

Review

Fractionation, characterization and speciation of heavy metals in composts and compost-amended soils

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Speciation of heavy metals in soils determines the availability for metals for plant uptake and potential for contamination of groundwater following application of composts to agricultural lands. Methods used to characterize heavy metals in solid phase of composts and compost amended soils include physical fractionation and chemical extraction. Chemical extraction schemes are most frequently used approach to fractionate trace metals in soils, sewage sludge and composts. Several variations exist in the sequential extraction procedures. These variations include reagent types, strength, volume and extraction time. A main drawback shared by all sequential extraction schemes is that the procedures themselves are complex and time consuming. This setback has been overcome by the use of ultrasound accelerated extraction which reduce the extraction time for the entire extraction steps to about 90 minutes allowing composting process to be monitored more frequently which help to provide detailed understanding of the partitioning behaviour of heavy metals. In spite of the variability the sequential extraction schemes, they all aimed at correlating each fraction with the mobility and plant availability of each metal. Several studies have shown that phase association of heavy metal in composts include water-soluble, exchangeable, precipitated as discrete phases, co-precipitate in metal oxides and adsorbed or complexed by organic ligands and residual forms. The phase association and solubility of metals changes over composting time thereby altering metal availability. It is apparent that the positive effects of resulting from compost application far outweigh the negative effect, but more research is needed on a wide range of municipal solid waste compost with more precise determination of the fate of municipal solid waste compost applied trace metals in the environment.

Key words: Fractionation, speciation, heavy metal, bioavailability, composts, compost-amended soils.

INTRODUCTION

The concept of recycling waste nutrient and organic matter back to agricultural land is feasible and desirable. Land application represents an economically desirable outlet for the producers of a waste and a potential cheap source of organic matter and fertilizer elements for landowners (Iwegbue et al., 2006a). In addition to the

potential beneficial components, some waste materials may also contain non-essential elements, persistent organic compounds and microorganisms that may be harmful to plants (Kurihara, 1984; Mullin and Mitchell, 1994; Iwegbue et al., 2005).

The presences of heavy metals in composts raise serious concern about the adverse environmental impact as a result of excessive compost application to agricultural lands. High and excessive accumulation of heavy metals in soil and other media may eventually contaminate both human and animal food chain (He et al., 1992; Iwegbue et al., 2005). Because of this, many

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Table 1. Heavy metals limits (mg/kg) for several countries with compost regulations or standards, as modified from Van Der Warf et al. (2002).

Element	Countries												
	A	A ^b Class 2 ^c	B Agr	B Park	CH	DK	F	D	I	NL	NL	Sp	CAN ^d
Arsenic	-	-	-	-	-	25	-	-	10	25	15	-	13
Boron	100	-	-	-	-	-	-	-	-	-	-	-	-
Cadmium	4	1	5	5	3	1.2	8	105	105	2	1	40	3
Chromium	150	70	150	200	150	-	-	100	100	200	70	750	210
Cobalt	-	-	10	20	25	-	-	-	-	-	-	-	34
Copper	400	100	100	500	150	-	-	100	300	300	90	1750	100
Lead	500	150	600	1000	150	120	800	150	140	200	120	1200	150
Mercury	4	1	5	5	3	1.2	8	1.0	1.5	2	0.7	25	0.8
Nickel	100	60	50	100	50	45	200	50	50	50	20	400	-
Selenium	-	-	-	-	-	-	-	-	-	-	-	-	2
Zinc	1000	400	1000	1500	500	-	-	400	500	900	280	4000	500

^aCountry codes: A: Austria; B: Belgium; CH: Switzerland; DK: Denmark; F: France; D: Germany; I: Italy; NL: Netherlands; SP: Spain. CaM: Canada U.S.A.: United state of American: JP = Japan

^bCalculated on 30% organic matter basis.

^cNotes: Class-2 versus class 1 or class A versus AA; Agr: agricultural use; Park: horticultural use.

^dDetermined from nitric acid digest.

countries in the world have established specific guidelines and standards for application of composts in agricultural lands. However, these guidelines are lacking in most African countries. The guidelines, which are generally based on phytotoxic effects and limited to plant uptake studies normally specify the maximum allowable total metal concentration and exhibit considerable variation. Heavy metals limits (mg/kg) for some countries of the world with composts regulations or standards is given in Table 1.

An appreciation of the effect of heavy metals in composts on crops can only be attained from precise knowledge of the heavy metal speciation and the response to plant species. In addition, speciation will determine metal mobility and hence potential contamination of ground water following compost application. Although speciation schemes to examine the solid and solution phase of wastes and waste amended soils are subject to analytical limitations. Despite uncertainties as the selectivity of the various extractants and possible problem due to redistribution and readsorption phenomena, procedures provides qualitative information on forms, association, bioavailability, their potential effects and guidelines for land application.

This review examines the various speciation schemes that have been applied to composts and compost amended soil with the view of describing the most effective scheme. It will, however concentrate on the environmental significance rather than the techniques used to measure heavy metals.

HEAVY METALS DISTRIBUTION IN COMPOSTS

Trace metals composition of composts varies widely depending on the sources, composting process (He et al., 1992) and geographical location (Krogmann, 1999). The levels of heavy metals in municipal solid waste composts have been reported for many countries in the world by several authors (Watanabe and Kurihara, 1982; Sridhar and Bammekke 1986; He et al., 1992; Krogmann 1999, Koivula et al., 2000) (see Table 2). Like soils, sediments and sludge, trace metals can exist in a variety of forms in composts. These forms include (i) water-soluble, (ii) exchangeable, (iii) linked to organic substances, (iv) occluded or co-precipitated with oxides, carbonates and phosphates, or other secondary minerals and (v) ions in the crystalline lattices of the primary minerals (Emmerich et al., 1982; Lake et al., 1984; Petruzzelli, 1989; He et al., 1992; Iwegbue et al., 2006b,c). The first three chemical forms are considered to be balanced among themselves; this equilibrium is influenced by pH and the concentrations of metals and ligands. The metals present in these forms are considered to be most available forms of plant nutrition, each successive form representing less availability (Petruzzelli, 1989; Iwegbue et al., 2006b).

