10 Chemical Association of Trace Elements in Soils Amended with Biosolids: Comparison of Two Biosolids

Kenneth S. Sajwan, S. Paramasivam, A.K. Alva, and J. Afolabi

CONTENTS

ABSTRACT

Understanding the chemical association of trace elements in soils amended with biosolids is very important because it determines their availability within and mobility beyond the rhizosphere. A sequential extraction method was used to determine the various chemical associations (exchangeable, sorbed, organic, carbonates, and sulfides) of Mn, Zn, Cu, Cd, Cr, Pb, and Ni at the end of sorghum–Sudan grass growth (65 days) in Candler fine sand (pH = 6.8) and in Ogeechee loamy sand (pH = 5.2) amended with sewage sludge (SS), which was obtained from two different sources at application rates of 0, 24.7, 49.4, 98.8, and 148.2 Mg ha^{-1}. Results of this study indicated that, irrespective of the soil type, Zn, Cd, Cr, Ni, Pb, and Mn in the labile fractions (exchangeable + sorbed) were almost nondetectable. Therefore, their availability to plants and mobility beyond the rhizosphere would be substantially low unless further transformations occurred from other fractions.

Results also indicated that the presence of substantial amounts of trace elements studied were in the sulfide (HNO_3) and organic (NaOH) fractions, irrespective of soil type. The exceptions were Pb, which was mainly present as carbonate (Na_2EDTA) fraction, and the remaining Pb equally as sulfide (HNO_3) and organic (NaOH) fractions. Furthermore, results indicated that the Cd was mainly present as carbonate (Na_2EDTA) fraction. Irrespective of soil type, source, and rate of SS application, summation of quantities of various fractions of all the trace elements studied through sequential extraction procedure were 1 to 7% lower than those of total quantities of these trace elements extracted with 4 M HNO_3 on fresh soil samples. They were also 5 to 20% lower than that of total trace elements determined on acid digestion described by the USEPA method. It was further evident that the application of SS shifted the solid phases containing the trace elements in soils away from those extractable with more severe reagents, such as 4 M HNO_3, to those extractable with milder reagents, such as dilute NaOH and Na_2EDTA.

10.1 INTRODUCTION

The agricultural use of biosolids has been a common practice in waste disposal in recent decades. Extensive research on the use of one of the biosolids (BS), SS, during the past three decades has helped to realize the beneficial effects of land application of biosolids. This resulted in renewed public interest in reusing and recycling of sewage sludge from wastewater treatment plants and a dramatic increase in land application of SS from 20 to 54% in the U.S. [1]. The traditional methods of organic waste disposal (landfilling, incineration, ocean dumping) are being restricted or outlawed due to air- and water-quality concerns.

Furthermore, wastewater treatment plants in cities around the world still encounter serious problems in disposing of SS; because of odor, high acidity, and levels of some heavy metals in excess of critical limits, public acceptance is lacking. This has caused exploration of alternative disposal methods. These endeavors have resulted in production of ash by incinerating dewatered activated sludge (ISS) and weathered ash (WISS) by dissolving and storing the incinerated by-product in ash ponds by wastewater treatment plants. Despite all this, the beneficial effects of amending soils with various organic amendments, including the use of sewage sludge, are still dramatically on the rise.

Most of these materials contain plant nutrients and organic matter and are beneficial in many ways to soils by improving their productivity. However, depending on origin and form, they contain variable amounts of trace elements such as Cu, Zn, Pb, Cr, Cd, and Ni, which tend to accumulate within the topsoil of the rhizosphere. Some of these elements can cause phytotoxicity and also pose toxicity problems to animals if any of these plants is used for grazing purpose. However, biosolids applications can also reduce trace element toxicity by redistributing them into various, less available forms [2]. Conversely, the slow mineralization of organic matter in biosolids could release various trace elements into more soluble forms [3]. The dynamics of sludge organic carbon appear, therefore, as a potential parameter driving the fate of trace elements in soil.

Research on the possible adverse effects of trace elements' accumulation in agricultural soils amended with municipal sewage sludge has begun to focus on the chemical forms of these elements in relation to their uptake by plants [4,5]. Later, scientists utilized a sequential extraction technique with various extractants to extract various chemical forms of these elements in the solid phase [2,6–9]. This chapter presents the results of a fractionation study of Mn, Zn, Cu, Cd, Cr, Pb, and Ni conducted at the end of a 65-day plant uptake experiment, and their chemical association in two soils amended with SS at varying rates from two different sources. This chapter also attempts to predict the potential fate of these trace elements with respect to mobility beyond the rhizosphere.

