Impact of Repeated Addition of Swine Manure and Cattle Manure on Cu and Zn Amount and Distribution in a Saskatchewan Soil

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Abstract

Increasing use of animal manures in Saskatchewan requires information on the fate and distribution of residual manure copper (Cu) and zinc (Zn) in Saskatchewan soils. To address this issue, the amounts of soil Cu and Zn in various inorganic and organic fractions were investigated in a field crop research plot (Cudworth association soil) with a five year history of annual application of liquid swine manure and solid cattle manure, and in two grassland field research plots (Meota and Oxbow association soils) that had received annual application of liquid swine manure for three years. The annual rates of manure application were based on N contents in the manures, and were equivalent to approximately 0, 100, 200 and 400 kg total N ha^{-1} yr^{-1} in the field crop plots, and 0 and 100 kg total N ha^{-1} yr^{-1} in grassland plots. In both the field crop and grassland manured plots there were no substantial increases in total Cu and Zn in soils associated with manure application. Some increases in the moderately labile Cu and Zn fractions were observed in treatments with large amounts of animal manures applied every year. The liquid swine manure had less effect on increasing labile Cu and Zn fractions than cattle manure. These results indicate that annual addition of animal manures at rates of approximately 100 kg N ha^{-1} for 3 to 5 years does not constitute an environmental risk from Cu and Zn loading in these soils.

<u>Key Words</u>**:** Cu fraction, Zn fraction, sequential Cu extraction, sequential Zn extraction, urea, swine manure, cattle manure

INTRODUCTION

Animal manures have been applied to agricultural lands to derive benefit from the essential nutrients and organic matter contained in these materials. However, there is concern over accumulation in the soil of heavy metals present in animal manures and other organic wastes because of increased and repeated use of manures in agriculture (Smith 1994). For example, soil receiving repeated applications of poultry litter for several years has exhibited high concentrations of extractable copper and zinc (Kingery et al. 1994; Van der Watter et al. 1994). Significant increases in DTPA extractable Cu and Zn after use of cattle and swine manures have also been documented (Eneji et al. 2001). The risk associated with the accumulation of trace metals in soils due to use of organic wastes includes phytotoxicity and the increased entry of toxic metals into the food chain (Heckman et. 1987) as well as in the deterioration of surface water and groundwater quality (Wood et al. 1999). However, the above risks are difficult to directly assess through determining the total contents of metals in the organic wastes because the physico-chemical forms of the metal in the manure strongly affect their mobility, reactivity and availability to plants.

To provide more insight into the fate of metals in the soil following land application of organic amendments, sequential extraction procedures have been introduced to divide the metal contents in organic amendments and soils into various fractions, using a series of chemical extractants to remove metals from different physico-chemical pools. Results obtained with these methods are difficult to directly compare because of the diversity of procedures employed, and do not identify specific metal species since each extraction step does not remove single and well established chemical forms of metals, but usually a mixture of compounds. However, information derived from these procedures is potentially valuable in predicting metal bioavailability and transformations between chemical forms in soils (Jenne and Luoma 1977). Silviera and Sommers (1977) extracted Cu, Zn, Cd and Pb in soil-sludge mixtures and found a large variability in each fraction, indicating that the metals added to soil in different sludges may occur in several chemical forms. In this study, we evaluated and compared the effects of repeated applications of liquid swine manure and solid cattle manure on the amounts and distribution of Cu and Zn among various chemically distinguishable labile and stable Cu and Zn fractions in both cropped land and grassland in the Black soil zone in East-Central Saskatchewan.

