EFFECTS UPON GROWTH AND NUTRIENT COMPOSITION OF CORN (ZEA MAYS) PLANTS GROWN ON TWO DIFFERENT TEXTURED MICHIGAN SOILS CONTAMINATED WITH NICKEL AND CADMIUM

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ABSTRACT

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By

Mary Frances Traynor

Rubicon sand (Muskegon County, Michigan), and Morley clay loam (Washtenaw County, Michigan) were treated with $NiCl_2$ and $CdCl_2$ and cropped with corn under greenhouse conditions.

Nickel and Cd were applied in equal milliequivalent concentrations ranging from 0.05 to 1.00 milliequivalent of metal/100 g air-dried soil. Treatments were replicated three times and a control set was included. Rubicon sand was adjusted by liming with $CaCO_3$ to a pH of 6.7; the native pH of Morley clay loam was 6.7-6.8. Plant and soil samples were analyzed for Cd, Cu, Fe, Mn, Ni, and Zn by atomic absorption spectrophotometry.

Cadmium contamination of both soils resulted in severe growth retardation at all levels of treatment. Increasing concentration of Cd in the soil resulted in an increase in Cd concentration and uptake by the plants.

Nickel contaminated soil did not retard plant growth significantly. Increasing levels of applied Ni created a significant soil x level interaction. At the higher levels of treatment, more Ni was taken up by plants grown on Morley clay loam than those grown on Rubicon sand.

Cadmium was more extractable than Ni from both soils. Less Ni was removed by extraction from Rubicon sand than Morley clay loam. Plants grown on both soils took up more Mn with increasing level of Ni treatment. The Cd treated Morley clay loam caused a decrease in plant Mn uptake.

Concentrations of Cu, Fe, and Zn were not affected by metal treatment; uptake of these metals was affected.

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TABLE OF CONTENTS

page

LIST OF TABLES

Table page

CHAPTER 2

CHAPTER 3

Table page

APPENDIX

INTRODUCTION

The distribution of heavy metals from naturally occurring ores to various products and wastes is a result of man's activities in altering his environment. Some metals (Zn, Cu, Mn) are essential micronutrients for all living organisms; whereas, others (Ni, Cd, Hg) are not known to have any essential role in life processes. Both types of metals can result in deleterious effects if present in excess of the requirements of plants and animals (2).

Cadmium in all of its chemical forms is toxic to living species (13). The ubiquitous toxicity of Cd constitutes the basis for enviornmental concern. Nickel, being ten times as toxic as Zn, is also very injurious to plants (46, 69, 71).

Due to the potential toxicity of these elements in the environment this study was initiated to determine the effects of the growth of corn (Zea mays) plants propagated on two different textured soils contaminated with Ni and Cd; the inactivation of these metals by the soil; the release of other nutrients, and the effect upon the nutrient composition of the crop. These properties are of essential importance in the determination of a soil which would be suitable for use as a waste disposal area for materials containing Cd and Ni.

CHAPTER 1

LITERATURE REVIEW

Chemical Properties of Cadmium

The behavior of Cd in its various modes of production, application, dissipation, and toxicity is intimately related to its position in the periodic chart of the elements. Cadmium is chemical element number 48 and has an atomic weight of 112.40. The only stable valence exhibited by Cd is two. Zinc, Cd and Hg follow directly after the so-called transition elements. The behavior of Cd in soils, rivers, lakes and the oceans may be strongly influenced by the fact that cadmium ion (Cd^{++} atomic radius @ 25 C°is 1.489 A) has the same charge and is nearly the same size as calcium ion (Ca^{++} atomic radius @ 25°C is 1.971 A). It, therefore, can readily replace this abundant element in minerals and sediments (3). Baes (3) postulates that the toxicity of Cd stems in part from its ability to displace its neighboring element, Zn, and bind itself more strongly to the nitrogen and sulfur groups of enzymes. The most important donor atoms which link metal ions to biological molecules are oxygen (O), nitrogen (N), and sulfur (S). Baes (3) has reported that Cd is held more tightly than, and should replace Mn^{++} and Fe^{++} from nitrogen donors. Additionally, Cd is bound to S more strongly than all of the essential metals except Cu.

Cadmium in Soil and Plants

Vinogradov (70) has discussed the geochemistry of Zn, and hence Cd in soils. He has found that parent rock materials of basaltic origin have a higher Cd content than those of granitic rocks. Lagerwerff (32) reports typical low, average, and high concentrations of Cd in soils of 0.11, 0.34, and 0.56 ppm, respectively. Schroeder (59) reports a Cd content of 0.15 ppm for unfertilized field soil, 0.8 ppm for tilled but unfertilized soil and 3.38 ppm for (phosphate) fertilized soil. In areas of suspected Cd contamination in rice (*Oryza sativa* L.) fields in Japan, concentrations of 1-50 ppm have been reported.

Studies of plants grown on contaminated soils indicated that plants can readily absorb Cd from soil (25, 26, 33, 37). John, et al. (24) found that Cd in radish and lettuce plants was significantly related to the ability of the soil to adsorb Cd. Lagerwerff (32), however, found significant increases in radish yields which coincided with increases in the Cd and Zn content of soils. This was perhaps due to alleviation of Zn deficiency. Turner (67) has reported the effect of Cd on Cd and Zn uptake by selected vegetable species from solution cultures. He found variations in response to Cd treatment between species, particularly sensitive to Cd damage. Most species apparently tolerated Cd levels in nutrient solution up to 0.1 ug/ml. He noted an increase in Zn uptake resulting from Cd treatment. Haghiri (17) showed that although foliar-applied Cd was readily translocated into various parts of soybeans, uptake of Cd via the root system was significantly higher. He showed that Cd in various parts of the soybean plant decreased in the following order: stem>leaves>pods>beans. Soybean plants appear to be more sensitive to Cd than wheat. In general, there is a depression in yield due to soil-applied Cd. Preliminary studies by Allaway (1) indicated that plant growth depression due to Cd toxicity tended to occur after plants had accumulated approximately 3 ppm of this metal. Page (45) states that plants cultured in soils containing soluble Cd will absorb substantial amounts of this element. He also points out that competitive effects of other ions, particularly zinc, may influence the amounts of Cd absorbed by plants. Finding that the uptake of Cd by plants is significantly related to the ability of the soil to adsorb Cd, John (24), has described Langmiur adsorption isotherms for 30 soils from British Columbia. He has determined the adsorption maximum and a coefficient relating to the bonding energy of the soil for Cd. The influence of 13 soil characteristics upon these coefficients was investigated.

