids. Liming did not affect grain content of other trace elements. Grain Mo increases were small and should not pose any risk to human or animal health. The high biosolids rate was approximately 7.5 times greater than the agronomic rate for 40 bu acre⁻¹ of dryland wheat in Oklahoma. Assuming Mo phytoavailability does not change with time, the effect of two years of 540 kg N ha⁻¹ biosolids represents 15 years of biosolids application at agronomic rate for dryland wheat. In this case, 15 years of biosolids application, at agronomic rates, should have little or no effect on As, Mo, or Se uptake in grain and pose little risk to human or animal health.

INTRODUCTION

Several trace elements exist as anionic complexes with oxygen ligands or as "oxyanions". Some trace element oxyanions frequently used by society include arsenic (As), molybdenum (Mo), and selenium (Se) (Alloway, 1990). Arsenic has been used as pesticides, wood preservatives, and as growth

promoters in poultry and swine. Molybdenum is used as an alloy to harden steel and as a catalyst for refining petroleum products. Selenium is used in photocells, solar cells, rectifiers, and as a photographic toner (Hammond, 1981). Molybdenum, selenium, and perhaps arsenic are required by living organisms but excessive exposure to these trace elements may be toxic. Normal plant Mo content range from 0.8 to 5 mg kg⁻¹ but Mo levels of >10 mg kg⁻¹ and low feed Cu (< 4 mg kg⁻¹) can result in molybdenosis in cattle (Adriano, 1986; Gupta and Lipsett, 1981). Livestock need forage and feeds that contain > 0.1 mg Se kg⁻¹ but concentrations > 3 mg Se kg⁻¹ can be toxic. There are plants that are Se accumulators and contain 1000 to 10,000 mg Se kg⁻¹ (Adriano, 1986). Cereals usually contain < 0.5 mg As kg⁻¹ and rarely exceed 1 mg As kg⁻¹. Toxicity occurs in sensitive crops when tops contain 20 to 100 mg As kg⁻¹ (Adriano, 1986).

Land application has been an attractive alternative for disposal of municipal biosolids. The nutrient and organic matter additions are beneficial to soil fertility, yet biosolids contain pollutants used by society. Major pollutants in biosolids are Zn, Cu, Pb, Ni, Cr and Cd and minor pollutants include As, Mo, and Se. In a study conducted of 208 biosolids across the United States, the 50th and 98th percentile contents (in parenthesis in mg kg⁻¹) are As (10,48), Cd (7,31), Mo (9,43), Se (5,19), and Zn (1202,4310) (U.S. EPA, 1988). Because of their potential impacts on human and environmental health, there is much concern from the accumulation and uptake of heavy metals and trace elements associated with land application of biosolids. Contaminants that occur in large concentrations in biosolids, or are known to accumulate in crops (Cd, Cu, Cr, Ni,

Pb, and Zn), have been extensively studied (Chaney, 1994). However, limited studies have been conducted on minor contaminants including As, Mo, and Se. Significant increases of As did not occur in corn grain and stover, soybean grain, or Swiss chard from soils amended with As containing biosolids (Ritter and Eastburn, 1978; Chaney et al., 1978). However, fodder rape was shown to have greater than 50 percent increase in As content over the control (Andersson and Nilsson, 1972). Only one study where a Mo contaminated (1500 mg Mo kg⁻¹) sludge showed any significant increase in plant concentrations of Mo (Pierzynski and Jacobs, 1986b). Both Swiss chard and fodder rape showed insignificant uptake of Se from biosolids (Chaney et al., 1978; Andersson and Nilsson, 1972). Cadmium in grain is measured because Cd is known to accumulate in wheat and affect grain quality, while Zn is measured because risk to human health is based on Zn/Cd content of grain (Chaney, 1994).

Recently, a new rule promulgated by U.S. EPA limits land application of biosolids based on As, Mo, and Se (U.S. EPA, 1993). Biosolids that exceeds 100 mg Se kg⁻¹ or 75 mg Mo kg⁻¹, or 75 mg As kg⁻¹ cannot be land applied. Also, biosolids land application cannot exceed cumulative amounts of 41 kg As ha⁻¹, 420 kg Mo ha⁻¹, or 100 kg Se ha⁻¹. Although these guidelines were based on uptake of contaminants by crops and risk to human and animal health, only limited information from few studies that documented uptake of As, Mo, and Se were available. More information is needed to document uptake of these oxyanions by crops to evaluate their risk to human and animal health and strengthen federal guidelines.

The objectives of this study were to determine the uptake of oxyanions (As, Mo, Se) along with Cd and Zn in wheat on biosolid-amended soils and the effects of lime addition on uptake.

MATERIALS AND METHODS

Approach

The uptake of three oxyanions (arsenic, molybdenum, and selenium) by hard red winter wheat (*Triticum aestivum* L.), from biosolids amended soils was determined. Biosolids were applied at five rates to a winter wheat field experiment for two consecutive years. The accumulation of the oxyanions, Cd, and Zn in soil and wheat grain was determined each year. Statistical methods used were analysis of variance and contrasts (SAS, 1988).