MATERIALS AND METHODS

Soil and manure used

Soils used in this study were from two different field manure experiments. One is a long-term trial testing effects of repeated use of manure in annually cropped lands where liquid swine manure and solid cattle manure had been applied annually for 5 years when the soils were sampled. The second experiment covers three years of low disturbance injection of liquid swine manure directly into grassland (Brome grass and Russian wild rye grass). Soils from the annual cropping trials were collected from plots in east-central Saskatchewan near Dixon, where the soil type is a Black Chernozem (Cudworth Association) of loamy texture. In the field trials, described in detail by Mooleki et al. (2002), swine and cattle manures have been applied at low, medium and high rates every year since the fall of 1996. Liquid swine manure is injected into the soil in 30 cm bands while cattle manure is broadcast and incorporated. Treatments sampled for the metal distribution study included the control and manure applied at three different rates (low, medium and high) equivalent to approximately 100, 200 and 400 kg total N ha^{-1}, and urea application at 50, 100 and 200 kg N ha^{-1} as comparisons. Soils from the grassland were collected from research plots near Burr (Brome grass) and Lanigan (Russian wild rye) in Saskatchewan, where the soil types are Meota (Black sandy loam) and Oxbow (Black sandy loam to loamy sand) associations, respectively. There were also three rates applied in the grassland field trials, but only soils from the low rate (100 kg total N ha^{-1}) treatments were used in this study since only the low rate was applied each year in the three year study. The field crop and grassland trials are set up as randomized complete block design experiments with four replicates of each treatment.

Soils were sampled from each plot (0-15 cm) after crop harvest in the fall of 2001. Three cores were taken from each plot randomly and mixed thoroughly to provide a composite sample. Visible crop residues were removed. After being shipped to the lab, soil samples were further air-dried, crushed, passed through 2-mm sieve, mixed, and stored at room temperature before analysis. Basic soil characteristics were measured on soil samples from the control plots that had never received manure (Table 1). Soil organic C was measured by dry combustion method using Leco carbon analyzer (LECO© Corporation, 1987). Total Cu and Zn was determined by digestion using Aqua Regia-HF-HNO_3 and HCl (Shuman, 1979) and determined by atomic absorption spectrometry (Baker and Amacher, 1982). Available Cu and Zn were extracted with DTPA and measured using atomic absorption spectrometry (Baker and Amacher, 1982). The selected soil characteristics are summarized in Table 1.

Table 1. Some characteristics of soils (Black Chernozem) used in the experiment.

Soil	Total	Total		Extractable (DTPA)	
Association	Soil Organic Carbon	Cu	Zn	Cu	Zn
	%	------------------ mg kg^{-1}	------------------		
Cudworth	1.9	19.2	71.7	0.88	0.93
Meota	1.4	12.6	62.5	0.73	1.59
Oxbow	1.5	13.9	71.6	0.77	1.85

The swine manure applied in the field was liquid effluent obtained from an agitated single-cell earthen storage unit, and cattle manure was stockpiled, homogenized cattle feedlot penning manure. Rates of nutrients applied in the field trials were calculated based on nutrient content of manure measured in samples collected during application. Total Cu and Zn in the manures were measured using atomic absorption spectrometry after acid digestion (Baker and Amacher, 1982). Rates of Cu and Zn applied yearly as manure for the growing seasons were calculated based on the concentration of manure-Cu and Zn measured and the application rate of manure product. The rates of total Cu and Zn applied as liquid swine manure and solid cattle manure are reported in Table 2.

Crops grown in the field crop study were Argentine canola (*Brassica napus, L.*) in 1997, hard red spring wheat (*Triticum aestivum, L.*) in 1998, Hulless barley (*Hordeum vulgare, L.*) in 1999, and again Argentine canola (*Brassica napus, L.*) in 2000 and hard red spring wheat (*Triticum aestivum, L.*) in 2001. Grasses grown in the grassland were Smooth Brome in Burr and Russian Wild Ryegrass in Lanigan, and cut in summer (June or July).

Table 2. Total Cu and Zn added in liquid swine manure and solid cattle manure at the field crop (Cudworth) and grassland (Meota, Oxbow) trials.