Sources of Cadmium

The natural geochemical partnership of Cd and Zn, reported by Vinogradov (70) accounts for an unusual rate of mobilization into man's environment. The release of Zn and its associated Cd into the environment in the manufacturing and recycling operations occur in two ways: (1) by volatilization and release of the metals or their compounds to the atmosphere, and (2) by release to streams in aqueous operations such as electrolysis and wet chemical processes (15). The apparent U.S. demand for Cd in 1968 was 13,328, 000 pounds which was predominantly used in plating, pigments, plastic stabilizers and metallurgy (15). Approximately 97% of the demand for Cd is in dissipative uses such as paints, plastics or plating (15). Geographically, 58% of the Cd-consuming industry of the U.S., according to a Bureau of Mines Survey (15) is in states bordering the Great Lakes, of these, Michigan accounts for 8%.

Cadmium in roadside plants and soils, decreasing with distance from the traffic, was attributed to Cd as an impurity in Zn-containing additives in motor oils and Zn compounds used in vulcanization of rubber tires (33, 34). Cadmium in the atmosphere, and the subsequent settling of the airborne particles on vegetation and soils, predominantly originates from smelting and electroplating of metals (27, 31, 39). Particulate fallout from such metallurgical processes was cited as a source of excessive amounts of the heavy metals in soils near a battery smelter (25). The industrial contribution to Cd enrichment of soil in Grand Rapids, Michigan, was documented by Klein (28). He found that soils of residential and agricultural areas had less Cd and Ni than industrial soils by a factor of about 1.4. Tsuchiya (66) postulated that the Cd, Zn, Pb mining operations and the run-off from waste piles at an upstream site were responsible for contamination of water and rice in Japan. Apart from its association with Zn, Cd compounds used as fungicides (25, 33, 51) and Cd present in superphosphate fertilizer (56) also resulted in the entry of heavy metals into the soil.

Cadmium in Water and Air

Bowen (6) has given concentrations of Cd found in water, air, plants and soils. In nonpolluted areas the normal concentration of Cd in water is 1 ppb. However, values greater than 10 ppb have been reported for natural waters and water for consumption (12). Cadmium enters surface waters from various industrial and agricultural sources and into processed drinking water supplies from pipes, water heaters, etc. Normal wastewater processing removes only a portion of the metal before returning the water to a surface stream for reuse. Since the water is reused for drinking water, irrigation, livestock watering, and aquatic life, some Cd may reenter the biological processes (19, 30).

Cadmium in the air varies with distance from a

Cd-emitting source. Hise and Fulkerson (19) reported that the yearly mean concentration of Cd in the air at lower Manhattan was 0.023 ug/m^3 while at a nonsuburban site it was 0.003 ug/m^3. They report that the average intake by inhalation is very small compared to that from food. Measurements of metal aerosols have been reported for several cities (21, 35, 36, 58).

Cadmium in Human Health

Cadmium, although not present in as large of quantities as other metals is much more toxic. Poisoning by this element can occur by intake or injection of Cd salts or by inhalation of CdO. Carroll (7) has made a good correlation between cardiovascular death rates and the concentration of Cd in the air as an industrial pollutant. Cadmium toxicity in mammals is well established (57). Experiments with mammals have shown Cd and its compounds can induce malignant tumors in rats (16). Evidence for the accumulation of Cd in human kidneys and livers, and the possible effects on human health have been reported (48, 49, 54, 55). More intensive study of Cd in soils and plants originated when recent reports associated the excessive accumulation of this heavy metal in man with hypertension (54), emphysema, chronic bronchitis (38) and the "ouch-ouch" disease (66). Although magnitudes of this metal in different matrices are small, man accumulates Cd in his kidney and liver (55).

Cadmium in Foodstuffs

Food is man's largest source of Cd intake. The Cd content of individual foods and of total diet have been analyzed many times with widely varying results (12, 42, 50, 59). Fruits rank the lowest in Cd content, whereas animal liver and kidney and shellfish have the highest contents. Variations may be accounted for by: (a) regional differences in soil and water, (b) agricultural chemicals used, (c) tendency for plant or animal to retain or concentrate Cd, (d) processing procedures, and, (e) sampling and analytical procedures (19).

Chemical Properties of Nickel

Nickel occurs in nature mainly in combination with As, At and S. Only Ni^{++} occurs in the ordinary chemistry of the element. The chemistry of Ni is not simple because of the existence of complex interconversions of various structures, i.e., octahedral, tetrahedral and square, as well as the formation of polymers by sharing of ligand atoms (8).

Stability diagrams for chelates of Cd^{++} and Ni^{++} have been presented by Norvell (43) to illustrate one method of estimating the influence of chelating agents on the solubility of potentially hazardous heavy metals in soils. The effectiveness of the chelating agents as chelates for Ni^{++} in calcareous soils would be in the order: DTPA, HEDTA, EDTA>CDTA>NTA>EDDHA>CIT>OX, EGTA,P_3O_{10} (diethylenetriamine-penaacetic acid, hydroxyethylethylenediaminetriacetic acid, ethylenediaminetetraacetic acid, cyclohexanediaminetetraacetic acid, nitrilotriacetic acid, ethylenediaminedi-O-hydroxyphenylacetic acid, citric acid, oxalic acid, ethyleneglycol-bis(2-aminoethylether)tetraacetic acid, and triphosphoric acid, respectively). Clearly, DTPA, HEDTA, EDTA, and CDTA could most effectively increase the solubility of Ni^{++} in soils (43). Schnitzer and Skinner (52, 53) have determined stability constants for Ni^{++}, Pb, Mn and fulvic acid. Their log K values for metals of the first transition series fail to follow the Irving-William's stability series (62). Stability constants reported for metal-soil organic-matter complexes are generally lower than those for complexes of the same metal with commercial chelating agents, such as EDTA and HEDTA.

Nickel in Soil and Plants

Vanselow (68) has noted that there are soils in scattered regions of the United States that have sufficient concentrations of Ni^{++} to be phytotoxic. Patterson (46) and Hodgson (20) have reported the range of total Ni in normal soils to be between 5 and 20 ppm but may be as high as 2000 ppm in soils derived from ultrabasic igneous rocks (serpentine), definitely a phytotoxic concentration. Massey (40) has conducted a study on soils contaminated from mining operations in Kentucky. Of the three metals investigated, Cu, Zn, and Ni, nickel is the most likely to remain in solution in toxic amounts after the pH is raised by liming. He found that approximately 4.3, 2.5 and 1.4 ppm Ni would be found in solution at pH of 4.5, 5.5 and 6.5, respectively. This is compared to 2.5 ppm which is toxic to oats (46, 50). Plants affected by Ni toxicity show two types of symptoms, one specific to the element such as white longitudinal striping in oats, and the other, chlorosis and necrosis characteristic of induced iron deficiency.