Field Experiment

A winter wheat field experiment was established at the Efav Experiment Station (Oklahoma State University, Stillwater, OK) in the fall of 1993 and 1994. The site was grown in Bermudagrass without any tillage or fertilization for more than 10 years prior to beginning this experiment. Biosolids were applied at five rates to a winter wheat field experiment for two consecutive years. The experimental design was a randomized complete block with three replications. Biosolids, anaerobic-digested sewage sludge from Stillwater, OK, were added at 5.6, 11.2, 22.4, 33.6, and 67.2 MT ha⁻¹. Assuming 20% mineralization rate of N (U.S. EPA, 1993), these rates correspond to treatments of 0, 45, 90, 180, 270,

and 540 kg N ha⁻¹ yr⁻¹ of plant available N (Table 1). Three additional treatments included ammonium nitrate (AN) at 540 kg ha⁻¹ yr⁻¹, AN at 540 kg N ha⁻¹ yr⁻¹ with 4.48 Mg ha⁻¹ lime, and Biosolids at 540 kg N ha⁻¹ yr⁻¹ with 4.48 Mg ha⁻¹ lime (Table 1). Lime was only added in the first application year. The soil at this site is a Norge loam (fine, mixed, thermic Udertic Paleustoll). Baseline soil characteristics and biosolid analysis are reported in Table 2. Hard red winter wheat (*Triticum aestivum* L.) was used in this experiment. Wheat varieties and seeding rates, treatment application, soil sampling and harvest dates are reported in Table 3.

Soil and Grain Analysis

Surface soil samples (0-15 cm) were collected from all plots following harvest in 1994 and 1995. Soil samples (< 2mm) were analyzed for pH and wet digested in nitric-perchloric acid. These digests were analyzed for Cd, Mo, and Zn using direct nebulization Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The soil digests were also analyzed for As and Se using hydride generation ICP-AES. Biosolids from both years were wet digested and analyzed in the same manner as soil. Soil pH was determined in 1:2 soil:0.01M CaCl₂ using a combination glass electrode (McLean, 1982). Organic C and Total N were determined using dry combustion. Biosolids or soil wet digestion was performed by a modification of the method described by Amacher (1996). In this method, soil (10g) was placed into a 125 mL beaker. Then 20 mL of trace metal grade HNO₃ was added and heated at 150°C on a hot plate until

almost dry. Twenty milliliters of trace metal grade HClO_4 was then added and heated at $215\text{ }^\circ\text{C}$ until thick white fumes appeared and then refluxed until digest was no longer brown in color ($\sim 2\text{h}$). Digests were then removed from hot plate and allowed to cool. Finally, 10 mL of trace metal grade HCl was added and heated at 120°C for 30 minutes. This was allowed to cool and contents were quantitatively transferred into a vacuum filter with $0.45\text{ }\mu\text{m}$ Supor® membrane filters (Gelman Sciences, Ann Arbor, MI). Filtered digests were transferred into 50 mL volumetric flasks and diluted to volume with deionized-distilled water.

Wheat grain from each plot was harvested both years. The grain was wet digested using nitric acid and were analyzed for total Cd, Mo, and Zn by direct nebulization ICP-AES. Arsenic and Se in the digests were analyzed by hydride generation ICP-AES. Wet digestion of the wheat grain was performed as described by Zarcinas et al. (1987). Grain (2g) was placed into calibrated 50 mL digestion tubes and 15 mL of trace metal grade HNO_3 was added and set overnight in a fume hood. Tubes were then heated at $120\text{ }^\circ\text{C}$ for 2 hours and then at $140\text{ }^\circ\text{C}$ until there was approximately 1 mL of digest in tube. Tubes were removed from heat and allowed to cool. Then 6 mL of trace metal grade HCl was added and heated at $120\text{ }^\circ\text{C}$ for 30 minutes. Samples were allowed to cool and diluted with deionized-distilled water to the 25 mL mark on tube. Digest were then vacuum filtered using $0.45\mu\text{m}$ Supor® membrane filters.

ICP-AES Analysis

The type of elemental analysis by ICP-AES (Hydride Generation or Direct Nebulization) used depended on the element of interest. Hydride Generation was used for low level As and Se analysis ($< 1 \text{ mg L}^{-1}$ in solution). Digests were measured for Se without any modifications to the digest. For As analysis, 3 mL of a 10% (w/v) KI and 1% (w/v) ascorbic acid solution was added to 10 mL of digest to reduce any As(V) to As(III) for Hydride Generation. Arsenic and Se were then measured using a Hydride Generator connected to a Fision's, Maxim Inductively Coupled Plasma - Atomic Emission Spectrophotometer (ICP-AES). The conditions for the Hydride generator and the ICP-AES are shown in Table 4.

Direct Nebulization ICP-AES was used for Cd, Mo, and Zn. The ICP-AES conditions were as follows: Forward Power at 1100 W, Plasma flow at 1.05 L min^{-1} , Carrier flow at 0.5 L min^{-1} , Sample Pump speed at 2.2 mL min^{-1} , Cd wavelength 228.804 nm, Mo wavelength 202.031 nm, and Zn wavelength of 206.198 nm.

RESULTS AND DISCUSSION

The effects of biosolids on trace element content in soil samples in 1994 and 1995 are shown in Figure 1. Biosolids application did not increase As and Se content in soil (Fig. 1; Table 5). Biosolids increased Zn and Mo soil content for both years. There were small but significant increases in soil Cd from

biosolids application in 1994 but not in 1995. Increases in soil content was directly related to their biosolids content of Zn > Mo > As > Cd > Se (Table 2).

The effect of biosolids on trace element content in wheat grain is shown in Figure 2. The application of biosolids linearly increased Mo content in grain in 1995 from 0.4 to 0.8 mg kg⁻¹ but not in 1994 (Fig 2; Table 6). These increases are much less than 10 to 20 mg Mo kg⁻¹ feed associated with molybdenosis and should not increase risk to human or animal health. Barbarick et al. (1995) found that wheat grain Mo was < 1 mg kg⁻¹ and did not significantly change after eleven annual application of biosolids to dryland wheat. Pierzynski and Jacobs (1986b) found that Mo concentrations in corn grain increased with sludge application from 0.6 to 6.9 when 94 Mg ha⁻¹ of a molybdenum-contaminated (1500 mg kg⁻¹) sewage sludge was used. The content and phytoavailability of Mo in their contaminated sewage sludge likely caused the tenfold increase in grain Mo. This contaminated sewage sludge greatly exceeds the ceiling limit of 75 mg Mo kg⁻¹ and could not be land applied under current federal regulations (U.S. EPA, 1993).

