

AVAILABILITY AND DISTRIBUTION OF HEAVY METALS
FROM SEWAGE SLUDGE IN THE PLANT-SOIL CONTINUUM

by

Bruce D. Rappaport

Committee Co-chairmen: David C. Martens

Raymond B. Reneau, Jr.

Agronomy

(ABSTRACT)

An investigation was conducted using in situ lysimeters (1.5 m x 2.3 m) to determine Cd, Cu, Ni, and Zn availabilities for barley (Hordeum vulgare L.) and corn (Zea mays L.) grown on four sludge-amended soils. These lysimeters were constructed in Acredale silt loam (Typic Ochraqualf), Bojac loamy sand (Typic Hapludult), Davidson clay loam (Rhodic Paleudult), and Groseclose silt loam (Typic Hapludult) soils. An aerobically digested sewage sludge from a sewage system with major industrial inputs was applied at rates of 0, 42, and 84 dry Mg ha⁻¹ to the lysimeters in the poorly-drained Acredale soil. Rates of 0, 42, 84, 126, 168, and 210 dry Mg ha⁻¹ were applied to the lysimeters in the well-drained Bojac, Davidson, and Groseclose soils.

Tissue metal concentrations were determined in 1984 and 1985 for a three crop rotation, which consisted of corn, barley, and corn on the Acredale soil. Increases in

sludge-borne Ni and Zn led to increases in Ni and Zn concentrations in corn earleaf, corn grain, and barley silage. Copper concentration was increased in barley silage but not in corn grain and stover. On this poorly-drained soil, metal movement did not occur below the Ap horizon even when Cu was applied in excess of USEPA guidelines. Although there were increases in metal levels, all four metals were within the range considered normal for corn and barley growth.

Soil, corn, and barley plants were sampled in 1984 and 1985 to determine Cd, Cr, Cu, Ni, and Zn availabilities for crops grown on the sludge-amended Bojac, Davidson, and Groseclose soils. Levels of DTPA-extractable Cd, Cu, Ni, and Zn in the Ap horizon of these soils increased linearly with sludge rate. Corn grain and stover yields were not decreased on the Bojac, Davidson, and Groseclose soils when 4.5, 5105, 760, 43.0, 135, and 620 kg ha⁻¹ of Cd, Cr, Cu, Ni, Pb, and Zn were added as a sludge-amendment. Copper and Zn applied in excess of 480 and 60 kg ha⁻¹ of USEPA guidelines, respectively on the Bojac, Davidson, and Groseclose soils were not phytotoxic to corn plants in 1984. Corn and barley tissue sampled for three consecutive seasons had Cr concentrations <2.8 mg kg⁻¹.

IN MEMORY OF
AND

If you lead a life of "have to"
nothing can be accomplished, but
if you "want to" all frontiers
can be conquered, because of
belief in one's self.

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Chapter I
INTRODUCTION

Land application of municipal and industrial sludge (solids) can provide an acceptable method of waste management. The nutrients in sludge, particularly N and P, can supplement soil nutrients and decrease fertilizer inputs for crop production. A major concern with regard to land application of sludge is that certain constituents in sludge may be either phytotoxic or harmful to animals and humans. Sludge amendments to agricultural land can result in an accumulation of potentially hazardous trace metals such as Cd, Cr, Cu, Ni, Pb, and Zn in the upper horizons of soil.

The phytotoxic effects of sludge-borne metals are dependent upon heavy metal contents in the sludge, chemical properties of the sludge, soil chemical reactions, and plant factors. This dissertation is the product of four research projects on trace metal extractions and movement in sewage sludge-amended soils. Each research project is presented as a self-contained chapter. The objectives of the research presented in each chapter are as follows:

- a. Chapter 2. To evaluate the efficiency of the DTPA and dilute HCl-H₂SO₄ procedures as extraction methods for prediction of Zn uptake by corn (Zea mays L.) plants grown on sludge-amended soils.

- b. Chapter 3. To determine if high chrome-sludge is an environmental hazard when used as a soil amendment.
- c. Chapter 4. To evaluate if Cd, Cu, Ni, and Zn are a rate limiting factor for plant growth on poorly-drained sludge-amended soils, and to evaluate the potential for groundwater contamination from leaching of heavy metals in these soils.
- d. Chapter 5. To determine the availability of elevated metal concentrations in sludge applied to agricultural land.

Chapter II

PREDICTION OF AVAILABLE ZINC IN SEWAGE SLUDGE-AMENDED SOILS

B. D. Rappaport, D. C. Martens, T. W. Simpson,
and R. B. Reneau, Jr.

2.1 ABSTRACT

A routine soil test would be helpful for management of agricultural soils amended with sewage sludge high in Zn. Fourteen field sites were selected in the Coastal Plain, Piedmont, and Ridge and Valley regions of Virginia to evaluate the suitability of the dilute HCl-H₂SO₄ and DTPA soil extractants for prediction of Zn uptake by corn (Zea mays L.). Soil and corn tissue samples were collected from these sites where sewage sludge had been applied previously. Multiple regression analysis was used to assess the forms of soil Zn extracted by dilute HCl-H₂SO₄ and DTPA. The exchangeable and specifically sorbed, organically bound and noncrystalline hydroxide and oxide bound Zn fractions were tested to develop prediction equations.

Dilute HCl-H₂SO₄ extracts were related to the three Zn fractions ($R^2 = 0.98^{**}$), whereas organically bound Zn was the only Zn fraction related to DTPA-extractable Zn ($r = 0.96^{**}$). Earleaf Zn concentration correlated more closely

with DTPA-extractable Zn ($r = 0.64^*$) than with dilute HCl-H₂SO₄ extractable-Zn ($r = 0.35$). The earleaf Zn concentration was studied as a function of either DTPA- or dilute HCl-H₂SO₄-extractable Zn, exchangeable and specifically sorbed Zn, organically bound Zn, and noncrystalline hydroxide and oxide bound Zn. Inclusion of the above fractions in a multiple regression analysis did not improve the relationship between earleaf Zn concentration and dilute HCl-H₂SO₄-extractable Zn. A coefficient of multiple determination ($R^2 = 0.77^{**}$) was obtained between earleaf Zn concentration and a two variable regression equation comprised of DTPA-extractable Zn and organically bound Zn. The negative regression coefficient for organically bound Zn indicated that a portion of this fraction, which was extracted by the DTPA, did not supply Zn to corn plants.

2.2 INTRODUCTION

Various soil extractants have been evaluated for estimation of plant available Zn from sewage sludge-amended and nonamended agricultural soils. These extractants include the dilute double acid procedure (0.05 M HCl + 0.0125 M H₂SO₄) developed by Nelson et al. (1953) and the DTPA (diethylenetriaminepentaacetic acid) method developed by Lindsay and Norvell (1969). Other Zn extractants, which have been

tested; are EDTA (ethylenediaminetetraacetic acid)- $(\text{NH}_4)_2\text{CO}_3$ (Trierweiler and Lindsay, 1969), NH_4OAc (Andersson, 1975) and ammonium oxalate (Macias, 1973). Of these soil extractants, DTPA has been the most widely used to estimate available Zn in soils (Haq et al., 1980; Lindsay and Norvell, 1978; Silveira and Sommers, 1977; Street et al., 1977).

In a greenhouse study, Haq and Miller (1972) used 85 Ontario soils with a wide range of chemical and physical properties to evaluate the reliability of the DTPA soil test to predict Zn concentration in corn tissue (Zea mays L.). They observed that DTPA-extractable Zn accounted for 36.4% of the variability in Zn concentration in corn plants. The suitability of DTPA to predict Zn concentration in swiss chard (Beta vulgaris L. 'Fordhook Giant') was tested by Haq et al. (1980). The swiss chard was grown on 46 Ontario soils with varying degrees of metal contamination. They reported a r value of 0.81** between DTPA-extractable Zn and Zn concentration in swiss chard. Singh and Narwal (1984) indicated that DTPA might be an effective extractant for prediction of Zn availability to fodder rape (Brassica napus L. 'Kenton'). In a field study by Latterell et al. (1978), a linear relationship occurred between DTPA-extractable Zn and Zn concentration in edible snapbean (Phaseolus vulgaris L. 'Tendergreen') tissue ($r = 0.90^{**}$) and in leaf tissue (r

= 0.97**). This research was conducted on a sludge-amended Hubbard coarse sand (Udorthentic Haploboroll).

Korcak and Fanning (1978) investigated the effect of $ZnSO_4$ application on Zn concentration by corn grown in the greenhouse on Collington sandy loam (Typic Hapludult), Manor sandy loam (Typic Dystrochrept) and Downer loamy sand (Typic Hapludult). They obtained r values from 0.78** to 0.95** between DTPA-extractable Zn and concentrations of this micronutrient in corn plants when the soils were limed to pH 6.5. Where the pH levels of the three soils ranged from 5.0 to 5.6, r values between the variables ranged from 0.84** to 0.97**.

Multiple regression equations which consisted of either soil pH or soil pH + (soil pH)² and DTPA-extractable Zn were used by Haq and Miller (1972) to estimate Zn concentration of corn plants from soils. Inclusions of these variables in the regression equation increased the R² from 0.36** to 0.70** and 0.76**, respectively. Haq et al. (1980) included an interaction variable, DTPA-extractable Zn x pH, with DTPA extractable Zn in their equation for prediction of Zn plant uptake by swiss chard and noted that the R² increased from 0.65** to 0.80**. Lindsay and Norvell (1978) suggested that soils with pH values which are <7.0 should have a pH factor with DTPA extractable Zn in the regression equation.

Most investigations which relate DTPA extractable Zn to plant uptake of Zn have been conducted under greenhouse rather than field conditions. Sommers (1980) indicated that lower concentrations of metals in plant tissue often occur from field experiments than from greenhouse pot trials due possibly to differences in soil pH. Logan and Chaney (1983) have further noted some dissimilarities in toxic element uptake by plants grown in the greenhouse versus the field. They suggested that higher levels of uptake occur under greenhouse conditions due to: 1) use of $\text{NH}_4\text{-N}$ fertilizers which result in a lower pH in pots than in the field, 2) higher soluble salt levels due to a smaller soil volume, 3) plant root confinement, and 4) abnormal watering patterns and relative humidity conditions in the greenhouse.

The purpose of this research was to evaluate the efficiency of the DTPA and dilute $\text{HCl-H}_2\text{SO}_4$ extractants as methods for prediction of Zn uptake by corn plants grown in the field on sludge-amended soils. The dilute $\text{HCl-H}_2\text{SO}_4$ extractant was chosen for study because it is the most widely used soil extractant in southeastern United States (Donohue and Issac, 1983). Selection of the DTPA extractant was based on its prevalent usage in various regions of the United States.

2.3 MATERIALS AND METHODS

Fourteen field sites (Table 1) planted to seven corn varieties were selected in the Coastal Plain, Piedmont, and Ridge and Valley regions of Virginia for this study. These sites were on soils which had received one or more applications of sewage sludge.

2.3.1 A. Field Experimentation

An experimental plot 6.1-m in length by four rows of corn wide was established on each soil in July 1983. The soil was classified and soil samples were collected from the Ap horizon (0- to 15-cm depth) when corn plants were in the early silk growth stage. Soil samples consisted of a composite of 10 soil cores taken with a stainless steel probe 1.9-cm in diameter. Soil samples were obtained by the same procedure from nearby non-sludge amended corn fields of the same soil series as the 14 sludge-amended soils to determine native soil Zn concentrations.

Corn silage was harvested from 6.1-m sections of two center rows in each plot and adjusted to 650 g H₂O kg⁻¹. Corn silage yields on the 14 soils ranged from 15,090 to 47,310 kg ha⁻¹. Relatively high average silage yields, 44,810 kg ha⁻¹, were obtained on irrigated soils; whereas, droughty conditions contributed to an average of 22,200 kg

Table 1 - Classification and chemical and physical properties of the 14 soils under study.

Soil No.	Soil Classification		pH	Organic Matter g kg ⁻¹	Non-crystalline			Particle size distribution			
	Soil series	Taxonomic class			Al	Fe	Mn	Sand	Silt	Clay	Texture
					----- mg kg ⁻¹ -----			----- % -----			
1	Acredale	Typic Ochraqualf; fine-silty, mixed, thermic	5.9	27	779	1340	7	32.3	62.3	5.4	silt loam
2	Caroline	Typic Paleudult; clayey, mixed, thermic	6.0	23	860	712	52	60.0	36.5	3.5	sandy loam
3	Goldsboro	Aquic Paleudult; fine-loamy, siliceous, thermic	5.9	23	924	1740	171	63.3	24.8	11.9	sandy loam
4	Kempsville	Typic Hapludult; fine-loamy, siliceous, thermic	6.2	21	688	1170	49	67.5	23.2	9.3	sandy loam
5	Suffolk	Typic Hapludult; fine-loamy, siliceous, thermic	5.8	23	773	1280	104	68.5	19.2	12.3	sandy loam
6	Molena	Psammentic Hapludult; sandy, mixed, thermic	6.2	26	3010	3060	239	81.2	11.5	7.3	loamy sand
7	Pamunkey	Ultic Hapludalf; fine-loamy, mixed, thermic	6.3	25	1070	3600	723	78.0	9.3	12.7	sandy loam
8	Braddock	Typic Hapludult; clayey, mixed, thermic	5.0	25	974	1710	171	50.1	31.4	18.5	loam
9	Cullen	Typic Hapludult; clayey, mixed, thermic	5.0	34	2190	2370	61	42.1	35.8	22.1	loam
10	Jackland	Typic Hapludalf; fine, montmorillonitic, mesic	5.9	32	1310	9650	1620	24.5	51.1	24.4	silt loam
11	Frederick	Typic Paleudult; clayey, mixed, mesic	5.9	26	766	1260	692	27.8	53.1	19.1	silt loam
12	Timberville	Fluventic Dystrochrept; fine-loamy, mixed, mesic	5.5	50	1720	3040	1700	34.2	51.1	14.7	silt loam
13	Endcav	Typic Hapludalf; very fine, mixed, mesic	6.4	22	824	1820	481	24.5	60.1	15.4	silt loam
14	Edom	Typic Hapludalf; fine, illitic, mesic	5.5	22	1040	1830	346	10.4	64.3	25.3	silt loam

ha⁻¹ on nonirrigated soils. The wide range in soil moisture provided a severe test for the relationship between Zn tissue concentration and extractable Zn.

2.3.2 B. Soil Analyses

Soil samples were air-dried and ground to pass a 10-mesh (2-mm) stainless steel sieve. Soil pH was determined in a 1:1 soil-to-water suspension after equilibration for 1-h (McLean, 1982). Organic matter was determined colorimetrically after wet oxidation with Na₂Cr₂O₇ (Peech et al., 1947). Particle size distribution was determined by the pipet method (Day, 1965). Total Zn was analyzed by atomic absorption spectrophotometry (AAS) after digesting samples in an aqua regia-HF mixture (Bernas, 1968). The procedures reported by Baker and Amacher (1982) were followed for determination of dilute HCl-H₂SO₄- and DTPA-extractable Zn. All soil analyses were completed in duplicate.

