Comissão 3.5 - Poluição, remediação do solo e recuperação de áreas degradadas

ASSESSMENT OF BIOAVAILABILITY OF HEAVY METALS AFTER VERMICOMPOSTING IN THE PRESENCE OF ELECTRONIC WASTE

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ABSTRACT

Heavy metals contained in electronic waste, if discarded improperly, can become bioavailable after vermicomposting, posing a risk to the environment. Small-scale vermicomposting experiments were carried out with printed circuit boards (PCBs) to investigate the migration of heavy metals (Cu, Pb, Zn, Ni, and Sn) to the final compost, as well as the mobility and bioavailability of these metals. High total levels of Pb, Sn and Cu in samples of manure with electronic waste (MEW) and vegetables with electronic waste (VEW) were detected. Based on the initial metal levels in the PCBs and their concentration in the resulting compost, the order of migration of these metals to the MEW and VEW samples was Sn (23.1 %)>Pb (18.4 %)>Ni (4.63 %)>Zn (0.46 %)>Cu (0.14 %) and Sn (24.3 %)>Pb (23.6 %)>Ni (11.33 %)>Zn (1.76 %)>Cu (0.60 %), respectively. Mobility and bioavailability of these metals in the compost were evaluated by three-stage sequential extraction, where F1 was the exchangeable fraction, F2 the organic fraction and F3 the residual fraction. The bioavailability factor (BF) was calculated by the ratio of the sum of fractions F1 and F2 divided by the total sum of the fractions (F1 + F2 + F3). The highest bioavailability factor (BF = 0.92) was found for Pb, the heavy metal considered the greatest environmental concern in this study, indicating the high mobility and the possibility of becoming bioavailable of this metal.

Keywords: electronic waste, metal contamination, lead, sequential extraction.

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RESUMO: *AVALIAÇÃO DA BIODISPONIBILIDADE DE METAIS PESADOS APÓS VERMICOMPOSTAGEM EM PRESENÇA DE LIXO ELETRÔNICO*

Os metais pesados presentes no lixo eletrônico, descartado de forma inadequada, podem se tornar biodisponíveis após a vermicompostagem, representando risco ao ambiente. Foram realizados experimentos de vermicompostagem em pequena escala na presença de placas de circuito impresso (PCI) para investigar a migração de metais pesados (Cu, Pb, Zn, Ni e Sn) para o composto obtido, assim como a mobilidade e biodisponibilidade desses metais. Os resultados evidenciaram elevados teores totais de Pb, Sn e Cu nas amostras de esterco com resíduo eletrônico (ERE) e vegetais com resíduo eletrônico (VRE). Levando-se em consideração os teores iniciais dos metais nas PCIs e as concentrações dos mesmos no composto obtido, a ordem de migração desses metais para as amostras ERE e VRE foi Sn (23,1 %)>Pb (18,4 %)>Ni (4,63 %)>Zn (0,46 %)>Cu (0,14 %) e Sn (24,3 %)>Pb (23,6 %)>Ni (11,33 %)>Zn (1,76 %)>Cu (0,60 %), respectivamente. A avaliação da mobilidade e biodisponibilidade dos metais no composto foi realizada mediante a extração sequencial em três etapas, sendo F1 a fração trocável, F2 a fração orgânica e F3 a fração residual. O fator de biodisponibilidade (FB) foi obtido pela razão entre a soma das frações F1 e F2 pela soma total das frações (F1 + F2 + F3). O maior valor do FB (0,92) foi encontrado para o Pb, metal pesado considerado de maior preocupação ambiental neste estudo, o que indica alta mobilidade desse metal, podendo tornar-se biodisponível.

Palavras-chave: resíduo eletrônico, contaminação por metais, chumbo, extração sequencial.

INTRODUCTION

Electronic waste (e-waste) is the name given to residues of obsolete electronic equipment such as televisions, cell phones, computers, and other devices. From the point of view of material composition, e-waste can be defined as a mixture of various metals such as copper, aluminum, iron, zinc, nickel, lead, cadmium, and mercury, associated with various types of plastic and ceramic materials (Cui and Zhang, 2008).

The generation of e-waste is on the rise, mainly as a result of technological development that continuously shortens the life of electronic equipment. For example, cell phones are used for an average period of only 18 months before being replaced, even when still operational (EPA, 2011). Residues from electrical and electronic equipment already account for 8 % of municipal waste and constitute one of the fastest growing waste fractions (Widmer et al., 2005).

Brazil is considered one of the largest producers of electronic waste in emerging countries. It is currently estimated that about 679,000 Mg yr^{-1} of e-waste is generated (Rocha et al., 2009). Regarding cell phones, about 10 to 20 % of the phones produced in Brazil are discarded every year (Oliveira et al., 2012).

Waste Electrical and Electronic Equipment (WEEE) is often disposed of together with household waste in landfills or dumps, resulting in a natural composting process of organic matter together with e-waste. Several studies have addressed the contamination of landfills by heavy metals from electronic waste, demonstrating a growing concern regarding the potential negative environmental impact of this type of waste (Spalvins et al., 2008; Li et al., 2009; Kiddee et al., 2013).

Composting can be defined as a controlled aerobic process, mediated by a mixed colony of microorganisms. In a first, the so-called thermophilic phase, more intense biochemical oxidation reactions occur. During the second or maturation phase, humification occurs. The composting period essentially depends on the type of reactions in the process and the type of material to be composted. It generally varies between 25 and 35 days for the first phase and from 30 to 60 days for the second phase (Pereira Neto, 2007).