There was no increase in the grain contents of other trace elements (As, Cd, Se, Zn) for either year. Ritter and Eastburn (1978) found no increase in corn grain or soybean grain concentrations of As or Cd with increased sludge application rate. Application of biosolids to agricultural land was shown not increase Se uptake by crops (Dowdy et al., 1984; Logan et al., 1987). Cadmium and Zn levels in wheat increased significantly with application of sewage sludges (Kirleis et al., 1984; Zwarich and Mills, 1979). Hooda and

Alloway (1994) found sewage sludge application resulted in higher concentrations of Cd and Zn in ryegrass.

Molybdenum availability and uptake by plants increases with soil pH (Barber, 1995). The Mo content of a crop grown on a pH 5.0 soil will, on average, double if the soil is limed to pH 6.0 (Barber, 1995). A one-time application of agricultural lime was added in 1993 to the 540 kg treatment rates to determine the effect of liming on trace element uptake from biosolids. In addition to the unlimed and limed biosolids treatments, unlimed and limed ammonium nitrate treatments were used as a control to determine if the trace elements were coming from the biosolids. There were no significant differences between treatments for As, Cd, Se, and Zn contents in grain (Table 6; Table 7). Liming increased mean grain Mo from biosolids treatments from 0.69 mg kg⁻¹ to 1.18 mg kg⁻¹ in 1994 and to a lesser extent in 1995 from 0.75 mg kg⁻¹ to 1.13 mg kg⁻¹ (Table 6; Table 7). Liming increased mean grain Mo in ammonium nitrate treatments slightly from 0.26 mg kg⁻¹ to 0.69 mg kg⁻¹ in 1995. The Mo content of grain from the ammonium nitrate treatments was lower than biosolids treatments in both years (Table 6; Table 7). This evidence points toward greater Mo uptake from biosolids and that adding lime increases the plant uptake of Mo. However, the increased levels of Mo in grain did not reach levels that would pose risk to human or animal health (> 10 mg Mo kg⁻¹). Studies have shown that increases in soil pH enhances uptake of Mo in biosolids amended soils (Pierzynski and Jacobs, 1986a and 1986b; Chaney and Ryan, 1993).

CONCLUSIONS

Biosolids application to winter wheat plots for 2 years increased soil content of Cd, Mo, and Zn but not As or Se. Two years of biosolids application did not increase uptake of As, Cd, Se, and Zn by winter wheat grain. However, uptake of Mo did increase during the second year of the experiment. The addition of lime, to soils receiving the high sludge rate, increased the uptake of Mo compared to the unlimed biosolids treatment. This is consistent with increased solubility and availability of Mo associated with increases in soil pH. No other element showed significant differences between limed and unlimed treatments. Grain Mo increases were small and should not pose any risk to human or animal health. The 540 kg N ha⁻¹ biosolids rate was approximately 7.5 times greater than the agronomic rate for 40 bu acre⁻¹ of dryland wheat in Oklahoma (Allen and Johnson, 1993). Assuming Mo phytoavailability does not change with time, the effect of two years of 540 kg N ha⁻¹ biosolids represents 15 years of biosolids application at agronomic rate for dryland wheat. In this case, 15 years of biosolids application, at agronomic rates, should have little or no effect on As, Mo, or Se uptake in grain and pose little risk to human or animal health.

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Table 1. Biosolid treatment rates and sources applied to plots at EFAW, Stillwater, OK.

Treatment	1	2	3	4	5	6	7	8	9
N rate†	0	45	90	180	270	540	540	540	540
Fert source‡	Bio	Bio	Bio	Bio	Bio	Bio	Bio	AN	AN
Lime§	N	N	N	N	N	N	Y	N	Y

† Nitrogen Rate $\text{kg N ha}^{-1} \text{ yr}^{-1}$

‡ Fertilizer source: Bio = Biosolids; AN = ammonium nitrate

§ Lime, Ag lime applied at 4.48 Mg ha^{-1}

Table 2. Chemical characteristics† of Norge loam prior to biosolids application and chemical analysis of biosolids.

<u>Soil (0-15 cm)</u>										
pH	Organic C	Total N	As	Cd	Mo	Pb	Se	Zn		
	-----g kg ⁻¹ -----		-----mg kg ⁻¹ -----							
6.4	11.9	1.1	5.23	0.179	0.406	12.24	0.274	29.46		
<u>Biosolids</u>										
Year	pH	Total N	As	Cd	Cu	Mo	Ni	Pb	Se	Zn
		g kg ⁻¹	-----mg kg ⁻¹ -----							
1993	6.4	22	13.32	5.46	976	44.5	30.2	916	0.461	1115
1994	6.9	23	9.83	5.49	752	34.2	25.6	807	0.752	928

↺

† pH, soil or biosolids:0.01M CaCl₂ 1:2; Organic C and total N, dry combustion; metals, wet digestion with HNO₃, HClO₄ by ICP-AES.

Table 3. Wheat varieties and seeding rates; treatment application, planting and harvest dates used in this study.

Wheat variety	Seeding Rate	Treatment application date	Planting date	Harvest date
Karl	67 kg ha ⁻¹	October 6, 1993	October 7, 1993	June 8, 1994
Tonkawa	84 kg ha ⁻¹	October 13, 1994	October 14, 1994	June 15, 1995

Table 4. ICP conditions for As and Se analysis by Hydride Generation.

