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Effects of Nickel and Cadmium Contaminated Soils on Nutrient Composition of Corn Plants

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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 (meq) per 100 g soil. Treatments ranging from 0.05 to 1.00 meq 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 five 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 N HCl, 1 N NH_4O Ac or 0.005 M DTPA.

The Cd-treated soils retarded growth 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 predominantly 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 result 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 soil's ability to adsorb Cd.

Nickel occurs commonly in soils and plants in concentrations substantially higher than those normally present in animal tissue and fluid. A 0.3 to 0.5 mg Ni intake per day for human adults has been estimated (5, 13). Vanselow (18) reported that soil contains 10-1000 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 pressure 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. 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 offer 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: 1) The metals being precipitated or strongly bound to the soil complex, unavailable for plant uptake, 2) the metals passing through the soil profile and entering underground water supplies or 3) the metals being loosely bound to the soil complex and available for plant uptake. The latter two phenomena pose potential threats to human consumption of food and water originating from areas such as those used for water renovation.

Before utilizing a soil for the purpose of treatment of metal-bearing waste, properties of the

soil and the metals must be known: 1) The capacity of a soil for fixation of metals of this type. 2) The leaching potential of metal cations and anions in a specific soil. 3) 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 20mm stainless steel screen, air dried and stored in plastic containers. Samples for laboratory work were passed through a 2mm 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 I).

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 meq/100 g soil) as well as triplicate controls were utilized in the 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 20% by weight and were allowed to equilibrate for 1 week; then 12 kernels 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 a soil did not significantly increase plant Ni concentration and uptake except at the highest level of treatment, 294 ppm. (Tables II and III). These data indicate that corn plants have an effective mechanism for excluding Ni from uptake and/or translocation under the conditions studied. Data (Table II) 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. Soil extractions after cropping (Table VI) 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. Langmuir adsorption isotherm data indicated much of the Ni was inactivated through an adsorption mechanism. Manganese was desorbed by the soil as Ni levels were increased and the decreased Mn in soil solution resulted in increased Mn uptake by corn plants (Tables II, III, VI). 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 plant 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.

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 IV, V). 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. 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 VII). 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 the plants.

TABLE I
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TABLE II. SOIL TREATM
CORN GROWN
UNDE

Soil Treatment Nickel Meq/100g	ppm	Dry Weight g/plant
0.00	0	0.70
0.05	15	0.66
0.10	29	0.67
0.20	59	0.65
0.50	147	0.66
0.75	220	0.67
1.00	294	0.55
LSD (0.05)		NS

[1]Each value is the average of 3 r

TABLE III. SOIL TREATM
CORN GROWN ON
GR

Soil Treatment Nickel Meq/100g	ppm	Dry Weight g/plant
0.00	0	0.70
0.05	15	0.66
0.10	29	0.67
0.20	59	0.65
0.50	147	0.66
0.75	220	0.67
1.00	294	0.55
LSD (0.05)		NS

[1]Each value is the average of 3 replica

TABLE IV. SOIL TREATMI
OF CORN GROWI
SAND UNDE

Soil Treatment Cadmium Meq/100g	ppm	Dry Weight g/plant
0.00	0	0.70
0.05	28	0.53
0.10	56	0.40
0.20	112	0.44
0.50	281	0.29
0.75	422	0.32
1.00	562	0.25
LSD (0.05)		0.123

[1]Each value is the average of 3 repli

f metals of this type.
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ents, each in tripli-
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had distilled water
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stainless steel mill
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Cu, Fe, Mn, Ni and

e plant Ni concen-
II and III). These
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than 0.5 ppm Cd
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he soil after crop-
by the plants.