10.2 MATERIALS AND METHODS

10.2.1 SOILS

Surface horizons (0 to 15 cm) of Candler fine sand (sandy, hyperthermic, uncoated, Typic Quartzipsamments) from a University of Florida experimental citrus grove in Lake Alfred, Florida, and Ogeechee loamy sand (silicious, thermic Typic Ochragult) from a fallow land in Savannah, Georgia, were used to study the effect of application of varying rates (0, 24.7, 49.4, 98.8, and 148.3 Mg ha^{-1}) of two SS materials on elemental uptake by sorghum–Sudan grass. Each of these treatments was replicated three times. At the end of 65 days of the plant growth experiment, various amended surface soils were sampled for follow-up fractionation study with the help of a sequential extraction procedure to identify the chemical association of residual trace elements, which could aid in predicting the potential fate of the trace elements in soil amended with these materials.

Selected properties of the surface samples of the two soils used in this study determined by standard methods are listed in Table 10.1. Characterization data of sewage sludge are also presented

TABLE 10.1
Selected Properties of Sewage Sludge and Soils Used in the Study

Properties[a]	Units	TSS[b]	PSS[c]	Candler[d]	Ogeechee[e]
pH (1:1 water:soil)		7.2	6.9	6.8	2
K	mg kg^{-1}	1785.0	1206.0	47.6	64.9
Na	mg kg^{-1}	1497.0	670.8	4.9	38.2
P	mg kg^{-1}	18540.0	13250.0	112.8	206.0
Ca	mg kg^{-1}	18890.0	15980.0	169.2	284.3
Mg	mg kg^{-1}	2571.0	1632.0	62.4	62.2
Mn	mg kg^{-1}	203.2	91.2	62.5	14.1
Fe	mg kg^{-1}	17210.0	10420.0	591.4	661.5
Cu	mg kg^{-1}	246.9	219.5	38.4	1.2
Zn	mg kg^{-1}	597.1	542.5	13.7	3.0
Pb	mg kg^{-1}	29.1	47.2	20.9	4.9
Cd	mg kg^{-1}	10.4	4.1	<0.5	<0.5
Ni	mg kg^{-1}	19.6	16.6	<1.0	<1.0
Cr	mg kg^{-1}	80.8	27.4	7.4	4.3
Al	mg kg^{-1}	16890.0	10170.0	1216.0	1383.0
B	mg kg^{-1}	97.8	107.6	1.1	<1.0
S	mg kg^{-1}	10150.0	8972.0	46.1	74.7
Sand	g kg^{-1}	—		967.0	860.0
Silt	g kg^{-1}	—		8.0	100.0
Clay	g kg^{-1}	—		25.0	40.0
Organic C	g kg^{-1}	—		5.1	11.6
CEC	cmol kg^{-1}			2.2	3.9
Texture				Fine sand	Loamy sand

[a] Total elemental compositions were determined on acid digest by ICP-OES.
[b] Collected from Travis field water quality control plant of the city of Savannah (70% domestic and 30% industrial).
[c] Collected from President Street water quality control plant of the city of Savannah (99% domestic and 1% industrial).
[d] Collected near Lake Alfred in Polk County, Florida.
[e] Collected near Savannah in Chatham County, Georgia.

in the same table. Detailed textural characterization indicated that soil properties were rather uniform in the field from which soil samples were collected and throughout the upper 15 cm of the soil profile. Because the soils in the pot were homogeneously mixed with varying rates of amendments, representative dried subsamples were collected from variously amended pots at the end of the 65-day plant uptake experiment for chemical association of trace elements study.

10.2.2 TRACE ELEMENT FRACTIONATION

The soil samples from each pot at the end of the 65-day plant uptake study were used for fractionation of chemical forms of Mn, Zn, Cu, Cd, Cr, Pb, and Ni. The total content of Mn, Zn, Cu, Cd, Cr, Pb, and Ni in the soil samples was determined on filtered extracts obtained from 2-g samples, which were digested with 12.5 mL 4 *M* HNO_3 at 80°C for 16 h. The trace elements in triplicate 2-g samples were fractionated by a modified sequential extraction procedure used by Sposito et al. [8] to quantify exchangeable, sorbed, organically bound, and precipitated forms (as carbonate and as sulfide).

Each 2-g soil sample was weighed into 50-mL centrifuge tubes, and 25 g each of the following reagents were sequentially added and shaken for the time specified for each extractant in the order listed:

- 0.5 *M* KNO_3, 16 h (exchangeable)
- Deionized water, 2 h (three times and combine all three fractions together; sorbed)
- 0.5 *M* NaOH, 16 h (organically bound)
- 0.05 *M* Na_2 EDTA, 6 h (carbonate from)
- 4 *M* HNO_3 at 80°C for 16 h (sulfide form)

At the end of each extraction period, the soil suspension was centrifuged, the supernatant was decanted into Whatman no. 42 filter paper, and then filtrate was collected. The centrifuge tube with soil was weighed once after the addition of the extractant and again after the solution was filtered, to estimate the quantity of the entrained solution. The quantity of each subsequent extractant was adjusted to account for the entrained solution from the previous extraction. The concentration of trace elements in the filtered solution was determined by Perkin Elmer optical emission spectroscopy (inductively coupled plasma optical emission spectroscopy) RL 3100. The amount of various trace elements in the entrained solution was carried over into subsequent extraction. The contribution of various trace elements in the entrained solution from the previous extraction was used to correct calculations of various trace elemental content in the subsequent extraction.

