

Effect of composting on characterization and leaching of copper, manganese, and zinc from swine manure

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“Capsule”: *The three metals differed in potential for leaching and bioavailability, with Zn being the most available.*

Abstract

This research was conducted to study the influence of composting on the concentrations, water solubility, and phase association of Cu, Mn, and Zn from swine (*Sus domesticus*) feces. Composting of separated swine manure was performed in two piles for 122 days. The metal concentrations increased rapidly during the first 49 days and leveled off thereafter. All metal concentrations increased approximately 2.7-fold in the final compost due to decomposition of organic matter. A sequential extraction protocol was used to evaluate the humification process and partition metals into water-soluble, exchangeable, organically complexed, organically bound, solid particulate, and residual fractions. Temporal changes in the water-soluble fractions of Cu, Mn, and Zn were reflected by water-soluble organic C concentrations, which rapidly increased to a maximum at Day 18 and declined thereafter. An increase in the humic acid/fulvic acid ratio in Na₄P₂O₇ or NaOH extracts at various stages of composting represented the humification process. During composting, the major portions of Cu, Mn, and Zn were in the organically-bound, solid particulate, and organically complexed fractions, respectively. Metal distributions in different chemical fractions were generally independent of composting age and, thus, independent of respective total metal concentrations in the composts. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Swine manure; Composting; Heavy metal; Organic carbon; Sequential extraction; Fractionation

1. Introduction

Intensive livestock production generates large amounts of manure that are applied to limited land area in proximity to the manure source. Continuous heavy manuring may pose environmental problems, such as odor, pollution of ground and surface waters due to leaching and run-off of organics and nutrients, and soil accumulation of heavy metals (Wadman et al., 1987). In Taiwan, swine house manure is normally cleaned daily with groundwater down a sump where the solid fraction is separated from slurry through a mechanical sieve. Composting of solid fraction or separated swine manure (SSM) prior to land application may provide a better alternative for manure management.

The composting of organic wastes is mainly a biological decomposition process of organic materials, resulting in a net loss of total organic matter (OM) and a

concentration of inorganic constituents (He et al., 1995). The main products of the composting process are fully mineralized materials such as CO₂, H₂O, mineral ions, stabilized OM (mostly humic substances), and ash. Composting reduces the volume and weight of the raw material resulting in a stable product that can be applied to soil as a valuable fertilizer and soil amendment.

Several researches have shown that swine manure may contain high concentrations of Cu, Mn, and Zn because of feed additives (Mullins et al., 1982; Miller et al., 1986; Payne et al., 1988; L’Herroux et al., 1997). Most of these trace elements are retained mainly in the solid phase after solid–liquid separation from slurry (Giusquiani et al., 1998). As such, successive application of Cu, Mn, and Zn-rich SSM composts in agricultural soils may cause metals to accumulate to toxic levels (King et al., 1990).

In cases where the potential toxic metal concentrations of a compost are high, the leachability of metals associated with compost is of concern. Knowledge of the elemental concentration of a compost, however, does

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not allow for a prediction of its leachability and bio-availability. Studies have shown that the chemical form, rather than the total concentration, of an element is more important than total concentration in determining its availability for plant uptake or leachability into groundwater (Petruzzelli et al., 1989). Although several studies have assessed the leachability or bioavailability of elements in fresh swine manure, manure mixed with sawdust, and soils amended with swine manure (Mullins et al., 1982; Miller et al., 1986; Payne et al., 1988; L'Herroux et al., 1997; Tiquia et al., 1997), few similar studies have been conducted to evaluate the influence of composting on leaching of elements from SSM solids. Since decomposition of manure occurs through biological action and spontaneous chemical reactions, composting may influence the concentrations and chemical characterization of elements in SSM composts.

The objective of this work was to study the influence of composting on the concentrations, leachability, and chemical partitioning of Cu, Mn, and Zn in SSM solids. A sequential extraction protocol was used to evaluate the humification process and to determine the water-soluble fraction and the phase association of metals associated with SSM compost. These studies were designed to assess the potential leachability of Cu, Mn, and Zn and to identify factors that influence the leachability of these elements in SSM compost. This research may provide useful information for the successful utilization of SSM compost.

2. Materials and methods

2.1. Composting of SSM

The solid fraction or SSM obtained from separation of slurry was composted in two piles on an indoor concrete area at a swine farm where the swine were fed with a typical corn (*Zea mays* L.)/soybean [*Glycine max* (L.) Merr.] ration. The raw material was divided into two piles (about 1.5 m³ each) without forced aeration and composted for 122 days. The compost was turned, mixed, and sampled at 0, 3, 7, 12, 18, 25, 33, 49, 80, and 122 days. Water was added immediately after the compost was turned to maintain a moisture content of 50 to 60% (w/w). The samples (4 l) were placed in partially closed polyethylene bags, transported to the laboratory, and stored at 5°C. Smaller subsamples were air-dried and used for analyses. All measurements were conducted in triplicate for each composting pile.