	1997		1998		1999		2000		2001	
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
	kg ha^{-1}									
Swine Manure										
Meota (Low rate)			0.17	0.24	0.08	0.22	0.10	0.20		
Oxbow (Low rate)			0.20	0.28	0.54	0.88	0.50	0.80		
Cudworth - Low rate	0.20	0.20	0.14	0.05	0.40	0.70	0.10	0.20	0.10	0.20
Medium rate	0.40	0.40	0.28	0.10	0.80	1.40	0.20	0.40	0.20	0.40
High rate	0.80	0.80	0.56	0.20	1.60	2.80	0.40	0.80	0.40	0.80
Cattle Manure										
Cudworth - Low rate	0.90	1.60	0.80	0.70	0.30	0.07	0.40	0.90	0.60	0.80
Medium rate	1.80	3.20	1.60	1.40	0.70	1.40	0.80	1.80	1.20	1.60
High rate	3.60	6.40	3.20	2.80	1.40	2.80	1.60	3.60	2.40	3.20

Fractionation of Cu and Zn

The fractionation scheme used to determine discrete pools of soil Cu and Zn is a modified version (Liang et al., 1990) of the one proposed by Miller et al. (1986). In the fractionation, 2 g of air-dried soil were first extracted with 20 ml of 0.5 *M* $Ca(NO_3)_2$ (16 hrs), followed sequentially by 20 ml 0.05 *M* $Pb(NO_3)_2$ + 0.1 *M* $Ca(NO_3)_2$ (16 hrs), 20 ml 0.44 *M* CH_3COOH + 0.1 *M* $Ca(NO_3)_2$ (8 hrs), 20 ml 0.01 *M* $NH_2OH{\cdot}HCl$ + 0. 1 *M* HNO_3 (0.5 hr), 20 ml 0.1 *M* $K_4P_2O_7$ (24 hrs), and 10 ml 0.113 *M* $(NH_4)_2C_2O_4$ + 0.087 *M* $H_2C_2O_4$ (in darkness 4 hrs). After each extraction using a rotation shaker, the suspension was centrifuged for 10 min at 10000 rpm. The supernatants were collected and diluted 10 times with deionized water.

The residue left behind after the above extractions was washed twice, dried in a forced-air oven at 60ºC for 24 hrs, and ground to pass a 150 µm sieve. A 0.5 g subsample was placed in a Teflon beaker containing enough deionized water to cover the bottom. Aqua Regia HF-HNO_3 and HCl digestion method was used to determine the residual Cu and Zn (Shuman, 1979).

Unless otherwise noted above, all extraction procedures were conducted at room temperature. Samples were washed twice between extractions with 0.025 *M* $Ca(NO_3)_2$ to remove occluded solutions. After centrifugation, Cu and Zn in the supernatant from each of the above extractions was determined by atomic absorption spectrometry.

The first extraction fraction (Ex-) represents water soluble and exchangeable fractions of Cu and Zn in soil. The fraction extracted by $Pb(NO_3)_2$ (Pb-) are adsorbed Cu and Zn forms that can be displaced by Pb salt solution. The fraction extracted by CH_3COOH (Aci-) are mainly metals held on soil surfaces by covalent type bonding, termed "inner sphere" complexed metals (Sposito, 1984). The fractions extracted by $NH_2OH \cdot HCl$, $K_4P_2O_7$, and $(NH_4)_2C_2O_4$ are the structural (occluded) forms bound by Mn oxide (MnO-), organically (OM-) and by Fe and Al oxides (FeO-), respectively. The residual Cu and Zn (Res-) represent the metals strongly held within silicate mineral structures, which may be a substantial portion of the total Cu and Zn in soils.

Statistical Analyses

Differences in metal fractions among components were examined statistically based on the least significant difference (LSD) using standard analysis of variance techniques and multiple comparison via the Walter-Duncan k-ratio procedure. Computations were performed by the GLM procedure (SAS 1985).

RESULTS AND DISCUSSION

Forms of Cu and Zn

With the procedure we used, Cu and Zn in manure-amended soils were divided into 7 fractions to represent four categories. One is the exchangeable form (Ex-) that was extracted by Ca reagent

Table 3. Distribution of Cu fractions in a Cudworth soil after 5 years of annual manure applications.