Vermicomposting occurs in the presence of worms, which mediate of naturally integrated activities in the soil in a network that involves several organisms. In addition to worms, various microorganisms participate in this process, mainly bacteria, fungi, protozoa, and actinomycetes. Fungi have enzymes capable of degrading complex and polymeric substrates, e.g., polysaccharides such as cellulose, hemicellulose, lignin, starch, chitin and glycogen, and proteins such as casein, keratin and albumin. Some soil fungi produce citric acid and others chelating organic acids (Manahan, 2013). On the other hand, bacteria are generally effective in degrading simple soluble products.

When worms open galleries that allow their locomotion they ingest soil, digesting the equivalent of their own weight. Thus, channels and pores are created throughout the soil profile, facilitating the movement of gases, water and soluble compounds. Of all materials ingested by earthworms, about 60 % is converted into vermicompost. In a fast and efficient humification process, the earthworms ingest the recently formed organic matter and excrete it in the form of coprolites, which is a decomposed material. The result of this process is chemically stabilized vermicompost (Landgraf et al., 2005).

Although animal manure is the most widely used raw material for vermicomposting, other substrates are also well accepted by worms, including the organic part of domestic waste and plant residues from diverse origins; in summary, materials containing organic matter. The California red worm, *Eisenia foetida*, is the most suitable species for vermicompost production for being well suited for worm cultures, producing humus in a short time, and very prolific. The product obtained from vermicomposting, i.e., humus, has a high degree of degradation and stabilization in function of the mechanisms to which the original material was subjected, when exposed to peristalsis and the intestinal flora of the earthworms, providing a rapid and efficient degradation of the material. Vermicomposting occurs in a short period, transforming the state of the fresh organic material into a state of stabilization apparently similar to that observed in nature, although the humic acid structures of the resulting organic fractions differ from those of peat or soil (Landgraf et al., 2005).

Thus, the main objective of this study was to evaluate the bioavailability of heavy metals after vermicomposting with electronic waste in small-scale simulation trials to test the behavior of this type of waste in the vermicomposting process.

MATERIAL AND METHODS

Preparation and characterization of the electronic waste

The electronic waste (EW) sample was obtained from printed circuit boards (PCBs) of obsolete computers, from which the batteries had been removed. The PCBs were shredded to irregularly shaped pieces of approximately 9 cm^2. Part of this sample was ground in a hammer mill, resulting in two forms of the sample, chopped and ground. Approximately 7.0000 g of the ground sample were soaked in 105 mL aqua regia overnight, and then the system heated to 115 ± 5 °C under reflux for 2 h. After cooling, the samples were quickly filtrated through filter paper into a 250.00 mL volumetric flask, using 5 % v/v HCl solution for washing of the residue and also to fill the volumetric flask to the mark. In the filtrate, the concentrations of Cu, Pb, Zn, Ni, and Sn were determined in an atomic absorption spectrophotometer (Agilent Technologies 200 Series AA). The residue was dried in an oven at 50 ± 5 °C, cooled in a desiccator, weighed, calcined in a muffle furnace at 550 °C and reweighed. Calcination, cooling and weighing were repeated until reaching constant weight. It was assumed that the difference between the initial mass and the residue mass after digestion corresponded to the quantity of metals present in the sample, that the difference in residue weight before and after calcination corresponded to the content of volatile polymers and that the remaining weight after calcination would correspond to the refractory ceramic materials. In this way, the percentage contents of metals, polymers and ceramic materials were determined in the sample.

Preparation of boxes for vermicomposting

To simulate the situation in which electronic waste is disposed of together with household waste containing organic residues, experiments were carried out for vermicomposting of organic material from the university restaurant (UR) of the Federal University of Viçosa or cattle manure in the presence of printed circuit board particles with a size of approximately 9 cm^2. Small-scale experiments were installed in properly drained wooden boxes used as worm bins, with a volume of approximately 58 L ($0.30 \times 0.53 \times 0.37$ m = 0.0588 m^3). The assemblies were as follows: one box containing cattle manure and California red worms (*Eisenia foetida*) – control (MC); one box containing cattle manure, California red worms and about 2.0 kg of chopped circuit boards (MEW); one box containing vegetable residues from the preparation of meals at the UR and California red worms – control (VC); and one box containing vegetable residues, California red worms and about 2.0 kg of chopped circuit boards (PEW). All boxes were covered with sawdust, to prevent the release of odorous gases and also to maintain moisture. Importantly, the content of e-waste in the composting mass was around 3.5 % of the mass, inferred based on Spalvins et al. (2008), Kiddee et al. (2013) and Li et al. (2009). After blending the materials to be composted carefully, the boxes were placed in a well-ventilated area and covered to start the process. During the composting process, the temperature was monitored and the system maintained moist, according to recommendations of Pereira Neto (2007).

Sampling

Samples were collected in 90 days intervals, over a period of 360 days, at different points of the boxes to obtain a representative sample (total of 500 g). After removing the worms and chopped circuit boards, these portions were carefully mixed and quartered to ensure a homogenous sample. A part of the sample was used for moisture determination and the rest air-dried. The dried samples were ground, sieved through mesh Nº 80 (0.177 mm) and stored for subsequent analysis.