2.2. Chemical analyses

Ash content was determined by heating (400°C for 8 h) in a furnace (He et al., 1995). Total C and N were analyzed using a CHN analyzer on composts ground to

<0.25 mm (He et al., 1995). For total elemental analysis, samples were digested with concentrated HNO₃ + HClO₄ (Jones and Case, 1990). The digest was centrifuged at 12,000×g for 30 min, and the supernatant was filtered through 0.45-μm filter membranes for metals (Cu, Mn, and Zn) analysis.

2.3. Sequential extraction and fractionation

The procedure of He et al. (1995), selected for this study, is designed to partition trace elements in composts into six operationally defined fractions: water-soluble, exchangeable, organically complexed, organically bound, solid particulate, and residue fractions (Fig. 1). Their method places more emphasis on the organic fraction (either Na₄P₂O₇ or NaOH are effective in organic matter extraction) because of high organic matter content of SSM compost. Also, organics extracted by Na₄P₂O₇ or NaOH are further separated into humic acid (HA) and fulvic acid (FA) fractions.

Twenty grams of each compost were weighed into a 250-ml polycarbonate centrifuge tube and the following fractions obtained:

1. Water soluble. Compost sample was extracted with 200 ml of deionized water by shaking for 24 h.
2. Exchangeable. The residue from the water-soluble fraction was extracted with 200 mL of 1 M KCl for 24 h.
3. Organically complexed. The residue from the exchangeable fraction was extracted with 200 ml of 0.1 M Na₄P₂O₇ for 24 h. Add 5 g KCl (to flocculate colloid particles) before centrifugation; the residue was washed with 200 ml of deionized water by shaking 30 min, adding 5 g KCl, centrifuging, and discarding the washing.
4. Organically bound. The residue from the organically complexed fraction was extracted with 200 ml of 0.1 M NaOH for 24 h. The washing was repeated.
5. Solid particulate. The residue from the organically bound fraction was extracted with 200 mL of 4 M HNO₃ for 24 h.
6. Residual. The residue from the solid particulate fraction was digested with HNO₃ and HClO₄ acids.

After each successive extraction, separation was accomplished by centrifugation at 12,000×g for 30 min. The supernatants were removed with a pipette and filtered through 0.45-μm filter membranes.

The pH of the water extracts were measured. An aliquot (100 ml) of Na₄P₂O₇ and NaOH extracts was acidified to pH 1 with 3 M H₂SO₄ allowed to stand at room temperature for 24 h, and centrifuged to obtain the FA fraction (HA fraction discarded). All extracts, residue digests, and FA fractions from Na₄P₂O₇ and

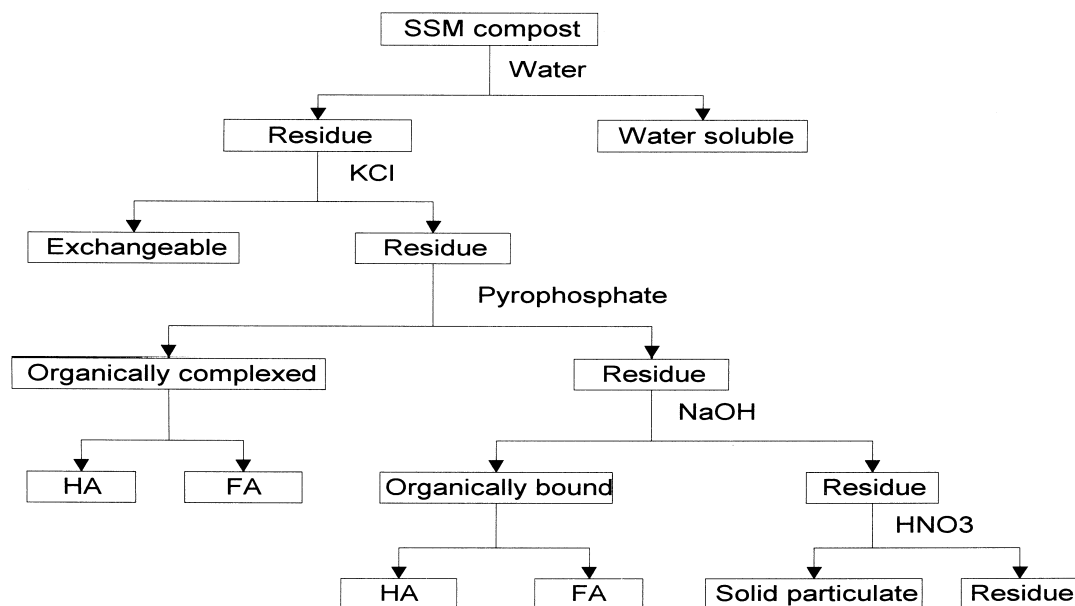


Fig. 1. Scheme for sequential extraction and fractionation of metals and organic C in composts.

NaOH extracts were stored at 5°C until analysis for Cu, Mn, Zn, and organic C (residue digest excluded).