Treatment	MnO-	OM-	FeO-	Res-	Total ^{Z}	DTPA
	------------------------------ mg Cu kg^{-1} soil ------------------------------					
Swine manure						

Control	1.14	5.10	3.31	11.7	18.1	0.84
SM[y] low	1.26	5.19	2.91	12.3	19.3	0.83
SM medium	1.34	5.51	3.38	12.1	19.3	1.01
SM high	1.76	5.79	3.94	13.2	20.3	1.36
Urea low	1.17	4.87	2.96	11.6	18.3	0.82
Urea medium	1.16	5.10	2.99	11.5	18.0	0.82
Urea high	1.21	5.40	3.21	12.0	19.2	0.97
LSD 0.05	0.30	0.86	0.66	0.88	1.31	0.25
Pr. > F	0.01	NS	0.05	<0.05	<0.05	<0.01
Cattle manure						
Control	1.34	5.37	2.95	11.8	20.2	0.91
CM[x] low	1.24	5.85	3.41	12.4	21.7	0.89
CM medium	1.20	7.02	3.86	11.8	21.6	0.95
CM high	1.22	6.72	4.09	11.9	21.0	1.00
Urea low	1.12	6.21	3.85	11.9	20.8	0.83
Urea medium	1.03	6.35	3.58	11.7	20.6	0.83
Urea high	1.13	5.97	3.80	11.6	21.2	1.01
LSD 0.05	0.22	0.85	0.66	1.2	1.9	0.24
Pr. > F	NS	0.01	<0.05	NS	NS	NS

[Z] = total Cu determined by acid digestion; [y]SM = Swine manure; [x]CM = Cattle manure

and may be considered a labile fraction. The second is the adsorbed component of Cu and Zn that was extracted by Pb reagent (Pb-), representing more loosely sorbed forms along with the acidic reagent (Aci-) for more strongly adsorbed forms and together may be considered moderately labile. The third category represents structural metal forms that include those occluded (bound) by hydrous oxides of Mn (MnO-) and organic matter (OM-) as well as hydrous oxides of Fe (Fe-) extracted by a weak reducing agent ($NH_2OH \cdot HCl$), oxidant ($K_4P_2O_7$) and oxalate reagent, respectively. Metals in the third category are moderately labile to stable. The last category are the metals that are held within silicate mineral structures, termed "residual," and extracted by HF-based acid digestion (Miller et al. 1986). The Cu and Zn in the last category are very recalcitrant and stable, being of very low bioavailability.

Table 4. Distribution of Cu fractions in two grassland soils after 3 years of annual swine manure applications.

Treatment	MnO-	OM-	FeO-	Res-	Total [Z]	DTPA
	----------	----------	mg P kg^{-1} soil	----------	----------	
Meota						
Control	0.91	4.12	1.60	7.67	12.6	0.73
Manure	0.75	4.26	1.71	7.73	13.6	0.73
Oxbow						

Control	0.65	4.51	2.95	7.63	13.9	0.77
Manure	0.82	4.64	3.32	7.51	15.4	1.21
LSD 0.05	0.24	0.53	0.37	0.84	0.78	0.87
Pr. > F						
Loc	NS	NS	<0.01	NS	0.05	NS
Trt	NS	NS	<0.10	NS	<0.01	NS
Loc*Trt	<0.10	NS	NS	NS	NS	NS

[Z] = total Cu determined by acid digestion.

In our study, the Cu in Ex-, Pb- and Aci- forms in all the treatments of all the soils tested was lower than the level that could be accurately detected. The percentages of total Cu in the MnO-, OM-, FeO-, and Res.- forms are 4.5 - 7.1%, 23.4 - 29.4%, 13.4 - 17.1% and 49.3 - 56.8% in field crop trial soils tested and 4.1 - 6.4%, 28.5 - 29.5%, 11.2 - 20.4%, and 46.0 - 53.6% in grassland trial soils tested, respectively (Tables 3 and 4). Zinc in the exchangeable fraction was also lower than the level that could be accurately detected. However, there was 1.2-2.7% of total Zn measured in the Pb-displaced form and 0.6 - 1.1% in the Aci- fraction of the field crop trial soils, and 2.5 - 3.9% in Pb- form and 1.7 - 2.8% in Aci-form measured in grassland trial soils. The percentage of total Zn in the MnO-, OM-, FeO-, and Res.- forms is 4.0 - 6.1%, 2.4 - 2.9%, 2.9 - 3.8%, and 83 - 88% in field crop trial soils, and 9.6 - 11.4%, 2.6 - 3.1%, 1.9 - 2.4% and 76.7 - 80.8% in grassland trial soils (Tables 5 and 6). It is not surprising that the highest percentage of Cu and Zn is found in the residual fraction associated with primary silicate minerals,

Table 5. Distribution of Zn fractions in a Cudworth soil after 5 years of annual manure applications.