The distribution of metals between the specific forms varies widely according to the individual metal and the characteristics of the compost, which depend on the physical, chemical and composting process. These parameters include pH, temperature, oxidation-reduction potential and the presence of complexing ligands. During

Table 2. Heavy metals levels (mg/kg) in composts from some countries of the world.

Heavy metal	USA He et al. (1995)	Nigeria Sridhar & Bammek e (1986)	Italy Giusquani et al (1992)	Germany Krogmann (1999)	Germany* Fricke et al. (1992)	Germany* Kehres (1990)	USA* Richard & Wood bury (1992)	Canada Hicklenton (1996)	(1999)	Japan Watanable & Kurihara (1982)	Finland** Kiovula et al (2000)	France De Haan (1988)	Netherland	Spain Gonzalez -villa et al. (1982)
Arsenic	7.7	-	-	-	-	4.8	-	7	2	2	-	-	-	-
Boron	6.9	-	-	-	-	-	-	10	30	-	-	60	60	-
Cadmium	3.3	1.76	5	29.6	0.78	0.57	1.1	3	2	2	0.17	7	6	0.04
Chromium	76.0	106.08	86	0.63	33.7	46.3	15	21	11	83	-	270	220	-
Cobalt	-	609.65	-	15.7	-	-	-	11	6	-	-	-	-	-
Copper	281	14.24	421	-	43.2	75.7	64	170	270	213	3.0	250	630	200
Iron	-	11847.27	11993	33.7	-	13.0**	-	-	-	-	-	-	-	-
Lead	234	7.87	863	6.7**	77.6	125	74	99	14	232	20	600	900	9
Manganese	501	575.94	311	67.6	-	603	-	-	-	-	-	600	400	500
Mercury	-	14.47	-	243	330*	327*	100*	1	1	2	0.03	4	5	-
Molybdenum	-	-	-	157*	-	-	-	12	9	-	-	-	-	0.76
Nickel	340	12.78	44	-	19.1	40.7	8	-	-	-	-	190	110	-
Selenium	1.7	-	-	7.7	-	-	-	1	1	-	-	-	-	-
Zinc	655	45.82	116	205	233	359	292	370	610	641	13.1	1000	1650	700

*mg mg⁻¹**g kg⁻¹

*Source separated biogenic waste.

composting, the species of heavy metal often changes thus altering the availability to plants, for example composted sludge (Chaney et al., 1975), which would also change metal availability (Simeoni et al., 1984). Plant availability of Cd, and Zn from composted sludge seems to be lower than uncomposted sludge (Chaney et al., 1975; Giordano et al., 1975; Simeoni et al., 1984).

Total trace metal composition of composts is of little importance in determining the total trace metal uptake by plants and consequently, contamination of the food chain since the different forms have different mobilities, bioavailabilities and potential environmental contamination. It is therefore, more important to know the distribution of each trace metals in the forms, than just the total content (Lake et al., 1984; Petruzzelli, 1989). The various techniques used to estimate heavy metal distribution in soils, and sewage sludge has been adopted for fractionation of heavy metals in composts and compost amended soils. There are two basic techniques. These techniques include (i) physical fractionation based on particle size and density, and (ii) chemical extraction based on selective dissolution of trace metals in different reagents.

Physical fractionation: The distribution of trace metals in different particle size and density fractions has been reported (Krauss et al., 1987; Petruzzelli et al., 1989a). These authors found that the fine dense fraction had the highest trace metal content and the coarse light fraction contained the least amount of each trace metals. The content of Pb, Cu, Zn, Ni, Cr, Cd and Hg in the coarse light fraction decreased by 65, 86, 52, 77, 47, 52 and 49%, respectively, as compared with the original compost (Krauss et al., 1987).

Chemical extraction: In order to determine heavy metal availability by means of chemical methods, two different approaches can be used, a single extraction with one reagent considered to be most suitable, or a sequential extraction with various chemical reagents in an increasing order of extractive force (Petruzzelli, 1989). The extraction with single solvent aims directly at the determination of the forms available for the plants, wherein these terms there must be agreement not only in the first 3 categories in the above mentioned lists, but all those metals which can move into the nutritional processes owing to slow alteration of the soil properties. Sequential extraction methods are frequently used to characterize and predict the mobility and bioavailability of heavy metals in compost and compost amended soils. They do, however lack uniformity in procedure, which can make it difficult to compare the results obtained in different studies. Infact the results obtained from different sequential extraction procedures may give very different answers about the geochemical phase within which an element exists. This problem has been solved to some extent by the introduction of the European commission's Bureau communautaire de Reference, BCR, three step sequential extraction method, which has made it possible to harmonize the extraction schemes for the determination

of extractable metals and can be used to enhance quality control of the whole analysis procedure, a key issue in interpreting this type of operational defined speciation (Ure et al., 1993, Song and Greenway, 2005).

In BCR method, the sample is subsequently extracted with three steps. The first step involves extracting with 0.11 molL^{-1} acetic acid which represent water and acid soluble as well as exchangeable fraction. The second step is the extraction with $0.1 \text{ molL}^{-1} \text{ NH}_4\text{OH.HCL}$, which represents the reducible fraction and the fraction combined with Fe/Mn oxides. The third step represents the fraction combined with organic materials, which is accomplished by extraction with $1.0 \text{ molL}^{-1} \text{ NH}_4\text{Ac}$ after the sample has been digested with H_2O_2 (Song and Greenway, 2005).