2.4. Metal and organic C analyses

Metal analyses of digest and extract solution and FA fractions from $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH extracts were performed using an atomic absorption spectrophotometer. Organic C analyses of extract solutions and FA fractions from $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH extracts were conducted with a total organic carbon analyzer. Trace element and organic C contents in the HA fraction of $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH extracts were not analyzed directly but were calculated by the difference between total and FA values.

2.5. Statistical analysis

All results are presented as the average value of two composting piles, and the data for each pile is the average of three replicates. Correlation analysis was conducted with the Statistical Analysis System (SAS Institute, 1987) software.

3. Results and discussion

3.1. Composting of SSM

The change in the C/N ratio and ash content reflects OM decomposition and stabilization during composting (Table 1). A rapid decrease in the C/N ratio and an increase in ash content occurred during the first 18 days,

followed by a slow change from Days 18 to 49 and a leveling off thereafter. The change in C/N ratio and ash content followed trends in many composting systems (Inbar et al., 1993; Iannotti et al., 1994; Chefetz et al., 1996) and exhibited three phases: (1) a rapid decomposition phase lasting for the first 18 days, during which most of the OM decomposed; (2) Days 18 to 49; and (3) a stationary phase from Days 49 to the end of the experiment, during which the rate of OM decomposition was extremely low. The ash content of the final compost was 50% of the final mass, indicating this material was half organic and half inorganic matter.

3.2. Condensation of metals

Since no leaching and runoff took place during composting, the total concentrations of Cu, Mn, and Zn increased with composting time and the corresponding loss of OM (Fig. 2). The total concentrations of Cu, Mn, and Zn increased from 343, 121, and 577 mg kg^{-1} , respectively, in raw material to 976, 331, and 1540 mg kg^{-1} , respectively, in mature compost, indicating 2.7–2.8 times enrichment of these elements during the process. Compared with a 25–40% increase in Cu and Zn concentrations in spent pig litter (Tiquia et al., 1997), 15–36% increase in cattle manure (Inbar et al., 1993), 50 to 100% in municipal solid waste (MSW; Leita and De Nobili, 1991), and no significant increase in poultry manure composting systems (Ihnat and Fernandes, 1996), this result indicates that metal concentrations in SSM during composting was greatly enhanced. This result suggests that the types of composting and raw materials are of major importance to metal condensation

Table 1
Chemical properties of separated swine manure at various stages of the composting process

| Composting time (days) | Ash (g kg ⁻¹) | C (g kg ⁻¹) | N (g kg ⁻¹) | C/N | pH ^a |
|------------------------|---------------------------|-------------------------|-------------------------|------|-----------------|
| 0 | 220 | 444 | 20.9 | 21.2 | 7.85 |
| 3 | 252 | 436 | 21.3 | 20.5 | 7.59 |
| 7 | 260 | 428 | 22.1 | 19.4 | 7.62 |
| 12 | 274 | 416 | 23.1 | 18.0 | 7.83 |
| 18 | 365 | 374 | 38.4 | 9.7 | 7.35 |
| 25 | 379 | 358 | 41.2 | 8.7 | 7.98 |
| 33 | 438 | 331 | 40.5 | 8.2 | 7.63 |
| 49 | 470 | 309 | 41.6 | 7.4 | 7.38 |
| 80 | 485 | 299 | 41.3 | 7.2 | 7.49 |
| 122 | 502 | 294 | 43.2 | 6.8 | 7.72 |

^a Measured on water extracts of compost samples.

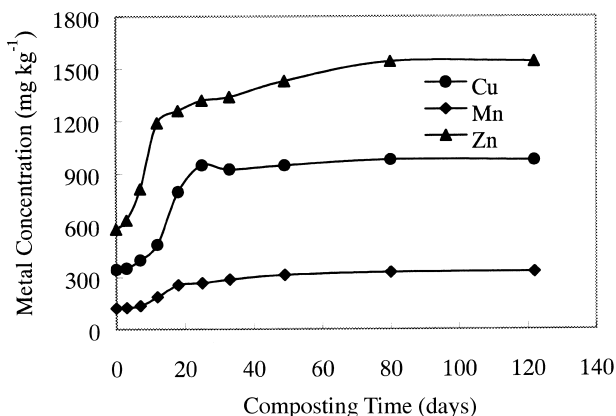


Fig. 2. Total concentrations of Cu, Mn, and Zn in separated swine manure during the composting process.

during composting. Major changes in the metal concentrations in SSM composts were recorded during the first 25 days of the process, paralleling the OM decomposition.

3.3. Water-soluble fractions of organics and metals

Water-soluble fractions of organics and metals are the most readily bioavailable in composts applied to soils (Leita and De Nobile, 1991).