Hydride Generation Conditions		ICP Conditions	
Reductant	1% NaBH ₄ in 0.1 M NaOH @ 3 ml min ⁻¹	Forward Power	1150 W
Blank Acid	3 M HCl @ 8 ml min ⁻¹	Plasma Flow	1.05 L min ⁻¹
Sample	make 3 M HCl @ 8 ml min ⁻¹	Carrier Flow	0.8 L min ⁻¹
KI (As only)	add 3 ml of 10%KI, 1% ascorbic acid solution per 10 ml sample	Wavelength	As193.761nm Se196.091nm

Table 5. F-values from statistical analysis of variance (ANOVA contrasts) for trace element contents of treated soils collected in 1994 and 1995.

Year	Contrasts	df	As	Cd	Mo	Se	Zn
1994							
	Treatment	6	0.75	3.00*	5.41**	1.25	5.66**
	N rate for Bio (linear)	1	0.44	10.4**	22.9***	3.14	25.2***
	N rate for Bio (quad)	1	2.74	6.79*	3.66	1.59	3.82
	Bio- Lime vs Unlimed	1	0.03	6.50*	2.26	0.03	3.76
	error	14					
1995							
	Treatment	6	0.71	1.76	4.71**		12.5***
	N rate for Bio (linear)	1	0.01	1.88	5.71*	nd	48.7***
	N rate for Bio (quad)	1	0.08	0.14	0.91	nd	5.97*
	Bio- Lime vs Unlimed	1	1.36	2.05	3.67	nd	4.27
	error	14					

Bio, Biosolids; AN, Ammonium Nitrate; nd, not determined.

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels respectively.

Table 6. F-values from statistical analysis of variance (ANOVA contrasts) for trace element contents in wheat grain collected in 1994 and 1995.

Year	Contrasts	df	As	Cd	Mo	Se	Zn
1994							
	Treatment	8	0.45	0.88	2.65*	0.37	0.13
	N rate for Bio (linear)	1	0.72	1.57	0.08	0.00	0.04
	N rate for Bio (quad)	1	0.08	0.24	1.85	2.02	0.01
	Bio Lime vs Unlimed	1	0.23	0.86	5.22*	1.14	0.23
	AN Lime vs Unlimed	1	0.48	0.17	2.00	0.04	0.01
	Unlimed Bio vs AN	1	0.02	0.98	1.39	0.62	0.00
	Limed Bio vs AN	1	0.00	0.40	4.20	0.00	0.33
	error df		14	17	18	17	17
1995							
	Treatment	8	0.35	1.33	3.68*	0.36	1.01
	N rate for Bio (linear)	1	0.00	0.31	5.60*	0.37	1.47
	N rate for Bio (quad)	1	0.40	1.46	0.17	1.54	0.06
	Bio Lime vs Unlimed	1	0.33	0.13	3.63	0.38	0.61
	AN Lime vs Unlimed	1	0.03	0.01	4.88*	0.07	1.70
	Unlimed- Bio vs AN	1	0.01	0.90	6.31*	0.09	1.00
	Limed- Bio vs AN	1	0.37	0.19	4.87*	0.00	1.23
	error df		14	16	18	18	17

Bio, Biosolids; AN, Ammonium Nitrate.

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels respectively.

Table 7. Mean trace element content in grain and soil pH from biosolids and ammonium nitrate treatments with and without lime at the 540 kg N ha⁻¹ rate.

Year	1994	Biosolids	Ammonium Nitrate	Biosolids + Lime	Ammonium Nitrate + Lime
		-----µg kg ⁻¹ -----			
As	mean	14.3	15.5	10.1	10.1
	sd	4.40	11.9	2.40	2.00
		-----mg kg ⁻¹ -----			
Cd	mean	0.011	0.031	0.027	0.039
	sd	0.015	0.016	0.013	0.011
Mo	mean	0.69	0.44	1.18	0.74
	sd	0.16	0.32	0.45	0.38
Se	mean	0.088	0.061	0.052	0.053
	sd	0.053	0.066	0.012	0.013
Zn	mean	27.8	29.5	27.8	27.5
	sd	1.80	10.8	1.05	1.90
Soil pH	mean	6.44	6.19	6.67	6.71
	sd	0.71	0.85	0.25	0.57
<hr/>					
Year	1995				
		-----µg kg ⁻¹ -----			
As	mean	14.1	15.4	7.20	13.9
	sd	6.00	16.6	2.50	11.4
		-----mg kg ⁻¹ -----			
Cd	mean	0.008	0.02	0.011	0.020
	sd	0.006	0.00	0.012	0.010
Mo	mean	0.75	0.26	1.13	0.69
	sd	0.45	0.23	0.12	0.07
Se	mean	0.107	0.087	0.065	0.069
	sd	0.110	0.080	0.003	0.042
Zn	mean	54.5	48.9	50.2	57.1
	sd	7.00	4.84	3.50	16.8
Soil pH	mean	6.51	6.22	6.93	6.84
	sd	0.81	0.99	0.31	0.56