Compost analysis

Physico-chemical parameters

Immediately after collection, the samples were heated to 105 ± 5 °C until reaching constant dry weight, to determine the water content (%). Each dry and ground sample was analyzed for the following parameters: pH (1:2.5 w/v in aqueous suspension), electrical conductivity (1:2.5 w/v in aqueous extract) and total organic matter (550 ± 10 °C for 4 h until reaching constant dry weight).

Determination of heavy metals

The total contents of the metals Cu, Pb, Zn, Ni, and Sn were determined by an atomic absorption spectrophotometer (Agilent Technologies 200 Series AA) after digestion of 0.2500 g of the sample with 4 mL HNO_3, 2 mL HF and 2 mL H_2O_2 in a microwave oven (Milestone-Ethos1), heated to 200 °C for 10 min and maintained at 1,200 watts for 20 min.

To analyze the mobility and bioavailability of metals present in the compost, a sequential extraction was performed in three steps, in triplicate, adapted from Egreja Filho et al. (1999) In the first step, the exchangeable fraction (F1) was extracted by adding potassium nitrate 1 mol L^{-1}, with pH adjusted to 7.00, to approximately 1.0000 g of the ground sample. The suspension was continuously stirred for 60 min, centrifuged for 15 min at 3000 rpm (1509 g) and filtered through filter paper for rapid filtration. Concentrated HNO_3 was added to the extract, which was heated, cooled and transferred to a 10.00 mL volumetric flask. The organically bound fraction (F2) was extracted from the residue of the first step by continuous shaking for 120 min in the presence of EDTA 0.05 mol L^{-1}, adjusted to pH 7.00. After centrifuging for 15 min at 3000 rpm (1509 *g*) and filtration through filter paper for rapid filtration, the extract was treated with concentrated HNO_3, heated, cooled and transferred to a 25.00 mL volumetric flask. The residual fraction (F3) was obtained from the residue of the second step, which was quantitatively transferred to a PTFE flask, to which 4 mL HNO_3, 2 mL HF and 2 mL H_2O_2 were added. The flasks were sealed and transferred to a microwave oven, where the temperature was increased to 200 °C in 10 min and maintained for 20 min at 1200 watts. After heating, the flasks were cooled and the digested material was transferred to a 25.00 mL volumetric flask and the volume completed with deionized water. At each step, the concentrations of Cu, Pb, Zn, Ni and Sn were determined by AAS for each compost sample.

Considering that the metal mobility decreases from the exchangeable fraction (F1) to the residual fraction (F3), the bioavailability factor (BF) was calculated for each metal as the ratio of the sum of the fractions F1 and F2 by the total sum of fractions F1 + F2 + F3 (Singh and Kalamdhad, 2012).

RESULTS AND DISCUSSION

Characterization of the electronic waste

In studies of different researchers, the EW described differs due to the heterogeneity of the samples, and mainly due to the different origins of PCB, obtained from equipment of different brands and ages (Yamane et al., 2011; Pant et al., 2012; Tuncuk et al., 2012).

In this study, the metals with highest proportion in the EW (56 %) (Figure 1) were copper with the highest percentage (22.9 %) followed by zinc (3.0 %), lead (2.6 %), tin (2.4 %), and nickel (0.4 %).

Physico-chemical parameters

During the composting experiments, the temperature remained in equilibrium with the environment, indicating that heat released from the biodegradation reactions was quickly transferred to the environment, as also occurs in composting under normal natural conditions. This fact can be attributed to the use of a composting mass of 58 kg and to the worms that create channels and pores by ingesting the material, facilitating the movement of gases, water and soluble components, as well as heat dispersion.

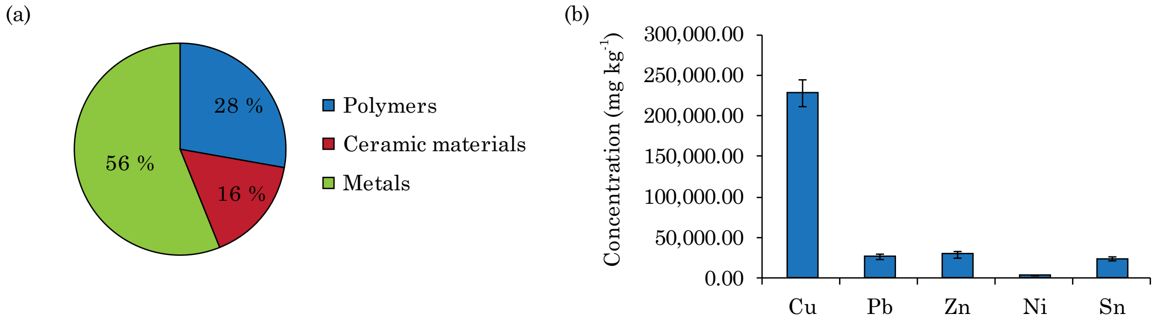

Figure 1. Determination of constituents of the electronic waste (EW) (a) percentage of polymers, ceramic materials and metals and (b) concentration of metals.

In controlled composting processes, moisture is restricted to a maximum of approximately 60 %. Control of excess moisture is critical to prevent anaerobiosis (cellular respiration in the absence of oxygen), which occurs when excess water occupies the empty spaces of the material. In this case, the production of leachates and malodorous gases are also generated (Pereira Neto, 2007). In the first sampling, after 90 days of composting, the moisture content was approximately 70 % in all trials (Figure 1), with acceptable variations in the other collections. In the final sampling, 360 days after the experiment, moisture contents of the composts were between 40 and 55 %, considered ideal by Silva et al. (2002) for composts marketed as organic fertilizers.