3.3.1. Water-soluble organic C

The water extract exhibited a slightly alkaline pH throughout the composting process (Table 1). The water-soluble organic C level rapidly increased to a maximum at Day 18 and declined thereafter (Fig. 3). As C compounds that are highly available (e.g. sugars, hemicellulose, organic and amino acids, and proteins) to microbes were degraded during the rapid decomposition phase, metabolic products were continuously released, resulting in an increase in water-soluble organic C. After the rapid decomposition phase, the substrate level was low and resulted in a reduction in soluble C. Water-

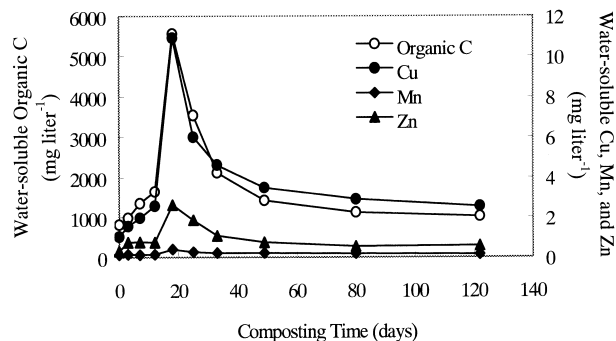


Fig. 3. Water-soluble organic C, Cu, Mn, and Zn concentrations during separated swine manure composting.

soluble fractions of organic C were small in the raw material (2%, expressed as percent of total compost organic C) and final compost (4%) but were substantial at the end of the rapid decomposition phase (up to 17.5%). Iannotti et al. (1994) found a similar water-soluble organic C trend for composting of MSW. Leita and De Nobile (1991) and Inbar et al. (1993), however, reported that water-soluble organic C declined throughout the composting process for MSW and cattle manure. These results suggest that the type of raw material and composting pattern are of major importance to the dissolution of organic C during composting.

3.3.2. Water-soluble fractions of metals

The increase in total concentrations during composting was not accompanied by a corresponding increase in the amount of water-soluble Cu, Mn, and Zn. Temporal changes in the water-soluble fractions of Cu, Mn, and Zn were reflected by changes in water-soluble organic C concentrations, which increased to a maximum at Day 18 and then declined (Fig. 3).

The water-soluble fraction of Cu (expressed as percent of the total concentration in the sample) increased from 3% in the raw SSM to 5% at Day 12, sharply increased to about 16% at Day 18, and gradually decreased to 3% in the mature compost. The water-extractable fractions of Mn or Zn increased from 1% in the raw material to 2% at Day 18 and then gradually decreased to 0.5% at the end of the process. This result indicates that composting substantially modifies Cu leachability in SSM compost and appears to have little influence on Mn or Zn leachability. The concentrations of Cu, Mn, or Zn in the water extracts during composting were highly correlated to water-soluble organic C concentrations with correlation coefficients of 0.98, 0.94, and 0.99, respectively. Dudley et al. (1986) found a similar trend for sludge-amended soils. Leita and De Nobile (1991) also found a similar Cu trend for MSW, but the solubility of Zn declined. Tiquia et al. (1997) found that the amounts of water-extractable Cu or Zn declined throughout the process during composting of

spent pig manure. The water-extractable fraction with Cu greater than Zn in SSM composts was similar to previous results reported for MSW sewage sludge compost or a mature MSW compost (Sims and Kline, 1991; Tisdell and Breslin, 1995).

3.4. Sequential extraction

3.4.1. Carbon distribution

The percentages of compost C extracted by sequential extraction with H₂O, KCl, Na₄P₂O₇, NaOH, and HNO₃ (one single extraction with each reagent) increased from 49% and leveled off at 60% of total compost C by Day 18 (Table 2). Water soluble fractions of organic C were small in the raw material (2%) and mature compost (4%) but were substantial at the end of the rapid decomposition phase (up to 17.5%; Table 2). The amount of KCl-extracted organic C was relatively small (1–3%) but showed a similar trend as that of the water extracts. Either Na₄P₂O₇ or NaOH-extracted organic levels increased from 4 or 14%, respectively, in the raw material to 21% in the mature compost, whereas HNO₃-extracted organic C decreased from 28 to 12%. Although organic C might have carried over from the water to the KCl extract and from the KCl to the Na₄P₂O₇ extract, the magnitude should be small. Carryover to the NaOH and HNO₃ extracts was eliminated by washing with water before changing extractants.

3.4.2. Humification of OM

Organic matter extracted with either Na₄P₂O₇ or NaOH is traditionally considered to be a humic substance (HS). In this study, the total level of HS increased during the composting process from 18.2% of total compost C in the raw material to 42.4% in the final compost (Table 3). Tiquia et al. (1997) found that total levels of HS increase from 10% of OM in the raw material to 16% of OM in the final compost during spent pig litter composting. Chefetz et al. (1996)

reported that 18% of organic matter was in the extracted humic form measured by repeated extraction (eight times) with NaOH throughout the MSW composting process. These results indicate a higher degree of humification of organic matter in SSM composts than in spent pig litter and MSW composts.