2.3.3 C. Soil Fractionation Procedures

Soil samples were fractionated to determine exchangeable and specifically sorbed, organically bound, and non-crystalline hydroxide and oxide bound Zn. Concentrations of Zn in solution for the various extracts were determined by

AAS. Methods followed for the fractionation procedure are outlined below.

1. Exchangeable and Specifically Adsorbed Zn (AA-Zn) - Five g of soil and 50 mL of 2.5% HOAc were shaken in 100 mL polypropylene centrifuge tubes for 24 h at 30°C. The shaking was completed at 180 cycles/min in a combination-reciprocating water bath shaker (Iyengar et al., 1981).

2. Organically bound Zn (Pyro-Zn) - This fraction was determined on a second subsample of soil using the procedure described by Bascomb (1968). One-half g of soil was shaken, as above, with 50 mL of 0.1 M $K_4P_2O_7$ for 16 h at 30°C in a 100 mL polypropylene centrifuge tube. The Pyro-Zn was computed by subtraction of AA-Zn from the amount extracted with 0.1 M $K_4P_2O_7$.

3. Noncrystalline oxide and hydroxide bound Zn (Ox-Zn) - Noncrystalline oxides of Al, Fe and Mn were solubilized by the method developed by McKeague and Day (1966) as modified by Miller (1981). Twenty-five mL of 0.1 M oxalic acid and 0.175 M ammonium oxalate, pH 3.25, were utilized in a 4 h dark extraction to obtain the noncrystalline oxide and hydroxide bound Zn. The Ox-Zn was computed by subtraction of 0.1 M $K_4P_2O_7$ -extractable Zn from the oxalate-extractable Zn.

2.3.4 D. Corn Tissue Analyses

Twelve corn earleaves were sampled at the early silk growth stage from the outside two rows of each plot. The corn earleaf samples were dried at 70°C for 72 h and ground to pass a 20-mesh (0.833-mm) sieve in preparation for Zn analysis. Duplicate 0.5-g subsamples of the ground tissue were digested in a HNO₃-HClO₄ acid mixture prior to the Zn determination by AAS.

2.3.5 E. Statistical Analyses

Relationships among earleaf Zn concentration, soil properties, Zn fractions, and DTPA- and dilute-HCl-H₂SO₄ extractable Zn were determined by Pearson correlation coefficients. Stepwise multiple regression analysis was used to assess the forms of soil Zn extracted by dilute HCl-H₂SO₄ and DTPA as a function of AA-Zn, Pyro-Zn, and Ox-Zn. Stepwise multiple regression and Maximum R² improvement techniques (Draper and Smith, 1981) were used to evaluate earleaf Zn concentration as a function of: 1) dilute HCl-H₂SO₄- or DTPA-extractable soil Zn, soil pH, (soil pH)² and the interaction term, extractable Zn x soil pH, and 2) dilute HCl-H₂SO₄- or DTPA-extractable soil Zn, AA-Zn, Pyro-Zn, and Ox-Zn. The best equation for prediction of earleaf Zn concentration was chosen on the basis of the closest Mallows

C(P) value to β and the lowest PRESS Statistic (Predicted Sum of Squares); where β is the number of coefficients in the regression equation and the PRESS Statistic is the lowest value as determined from a General Linear Model Procedure (Montgomery and Peck, 1982).

2.4 RESULTS AND DISCUSSION

Taxonomic classification indicated that the soils studied were representative of large agricultural areas in the Coastal Plain, Piedmont, and Ridge and Valley regions of the eastern United States. The amounts of Al, Fe, and Mn in noncrystalline hydroxide and oxide forms varied considerably in the 14 soils (Table 1). These soils ranged in pH from 5.0 to 6.4. Chaney (1982) recommended an initial soil pH of 6.5 when sludge is applied and a pH of 6.2 thereafter to decrease metal availability from sewage sludge application. Only 4 of the 14 soils studied had a pH \geq 6.2. Organic matter contents in the soils varied from 21 to 50 g kg⁻¹ with a mean of 27 g kg⁻¹.

Total Zn contents ranged from 30 to 181 mg kg⁻¹ in the 14 sludge-amended soils (Table 2). Native Zn concentrations in the 14 soil series ranged from 25 to 165 mg kg⁻¹. The mean Zn concentration in the non-sludge amended soils was 58 mg kg⁻¹, whereas, the mean concentration of Zn in the

Table 2 - Corn earleaf Zn, total Zn, DTPA- and dilute acid-extractable Zn and Zn fractions in the 14 soils under study.

Soil No.	Earleaf Zn	Total Zn	DTPA-ext. Zn	DA-ext. Zn	Zn fractions		
					AA-Zn	Pyro-Zn	Ox-Zn
----- mg kg ⁻¹ -----							
1	16.7	36	3.2	8.8	2.6	11.6	6.1
2	26.5	30	1.5	4.5	1.0	7.7	6.5
3	47.6	67	6.3	13.8	4.1	13.9	25.4
4	43.9	47	1.8	5.7	1.5	3.8	10.8
5	44.4	61	4.0	8.7	2.8	8.5	11.2
6	37.5	181	5.1	15.2	5.2	16.1	17.5
7	31.1	138	8.4	29.6	7.2	20.4	56.2
8	24.4	136	0.6	1.0	0.2	3.0	3.3
9	18.7	151	0.5	1.2	0.2	6.9	1.0
10	33.9	69	2.6	4.9	1.0	6.0	16.9
11	20.2	39	4.6	11.2	4.5	9.6	10.9
12	94.0	96	21.1	26.7	5.1	42.8	48.2
13	35.6	48	2.1	4.7	1.4	4.9	8.2
14	138.0	76	8.7	11.5	2.9	11.3	16.5

sludge-amended soils was 84 mg kg^{-1} . Zinc concentrations in the earleaves from the sludge-amended soils were within normal levels, except from soils 12 and 14 (Jones and Eck, 1973).

2.4.1 A. Relationships between Extractable Zinc and Soil Fractions

Multiple regression analyses were completed to assess the forms of soil Zn extracted by DTPA and dilute $\text{HCl-H}_2\text{SO}_4$. The AA-Zn, Pyro-Zn, and Ox-Zn fractions were tested to develop regression equations. Of these three Zn fractions, only Pyro-Zn was related to DTPA-extractable Zn ($r = 0.96^{**}$). The regression equation for the relationship is as follows:

$$\begin{aligned} \text{DTPA-ext. Zn (mg kg}^{-1}\text{)} &= & [1] \\ &-0.91 + 0.50[\text{Pyro-Zn (mg kg}^{-1}\text{)}]. \end{aligned}$$

The Pyro-Zn may not be limited, however, to only organically bound Zn. Potassium pyrophosphate probably extracted portions of noncrystalline Al, Fe, and Mn hydroxide and oxide bound Zn. This is indicated by the simple correlation coefficients between the total amount of Zn extracted by the $\text{K}_4\text{P}_2\text{O}_7$ and oxalate solutions ($r = 0.94^{**}$) and between Pyro-Zn and both organic matter ($r = 0.75^{**}$) and Mn in noncrys-

talline hydroxide and oxide forms ($r = 0.58^*$). Shuman (1983) indicated that $\text{Na}_4\text{P}_2\text{O}_7$ extracts larger quantities of soil metals than those present in the organic fraction. Pyrophosphate dissolves a portion of the Fe oxide and hydroxide fraction which results in an overestimation of the organic fraction (Shuman, 1982).

Dilute $\text{HCl-H}_2\text{SO}_4$ -extractable Zn was related to AA-Zn, Pyro-Zn, and Ox-Zn ($R^2 = 0.98^{**}$) by the following regression equation:

$$\begin{aligned} \text{Dilute HCl-H}_2\text{SO}_4\text{-ext. Zn (mg kg}^{-1}\text{)} &= [2] \\ &-0.53 + 1.84[\text{AA-Zn (mg kg}^{-1}\text{)}] \\ &+ 0.17[\text{Pyro-Zn (mg kg}^{-1}\text{)}] + 0.22[\text{Ox-Zn (mg kg}^{-1}\text{)}]. \end{aligned}$$

The relationship indicates that the dilute $\text{HCl-H}_2\text{SO}_4$ procedure extracts portions of Zn from each of the three fractions. The extraction mechanisms include; 1) solubilization of occluded Zn^{++} during dissolution of Al, Fe, and Mn hydroxides and oxides, and 2) displacement of Zn^{++} by H_3O^+ from negatively charged organic and inorganic soil components. The dilute $\text{HCl-H}_2\text{SO}_4$ procedure extracted more Zn from each of the 14 soils than the DTPA method (Table 2). The mean amount of dilute $\text{HCl-H}_2\text{SO}_4$ -extractable Zn was 10.5 mg kg^{-1} whereas the mean amount of DTPA-extractable Zn was 5.0 mg kg^{-1} . The difference in mean Zn concentrations bet-

ween dilute HCl-H₂SO₄- and DTPA-extractable Zn reflects dissolution and dissociation by the former procedure and chelation at a buffered pH of 7.3 by the latter. There was, however, a significant correlation ($r = 0.82^{**}$) between dilute HCl-H₂SO₄- and DTPA-extractable Zn for the 14 Virginia soils studied.

2.4.2 B. Soil Test Zinc

The independent variables, dilute HCl-H₂SO₄-extractable Zn, soil pH, (soil pH)², and the interaction term dilute HCl-H₂SO₄-extractable Zn x soil pH were tested to develop a prediction equation for earleaf Zn. A second model, dilute HCl-H₂SO₄-extractable Zn, AA-Zn, Pyro-Zn and Ox-Zn also was tested. In a stepwise regression procedure, the dilute HCl-H₂SO₄ extractable Zn did not meet the 0.15 level of significance for entry into either model one or two. However, when a Maximum R² Regression Improvement Procedure was utilized to predict earleaf Zn concentration as a function of model one, Zn in the earleaf was predicted by the following equation ($R^2 = 0.46^*$):

$$\begin{aligned} \text{Earleaf Zn (mg kg}^{-1}\text{)} &= 27.58 + 25.37[\text{DA (mg kg}^{-1}\text{)}] \quad [3] \\ &- 4.03[\text{DA (mg kg}^{-1}\text{)} \times \text{soil pH}], \end{aligned}$$

where DA is dilute HCl-H₂SO₄-extractable Zn.

Earleaf Zn concentration was studied as a function of DTPA-extractable Zn, soil pH, (soil pH)², and the interaction term DTPA-extractable Zn x soil pH. Inclusion of the pH variables, however, did not enter into the regression equation at the 0.15 probability level. Alternatively, earleaf Zn concentration was studied as a function of DTPA-extractable Zn, AA-Zn, Pyro-Zn, and Ox-Zn. Only DTPA-extractable Zn and Pyro-Zn entered into the model at the 0.15 probability level. The DTPA-extractable Zn, which accounted for 41% of the variation in earleaf Zn, was the first variable entered into the model. The second variable entered in the stepwise regression procedure, Pyro-Zn, improved the relationship from $r = 0.64^*$ to $R^2 = 0.77^{**}$ (Table 3).

The negative coefficient for Pyro-Zn in the equation (Table 3) suggests that DTPA extracted portions of organically bound and occluded Zn in noncrystalline hydroxides and oxides which were unavailable to the corn plants. Subtraction of Pyro-Zn from DTPA-extractable Zn in the regression equation provided a better estimate than other models for the available portion of Zn from the 14 sewage sludge-amended soils.

Table 3 - Stepwise multiple regression equations for prediction of corn earleaf Zn concentration by DTPA-extractable Zn.

Regression step	Regression equation	r	R ²	P>F
1	Zn in earleaf (mg kg ⁻¹) = 23.5 + 4.0 [DTPA-Zn (mg kg ⁻¹)]	0.64	----	0.013
2	Zn in earleaf (mg kg ⁻¹) = 41.7 + 16.4 [DTPA-Zn (mg kg ⁻¹) - 6.8 [Pyro-Zn (mg kg ⁻¹)]	---	0.77	0.001

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Chapter III

CHROMIUM CONCENTRATIONS IN CORN AND BARLEY GROWN ON SEWAGE SLUDGE-AMENDED SOILS

B. D. Rappaport, D. C. Martens, R. B. Reneau, Jr.,
and T. W. Simpson

3.1 ABSTRACT

The effect of Cr on plant growth from sludge application to agricultural soils is at present speculative. Field investigations were conducted in 1984 and 1985 in the Coastal Plain, Piedmont, and Ridge and Valley regions of Virginia to evaluate Cr uptake by corn (Zea mays L.) and barley (Hordeum vulgare L.) plants grown in sludge-amended soil. The sludge used was aerobically digested from a wastewater treatment plant with major industrial inputs. Rates of sludge application were 0, 42, 84, 126, 168, and 210 dry Mg ha⁻¹. These sludge rates correspond to chromium applications of 0, 1021, 2042, 3063, 4084, and 5105 kg ha⁻¹. The Cr concentrations in corn and barley tissue were low (<2.8 mg kg⁻¹) at all rates of Cr application on the soils under study.

When excessive levels of Cr are applied as sewage sludge and incorporated into agricultural soils at pH levels in the range of 5.5 to 7.0, Cr forms insoluble Cr hydroxide

which is non-mobile in soil. At soil pH levels >7.0 , however, trivalent Cr can be oxidized to hexavalent Cr, which exists in soil as the chromate or dichromate anion. Hexavalent Cr anions are mobile in soils, and therefore, are potential groundwater pollutants. To prevent plant uptake and leaching of hexavalent Cr, guidelines for land disposal of high Cr-sludges should account for the extremely low solubility of Cr hydroxide at pH levels in the range 5.5 to 7.0. Formation of insoluble Cr compounds in the pH range of 5.5 to 7.0 accounts for the low uptake of applied Cr by corn and barley in this investigation. It is necessary to adjust soil pH from 5.5 to 7.0 to ensure formation of insoluble Cr compounds and, thereby, to prevent movement of Cr into groundwater which may result in subsequent pollution of the Chesapeake Bay.

3.2 INTRODUCTION

An increase in land application of wastewater sludges has stimulated interest in the potential environmental pollution hazard of Cr-bearing sludges. Federal regulations have established that total Cr may not exceed $1 \mu\text{mole L}^{-1}$ in public water supplies (EPA, 1976, 1980). The World Health Organization (1973) estimated that intake of Cr by Americans varied from 5 to $100 \mu\text{g day}^{-1}$ and that assimila-

tion of Cr(III) ingested by drinking public water is unlikely. Adult urinary loss of Cr is 5 to 10 $\mu\text{g day}^{-1}$ and at least this much must be replaced to maintain balance. Scott (1972) concluded that Cr is important for glucose metabolism in animals and its activity is related to that of insulin. The hexavalent form of Cr [Cr(VI)], however, is an irritant and is corrosive to mucous membranes (National Academy Sciences, 1974).