This has been investigated by Crooke, et al. (9, 10, 11). The most likely mechanism for the production of induced iron deficiency is the replacement of iron by the toxic metal in some complex essential to normal metabolism (11). The necrosis produced by Ni might be the result of severe Fe deficiency (22) but Crooke et al. (10) showed that a high iron supply reduced the severity of necrosis no more than could be accounted for by the reduction in Ni content.

Hunter and Vergnano (22) described a wide range of crops exhibiting Ni toxicity symptoms. Plant species vary considerably in their susceptibility. Barley is resistant while wheat, ryegrass and beans are little affected. Oats, clover and potatoes are moderately affected, followed by turnips, swedes, cabbage and kale, with beet being the most sensitive crop. The distribution of absorbed Ni in plants depends on the species (22). Tiffin (65) has found negatively charged Ni in xylem exudates of various plants. Although liming has traditionally been used to control toxicities from developing, the hydrous oxides of Mn and Fe, which are nearly ubiquitous in clays, soils, and sediments, have been proposed by Jenne (23) to furnish the principal control on the fixation of Co, Ni, Cu, and Zn.

Patterson (46) has reported work conducted upon the pH of the soil and its effects upon Ni toxicity. He found that toxic symptoms developed in wheat plants grown on a soil of pH 5.1 with 80 and 160 ppm Ni applied. At pH 6.5 only slight toxicity symptoms occurred and at pH 7.5 none were visibly affected. Uptake of Ni by the plants was small at pH 6.5 and 7.5 at levels below 80 ppm Ni in soil. He found that Ni tends to concentrate in the grain, the content of which is between two and three times the level in straw. As a general guide it may be taken that if the total Ni in a soil is below 20 ppm at a pH of above 5.5 no damage to crops may be expected. At a pH level around 7.5 considerably higher levels of Ni can be safe; whereas in more acid soils even 5 to 10 ppm Ni can be toxic.

Nickel in Enzymatic Systems

Nickel is not known to be essential for plants or animals. Schroeder (58) believes that it behaves like an essential trace element because: (a) it is ubiquitous in the biosphere, (b) shows biological activity *in vitro*, affecting certain enzyme systems, (c) is toxic to mammals only in astringent doses, and, (d) has a low molecular weight and two interchangeable valencies.

Nickel activates several enzyme systems including arginase (18), carboxylase (61), acetyl coenzyme A synthetase

(72), and trypsin (63). It inhibits acid phosphatase under certain conditions (44) and catalyzes the enzymatic decarboxylation of oxalacetic acid (61). Nickel is found to be consistently present in ribonucleic acid (RNA) from diverse sources in concentrations many times higher than in the native material from which the RNA is isolated (64).

Nickel as a Carcinogenic Metal

The trace elements most extensively studied in mineral nutrition are Fe, Cu, Mn, and Mo. As the human body ages, a large number of these elements accumulate. When present in excess, they may be responsible for the induction of cancer. Adequate documentation exists for only a small number of these metals. Unequivocal experiments reveal that Ni, Cd, and some Cr compounds are true metal carcinogens (14). Pure metallic Ni and many of its compounds can be considered as causes of cancer (47). Nickel compounds found to be carcinogenic include Ni_3S_2, NiO, $NiCO_3$. These are soluble, insoluble and moderately soluble compounds. The target organ for this element is usually the muscle (14).

Human beings are constantly being exposed to carcinogenic hydrocarbons from the atmosphere. The lungs and liver inactivate these hydrocarbons by an induced enzyme system, benzyrene hydroxylase. Nickel inhibits this enzyme (64); thus, it may permit the hydrocarbon to exist for longer periods allowing a longer time for the carcinogen to interact with the tissues.

Nickel in Foodstuffs

Nickel occurs regularly in soils and plants in concentrations substantially higher than those normally present in animal tissues and fluids. Common pasture plants contain 0.5-3.5 ppm Ni on a dry weight basis (41, 60). Kent and McCance (27) give an estimate of 0.3 to 0.5 mg Ni/day, and Schroeder et al. (58) give a similar calculated range of 0.3-0.6 mg Ni/day for human adults. The amounts and proportions of the different classes of foodstuffs consumed result in intakes of Ni which vary greatly. Schroeder et al. (58) indicate that vegetarian diets supply more Ni than nonvegetarian diets. He estimates that 0.7-0.9 mg Ni/day is consumed in a vegetarian diet in comparison to 0.003-0.01 mg Ni/day of a diet high in refined foods and low in vegetables.

Data on the Ni content of foods are meager. Approximately 50 years ago Bertrand and Macheboeuff (4, 5) reported levels of 1.5 to 3.0 ppm Ni on a dry weight basis for green leafy vegetables and 0.15 to 0.35 ppm for fruits, tubers, and grains. Schroeder et al. (58) have recently confirmed these data.

CHAPTER 2

EFFECTS OF NICKEL AND CADMIUM CONTAMINATED SOILS ON NUTRIENT COMPOSITION OF CORN PLANTS[1]

Abstract

Rubicon sand from Muskegon County, Michigan was treated with $NiCl_2$ and $CdCl_2$ and cropped with corn. The nutrient status of the soil was determined before and after cropping by chemical extractions, and the plant tissue was analyzed for several metals.

Nickel and Cd were applied in equal amounts of milliequivalents per 100 g soil. Treatments ranging from 0.05 to 1.00 milliequivalent of metal/100 g soil were replicated three times. A control set was included. The soil was limed to a pH of 6.8.

The corn was harvested 5 weeks after planting. The dried, ground corn plant tissue was subjected to a nitric-perchloric acid digestion and analyzed for Cd, Cu, Fe, Mn, Ni and Zn by atomic absorption spectrophotometry. The soil metal levels after cropping were determined by extractions with 0.1 $\underline{N}$ HCl, 1 $\underline{N}$ NH_4OAc or 0.005 $\underline{M}$ DTPA.

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[1] Michigan Agricultural Experiment Station Journal Article No. 6416.