The levels of HA and FA in SSM compost at various stages of the process represent the humification process (Table 3). In general, fresh composts contain low levels of HA and higher levels of FA (Saviozzi et al., 1988; Chefetz et al., 1996), a trend also shown in this study. Of the humic substances extracted with Na₄P₂O₇ and NaOH, HA percentages increased, and FA levels decreased with time. The increasing level of HA represents the degree of humification and maturity of the compost. The HA/FA ratio is used commonly to determine compost stability and maturity. The HA/FA ratio of Na₄P₂O₇ extracts increased from 0.54 to 3.55 and that of NaOH increased from 0.28 to 1.08. A combined HA/FA ratio (i.e. weighted average of HA/FA ratios in Na₄P₂O₇ and NaOH extracts) may be more meaningful than an individual ratio for either Na₄P₂O₇ or NaOH extract as an index of maturity. The weighted HA/FA ratio increased from 0.33 in the raw material to 1.85 in the mature compost.

Thus, parameters such as ash content, C/N ratio, metal concentrations, extracted humic C, and the combined HA/FA ratio can be used as maturity indices. Linear correlation analysis (Table 4) reveals that all of these parameters were significantly ($P \leq 0.01$) correlated to each other and all were good indicators of SSM compost maturity.

3.4.3. Distribution of metals

Metals in the water-soluble fraction may be readily leachable and bioavailable in the environment. Metals in the exchangeable and organically complexed fractions are relatively labile and may be potentially bioavailable, and metals in the organically bound and solid

Table 2
Distribution of compost C in the various fractions as a percentage of total compost C during composting

| Composting time (days) | Extractable organic C | | | | | | Residue ^a |
|------------------------|-----------------------|-----|---|------|------------------|-------|----------------------|
| | H ₂ O | KCl | Na ₄ P ₂ O ₇ | NaOH | HNO ₃ | Total | |
| 0 | 2.1 | 0.8 | 4.1 | 14.1 | 28.0 | 49.1 | 50.9 |
| 3 | 2.6 | 0.9 | 4.5 | 14.9 | 28.0 | 50.9 | 49.1 |
| 7 | 3.6 | 1.0 | 4.9 | 15.4 | 27.4 | 52.3 | 47.7 |
| 12 | 4.6 | 1.1 | 6.9 | 16.3 | 26.6 | 55.5 | 44.5 |
| 18 | 17.5 | 2.8 | 11.9 | 14.3 | 13.8 | 60.3 | 39.7 |
| 25 | 11.9 | 2.1 | 12.7 | 15.6 | 16.4 | 58.7 | 41.3 |
| 33 | 7.7 | 1.6 | 16.1 | 19.7 | 15.6 | 60.7 | 39.3 |
| 49 | 5.5 | 1.5 | 19.4 | 21.5 | 13.6 | 61.5 | 38.5 |
| 80 | 4.4 | 1.2 | 19.4 | 20.8 | 14.9 | 60.7 | 39.3 |
| 122 | 4.0 | 1.1 | 21.0 | 21.4 | 12.4 | 59.9 | 40.1 |

^a Calculated by subtraction of total extracted organic C from compost C.

Table 3
Extracted humic C and its distribution in fulvic acid (FA) and humic acid (HA) fractions during separated swine manure composting

| Composting time (days) | Extracted humic C ^a (%) | Na ₄ P ₂ O ₇ extract | | | NaOH extract | | | Combined HA/FA ^c |
|------------------------|------------------------------------|---|---------------------|-------|--------------|---------------------|-------|-----------------------------|
| | | FA (%) | HA ^b (%) | HA/FA | FA (%) | HA ^b (%) | HA/FA | |
| 0 | 18.2 | 65 | 35 | 0.54 | 78 | 22 | 0.28 | 0.33 |
| 3 | 19.4 | 57 | 43 | 0.75 | 79 | 21 | 0.27 | 0.35 |
| 7 | 20.3 | 52 | 48 | 0.92 | 78 | 22 | 0.28 | 0.39 |
| 12 | 23.2 | 44 | 56 | 1.27 | 76 | 24 | 0.32 | 0.50 |
| 18 | 26.2 | 35 | 65 | 1.86 | 61 | 39 | 0.64 | 1.03 |
| 25 | 28.3 | 32 | 68 | 2.13 | 64 | 36 | 0.56 | 1.01 |
| 33 | 35.8 | 29 | 71 | 2.45 | 58 | 42 | 0.72 | 1.22 |
| 49 | 40.9 | 24 | 76 | 3.17 | 57 | 43 | 0.75 | 1.42 |
| 80 | 40.2 | 24 | 76 | 3.17 | 51 | 49 | 0.96 | 1.63 |
| 122 | 42.4 | 22 | 78 | 3.55 | 48 | 52 | 1.08 | 1.85 |

^a Sum of C extracted by Na₄P₂O₇ and NaOH (as shown in Table 2) as a percentage of total compost C.

^b Calculated by the difference between extract and FA values.

^c Weighted average of HA/FA ratios in Na₄P₂O₇ and NaOH extracts.