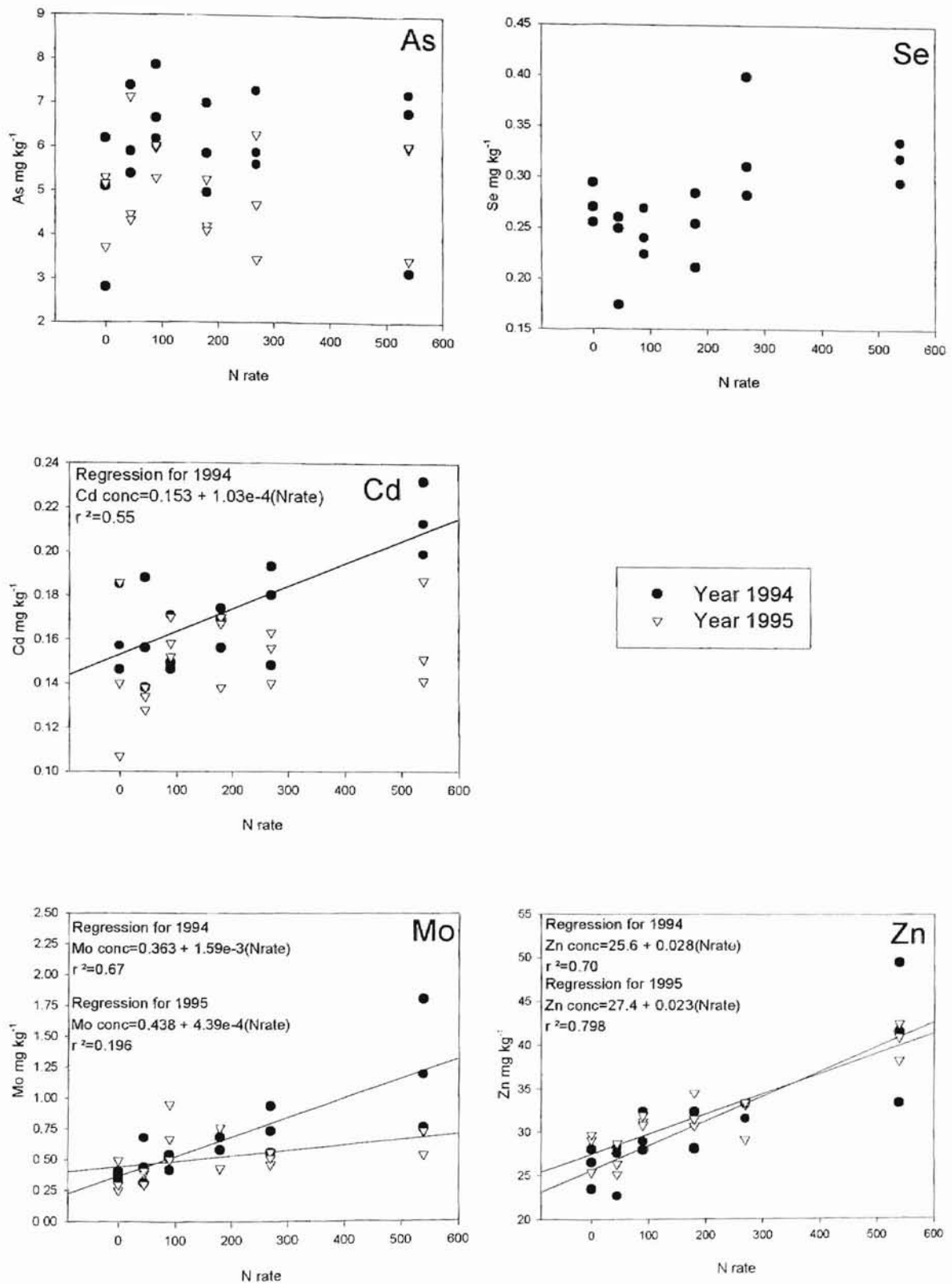


Figure 1. Soil trace element contents vs. N rate of biosolids years 1994 and 1995.

