



Revista Brasileira de Ciência do Solo

ISSN: 0100-0683

revista@sbc.org.br

Sociedade Brasileira de Ciência do Solo
Brasil

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Revista Brasileira de Ciência do Solo, vol. 38, núm. 1, 2014, pp. 166-176

Sociedade Brasileira de Ciência do Solo
Viçosa, Brasil

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INFLUENCE OF DIGESTION METHODS ON THE RECOVERY OF IRON, ZINC, NICKEL, CHROMIUM, CADMIUM AND LEAD CONTENTS IN 11 ORGANIC RESIDUES⁽¹⁾

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SUMMARY

There are currently many devices and techniques to quantify trace elements (TEs) in various matrices, but their efficacy is dependent on the digestion methods (DMs) employed in the opening of such matrices which, although “organic”, present inorganic components which are difficult to solubilize. This study was carried out to evaluate the recovery of Fe, Zn, Cr, Ni, Cd and Pb contents in samples of composts and cattle, horse, chicken, quail, and swine manures, as well as in sewage sludges and peat. The DMs employed were acid digestion in microwaves with HNO₃ (EPA 3051A); nitric-perchloric digestion with HNO₃ + HClO₄ in a digestion block (NP); dry ashing in a muffle furnace and solubilization of residual ash in nitric acid (MDA); digestion by using *aqua regia* solution (HCl:HNO₃) in the digestion block (AR); and acid digestion with HCl and HNO₃ + H₂O₂ (EPA 3050). The dry ashing method led to the greatest recovery of Cd in organic residues, but the EPA 3050 protocol can be an alternative method for the same purpose. The dry ashing should not be employed to determine the concentration of Cr, Fe, Ni, Pb and Zn in the residues. Higher Cr and Fe contents are recovered when NP and EPA 3050 are employed in the opening of organic matrices. For most of the residues analyzed, AR is the most effective method for recovering Ni. Microwave-assisted digestion methods (EPA3051 and 3050) led to the highest recovery of Pb. The choice of the DM that provides maximum recovery of Zn depends on the organic residue and trace element analyzed.

Index terms: *aqua regia*, heavy metals, manure, sewage sludge, compost, degree of humification.

⁽¹⁾ Study drawn from the end of course monograph of undergraduate studies of the first author, financed by FAPEMIG and CNPq. Received for publication on September 20, 2012 and approved on October 9, 2013.

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RESUMO: INFLUÊNCIA DE MÉTODOS DE DIGESTÃO NA RECUPERAÇÃO DE TEORES DE FERRO, ZINCO, NÍQUEL, CROMO, CÁDMIO E CHUMBO EM 11 RESÍDUOS ORGÂNICOS

A eficiência de determinação de teores de elementos-traço (ET) é dependente dos métodos de digestão (MD) empregados na abertura de matrizes, que, embora “orgânicas”, podem conter constituintes inorgânicos de difícil solubilização. Objetivou-se, em razão do emprego de cinco MD, avaliar a recuperação de teores de Fe, Zn, Cr, Cd, Pb e Ni em 11 amostras de composto comercial, composto de lixo, composto orgânico, esterco de bovino, esterco de codorna, esterco de equino, esterco de galinha, esterco de suíno, lodo de esgoto de duas origens e turfa. Os métodos de digestão estudados foram: digestão ácida por micro-ondas com HNO_3 (EPA 3051); digestão nítrico-perclórica com $\text{HNO}_3 + \text{HClO}_4$ em bloco digestor (NP); digestão seca em forno tipo mufla com solubilização da cinza residual com ácido nítrico (MUFLA); digestão em solução água régia ($\text{HCl}:\text{HNO}_3$) em bloco digestor (AR) e digestão ácida com $\text{HNO}_3 + \text{H}_2\text{O}_2$ e HCl (EPA 3050). O método da digestão seca é o que proporciona maior recuperação de Cd nos resíduos orgânicos, mas o método EPA 3050 pode ser uma alternativa para o mesmo fim. A digestão seca não deve ser empregada para determinar os teores de Cr, Fe, Ni, Pb e Zn nos resíduos; entretanto, Cr e Fe são recuperados quando a digestão é feita pelos protocolos nítrico-perclórico e EPA 3050 nas matrizes orgânicas. A água régia é o método de digestão mais eficiente em recuperar o Ni, para a maioria dos resíduos. Os métodos que empregam micro-ondas (EPA 3051 e 3050) propiciam a extração dos maiores teores de Pb. A escolha de método de digestão que propicia máxima recuperação de Zn está condicionada ao resíduo orgânico e elemento-traço analisados.