The Cd-treated soils retard grown more than Ni-treated soils indicating a greater toxicity due to Cd than to Ni for corn. Likewise, Cd was taken up by corn to a greater extent than was Ni.

Introduction

The natural geochemical partnership of Cd and Zn reported by Vinogradov (19) accounts for entry of Cd into the environment. Atmospheric Cd, and the subsequent settling of the airborne particles on vegetation and soils, originates predominatly from smelting and electroplating of metals (7). Apart from its association with Zn, Cd compounds used as fungicides (3, 9, 12) and Cd present in superphosphate fertilizer (14) also resulted in the entry of heavy metals into the soil.

Intensive study of Cd in soils and plants originated when recent reports associated the excessive Cd accumulation in man with hypertension (15), emphysema, chronic bronchitis (10) and the "ouch-ouch" disease (17).

In considering the soil-plant-animal-human system into which heavy metals may enter at any point and affect the entire system, one must direct attention to the most probable points of entry. Drinking water and diet are chief sources of Cd intake (16). Dustfall Cd enters water and food supplies in substantial amounts whereas Cd in inspired air contributes only 1-3% of the daily human intake. Cadmium level studies of plants grown on contaminated soils indicate that plants can readily absorb Cd from a soil (3, 4, 8). John, et al. (4) found that the Cd in radish and lettuce plants was significantly related to the soils' ability to adsorb Cd.

Nickel occurs commonly in soils and plants in concentrations substantially higher than those normally present in animal tissue and fluid. Kent and McCance (5) and Schroeder, et al. (13) estimate a 0.3 to 0.5 mg Ni intake per day for human adults. Vanselow (18) reported that soil contains 10 to 1000 ppm Ni and that soils in scattered regions of the United States have sufficient concentrations of Ni to be phytotoxic. Experimentation has shown that Ni, Cd and some Cr compounds are true metal carcinogens (1).

Increasing public concern with the problems of waste disposal have brought pressures to solve not only municipal but also industrial pollution problems. The metal-plating industry in particular is somewhat unique because the wastes are not principally organic in nature. But rather, they are toxic because they contain heavy metal ions (Cd, Cr, Cu, Ni, and Zn) which interfere with the metabolism of living systems. The need for treatment of these wastes and the fact that soil has a cation exchange capacity with specific bonding sites offers interesting possibilities for inactivation and renovation of these metal ions by wastewater application to soil.

If agricultural lands were (irrigated) over a period of time with effluent containing considerable quantities of heavy metals three phenomena could occur: (a) the metals being precipitated or strongly bound to the soil complex, unavailable for plant uptake, (b) the metals passing through the soil profile and entering underground water supplies, or,

(c) the response and nutrient composition of crops grown on this soil.

In an attempt to verify these points, research was initiated using a soil originating from a 10,000 acre disposal site near Muskegon, Michigan. A greenhouse study of the response of corn grown on Ni and Cd contaminated soil and the nutrient composition of the crop was done.

Methods and Procedures

Surface (0-4 in.) soil samples were collected from the site of the waste disposal area at Muskegon, Michigan. The soil was passed through a 20 mm stainless steel screen, air dried and stored in plastic containers. Samples for laboratory work were passed through a 20 mm plastic screen.

Soil physical analysis, pH, and organic matter content were determined by the MSU Soil Testing Laboratory. Cation exchange capacity was determined by the sodium saturation method (2) (Table 1).

Table 1. Characteristic properties of Rubicon sand, A horizon.

% Sand	89.38
% Silt	1.18
% Clay	9.44
% O.M.	2.16
C.E.C. (me/100g soil)	5.7
pH	5.0

A greenhouse project was designed to test the response of corn (Zea mays) to a soil contaminated with Cd and Ni; the inactivation of these metals by the soil; the release of other nutrients, and the effect upon the nutrient composition of the crop. Six treatments, each in triplicate, of $NiCl_2$ and $CdCl_2$ (0.05, 0.10, 0.20, 0.50, 0.75 and 1.00 me/100g soil) as well as triplicate controls were utilized in this experiment.

Two and a half kilograms of soil/pot received lime (to adjust pH to 6.8) fertilizer (NPK) and metal treatments, mixed in by hand. The pots, containing drainage holes, had distilled water added to 15% by weight and were allowed to equilibrate for 1 week, then 12 kernals were planted per pot. After emergence the seedlings were thinned to 8 plants/pot. Plants were harvested after five weeks of growth, dried in a forced air oven at 60°C and ground in a Wiley stainless steel mill with a 20 mesh screen. Soil core samples were removed from each pot and air-dried.

Plant samples were digested with a nitric-perchloric acid mixture then analyzed for Cd, Cu, Fe, Mn, Ni, and Zn on a Perkin-Elmer 303 atomic absorption spectrophotometer. The soil samples were equilibrated with three extractants: 0.005 M DTPA (diethylenetriaminepentaacetic acid) (11), 1 N NH_4OAc, and 0.1 N HCl, and analyzed for Cd, Cu, Fe, Mn, Ni and Zn.

Results and Discussion

Increasing levels of Ni when added to the soil, did not significantly increase plant Ni concentration and uptake, except at the highest level of treatment, 294 ppm (Tables 2 and 3). These data indicate that corn plants have an effective mechanism for excluding Ni from uptake and/or translocation under the conditions studied. Data (Table 2) indicate that very high levels of added Ni tended to reduce plant growth slightly, but the degree of toxicity was low. These results indicate that Ni was being removed from soil solution very quickly and effectively.

Table 2. Soil treatment, plant growth and metal content of corn grown on nickel-treated Rubicon sand under greenhouse conditions.[a]

Soil Treatment Nickel		Dry Weight	Plant Metal Concentration					
			Cd	Cu	Fe	Mn	Ni	Zn
me/100 g	ppm	g/plant	ppm					
0.00	0	0.70	0	15	102	50	15	37
0.05	15	0.66	0	18	156	63	15	38
0.10	29	0.67	0	20	158	74	16	44
0.20	59	0.65	0	16	132	82	19	47
0.50	147	0.66	0	18	148	94	16	34
0.75	220	0.67	0	20	148	98	19	40
1.00	294	0.55	0	17	144	116	25	31
LSD (0.05)		NS		ns	ns	13.0	6.4	ns

[a] Each value is the average of 3 replications.