Moisture loss during the composting process in the form of vapor produced by heat generation is a sign of organic matter decomposition (Kalamdhad et al., 2009). The formation of leachate and malodorous gases was not observed during the experimental period.

The pH is a parameter with great influence on the composting process, and the pH variation in the four trials during the composting process is in the figure 2. In general, the pH values were within the optimal growth ranges for bacteria (6.0-7.5) and fungi (5.5-8.0) (Singh and Kalamdhad, 2012). Initially, the pH values were between 6.5 and 7.5 for manure compost samples and around 8.5 for the compost samples of plant residues. During the experiment, these values were reduced and stabilized between 5.5 and 6.5, after 270 days. The reduction in pH can be explained mainly by the oxidation of organic C forming oxygenates, such as CO_2 and organic acids, as well as by NH_4^+ hydrolysis, resulting from the conversion of organic N in the decomposition process.

The pH value of the solution strongly influences not only the local dissolution of the biomass surface, but also the chemical solution of heavy metals: hydrolysis, complexation with organic and, or, inorganic ligands, redox reaction, precipitation, speciation, and biosorption of heavy metals (Singh and Kalamdhad, 2012).

Electrical conductivity is generally measured during composting because it reflects the salinity and may influence metal oxidation. In the first compost sampling after 90 days (Figure 2), electrical conductivity was near 2.00 mS cm^{-1} for all samples. Over time, these values increased to a point of stabilization close to 3.00 mS cm^{-1} for the manure compost samples and to around 9.00 mS cm^{-1} for plant compost samples. The pH reached a minimum value at the third sampling after 270 days (Figure 2), coinciding with the maximum conductivity, which

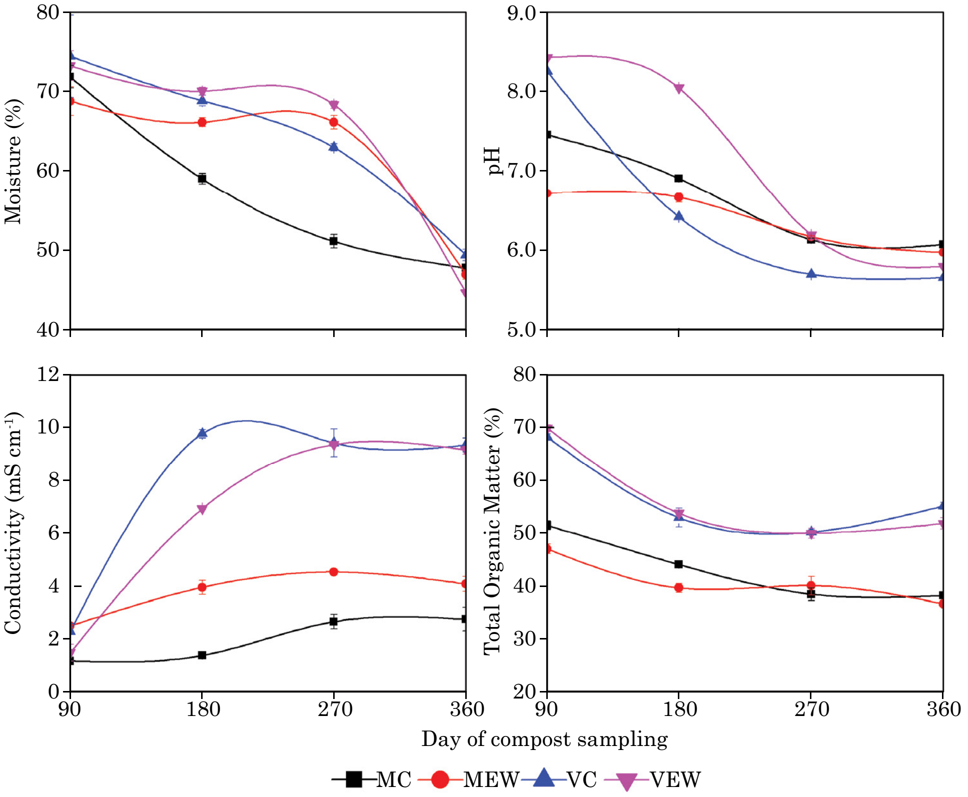

Figure 2. Diagram of variations in moisture, pH, electrical conductivity, and organic matter at compost sampling after 90, 180, 270 and 360 days. MC: manure control; MEW: manure electronic waste; VC: vegetable control; VEW: vegetable electronic waste.

suggests that the major contribution to conductivity increase is the intensified activity of the H^+ ion, also taking into consideration the salt concentration. This increase in electrical conductivity can be due to the release of soluble mineral salts and ammonium ions by the decomposition of organic matter (Kalamdhad et al., 2009).

No contribution to the increase in conductivity was observed due to the presence of PCBs in the PEW sample, since the conductivity values were the same in the control sample as in the EW sample in the third sampling. This suggests that the metals released from PCB are bound to the organic matter and do not contribute as free ions to increase conductivity.

The highest electrical conductivity values observed for the compost samples obtained from plant residues are probably due to a higher production of ammonium and nitrate ions, since fresh vegetables have a higher proportion of N (C/N ratio of less than 30:1).