Termos de indexação: água régia, metais pesados, esterco, lodo de esgoto, composto, grau de humificação.

INTRODUÇÃO

The concentration of trace elements (TEs) in organic residues is variable and tends to be low in plant material and high in some residues from industries, animal production systems or municipal waste and industrial facilities. The origin of residues in crop areas does not ensure a residue with low levels of TEs, and in the case of certain swine and poultry manures, feeding and farm management systems may lead to high Zn, Cu and Mn contents in the manures (Tedesco et al., 2008; Mattias et al., 2010). Agricultural use of residues in most countries considers the maximum concentration permitted and critical load of TEs applied on crop areas since the risk of contamination of water, soil, plants and harvested products is always present (Kabata-Pendias, 2011). In addition to strict observance of legislation related to safe discard of residues in the environment, the use of organic residues in agriculture implies careful assessment of their chemical composition and correct definition of the rate to be applied to soils (Abreu Junior et al., 2005; Silva, 2008).

Sample digestion processes prior to quantification of TEs includes closed or open digestion systems and the use of different combinations of acids, such as HNO_3 , HCl , HClO_4 , HF and others (Melo & Silva, 2008; Nemati et al., 2010; García-Delgado et al., 2012), as well as oxidants such as H_2O_2 . Due to their chemical composition, degree of polymerization and the presence of molecules resistant to digestion, the recovery of TEs in organic residues is subject to

variation (Abreu et al., 1996; Hseu, 2004; Nemati et al., 2010; García-Delgado et al., 2012). Therefore, DMs must be chosen considering the residue and the recovery rate of the trace element investigated (Hseu, 2004; García-Delgado et al., 2012). Hydrofluoric acid (HF) has been used in the extraction of TEs in different materials since it is capable of solubilizing metals bonded to silicates, enabling total digestion of the samples (Yafa & Farmer, 2006; Yawar et al., 2010; García-Delgado et al., 2012), and, hence, greater recovery of TEs (García-Delgado et al., 2012). When multiple chemical elements are analyzed, however, DMs that use HF should be avoided as they can overestimate the concentration of constituents in the residue, apart from the risk associated with handling the reagent (Marin et al., 2008). Moreover, HF can result in damage to the flame absorption spectrometer apparatus (Atgin et al., 2000). According to García-Delgado et al. (2012), microwave digestion with HF can decrease the recovery of some chemical elements due to the formation of calcium fluoroaluminates or precipitates of calcium fluoride in residues with high levels of calcium.

Wet digestion in open systems, according to Azcue & Mudrock (1994), is time consuming and subject to contamination and loss of some chemical elements by volatilization. In the case of muffle furnace digestion, if the analyte measured is volatile (as is the case of As, Cr, Pb and Cd), losses may occur by volatilization and/or adsorption of the chemical element onto the walls of the furnace due to the high combustion temperature, usually from 500-550 °C (Azcue & Mudrock, 1994), as well as cross-contamination of samples (EFSA, 2012).

The use of microwaves in wet digestion has greatly accelerated the determination of TEs and reduced the risk of contamination and loss of volatile chemical elements (Reis et al., 2011). However, according to Sastre et al. (2002), open systems allow the analysis of a larger number of samples and facilitate evaporation of acid and drying of the digests, thereby reducing analytical problems in stages subsequent to digestion. Zheljaskov & Warman (2002) verified that HNO_3 and NP digestion provided higher recovery of Cd and Pb as compared to breakdown of organic matrices in a muffle furnace (i.e., dry ashing). Hseu (2004) also described good results with HNO_3 digestion, mainly in regard to the recovery of Cd, Mn and Ni. This method is recommended by the author, based on cost, time and extraction efficiency. In a study developed by Abreu et al. (1996), however, the highest levels of TEs in residues were found when AR was employed in the digestion.