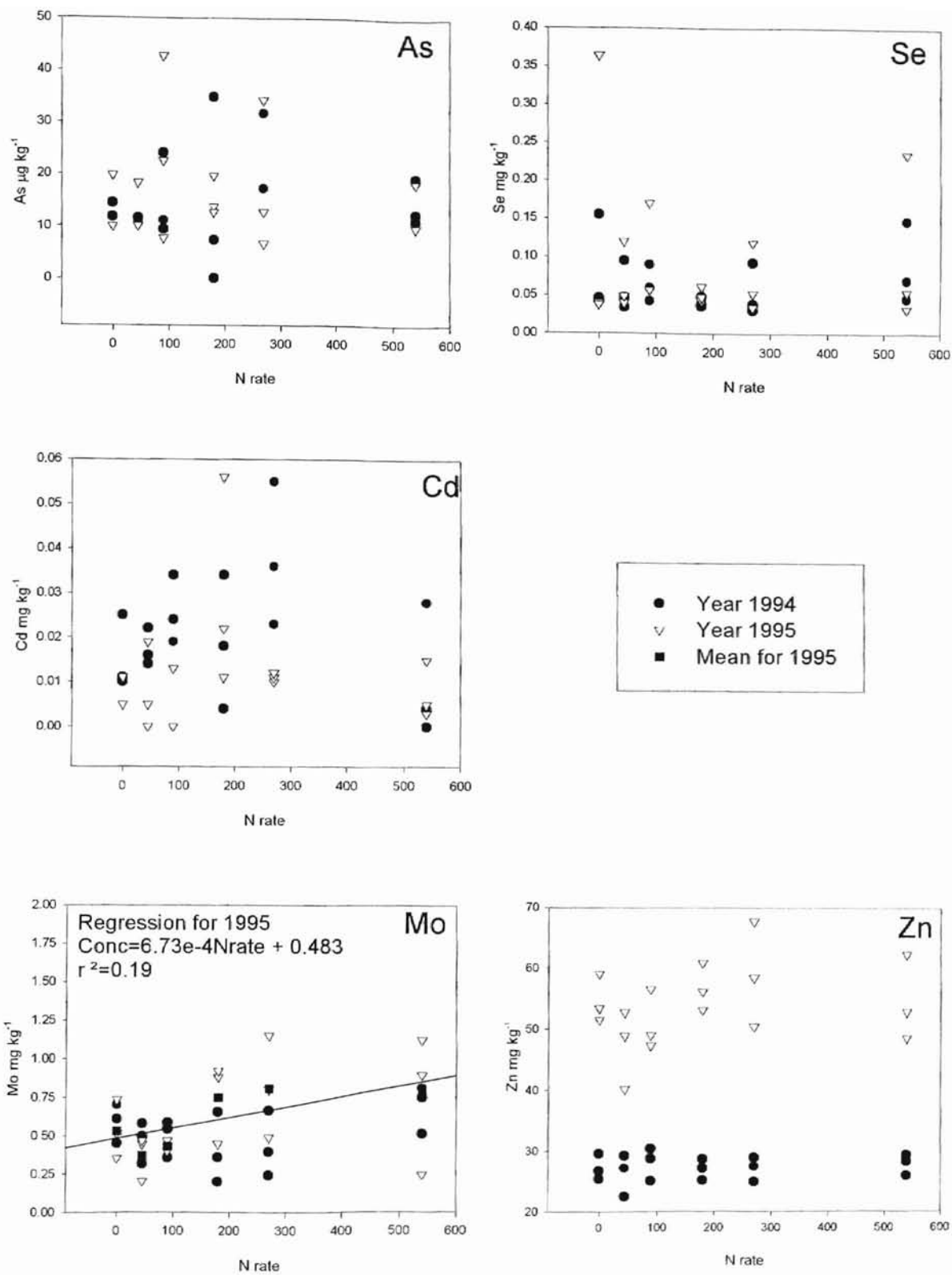


Figure 2. Grain trace element contents vs. N rate of biosolids for years 1994 and 1995.

APPENDIX A

Table A1. Soil pH and Soil EC data for treated soils.

Treatment	Rep	pH	EC ds m ⁻¹
Unlimed Control	1	3.60	2.40
Unlimed Control	2		2.50
Unlimed Control	3		2.50
Limed Control	1	7.30	2.20
Limed Control	2	7.50	2.25
Limed Control	3	7.30	2.25
Alum	1	7.20	2.20
Alum	2	7.60	2.20
Alum	3	7.40	2.20
CKD	1	7.10	2.30
CKD	2	7.60	2.30
CKD	3	7.70	2.35
Fe	1	7.60	2.20
Fe	2	7.60	2.20
Fe	3	7.70	2.30
Mn	1	6.50	2.95
Mn	2	7.00	2.95
Mn	3	7.00	3.00

Table A2. Arsenic solubility data of treated soils.

Treatment	Rep	NH ₄ Cl	Bray #1	PO ₄
		mg kg ⁻¹		
Unlimed Control	1	2.9	95.0	345
Unlimed Control	2	5.9	102.0	359
	mean	4.4	98.5	352
Limed Control	1	10.0	49.0	350
Limed Control	2	15.3	50.2	328
Limed Control	3	9.5	45.9	330
	mean	11.6	48.4	336
Alum	1	12.8	4.3	139
Alum	2	10.3	2.6	162
Alum	3	9.9	3.7	161
	mean	11.0	3.5	154
CKD	1	26.4	13.7	305
CKD	2	21.5	8.2	324
CKD	3	23.1	10.5	333
	mean	23.7	10.8	321
Fe	1	17.9	3.5	205
Fe	2	17.0	3.5	227
Fe	3	14.7	3.0	242
	mean	16.5	3.3	225
Mn	1	7.8	1.4	175
Mn	2	6.5	0.0	157
Mn	3	8.9	0.4	184
	mean	7.7	0.6	172

Table A3. Carrot weights and As concentration data.

Treatment	Rep	Weight		As Conc	
		Root	Shoot	Root	Shoot
		g		mg kg ⁻¹	
Unlimed Control	1	No Growth			
Limed Control	1	0.138	0.500	0.697	0.023
Limed Control	2	0.183	0.471	1.180	0.043
Limed Control	3	0.264	0.698	0.175	0.014
	mean	0.195	0.556	0.684	0.027
Alum	1	0.738	1.120	0.104	0.096
Alum	2	0.289	0.469	0.420	0.030
Alum	3	0.372	0.638	0.176	0.020
	mean	0.466	0.742	0.233	0.049
Fe	1	0.275	0.676	0.955	0.194
Fe	2	0.297	0.521	0.347	0.039
Fe	3	0.489	0.802	0.521	0.015
	mean	0.354	0.666	0.608	0.083
CKD	1,2,3	0.123	0.400	1.300	0.193
	mean	0.041	0.133		
Mn	1,2,3	0.080	0.019	0.822	0.086
	mean	0.027	0.006		

APPENDIX B

Table B1. Soil pH and soil trace element concentrations sampled 1994.