The organic residues are decomposed by soil organisms by incorporation of part of the C in the microbial tissue, while the rest is released as CO_2. As a general rule, only one-third of the carbon present in recent waste remains in the ground after the first months of decomposition (Landgraf et al., 2005). During the composting process, CO_2 is emitted from the compost mass as a final metabolic product (mineralization). Thus, the total organic C content decreases as composting progresses. Initially, organic matter is composed of carbohydrates, proteins, lipids, and woody compounds. The organic matter is decomposed and converted into stable humic compounds. Humic substances have the ability to interact with metal ions, to buffer the pH and act as a potential nutrient source for plants (Singh et al., 2009). Organic matter tended to decrease in the four trials of the experiment (Figure 2). Therefore, the organic matter content decreased as decomposition progressed and was quite stable in the second sampling after 180 days. Moreover, the control samples (MC; VC) showed the same behavior as samples with EW (MEW; PEW), despite the decrease in organic matter (Figure 2). The reduction in organic matter was related to the degradation activity of microorganisms and earthworms; since no difference was observed, it is suggested that the presence of EW does not decrease this activity.

Total metal contents in the compost

The raw material used for composting is relatively free of heavy metals, which can be confirmed by the low levels of Cu, Pb, Ni, and Sn found in the control samples (Figure 3). However, high contents of these elements in the samples of compost with electronic waste are strong indicators of contamination of the organic fraction by the non-compostable inorganic fraction rich in these metals (Figure 3). It can therefore be stated that this contamination occurred due to the oxidation of metals from EW in the composting environment, followed by migration of metal ions from the inorganic to the organic fraction. It is believed that the metals were oxidized by powerful oxidants produced by certain microorganisms, since according to Manahan (2013), 2-ketogluconic acid, a powerful oxidant, is produced by certain soil bacteria. When solubilizing metal ions, this oxidant contributes to the degradation of PCBs. Of the metals analyzed, Zn was found at highest levels in the control samples.

Considering the initial metal contents in the PCBs and their concentration in the resulting compost, the order of migration from the MEW and PEW samples was Sn (23.1 %)>Pb (18.4 %)>Ni (4.63 %)>Zn (0.46 %)>Cu (0.14 %) and Sn (24.3 %)>Pb (23.6 %)>Ni (11.33 %)>Zn (1.76 %)>Cu (0.60 %), respectively.

Although Cu is the metal with highest proportion in the EW, acting as an electrical conductor between components of the PCB with 22.9 % (Figure 3), the migration percentage to the compost from the MEW and PEW samples was lowest (0.14 and 0.60 %, respectively). These results may be considered consistent, since Cu is a noble metal, little reactive, with low standard oxidation potential (-0.337 volts). Furthermore, Cu is protected by a degradation-resistant lacquer layer.

Lead and Sn present in EW at the proportions of 2.63 and 2.43 %, respectively, migrated at the highest rates. From the MEW sample, 18.4 % Pb and 23.1 % Sn migrated to the compost. From the PEW sample, the migration levels of Pb and Sn were 23.6 and 24.3 %, respectively. These high migration levels evidence the oxidation of these metals as a result of the high standard oxidation potentials (+ 0.126 and + 0.136 volts, respectively). Another factor that may have contributed to the dissolution of these metals is that they are contained in welds exposed on the PCBs, unlike Cu, which is protected by a varnish layer.

Zinc had a slightly higher content (3.0 %) than Pb and Sn in EW, but its migration to the compost was much lower compared with these elements, in spite of having the highest standard oxidation potential (+ 0.764 volts) of the metals analyzed. From the MEW and PEW samples, 0.46 and 1.76 % migrated from the PCBs to the compost, respectively. An explanation for this phenomenon might be the passivation of Zn, since oxidation forms Zn oxide or hydroxide which, by the action of C gas, is transformed into Zn basic carbonate, $3Zn(OH)_2.ZnCO_3$, which covers the metal surface, preventing the progress of oxidation (Gentil, 2011).

Of the metals analyzed, Ni was the element at lowest concentration in the EW (0.37 %). The reason is that the batteries – the main source of this metal – were removed from the PCBs when preparing the sample. The migration percentages were 4.63 and 11.33 % from the MEW and PEW