Table 4
Correlation coefficients (*r*) between parameters used for separated swine manure compost maturity indices

| | Ash | C/N | Cu concentration | Extracted humic C | Combined HA/FA ratio |
|----------------------|-----|---------|------------------|-------------------|----------------------|
| Ash | | -0.96** | 0.95** | 0.98** | 0.99** |
| C/N | | | -0.99** | -0.90** | -0.94** |
| Cu concentration | | | | 0.90** | 0.93** |
| Extracted humic C | | | | | 0.97** |
| Combined HA/FA ratio | | | | | |

**Significance at the $P \leq 0.01$ level ($n = 10$).

particulate fractions are relatively immobile and may not be readily bioavailable. However, metals in the residual fraction are tightly bound and not expected to be released readily under natural conditions (He et al., 1995). The differences in the distribution patterns of Cu, Mn, and Zn in the SSM composts studied indicate that the potential mobility and bioavailability of these elements vary in the environment.

Results show that the distribution of Cu, Mn, and Zn in various fractions (water-soluble fraction excluded) were generally independent of composting age and of total metal concentrations (Fig. 4). The water-soluble fractions of Mn and Zn were both < 2% throughout the process and may be the most mobile and bioavailable fractions of the metals. The water-soluble fractions of Cu increased from 3% in the raw SSM to about 16% at Day 18, then decreased to 3% in the final compost. The exchangeable fractions of Cu, Mn, and Zn during the composting process were low, < 4, 2, and 1%, respectively. In general, only a small portion of total compost Cu, Mn, and Zn (< 5, 13, and 3%, respectively) remained in the final residue.

In the 10 composts at various stages of composting, the greatest amount of Cu was in the organically bound fraction, followed by the organically complexed, solid particulate, and water soluble fractions, with the smallest

amounts of Cu being associated with the exchangeable and residual fractions (Fig. 4). Approximately 70% of total Cu in these composts was associated with the organically bound and organically complexed fractions, which may have been due to a high affinity of Cu for organics (Stumm and Morgan, 1981). Though, there were some small changes in Cu distribution observed during the process; the organically complexed fractions tended to decrease, the organically bound fractions increased, and the water-soluble fractions increased to a maximum at Day 18 and then declined thereafter. Statistical analysis reveals that organically complexed or organically bound fraction of Cu was significantly correlated to ash, organic C, extracted humic C, HA/FA, and total Cu concentrations during the process ($P \leq 0.05$; Table 5).

At various stages of composting, the highest amounts of Mn were present in the solid particulate and organically complexed fractions, followed by the residual, organically bound, exchangeable, and water-soluble fractions (Fig. 4). In the mature compost, 47% of Mn was present in the solid particulate fraction, 39% with the organically complexed fraction, 8% with the residual fraction, 4% with the organically bound fraction, and 1% each with the exchangeable and water-soluble fractions. However, due to low total Mn content of the

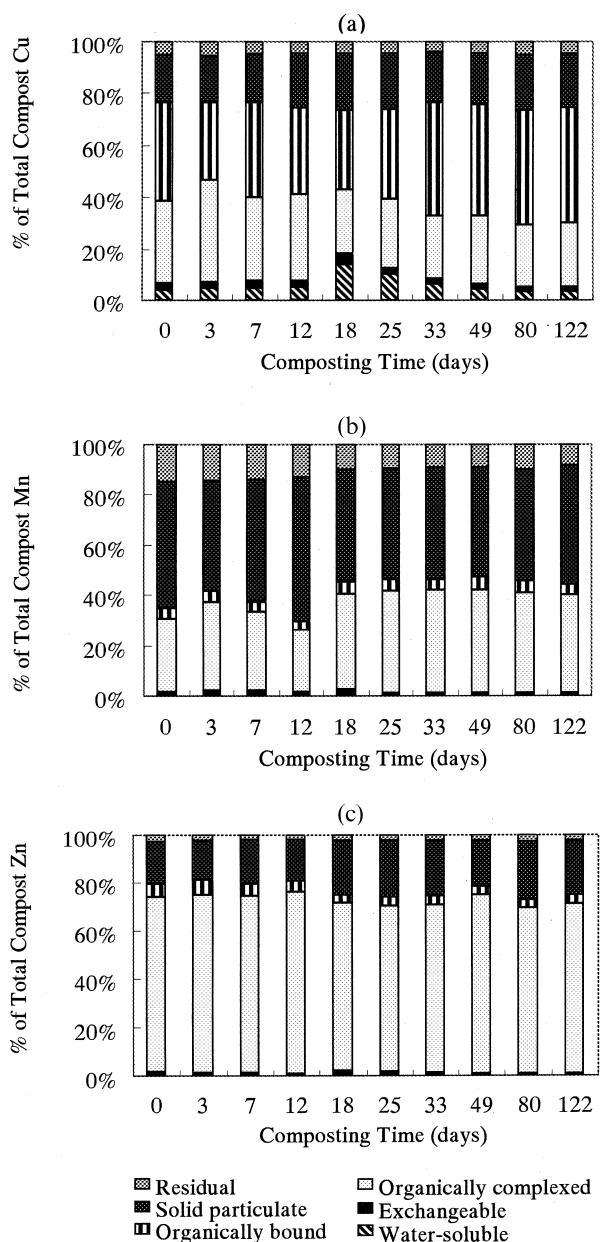


Fig. 4. Distribution of (a) Cu, (b) Mn, and (c) Zn in the various fractions by sequential extraction.