The extractants commonly used include H_2O , KNO_3 , $\text{Na}_4\text{P}_2\text{O}_7$, EDTA, and HNO_3 . Each extractant is targeted on a single form of each metal, for example H_2O for soluble, KNO_3 for exchangeable, $\text{Na}_4\text{P}_2\text{O}_7$ for organic matter bound, EDTA for carbonate and sulfide precipitated and HNO_3 for residual form of each metal (Lake et al., 1984; He et al., 1992). Other sequential extraction procedures that have been applied for composts (Silvera and Sommer, 1977, Tessier et al., 1979; Schalascha et al., 1982; Sposito et al., 1982; Chang et al., 1984; Sims and Kline, 1991; Fraser and Lum 1983; Tisdell and Breslin, 1995; Ma and Rao, 1997). However precise separation of trace metals is often a problem with available analytical techniques as result of overlap between fractions. Sposito et al. (1982) calculated the amount of metal extracted by a given extracting reagent according to the equation:

$$\mu\text{g extracted} = C \times W - C^1 \times M \quad \dots\dots\dots (1)$$

where C is the concentration ($\mu\text{g/g}$) of the metal in the extracted solution; C^1 is the concentration ($\mu\text{g/g}$) of the metal in the solution extracted in the preceding step of the sequence; and M is the mass of solution (g) carried over to the present extract from the preceding one; W (g) is the mass of the sample. This equation contains a correction factor for the amount of metals in solution entrained in the sample after the centrifugation which follows each extraction. This correction is made in lieu of washing the sample with deionized water after centrifugation because washing may lead to metal losses and therefore, low recovery of metal from a given extraction step.

Water-soluble fraction

The water soluble fraction is certainly the most biologically active. The high toxicity potential of this fraction is proven by the higher sensitivity exhibited by plants grown in hydroponic media. The water soluble fraction has highest potential of contamination of food chain, surface water and groundwater (Leita and De Nobili, 1991; He et

al., 1992). Leita and De Nobili (1991) investigated the water extractable fraction of Cd, Zn, Cu and Pb and changes in water soluble organic carbon during composting of municipal solid waste. The authors reported a progressive increase in the total metal concentrations during composting period was not accompanied by a corresponding increase in the water-extractable amounts of metals. The progressive increase in total metal concentration during composting is due to mineralization of organic matter (Koivula et al., 2000; Barker and Bryson, 2002; Leita and De Nobili 1991). The behavior of water-soluble fraction of heavy metal during composting is dependent on the pH changes as the composting progresses. Petruzzelli (1989) and Caviatti et al. (1993) also reported that increasing the pH of compost lowered the availability of heavy metals.

Leita and De Nobili (1991) reported that water extractable fraction of Pb and Zn decreased rapidly with composting time. Pb and Zn as percentage of total metal content decreased rapidly from 5.8 and 3.2% at the beginning to about 1.3 and <0.2% at the end of 160 days of composting respectively. A completely different and complex behavior was observed for Cu and Cd. Cadmium was characterized by extremely low extractable fraction at the beginning of composting. Water extracts contained <0.02 mgkg⁻¹. Afterward, Cd concentration increased rapidly within few days (Day 8-13), reaching about 37% of the total cadmium content. High variability in the water-soluble fraction of Cd was observed during the period from day 20 to 72 of composting. Afterward the amount decreased again to nearly non detectable levels. The water-extractable fraction of Cu increased slightly up to about 5% during the thermophilic phase, then decreased again and was less variable than Cd. The water-extractable fractions of Pb and Zn were highly correlated ($r=0.99^{***}$ and 0.98^{**} respectively) with concentrations of non humic decomposition products. Non humic substance, mainly composed of soluble polysaccharides, peptides and amino acid were as much as 90% of total soluble organic carbon during first days of composting. The concentration of Cu in the equilibrium solution was significantly correlated ($r=0.94^{**}$) only with the concentration of water-soluble humic carbon. No correlation was found for the water-soluble fraction of cadmium (Leita and De Nobili, 1991).

Canarutto et al. (1991) studied the water-soluble fraction of trace metal from composts. The authors reported that (i) water-soluble contents of Cu, Cd, Zn, Ni and Pb were lower after 60 days of composting than before composting and (ii) in most cases, water soluble trace metal were higher those sequentially extracted with KNO₃. Henry and Wescott (1992) determined the water extractable metal content in a Washington State (USA) commercially produced matured composts. The trend of solubility decreased in the order Ni > Cu > Zn > Cd > Cr > Pb with the corresponding values of 8.1, 4.1, 2.7, 2.5 1.4 and < 1%. Sims and Kline (1991) measured an identical

trend with values of from Ni to Pb of 2.9, 5, 4, 2.5 1 and 0.5% in MSW sewage sludge co-composts. The measured decrease in water extractable fractions of Cu, Zn, Cd, Cr and Pb were 17, 13.8, 8.5, 8.5 and 2.8%, respectively to 1% or less. Water extractable nickel reported by these authors decreased from 29.6 to 7.2%; still at much higher water soluble levels compared to other elements. For both studies, the decrease in the water extractability were slightly offset by increase (50-100%) in the total metal content of the compost during the same time as a result of organic matter loss (Henry and Wescott, 1992).

Tisdell and Breslin (1995) determined the total content and water solubility of cadmium (Cd), lead (Pb), Iron (Fe), copper (Cu), chromium (Cr), nickel (Ni) and zinc (Zn) using the synthetic acid rain water cascade (SRC) extraction protocols to access the environmental acceptability of MSW composts. The SRC leachable fractions of Cu, Zn, Cr, Pb and Fe was <6% in the Pembroke Pine compost and <10% in the St. Cloud compost. Nickel solubility, however, was high and variable in the composts studied. The SRC-extractable Ni ranged from 11.3% for Pembroke Pine compost to 56.2% for St. Cloud compost. The SRC extractable elements from the MSW composts studied decreased in the following order; Ni>Cu>Zn>Pb ~ Cd>Cr>Fe ~ Pb. The order of SRC-extractable fraction of Ni>Cu>Zn>Pb measure in the Pembroke Pines and St. cloud composts were similar to previously reported results (Henry and Wescott, 1992; Sims and Kline, 1991).