Table 3. Soil treatment, plant growth and metal uptake of corn grown on nickel-treated Rubicon sand under greenhouse conditions.[a]

Soil Treatment Nickel		Dry Weight	Plant Metal Uptake					
			Cd	Cu	Fe	Mn	Ni	Zn
me/100 g	ppm	g/plant	ug/plant					
0.00	0	0.70	0	10	71	35	10	26
0.05	15	0.66	0	12	104	42	10	25
0.10	29	0.67	0	13	104	50	11	29
0.20	59	0.65	0	10	86	53	12	32
0.50	147	0.66	0	12	97	62	10	22
0.75	220	0.67	0	13	99	66	13	27
1.00	294	0.55	0	10	81	64	14	17
LSD (0.05)		NS		ns	ns	14	ns	8.1

[a] Each value is the average of three replications.

Cadmium was much more toxic to the corn plants than was Ni. Addition of Cd to the soil resulted in severe plant growth retardation and elevated Cd concentration and uptake by plants (Tables 4 and 5). The plant growth decreased from 0.70 g/plant in the control to 0.29 g/plant at 281 ppm Cd added to the soil. Levels of plant Cd concentration rose from less than 0.5 ppm Cd to 131 ppm Cd with the same treatments. Cadmium was readily taken up and translocated in the plant and as a result was relatively toxic to the plants. As with Ni, Fe and Mn desorption by soils and concentration in plants was increased by increasing soil Cd levels.

Table 4. Soil treatment, plant growth and metal content of corn grown on cadmium-treated Rubicon sand under greenhouse conditions.[a]

Soil Treatment Cadmium		Dry Weight	Plant Metal Concentration					
			Cd	Cu	Fe	Mn	Ni	Zn
me/100 g	ppm	g/plant	ppm					
0.00	0	0.70	<1	15	107	50	15	37
0.05	28	0.53	26	13	185	71	10	56
0.10	56	0.40	47	14	171	73	15	43
0.20	112	0.44	55	13	206	67	16	37
0.50	281	0.29	131	19	146	84	15	33
0.75	422	0.32	131	10	149	95	12	36
1.00	562	0.25	133	12	128	86	15	30
LSD (0.05)		0.123	25.6	ns	54.8	21.0	ns	ns

[a] Each value is the average of 3 replications.

Table 5. Soil treatment, plant growth and metal uptake of corn grown on cadmium-treated Rubicon sand under greenhouse conditions.[a]

Soil Treatment Cadmium		Dry Weight	Plant Metal Uptake					
			Cd	Cu	Fe	Mn	Ni	Zn
me/100 g	ppm	g/plant	ug/plant					
0.00	0	0.70	<1	10	71	35	10	26
0.05	28	0.53	14	7	99	38	6	31
0.10	56	0.40	19	6	66	29	6	17
0.20	112	0.44	24	6	91	30	7	16
0.50	281	0.29	37	3	42	24	4	10
0.75	422	0.32	42	3	48	30	4	12
1.00	562	0.25	34	3	33	22	4	8
LSD (0.05)		0.123	10.0	2.1	27.4	ns	ns	13.4

[a] Each value is the average of 3 replications.

Soil extractants after cropping (Table 6) indicated that little Ni was extractable compared to the amount added to the soil. Most of the Ni was inactivated in a form that could resist removal by rather strong chemical treatments.

Therefore, most of the added Ni was probably not available to the corn plants. Langmiur adsorption isotherm data indicated much of the Ni was inactivated through an adsorption mechanism. Manganese was desorbed by the soil as Ni levels added were increased, and the increased Mn in soil solution resulted in increased Mn uptake by corn plants (Tables 2, 3, 6). Although the chemical extractants removed only a small part of the Ni added to the soil, the amount extracted correlated well with the amount of Ni added in the original treatment. There was a poor correlation between plant growth or Ni uptake and the amount of Ni added or soil extractable Ni. Except for the increased Mn concentration and a possible increase in plant Fe concentration due to soil Ni addition, the treatments had no effect on metal composition of the plants or on the relative amounts of metals extractable from the Rubicon sand.

Table 6. Soil treatments and soil extractable metal concentrations of Rubicon sand.[a]

Soil Treatments		Soil Metal Concentration					
Nickel		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
me/100 g	ppm	ppm Ni			ppm Mn		
0.00	0	<1	<1	<1	18	5	2
0.05	15	8	4	<1	23	5	3
0.10	29	17	8	<1	15	5	7
0.20	59	31	15	2	19	8	4
0.50	147	73	40	7	21	8	7
0.75	220	96	57	19	28	9	5
1.00	294	155	81	24	10	8	6
LSD (0.05)		21.0	5.7	5.6	8.8	ns	1.5

[a] Each value is the average of 3 replications.

The soil extraction of most metals was not influenced by Cd additions, but the Cd remained more soluble and extractable than did the Ni (Table 7). Relative amounts of Cd extracted from the soil after cropping correlated well with the Cd added to the soil and the amount taken up by plants.

Table 7. Soil treatments and soil extractable metal concentrations of Rubicon sand.[a]

Soil Treatments		Soil Metal Concentration					
Cadmium		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
me/100 g	ppm	----- ppm Cd	--------		----- ppm Mn	--------	
0.00	0	<1	<1	<1	18	5	2
0.05	28	22	23	10	7	5	2
0.10	56	46	41	16	15	4	2
0.20	112	92	79	40	13	7	3
0.50	281	239	206	116	10	9	6
0.75	422	319	309	181	14	11	11
1.00	562	378	364	224	10	11	10
LSD (0.05)		38.9	38.8	31.9	ns	2.9	2.2

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[a] Each value is the average of 3 replications.

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CHAPTER 3

INFLUENCE OF NICKEL AND CADMIUM CONTAMINATION OF RUBICON SAND AND MORLEY CLAY LOAM UPON CORN GROWTH AND METAL COMPOSITION AND EXTRACTABLE SOIL METALS

Abstract

For a greenhouse investigation, Rubicon sand and Morley clay loam were contaminated with $NiCl_2$ and $CdCl_2$ by metal additions ranging from 0.05 to 1.00 me/100 g of soil. Rubicon sand was adjusted to a pH of 6.7-6.8 with $CaCO_3$ while the Morley clay loam was at a native pH of 6.7-6.8. The soils were planted to corn after being equilibrated with the metal additions for one week. The plants were harvested after five weeks of growth and analyzed for Cd, Cu, Fe, Mn, Ni and Zn after being dried in a forced-air oven at 60°C.

Separate air-dry soil samples which were obtained after plant harvest, were extracted with 0.1 N HCl, and 0.005 M DTPA. Each extract was analyzed for Cd, Cu, Fe, Mn, Ni and Zn.