The concentrations of total trace elements were also determined by USEPA method no. 3050 [10]. This method (second method) involved digestion of 1.0 g soil in 10 mL of HNO_3. Then the solution was cooled and an additional 5 mL of concentrated HNO_3 was added and refluxed twice for 30 min each time. After the solution was cooled, 3 mL of 30% H_2O_2 was carefully added and refluxed in a block digester to obtain a clear solution. Then, 5 mL of concentrated HCl and 10 mL of deionized water were added and refluxed without boiling. The solution was then cooled and quantitatively transferred into 50 mL volumetric flask and volumized to 50 mL with deioinzed water. Total trace elemental concentrations in diluted digest was determined using Perkin Elmer optical emission spectroscopy (inductively-coupled plasma optical emission spectroscopy) RL 3100.

10.3 RESULTS AND DISCUSSION

10.3.1 TOTAL TRACE ELEMENT CONTENTS

The total elemental contents in soils amended with varying rates of two different sources of sewage sludge were determined by two different methods, as described under Section 10.2. However, total

TABLE 10.2
Effect of Soil Type and Rate of Raw Sewage Sludge Amendment on Total Content of Various Trace Elements at End of 65-day Sorghum–Sudan Grass Growth

Soil[a]	Source and amendment rates (Mg ha^{-1})	Cu (mg kg^{-1})[b]	Zn	Cd	Cr	Pb
	[PSS]					
Candler fine sand [FS]	0.0	16.92	8.10	0.06	1.92	2.46
	24.7	25.10	19.46	0.07	2.13	3.06
	49.4	31.20	31.15	0.13	2.69	9.26
	98.8	44.61	44.83	0.19	5.14	13.48
	148.3	56.25	58.88	0.20	6.27	16.09
Ogeechee loamy sand [GS]	0.0	8.78	8.89	0.07	6.32	11.71
	24.7	13.30	21.71	0.16	6.52	13.46
	49.4	23.14	36.51	0.20	9.01	15.84
	98.8	51.95	78.83	0.45	13.33	26.23
	148.3	63.17	121.96	0.51	14.71	42.38
	[TSS]					
Candler fine sand [FS]	0.0	12.92	7.21	0.06	2.54	5.13
	24.7	18.33	14.29	0.11	3.38	5.75
	49.4	22.67	46.69	0.36	5.83	6.97
	98.8	57.54	89.13	0.78	10.35	9.68
	148.3	75.00	141.25	1.29	15.40	11.88
Ogeechee loamy sand [GS]	0.0	4.33	3.38	0.05	5.43	5.88
	24.7	10.29	22.46	0.21	7.30	7.19
	49.4	15.00	42.88	0.46	9.66	8.31
	98.8	46.08	100.71	1.17	15.29	15.49
	148.3	59.67	142.08	1.56	20.27	18.75
LSD ($p = 0.05$)		3.12	5.84	0.10	0.43	1.53

[a] Labels next to the soil names in the parentheses [FS] and [GS] represent Florida soil and Georgia soil, respectively. [TSS] and [PSS] represent sewage sludge materials from Travis field and President Street water quality control plants in Savannah, Georgia.

[b] Numbers presented are means of three replicate sample analyses.

Note: LSD values were calculated for total trace element contents determined by HNO_3 acid digestion in soils amended with varying rates of two different sources of sewage sludge and collected at the end of 65 days of plant growth (U.S. Environmental Protection Agency, 1986, in: *Test Methods for Evaluating Solid Waste*. 3rd ed. USEPA SW-S846. U.S. Gov. Print. Office, Washington, D.C. 30501–30594USEPA, 1986).

content of Cu, Zn, Mn, Cr, and Pb in the soil samples-determined digestion step employed by USEPA method [10] is listed in Table 10.2. It is interesting to note that the trace element contents of the two soils, at any level of sewage sludge application, reflected the trace element composition of the sewage sludge. The order of trace element content in original sewage sludge material in TSS is Zn > Cu > Cr > Pb > Ni >Cd; this order in PSS material is Zn > Cu > Pb > Cr > Ni > Cd. The order of trace element content in unamended (preplant) Candler fine sand of Florida is Mn > Cu > Pb > Zn > Cr > Ni > Cd and, in unamended (preplant) Ogeechee loamy sand of Georgia, it is Mn > Pb > Cr > Zn > Cu > Ni > Cd (Table 10.1).