Sequential chemical extraction

Various sequential chemical extraction schemes have been adopted for composts and composts-amended soils. These schemes vary in reagent types, volume, strength and extraction time. In spite of the variability in reagents and modification of approaches, they all aimed at correlating each fraction with plant bioavailability. Garcia et al. (1990) studied the simplest sequential chemical extraction technique with CaCl₂ and diethylene triamine pentacetic acid (DTPA) to examine the extractability of metals over composting time. The authors reported that CaCl₂ extractable Fe, Cu, Mn, Zn, Ni and Pb as percentage of total metal content decreased from 84.7, 3.2, 5.0, 2.4, 3.9 and 7.5% at the beginning to 2.7, 0.5, 0.7, 0.3, 0 and 3.5%, respectively, after 90 days of composting. DTPA extractable Fe, Mn, Ni and Pb decreased from 6 to 11%, 22.6 to 9.8%, 4.9 to 3.8% and 26.1 to 21.1%, respectively, but DTPA extractable Cu and Zn increases from 14 to 18% and 27.1 to 35.2%, respectively. DTPA always extract considerably more trace metals than CaCl₂ except for Fe, in which CaCl₂ extracted more Fe than DTPA. This suggested that the organic compounds bound more trace metals than held on the exchange sites.

Gregson et al. (1988) sequentially extracted Pb from compost, the extractants applied include calcium chloride (CaCl₂) (0.5 M) for exchangeable and soluble metal;

acetic acid (0.05 M) for adsorbed; pyrophosphate (0.3 M) for organically bound; acid oxalate + 0.1 M oxalic acid and 0.175 M ammonium oxalate for Fe and Mn oxides occluded/or precipitated ions and nitric acid for the residual fraction. The calcium chloride and acetic acid extractable fractions represent the most readily "available" pool for uptake. The authors found that greater amount of Pb sequentially extracted are in the pyrophosphate fraction i.e. organically bound fraction. The acetic acid and oxalate-extractable fraction are similar. Pb in the nitric acid extractable fraction account for about only 10% of the total lead in the compost.

Petruzzelli (1989) sequentially extracted Cu, Pb, Cr, Cd, Ni from two composts derived from the organic fraction of urban waste. In the adopted procedure, H₂O for water-soluble metals which represents the most mobile and immediately bioavailable fraction of the total content, KNO₃ for exchangeable metals - KNO₃ extracted metals are linked to the surface by coulombic forces, by mean of exchange reaction and while DTPA extracted heavy metals adsorbed or complexed by organic matter according to the stability constants of the complexed. All the three extractable forms are to be considered bioavailable. The author reported <0.01 µg g⁻¹ for water extractable Pb, Cr, Cd, Ni and 1 to 1.5 µg g⁻¹ for water extractable Zn and 2.5 to 5.4 µg g⁻¹ for water-extractable copper. DTPA extracted more metals compared with KNO₃. The amount of metal extracted by the reagents were less than 6% of the total metal content of the composts in all cases except for Cd (11% was extracted from one compost).

Canarrutto et al. (1991) reported the effect of composting time on the sequential extraction Cu, Cd, Zn, Ni and Cr with water, KNO₃, and EDTA. The results indicated that (i) water-soluble trace metals decreased rapidly with composting time. (ii) The amount metal in water extractable fraction were greater than the amount extractable by KNO₃ (iii) EDTA extracted the greatest amounts of trace metals and (iv) total amount of metals extractable by the three reagents decreased with composting time. This is due to complexation by humified organic compounds and changes in pH with composting time.

Tisdell and Breslin (1995) reported the sequential extraction procedure that partition elements into five distinct fractions using multiple extraction of the compost using a more aggressive leaching solution. The five fractions are identified as (i) exchangeable metal ions (1 M MgCl₂ at pH 7) (ii) carbonate bound metal ions (1 M sodium acetate at pH 5) (iii) metal ions bound iron and manganese oxides (0.04 M hydroxylamine hydrochloride (HONH₂HCl) in 25% acetic acid (iv) metal bound to organic matter (0.02 M nitric acid and 30% hydrogen peroxide at pH 2 and 90°C followed by 1.2 M ammonium acetate in 10% nitric acid and (v) residual bound metal ions (HF-H₃BO₂ acid digestion) the SCE protocol for fractions 1 through 4 are described in Tessier et al. (1979) and Fraser and Lum (1983). Fraction 5, residual phase, was extracted using a hydrofluoric-boric acid dige-

stion technique (Silberman and Fisher, 1979). The total content, phase association, and water solubility of cadmium (Cd), lead (Pb), iron (Fe), copper (Cu), nickel (Ni), chromium (Cr) and zinc (Zn) was determined using sequential chemical extraction and synthetic acid rain cascade (SRC) extraction protocol to assess the environmental acceptability of MSW composts. The results showed that with the exception of Cd, the exchangeable fractions of Pb, Cr, Cu, Ni and Fe were less than 4%. The exchangeable fraction of Cd was 12.8 and 10.3% for St. Cloud and Pembroke Pine composts, respectively. Sodium-acetate-extractable Cd and Zn were highest (20-30%); followed by Pb and Ni (4-10%) and Fe, Cr and Cu (<4%). The partition of element within the HONH₂HCl - nitric acid - H₂O₂ and HF-H₃BO₃ extractable fractions of the composts were similar in both composts. The hydroxylamine hydrochloride-extractable fractions of the composts contained >45% of the Zn, 25 to 30% of the Pb, Cd and Ni, 10 to 22% of Fe and Cr and < 5% of the Cu. The nitric acid-H₂O₂ extractable fraction contained between 10 to 20% of the Cd and Zn, 20 to 40% of the Fe, Cr, Ni and Pb, and between 70 to 80% of the Cu associated with MSW composts. Less than 20% of the Cd, Pb and Cu, 20 to 33% of the Pb and Ni and >50% of Fe and Cr were extracted from the HF-H₃BO₃ fraction of the St. Cloud and Pembroke Pine composts.