final SSM compost (331 mg kg^{-1}) compared with soil Mn content of $1000\text{--}3000 \text{ mg kg}^{-1}$ (Alloway, 1995), it is unlikely that application of SSM composts to soils will cause Mn toxicity to plants. In fact, Chaney and Ryan (1993) are concerned that application of alkaline biosolids can result in Mn deficiency in susceptible crops. Organically complexed or organically bound fraction was significantly correlated to ash, organic C, C/N, extracted humic C, HA/FA, and total Cu concentrations ($P \leq 0.05$; Table 5), while the residual fraction was strongly correlated to these parameters ($P \leq 0.01$).

At various stages of composting, the major and approximately the same amounts (71%) of Zn were in the organically complexed fraction, with moderate

amounts occurring in the solid particulate fraction, a small amount being associated with the organically bound and residual fractions, and the lowest with the water-soluble and exchangeable fractions. Approximately 70% of total compost Zn was in the organically complexed fraction, indicating its potential environmental mobility. Exchangeable, organically bound, or solid particulate fraction was significantly correlated to ash, organic C, C/N, extracted humic C, HA/FA, and total Cu concentrations during the process ($P \leq 0.05$; Table 5).

The distribution of these elements in the various fractions by sequential extraction during composting reveals that the readily leachable fraction (water-soluble fraction) of elements (% of total compost metals) in SSM compost decreased in the order $\text{Cu} > \text{Mn} \approx \text{Zn}$, whereas the potential mobility of these elements was generally in the order $\text{Zn} > \text{Cu} > \text{Mn}$. Our results were consistent with those of Miller et al. (1986) and L'Herroux et al. (1997), who found a similar pattern of Cu and Zn in the solid fraction of raw pig slurry. He et al. (1995) also found a similar Mn and Zn trend for MSW composts, but most of the Cu was present in the solid particulate fraction. Tisdell and Breslin (1995) found that Cu in MSW composts was concentrated in the organic fraction.

3.4.4. Distribution of metals in fulvic acid and humic acid fractions

Humic substances have a relatively high capacity to complex with trace metals (Stevenson, 1982). Humic fractions (HA and FA) may differ in complexing trace metals as well as in affinity toward individual metal ions (Stevenson, 1982). It is generally believed that HA represents more stable and condensed forms of humic substances than FA (Stevenson, 1982). Some non-humic substances, such as low molecular weight polysaccharides, amino acids, and phenolic acids, are recovered as FA based on the operational definition of FA (He et al., 1995). Therefore, relative distributions of trace metals in HA and FA may be used to predict the stability or mobility of trace metals in the environment after SSM compost application.

Most Cu, Mn, and Zn were recovered in FA from either $\text{Na}_4\text{P}_2\text{O}_7$ or NaOH extracts throughout the composting process (Table 6). As high as 99–100% of Cu in either $\text{Na}_4\text{P}_2\text{O}_7$ or NaOH extracts and Mn in $\text{Na}_4\text{P}_2\text{O}_7$ extracts from raw SSM were retained in the FA fraction and as composting proceeded, the percentage decreased to 72–77% in the mature compost. This result suggests that although Cu and Mn associated with organic components in SSM are less stable during the composting process, they tend to be more stable with composting age. The distribution of Mn in the NaOH extract and Zn in either $\text{Na}_4\text{P}_2\text{O}_7$ or NaOH extracts in FA and HA remained constant during composting. Therefore,

Table 5
Matrix correlation (coefficient of correlation r) of Cu, Mn, and Zn extractions with composting parameters

| | pH | Ash | Organic C | C/N | Extracted humic C | humic acid/fulvic acid | Total metal ^a |
|-----------------------|-------|---------|-----------|--------|-------------------|------------------------|--------------------------|
| <i>Cu</i> | | | | | | | Cu |
| Water-soluble | 0.15 | -0.03 | 0.05 | -0.23 | -0.19 | -0.05 | 0.20 |
| Exchangeable | 0.05 | -0.57 | 0.60* | 0.38 | -0.68* | -0.54 | -0.42 |
| Organically complexed | 0.09 | -0.83* | 0.83* | 0.90** | -0.77* | -0.83* | -0.89* |
| Organically bound | -0.18 | 0.73* | -0.75* | -0.59 | 0.81* | 0.72* | 0.60* |
| Solid particulate | 0.07 | 0.54 | -0.55 | -0.68* | 0.46 | 0.58 | 0.68* |
| Residual | -0.16 | -0.35 | 0.35 | 0.52 | -0.30 | -0.30 | -0.50 |
| <i>Mn</i> | | | | | | | Mn |
| Water-soluble | -0.05 | -0.57 | 0.60* | 0.39 | -0.67* | -0.55 | -0.47 |
| Exchangeable | -0.44 | -0.58 | 0.61* | 0.65* | -0.58 | -0.54 | -0.67* |
| Organically complexed | -0.16 | 0.80* | -0.78* | -0.84* | 0.72* | 0.75* | 0.76* |
| Organically bound | -0.42 | 0.70* | -0.70* | -0.71* | 0.65* | 0.66* | 0.65* |
| Solid particulate | 0.24 | -0.51 | 0.49 | 0.55 | -0.42 | -0.46 | -0.44 |
| Residual | 0.08 | -0.95** | 0.94** | 0.99** | -0.89* | -0.93** | -0.97** |
| <i>Zn</i> | | | | | | | Zn |
| Water-soluble | 0.24 | -0.27 | 0.28 | 0.01 | -0.40 | -0.25 | -0.15 |
| Exchangeable | 0.08 | -0.88* | 0.89* | 0.82* | -0.90** | -0.85* | -0.94** |
| Organically complexed | -0.20 | -0.54 | 0.54 | 0.66* | -0.41 | -0.57 | -0.51 |
| Organically bound | 0.17 | -0.85* | 0.85* | 0.93** | -0.78* | -0.83* | -0.89* |
| Solid particulate | 0.06 | 0.78* | -0.78* | -0.87* | 0.68* | 0.78* | 0.78* |
| Residual | -0.01 | -0.12 | 0.10 | 0.17 | -0.11 | -0.06 | -0.32 |