However, at the end of 65-d sorghum–Sudan grass growth, the order of total trace element in soils amended with varying rates of different sewage sludge material varied according to their source of SS. The order of total trace element contents amended with TSS in both soils was Zn > Cu > Cr > Pb > Cd; this order in PSS amended soils was Zn > Cu > Pb > Cr > Cd (Table 10.2). Interestingly, Ni was virtually nondetectable and therefore the concentrations of Ni were not

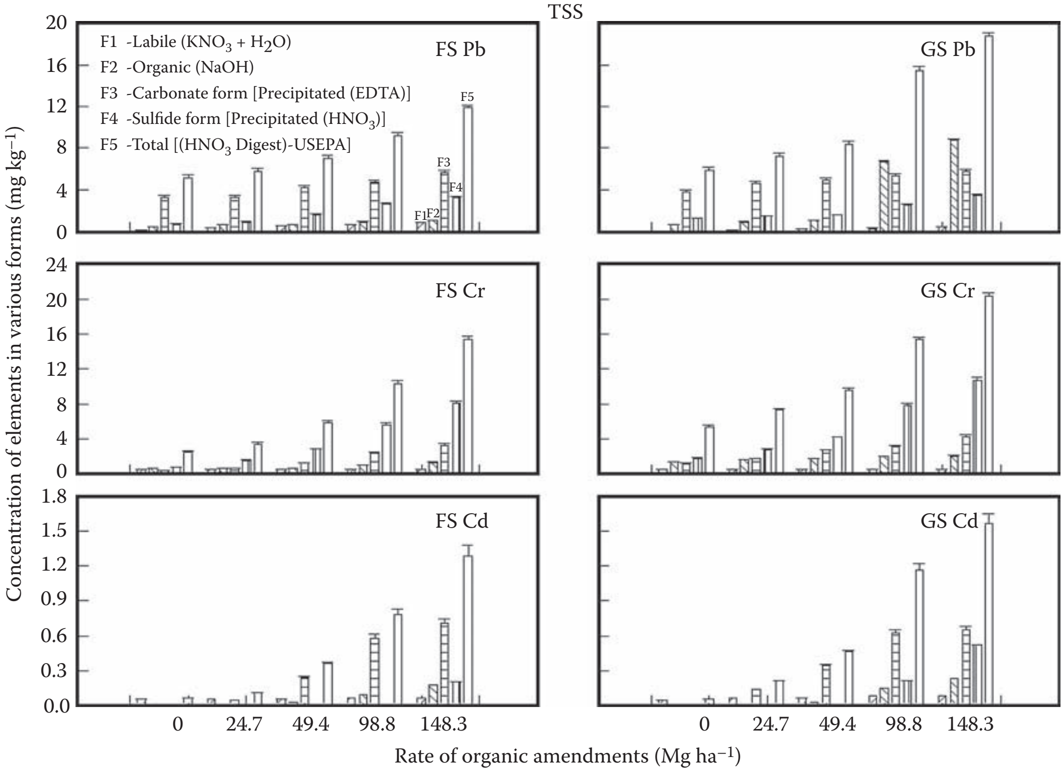

FIGURE 10.1 Distribution of Cd, Cr, and Pb into various chemical fractions at the end of 65-day sorghum–Sudan growth in sandy and loamy sand soils amended with various rates of industrial (70% domestic and 30% industrial — TSS) sewage sludge material obtained from a water quality-control plant in Savannah, Georgia.

presented in Table 10.2. Disappearance of Ni is attributed to greater uptake by sorghum–Sudan grass. A significant amount of Ni accumulation was observed in shoots and roots of sorghum–Sudan grass; Pb accumulation was observed mostly in roots. Accumulation of Ni in roots was greater than in shoots of sorghum–Sudan grass. Furthermore, in both soils, total trace element concentrations increased approximately proportionally to the application rates of different sewage sludge materials used to amend these soils.

10.3.2 DISTRIBUTION OF TRACE ELEMENTS INTO VARIOUS FRACTIONS

The chemical association of various residual trace elements in the soils amended with varying rates of different sources of sewage sludge at the end of sorghum–Sudan crop growth was determined by sequential extraction procedures. This procedure would help to identify the relative proportions of "exchangeable," "sorbed," "organic," "carbonate," or "sulfide" forms of these trace elements. Figure 10.1 through Figure 10.4 present distribution of various trace elements among these various fractions in soil amended with these two sewage sludge materials, along with total elemental contents determined by the USEPA method [10].

Theoretically, summation of various fractions of any trace elements should be equal to the total amount of that element extracted from fresh soil with 4 M HNO_3 digest. Total amount of various trace elements determined by 4 M HNO_3 digest is not presented here. The experimental precision at any step of the sequential extraction procedure was always better and the sum of extracted trace elements was always near, though usually systematically about 1 to 7% lower, than the total trace