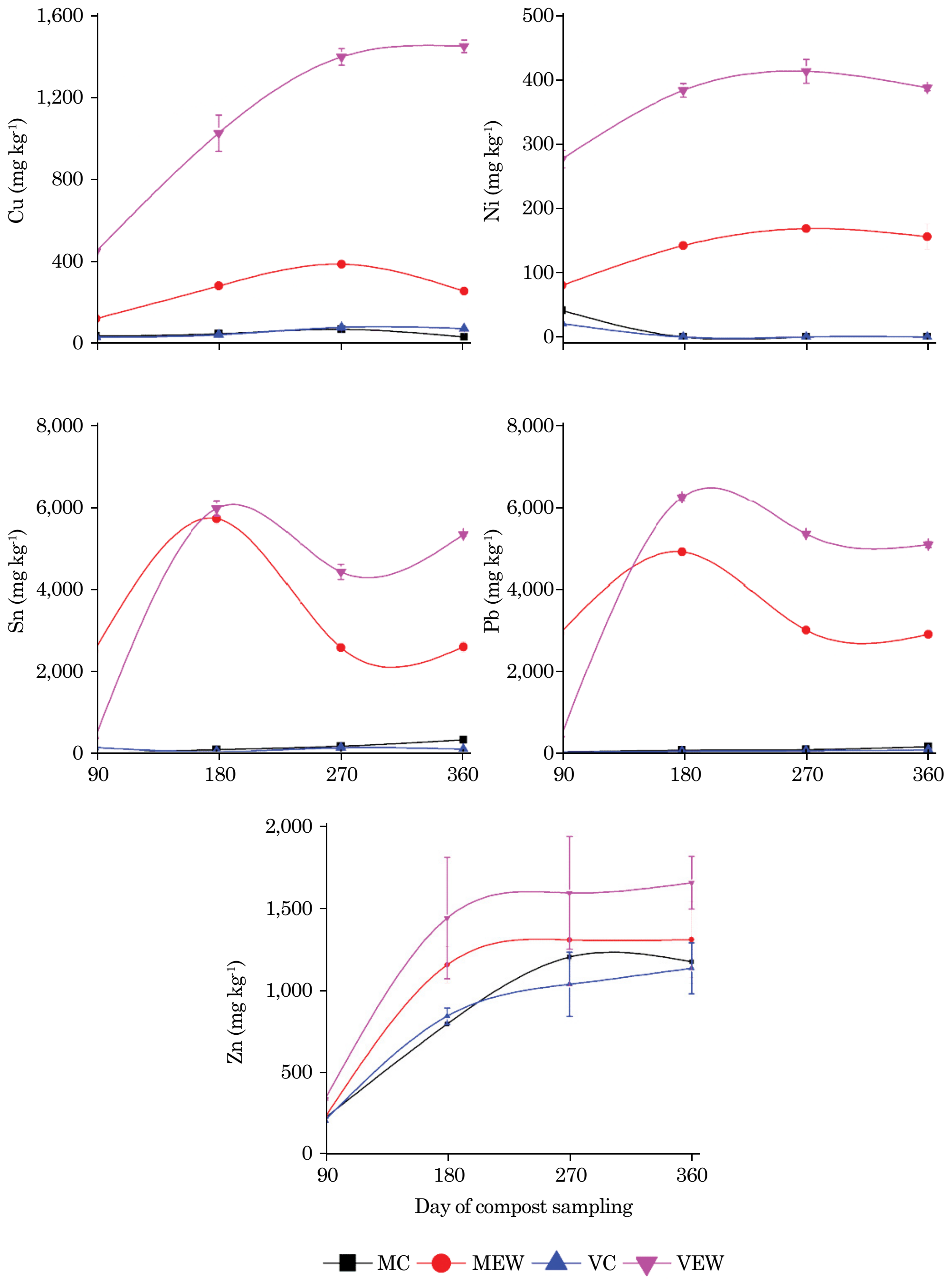

Figure 3. Total metal content (Cu, Ni, Pb, Sn, and Zn) in the compost samples.

samples, respectively. Considering the high standard oxidation potential (+ 0.250 volts), the migration percentages were low, compared to lead and tin.

Bioavailability and mobility of heavy metals in the compost

The total metal concentration after digestion of the compost sample with a strong acid may be considered a general indicator of environmental contamination. However, the total metal concentration does not provide information about the risk of mobility and bioavailability, which depend on the chemical form of the element. The sequential chemical extraction procedure can provide an understanding of metal fractions with different natures and allow a prediction of the mobility of metals, bioavailability and leaching rates. The mobility and bioavailability of metals decrease approximately in the order of the extraction sequence (Singh and Kalamdhad, 2012).

Thus, the mobility and bioavailability of metals in the compost were evaluated based on the sequential extraction of fraction F1 – exchangeable fraction, F2 – organically bound fraction and F3 – residual fraction (Tables 1 and 2).

In relation to Cu, the fractions F2 and F3 predominated in all trials; in the MEW and PEW samples, Cu occurred in the fractions F2 (71.1 %)>F3 (28.5 %)>F1 (0.45 %) and F2 (83.4 %)>F3 (16.1 %)>F1(0.57 %), respectively. The higher Cu content in the F2 fraction for PEW in relation to MEW may be justified by the higher organic matter content (Figure 2) of this sample. These high Cu contents in the F2 fraction are probably due to metal complexation by organic functional groups, e.g., carboxyl, carbonyl, phenolic and aminic groups present in humic substances formed in the composting process.

The bioavailability factor (BF) for Cu in the MEW and PEW samples was 0.72 and 0.84, respectively, indicating high mobility of the metal in the compost and potential bioavailability. The chemical affinity for the Cu(II) ion of humic substances is greater (Nachtigal et al., 2007), as observed here for the organically bound fraction. This affinity may be related to the larger ionic radius of copper, resulting in a smaller hydrated radius. Electronegativity may be another factor that contributes to greater Cu-organic matter affinity. In addition to all this, water-soluble humic substances have high levels of carboxylic groups that readily complex with Cu.

The stability constants of the metal-humic substance complexes depend on the nature of the organic matter, the metal, and also on other factors, e.g., ionic strength and pH of the environment (Singh and Kalamdhad, 2012).