^a Total metal: digestion with HNO₃ + HClO₄.

*Significance at the $P \leq 0.05$ level ($n = 10$).

**Significance at the $P \leq 0.01$ level ($n = 10$).

Table 6
Distribution of Cu, Mn, and Zn in fulvic acid (FA) and humic acid (HA) fractions of Na₄P₂O₇ and NaOH extracts during the composting process

| Composting time (days) | Cu | | | | Mn | | | | Zn | | | |
|------------------------|---|-----------------|------|-----------------|---|-----------------|------|-----------------|---|-----------------|------|-----------------|
| | Na ₄ P ₂ O ₇ | | NaOH | | Na ₄ P ₂ O ₇ | | NaOH | | Na ₄ P ₂ O ₇ | | NaOH | |
| | FA | HA ^a | FA | HA ^a | FA | HA ^a | FA | HA ^a | FA | HA ^a | FA | HA ^a |
| 0 | 99 | 1 | 100 | 0 | 100 | 0 | 89 | 11 | 99 | 1 | 100 | 0 |
| 3 | 99 | 1 | 100 | 0 | 100 | 0 | 83 | 17 | 100 | 0 | 100 | 0 |
| 7 | 97 | 3 | 99 | 1 | 97 | 3 | 86 | 14 | 99 | 1 | 99 | 1 |
| 12 | 92 | 8 | 95 | 5 | 92 | 8 | 86 | 14 | 97 | 3 | 100 | 0 |
| 18 | 86 | 14 | 96 | 4 | 89 | 11 | 98 | 2 | 98 | 2 | 100 | 0 |
| 25 | 85 | 15 | 89 | 11 | 83 | 17 | 94 | 6 | 100 | 0 | 100 | 0 |
| 33 | 84 | 16 | 82 | 18 | 87 | 13 | 99 | 1 | 96 | 4 | 100 | 0 |
| 49 | 81 | 19 | 83 | 17 | 85 | 15 | 98 | 2 | 91 | 9 | 99 | 1 |
| 80 | 75 | 25 | 77 | 23 | 82 | 18 | 94 | 6 | 96 | 4 | 100 | 0 |
| 122 | 72 | 28 | 73 | 27 | 77 | 23 | 87 | 13 | 93 | 7 | 100 | 0 |

^a Calculated by subtraction of metals in FA from metals in total extract.

composting age had little influence on Zn stability with regards to association with organic components in SSM. He et al. (1995) also found that most of the Mn and Zn in mature MSW compost was recovered in FA fractions, but more Cu was retained in HA than in FA fractions.

4. Conclusions

This article demonstrates that metal concentrations as well as ash content, C/N ratio, extracted humic C, and

weighted HA/FA ratio were each good indicators of SSM compost stability and maturity. All of these parameters reveals that the SSM compost, described in this study, was mature and stable after about 80 days of composting. Although Cu, Mn, and Zn concentrations increased approximately 2.7-fold in the final compost, the results of this study show that the leachability of these elements in final compost is likely low. However, enhanced leaching of Cu (up to 16% of total compost Cu) at the end of rapid decomposition phase due to substantial dissolution of organic C (17.5% of total compost

C) indicates that application of immature SSM compost on soil may not be a risk-free management practice. Composting age and metal concentration appear to have little influence on water-soluble fractions of Mn and Zn and the distribution of Cu, Mn, and Zn among the different extractable forms. Copper was primarily in the organically bound fractions during the composting process. Manganese was mainly associated with the solid particulate fractions. Zinc was concentrated in the organically complexed fractions. The distribution of the three metals in the various fractions indicates their differences in potential leachability and bioavailability. Of the elements studied, Zn in SSM compost appeared to be the most potentially leachable and bioavailable.

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