Results indicate that Rubicon sand is more capable of bonding Ni than is Morley clay loam. Nickel levels affected yield only at the highest level of treatment on both soils. Manganese was released by each soil with increasing level of

Ni. Cadmium caused severe toxicity symptoms on plants grown on either soil with growth retardation even at the lowest level of Cd addition. Extractable Cd was similar for both soils at each level of treatment. Concentration of Cu, Fe, and Zn were not affected by metal treatment; uptake of these metals was affected.

Introduction

The increasing needs for alternative methods of wastewater disposal for industrial, agricultural and domestic uses have resulted in efforts to utilize the natural filtering system of the soil. Industrial wastewaters, in particular, may contain heavy metals (Cd, Cr, Cu, Ni, and Zn) which are toxic and interfere with the metabolism of living systems.

Intensive studies of Cd in soils, plants, animals and humans originated after several cases of Cd poisoning were reported in Japan as a result of run-off from wastepiles at mining operations (12). Considerable investigation has also been conducted to determine the sources of Cd pollutants in the environment (6, 9, 10, 14). In order to ascertain the influence of Cd upon plants and various food crops, a number of investigators (3, 4, 5, 7, 11, 13) have initiated programs of study.

Most of the metals which are potentially hazardous in the environment belong to the transition elements of the periodic table. The electrode potentials of these elements indicate a tendency to yield aqueous solutions of their ions. However, the concentrations of metal ions are found to be lower than predicted by solubility due to their adsoprtion and/or coprecipitation with other compounds. Due to their electronic structure, the transition metals form a large number of complex compounds; therefore, chelating agents which may be present in wastewater may therefore cause an apparent increase in the solubility of the metal (1).

It would be very useful to know how different textured soils respond to heavy metal contamination. Therefore, before using soils to treat wastewaters, certain properties of the soil and metals must be known: (a) the capacity of a soil for fixation of metals of this type; (b) the leaching potential of metal cations and anions in a specific soil; and (c) the response and nutrient composition of crops grown on this soil and the differences between soil types.

Methods and Procedures

Rubicon sand from Muskegon County and Morley clay loam from Washtenaw County, Michigan were obtained from the top four inches of the profile. The soils were passed through a 20 mm stainless steel screen, air-dried and stored in plastic containers. Samples for laboratory work were passed through a 2 mm plastic screen and were used on an air-dry basis.

Soil physical analysis, pH and organic matter content were determined by the MSU Soil Testing Laboratory. Cation exchange capacity was determined by the sodium saturation method (2) (Table 1).

Morley clay loam contains twice the amount of organic matter as Rubicon sand. It also has a much higher cation exchange capacity and more surface area due to the higher clay content.

Table 1. Characteristic properties of Rubicon sand, A horizon and Morley clay loam, A_p horizon.

Soil	% Sand	% Silt	% Clay	% O.M.	CEC	pH
Rubicon sand	89.38	1.18	9.44	2.16	5.7	5.0
Morley clay loam	40.40	28.72	30.88	4.17	14.9	6.7

Six treatments each in triplicate, of $NiCl_2$ and $CdCl_2$ (0.05, 0.10, 0.20, 0.50, 0.75, and 1.00 me/100 g soil) [15, 29, 59, 147, 220 and 294 ppm Ni; 28, 56, 112, 281, 422 and 562 ppm Cd], as well as triplicate controls were used in the greenhouse experiment. Two and a half kilograms of soil per pot received lime (to adjust to pH 6.8 on the Rubicon sand). The Morley clay loam had a native soil pH of 6.7. Fertilizer (NPK) and metal treatments were mixed in by hand. The pots, containing drainage holes with filter paper on the bottom, had distilled water added to 20% and 15% by weight for Morley clay loam and Rubicon sand, respectively. They were allowed to equilibrate for one week and were then arranged in a randomized complete block design. Twelve kernels of corn were planted per pot. After emergence the plants were thinned to 8 plants per pot and were harvested after five weeks of growth. All plants were dried in a forced air oven at 60°C and ground in a Wiley stainless steel mill with a 20 mesh screen. Soil core samples were removed from each pot after plant harvest and were air-dried.

Plant samples were digested with a nitric-perchloric acid mixture. Separate subsamples were equilibrated with 2 extractants; 0.005 M DTPA (diethylenetriaminepentaacetic acid) (8), and 0.1 N HCl (hydrochloric acid). Both plant and soil samples were then analyzed for Cd, Cu, Fe, Mn, and Zn on a Perkin-Elmer 303 atomic absorption spectrophotometer.

Results and Discussion

Results indicate that nickel treatments did not result in toxicity to the plants grown on either soil type; however, there was a slight decrease in yield with increasing level of treatment. There is a significant soil-level interaction of Ni concentration and uptake by the plants. At the higher levels of treatment the plants grown on the Morley clay loam concentrated more Ni than those grown on the Rubicon sand (Table 2). A significantly greater amount of Ni was extractable from the Morley clay loam than from the Rubicon sand. There was a good correlation between level of treatment and 0.1 N HCl extractable Ni on both soils (Table 3). With increasing level of metal treatment on both soils, plants took up significantly more Mn; 50-60 percent more than the control plants. Plants grown on Morley clay loam took up more Mn at each level of treatment than did those grown on Rubicon sand (Table 2). Soil extractions (Table 1a) indicated that the Morley clay loam contained considerably more Mn (5-7 times more) than the Rubicon sand and more Mn was extractable with each level of treatment. Soil extractions (Table 1a) indicate the Rubicon sand contained 3.3 times more extractable Fe than Morley clay loam. However, Fe uptake by the plants was not affected by soil type or treatment (Table 2a). Copper and Zn concentration and uptake were not affected (Table 2a); soil extractions likewise were not affected.

Table 2. Comparison of yield and nickel and manganese concentration and uptake by corn plants grown for 5 weeks on nickel-treated Rubicon sand and Morley clay loam.