Chromium ranges from trace concentrations to 250 $\mu\text{g g}^{-1}$ as chromic oxide in soil. Concentrations of Cr are usually higher in soils derived from basalt or serpentine. High Cr levels exist in ultramafic igneous rocks, shales and clays, and in phosphorites. Chromium concentrations in phosphorites range from 30 to 3000 $\mu\text{g g}^{-1}$. Phosphorites are used as fertilizers and are a source of soil Cr contamination as are limestones (National Academy Sciences, 1974).

Chromium is present in soil in either the trivalent [Cr(III)] or hexavalent [Cr(VI)] oxidation state. Two forms of Cr(III) may exist in soil, these include the trivalent Cr cation (Cr^{+3}) and the chromium oxide anion (CrO_2^-). Two forms of Cr(VI) that may exist in soils include the chromate and dichromate anions, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, respectively (Reisenauer, 1982). Hexavalent Cr is toxic to plants, mobile in soils, and exists as a potential ground water pollutant

(Bartlett and Kimble, 1976a; Bartlett and James, 1979; Shivas, 1980). It is important to consider the valence state in regard to the environmental implications of Cr-sludge application to soil. Since Cr(VI) is more toxic and mobile in soils than Cr(III), we must consider the possibility that Cr(III) might convert to Cr(VI) and vice versa. In the development of guidelines for the land disposal of high Cr wastes, it was assumed that the extremely low solubility of $\text{Cr}(\text{OH})_3$ at pH levels >5.5 would prevent both plant uptake of Cr and downward movement of Cr into ground water (USEPA, 1977).

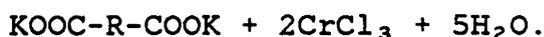
Until 1976, chemical reactions of Cr in soils were largely speculative. Bartlett and Kimble (1976a) showed that, as solution pH was raised above 4, solubility of Cr(III) decreased. Mertz (1969) as cited by Bartlett and Kimble (1976a) assumed that the Cr precipitate consisted of macromolecules with Cr ions in six coordination complexes with water and hydroxyl groups. Trivalent Cr and Al chemistry are similar in soils. Both cations tend to be octahedrally coordinated. In addition, both Cr(III) and Al become anions in soil when the pH is greater than neutral. Research by Bartlett and Kimble (1976b) has shown that the pH-solubility curve of Cr(VI) in the presence of excess Al is quite similar in shape to that of phosphate with excess Al. Hexa-

valent Cr has been shown to become completely insoluble near pH 6 and to become soluble again above pH 8. It is probable that portions of Cr(VI) coprecipitate with Al in soils. All of the soils studied adsorbed Cr(VI) except one with a CaCO₃ horizon. The orthophosphate present in the soils competed for adsorption sites and prevented Cr(VI) adsorption.

Chromium studies in soils show that the presence of organic matter brings about spontaneous reduction of some Cr(VI) to Cr(III) even at pH levels above neutrality. Hexavalent Cr reduction does not occur in soils low in organic matter unless an energy source is provided (Bartlett and Kimble, 1976b). They developed the following equation to explain the reduction of Cr(VI) along with the oxidation of a hypothetical compound:

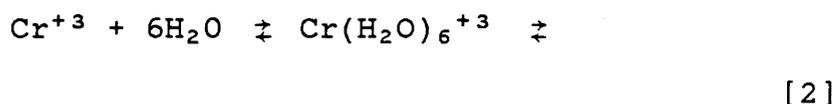


[1]

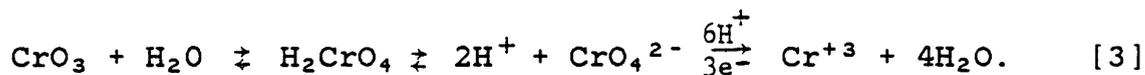


This equation was developed with the understanding that 3 meq of HCl were required to prevent a pH rise during the reduction of 1 mmole of Cr(VI). Bartlett and Kimble (1976b) showed that, with the addition of HCl three times the molar quantity of Cr(VI), the pH after reduction exactly equaled the pH of the system which received Cr(III) directly.

Additions of Cr(III) to soil has resulted in pH decreases. Soil pH decreased from 4.5 to 3.9 where Bartlett and Kimble (1976b) applied 10 μ mole of $\text{CrCl}_3 \text{ g}^{-1}$. Grove and Ellis (1980a) proposed that water-soluble Cr(III) compounds added to soils account for pH decreases and for reversion of resulting Cr compounds to the less soluble Cr_2O_3 :



The CrO_3 [Cr(VI)] incorporated into soil hydrolyzes rapidly to H_2CrO_4 and subsequent dissociation of H_2CrO_4 causes a temporary decrease in soil pH (Grove and Ellis, 1980a) as shown by equation (3):



Reduction of Cr(VI) to Cr(III) is dependent upon the availability of both protons and electrons. Hexavalent Cr reduction, therefore, proceeds more rapidly in acid than in alkaline soils (Cary et al., 1977). This reductive step will increase the soil pH slightly. The electron donor would be either soil organic matter or Mn (Bartlett and Kimble, 1976b; Bartlett and James 1979). Bartlett and Kimble

(1976b) have shown that Cr(VI) reduction is inhibited in the absence of organic matter. After Cr(VI) is reduced by the reactions of equation (3), the reduced Cr enters the reaction pathway of equation (2).

Although early research by Bartlett and James (1976a) indicated that the oxidation of Cr(III) to Cr(VI) did not occur in soil, it was later shown that a fresh moist field soil will oxidize substantial quantities of Cr(III) to Cr(VI). Bartlett and James (1979) indicated that, in the earlier research, Bartlett and James (1976a) used an air dried soil devoid of oxidized Mn. Bartlett and James (1979) have shown that the oxidation of Cr(III) to Cr(VI) in soils is the result of Mn reduction. Specifically, their research indicated that oxidation of Cr(III):

1. Did not occur in soils low in Mn,
2. Did not occur in acid soils if Mn was in the reduced form,
3. Was accompanied by an increase in reduced Mn, and
4. Occurred at nominal concentrations when oxidized Mn was converted to a reduced form by drying.

Bartlett and James (1979) reported that, of 20 possible couplings of Cr and Mn half reactions, 16 of these couplings

would give spontaneous reactions for the formation of Cr(VI). Oxidation therefore appears to occur in soil in the presence of oxidized Mn, which serves as the electron acceptor.

Chromium(III) added to soils as a metal ion is rapidly adsorbed and/or hydrolyzed, and precipitated in the absence of soluble complexing ligands. The Cr(III) applied to soils as waste amendments, however, may remain soluble due to the addition of organic acids (James and Bartlett, 1983a). James and Bartlett (1983a) showed that citric acid, fulvic acids, and water soluble organic matter, prevented Cr(III) precipitation in solution above pH 5.5. One year after an application of 750 μ moles of Cr-citrate per 100 g of soil, soluble Cr (75 μ moles per 100 g) was still present in the soil regardless of pH. The disappearance of soluble Cr-citrate may involve the adsorption of the chelate as an anion or uncharged species by soils rich in iron oxide or kaolinite (Grove and Ellis, 1980b).

Compounds capable of chelating Cr(III) or reducing Cr(VI), such as citric acid, may be present in organic waste materials added to soils or may form during decomposition. The solubility of Cr may be affected by the interaction between oxidation-reduction and organic complexation in soils. The addition of an organic ligand such as citrate can in-

crease Cr solubility [Cr(VI)] by facilitating Cr(III) oxidation. Chromium-citrate is more soluble in soil than Cr(OH)₃ and is oxidized more slowly over a longer period of time. This phenomena probably reflects the fact that the chelate is not rapidly precipitated by soils and that the addition of an organic ligand such as citrate can facilitate reduction of Cr(VI) (James and Bartlett, 1983b). The objective of this research was to determine if high chrome-sludges are an environmental hazard when used as soil amendments.

3.3 MATERIALS AND METHODS

3.3.1 A. Field experimentation

Field experiments were conducted to evaluate corn (Zea mays L.) and barley (Hordeum vulgare) response to applications of an aerobically digested sludge from a wastewater treatment plant with high Cr influent. Rates of sludge application were 0, 42, 84, 126, 168, and 210 dry Mg ha⁻¹. These sludge rates correspond to Cr applications of 0, 1021, 2042, 3063, 4084, and 5105 kg ha⁻¹.

The field experiments were conducted at three sites in the Coastal Plain, Piedmont, and Ridge and Valley physiographic regions of Virginia. The field experiments were located on Bojac loamy sand (coarse-loamy, mixed, thermic Typic Hapludult; pH, 6.3; CEC, 5.4 cmol(+)kg⁻¹), on Davidson

clay loam (clayey, kaolinitic, thermic Rhodic Paleudult; pH, 6.3; CEC, 12.5 cmol(+)kg⁻¹), and on Groseclose silt loam (clayey, mixed, mesic Typic Hapludult; pH, 6.0; CEC, 9.3 cmol(+)kg⁻¹).

Field plots consisted of in situ lysimeters to limit the size of the field experiments required for sludge applications and to prevent movement of the sludge components from the experimental area. The lysimeters consisted of an isolated volume of soil, 2.3 by 1.5 m and 0.9-m deep. A randomized complete block design with four replicates was used at the three experimental sites.

Corn crop. The three experimental sites were planted to 'Pioneer 3192' field corn in the spring of both 1984 and 1985. In the spring of 1984, 200 kg N ha⁻¹ was applied to the control treatment. In the spring of 1985, 250 kg N ha⁻¹ was applied to the control and the sludge treatments. After stands were established, seedlings were thinned to a population of 57,300 plants ha⁻¹ (23,200 plants A⁻¹). Corn grain yields were determined at plant maturity in the fall and were adjusted to 155 g H₂O kg⁻¹.

Barley crop. Barley variety 'Henry' was planted in 18-cm rows at a seeding rate 134.5 kg ha⁻¹ in the fall of 1984. Nitrogen was applied to the control treatment at the rates of 20 and 80 kg ha⁻¹ in late fall and early spring.

Barley silage yields were determined from the Bojac soil at Feekes' growth stage 7 to 9 and silage yields from the Davidson and Groseclose soils at Feekes' growth stage 10.3 to 10.5 (Large, 1954). Barley silage yields were adjusted to 650 g H₂O kg⁻¹.

3.3.2 B. Tissue analyses

Ten corn earleaves were sampled at the early silk growth stage and corn grain was harvested from the entire plot at physiologic maturity. Barley plants were harvested 2.5 cm above the soil surface in the spring as previously described. The earleaf, grain, and barley samples were dried at 70°C for 72 h and ground to pass a 20-mesh (0.833 mm) sieve in preparation for Cr analyses. One-half gram subsamples of the ground corn and barley tissue, and grain were digested in a HNO₃-HClO₄ acid mixture prior to determination of Cr by flameless atomic absorption spectroscopy.

3.3.3 C. Statistical analyses

Crop yield response and plant nutrient levels for the evenly spaced sludge application rates were analyzed by orthogonal polynomial and contrast comparison analyses.

3.4 RESULTS AND DISCUSSION

Studies of potential metal toxicities in soils can be divided into two categories: (1) the phytotoxicity from the application of highly soluble metal salts and (2) the impact on the food chain of heavy metals applied to agricultural soils as organic waste amendments. The second category is of primary environmental concern because of increased interest in land disposal of sludge. The criteria used for land application of sludge-borne metals has been described (USEPA, 1983). These regulations were designed to limit the cumulative loading rates of Cd, Cu, Ni, Pb, and Zn in agricultural cropland to levels which would not adversely affect human health. Certain states have adopted more conservative regulations than outlined in federal guidelines. Sludges added to soils increase organic matter which improves soil properties and water holding capacity. Sludges may contain adequate quantities of macronutrients such as N and P for crop production. As long as the application rate does not exceed the crop N requirement, the potential for groundwater contamination of NO_3^- is no greater from sludge application than from commercial fertilizer application (Chaney, 1982). Unlike the cumulative loading rate guidelines for Cd, Cu, Ni, Pb, and Zn to agricultural cropland, the effect of Cr from sludge application to agricultural land is at present speculative.

In the first field experiments during 1984 corn grain yields were consistently higher on all three soils at the highest sludge application rate compared with the control inorganic N treatment (200 kg N ha^{-1}). Yields at the highest sludge application rate were 12,600, 10,810, and 13,220 kg ha^{-1} on Bojac loamy sand, Davidson clay loam, and Groseclose silt loam, respectively. Orthogonal polynomial comparison analysis indicated that corn grain yields increased linearly ($P = 0.01$) as a function of the five evenly spaced sludge applications for the Bojac, Davidson, and Groseclose soils. The plants appeared healthy throughout the first growing season with no apparent visual toxicity symptoms.

Corn earleaf tissue, sampled at the early silk stage, had Cr levels which ranged from 402 to 945, 70 to 233 and 70 to 333 ng g^{-1} (ppb) for the Bojac, Davidson, and Groseclose, respectively. The Cr concentrations in corn earleaves, averaged over all treatments, were 647, 212 and 132 ng g^{-1} (ppb) for the Bojac, Groseclose, and Davidson soils, respectively. Based on contrast analyses, the Cr concentrations in the earleaves from the Bojac, a coarse textured well drained soil, was higher ($P=0.01$) than in the earleaves from the finer textured Groseclose, and Davidson soils. Chromium was nondetectable [$<70 \text{ ng g}^{-1}$ (ppb)] in the corn grain from all sludge application rates for the three soils.

Barley was planted in the fall of 1984 as a winter cover crop and harvested for silage in early spring 1985 prior to a second season of corn. Silage yields for the inorganic N control treatment (100 kg N ha^{-1}) were 9890, 9670, and $10,730 \text{ kg ha}^{-1}$ compared to the highest sludge application rate ($210 \text{ dry mt ha}^{-1}$) which yielded 8680, 9100, and 9670 kg ha^{-1} for the Bojac, Davidson, and Groseclose soils, respectively.

Based on contrast comparison analysis there was no difference in the Cr concentration in the silage for the no N control treatment compared with the five sludge application rates for each of the three soils. Chromium levels in the silage ranged from 1000 to 2748, 860 to 1890, and 560 to 1100 ng g^{-1} (ppb) for the Bojac, Davidson, and Groseclose soils, respectively. The Cr concentrations in the silage, averaged over all treatments, were 1602, 1342, and 878 ng g^{-1} (ppb) for the three soils, respectively.