There is no ideal method for maximum recovery of TEs in organic matrices, and the lack of standardization in the aforementioned methods hampers comparison of results from different studies (Yafa & Farmer, 2006). It is unlikely that the choice of a single DM would result in maximum extraction efficiency for all TEs; thus, in relation to recovery of TE, there is a great need to study the effect of different DMs in opening diverse organic matrices. This will require evaluation of different combinations of acids and oxidizing agents for the digestion of organic materials, which often have a great variety of constituents. The aim of this study was to evaluate the effect of five DMs (EPA 3051, NP, MDA, AR and EPA 3050) on recovery of Fe, Zn, Ni, Cr, Cd and Pb contents in samples of manures, composts, peat and sewage sludges.

MATERIALS AND METHODS

Residues studied

This study was conducted at the Universidade Federal de Lavras (Federal University of Lavras), Minas Gerais (MG), Brazil, and the analyses were performed at the Laboratory of Soil Organic Matter Studies (LEMOs) and the Environmental Geochemistry Laboratory, both belonging to the Soil Science Department. Organic residues were collected in municipalities of the states of Minas Gerais and São Paulo, and the following types of waste were analyzed: commercial compost (C.COM) (Passos, MG), garbage compost (G.COM), organic compost (O.COM), cattle manure (BOV) (Lavras, MG), quail manure (QUAI) (Lavras, MG), horse manure (HOR), chicken manure (CHIC) (Lavras, MG), swine manure (SWI) (Oliveira, MG), urban sewage sludge (SL1), industrial sewage sludge (SL2) and peat (PEAT). In relation to the manures, only fresh materials were sampled (i.e., not composted, with a low degree of humification).

The BOV was collected on a dairy cattle farm; the HOR in facilities whose floor was not covered by bedding or any other material; and, finally, the SWI was collected on a farm with pigs in the finishing phase, and only the solid fraction of the fresh manure was sampled. In regard to their chemical composition, CHIC, QUAI and SWI were distinguished by their higher nutrient concentration, compared to BOV and HOR, which may be due to the balanced feeding and mineral supplements furnished to the first group. Thus, N, P, Ca and K contents and micronutrients were much more abundant in the manure from smaller confined animals than in those produced by large animals such as cows and horses. The SL1 was obtained from a city of around 200,000 inhabitants and it is composed of sewage from residences; therefore, in relation to the SL1 (essentially derived from processing of industrial sewage, the SL2 contained higher levels of TEs, although both of them were stabilized, composted and rich in humic material. The PEAT was collected in the municipality of Boa Esperança, MG. It is a carbon-rich soil with chemically stabilized organic functional groups and a significant presence of C-humic substances. The composts evaluated, for their part, were already completely decomposed, rich in humic material and had low levels of labile carbon. The C.COM was derived from the composting of poultry manure and sugarcane bagasse; the O.COM originated from a previous stage of substrate manufacturing, composed of a mixture of decomposed pine bark, peat and manure; and the G.COM was produced from the composting of an organic matrix which had been separated from the solid residues of garbage processing units. More details related to the chemical and physical composition and data regarding the nature of the organic residues investigated can be obtained in Melo & Silva (2008) and Higashikawa et al. (2010). After collection, the residue samples were dried (70 °C) in an oven with assisted air circulation, sieved (<0.25 mm) and placed in a desiccator for subsequent analysis.

Digestion methods

Microwave-assisted acid digestion (EPA 3051)

This protocol is based on the method proposed by the US Environmental Protection Agency - USEPA (USEPA, 1998). Digestion was performed using a Multiwave microwave and 50 mL high-pressure modified polyethylene vessels. Samples were weighed to 0.5 g and then 10 mL of HNO_3 was added to each digestion vessel. The containers were sealed, placed in the microwave and heated for 10 min (0.76 MPa, 175 °C). Prior to dilution and filtering, some digests exhibited a dark brown to light yellow color, indicating incomplete digestion of more humified matrices. Similar conditions were observed in the samples of sewage sludge and garbage compost. In these cases, an additional 4 mL of HNO_3 was added and digestion

was reinitiated. The digests were then solubilized in 10 mL of double-distilled water (DDW) and filtered with qualitative cellulose filter paper (pore diameter of 0.45 μm). After this step, quantification of the TEs was performed using an atomic absorption spectrophotometer. Digestion was carried out with triplicates for each residue; three blanks and standard samples for each batch of samples were digested in the microwave.