TABLE I. CHARACTERISTIC PROPERTIES OF RUBICON SAND, A HORIZON

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

TABLE II. SOIL TREATMENT, PLANT GROWTH AND METAL CONTENT OF CORN GROWN ON NICKEL-TREATED RUBICON SAND UNDER GREENHOUSE CONDITIONS.[1]

Soil Treatment Nickel		Dry Weight	Plant Metal Concentration					
			Cd	Cu	Fe	Mn	Ni	Zn
Meq/100g	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

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

TABLE III. SOIL TREATMENT, PLANT GROWTH AND METAL UPTAKE OF CORN GROWN ON NICKEL-TREATED RUBICON SAND UNDER GREENHOUSE CONDITIONS.[1]

Soil Treatment Nickel		Dry Weight	Plant Metal Uptake					
			Cd	Cu	Fe	Mn	Ni	Zn
Meq/100g	ppm	g/plant	μg/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

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

TABLE IV. SOIL TREATMENT, PLANT GROWTH AND METAL CONTENT OF CORN GROWN ON CADMIUM-TREATED RUBICON SAND UNDER GREENHOUSE CONDITIONS.[1]

Soil Treatment Cadmium		Dry Weight	Plant Metal Concentration					
			Cd	Cu	Fe	Mn	Ni	Zn
Meq/100g	ppm	g/plant	ppm					
0.00	0	0.70	0	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

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

TABLE V. SOIL TREATMENT, PLANT GROWTH AND METAL UPTAKE OF CORN GROWN ON CADMIUM-TREATED RUBICON SAND UNDER GREENHOUSE CONDITIONS.[1]

Soil Treatment Cadmium		Dry Weight	Plant Metal Uptake					
			Cd	Cu	Fe	Mn	Ni	Zn
Meq/100g	ppm	g/plant	μg/plant					
0.00	0	0.70	0	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

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

TABLE VI. SOIL TREATMENTS AND SOIL EXTRACTABLE METAL CONCENTRATIONS OF RUBICON SAND.[1]

Soil Treatments Nickel		Soil Metal Concentration					
		HCl	DTPA	NH_4OAc	HCl	DTPA	NH_4OAc
Meq/100g	ppm	ppm Ni			ppm Mn		
0.00	0	0	0.3	0	18	5	2
0.05	15	8	4	0	23	5	3
0.10	29	17	8	0	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

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

TABLE VII. SOIL TREATMENTS AND SOIL EXTRACTABLE METAL CONCENTRATIONS OF RUBICON SAND.[1]

Soil Treatment Cadmium		Soil Metal Concentration					
		HCl	DTPA	NH_4OAc	HCl	DTPA	NH_4OCa
Meq/100g	ppm	ppm Cd			ppm Mn		
0.00	0	0	0	0	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

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

ACKNOWLEDGMENT

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Inquirer: T. C. Hutchinson, U

Q. We find Ni in solution to be toxi
and others have found 10 ppm
levels of greater than 100 ppm h
comment on this anomaly?

A. Nickel in solution is much more
great proportion of the nickel ad
of organic matter. This is evid
insignificant effect, then, upon
fixed on the cation exchange col
nutrient solution would be ver

Inquirer: D. J. Horvath, West

Q. Ni data in literature are in con
Paterson - Please comment.

A. Data from this experiment indic
the soil solution very quickly a
form that resisted removal by r
fore, not available for plant upt
cate that Ni is being inactivate

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DISCUSSION

Inquirer: T. C. Hutchinson, University of Toronto, Toronto, Ontario, Canada

Q. We find Ni in solution to be toxic to seedlings of many vegetables at less than 2 ppm. DeKoch and others have found 10 ppm to be toxic to many species. In your data extractable soil Ni levels of greater than 100 ppm had no significant effect on growth nor was it taken up. Can you comment on this anomaly?

A. Nickel in solution is much more readily available for plant uptake than is Ni in a soil system. A great proportion of the nickel added to the soil is fixed or complexed by the exchange capacity of organic matter. This is evident by the replacement of Ni for Mn when Ni is added. The insignificant effect, then, upon growth at levels of Ni up to 100 ppm is attributed to its being fixed on the cation exchange column and not available for plant uptake. This amount of Ni in a nutrient solution would be very toxic to plant growth.

Inquirer: D. J. Horvath, West Virginia University, Morgantown, West Virginia

Q. Ni data in literature are in conflict re: toxicity and tissue concentration - data of Wick and Paterson - Please comment.

A. Data from this experiment indicated that Ni toxicity was low. The Ni is being removed from the soil solution very quickly and effectively. A great portion of the Ni was inactivated in a form that resisted removal by rather strong chemical treatments. Most of the Ni was, therefore, not available for plant uptake. Data obtained from Langmuir adsorption isotherms indicate that Ni is being inactivated through an adsorption mechanism as Mn is released.