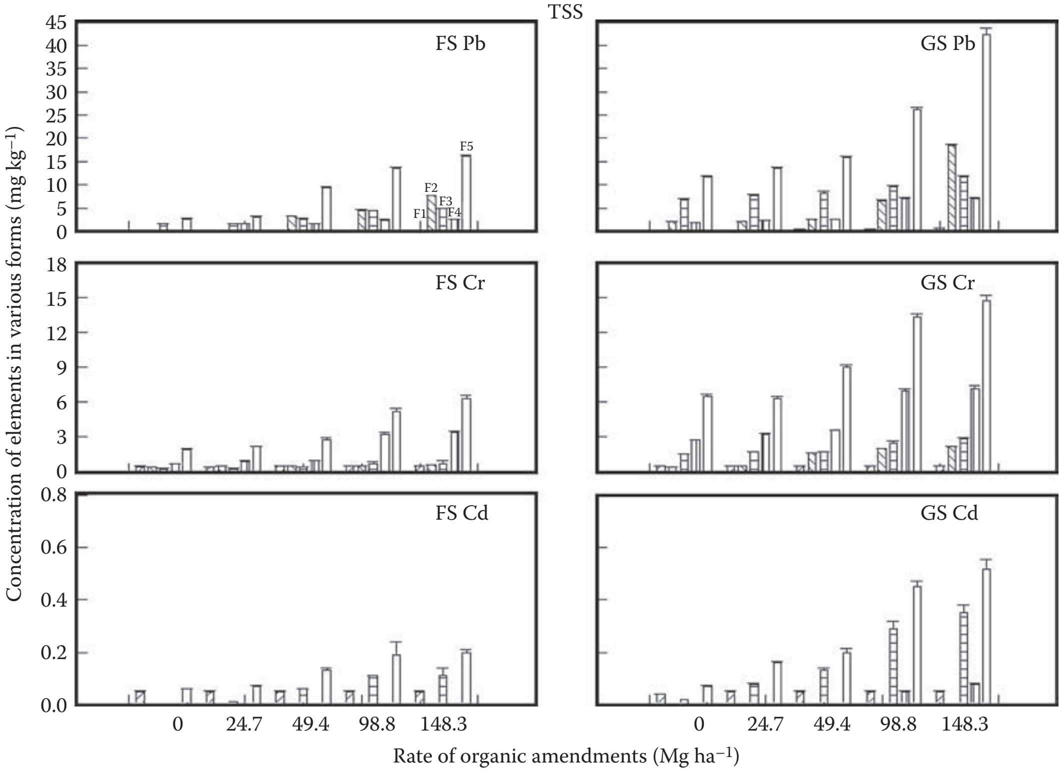

FIGURE 10.2 Distribution of Cd, Cr, and Pb into various chemical fractions at the end of 65-day sorghum–Sudan growth in sandy and loamy sand soils amended with various rates of domestic (99% domestic and 1% industrial — PSS) sewage sludge material obtained from water quality control plant in Savannah, Georgia.

elemental contents determined by 4 HNO_3 digest on fresh samples. These deviations were perhaps due to some experimental errors. However, the summation values for various trace elements reported in this study were about 5 to 20% lower than that of total trace elements contents determined by HNO_3 + HCl and H_2O_2 digestion procedures [10] and reported in Table 10.2.

The overestimation of total trace element contents by the USEPA method compared to that of the other two procedures is basically due to recovery of trace elements from organic material through the oxidation process. Chemical association (fractionation) study data were presented only for Cd, Cr, Pb, Cu, Zn, and Mn. However, the trace element Ni was nondetectable for all the fractions studied and therefore was not reported.

10.3.2.1 Exchangeable Fraction

Exchangeable fractions of various trace elements are defined as the amount that could be extracted with 0.5 KNO_3 during the first step of the sequential extraction procedure. In this study, irrespective of soil type, source, and rates of sewage sludge application, presence of very low to nondetectable amounts of Cd and Cr were evident as exchangeable fraction. However, presence of Mn in exchangeable fraction accounted for about 15% of the total contents in the soil at the end of 65 days of sorghum–Sudan growth. Other trace elements, such as Zn, Cu, and Pb in exchangeable form, accounted for only 1 to 4% of the total. Actual quantities of all the trace elements increased with increasing rates of sewage sludge amendments, irrespective of soil types or source of sewage sludge.