Nickel		Soil	Yield	Nickel		Manganese	
				concentration	uptake	concentration	uptake
me/100 g	ppm		g/plant	ppm	ug/plant	ppm	ug/plant
0.00	0	RUB	0.70	15	10	50	35
		MOR	0.72	9	7	83	59
0.05	15	RUB	0.66	15	10	63	42
		MOR	0.65	11	8	66	43
0.10	29	RUB	0.67	16	11	74	50
		MOR	0.70	14	10	74	52
0.20	59	RUB	0.65	19	12	82	53
		MOR	0.71	17	12	108	77
0.50	147	RUB	0.66	16	10	94	62
		MOR	0.67	26	17	141	94
0.75	220	RUB	0.67	19	13	98	66
		MOR	0.67	25	16	159	105
1.00	294	RUB	0.55	25	14	116	64
		MOR	0.50	80	40	187	91
LSD (0.05) (Soil X Level)			ns	12.5	7.0	32.2	18.2
LSD (0.05) (Soil)			ns	+	+	+	+
LSD (0.05) (Level)			0.081	+	+	+	+

+Not calculated due to a significant Soil X Level interaction.

Table 3. Comparison of nickel concentrations extractable from Rubicon sand and Morley clay loam.

Nickel		Soil	0.1 N HCl	0.005 M DTPA
me/100 g	ppm		ppm Ni	
0.00	0	RUB	<1	<1
		MOR	<1	<1
0.05	15	RUB	8	4
		MOR	10	8
0.10	29	RUB	17	8
		MOR	18	16
0.20	59	RUB	31	15
		MOR	40	35
0.50	147	RUB	73	40
		MOR	108	82
0.75	220	RUB	96	57
		MOR	163	123
1.00	294	RUB	155	81
		MOR	219	155
LSD (0.05) (Soil X Level)			14.7	5.8
LSD (0.05) (Soil)			+	+
LSD (0.05) (Level)			+	+

[+] Not calculated due to a significant Soil X Level interaction.

It would be expected that more Ni would be extractable from the Rubicon sand than from the Morley clay loam which has a high cation exchange capacity and organic matter content. The high Fe concentration of the Rubicon sand may be responsible for complexing the Ni in a form not extractable with 0.1 N HCl. The fact that the Rubicon sand was limed may also be responsible for this phenomenon; the formation of insoluble $NiCO_3$ may have taken place.

It appears that Ni is replacing Mn from its' bonding site on both soils and making it more available for plant uptake. However, the Morley clay loam contains 5-7 times as much Mn as the Rubicon sand but the plants grown on the Morley clay loam take up only one and one half times as much Mn as those grown on Rubicon sand. The Ni on the Rubicon sand may be replacing more Mn hence making it available for uptake and the Ni then being fixed to the Mn sites.

Both soils contaminated with Cd caused severe plant growth retardation and toxicity. Soil type and treatment level significantly affected yield (Table 4). Cadmium uptake by the plants was significantly affected by increasing level of treatment. There was no significant soil x treatment interaction in plant Cd uptake. Soil extractions (Table 5) indicate a significance due only to level of treatment. Extractable Cd from both soils is similar at each treatment level.

Plant Mn uptake was not affected by soil type. There was, however, a significant soil x treatment interaction (Table 3a). With increasing level of treatment, less Mn was taken up by the plants. Uptake by plants grown on Morley clay loam decreased much more than those grown on Rubicon sand. Soil extractions (Table 4a) indicate a higher Mn content in the Morley clay loam than the Rubicon sand.

Iron uptake was significantly affected by both soil type and level of treatment (Table 3a). Increasing level of treatment caused less Fe to be taken up by the plants. Soil extractions, (Table 4a), however, showed no significant affect due to treatment. There was a significant difference due to soil type. The Cu and Zn uptake by the plants decreased significantly with level of treatment. This may correspond to the plants gradually dying at the higher levels of treatment.

Table 4. Comparison of yield and cadmium concentration and uptake by corn plants grown for 5 weeks on cadmium-treated Rubicon sand and Morley clay loam.

Cadmium		Soil	Yield	Cadmium concentration	Cadmium uptake
me/100 g	ppm		g/plant	ppm	ug/plant
0.00	0	RUB	0.70	<1	<1
		MOR	0.72	<1	<1
0.05	28	RUB	0.53	26	14
		MOR	0.48	28	13
0.10	56	RUB	0.40	47	19
		MOR	0.46	40	18
0.20	112	RUB	0.44	55	24
		MOR	0.33	55	18
0.50	281	RUB	0.29	131	37
		MOR	0.23	117	27
0.75	422	RUB	0.32	131	42
			0.16	198	31
1.00	503	RUB	0.25	133	34
		MOR	0.20	422	43
LSD (0.05) (Soil X Level)			0.101	71.6	ns
LSD (0.05) (Soil)			+	+	ns
LSD (0.05) (Level)			+	+	7.9

[+] Not calculated due to a significant Soil X Level interaction.

Table 5. Comparison of cadmium concentrations extractable from Rubicon sand and Morley clay loam.

Cadmium		Soil	0.1 N HCl	0.005 M DTPA
me/100 g	ppm		ppm Cd	
0.00	0	RUB	<1	<1
		MOR	<1	<1
0.05	28	RUB	22	23
		MOR	22	14
0.10	56	RUB	46	41
		MOR	44	28
0.20	112	RUB	92	79
		MOR	96	85
0.50	281	RUB	239	207
		MOR	211	223
0.75	422	RUB	319	309
		MOR	297	325
1.00	562	RUB	378	364
		MOR	378	367
LSD (0.05) (Soil X Level)			ns	ns
LSD (0.05) (Soil)			ns	ns
LSD (0.05) (Level)			19.5	27.6

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CHAPTER 4

SUMMARY AND CONCLUSIONS

A greenhouse study was conducted to evaluate the response of corn to two different textured soils contaminated with Cd and Ni; the release of other nutrients, and the effect upon the nutrient composition of the crop. The results from these experiments are summarized below.

1. Dry weight production was affected only at the highest level of treatment on Ni-contaminated Rubicon sand and Morley clay loam.

2. There was no significant increase in Ni concentration or uptake on Ni-contaminated Rubicon sand. However, a significant increase in Ni concentration and uptake occurred with increasing treatment on Morley clay loam. There was a significant soil x level interaction of plant Ni concentration and uptake.

3. A very significant increase in plant Mn concentration and uptake was found on both soils with increasing metal treatment.

4. A decrease in plant Fe concentration and uptake occurred on Ni-contaminated Morley clay loam. Rubicon sand showed no changes in plant Fe concentration or uptake. Rubicon sand naturally contains three times as much extractable

Fe as Morley clay loam.

5. Extractable Ni levels from Morley clay loam were much higher than extractable levels from Rubicon sand. These differences may have resulted from the addition of $CaCO_3$ to Rubicon sand when raising the pH to 6.7. The Morley clay was at a higher pH naturally and no $CaCO_3$ was added. The $CaCO_3$ could then bind the Ni in a precipitated form and result in less Ni being extractable from the Rubicon sand.