Corn earleaf tissue, sampled at the early silk stage from the corn in 1985 had Cr levels which ranged from 620 to 1100, 220 to 450, and 320 to 660 ng g^{-1} (ppb) for the Bojac, Davidson, and Groseclose soils, respectively. The Cr concentrations in corn earleaves, averaged over all treatments were 877, 430, and 343 ng g^{-1} (ppb) for the Bojac, Groseclose, and Davidson soils, respectively. The Cr levels in

the 1985 corn earleaves (as in 1984) from the Bojac soil, averaged over all treatments was higher, ($P=0.01$) than in the earleaves from the Groseclose and Davidson soils. Stoltenwerk and Grove (1985a) showed that very little adsorption of Cr(VI) occurred in soil after removal of Fe oxide and hydroxide coatings with $\text{Na}_2\text{S}_2\text{O}_4$. They concluded that Cr(VI) was adsorbed by these coatings. In agreement with this, the Cr concentration in the earleaves of corn sampled in 1984 and 1985 from the Davidson soil, with a high Fe oxide and hydroxide content, was lower than from the Bojac, and Groseclose soils. James and Bartlett (1983c) have shown that the adsorption reaction with $\text{Fe}(\text{OH})_3$ removed 78% of applied Cr(VI) and that liming decreased exchangeable Cr(VI) by 71%. Present data indicate that the excessive Cr levels applied as an organic amendent to the three diverse Virginia soils was not detrimental to corn or barley production.

Investigations on the effects of Cr application have indicated that increases in Cr metal concentrations of plant tissue have occurred on some soils. Mortvedt and Giordano (1975) showed that the addition of Cr(VI) as Na_2CrO_7 at $320 \mu\text{g g}^{-1}$ resulted in Cr concentrations of $29 \mu\text{g g}^{-1}$ in corn tissue while the application of Cr(III) resulted in $2.8 \mu\text{g g}^{-1}$. The application of $1360 \mu\text{g g}^{-1}$ of Cr in sewage sludge, however, resulted in $1.5 \mu\text{g g}^{-1}$ of Cr in the tissue with no

decrease in grain yield. Cunningham et al. (1975) showed that Cr in corn tissue was higher from inorganic salt treatments than from Cr treatments from organic wastes. Chromium acetate applied at the rate of $700 \mu\text{g g}^{-1}$ increased tissue Cr levels from $<3 \mu\text{g g}^{-1}$ to $46 \mu\text{g g}^{-1}$, whereas the application of $697 \mu\text{g g}^{-1}$ of Cr in treated sludge increased tissue Cr concentration to only $8 \mu\text{g g}^{-1}$. Kelling et al. (1977) reported that 110 kg ha^{-1} of Cr applied as sewage sludge did not increase plant tissue levels of either rye (Secale cereale) or sorghum-sudangrass (Sorghum-sudanese). In a comparative yield study, Sykes et al. (1981) indicated that application of $500 \mu\text{g g}^{-1}$ of Cr as tannery sewage sludge did not affect lettuce (Lactuca sativa) and radish (Raphanus sativus) yields and that $\text{Cr}(\text{OH})_3$ application at a rate of $500 \mu\text{g g}^{-1}$ of Cr did not affect bean (Phaseolus spp.) yield. In contrast, there was a decrease in bean yield from application of $500 \mu\text{g g}^{-1}$ as tannery sewage sludge.

Transformations of chemical species can occur in sludge-soil mixtures following incorporation of high chrome-sludge into soil. Plant available levels are controlled by chemical equilibrium processes. Added Cr to soils by sludge-amendments are chelated by or adsorbed to soil organic matter or Al, Fe, or Mn hydrous oxides. In the worst case scenario of excessive Cr application rates to soils,

little organically amended Cr will enter the plant-food chain. Chromium is so strongly chelated in plant root cells that very little is translocated to crop shoots (Chaney, 1982). Chaney (1983) has reviewed chrome wastes from the tanning industry and pointed out that the USEPA removed Cr tanning waste from the hazardous waste list in 1980 due to the presence of Cr(III) rather than the Cr(VI) form.

3.5 CONCLUSIONS

Soluble and toxic Cr(VI) formed in or added to soils may be removed by anion adsorption or precipitation or by reduction to low-solubility cationic forms. At soil pH levels >6.4 , HCrO_4^- dissociates to CrO_4^{2-} . Soil pH affects the form of Cr(VI) reacting with soil and the rate of reduction of Cr(VI) to Cr(III). Liming soils, which contain Al and Fe sesquioxides and kaolinite, decrease, exchangeable Cr(VI) due to a decrease in positive charge on the soil colloids as pH is increased above the minerals zero point charge. In aerobic soils easily oxidized organic compounds will act as reducing agents for Cr(VI).

Soil acidifying compounds and reducing agents such as organic matter addition can be incorporated in the soil to promote Cr(VI) reduction. After Cr(VI) reduction, limestone may be added to form more insoluble Cr compounds.

Long term implications of Cr waste amendments to agricultural soils on pollution of ground water are not completely understood. Even though experimental data indicate that adsorption reactions will minimize Cr as a source of ground water contamination, Cr desorption data are required to evaluate the full potential of Cr(VI) pollution in the Chesapeake Bay. It is recommended that the method outlined by Stollenwerk and Grove (1985b) be followed for monitoring levels of Cr(VI) in groundwater and in the Chesapeake Bay. Caution is required for current standard water analysis techniques can result in reduction of Cr(VI) to Cr(III) by sample acidification and by impurities such as NO_2 present in HNO_3 . This reduction reaction of Cr(VI) could lead to erroneous values for the potential pollutant.

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Chapter IV

HEAVY METAL ACCUMULATION IN CORN AND BARLEY GROWN ON A SLUDGE-AMENDED TYPIC OCHRAQUALF

B.D. Rappaport, D.C. Martens, R.B. Reneau, Jr.,
and T.W. Simpson

4.1 ABSTRACT

A field experiment was conducted during the 1984 and 1985 growing seasons in the Atlantic Coastal Plain region to evaluate heavy metal accumulation in corn (Zea mays L.) grain and stover and in barley silage (Hordeum vulgare L.) grown on a poorly drained, sludge-amended soil. The study was conducted using in situ lysimeters (1.5 m x 2.3 m) on Acredale silt loam (fine-silty, mixed, thermic, Typic Ochraqualf) with a CEC of 6.9 cmol(+)kg⁻¹ and a pH of 6.6. An aerobically digested sludge from a wastewater treatment plant with major industrial inputs was applied to the lysimeters in 1984 at rates of 0, 42, and 84 dry Mg ha⁻¹. At the highest application rate, 1.8, 304, 17.2, and 248 kg ha⁻¹ of Cd, Cu, Ni, and Zn were applied, respectively. Cadmium concentration was <0.01 mg kg⁻¹ in the corn grain in both 1984 and 1985. Sludge application increased the concentration of Ni and Zn in the corn grain in 1984 and 1985. Levels of Cd and Cu were unaffected by sludge application in the corn

grain for both years. Copper, Ni, and Zn levels were increased in the barley silage by sludge application. Levels of DTPA-extractable metal in the Ap horizon were increased by sludge application and were 0.25, 60, 2, and 30 mg Cd, Cu, Ni, and Zn kg^{-1} in the highest sludge treatment, respectively. The DTPA-extractable Cd, Cu, Ni, and Zn within the soil profile indicated no downward metal movement. On this poorly-drained soil, phytotoxicity due to metals did not occur even where Cu was applied in excess of the USEPA recommended cumulative application guidelines of 280 kg ha^{-1} .

4.2 INTRODUCTION

Land application of sewage sludge to agricultural soils has continually increased as a sludge management option in the last century (Pahren, 1980). For example, application of municipal and industrial wastewater sludges to agricultural land has increased from <200 ha to >8,900 ha from 1980 to 1985 in Virginia. To provide health protection and to maintain water quality, it is essential that the solids (sludge) removed during sewage treatment are properly managed. Land application of sewage sludge is frequently the best management alternative for maintenance of water quality. While application of wastewater sludge to agricultural land has proven to be a satisfactory method of waste management, it is not without knowledge gaps.

Limited information is available on the accumulation of metals in the food-chain and on the metal contamination of ground and surface waters from land application of sludges on poorly-drained soils. Several states limit the application of sewage sludge to soils based on a minimum depth to a seasonal high water table (Flanders and Woodbury, 1983; Florida Department of Environmental Regulations, 1985; Indiana Stream Pollution Control Board, 1982; Ohio EPA, 1983; Wisconsin Department of Natural Resources, 1985). If sludge is applied to soils that are anaerobic for extended periods, metals may be in different and potentially more mobile and available forms than in well-drained soils. Sims and Patrick (1978) have shown generally greater amounts of Cu and Zn in a Mhoon silty clay loam (Typic Fluvaquent) in the exchangeable and organic fractions at low pH and Eh than at high pH and Eh levels.

Jones et al. (1975) studied the concentration of Cd and Zn in the earleaf and grain of corn (Zea mays L.) grown on a Blount silt loam (Aeric Ochraqualf) amended with an anaerobic digested sludge. The maximum rates of Cd and Zn additions over a four year period were 78.2 and 1806 kg ha⁻¹, respectively. Corn grain Cd and Zn were increased (p = 0.05) from 0.14 to 0.92 and 24.3 to 53.3, and leaf Cd and Zn were increased (p = 0.05) from 0.20 to 10.30 and 28.3 to

259.3 mg kg⁻¹ by sludge application, respectively. After an additional application of sludge the following year which provided a five year cumulative total of 81 and 1905 kg ha⁻¹ of Cd and Zn, levels in the corn earleaf were increased. The concentrations of Cd and Zn in the earleaf were >20 and 380 mg Kg⁻¹ with no decrease in corn grain yields (Hinesly et al., 1977). Three and four years after termination of sludge application, grain from sludge-treated and control plots did not differ in either Cd or Zn concentration (Hinesly et al., 1979). However, agricultural tile was used to provide drainage in this soil, thereby reducing water table fluctuations. The results of these studies may not be typical for poorly-drained soils due to less anaerobic soil conditions.

Limited criteria is available to assess heavy metal availability after sludge application to poorly-drained soils. These soils are often low in hydrous oxides that can adsorb and occlude metals. If sludge-borne heavy metals are not more available on poorly-drained soils, then these soils could serve as sites for land application of sewage sludge.

Field experimentation is needed to determine the accumulation of heavy metals in agronomically important crops grown on sludge-amended soils which developed under reduced conditions. This two year field experiment was initiated on

a poorly-drained soil to determine if Cd, Cu, Ni, and Zn from sludge application are rate limiting factors for corn and barley production and to evaluate the potential for groundwater contamination from leaching of heavy metals applied in sewage sludge. A sludge Cu application rate in excess of that in USEPA guidelines (1983) was applied to the soil.

4.3 MATERIALS AND METHODS

A field experiment was conducted in the Atlantic Coastal Plain to evaluate corn and barley (Hordeum vulgare L.) response to application of an aerobically digested sewage sludge from a sewage system with major industrial inputs. The field experiment was located on Acredale silt loam (fine-silty, mixed, thermic, Typic Ochraqualf); a soil with a low sesquioxide content. Soils and plants were sampled for three consecutive crops. The cropping sequence consisted of corn, barley, and corn from 1984 to 1985.

4.3.1 A. Field Experimentation

Experimental plots were in situ lysimeters constructed in a manner to prevent lateral movement of sludge components from plot to plot. The lysimeters consisted of an isolated volume of soil, 2.3 by 1.5 m and 0.9-m deep. Isolation of

this soil volume was accomplished by digging a ditch 20-cm wide to a depth of 0.9 m and then wrapping these soil blocks with 10 mil polyethylene film. Aluminum flashing was placed around all plots to limit lateral surface movement and runoff. Connection of the aluminum flashing to the plastic ensured total lateral isolation.

Sewage sludge was applied to the lysimeters at rates of 0, 42, and 84 dry Mg ha⁻¹ (Table 4). These treatments were arranged in a randomized complete block design with four replicates. The sludge had a pH of 6.2, and a water content (105°C) of 370 g H₂O kg⁻¹. The elemental analyses of the dry sludge was 31,660, 1,080, and 16,000, mg kg⁻¹ P, K, and organic N, respectively. There was limited inorganic N since the sludge was dewatered on sand beds which allowed for maximum NH₃ volatilization and NO₃⁻ leaching losses. Heavy metal concentrations in the sludge were 21.5, 24,300, 3,654, 206, 640, and 2,982 mg Cd, Cr, Cu, Ni, Pb, and Zn kg⁻¹ on a dry weight basis. The sludge was incorporated into the soil to a = 20-cm depth.

The experimental area was planted to 'Pioneer 3192' field corn in the spring of both 1984 and 1985. After stands were established, seedlings were thinned to a population of 57,300 plants ha⁻¹. In the spring of 1984, 200 kg N ha⁻¹ was applied to the control treatment. In the spring of

Table 4. Amount of heavy metals applied to the Acredale soil from sewage sludge application.

Dry sludge application	Heavy metal application			
	Cd	Cu	Ni	Zn
Mg ha ⁻¹	----- kg ha ⁻¹ -----			
0	---	---	---	---
42	0.9	152	8.6	124
84	1.8	304	17.2	248

1985, 250 kg N ha⁻¹ was applied to the control and the sludge treatments. The control treatment was amended with P and K, whereas the sludge plots were amended with only K. Levels of P and K application were in accordance with soil test recommendations. Ten corn earleaves were sampled at the early silk growth stage. Corn grain and stover were harvested at physiological maturity and yields were adjusted to 155 and 650 g H₂O kg⁻¹, respectively.

Barley, variety 'Henry', was planted in 18-cm rows at a seeding rate of 134.5 kg ha⁻¹ in the fall of 1984. Ammonium nitrate was applied to the control treatment at the rate of 20 and 80 kg N ha⁻¹ in late fall and early spring, respectively. Concentrated superphosphate and muriate of potash were applied in the fall to the control and sludge treatments prior to planting. Levels of P and K application were in accordance with soil test recommendations for barley production. Barley plants were harvested 2.5 cm above the soil surface for measurement of silage yields at Feekes' growth stage 7 to 9 (Large, 1954). The yields were adjusted to 650 g H₂O kg⁻¹.

4.3.2 B. Tissue Analyses

The earleaf, grain, stover, and barley samples were dried at 70°C for 72 h and ground to pass a 20-mesh (0.833 mm) sieve in preparation for analyses. Subsamples (0.5 g) of the ground corn and barley tissue were digested in a HNO₃-HClO₄ acid mixture prior to determination of Cd and Ni by flameless and of Cu and Zn by flame atomic absorption spectrophotometry (AAS).

4.3.3 C. Soil Analyses

A composite of 10 soil cores obtained from the 0- to 15-cm surface layer prior to sludge application were air-dried and were ground to pass a 10-mesh (2-mm) stainless steel sieve in preparation for laboratory analyses. Soil pH was measured in a 1:1 soil-to-water suspension after equilibration for 1 h (McLean, 1982). Organic matter was determined colorimetrically after wet oxidation with Na₂Cr₂O₇ (Peech et al., 1947). Particle size distribution was measured by the pipet method (Day, 1965). Cation exchange capacity of the soil was obtained by Ca saturation with subsequent displacement by Mg buffered at pH 7.0 (Rich, 1961). Electrical conductivity was determined by the method outlined by Rhoades (1982), except that a 1:2 soil-to-water (v/v) and a 1 h equilibration was used.