Treatment	Pb-	Aci-	MnO-	OM-	FeO-	Res-	Total [Z]	DTPA
	------ mg Zn kg^{-1} soil ------							
Swine manure								
Control	0.88	0.63	3.28	1.82	2.45	66.8	68.4	0.75
SM[y] low	1.36	0.57	3.03	1.93	2.46	67.2	75.7	1.08
SM medium	1.44	0.62	3.37	1.97	2.55	64.8	73.1	1.28
SM high	1.87	0.96	3.51	2.14	2.75	64.5	74.1	2.06
Urea low	0.88	0.49	2.77	1.88	2.69	60.5	72.1	0.78
Urea medium	0.91	0.51	3.23	1.84	2.65	65.9	67.9	0.80
Urea high	1.08	0.53	3.36	2.05	2.76	12.0	74.9	0.93
LSD 0.05	0.52	0.17	0.68	0.32	0.42	7.8	8.2	0.32
Pr. > F	<0.01	<0.01	NS	NS	NS	NS	NS	<0.01
Cattle manure								
Control	1.10	0.50	3.76	2.06	2.27	68.9	74.9	1.10

CM[x] low	1.58	0.64	3.66	2.20	2.39	69.7	80.2	1.31
CM medium	2.08	0.85	4.24	2.28	2.55	67.4	79.3	1.89
CM high	2.10	0.80	4.15	2.04	2.61	68.1	77.5	1.90
Urea low	1.30	0.79	4.62	2.15	2.89	62.4	70.3	1.35
Urea medium	1.04	0.60	3.49	2.04	2.61	66.2	72.1	1.10
Urea high	1.31	0.70	4.01	1.98	2.41	68.8	75.4	1.38
LSD 0.05	0.68	0.20	1.12	0.46	0.30	7.9	11.7	0.76
Pr. > F	0.01	<0.05	NS	NS	0.01	NS	NS	NS

[Z] = total Zn determined by acid digestion; [y]SM = Swine manure; [x]CM = Cattle manure;

as soils of the Canadian Prairies are rich in silicate clays and relatively unweathered. A high proportion of Cu was found to be associated with OM- (Tables 3 and 4), which is anticipated given the relatively high organic matter content of Black Chernozemic soils. Other studies have reported that Cu in the manure itself is also strongly associated with the organic matter fraction (Mullins et al., 1982; Payne et al., 1988; Canet et al., 1997).

Table 6. Distribution of Zn fractions in two grassland soils after 3 years of annual swine manure applications.

Treatment	Pb-	Aci	MnO-	OM-	FeO-	Res-	Total [Z]	DTPA
	---------- mg Zn kg^{-1} soil ----------							
Meota								
Control	2.31	1.15	6.97	1.80	1.64	54.4	62.5	1.59
Manure	2.92	1.94	7.04	2.00	1.62	54.4	67.0	2.83
Oxbow								
Control	2.03	2.03	7.71	2.17	1.49	64.9	71.6	1.85
Manure	3.15	2.05	9.11	2.45	1.83	61.3	75.2	2.92
LSD 0.05	0.70	0.57	0.62	0.57	0.35	4.70	5.53	0.84
Pr. > F								
Loc	NS	NS	<0.01	NS	NS	<0.01	<0.01	NS
Trt	<0.01	0.05	<0.01	NS	NS	NS	<0.05	<0.01
Loc*Trt	NS	<0.10	<0.01	NS	NS	NS	NS	NS

[Z] = total Zn determined by acid digestion.

Effect of Manure and Urea on Total Cu and Zn in Soil

Soil total Cu and Zn were not significantly increased by the addition of swine and cattle manure (Tables 3, 4, 5 and 6), but were significantly different among soils (Tables 4 and 6). The reason for lack of significant differences in total Cu and Zn as related to manure amendment may be because of the relatively low amounts of Cu and Zn added over the years of manure application (Table 2) such that, even at high rates of manure application, there was not enough to cause a significant build up. Similar results were reported by Canet et al. (1997) who found that there was no significant increase in total soil Cu and Zn after repeated use of sheep manure for 7 years in Spain. Significant increases in metal contents in soils amended with sewage sludge and municipal solid waste compost was observed, but not in the manure treatment due to low content of metals in the manure (Canet et al., 1997).