Nitric-perchloric digestion

We used the method proposed by Tedesco et al. (1995), with modifications. Samples were weighed to 0.5 g and transferred to digestion tubes. Following sample preparation, 6 mL of HNO_3 was added to each digestion tube and the tubes were allowed to sit overnight. Glass funnels were placed in the neck of the tubes during predigestion as a cover and to reflux acid fumes generated during digestion (Tedesco et al., 1995). Tubes were randomly placed in a digestion block to minimize the effect of spatial temperature variation within the block and gradually heated to 140 $^{\circ}\text{C}$. The samples were then digested until approximately 1 mL of acid remained; however, when there was no clear colorless endpoint, an additional 3 mL of HNO_3 was added to each tube and evaporated off until 1 mL of the digest remained. Tubes were then removed from the block and cooled to room temperature. After cooling, 2 mL of HClO_4 was added and the digests were placed back into a preheated block and heated at 190 $^{\circ}\text{C}$ for 2 additional hours. Samples were removed from the block, cooled to room temperature, solubilized and filtered as described in the EPA 3051 method.

Modified dry ashing

Dry ashing in a muffle furnace is based on Melo & Silva (2008) and Azcue & Mudroch (1994), with modifications, which are described below. After weighing 0.5 g of each residue, samples were transferred to crucibles and dried at 105 $^{\circ}\text{C}$ in an oven with assisted air circulation to remove all residual water before ashing. The vessels were then placed in the muffle furnace and gradually heated (50 $^{\circ}\text{C}$ every 30 min) from room temperature to 550 $^{\circ}\text{C}$ and ashed for 2 h. After cooling, the residual ash was dissolved in 8 mL of HNO_3 and the digests were then solubilized and filtered as described in the previous methods for determination of TEs.

Aqua regia digestion

Samples were weighed to 0.5 g and transferred to digestion tubes, to which 10 mL of aqua regia (McGrath & Cunliffe, 1985; $\text{HCl}:\text{HNO}_3$, 3:1, v/v) were added and left to sit overnight under reflux conditions. The block was gradually heated from ambient temperature to 180 $^{\circ}\text{C}$ and the samples were processed until 1 mL of acid remained, similar to NP digestion. When there was no clear colorless endpoint, an

additional 4 mL of AR was added and evaporated off to a volume of about 1 mL. The extracts were then solubilized and filtered as previously described.

Acid digestion with $\text{HNO}_3 + \text{H}_2\text{O}_2$ (EPA 3050)

Following the EPA 3050 method proposed by USEPA (1998), 1 g extracts of the residue were weighed and transferred to digestion tubes, to which 10 mL of HNO_3 were added. After being placed in a digestion block, the samples were heated to 95 \pm 5 $^{\circ}\text{C}$ for 10 min. After cooling, an additional 5 mL of HNO_3 were added and evaporated off at 95 \pm 5 $^{\circ}\text{C}$ for 2 more hours. Then the samples were cooled, and 2 mL of DDW and 3 mL of 30 % H_2O_2 were added. The samples were then placed in the block for 2 more hours at 95 \pm 5 $^{\circ}\text{C}$. Finally, the samples were cooled, each received 5 mL of HCl and 10 mL of DDW and then they were reheated for 5 min at 95 \pm 5 $^{\circ}\text{C}$. Finally, the digests were filtered and placed in plastic containers.

Multi-elemental analysis

After digestion, the extracts were subjected to multi-elemental analysis in an atomic absorption spectrophotometer with a graphite furnace (Hitachi Z-8100, Japan) in order to determine the concentrations of Cd, Cr, Fe, Ni, Pb and Zn in the organic residues. In the case of Fe, due to its high levels in the residues, readings in the graphite furnace were not necessary, only readings in the atomic absorption apparatus in an air-acetylene flame.