Noncrystalline and crystalline Al, Fe, and Mn were extracted by adding 100 mL of Tamm's solution (0.1 M oxalic acid and 0.175 M ammonium oxalate, pH 3.25) to 2 g of soil in a 250 mL beaker as described by Sampath (1980). Extractions were performed in duplicate. Aluminum was determined by AAS using a high temperature N₂O-acetylene flame. Iron and Mn were determined by use of an air-acetylene flame.

Mineralogical Analyses. The <2- μ m clay fraction was separated from the composite soil sample (0-15 cm depth) as described by Jackson (1979). Clay separates were mounted on porous ceramic tiles for X-ray diffraction analysis. Two ceramic tiles were prepared for each sample, one saturated with K and the other Mg saturated and glycerol solvated and washed free of excess salts. The Mg and K saturated tiles were subjected to heat treatments of 25 and 110°C, and 25, 110, 300, and 550°C, respectively. Analyses were performed on a GE/Diano XRD-8300 AD X-ray diffractometer equipped with a graphite crystal monochromator and controlled by a DEC LSI-11 computer. The samples were scanned at 2° 2 θ using CuK α radiation. Quantitative analyses of the clay separate was determined by differential scanning calorimetry (DSC). Samples were run in a DuPont DSC cell using a N₂ atmosphere from 50 to 625°C (20°C/min.) and controlled by a DuPont 1090 thermal analyzer.

Heavy Metals. Soil samples were collected from the 0- to 15-cm depth from all plots when corn plants were in the early silk growth stage in 1984 and 1985. The procedure reported by Baker and Amacher (1982) was followed for determination of DTPA-extractable Cd, Cu, Ni, and Zn. DTPA-extractable Cd and Ni were analyzed by flameless AAS, and Cu and Zn were analyzed by flame AAS.

To evaluate downward movement of applied metals, DTPA-extractable Cd, Cu, Ni, and Zn were determined with depth for three replicates of the control and the 84 dry Mg ha⁻¹ treatments in the fall of 1985. Samples from the Ap horizon were divided into upper and lower portions of this horizon, which were 0-12 and 12-25 cm, respectively. The remainder of the profile was sampled in 15-cm increments to a depth of 85 cm.

4.3.4 D. Statistical Analyses

Corn grain, corn stover, and barley yields; Cd, Cu, Ni, and Zn uptake and concentrations in the plant tissue; and DTPA-extractable Cd, Cu, Ni, and Zn were evaluated by analysis of variance and the least significance difference test. A two-sample t test was used to evaluate downward movement of DTPA-extractable Cu and Zn (Steel and Torrie, 1980). The 0.05 level of probability was chosen for mean separation.

4.4 RESULTS AND DISCUSSION

The Acredale soil had a pH of 6.6 in the spring of 1984 prior to sludge incorporation and cropping (Table 5). The relatively low CEC of the soil reflects a low clay content as well as the dominance of kaolinite in the mineralogical suite. The soil contained relatively little crystalline and noncrystalline hydroxides and oxides of Al, Fe, and Mn. Long-term leaching losses as a result of a high seasonal fluctuating water table in this profile for extended periods of time, explain this low sesquioxide content.

At early corn silk in July 1984, the pH of the 0, 42, and 84 dry Mg ha⁻¹ sludge treated plots did not differ and ranged from 5.9 to 6.0. The sludge addition increased the organic matter content and soluble salt levels from 2.2 to 3.9 g kg⁻¹ and 0.9 to 1.3 S m⁻¹ x 10⁻² from the control to 84 dry Mg ha⁻¹ treatment, respectively. Bower and Wilcox (1965) reported that salinity effects are usually negligible for saturation extracts of <0.2 S m⁻¹.

4.4.1 A. Metal Extractability

Levels of DTPA-extractable metals in the Ap horizon were increased by sludge rate in 1984 and 1985 (Fig. 1). DTPA-extractable Cu and Zn within the soil profile indicated no downward movement of applied metals (Table 6). Cadmium

Table 5. Chemical, physical, and mineralogical properties of the Ap horizon of the Acredale soil under study.

pH	Organic matter	CEC	Crystalline & noncrystalline			Particle-size distribution				Mineralogical suite of < 2 μ m clay fraction [†]
			Al	Fe	Mn	Sand	Silt	Clay	Texture	
	g kg ⁻¹	cmol(+)kg ⁻¹	----- mg kg ⁻¹ -----			----- % -----				
6.6	23	6.9	1610	3400	12	37.8	52.3	9.9	sil	K ₁ , M ₂ , HIV ₃ , Q=V=C ₄ , MO ₅ , F=ML ₆ ,

[†] C=chlorite, F=feldspars, HIV=hydroxy interlayered vermiculite, K=kaolinite, M=mica, ML=regularly interstratified mineral, MO=montmorillonite, Q=quartz, and V=vermiculite; subscripts 1-6 range from most to least abundant.

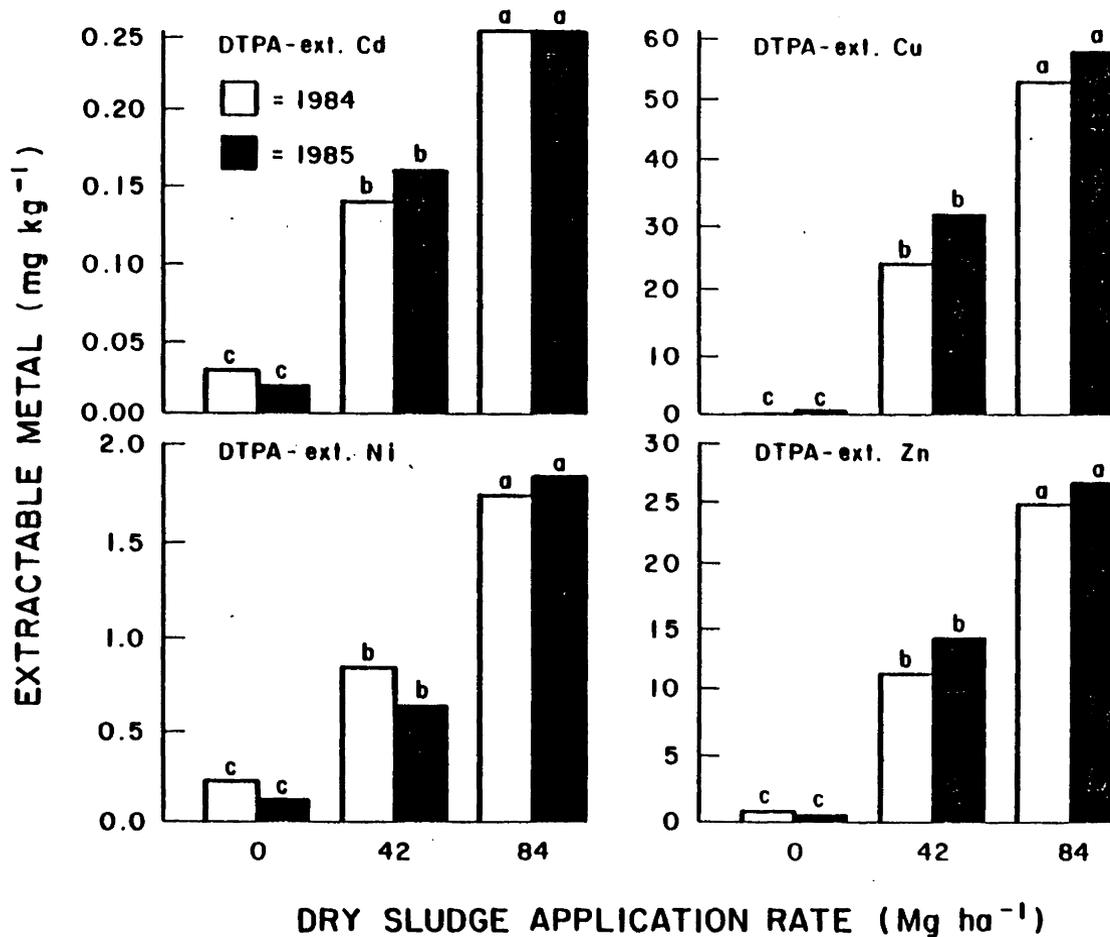


Figure 1. Effect of sludge application on DTPA-extractable Cd, Cu, Ni, and Zn in the Ap horizon of the Acredale soil in 1984 and 1985. Means for each year for each parameter followed by different letters are significantly ($p = 0.01$) different.

Table 6. Amounts of DTPA-extractable Cu and Zn in six layers of the Acredale soil 1.5 years after sludge application.

Depth --cm--	Dry sludge application, Mg ha ⁻¹			
	0	84	0	84
	mg ext. Cu ha ⁻¹		mg ext. Zn ha ⁻¹	
0-12	0.2b [†]	51a	0.2b	25a
12-25	0.2b	22a	0.1b	8a
25-40	0.2a	0.2a	0.2a	0.1a
40-55	0.1a	0.1a	0.1a	0.1a
55-70	0.2a	0.2a	0.1a	0.1a
70-85	0.2a	0.2a	0.1a	0.1a

[†]Row means for each metal followed by different letters are significantly (P = 0.05) different.

and Ni were $<0.02 \text{ mg kg}^{-1}$ below the Ap horizon. Adsorption and occlusion reactions in soil govern heavy metal mobility in the soil environment. The increase in organic matter in the soil from sludge application may have been an important determinant for maintaining metals in nonmobile forms (McLaren and Crawford, 1973; Sommers and Nelson, 1978). The Al and Fe hydrous oxides, in the soil could have selectively removed metals from solution (Kinniburgh et al., 1976). Portions of the metals sorbed on the surfaces of hydroxides and oxides may have become occluded and nonreactive (Jenne, 1968). Other studies have shown that applied metals remain in the zone of incorporation (Mullins et al., 1982; Higgins, 1984).

4.4.2 B. Yields

Corn grain and stover harvested in 1984, and barley silage harvested in the spring of 1985 were consistently higher from the control treatment than from the sludge treatments (Table 7). These decreases in yields are attributable to N deficiency (Scott et al., 1985). Experimental results of a laboratory study, under anaerobic conditions estimated that much less than 10% of the N in the sludge mineralized during the first growing season (Scott et al., 1985). If the heavy metal concentration of the plant tissue is used

Table 7. Effect of sludge application in 1984 on corn grain and stover, and barley silage yields in 1984 and 1985.

Dry sludge application	Corn yield (1984) [†]		Barley yield (1984-1985) [‡]	Corn yield (1985)	
	Grain	Stover	Silage	Grain	Stover
Mg ha ⁻¹	----- kg ha ⁻¹ -----				
-- [§]	8,100a [¶]	27,900a	8,200a	9,700a	19,200a
42	3,200b	17,100c	2,400c	9,700a	21,300a
84	3,600b	19,900b	3,100b	9,000a	20,500a

[†]The grain and stover yields were adjusted to 155 and 650 g H₂O kg⁻¹, respectively.

[‡]Barley silage yields were determined at Feekes' growth stage 7 to 9 and adjusted to 650 g H₂O kg⁻¹.

[§]Nitrogen was applied to the control treatment at the rate of 200, 250, and 100 kg ha⁻¹ as NH₄NO₃ for corn production in 1984 and 1985, and for barley production, respectively.

[¶]Column means followed by different letters are significantly (p = 0.05) different.

for diagnostic phytotoxic affects, all four metals (Tables 8 and 9) were within the range considered to be normal for barley and corn growth (Page et al., 1981; Chapman, 1966). This is further evidence that the yields were influenced by the N-mineralization rate rather than by metal accumulation.

In the spring of 1985, 250 kg N ha⁻¹ was applied to the control and sludge treatments to eliminate the N deficiency in the second crop of corn. Corn grain and stover yields ranged from 9,000 to 9,700 and 19,200 to 21,300 kg ha⁻¹ in 1985, respectively, and were not decreased by sludge application (Table 7). These data indicate that no decrease in yield occurred from the high rates of Cr and Cu applied in the sewage sludge. Rappaport et al. (1986) concluded that Cr must exist as Cr⁺⁶ in soil to pose an environmental hazard with respect to a decrease in yield or to a phytotoxicity.

4.4.3 C. Metal Concentrations in Tissue

First-Crop. Concentrations of Cd in the corn earleaf were not increased in 1984 from sludge application (Table 8). Cadmium, however, was increased in the corn stover in 1984. The control treatment Cd stover concentration was 0.03 mg kg⁻¹ and increased to 0.13 and 0.07 mg kg⁻¹ in the 42 and 84 dry Mg ha⁻¹ sludge treatments, respectively. Cad-

Table 8. Elemental composition of corn earleaves, grain, and stover on the sludge treatments of the field study in 1984 and 1985.

Dry sludge application	Year							
	1984				1985			
	Cd	Cu	Ni	Zn	Cd	Cu	Ni	Zn
Mg ha ⁻¹	<u>Earleaf concentration, mg kg⁻¹</u>							
-- [†]	0.07a [‡]	8.0a	0.23b	21a	<0.01	7.8a	0.54a	14c
42	0.07a	6.1b	0.36ab	18a	<0.01	7.7a	0.66a	27b
84	0.06a	4.9c	0.54a	28a	<0.01	8.2a	0.66a	31a
	<u>Grain concentration, mg kg⁻¹</u>							
--	<0.01	4.5a	0.39b	30b	<0.01	2.2a	0.11b	17b
42	<0.01	3.8a	1.04a	40a	<0.01	2.9a	0.34a	28a
84	<0.01	3.9a	1.34a	36ab	<0.01	2.3a	0.37a	26a
	<u>Stover concentration, mg kg⁻¹</u>							
--	0.03c	4.9a	0.75a	14b	0.02a	6.6a	0.14a	10c
42	0.13a	5.3a	1.32a	50a	0.02a	6.9a	0.18a	37b
84	0.07b	4.5a	1.33a	53a	0.03a	6.7a	0.18a	45a

[†] Nitrogen was applied to the control treatment at the rate of 200 and 250 kg ha⁻¹ as NH₄NO₃ in 1984 and 1985, respectively.

[‡] Column means for each parameter followed by different letters are significantly (p = 0.05) different.

Table 9. Effect of rate of sludge application on metal concentration and uptake in barley silage on the Acredale soil in 1985.

Dry sludge application	Metal			
	Cd	Cu	Ni	Zn
Mg ha ⁻¹	<u>Silage concentration, mg kg⁻¹</u>			
-- [†]	0.12a [‡]	1.0b	0.51b	12.0c
42	0.13a	2.5a	0.92a	31.7b
84	0.14a	2.8a	0.74a	35.0a
	<u>Silage uptake, g ha⁻¹</u>			
--	0.3a	2.9a	1.5a	34.4a
42	0.1b	2.0b	0.8b	26.0b
84	0.1b	3.0a	0.8b	37.5a

[†] Nitrogen was applied to the control treatment at the rate of 100 kg ha⁻¹ as NH₄NO₃.