	Rep	0	45	90	180	270	540	540+Lime
Soil pH 94	1	6.02	6.3	6.41	6.21	5.98	6.6	6.5
	2	5.93	6.06	6.82	5.92	6.33	5.66	6.56
	3	6.98	6.39	6.68	6.67	6.9	7.06	6.96
	average	6.3	6.3	6.6	6.3	6.4	6.4	6.7
	Stdev	0.6	0.2	0.2	0.4	0.5	0.7	0.3
Soil As 94	1	5.1	5.9	7.1	5.8	6	7.2	7
	2	6.2	7.4	7.9	4.9	7.3	7.1	6.3
	3	3	5.4	6.2	7.2	5.9	3.1	5
	average	4.8	6.2	7.1	6.0	6.4	5.8	6.1
	Stdev	1.6	1.0	0.9	1.2	0.8	2.3	1.0
Soil Cd 94	1	0.16	0.14	0.17	0.16	0.18	0.21	0.21
	2	0.18	0.19	0.15	0.17	0.15	0.232	0.17
	3	0.15	0.16	0.15	0.17	0.19	0.2	0.16
	average	0.16	0.16	0.16	0.17	0.17	0.21	0.180
	Stdev	0.02	0.03	0.01	0.01	0.02	0.02	0.026
Soil Mo 94	1	0.34	0.43	0.41	0.68	0.56	1.19	1.11
	2	0.4	0.31	0.52	0.57	0.73	1.8	0.89
	3	0.37	0.68	0.54	0.68	0.93	0.75	0.88
	average	0.37	0.47	0.49	0.64	0.74	1.25	0.960
	Stdev	0.03	0.19	0.07	0.06	0.19	0.53	0.130
Soil Pb 94	1	12.32	16.22	20.42	21.29	20.28	34.94	33.85
	2	12.46	17.04	20.64	17.69	27.4	54.2	30.54
	3	9.85	14.41	16.8	19.71	25.45	24.39	28.12
	average	11.54	15.89	19.29	19.56	24.38	37.84	30.84
	Stdev	1.47	1.35	2.16	1.80	3.68	15.12	2.88
Soil Se 94	1	0.27	0.249	0.24	0.284	0.282	0.232	0.315
	2	0.255	0.26	0.224	0.254	0.399	0.335	0.241
	3	0.294	0.174	0.269	0.211	0.31	0.319	0.219
	average	0.273	0.228	0.244	0.250	0.330	0.295	0.258
	Stdev	0.020	0.047	0.023	0.037	0.061	0.055	0.050
Soil Zn 94	1	29.2	31.3	35.3	41	60.9	55.3	52
	2	31.5	33	36.1	33.7	40.7	55.1	42.7
	3	28.4	29	31.6	34.4	38.4	42	38.5
	average	29.70	31.10	34.33	36.37	46.67	50.80	44.4
	Stdev	1.61	2.01	2.40	4.03	12.38	7.62	6.9

Table B2. Soil pH and soil trace element concentrations sampled 1995.

	Rep	0	45	90	180	270	540	540+Lime
Soil pH 95	1	5.97	6.55	6.49	6.25	6.25	6.79	6.8
	2	5.74	5.99	7.12	5.62	6.55	5.59	6.71
	3	7.06	6.28	6.57	6.62	6.76	7.14	7.28
	average	6.3	6.3	6.7	6.2	6.5	6.5	6.9
	Stdev	0.7	0.3	0.3	0.5	0.3	0.8	0.3
Soil As 95	1	5.97	6.55	6.49	6.25	6.25	6.79	6.8
	2	5.74	5.99	7.12	5.62	6.55	5.59	6.71
	3	7.06	6.28	6.57	6.62	6.76	7.14	7.28
	average	6.26	6.27	6.73	6.16	6.52	6.51	6.93
	Stdev	0.71	0.28	0.34	0.51	0.26	0.81	0.31
Soil Cd 95	1	0.19	0.14	0.15	0.17	0.16	0.15	0.17
	2	0.14	0.13	0.17	0.17	0.16	0.19	0.19
	3	0.11	0.13	0.16	0.14	0.14	0.15	0.19
	average	0.15	0.13	0.16	0.16	0.15	0.16	0.183
	Stdev	0.04	0.01	0.01	0.02	0.01	0.02	0.012
Soil Mo 95	1	0.5	0.39	0.36	0.42	0.46	0.73	0.75
	2	0.25	0.3	0.95	0.76	0.56	0.73	1.09
	3	0.3	0.41	0.5	0.43	0.51	0.55	0.8
	average	0.35	0.37	0.60	0.54	0.51	0.67	0.88
	Stdev	0.13	0.06	0.31	0.19	0.05	0.10	0.18
Soil Pb 95	1	11.5	13.71	16.13	15.59	15.78	20.43	25.82
	2	11.81	15.02	16.82	24.02	21.95	31.36	24.7
	3	11.31	12.77	18.63	15.04	16.33	22.16	30.84
	average	11.54	13.83	17.19	18.22	18.02	24.65	27.12
	Stdev	0.25	1.13	1.29	5.03	3.41	5.88	3.3
Soil Zn 95	1	29.02	28.67	31.23	30.63	29.06	38.15	37.53
	2	25.37	26.28	31.86	34.43	33.08	40.82	40.05
	3	29.71	25.07	30.74	31.52	29.71	41.46	37.12
	average	28.03	26.67	31.28	32.19	30.62	40.14	38.23
	Stdev	2.33	1.83	0.56	1.99	2.16	1.76	1.59

Table B3. Wheat grain trace element content for 1994.