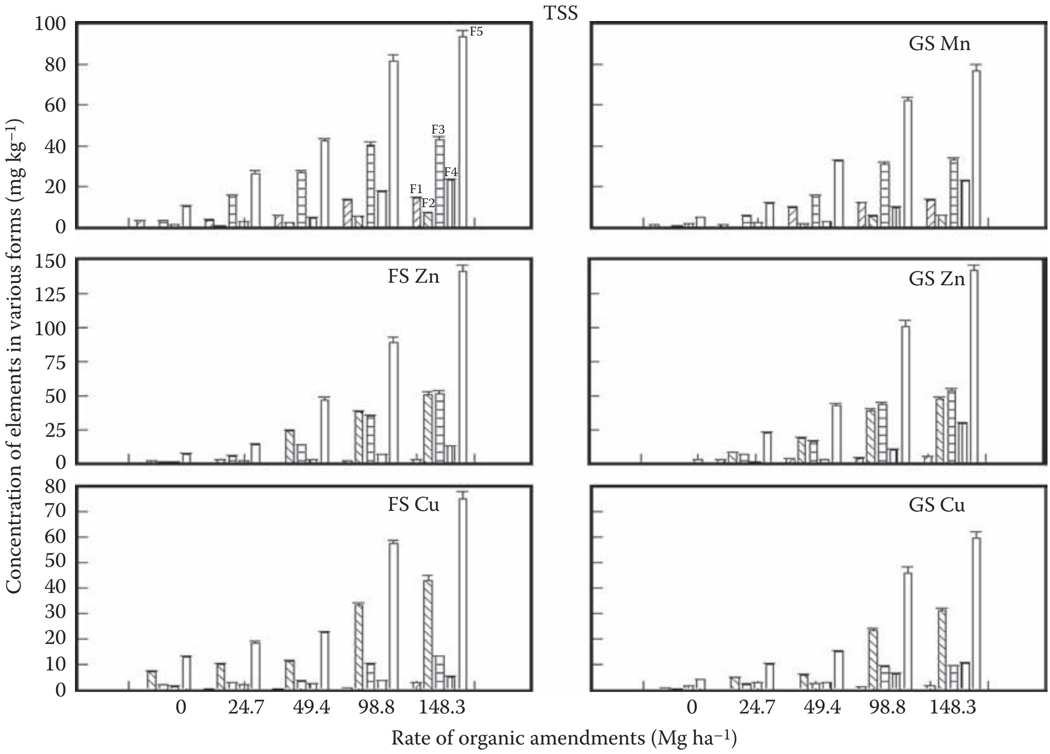

FIGURE 10.3 Distribution of Cu, Zn, and Mn into various chemical fractions at the end of 65-day sorghum–Sudan growth in sandy and loamy sand soils amended with various rates of industrial (70% domestic and 30% industrial — TSS) sewage sludge material obtained from water quality control plant in Savannah, Georgia.

10.3.2.2 Sorbed Fraction

Sorbed fractions of various trace elements are defined as the amount that could be extracted with deionized water as a second step in the sequential extraction procedure following the KNO_3 extraction step. Except for Cd and Cr, all the other trace elements studied (Zn, Cr, Pb, and Mn) in sorbed fraction were quantitatively smaller compared to that of the exchangeable form. The sorbed fraction of Cr accounted for about 2.6 to 22.0% of its respective total content; the sorbed Cd accounted for 5 to 85% of its respective total content.

10.3.2.3 Labile Fraction

Amounts of exchangeable and sorbed fractions were added together and presented as labile components of all these trace elements in Figures 10.1 through Figure 10.4. The labile fraction is the fraction that is readily available for plant uptake or leaching. Therefore, having more labile fraction of any of these trace elements would pose a serious concern because they can cause toxicity problems or groundwater contamination due to loading. The relationships among various fractions for various trace elements — how these various fractions are affected by soil type, sewage sludge source, and rates of amendments — are shown at a glance in Figure 10.1 through Figure 10.4. Overall, this labile fraction is substantially very low compared to other fractions.