[‡] Column means for each parameter followed by different letters are significantly (p = 0.05) different.

mium in the corn grain was $<0.01 \text{ mg kg}^{-1}$ which is well below 0.9 mg kg^{-1} considered to be the normal concentration in corn grain (Kirkham, 1975).

Copper concentrations in 1984 earleaf samples were decreased by the addition of sludge to the plots (Table 8). Levels of Cu decreased from 8.0 to 4.9 mg kg^{-1} in the control treatment to the highest sludge application rate, respectively. Soil Cu^{+2} solubilized during the first year may have formed stable ligand complexes with the organic matter additions to the soil by the sludge treatments (McLaren and Crawford, 1973). The affinity of Cu^{+2} for organic matter would explain the decreased Cu concentration in the earleaf during the first corn crop.

Nickel concentrations in 1984 in the corn earleaf and grain were increased as a result of sludge application (Table 8). The concentration of Ni in the grain was increased more than threefold by the application of 17.2 kg ha^{-1} of Ni in the 84 dry Mg ha^{-1} sludge treatment. The concentration of Ni, however, was below levels reported to cause phytotoxicity (Hutchinson, 1981).

Residual-Crops 2 and 3. After corn harvest in 1984, the experimental plots were planted to barley in the fall of 1984 and to corn in the spring of 1985, respectively to assess residual metal accumulation in these crops. Sludge ap-

plication did not increase Cd concentration in the barley silage (Table 9). Cadmium uptake, however, was higher in the control treatment barley silage due to the higher yield (Table 7). Cadmium was $<0.01 \text{ mg kg}^{-1}$ in the corn grain and in the earleaf in 1985. This is in contrast to a greenhouse study by King and Dunlop (1982) where the addition of sludge to supply 0, 2, 4, and 8 kg Cd ha⁻¹ to a Wasda soil (fine-loamy, mixed, acid, thermic Histic Humaquept) increased the Cd concentration in corn grain ($r^2 = 0.75^{**}$). In their study the Cd concentration ranged from 0 to 6 and 0 to 0.25 mg kg⁻¹ in the corn stover and corn grain, respectively.

Copper levels were increased in the barley silage as a result of sludge application (Table 9). Concentrations of Cu in the 1985 corn earleaf, grain, and stover were not increased by sludge additions (Table 8). Grain and stover Cu concentrations during the two croppings of corn ranged from 2.2 to 4.5 and 4.5 to 6.9 mg kg⁻¹, respectively. Chaney (1975) concluded that increases in soil Cu lead to small increases in plant-shoot Cu levels due to Cu accumulation in the plant roots rather than shoots. The increase in barley silage Cu may be due to a concentration affect due to a decrease in yield.

Nickel and Zn were increased in the barley silage as a result of increased sludge additions (Table 9). Nickel and

Zn concentrations in the 1985 corn grain were increased as a result of sludge application (Table 8). The concentration of Ni was increased more than threefold by the application of 17.2 kg ha⁻¹ of Ni in the 84 dry Mg ha⁻¹ sludge treatment. Zinc concentration in the barley silage increased from 12 to 35 mg kg⁻¹ (Table 9).

In summary, increases in sludge borne Ni and Zn led to increases in Ni and Zn concentrations in corn earleaf, grain, and barley silage and in Zn stover concentrations. An increase in rate of sludge-borne Cu did not increase grain and stover Cu concentrations but increased barley silage Cu concentration. Cadmium, Cu, Ni, and Zn concentrations in the plant tissue are similar to those reported in other field investigations in which sewage sludge was used as the metal source (Dowdy and Larson, 1975; Hinesly et al., 1977; Scheaffer et al, 1979).

On this poorly-drained soil, neither metal phytotoxicity nor metal movement within the soil profile occurred even when Cu was applied in excess of USEPA (1983) guidelines. Although this soil was low in Al and Fe hydrous oxides and clay, had a low CEC, and was anaerobic for periods of time which made it a prime candidate for increased metal mobility and uptake, there were no detrimental affects on crop production from applied metals. Overall, it can be concluded

that addition of sludge from 0 to 84 dry Mg ha⁻¹ was not rate limiting with respect to a decrease in crop yield by a large increase of metal uptake due to metal phytotoxicity. Even though there were increases in metal concentrations all four metals were within the range considered to be normal for barley and corn growth (Chapman, 1966; Jones, 1967; Melsted et al., 1969; Page et al., 1981).

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Chapter V

HEAVY METAL AVAILABILITY IN SOILS TREATED WITH A SEWAGE SLUDGE WITH ELEVATED METAL LEVELS

B.D. Rappaport, D.C. Martens, R.B. Reneau, Jr.,
and T.W. Simpson

5.1 ABSTRACT

A study was conducted in 1984 using in situ lysimeters (1.5 m x 2.3 m) to determine Cd, Cu, Ni, and Zn availabilities for corn (Zea mays L.) grown on sludge-amended soils. These lysimeters were constructed in a Bojac loamy sand (Typic Hapludult), Davidson clay loam (Rhodic Paleudult), and Groseclose silt loam (Typic Hapludult) located in the Coastal Plain, Piedmont, and Ridge and Valley provinces of Virginia, respectively. An aerobically digested sludge from a wastewater treatment plant with major industrial inputs was applied to the lysimeters at rates of 0, 42, 84, 126, 168, and 210 dry Mg ha⁻¹. The highest sludge rate corresponded to an application of 4.5, 760, 43.0, and 620 kg Cd, Cu, Ni, and Zn ha⁻¹, respectively. Corn grain and stover yields at the three locations increased linearly as a function of increased sludge application ($r^2 > 0.92^{**}$). Metal concentrations in the grain and earleaves for corn grown on the three soils were within normal levels. Levels of DTPA-

extractable metals in the Ap horizon of the three soils increased linearly ($r^2 = 0.95$ to 0.98^{**}) with rate of sludge application. Maximum DTPA-extractable metal levels were 0.6, 150, 4.0, and 75 mg kg⁻¹ for Cd, Cu, Ni, and Zn, respectively. The order of magnitude of DTPA-extractable metals for the soils were Cu>Zn>Ni>Cd which reflected the trace metal composition of the sludge. Relatively low correlations ($r^2 \leq 0.58^{**}$) occurred between DTPA-extractable Cd, Cu, Ni, and Zn and the respective metal concentration in corn earleaves for each of the three soils. Phytotoxicity did not occur in the corn grown on three diverse soils even when Cu and Zn were applied in excess of USEPA guidelines.

5.2 INTRODUCTION

Sewage sludge is the residue produced from the treatment of sewage in rural areas and in large cities with a diversity of industries. Often sewage from residential areas is comprised primarily of domestic wastewater, food residues, and stormwater. Sewage from large cities contains industrial chemicals and stormwaters which may carry metals from atmospheric pollutant sources such as partial combustion of coal and petroleum products (Sommers, 1977). Heavy metal contamination in the food-chain is one of the factors which may limit the agricultural use of sewage sludge on agricultural land (CAST, 1976, 1981; USEPA, 1983).

When metals are added to soils as sludge-amendments, there is limited downward movement and, consequently, metals remain in the Ap horizon (Page, 1974). As a result, there is an increase in the labile pool of metals in the plow layer. A soil extractant is needed for the humid southeastern region of the United States to evaluate heavy metal availabilities in sludge-amended soils. The soil extractant is needed as an integral part of a monitoring program to prevent yield reductions and metal contamination of the food-chain from the dissolution of sludge metals.

The DTPA soil test (0.005 M, pH 7.3) developed by Lindsay and Norvell (1969) has been widely used to identify micronutrient deficiencies in near neutral and calcareous soils (Follett and Lindsay, 1971; Lindsay and Norvell, 1978; Mashhady, 1983). This procedure has been used extensively to assess heavy metal availability from sludge-amended soils (Gaynor and Halstead, 1976; Korcak and Fanning, 1985; Rappaport et al., 1986; Singh, 1981). Rappaport et al. (1986) related DTPA-extractable Zn to Zn concentrations in corn on 14 sludge-amended soils in the Coastal Plain, Piedmont, and Ridge and Valley regions of Virginia. Their research showed a significant coefficient of multiple determination ($R^2 = 0.77^{**}$) between corn earleaf Zn concentration and a two variable regression model comprised of DTPA-extractable Zn and organically bound Zn.

Limited information is available in the literature on phytotoxicity from sludge application where metal concentrations were applied in excess of the USEPA (1983) guidelines. Cunningham et al. (1975) conducted greenhouse research with four diverse municipal sludges on corn production on Warsaw sandy loam (Typic Argiudoll). Concentrations of Cu, Ni, and Zn in the sludge ranged from 300 to 943, 120 to 853, and 968 to 6,074 mg kg⁻¹, respectively. After a six week growing period, the concentrations of Cu, Ni, and Zn in the corn ranged from 5.8 to 24.6, 4.5 to 16.9, and 87 to 569 mg kg⁻¹. Corn yields increased at sludge rates of 125 and 251 Mg ha⁻¹ and decreased at 502 Mg ha⁻¹ sludge rate. The decreases were attributed to toxic concentrations of heavy metals and to high soluble salt levels.

Dowdy et al. (1978) investigated the influence of 1400 Mg ha⁻¹ of sludge application over a three-year period on Zn concentration in beans (Phaseolus vulgaris L. var. 'Tendergreen') grown in the field on Hubbard coarse sand (Udorthentic Haploboroll). They reported that, although 1,520 kg Zn ha⁻¹ had been applied, Zn levels never exceeded 60 mg kg⁻¹ in the edible bean tissue. Copper was applied in excess of 260 kg ha⁻¹ and was increased in the edible tissue from 2 mg in the control to 8 mg kg⁻¹ where sludge was applied. Copper and Zn were applied in excess of the USEPA (1983) guidelines by 10 and 1240 kg ha⁻¹, respectively.

The objectives of this investigation were to investigate the relationship between DTPA-extractable Cd, Cu, Ni, and Zn and concentrations of the respective metals in corn tissue and to determine whether Cd, Cu, Ni, and/or Zn are rate limiting factors where sludge was used as a soil amendment for corn production on three well-drained soils. Sludge Cu and Zn application rates in excess of those in USEPA guidelines (1983) were applied to the soils.

5.3 MATERIALS AND METHODS

5.3.1 A. Field Experimentation

In situ lysimeters were constructed to study heavy metal availability and accumulation of metals in corn from application of an aerobically digested sewage sludge from a sewage system with major industrial inputs. Studies were conducted on Bojac loamy sand (coarse-loamy, mixed, thermic Typic Hapludult), Davidson clay loam (clayey, kaolinitic, thermic Rhodic Paleudult), and Groseclose silt loam (clayey, mixed, mesic, Typic Hapludult). These soils were located in the Coastal Plain, Piedmont, and Ridge and Valley regions of the eastern United States, respectively. Soils with diverse chemical and physical properties (Table 10) were selected for this research to ensure wide applicability of the experimental results.

Table 10. Classification, chemical, and physical properties of the Ap horizon of the soils under study.

Soil classification		pH	Organic matter	CEC	Amorphous & crystalline			Particle-size distribution			
Soil series	Taxonomic class				Al	Fe	Mn	Sand	Silt	Clay	Texture
			g kg ⁻¹	cmol(+)kg ⁻¹	mg kg ⁻¹			%			
Bojac	Typic Hapudult; coarse-loamy, mixed, thermic	6.3	16	5.4	2,430	9,070	80	64.0	27.8	8.2	ls
Davidson	Rhodic Paleudult; clayey, kaolinitic, thermic	6.3	18	12.5	4,740	42,500	1,280	15.3	47.1	37.6	cl
Groseclose	Typic Hapludult; clayey, mixed, mesic	6.0	25	9.3	2,610	9,030	580	20.7	59.3	20.0	sil

The Davidson soil is a fine textured highly weathered soil with high levels of crystalline and noncrystalline Al, Fe, and Mn (Table 10). The Groseclose soil, a fine-textured upland soil, is developed from calcareous parent material. The Bojac soil is a coarse-textured, well drained soil which developed from marine sediments. The dominant clay minerals in the Ap horizon of the Bojac and Groseclose soil were kaolinite and hydroxy interlayered vermiculite (Table 11). The Ap horizon of the Davidson contained primarily kaolinite and some 14-A° hydroxy interlayered vermiculite.

The lysimeters were constructed in a manner to prevent movement of sludge components from plot to plot. The lysimeters consisted of an isolated volume of soil, 2.3 by 1.5 m and 0.9-m deep. Isolation of this soil volume was accomplished by excavating a ditch 20-cm wide to a depth of 0.9 m and then wrapping these soil blocks with 10 mil polyethylene film. Aluminum flashing was placed around all plots to limit lateral surface movement and runoff. Connection of the Al flashing to the plastic ensured total lateral isolation.

Sewage sludge was applied to the lysimeters in the three soils at rates of 0, 42, 84, 126, 168, and 210 dry Mg ha⁻¹ (Table 12). These treatments were arranged in a randomized complete block design with four replicates on the Bojac and Groseclose soils and three replicates on the Da-

Table 11. Mineralogical properties of the Ap horizon of the soils under study.

Soil series	Mineral suite of < 2 μ m clay fraction [†]									
	C	F	G	HIV	K	M	ML	MO	Q	V
----- % -----										
Bojac	11	5	2	31	27	10	2	5	7	-- [‡]
Davidson	--	2	1	14	68	2	5	5	3	--
Groseclose	4	4	Tr [§]	33	26	14	2	4	8	5

[†] C = chlorite, F = feldspars, G = gibbsite, HIV = hydroxy interlayered vermiculite, K = kaolinite, M = mica, ML = regularly interstratified mineral, MO = montmorillonite, Q = quartz, and V = vermiculite.

[‡] Non-detectable.

[§] Trace amounts detected.

Table 12. Amounts of heavy metals applied to the soils from sewage application.

Dry sludge application	Heavy metal application			
	Cd	Cu	Ni	Zn
Mg ha ⁻¹	----- kg ha ⁻¹ -----			
0	---	---	---	---
42	0.9	152	8.6	124
84	1.8	304	17.2	248
126	2.7	456	25.8	372
168	3.6	608	34.4	496
210	4.5	760	43.0	620

vidson soil. The sludge had a pH of 6.2 and a water content (105°C) of 370 g H₂O kg⁻¹. The elemental analyses of the dry sludge was 31,660, 1,080, and 16,000 mg kg⁻¹ of P, K, and organic N, respectively. There was limited inorganic N since the sludge was dewatered on sand beds which allowed for maximum NH₃ volatilization and NO₃⁻ leaching losses. Heavy metal concentrations in the sludge were 21.5, 24,300, 3,654, 206, 640, and 2,982 mg Cd, Cr, Cu, Ni, Pb, and Zn kg⁻¹, respectively on a dry weight basis. The sludge was incorporated into the soil to ≈ 20-cm depth.