The partitioning of metals in the swine manure composts (SMC) was performed using the sequential extraction procedure of Tessier et al. (1979); in this procedure, the distribution of metal among the exchangeable, carbonate, oxides, organic and residual was elucidated based in solubility of metal in the different reagents (Hsu and Lo, 2000). Fractional totals of Cu, Mn and Zn was within 100±12% of the total metals, indicating good recovery. The results showed that the distribution of Cu, Zn and Mn in the various fractions (expressed as percentages of total concentration) were generally independent of the respective total metal concentration in the compost. The exchangeable fractions of metal in the eight composts were < 4% (Cu), 13% (Mn) and 2% (Zn). Greater percentage of copper was associated with the organic fraction (47-55%), which may have been due to copper affinity for organics. The Fe-Mn oxide fraction was the next abundant fraction (30-40%). Since approximately 90% of the copper in these composts was associated with organic and oxides fractions, organic complexation and inorganic sorption probably controlled solubility in swine manure composts. Greater percentage of Mn was associated with Fe-Mn oxides fraction (37-59%) except for 2 composts that had greatest Mn concentration in the carbonate fraction. For all composts, the mean percentage of Mn associated with the various fractions were 48% (oxides), 29% (carbonate) 13% (organic), 6% (exchangeable), the greatest concentrations of Zn in the composts except for two of composts, in which Fe-Mn oxides fraction had the greatest amounts of Zn. Zn occupied the carbonate and oxide fractions in more than

70% of the compost. This indicates its potential environmental metal leachability (Hsu and Lo, 2000). Acid environment enhances the mobility of metal in the environment. Metals bound to carbonate are sensitive to pH changes and they are leached by lowering the pH (Pere-Cid et al., 1999)

He et al. (1995) used a modified procedure to separate trace metals into; water-soluble (H_2O), exchangeable (KCl), complexed ($Na_4P_2O_7$), organically bound (NaOH), solid particulate (HNO_3) and residual (HNO_3-HClO_4 digestion) forms. Compared with other previously described schemes, this method placed more emphasis on the organic fraction (both $Na_4P_2O_7$ and NaOH are effective in organic matter extraction) because high organic matter content of MSW composts and less emphasis on the mineral fraction (such as carbonate, sulfide and Fe/Mn oxides) because a major component of the mineral in MSW glass, which, except for lead crystals, has low trace metal content. Similar to other procedures, this is also operationally defined and these overlaps between fractions exist. The authors suggested that (i) trace metals extracted by water, KCl and $Na_4P_2O_7$ are relatively labile and thus may be potentially available; (ii) trace metals extracted by NaOH and HNO_3 are relatively immobile and may not be readily available; and (iii) trace elements in the residual forms are completely immobile and not bioavailable.

The amount of Cd, Cr, Cu, Pb and Zn extracted by water and KCl are generally small except for zinc and copper in one of the compost sample and Cd in three composts. Substantial amount of Mn and Ni was found water-soluble and KCl extractable fraction (as high as 20% total compost metal content). Also significant amount of trace metals was extracted with $Na_4P_2O_7$. More than 50% (as high as 80% in some cases) of total compost Zn was extracted by this reagent, indicating that much of the Zn in the composts may be potentially mobile. Much lower amount of trace metals were extracted with NaOH than with $Na_4P_2O_7$ except for Ni and Zn. Because of the affinity of Ni and Cu for humified organic matter, a single extraction with $Na_4P_2O_7$ would not have removed all the Ni and Cu bound to more stabilized organic matter and subsequently extracted with NaOH. Extraction with HNO_3 dissolved the largest portion of the composts metals except for Ni and Cr. Forms of metal extracted by HNO_3 include carbonate, phosphate, sulfide minerals, Fe and Mn oxides, and even elemental metals. The authors reported that only a small portion of compost metals remained in the final residue, but as high as 50% of the total Ni and or still remained; probably as metallic (or alloy) form, silicate minerals, glass and inert plastics (He et al. 1995). Qia and Ho (1996) found that the addition of red mud prior to composting not only reduced leachability and plant availability of heavy metals in the compost, but also significantly reduced the level of metals extractable by acid digestion composting of sewage sludge and limed lowered the extractable copper, manga-

nese, zinc and nickel relative to unlimed sewage sludge compost, although lime addition of 1% by mass was recommended for maximum effectiveness.

Wong and Foag (2000) conducted experiments to reduced the bioavailability of heavy metals through raising the pH of the compost mass. Fe-Mn oxide bound Pb increased from 6.62 to 8.47 $mg\ kg^{-1}$ during composting. Organic matter and sulphides-bound Pb rose from 4.79 to 7.97 $mg\ kg^{-1}$ and was 66.4% higher than that in the raw sludge. The increase in the five fractions concentrations may be attributed to the weight losses of the materials during composting process through mineralization of organic matter.

Hsu and Lo (2001) concluded that metal distribution in different chemical fractions was generally independent of composting age and, thus, independent of respective metal concentrations in the compost. Nevertheless, Garcia et al. (1995) found that co-compost of the sewage sludge with Cd, Cu, Zn and Ni, presents less risk of metals in the wastes being to soils being used by plants. Because of the loss of carbon during composting, the concentration of metallic contaminant in solid wastes may be increased. Pare et al. (1999) reported increases in the total concentration of some residual heavy metals, ranging from 26 to 145% increases after 41 days to composting of biosolid and municipal solid wastes; concentrations of some other metals remained constant or decreased during composting. Sequential extraction of metals indicated a decline in soluble component and an increased in residual, organically bound forms (Pare et al., 1999). Pare et al. (1998) determined the amount of water-soluble and acid hydrolysable carbon compounds remained somewhat constant, but that non hydrolysable nitrogen-containing compounds greatly increased (Pare et al., 1998, 1999) suggesting that the stabilized organic matter formed complexes with metals and restricted the mobility of the metals and their availability for plant absorption. However, some times as in nature, composting may release contaminating metals from organic combination by degradation of the organometallic complexes, leading to increased bioavailability (Heyes et al., 1988).

Mobility of metals in compost varies with their speciation. Sawhney et al. (1996) noted that leaching of arsenic (more than 20% of the initial arsenic content of compost) was much higher than leaching of cadmium, chromium, nickel and lead (about 3% of the total initial content). Leaching of arsenic declined rapidly with time before reaching a baseline, indicating that initial leaching was of water soluble salts or exchangeable ions and that solid phases governed the subsequent slow-release processes.