Effect of Manure and Urea on Cu and Zn Fractions in Soil

Copper and zinc fractions responded differently to the addition of manure and urea in the field crop trial soils (Tables 3 and 5). The inability to distinguish the exchangeable (Ex-) Cu and Zn in all the treatments in both cropland and grassland soils tested reflects the limited importance of this fraction in Canadian prairie soil (Liang et al, 1990 and 1991) and showed that manure additions did not lead to the accumulation of exchangeable Cu and Zn, and of Cu in the adsorbed fractions (Pb-replaceable and acid reagent-extractable fractions).

The structural fractions also showed little change after 3 - 5 years of annual cattle or swine manure application in either cropland or grassland soils compared to urea fertilizer treatment and/or the unfertilized control. There is a trend of increased Mn-oxide associated Cu in swine manure treatments, and the highest rate of swine manure had significantly higher MnO-extractable Cu than the other treatments. A similar trend was observed in DTPA-extractable Cu in which the highest level of swine manure addition led to a small but significant increase in DTPA-Cu in the field crop land. Although MnO-Cu may be considered to be structural forms of Cu, this form is the least stable form among the all the fractions in this category and is likely extracted by DTPA. There is a strong correlation between MnO-Cu and DTPA-Cu ($R^2 = 0.92$) for swine manure treatments. There were no significant increases in MnO-Cu and DTPA-Cu after application of swine manure in the grassland trial soils, which can be attributed to the low rate of manure application and only three years of application.

Moderately labile Zn (both Pb- and Aci- adsorbed forms) were detected and results showed significant increases in this fraction in swine and cattle manure treatments in the field crop trial soils, especially for the medium and high rates applied. In the grassland trial soils an increase of moderately labile Zn was less than in the field crop trials, probably due to low application rate and only three years application of swine manure. Results showed that zinc in the Pb- fraction was significantly increased only in Meota soil and Aci-fraction only in Oxbow soil (Tables 4 and 6). A small but significant increase of DTPA-Zn was also observed in both the field crop and grassland soils. Stable Zn fractions (MnO-, OM-, FeO- and residual) and Cu fractions (OM-, FeO- and residual-) were not influenced by manure application, indicating a limited proportion of manure Zn and Cu was added or transferred to these fractions. These results suggest the stable fractions are not significant short-term storehouses of manure metals, and thus added metals reside in labile forms. Long-term manure additions have been reported to increase the Cu and Zn forms in the labile and moderately labile fractions and also increased total Cu and Zn content (Han et al., 1999). Han et al. (1999) reported that Cu and Zn accumulation in poultry manure-amended soils were significantly higher than non-amended soils, and suggested that the Cu and Zn in the long-term amended soil are potentially bioavailable and mobile. This could be because of an important cumulative effect of manure additions and a decrease in the soil metal adsorption as fixation sites become saturated. However, this was not the case in our study as after 5 years of repeated application of swine or cattle manure in field crop trials and 3 years in grassland trials, the increase in labile and moderately labile copper and zinc was small, in line with the low rates of addition of these metals as well as reflecting removal of the metals through crop or grass harvest.

CONCLUSION

Annual application of liquid swine manure or solid cattle manure for 5 years in a field crop trial and 3 annual applications of swine manure in a grassland trial did not contribute to substantial increases in total Cu and Zn in Black Chernozem soils in east-central Saskatchewan. Some moderately labile Cu and Zn fractions, especially Zn, increased only when large amounts of swine manure and cattle manure were applied. In general, liquid swine manure had less effect on increasing labile Cu and Zn fractions than cattle manure. Given that the low and medium rate, 100 - 200 kg N ha^{-1} as manure per year is considered agronomically optimal in this region (Mooleki et al., 2002), concerns about Cu and Zn loading after three to five years of recommended application in these soils are limited.

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