The experimental sites were planted to 'Pioneer 3192' field corn in the spring of 1984. After stands were established, seedlings were thinned to a population of 57,300 plants ha⁻¹. Two hundred kg of N ha⁻¹ as NH₄NO₃ was applied to the control treatment. Muriate of potash was applied to all treatments, and triple superphosphate was applied only to the control treatment. Inorganic fertilizer amendments were based on soil test recommendations. Corn grain and stover yields were determined at physiologic maturity in the fall of 1984. The corn grain and stover yields were adjusted to 155 and 650 g H₂O kg⁻¹, respectively. A composite sample of 10 earleaves was collected from all plots when corn plants were in the early silk growth stage.

5.3.2 B. Tissue Analyses

Corn earleaf and grain samples were dried at 70°C for 72 h and ground to pass a 20-mesh (0.833-mm) sieve. Subsamples (0.5 g) of the ground tissue were digested in a HNO₃-HClO₄ acid mixture prior to determination of Cd and Ni by flameless and of Cu and Zn by flame atomic absorption spectrophotometry (AAS).

5.3.3 C. Soil Analyses

Soil samples were collected with a stainless steel probe (1.9-cm diameter) prior to sludge application, air-dried, and ground to pass a 10-mesh (2-mm) stainless steel sieve in preparation for laboratory analyses. Soil pH was measured in a 1:1 soil-to-water suspension after equilibration for 1-h (McLean, 1982). Organic matter was determined colorimetrically after wet oxidation with Na₂Cr₂O₇ (Peech et al., 1947). Particle size distribution was obtained by the pipet method (Day, 1965). Cation exchange capacity (CEC) of the soils was determined by Ca saturation with subsequent displacement by Mg, buffered at pH 7.0 (Rich, 1961).

Soil samples were obtained from the Ap horizon of each plot (10 cores/plot) when corn was in the early silk growth stage. These samples were prepared for DTPA extractable Cd, Cu, Ni, and Zn analyses by aforementioned procedures. The

procedure reported by Baker and Amacher (1982) was followed for determination of the DTPA-extractable metals.

Noncrystalline and crystalline Al, Fe, and Mn were extracted by adding 100 mL of Tamm's solution (0.1 M oxalic acid and 0.175 M ammonium oxalate, pH 3.25) to 2-g of soil in a 250 mL beaker as described by Sampath (1980). Aluminum was determined by AAS using a high temperature N₂O-acetylene flame. Iron and Mn were determined using an air-acetylene flame.

Mineralogical Analyses. The <2- μ m clay fraction was separated from whole soil from each location at a depth of 0-15 cm, as described by Jackson (1979). Clay separates were mounted on porous ceramic tiles for X-ray diffraction analysis. Two ceramic tiles were prepared for each sample, one saturated with K and the other Mg saturated, glycerol solvated, and washed free of excess salts. The Mg and K saturated tiles were subjected to heat treatments of 25 and 110°C, and 25, 110, 300, and 550°C, respectively. Analyses were performed on a GE/Diano XRD-8300 AD X-ray diffractometer equipped with a graphite crystal monochromator and controlled by a DEC LSI-11 computer. The samples were scanned at 2° 2 θ using CuK α radiation. Quantitative analyses of the clay separates were determined by differential scanning calorimetry (DSC). Samples were run in a DuPont DSC cell

using a N₂ atmosphere from 50 to 625°C (20°C/min) and controlled by a DuPont 1090 thermal analyzer.

5.3.4 D. Statistical Analyses

Crop yield responses to the evenly spaced sewage sludge applications were analyzed by orthogonal polynomial comparisons. Metal concentrations in corn tissue and DTPA-extractable metals were evaluated by analyses of variance and the least significant difference (LSD) test. Relationships among earleaf metal concentrations and DTPA-extractable metals were determined by Pearson correlation coefficients. Only sludge treatments were included in these correlations. The 0.05 level of probability was chosen for these statistical techniques (Steel and Torrie, 1980).

5.4 RESULTS AND DISCUSSION

The levels of Cd, Cu, Ni, and Zn incorporated into the soils in 1984 from the sludge application are shown in Table 12. The three soils had a CEC levels between 5 to 15 cmol(+)kg⁻¹ (Table 10). Soil pH levels in the in situ lysimeter plots (Table 13) at early corn silk were below the USEPA (1983) suggested pH level of ≥6.5 for sludge-amended soils. The USEPA (1983) recommended maximum cumulative sludge metal application for cropland with a soil CEC of 5

Table 13. Soil pH on three soils at early corn silk in 1984.

Dry sludge application	Soil series		
	Bojac	Davidson	Groseclose
Mg ha ⁻¹	pH		
0	6.1ab [†]	5.7b	5.7a
42	6.2a	6.0a	6.0a
84	6.1ab	5.8ab	5.9a
126	5.8c	5.9a	5.9a
168	6.0bc	5.9a	5.9a
210	6.0bc	5.9a	5.9a

[†]Column means for each soil followed by different letters are significantly (P = 0.05) different.

to 15 cmol(+)kg⁻¹ of 10, 280, 280, and 560 kg Cd, Cu, Ni, and Zn ha⁻¹, respectively. Levels of Cu and Zn were applied in excess of recommended maximum loading rate by 480 and 60 kg Cu and Zn ha⁻¹ at the high treatment (Table 12). The high sludge loading rates provided an appropriate test of the applicability of the USEPA (1983) guidelines for the three soils.

5.4.1 A. Corn Grain and Stover Yields

Grain and stover yields from the three locations increased linearly as a function of the five evenly spaced sludge rates (Figures 2 and 3). Corn grain yields from the control treatment were 11,600, 9,900, and 10,100 and from the highest sludge application treatment were 12,600, 10,800, and 13,200 kg ha⁻¹ on Bojac, Davidson, and Groseclose soils, respectively. These yield increases were due to increased available N as a result of sludge application (Scott et al., 1985). The corn grain and stover yields were not decreased on the three soils where up to 4.5, 5105, 760, 43.0, 135, and 620 kg Cd, Cr, Cu, Ni, Pb, and Zn ha⁻¹ were added in a single sludge application, respectively.

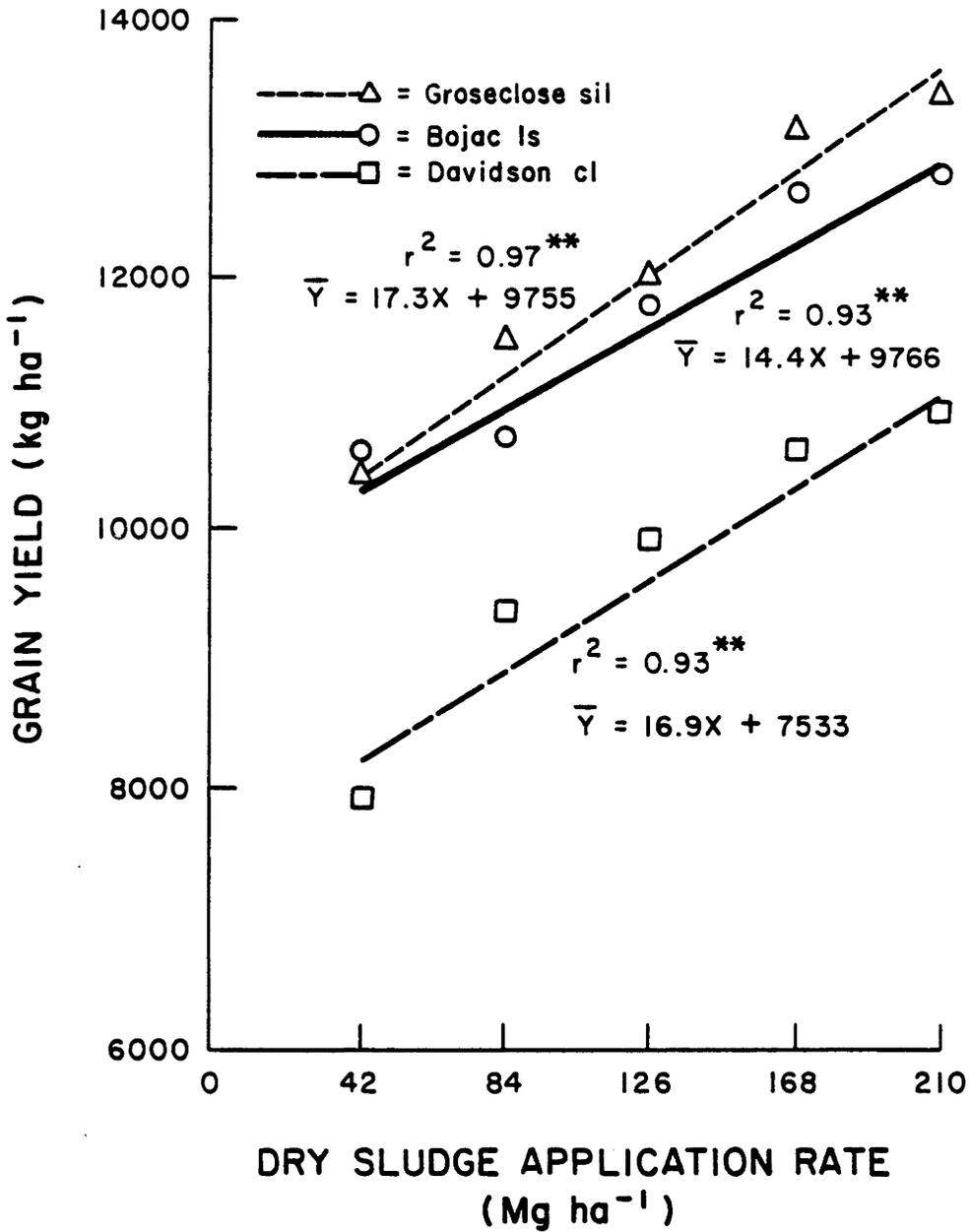


Figure 2. Effect of sludge application on corn grain yield on three soils in 1984.

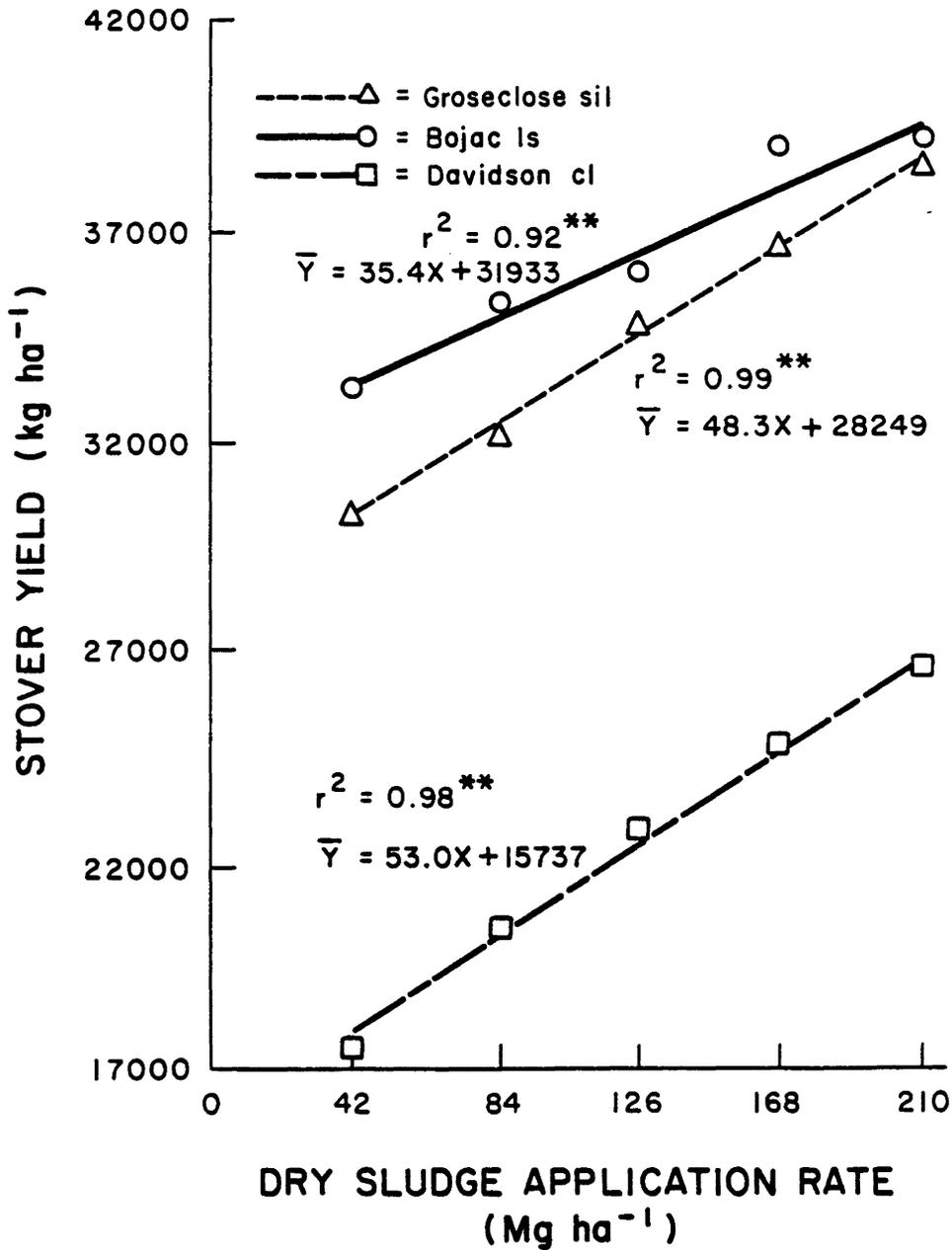


Figure 3. Effect of sludge application on corn stover yield on three soils in 1984.

5.4.2 B. Metal Extractability

DTPA-extractable Cd, Cu, Ni, and Zn in the three soils increased as a function of increasing sludge application rate (Figure 4). The order of magnitude of the DTPA-extractable metals for the soils were Cu>Zn>Ni>Cd. These results reflect the trace metal composition of the sludge which was of the same order. Previously, Sposito et al. (1984) showed that the total (4 M HNO₃) trace metal contents of two soils, a Greenfield sandy loam (Typic Haploxeralf) and a Domino loam (Xerollic Calciorhid), at any level of sludge application reflected the trace metal composition of the sludge.