Table 1. Metal concentrations determined by sequential extraction (F1, F2 e F3) of the compost obtained from cattle manure

Day	Manure Control (MC)			Manure + electronic waste (MEW)		
	F1(1)	**F2(2)**	**F3(3)**	**F1(1)**	**F2(2)**	**F3(3)**
			Cu (mg kg^{-1})			
90	1.04 ± 0.17	11.62 ± 1.43	48.60 ± 1.03	1.55 ± 0.13	42.54 ± 2.99	101.84 ± 5.54
180	1.27 ± 0.12	29.58 ± 1.30	34.50 ± 8.71	2.82 ± 0.51	177.15 ± 3.54	110.74 ± 14.97
270	0.53 ± 0.10	28.74 ± 0.74	42.19 ± 0.94	1.49 ± 0.04	234.80 ± 5.53	94.10 ± 14.50
360	0.40 ± 0.07	27.80 ± 4.38	40.74 ± 6.30	1.32 ± 0.06	173.13 ± 8.51	95.12 ± 8.43
			Pb (mg kg^{-1})			
90	8.08 ± 1.72	13.36 ± 1.22	77.72 ± 9.85	14.65 ± 4.00	1,620 ± 206	1,792 ± 143
180	0.15 ± 0.01	25.33 ± 1.04	76.38 ± 11.54	1.49 ± 0.34	4,104 ± 297	439.40 ± 37.81
270	0.12 ± 0.07	22.33 ± 1.84	87.50 ± 8.02	0.33 ± 0.14	2,865 ± 139	264.39 ± 63.60
360	0.06 ± 0.01	32.00 ± 1.41	77.82 ± 5.97	0.34 ± 0.07	2,711 ± 65	366.36 ± 75.31
			Sn (mg kg^{-1})			
90	ND	ND	215.17 ± 53.15	ND	ND	2,142 ± 291
180	ND	ND	141.47 ± 23.22	ND	48.30 ± 1.26	5,686 ± 311
270	ND	ND	136.41 ± 10.28	ND	68.39 ± 13.42	2,261 ± 31
360	ND	ND	126.38 ± 4.64	ND	44.67 ± 5.99	2,223 ± 103
			Zn (mg kg^{-1})			
90	4.57 ± 0.63	89.18 ± 1.77	100.88 ± 9.68	4.42 ± 0.27	86.12 ± 13.31	119.84 ± 14.87
180	0.17 ± 0.19	199.73 ± 3.69	732.12 ± 121.3	0.39 ± 0.28	346.39 ± 26.60	956.61 ± 37.35
270	0.03 ± 0.01	205.15 ± 1.92	816.17 ± 127.2	0.38 ± 0.07	393.10 ± 13.74	807.42 ± 181.3
360	0.74 ± 0.35	213.08 ± 8.48	823.08 ± 187.0	0.65 ± 0.44	364.00 ± 9.70	777.45 ± 255.7
			Ni (mg kg^{-1})			
90	ND	ND	ND	0.52 ± 0.27	13.50 ± 2.10	60.21 ± 1.55
180	ND	ND	ND	0.43 ± 0.10	76.69 ± 12.57	83.85 ± 1.67
270	ND	ND	ND	0.46 ± 0.03	102.98 ± 5.94	52.37 ± 26.97
360	ND	ND	ND	0.40 ± 0.04	95.42 ± 8.22	36.62 ± 17.69

(1) F1: exchangeable fraction, extracted by potassium nitrate 1 mol L^{-1}, pH 7.00; (2) F2: organically bound fraction, extracted from the residue of the first step in the presence of EDTA 0.05 mol L^{-1}, pH 7.00; (3) F3: residual fraction, obtained from the residue of the second step, quantitatively transferred to a PTFE flask, in the presence of 4 mL HNO_3, 2 mL HF and 2 mL H_2O_2.

Lead was predominant in the fractions F2 and F3 in all trials; in the MEW and PEW samples the fractions were ranked as F2 (91.55 %)>F3 (8.45 %)>F1 (0.01 %) and F2 (91.77 %)>F3 (8.22 %)>F1 (0.01 %), respectively. The high levels of this metal in fraction F2 indicate its complexation with humic substances formed by composting. The organically bound lead can be considered potentially available to plants, despite its lower mobility (Singh and Kalamdhad, 2012). Therefore, environmental changes such as variations in pH, redox potential and of organic compounds can make this metal readily available.

The bioavailability factor (BF) for Pb, the heavy metal of greatest environmental concern, in the MEW and PEW samples was 0.92. Due to this high bioavailability factor of Pb, phytotoxicity is possible.

Tin was not detected in fraction F1 in any trial, but occurred predominantly in fraction F3; in the MEW and PEW samples, it was detected in the fractions F3 (97.06 %)>F2 (2.94 %) and F3 (98.22 %)>F2 (1.78 %), respectively. The high concentrations in fraction F3 indicate that this metal is probably bonded to organic groups of the compost by more energetic bonds, which may make it more covalent.

The bioavailability factor (BF) for Sn in the sample of MEW and PEW was 0.03 and 0.02, respectively. These values indicate that the bioavailability of this metal is low under natural conditions, and that it should therefore not enter the food chain.

Zinc occurred primarily in the fractions F2 and F3 in all trials; in the samples MEW and PEW it occurred in the fractions F3 (67.23 %)>F2 (32.73 %)>F1 (0.03 %) and F3 (63.96 %)>F2 (36.02 %)>F1 (0.02 %), respectively. The high content in fraction F3 suggests that this metal is not bioavailable, however a reasonable quantity was found in fraction F2, which may become bioavailable due to changes in environmental conditions. The toxicity of this metal is not high, as that of lead, but in fact it is an essential micronutrient for plants.