6. Extractable soil Mn concentrations increased significantly with increasing Ni treatment on Morley clay loam, but there was no significant change in extractable soil Mn concentration on Rubicon sand.

7. Other elements (Cu, Fe, Zn) extractable from the soil were not significantly affected by Ni treatment.

8. At all levels of treatment, Cd drastically decreased plant dry-weight production on both soils.

9. Plant Cd concentration and uptake increased with increasing Cd treatment.

10. Plant Mn concentration and uptake increased with increasing Cd treatment on Rubicon sand. Cadmium treatment increased plant Mn concentration but decreased Mn uptake on Morley clay loam.

11. Generally there was a decrease in plant Fe uptake with increasing levels of applied Cd on both soils. Other than a decrease in Zn uptake with Cd treatment on Morley clay loam the uptake of other elements were not influenced.

12. Comparable levels of extractable Cd were obtained from both soils and a high percentage of the applied Cd was easily extractable after cropping.

13. No significant change in extractable soil Mn concentration occurred with treatment of Cd on either soil.

14. Other elements extractable from the soil were not significantly affected by Cd treatment.

15. At all levels of treatment, Cd appeared to be much more toxic than did Ni.

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APPENDIX

Table la. Comparison of iron and manganese concentrations extractable from nickel-treated Rubicon sand and Morley clay loam.

Nickel		Soil	0.1 N HCl	0.005 M DTPA	0.1 N HCl	0.005 M DTPA
me/100 g	ppm		--- ppm Fe ----		--- ppm Mn -----	
0.00	0	RUB	70	47	18	5
		MOR	21	45	128	37
0.05	15	RUB	71	48	23	5
		MOR	21	44	107	32
0.10	29	RUB	75	51	15	5
		MOR	22	46	108	36
0.20	59	RUB	70	45	19	8
		MOR	20	43	100	38
0.50	147	RUB	61	41	21	8
		MOR	25	42	145	35
0.75	220	RUB	59	45	28	9
		MOR	24	41	160	41
1.00	294	RUB	62	39	10	8
		MOR	26	40	167	36
LSD (0.05) (Soil X Level)			10.5	ns	14.9	ns
LSD (0.05) (Soil)			+	1.5	+	2.7
LSD (0.05) (level)			ns	2.9	+	ns

+Not calculated due to a significant Soil X Level interaction.

Table 2a. Comparison of iron, copper and zinc concentration and uptake on nickel-treated Rubicon sand and Morley clay loam.

Nickel		Soil	Copper		Iron		Zinc	
			conc.	uptake	conc.	uptake	conc.	uptake
me/100 g	ppm		ppm	ug/plant	ppm	ug/plant	ppm	ug/plant
0.00	0	RUB	15	10	102	71	37	26
		MOR	18	13	151	108	50	36
0.05	15	RUB	18	12	156	104	38	25
		MOR	18	12	126	89	46	30
0.10	29	RUB	20	13	158	104	44	29
		MOR	21	15	132	92	45	32
0.20	59	RUB	16	10	132	86	47	32
		MOR	18	13	107	76	43	30
0.50	147	RUB	18	12	148	97	34	22
		MOR	26	17	130	87	54	36
0.75	220	RUB	20	13	148	99	40	27
		MOR	18	12	99	66	55	36
1.00	294	RUB	17	10	144	80	31	17
		MOR	16	8	100	49	55	27
LSD (0.05) (Soil X Level)			ns	ns	42.3	ns	ns	ns
LSD (0.05) (Soil)			ns	ns	+	ns	5.5	3.5
LSD (0.05) (Level)			ns	3.3	+	ns	ns	ns

[+] Not calculated due to a significant Soil X Level interaction.

Table 3a. Comparison of copper, iron, manganese and zinc concentrations and uptake by corn plants grown for 5 weeks on cadmium-treated Rubicon sand and Morley clay loam.

Cadmium		Soil	Copper		Iron		Manganese		Zinc	
			conc.	uptake	conc.	uptake	conc.	uptake	conc.	uptake
me/100 g	ppm		ppm	ug/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant
0.00	0	RUB	15	10	102	71	50	35	37	26
		MOR	18	13	151	108	83	59	50	36
0.05	28	RUB	13	7	185	99	71	38	56	31
		MOR	18	9	114	55	68	33	54	26
0.10	56	RUB	14	6	171	62	73	29	43	17
		MOR	19	9	130	59	64	29	60	28
0.20	112	RUB	13	6	206	91	67	30	37	16
		MOR	13	4	155	51	87	29	36	12
0.50	281	RUB	12	3	146	42	84	24	33	10
		MOR	10	2	111	26	110	26	49	11
0.75	422	RUB	10	3	148	48	95	30	36	12
		MOR	11	2	95	15	105	17	47	8
1.00	562	RUB	12	3	128	33	86	22	30	8
		MOR	11	1	203	20	156	15	48	5
LSD (0.05) (Soil X Level)			ns	2.5	50.9	21.9	21.5	9.6	ns	ns
LSD (0.05) (Soil)			1.5	ns	ns	+	+	ns	7.3	ns
LSD (0.05) (Level)			2.8	+	+	+	+	+	ns	7.8

[+] Not calculated due to a significant Soil X Level interaction.

Table 4a. Comparison of iron and manganese concentrations extractable from cadmium-treated Rubicon sand and Morley clay loam.

Cadmium		Soil	0.1 N HCl	0.005 M DTPA	0.1 N HCl	0.005 M DTPA
me/100 g	ppm		--- ppm Fe ---		--- ppm Mn ---	
0.00	0	RUB	70	47	18	5
		MOR	21	45	128	39
0.05	28	RUB	52	54	7	5
		MOR	25	48	170	30
0.10	56	RUB	65	56	15	4
		MOR	23	32	133	15
0.20	112	RUB	73	49	13	7
		MOR	23	34	151	22
0.50	281	RUB	66	48	10	9
		MOR	23	32	154	34
0.75	422	RUB	78	53	14	11
		MOR	22	30	127	26
1.00	562	RUB	83	39	10	11
		MOR	22	24	137	23
LSD (0.05) (Soil X Level)			13.3	6.0	17.5	5.9
LSD (0.05) (Soil)			+	+	+	+
LSD (0.05) (Level)			ns	+	+	+

+Not caluclated due to a significant Soil X Level interaction.