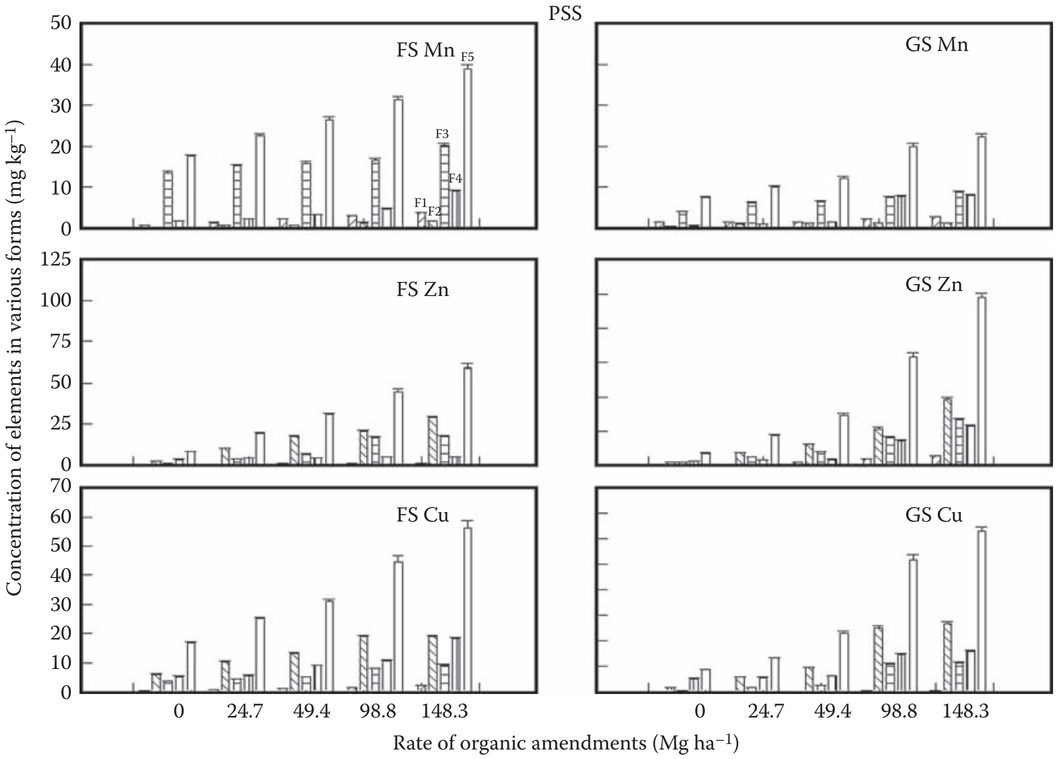

FIGURE 10.4 Distribution of Cu, Zn, and Mn into various chemical fractions at the end of 65-day sorghum–Sudan growth in sandy and loamy sand soils amended with various rates of domestic (99% domestic and 1% industrial — PSS) sewage sludge material obtained from water quality control plant in Savannah, Georgia.

10.3.2.4 Organic Fraction

Organically bound fractions of trace elements are defined as the amount that could be extracted from soil with 0.5 NaOH for 16 h of equilibration under shaking conditions. This is the third step following, KNO_3 and water extraction steps in the sequential extraction procedure described by Sposito et.al. [8]. Among the trace elements studied for various chemical associations, residual Cu at the end of sorghum–Sudan crop growth in soils amended with varying rates of different sources of sewage sludge accounted for about 32 to 59% of the total Cu as in organic form. Similarly, Zn accounted for about 21 to 57% of the total Zn, and Pb accounted for about 7 to 48% of the total in organic form.

Furthermore, it was observed that the organic form of Cu almost doubled in actual quantity at low to moderate rates of sewage sludge amendment in Candler fine sand from Florida compared to that of Ogeechee loamy sand of Georgia for the corresponding rate of amendment application (Figure 10.3 and Figure 10.4). A somewhat similar trend was observed for Zn but not prominently as for Cu. The amount of organic fraction of Cu and Zn was not substantially affected by rate of amendment application at medium to higher rates, but a greater increase was observed at the highest rate of amendment application (148.3 Mg ha^{-1}). The organic fraction of Pb increased with increasing rates of amendment application and the increase in actual quantities was great at the highest rate of sewage sludge application. Organic fraction was very prominent in Ogeechee loamy sand of Georgia compared to that in Candler fine sand of Florida. In contrast, the organic form of Cr was higher at all application rates of sewage sludge in Ogeechee loamy sand, but not in Candler fine sand from Florida (Figure 10.1 and Figure 10.2).

10.3.2.5 Carbonate Fraction

The carbonate forms of trace elemental fractions are defined as the amount that could be extracted from soil with 0.05 Na-EDTA for 6 h of equilibration under shaking conditions. This step is the fourth following the extraction of organic fraction with 0.5 NaOH. All the trace elements studied in this study showed carbonate fraction in both soils amended with sewage sludge. However, among all the trace elements, a major portion of residual Pb, Cd, and Mn were present as carbonate, irrespective of source of sewage sludge and type of soil.

Among these three trace elements, about 50 to 60% of total residual Mn was present as carbonate form, irrespective of soil type and rate of sewage sludge application. The carbonate fraction of total Cd accounted for about 50 to 70% and the Pb carbonate fraction accounted for about 28 to 65% of the total Pb in both soils, irrespective of source of sewage sludge. Even though relative proportions of carbonate forms of Cu and Zn in soils amended with both sewage sludge materials and in both soils were somewhat comparable, the actual quantity of Cu present as carbonate form was greater in Candler fine sand from Florida and the actual quantity of Zn present as carbonate form was greater in Ogeechee loamy sand of Georgia. The carbonate form of Cr accounted only for 12 to 25% of the total Cr present in residual soil, irrespective of soil type and source of sewage sludge.

10.3.2.6 Sulfide Fraction

Trace elements in sulfide forms are generally extracted with the help of 4 HNO_3 as the last step in the sequential extraction procedure described by Sposito et. al. [8]. All the trace elements studied in soils amended with sewage sludge indicated greater percentages present as sulfide form. In addition, irrespective of trace elements, the sulfide form of trace elements (Cu, Zn, Cr, Cd, Pb, and Mn) increased with increasing amount of sewage sludge application. In terms of actual quantity (Cr > Pb > Cd), quantities of Cd, Pb, and Cr were comparatively less when compared with other trace elements studied. Even though actual quantity of Cr was less, this represented about 29 to 65% of the total Cr content. Furthermore, about 5 to 30% of total Cu and Zn was present as sulfide form. Similarly, about 8 to 39% of total Mn was present as sulfide form.