Correlation analyses were completed to assess the relationship between DTPA-extractable metal and earleaf metal concentration. Coefficients of simple correlations of 0.62* and 0.58* were obtained between DTPA-extractable Cu and Zn and concentration of these heavy metals in the earleaf from the Davidson soil. The correlation coefficient between DTPA-extractable Zn and the concentration of this micronutrient in the earleaf from the Groseclose soil was $r = 0.65^{**}$. Negative correlation coefficients of $r = -0.69^{**}$ and $r = -0.76^{**}$, were obtained between Cd and Ni concentrations in the earleaf and DTPA-extractable Cd and Ni for the Davidson soil, respectively. These inverse relationships probably reflect dilution in the metal concentration due to

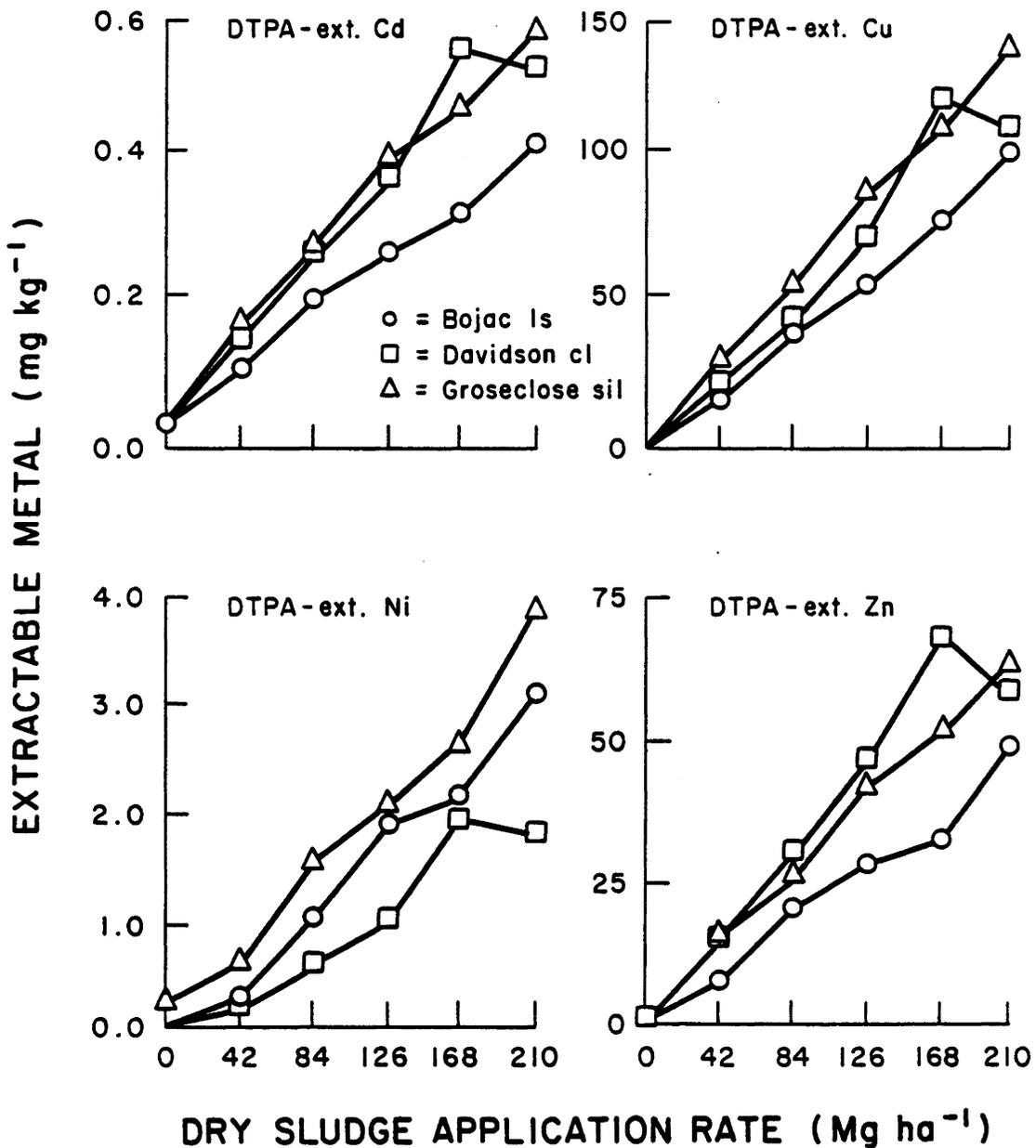


Figure 4. Effect of sludge application on DTPA-extractable Cd, Cu, Ni, and Zn in the Ap horizon of three soils in 1984.

the yield increase from N application. Correlations were nonsignificant between DTPA-extractable Cd, Cu, Ni, and Zn and concentrations of the respective metals in earleaves for the combined data from the three soils.

These relatively low correlations are possibly due to the small increases in plant tissue concentration with the increasing sludge rate. Hinesly et al. (1978) suggested that some critical level of Cd or Zn in corn ear leaves must exist before concentrations in grain are increased significantly. Their research showed that leaf-Zn and grain-Zn concentrations were correlated for 20 corn inbreds grown on all sludge treated plots. For the control treatment and one-quarter maximum sludge treatment, however, Zn concentrations in corn grain and leaves were unrelated. Similar results were shown for Cd. Chaney (1975) concluded that increases in soil Cu lead to small increases in plant-shoot Cu levels due to accumulation in plant roots rather than shoots, whereas increases in soil Zn, however, lead to large increases in plant-shoot Zn.

An inherent problem associated with the prediction of metal availability in sludge-amended soils for the determination of metal levels in plant tissue is the heterogeneous composition of complexing sites in soil systems and the competition among cations present in soil solution for these

sites. At low rates of metal application, the soil may control metal ion activities in solution available for plant uptake. Corey (1981) has referred to the possibility that relatively pure precipitates of specific metals may exist in discrete form in some sludges and that, where high rates of these sludges are applied to soils, solubility of the precipitates controls metal ion activities in soil solution. The differences in metal selectivity coefficients, along with other soil and plant factors make prediction of metal availability in sludge-amended soil difficult.

This field research indicates that the DTPA extractant provides an estimate of the amounts of applied heavy metals in sludge-amended soils. The DTPA-extractable metal levels increased with sludge rate and reached a maximum of 0.6, 150, 4.0, and 75 mg for Cd, Cu, Ni, and Zn kg^{-1} , respectively without any metal phytotoxicity. Rappaport et al. (1986) showed that a portion of Zn extracted from sludge-amended soils with DTPA is plant unavailable. High DTPA-extractable Cu and Zn also were reported in other investigations where either sludge or metal enriched-sludge were applied to soils (Korcak and Fanning, 1978; MacLean and Dekker, 1978; Mitchell et al., 1978). Gaynor and Halstead (1976) showed that sludge greatly increased DTPA-extractable levels of Cd, Cu, and Zn, but not Ni.

5.4.3 C. Plant Metal Concentration

Metal concentrations in corn earleaf and grain grown on the three soils are shown in Table 14. Concentration of Cd in the corn grain ranged widely among treatments within each experimental location. Giordano et al (1975) applied 2.5, 5.0, and 10.0 kg ha⁻¹ of sludge borne Cd and showed concentrations of Cd in corn grain from 0.9 to 1.2 mg kg⁻¹. Cadmium in the corn grain was well below the 0.9 mg kg⁻¹ considered normal for corn grain (Kirkham, 1975). Sludge application did not increase Cu concentrations in earleaves from plants grown on the three soils (Table 14). An increase in Cu concentration in corn grain occurred only on the Davidson clay loam. The normal Cu concentrations in earleaves sampled at the early silk growth stage range from 3 to 15 mg kg⁻¹ and for mature corn range from 1 to 5 mg kg⁻¹ for non-sludged soils (Jones and Eck, 1973). Copper concentrations in earleaves and grain were within these respective ranges even where sludge-borne Cu application to the three soils exceeded the recommended rate in USEPA guidelines (1983) by approximately threefold.

Nickel concentrations were not increased in the corn earleaf and grain harvested from the Davidson soil. There were increased levels of Ni, however, in the corn earleaf and grain harvested from the Bojac and Groseclose soils (Ta-

Table 14. Elemental composition of the corn earleaves and grain from the sludge-amended soils under study in 1984.

Dry sludge application	Earleaf concentration				Grain concentration			
	Cd	Cu	Ni	Zn	Cd	Cu	Ni	Zn
Mg ha ⁻¹	----- mg kg ⁻¹ -----							
	<u>Bojac loamy sand</u>							
-- [†]	0.31a [‡]	9.4a	0.54b	66a	0.02a	4.8a	0.44b	31a
42	0.30a	6.1c	1.02a	69a	0.01a	5.1a	0.64ab	33a
84	0.30a	6.6abc	0.88a	68a	0.02a	4.6a	0.58b	33a
126	0.32a	9.6a	0.94a	56a	0.01a	4.0a	0.62b	34a
168	0.25a	6.5bc	0.80a	60a	0.01a	4.3a	0.66ab	30a
210	0.28a	6.5bc	0.84a	71a	0.01a	4.9a	0.88a	36a
	<u>Davidson clay loam</u>							
--	0.09a	8.9a	0.38a	21b	<0.01a	4.0b	0.10a	22b
42	0.07ab	6.1b	0.41a	21b	-- [§]	5.1ab	0.90a	27ab
84	0.04bc	8.4a	0.36a	25ab	--	5.8a	0.90a	30ab
126	0.03c	8.9a	0.31a	26ab	--	5.6a	0.49a	31a
168	0.02c	9.1a	0.20a	28a	0.08a	4.7ab	0.33a	26ab
210	0.04bc	8.6a	0.23a	27ab	0.49a	4.7ab	0.35a	23ab
	<u>Groseclose silt loam</u>							
--	0.05c	8.8a	0.28b	22c	0.09b	4.2abc	0.44c	28a
42	0.12ab	9.1a	0.39ab	28c	0.06b	3.2c	0.56bc	26a
84	0.14a	9.3a	0.42a	39b	0.06b	3.7bc	0.62abc	25a
126	0.08bc	8.9a	0.35ab	40b	0.05b	4.0abc	0.82abc	32a
168	0.05c	10.5a	0.36ab	48a	0.36ab	4.9a	1.07a	31a
210	0.10ab	9.3a	0.46a	45ab	0.65a	4.7ab	1.02ab	32a

[†] Nitrogen was applied to the control treatment at the rate of 200 kg ha⁻¹ as NH₄NO₃ prior to planting.

[‡] Column means for each soil followed by different letters are significantly (P = 0.05) different.

[§] Sample not analyzed.

ble 14). Corn earleaf and grain harvested from the Bojac soil were 0.54 and 0.44 for the control and 0.84 and 0.88 mg kg⁻¹ for the highest sludge rate. Corn earleaf and grain harvested from the Groseclose soil were 0.28 and 0.44 for the control and 0.46 and 1.02 mg kg⁻¹ for the highest sludge rate. There is a dearth of literature on Ni availability in sludge-amended soils. However, it has been shown (Soon et al., 1980) that, similar to the experimental results on the Bojac and Groseclose soils, Ni accumulation occurred in corn stover and grain where plants were grown on a sludge-amended Conestoga loam (Aquic Mollic Eutrochrept).

Concentrations of grain Zn were not increased from sludge application on the Bojac and Groseclose soils, but were increased in the grain harvested from only the 126 Mg ha⁻¹ sludge application rate for the Davidson clay loam (Table 14). Zinc concentrations in ear leaves usually varied directly with increasing levels of applied Zn on the Groseclose soil. Increases in Zn concentrations in corn earleaves and grain, have been reported in other studies where sludges were applied to soils (Cunningham et al., 1975; Gaynor and Halstead, 1976)

Nickel and Zn levels in the corn usually varied with increasing rates of sludge application, whereas Cd and Cu generally resulted in small increases (Table 14). In sum-

mary, metal concentrations in the grain and earleaves from the three sludge-amended soils (Table 14) were within normal levels (Allaway, 1968; Hutchinson, 1981; Jones and Eck, 1973; Page et al., 1981). The application of sludge was not rate limiting on the three soils under study with respect to a decrease in crop yield or increase in metal concentrations. It should be pointed out, however, that the potential hazard of plant available heavy metals in soil could pose a threat to soil productivity and water quality if loading rates of sludge-borne metals are not regulated. However, data indicate that when sludge is applied at a rate that does not exceed the crops N requirement and when metals are applied within USEPA (1983) guidelines, the use of sludge on agricultural land as a disposal alternative on well-drained soils has environmental and economic advantages.

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Chapter VI

SUMMARY AND CONCLUSIONS

This research was conducted to fill knowledge gaps and to better understand heavy metal availabilities in sludge-amended soils in the eastern United States. In this investigation, information was obtained on the suitability of the dilute HCl-H₂SO₄ and DTPA soil extractants for prediction of Zn uptake by corn, on the accumulation of Cr in corn and barley from soils amended with a high chrome-sludge, and on heavy metal availabilities in crops grown on sludge-amended soils. The specific findings from this research are listed below.

1. Corn earleaf Zn concentration correlated more closely with DTPA-extractable Zn ($r = 0.64^*$) than with dilute HCl-H₂SO₄-extractable Zn ($r = 0.35$) on 14 sludge-amended soils.
2. Dilute HCl-H₂SO₄-extractable Zn was related to exchangeable and specifically adsorbed Zn, organically bound Zn, and noncrystalline hydroxide and oxide bound Zn ($R^2 = 0.98^{**}$) for 14 sludge-amended soils.
3. A coefficient of multiple determination ($R^2 = 0.77^{**}$) for 14 sludge-amended soils was obtained

between corn earleaf Zn concentration and a two variable regression equation comprised of DTPA-extractable and organically bound Zn.

4. The dilute HCl-H₂SO₄ and DTPA reagents extracted soil Zn fractions from 14 sludge-amended soils which were unavailable for uptake by corn plants.
5. The concentration of Cr in corn and barley tissue sampled during a two year field experiment was <2.8 mg kg⁻¹, although the six treatment rates of sludge supplied 0, 1021, 2042, 3063, 4084, and 5105 kg Cr ha⁻¹ on a Bojac loamy sand, Davidson clay loam, and Groseclose silt loam. Formation of insoluble Cr compounds in the pH range of the soils may have accounted for the low concentration of Cr in the corn and barley tissue.
6. Although the Acredale soil is poorly-drained and should be a prime candidate for increased metal mobility and uptake, there were no detrimental effects on crop production from applied metals. Neither metal phytotoxicity nor metal movement occurred within the soil profile where Cu was applied in excess of USEPA guidelines.

7. Sludge Cu and Zn applied in excess of 480 and 60 kg ha⁻¹ of USEPA guidelines to Bojac loamy sand, Davidson clay loam, and Groseclose silt loam did not increase metal levels in corn grain and earleaf above normal levels in plants grown on non-sludged soils.
8. Relatively low correlations ($r \leq 0.76^{**}$) occurred between DTPA-extractable Cd, Cu, Ni, and Zn and the respective metal concentration in corn earleaves for plants grown on three sludge-amended soils. These relatively low correlations are possibly due to the small increases in plant tissue concentration with increasing sludge rate. Differences in soil and plant factors make prediction of metal availability in sludge-amended soils difficult. At low rates of sludge-borne metal application, the soil may control metal solubility and, at high rates, the sludge may govern metal availability.
9. Findings in this field and laboratory research add reliability to the USEPA (1983) guidelines for total cumulative application of sludge-borne metals.

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