Analytical quality of the results

For each batch of digestion, blank samples were used to verify the precision of the methods employed and to control possible contamination. For this purpose, the detection limit (DL) was calculated for the DMs and TEs using the following equation: $\text{DL} = 3 \times \text{SD}$ (Juranovic et al., 2003), where SD is the standard deviation of the five blank samples for each TE and DM. The DL values calculated are shown in table 1.

In all the analytical procedures carried out and also in the multi-elemental characterization of the solution and certified sample, pure reagents (ACS grade), and double-distilled water were used. The certified sample analyzed in the study was industrial sewage sludge (BCR 146-R). Three replicates per batch for each DM/organic residue combination were used in this study.

Statistical analysis

The attributes evaluated were subjected to analysis of variance and the averages were grouped through the Scott-Knott cluster method ($\alpha = 5\%$). We performed factorial partitioning split in analysis of variance to assess the effect of different DMs on the recovery levels of TEs for each of the eleven organic residues analyzed.

Table 1. Detection limits for the different digestion methods and trace elements in accordance with the five replicates used for blank samples

Trace element	Digestion method				
	EPA 3051A	Nitric-perchloric	Modified dry ashing	<i>Aqua regia</i>	EPA 3050
	mg kg ⁻¹				
Cd	0.09	0.03	1.41	0.12	0.001
Cr	2.19	2.34	0.30	3.51	1.170
Ni	0.38	2.94	0.11	11.6	0.002
Pb	0.12	0.66	0.33	1.77	0.009
Fe	38.2	221	460	52.7	264
Zn	1.59	4.89	10.6	13.2	6.27

All analyses were carried out using SISVAR (Ferreira, 2003).

Study of the triple interaction by principal component analysis.

For the study of the interactions between organic residues, TEs and DMs, we used principal component analysis (PCA) with application of the Tucker multiway model (Leibovici & Sabatier, 1998). Due to differences in units and in the magnitude of TE contents, data was first standardized to meet the premise of the aforementioned method. From the residuals of the fitted model, a three-way array was built. In matrix notation, the model allows estimation of arrays A, B and C, which represent the eigenvalues of the interactions and the core array G that estimates the relationship among the three dimensions (Residues, TEs and DMs). The algorithm used was proposed by Kroonenberg & Deleeuw (1980), and for the best model arrangement, the procedure proposed by Timmerman & Kiers (2000) was used.

Results were interpreted graphically through joint conditional biplots using the following combinations: Organic Residues × TEs, as a function of DMs; Organic Residues × DMs, as a function of TEs; and TEs × DMs, as a function of Organic Residues. All analyses were performed using R software and the “PTAk” package (R Development Core Team, 2011; Leibovici & Sabatier, 1998).

RESULTS AND DISCUSSION

The recovery of the TEs of the certified sample (BCR 146-R) ranged from 55 to 116 % for Cd, 78 to 118 % for Cr, 50 to 91 % for Fe, 91 to 98 % for Ni, 50 to 65 % for Pb and 77 to 125 % for Zn (Figure 1). When we calculated the average recovery of a given TE for the five DMs, we found recovery of 83 % of Cd, 89 % of Cr, 75 % of Fe, 93 % of Ni, 56 % of Pb and 90 % of Zn in the BCR 146-R. The recovery

rates of TEs in the certified sample, in general, are within the acceptable range and similar to those described in Nemati et al. (2010); they are also consistent with those found by Hseu (2004), except for Pb, whose recovery ranged from 74 to 96 %, a value higher than the value observed in this study. The recovery rates of TEs obtained by García-Delgado et al. (2012) with the use of different DMs ranged from 80 to 123 %, and for Pb, specifically, the recovery rate (90 to 115 %) was significantly higher. Hseu et al. (2002) also reported a wide variation in the recovery of Pb (32-143 %) for different certified samples.

The recovery of the TEs in all methods examined only approaches their total content since these methods are not capable of dissolving silicates, but they are effective in solubilizing metals bonded to organic constituents (Zheljaskov & Warman, 2002). The digests obtained by NP presented a clear colorless endpoint (i.e., no residual material). For determination of Cd (Figure 1), the results indicate that the greatest recovery was obtained by the MDA method for seven residues (QUAI, HOR, CHIC; O.COM; SL1, SL2 and G.COM). In the case of QUAI and HOR, only the MDA method recovered the greatest contents of Cd (Figure 1).