Song and Greenway (2002) applied the BCR sequential extraction protocol to study of fractionation of eight elements in four open-air windrow-composting processes. After the three extraction of eight elements, the extraction solution was analysed using ICP-MS. The

elemental partitioning profiles for nickel in a mixed composting processes showed that the fraction of Ni extracted with acetic acid decreased with increasing composting time whereas the fraction of nickel combined with humic acid increased with the increase of compost time. Greenway and Song (2004) used the accelerated sequential extraction method to investigate the elemental leach ability in compost using a kinetic approach. These leaching experiments provide useful and rapid information about how easily an element can be leached from its matrix. A non-selecting leaching agent (such as ethylene diamine tetracetic acid, EDTA) is usually chosen to carry out the leaching experiment and this allowed passage through dried samples packed into burette columns. The eluents collected at different time intervals are subject to metal analysis using ICP-MS by recording the amount of leached metal versus found taken with a given reagent, a kinetic leaching curves was obtained. A non-linear regression model was the applied such that the leached species can be catalogued into two components i.e. those which are easily extracted (labile species) and those which are extracted more slowly (non-labile species). From the regression parameter obtained, the lability of the element in compost could be quantitatively defined (Greenway and Song, 2004) from the regression parameters. It was concluded that 25.6% of Zn could be catalogued as labile fractions and rest of zinc was non labile, which meant the later fraction was too likely to be leached out from the compost by EDTA (Greenway and Song, 2004).

Zheng et al. (2004) reported changes that occur to Pb speciation, distribution and bioavailability during the course of composting. The concentration of total Pb and the five fractions were increased during the while stage of compost. However, the percentage distribution with respect to total Pb were changed in the following; exchangeable, bound to Fe-Mn oxides and bound to carbonates Pb with respect to total increased, while the percentages of bound to organic matter and sulphides, and residual Pb with respect to total Pb were decreased during composting. The data indicates that the quantity of Pb in the less toxic portion, such as consisting of organic matter and sulphide bound and residual Pb, was increased, and that the contamination and bioavailability of heavy metal Pb in sewage sludge was reduced during composting.

Haug et al. (2005) reported changes in the speciation and DTPA extractable copper and zinc during humification of organic matter in pig manure composts. Composting of pig manure resulted in a significant reduction in percentage of water soluble, exchangeable, carbonate and Fe-Mn oxides fractions of copper and zinc and increase in organic and residual fraction of Cu and Zn. The water soluble fraction of copper decreased from 13% to 2.8; while in Zn, it decreased from 2.72 to 2.09%. Exchangeable fraction of Cu decreased from 3.7 to 2.06%; while for Zinc, it decreased from 7.87 to 2.98% after 63

days of composting. The organic fraction of copper increased from 32.7 to 41.6%; for zinc, it increased from 7.56 to 12.3%. Residual fraction of Cu and Zn increased from 29.9 to 40% and 34 to 36%, respectively.

The content of DTPA extractable copper and zinc decreased along with composting process. DTPA-Cu decreased from 15.7 mg/kg of the initial compost to 11 mg/kg of the product, while DTPA-Zn decreased from 119.85 to 94.9 mg/kg. The reduction of DTPA extractable Cu was 27.0%, while DTPA-Zn was 20.8% after composting for 63 days. The authors concluded that composting of pig manure for 63 days was more efficient in reducing the bioavailability of Cu than Zn (Haug et al., 2005).

A main drawback shared by all sequential extraction schemes, however, is that the procedures themselves are complex and very time consuming. This is because the extraction procedure takes several hours, while the sample is mechanically shaken to allow heterogeneous system to approach equilibrium. A whole protocol, which typically contains three to 5 steps, often takes several days to complete, which make the sequential extraction method inappropriate for frequent environmental monitoring. One approach to overcome this is to use the ultrasound accelerated extraction method. For example, in the standard BCR method each step took only 5 min due to the much more rapid extraction process. This ultrasound extraction method was compared with the traditional BCR reference material and this confirmed that result is comparable (Song and Greenway, 2004, 2005). The speed of the new extraction method provided two advantages; first, it allowed the composting process to be monitored more frequently which helps to provide a more detailed understanding of the partitioning behaviours of heavy metals. Second, it allow one extra step to be included into the BCR sequential extraction procedure. This extra step was designed to look at the portion of the elements combined with humic substances, and this involved extraction 0.1 molL^{-1} sodium pyrophosphate solution before the residue was digested with hydrogen peroxide (Song and Greenway, 2005).

DISTRIBUTION OF TRACE METALS IN FULVIC AND HUMIC ACID FRACTIONS

The prospect of a significant increase in concentration of potential harmful metals in soil because of waste application has stimulated interest in the chemistry of trace metal interaction with organic components of the waste (Holtzclaw et al., 1978). Humic substances - have a relatively high capacity to complex metals as well as affinity towards individual metal ion (Holtzclaw et al., 1978; Steveson, 1982; He et al., 1992; Hsu and Lo, 2000). The relative distributions of trace metals in humic acid (HA) and fulvic acid (FA) may be used to predict the stability or mobility of trace metals in the environment after MSW compost application (He et al., 1995). The relative distribution of

trace heavy metals in FA and HA fraction from $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH extracts varied depending on both individual elements and compost. The distribution patterns of trace metals in HA and FA indicates that (i) Cr and Cu were recovered in HA than FA in both $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH extracts (ii) more Mn, Ni and Zn were recovered in the FA than in HA in both $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH extracts and (iii) the distribution pattern of Pb and Cd is a function the extractant used. The distribution pattern suggested that Cr and Cu are associated with organic component of the municipal solid waste compost are more stable, thus less labile compared with Mn, Ni and Zn in similar form (He et al., 1995). In contrast, Petruzzeli et al. (1980) and Canarutto (1991) reported that most compost Cd, Cr, Cu, Ni Pb and Zn extracted with 0.5 M NaOH was recovered in the FA fraction. This difference in the distribution pattern is due the fact that (i) different composts were used, (ii) compost were pre-extracted with H_2O , KCl and $\text{Na}_4\text{P}_4\text{O}_7$ —this might have extracted substantial amount of metals, whereas direct extraction with NaOH was used in the study of Petruzzeli et al. (1980) and Canarutto et al. (1991), and (iii) a higher concentration was used by Petruzzeli et al (1980) and Canarutto et al. (1991) have a significant effect on the distribution of humic substance metals in FA and HA fractions.