Table 2. Metal concentrations in the compost from vegetable residues determined by sequential extraction (F1, F2 e F3)

Day	Vegetable control (VC)			Vegetable + electronic waste (VEW)		
	F1[(1)]	F2[(2)]	F3[(3)]	F1[(1)]	F2[(2)]	F3[(3)]
			Cu (mg kg^{-1})			
90	2.49 ± 0.32	19.90 ± 0.92	27.61 ± 0.17	18.98 ± 2.60	262.42 ± 23.23	214.85 ± 16.65
180	1.08 ± 0.11	35.03 ± 1.97	27.61 ± 0.17	15.21 ± 0.64	675.28 ± 10.88	214.85 ± 16.65
270	0.44 ± 0.08	36.47 ± 1.74	33.60 ± 1.08	4.77 ± 0.20	698.55 ± 23.75	134.58 ± 9.74
360	0.54 ± 0.08	34.24 ± 2.03	40.39 ± 2.26	5.75 ± 0.12	766.44 ± 27.08	236.04 ± 12.74
			Pb (mg kg^{-1})			
90	8.88 ± 0.44	24.88 ± 7.83	46.57 ± 1.79	8.26 ± 0.80	464.94 ± 39.82	109.04 ± 3.14
180	0.21 ± 0.06	26.61 ± 0.63	27.61 ± 0.17	1.66 ± 0.25	4,059 ± 385	214.85 ± 16.65
270	0.17 ± 0.07	30.32 ± 4.20	62.81 ± 10.40	0.41 ± 0.07	4,840 ± 109	433.67 ± 9.37
360	0.06 ± 0.01	29.36 ± 1.43	80.31 ± 11.69	0.36 ± 0.11	4,584 ± 70	1,025 ± 169
			Sn (mg kg^{-1})			
90	ND	ND	129.98 ± 26.55	ND	ND	262.38 ± 18.36
180	ND	ND	129.86 ± 11.29	ND	68.11 ± 5.13	5,354 ± 333
270	ND	ND	120.00 ± 11.60	ND	86.40 ± 1.61	4,759 ± 133
360	ND	ND	122.30 ± 7.33	ND	79.66 ± 8.50	3,815 ± 152
			Zn (mg kg^{-1})			
90	5.78 ± 0.64	131.99 ± 5.41	72.54 ± 3.64	6.49 ± 0.64	254.19 ± 19.79	102.65 ± 17.88
180	0.54 ± 0.10	249.18 ± 23.94	770.92 ± 94.25	0.39 ± 0.28	517.20 ± 13.56	863.42 ± 25.41
270	0.26 ± 0.02	287.69 ± 4.90	652.96 ± 57.89	0.26 ± 0.06	460.67 ± 15.45	817.94 ± 12.77
360	0.54 ± 0.05	297.59 ± 8.69	1004 ± 287	0.80 ± 0.20	683.96 ± 21.24	968.59 ± 28.44
			Ni (mg kg^{-1})			
90	ND	ND	ND	10.16 ± 1.92	133.69 ± 2.70	81.97 ± 2.53
180	ND	ND	ND	2.57 ± 0.20	233.76 ± 5.05	66.89 ± 2.46
270	ND	ND	ND	2.14 ± 0.07	267.16 ± 2.60	52.08 ± 8.33
360	ND	ND	ND	2.65 ± 0.24	284.69 ± 11.69	84.00 ± 13.65

(1) F1: exchangeable fraction, extracted by potassium nitrate 1 mol L^{-1}, pH 7.00; (2) F2: organically bound fraction, extracted from the residue of the first step in the presence of EDTA 0.05 mol L^{-1}, pH 7.00; (3) F3: residual fraction, obtained from the residue of the second step, quantitatively transferred to a PTFE flask, in the presence of 4 mL HNO_3, 2 mL HF and 2 mL H_2O_2.

The bioavailability factor (BF) for Zn in the MEW and PEW samples was 0.33 and 0.36, respectively. Availability of Zn is influenced by the total Zn content, pH, organic matter content and the availability of adsorption sites (Singh and Kalamdhad, 2012).

Nickel was not detected in control samples, and occurred predominantly in the fractions F2 and F3 in the composted samples in the presence of EW, where in the samples MEW and PEW it occurred in fractions F2 (66.09 %)>F3 (33.61 %)>F1 (0.30 %) and F2 (83.13 %)>F3 (16.21 %)>F1 (0.67 %), respectively. The high levels of this metal in fraction F2 indicate its complexation with humic substances formed in the composting process. However, the Ni^{2+} cation forms complexes with less stable organic ligands than those with Cu^{2+} (Singh and Kalamdhad, 2012).

The bioavailability factor (BF) for Ni in the MEW samples was 0.66. In the PEW samples, BF was 0.84, indicating high mobility, which can make it bioavailable. It should be noted that the Ni content in the compost was the lowest of the metals studied, in view of the lower proportional content in the EW.

CONCLUSIONS

The migration order of metals from electronic waste to compost was the same in the manure with electronic waste and vegetables with electronic waste samples: Sn>Pb>Ni>Zn>Cu. Compost contamination with heavy metals occurred due to oxidation of the metals from electronic waste in the composting environment, followed by migration of metal ions from the inorganic to the organic fraction.

The order of the bioavailability factor was Pb>Cu>Ni>Zn>Sn in the manure with electronic waste and vegetables with electronic waste samples, where a value of 0.92 was found for Pb, the heavy metal of greatest environmental concern in this study. The high mobility of this metal in the compost can make it bioavailable, proving that electronic waste should not be disposed of together with organic waste.

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