The concentrations of Cd ranged from 0.01 to 29.7 mg kg⁻¹, with the highest recovery observed for the MDA and EPA 3050 methods for most of the residues evaluated. For SL1, however, we verified that the NP and MDA methods are efficient in extracting Cd, and, for SL2, AR and MDA were similar and provided the highest recovery of Cd (Table 2). Based on the results obtained, EPA 3051A cannot be used for determination of Cd in the residues investigated, as is also the case of AR, considering most of the organic residues. Results obtained by Hseu (2004) indicated that HNO₃ digestion was the most effective in recovering Cd for most of the composts evaluated, whereas NP and dry ashing led to lower recovery of this element, except for SWI, CHIC and G.COM, whose results were similar for the different DMs. The high vapor pressure of Cd, along with the risk of cross-

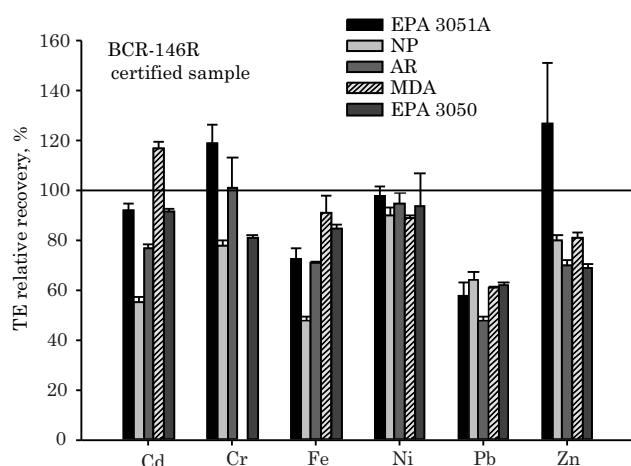


Figure 1. Relative recovery (100 % value corresponds to the level of the corresponding TE in the certified sample) of trace elements (TEs) in the certified industrial sewage sludge (BCR 146-R) through the use of the different digestion methods. NP: nitric-perchloric, AR: aqua regia, MDA: modified dry ashing.

contamination between samples, may have caused errors in the determination of this element in open digestion systems (EFSA, 2012). For these reasons, even if the MDA method is effective in recovering the Cd of some residues, EPA 3050, an open digestion method, seems to be more adequate for determining this element.

In relation to Cr (Table 2), the values ranged from 0.02 to 256 mg kg⁻¹, and the results indicated the greatest recovery by the NP and EPA 3050 methods, followed by AR digestion. The EPA 3050 method led to the highest recovery of Cr in 7 of the 11 residues analyzed, followed by the NP method for O.COM, PEAT and SL1. In fact, for SWI and C.COM, the highest levels of Cr were observed in AR digestion. For PEAT and SL1, NP led to the highest recovery of Cr. For most of the residues, EPA 3050 seemed more appropriate for recovery of Cr, although it is not possible to exclude NP as an alternative method for the same purpose. The EPA 3051A method presented high recovery of Cr only for the SL1 sample; however, there is the possibility of using another DM for the same purpose. Therefore, EPA 3051 was not suitable for maximum recovery of Cr in the organic residue.

Hseu et al. (2002) used different methods to determine total contents of Cd, Cr, Cu, Ni, Pb and Zn in sediments from freshwater and soil and found that the mixture of HF-HNO₃-HClO₄-H₂SO₄ in a hot plate led to the highest recovery of Cr. According to Hseu (2004), the dry ashing method recovered a higher amount of Cr as compared to other methods since calcination at high temperatures allows greater extraction of refractory metals, such as Cr (Hseu, 2004). In this study, dry ashing digestion did not

exhibit the same efficiency in determining Cr, given the lower recovery rate of the element in relation to other DMs.