Base-extracted humic substance from the swine manure compost resulted in an average removal of 86% (of the total) Cu, 6% Mn and 14% Zn. The higher extractability of copper may be due to high dissolved concentrations of organic matter, which can strongly complex with the metal. In contrast to Cu, Mn and Zn solubility was low using NaOH. The major portions (80% on average) Cu, Mn and Zn extracted with NaOH were recovered in the non humic fraction (NHF), and only small fractions remained in HA and FA (Hsu and Lo, 2000).

Haug et al. (2005) reported the distribution of copper and zinc in HA and FA extracted during humification organic in pig manure composts. The content of Cu in HA fraction increased significantly from 134 to 433 mg/kg^{-1} . The increase of Zn in HA fraction was less obvious, which increased from 113.7 to 170 mg/kg^{-1} . In the case of FA fraction, Zn increased from 601.7 to 1703 mg/kg^{-1} but no significant change of Cu concentration in FA fraction was observed after composting. This suggested that HA fraction had more affinity towards for stable complex formation as compared to Zn which showed more affinity towards FA fraction for stable complex formation.

CHEMICAL FRACTIONATION AND PLANT UPTAKE OF HEAVY METAL IN SOILS AMENDED WITH COMPOSTS

Heavy metals are associated with different soil components in different ways, and these associations determine their mobility and availability (Kabala-Pendias and Pen-

dias, 1991; Singh, 1997; Ahumada et al., 1999; Kabala and Singh, 2001). Water soluble and exchange-able forms are considered readily mobile and available to plants, while metals incorporated into the crystalline lattices of clays appears relatively inactive. The other forms precipitated as carbonate, occurred in Fe, Mn and Al oxides or complexed with organic matter—could be considered relatively active or firmly bound, depending upon the actual combination of physical properties of soil (Sposito et al., 1982; Shuman 1985; Kabala and Singh, 2001). Thus, soil texture (clay content) pH, organic matter, and Fe-Mn oxides have been found to be the most important soil properties influencing the lability and biological uptake of heavy metals (Iyengar et al., 1981; Narwal and Singh, 1988; Ma and Rao, 1997; Karczewska et al., 1988; Kabala and Singh, 2001).

Sequential chemical extraction schemes are considered to be a great value than single extractant in the determining metal distribution in composts and compost amended soils. Reagents utilized were chosen on the basis of their selectivity and specificity towards particular physicochemical form, although variations in reagent strength, volume and extraction time between the schemes are apparent (Lake et al., 1984). The major aim of extracting trace metals with various reagents from composts is to estimate the relative distribution and consequently identify which form(s) has high potential for plant uptake (bioavailability) and water contamination (He et al., 1992). Trace metal in the soluble, exchangeable and organically bound forms are believed to be highly available for plant uptake (Petruzzelli, 1989; He et al., 1992). It is often difficult to quantify trace metals in these forms with the current techniques. Therefore, a statistical approach is needed to correlate trace metal extracted by specific reagent with uptake by a plant test.

The surface horizons of two field soils that has been amended with a series of reagents (KNO_3 , H_2O , NaOH, EDTA (ethylene dinitrotetraacetic acid), HNO_3 in sequence and with DTPA (1,4,7-triazeheptane-1,1,7,7-pentaacetic acid) to characterize the zinc pool in the soil with respect to lability and bioavailability. Statistical correlation analysis, comparing extracted Zn fractions with the concentrations of Zn in the leaves of barley (*Hordeum vulgare L*) grown on the soils. The author concluded that (i) zinc extracted by KNO_3 and H_2O in sequence is associated with the highly labile, soluble pool, dominated by Zn^{2+} , which determines the immediate bioavailability (ii) Zn extracted by KNO_3 , H_2O and NaOH in sequence has a strong, positive 1:1 correlation with DTPA extractable zinc and, therefore, is associated with labile, plant available Zn pool. (iii) EDTA extractable Zn represent a reservoir of potentially bioavailable Zn and (iv) HNO_3 -extractable Zn is associated with non labile pool that is not bioavailable. The relationships between extracted Zn fractions and bioavailability were applicable to both soil investigated and did not depend on the type of sludge and length of lime of sludge application (LeClaire et al.,

1984).

The effect of small scale composting on heavy metal was studied by Simeoni et al. (1984). Lettuce (*Lactuca sativa*) and oat (*Avena sativa*) was grown in pots containing composted and uncomposted sludge addition at rates equivalent to 0, 60, 120 and 240 mg/ha to acidic red feather loamy sand (Lithic Cryoboralfs) and a neutral nunn clay loam (*Aridic Argiustolls*). After seven weeks, dry matter yield were measured and soil and plant sample were analysed for contain of Cd, Cu and Zn. Addition of compost produced greater yields in both species than addition of sludge due to lower soluble salt content and the zinc availability of the compost. The higher application rate maintained a higher pH on the loamy sand, which possibly decreased Cd and Pb availability to plants. Leaching of soluble copper complexed during composting might have contributed to 40% decrease in sludge Cu content. Composting increased the humic acid, decreased the β -humus and change Cu and Cd distribution in sludge organic matter.