	Rep	0	45	90	180	270	540	540+lime	540 AN	540 AN+lime
Grain As 94	1	.	.	24	0	31.75	12.4	11.78	11.68	10.36
	2	11.75	11.56	11.1	34.9	17.25	19.25	h98.4	28.78	11.96
	3	14.375	11.34	9.4	7.3	h83.4	11.13	8.4	5.94	8.03
	average	13.1	11.5	14.8	14.1	24.5	14.3	10.09	15.47	10.12
	Stdev	1.9	0.2	8.0	18.4	10.3	4.4	2.4	11.88	1.98
Grain Cd 94	1	0.011	0.014	0.024	0.004	0.036	0	0.042	0.019	0.046
	2	0.025	0.016	0.034	0.034	0.055	0.028	0.021	0.042	0.044
	3	0.01	0.022	0.019	0.018	0.023	0.004	0.019	h0.54	0.026
	average	0.015	0.017	0.026	0.019	0.038	0.011	0.027	0.031	0.039
	Stdev	0.008	0.004	0.008	0.015	0.016	0.015	0.013	0.016	0.011
Grain Mo 94	1	0.606	0.315	0.355	0.197	0.665	0.748	0.797	0.07	0.39
	2	0.699	0.577	0.54	0.358	0.242	0.809	1.072	0.59	0.69
	3	0.448	0.493	0.583	0.655	0.394	0.512	1.667	0.65	1.15
	average	0.584	0.462	0.493	0.403	0.434	0.690	1.179	0.44	0.74
	Stdev	0.127	0.134	0.121	0.232	0.214	0.157	0.445	0.32	0.38
Grain Se 94	1	0.042	0.034	0.043	0.039	0.039	0.046	0.061	0.048	0.044
	2	0.045	0.095	0.09	0.036	0.031	0.07	0.056	0.133	0.063
	3	0.155	0.047	0.06	0.049	0.093	0.147	0.039	0.003	
	average	0.081	0.059	0.064	0.041	0.054	0.088	0.052	0.061	0.053
	Stdev	0.064	0.032	0.024	0.007	0.034	0.053	0.012	0.066	0.013
Grain Zn 94	1	29.6	27.2	30.4	28.6	24.9	29.3	24.2	28.51	26.64
	2	25.4	29.2	28.7	27.1	28.9	28.2	41.9	27.02	26.12
	3	26.8	22.5	25.0	25.1	27.4	25.9	22.3	h113.69	29.67
	average	27.2	26.3	28.0	26.9	27.1	27.8	29.5	27.77	27.48
	Stdev	2.1	3.5	2.7	1.8	2.0	1.8	10.8	1.05	1.92

Table B4. Wheat grain trace element content for 1995.

	Rep	0	45	90	180	270	540	540+lime	540 AN	540 AN+lime
Grain As 95	1	19.8	h96.6	22.6	19.6	12.8	18.3	5.5	7.625	7.075
	2	10.0	18.3	42.8	13.8	34.3	9.9	.	4.16	7.5125
	3	h73.5	10.1	7.7	12.7	6.7	h97.5	9.0	34.5	27.06
	average	14.9	14.2	24.4	15.4	17.9	14.1	7.2	15.43	13.88
	Stdev	6.9	5.8	17.6	3.7	14.5	6.0	2.5	16.61	11.41
Grain Cd 95	1	h0.336	0.019	0.000	0.056	0.010	0.003	0.010	0.01	0.01
	2	0.005	0.000	0.013	0.022	0.011	0.005	0.023	0.01	0.03
	3	0.011	0.005	0.000	0.011	0.012	0.015	0.000	0.02	h6.24
	average	0.008	0.008	0.004	0.030	0.011	0.008	0.011	0.02	0.02
	Stdev	0.004	0.010	0.008	0.023	0.001	0.006	0.012	0.00	0.01
Grain Mo 95	1	0.353	0.444	0.467	0.882	0.804	0.895	1.146	0.48	0.70
	2	0.516	0.465	0.429	0.447	0.490	0.245	1.239	0.01	0.76
	3	0.734	0.203	0.400	0.923	1.153	1.120	0.997	0.28	0.62
	average	0.534	0.371	0.432	0.751	0.816	0.753	1.127	0.26	0.69
	Stdev	0.191	0.146	0.034	0.264	0.332	0.454	0.122	0.23	0.07
Grain Se 95	1	0.041	0.040	0.057	0.062	0.035	0.055	0.067	0.038	0.054
	2	0.038	0.120	0.170	0.044	0.053	0.033	0.061	0.043	0.116
	3	0.364	0.049	0.057	0.048	0.119	0.234	0.067	0.179	0.036
	average	0.148	0.070	0.095	0.051	0.069	0.107	0.065	0.087	0.069
	Stdev	0.187	0.044	0.065	0.009	0.044	0.110	0.003	0.080	0.042
Grain Zn 95	1	53.4	48.9	47.3	56.1	58.4	62.3	48.8	53.68	68.93
	2	51.5	52.7	56.5	60.9	67.7	48.5	54.1	44.00	45.23
	3	59.0	40.2	49.0	53.1	50.4	52.8	47.6	49.17	h300.5
	average	54.6	47.2	50.9	56.7	58.8	54.5	50.2	48.95	57.08
	Stdev	3.9	6.4	4.9	3.9	8.7	7.0	3.5	4.84	16.76

VITA

Eric McMasters Hanke

Candidate for the Degree of

Master of Science

Thesis: REMEDIATION OF ARSENIC CONTAMINATED SOIL AND TRACE
ELEMENT AVAILABILITY TO WINTER WHEAT IN
BIOSOLIDS AMENDED SOILS

Major Field: Agronomy

Biographical:

Personal Data: Born in Oklahoma City, Oklahoma, On July 1, 1971, the son of Harold and Nancy Hanke.

Education: Graduated from John Marshall High School, Oklahoma City, Oklahoma in May 1989; received Bachelor of Science degree in Agronomy (Soil Science option) from Oklahoma State University, Stillwater, Oklahoma in December 1994. Completed the requirements for the Master of Science degree with a major in Agronomy at Oklahoma State University in May, 1997.

Experience: Graduate Research Assistant, Department of Agronomy, Oklahoma State University, January 1995 to present.
Undergraduate Research Assistant, Department of Agronomy, Oklahoma State University, August 1994 to December 1994.
Mechanics Apprentice, Mike's Garage Inc., Oklahoma City, Oklahoma during summer breaks from May 1989 to August 1994.

Professional Organizations: American Society of Agronomy, Soil Science Society of America.