The concentration of Fe (Table 2) ranged from 35.1 to 30,327 mg kg⁻¹, and the highest recovery was observed from EPA 3051A, EPA 3050, NP and AR. In the case of CHIC, EPA 3050 was the only DM that led to higher recovery of Fe; EPA 3051A showed the highest recovery of Fe for SL1. The MDA method proved to be unsuitable to recover Fe, so its use should be avoided for analysis of the residues examined in this study. The NP and EPA 3050 methods stood out in terms of Fe recovery; however, the choice of a DM for recovery of a given chemical element is conditioned on the organic residue to be analyzed.

The Ni contents in the residues ranged from 0.12 to 147 mg kg⁻¹, and AR digestion led to the highest recovery of this element in 8 of the 11 residues evaluated, especially for C.COM and CHIC samples. The dry ashing method, for its part, led to the lowest recovery of Ni for the residues analyzed, except for the O.COM. Hseu (2004) did not find any significant difference among four different DMs for Ni; however, according to the author, the use of HNO₃ recovered more Ni compared to the others protocols, except for poultry litter and soybean meal. Nemati et al. (2010) conducted a comparative study with open digestion and microwave-assisted DMs for determination of Zn, Cu, Cr, Ni, Pb and Cd in shrimp sludge compost and concluded that microwave-assisted digestion led to the greatest recovery for all the elements evaluated.

The levels of Pb and Zn in the residues ranged from 0.36 to 192 mg kg⁻¹ and from 10.1 to 893.33 mg kg⁻¹, respectively (Table 2). It was observed that, in general, the EPA 3051A and EPA 3050 methods presented the highest recovery of Pb and Zn, for most residues. Pelozato et al. (2011), comparing extraction methods, observed better efficiency from the EPA 3050 method, which was able to extract higher amounts of Cd, Cu and Zn in soil samples. According to Nemati et al. (2010), microwave-assisted digestion (EPA 3051A) is most recommended for determining Zn. A study conducted by Hseu (2004) found good results with HNO₃ and H₂SO₄ for recovering Zn, mainly when investigating composted materials. However, Yawar et al. (2010) pointed out that the use of H₂SO₄ may reduce sensitivity for metal detection. Hseu et al. (2002) presented results similar to those obtained in this study for soils and sediments as they verified that nitric acid digestion was the most appropriate for analyzing total Pb. According to these authors, the use of sulfuric acid is not recommended for determining Pb since it precipitates the metal, underestimating the content of this chemical element.

From the data presented in figure 2a, inferences can be made about the effect of different DMs on levels of recovery of TEs in organic residues, and it is possible to observe which residues showed similar (or discrepant) levels of TEs or *vice-versa*. In general, the

Table 2. Contents of trace elements (TEs) in 11 organic residues after use of the five digestion methods investigated