Sims and Kline (1991) used a sequential extraction method (KNO_3 , H_2O , NaOH , $\text{Na}_2\text{-EDTA}$, HNO_3) to determine the soil fractions and plant availability of Cd, Cr, Cu, Ni Pb and Zn in three Atlantic coastal plain soils amended with four rates of co-composted sewage sludge (CCSS 0, 11, 22 and 44 kg/ha) limed to four pH (pH 5.3 – 7.2) and used to grow wheat (*Triticum aestivum* L) and soybean (*Glycine max* L) under greenhouse condition. The average (across soils) increase in total soil Cd, Cr, Cu, Ni, Pb and Zn, at the highest rate of application of the co-composted sewage sludge was 0.1, 2, 7, 5, 14 and 14 mg/kg respectively. The distribution of all metals, except Cd, differed in the NaOH , and EDTA fractions and less in the HNO_3 form in the unamended soil. The more labile fraction (KNO_3 , H_2O) of Cu, Ni, Pb and Zn, but not Cd and Cr, increased slightly (<1 mg/kg) when CCSS was added. Liming usually resulted in minor (<5%) changes in the distribution of Cd, Cr, Ni and Pb among the soil fractions. However, liming consistently decreased NaOH extractable copper and ($\text{KNO}_3 + \text{H}_2\text{O}$) extractable Zn, and increase the percentage of these metals in the EDTA and HNO_3 fractions. Amendment with CCSS reduced wheat dry matter production in all soils, probably from decreased N availability caused by high C/N ratio (52:1) of the compost, and slightly increased soybean growth (6-12%). The CCSS had little effect on concentrations of Cd, and/or Pb in either crop, but consistently increased Cu, Ni and Zn in vegetative tissue of wheat and soybean and Ni and Zn in soybean grain. Liming decreased Mn and Zn in the wheat and soybean, and Ni in soybean grain, but rarely affected plant Cd, Cr, Cu or Pb with exception of Zn consistent correlation between total metal content or individual metal fraction and plant metal concentrations or uptake was observed. However, significant multiple regression model between soil metal fractions, pH and metal concentration in the wheat was obtained for Ni ($R^2=0.42^{***}$ - 0.86^{**}), Cu ($R^2=0.37^{**}$ - 0.57^{***}) and Zn (R^2

$=0.62^{**}$ - 0.82^{**}) with all three soils (Sims and Kline, 1991). Petruzzelli et al. (1989b) evaluated the up take by corn and chemical extractability of heavy metals from a four years compost treated soil. The authors reported that cadmium content of the grain, remained unaltered in the first 2 years, and increased in the third year of the experiment and maintain this value in the last year. On the contrary, the cadmium content in the root portion increased from 0.22 to 1.31 mgkg^{-1} over the years particularly after compost addition (more than 55%). At the end of the experiment the authors found that Cd in the corn root from treated plot was nearly six times greater than those from untreated plots. Composts addition produced an increase in the concentrations of these metals in grains of more than 35% and about 75% for Zn and Cu, respectively. Only in the 4th year Ni concentration increases in the root while the content of Pb and Cr in corn was generally unaffected by compost application. The authors concluded that the extractability of heavy metals changes with time. However the extractable amount is rather small with respect to the total heavy metal content of the compost.

Plant uptake studies are of primary importance in the evaluation of environmental contamination arising from heavy metals in soils. Several studies have demonstrated that land application of waste containing heavy metals will result an increased plant uptake of heavy metals. Availability of applied metals to plants depends on the soil characteristics, the composition of waste, metals species and application rate (Mullin and Mitchell, 1994). However, heavy metal bioavailability can be influenced by the variation in soil salinity since metals mobility could be greatly enhanced by the quantities of salts present because of the competing effects on the adsorbing surfaces of the soils (Petruzzelli et al., 1985). Several studies have confirmed the hypothesis that only total metal composition of compost as an index of possible environmental hazard could be misleading even though soil samples from treated plots exhibited a certain tendency towards higher heavy metals extractability thus suggesting that further addition of compost could modify heavy metals bioavailability.

Heavy metal uptake by plants varies considerably among species and also among genotypes within a species. For example, leafy vegetables such as Lettuce (*Lactuca sativa* L), swiss chard (*Beta vulgaris*), tobacco (*Nicotina tabacum* L), spinach (*Spinacia oleracea* L) and curlycress (*Arabio psisthaliana* L) take up more cadmium than crops like corn (*Zea mays* L), soybean (*Glycine max* L) wheat (*Triticum aestivum* L) and forage (Mullin and Mitchell, 1994).

Conclusion

Total trace metal composition of composts and compost amended soils are of little importance in determining the total trace metal uptake by plants and consequent level of

risk from these elements for plants and the food chain, since the different forms have different mobilities, bioavailabilities and potential environmental contamination. Several studies have shown that phase associations of metal include water soluble, exchangeable, precipitated as discrete phase, co-precipitated in metal oxides, and adsorbed or complexed by organic ligand and residual fractions. The phase association and solubility of metal changes over composting time thereby altering metal availability.

Soil solution is the interface between the root system and the soil, and therefore the concentration and chemistry of heavy metals in the solution form is closely related to their mobility and bioavailability. Both physical and chemical fractionation has been exploited in the characterization of heavy metals in the solid phase of composts and compost amended soils. Sequential chemical extraction procedures are the most frequently used approach. These procedures vary in approach, specificity, reagent types, strength, volume and extraction time. In spite of these variations, the procedures are directed towards correlating each fraction with mobility and plant availability. Chemical extraction does not represent a definitive method of analytical speciation but give only a approximate idea, and the bioassay tests can only partially reproduce a complete field test situation but both separately or used together can significantly help in evaluating the level of risk of heavy metals. The interaction of heavy metal with the organic fraction of the composts has stimulated interest in the distribution of metals among the humic and non humic fraction of the composts and compost amended soils. Humic substances have the relative capacity to complex metals as well as affinity towards individual metal ion. The relative distribution of metal in humic acid (HA) and fulvic acid (FA) may be used as an index for predicting the stability or mobility of trace metals in the environment after MSW compost application. However limited studies have been carried out in these areas.

In most African countries, there are little or no information available on the levels of heavy metals in composts and compost-amended soils. In contrast, extensive works have been directed to the characterization and prediction of mobility and bioavailability of heavy metal in composts and composts amended soil in Europe and U.S.A. Since both soils and composts generated in Africa may be considerably different from those of Europe and U.S.A, it is therefore necessary for African researchers to pay more attention to this field. Specifically more effort should be in the following directions (i) interaction between organic components and trace metals and compost amended soil; (ii) phase association of heavy metals in compost and compost amended soils; (iii) correlation between extractability and bioavailability and (iv) development of specific guidelines and standards for application of composts in agricultural lands. Hopefully, information obtained from studies of these topics will provide a sound basis

is for both Federal and State governments to establish guidelines on compost production and application, and for the general public to make objective judgment on composting as a sustainable solution to organic waste management.

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