10.4 GENERAL DISCUSSION AND CONCLUSION

The accumulation of Zn, Cu, Cr, Pb, Ni, Cd, and Mn in soils amended with sewage sludge was found to be governed by the content of the metals in amendment source and rate of sewage sludge application, and also the influence of plant growth and uptake. Soil properties, trace metal content, and rate of sewage sludge application appeared to play a role in determining the amounts of various fractions of trace elements. In general, it was evident that Ogeechee loamy sand of Georgia had greater specific trace element content at a particular SS application rate compared to that of Candler fine sand from Florida. Even though both SSs had substantially greater amounts of Ni (Table 10.1) prior to the application to these soils, no detectable amount of Ni was found in soils as any of those chemical fractions studied at the end of the 65-day sorghum–Sudan crop growth. Absence of Ni in residual soil was an indication of plant uptake; this was confirmed by the experimental data obtained by analyzing plant roots and shoots. However, the plant accumulation of Ni data is not presented in this chapter.

The actual quantity of labile Cu, Cr, Cd, and Pb in the soils, which was extractable with KNO_3 and H_2O, was very low, averaging between 0.0 to 3.0 mg L^{-1}, regardless of the types of soils and source and rate of SS application. However, for Zn and Mn, the KNO_3 extractable fraction was substantially greater compared to that of the H_2O extractable fraction. Combined (KNO_3 + H_2O) fractions for Zn accounted for between 2.5 and 10.0% of the total Zn; for Mn, they accounted for between 3 and 25% of the total Mn. The low amount of trace elements in the KNO_3 + H_2O fraction could signify a low availability of these elements to crop plants because the readily soluble form of a trace metal is often regarded as the most bioavailable form. However, the bioavailable forms are related to several properties and reactions within the soils [11,12] and several chemical extractants developed to represent plant absorption may extract trace elements from several fractions [13].

The application of sewage sludge to the field soils is expected to reduce the HNO_3 (sulfide) fraction percentages for all of the trace elements, regardless of the type of sewage sludge or soil, due to their acidic nature during their decomposition. This trend was generally observed with sewage sludge application for most of the trace elements studied in this experiment with the exception of Cr. The sulfide fraction of Cr represented about 28 to 62% of the total Cr content, which represents the slowly available fraction. It is also generally observed that the application of sewage sludge tended to increase percentages of NaOH (organic) fraction. Trace elements, such as Zn, Cu, and Pb, very closely followed this trend in the study, as expected. However, Cd and Mn did not follow this trend. In contrast, a significant portion (about 19 to 80%) of residual Cd and Mn was present as carbonate fraction, irrespective of soil type and source of sewage sludge.

Irrespective of soil type and source of sewage sludge material, the organic form of Cu for Cu and Zn was the predominant Cu form in residual soil amended with sewage sludge. However, the next greater percentage of Cu and Zn was precipitate form and the source of sewage sludge to a certain extent determined whether it was in sulfide form or carbonate form of precipitate. However, in general, a greater percentage of Zn was present as carbonate (Na_2EDTA) fraction irrespective of soil type or source of sewage sludge. In the case of Cu, a greater percentage of Cu was present as sulfide (HNO_3) in both soils receiving sewage sludge exclusively from a domestic source; the carbonate form of residual Cu was second dominant in both soils receiving sewage sludge from industrial and domestic mixture.

A major portion of Cr present as sulfide (HNO_3) fraction, irrespective of soil types, accounted for about 29 to 62% of total Cr. Relative proportions of various fractions of Pb were affected mainly by soil type; a quantitatively greater amount of Pb in any fraction was generally found in Ogeechee loamy sand compared to that of Candler fine sand of Florida. Among the various fractions studied, a quantitatively greater amount of Pb was present as organic (NaOH) fraction. Irrespective of soil type and source of sewage sludge precipitate form of Pb (carbonate or sulfide form) was the next dominant form Pb in residual soil. Irrespective of the soil type, and source of sewage sludge, the carbonate form of Cd and Mn was the dominant form present in residual soils. The various fractions of Mn were in the following order: $Na_2EDTA > HNO_3 > H_2O > NaOH > KNO_3$. For Cd, the order of fraction was $Na_2EDTA > H_2O > HNO_3 > NaOH > KNO_3$.

It is evident that the application of sewage sludge shifted the solid phases containing Cu, Zn, Cr, Pb, Cd, Ni, and Mn in the soils away from those extractable with more severe reagents, such as 4 HNO_3, to those extractable with milder reagents such as dilute NaOH, NaEDTA, KNO_3, and H_2O. It was further evident that exchangeable (KNO_3) and sorbed (H_2O) fractions were substantially low and the major portion of the trace elements was in organic (NaOH) and carbonate (NaEDTA) and sulfide (HNO_3) fractions. This shift suggests that sewage sludge application would provide the trace elements in labile chemical forms that could be more readily available to crop plants with time. In the meantime, presence of substantially low amounts of exchangeable plus sorbed (labile) fractions of all the trace elements in sewage sludge-amended soils indicated very low mobility beyond the rhizosphere.

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