Organic residue	Digestion method				
	EPA 3051A	Nitric-perchloric	Modified dry ashing	<i>Aqua regia</i>	EPA 3050
	mg kg ⁻¹				
	Cd				
C. COM	0.03 c	0.22 a	0.02 c	0.14 b	0.27 a
G. COM	0.07 c	0.68 b	11.0 a	0.48 b	10.6 a
O. COM	0.07 c	0.57 b	16.0 a	0.33 b	12.4 a
BOV	0.03 a	0.12 b	0.07 b	0.04 a	9.55 a
QUAI	1.19 c	1.24 c	17.5 a	1.05 c	5.21 b
HOR	0.02 d	0.22 c	10.4 a	0.09 d	1.25 b
CHIC	0.30 c	0.04 d	17.9 a	0.33 c	12.7 a
SWI	0.04 c	0.30 b	0.01 c	0.36 b	8.26 a
SL1	9.18 b	12.2 a	12.2 a	0.17 c	6.48 b
SL2	0.07 e	0.17 d	21.0 a	29.7 a	7.12 c
PEAT	0.01 b	0.07 b	0.05 b	0.02 b	9.73 a
	Cr				
C. COM	80.6 d	102.9 b	90.2 c	183 a	81.6 d
G. COM	0.02 d	24.8 a	3.15 c	14.7 b	24.9 a
O. COM	12.5 d	65.7 a	12.9 d	37.5 c	57.0 b
BOV	49.2 c	75.2 b	21.5 d	76.4 b	256 a
QUAI	0.11 d	16.7 a	0.74 c	12.2 b	16.6 a
HOR	26.9 d	74.5 b	24.0 d	46.5 c	97.8 a
CHIC	0.02 d	1.03 c	2.44 c	8.63 b	15.3 a
SWI	2.04 d	16.1 b	1.08 d	5.10 c	12.6 a
SL1	99.5 a	106.6 a	95.5 a	7.74 b	5.10 b
SL2	7.34 c	8.31 c	0.62 d	106 b	144 a
PEAT	4.64 b	17.5 a	2.03 b	14.3 b	11.3 b
	Fe				
C. COM	9410 b	11351 a	4742 c	11597 a	10395 a
G. COM	24100 a	23151 a	11462 c	19090 b	21908 a
O. COM	13729 c	24377 b	8829 d	16425 c	30327 a
BOV	10287 a	11962 a	2541 b	12230 a	482 c
QUAI	254 d	1936 b	154 e	737 c	18967 a
HOR	8722 b	13513 a	4266 c	9807 b	12295 a
CHIC	175 d	326 c	35.1 e	966 b	5492 a
SWI	1881 b	2199 a	685 c	1738 b	1613 b
SL1	22679 a	12814 b	13699 b	7782 c	1740 d
SL2	5776 c	9162 b	2798 d	16211 a	555 e
PEAT	28972 a	26128 b	11639 c	30147 a	2480 d
	Ni				
C. COM	80.7 b	31.5 d	63.8 c	147 a	14.6 e
G. COM	15.5 b	21.1 a	1.10 c	26.0 a	17.8 b
O. COM	15.0 c	22.0 b	26.5 b	33.8 a	26.6 b
BOV	2.81 c	22.4 a	0.29 d	20.6 a	10.3 b
QUAI	48.5 a	2.53 c	0.42 d	15.2 b	19.3 b
HOR	1.10 c	21.0 b	0.12 d	19.4 b	54.5 a
CHIC	4.12 c	2.68 d	1.14 d	18.4 a	8.63 b
SWI	0.64 c	1.88 b	0.75 c	15.8 a	12.0 a
SL1	21.2 b	35.1 a	2.02 d	23.7 b	12.6 c
SL2	3.70 c	17.9 b	3.34 c	26.7 a	10.1 b
PEAT	2.13 c	13.3 b	0.56 d	19.6 a	14.3 b

Continue...

Table 2. Cont.

Organic residue	Digestion method				
	EPA 3051A	Nitric-perchloric	Modified dry ashing	<i>Aqua regia</i>	EPA 3050
	mg kg ⁻¹				
	Pb				
C. COM	0.54 c	3.97 b	0.50 c	3.20 b	22.8 a
G. COM	116 a	124 a	88.0 b	92.8 b	79.8 b
O. COM	2.97 c	12.9 b	3.30 c	8.92 b	18.3 a
BOV	19.9 a	7.65 b	0.36 c	5.59 b	8.03 b
QUAI	32.0 a	1.97 b	0.50 c	1.34 b	29.0 a
HOR	1.58 c	6.19 a	1.15 c	4.29 b	4.92 b
CHIC	37.1 a	1.89 b	0.69 c	1.95 b	2.13 b
SWI	0.97 b	3.98 a	0.68 b	4.52 a	3.19 a
SL1	171 a	48.9 b	114 a	15.2 c	10.9 c
SL2	35.2 b	35.2 b	1.13 c	1.09 c	192 a
PEAT	2.13 b	13.3 a	0.56 c	19.6 a	14.3 a
	Zn				
C. COM	138 b	112 b	80.0 c	56.5 c	254 a
G. COM	286 a	184 c	252 b	239 b	299 a
O. COM	162 b	156 b	152 b	128 c	198 a
BOV	36.7 c	64.7 b	55.5 b	58.9 b	70.8 a
QUAI	826 a	752 b	618 c	784 b	51.1 d
HOR	274 a	256 b	167 c	189 c	152 c
CHIC	468 b	396 c	430 b	538 a	338 c
SWI	893 a	669 c	469 d	519 d	725 b
SL1	357 c	586 a	459 b	54.5 d	351 c
SL2	62.5 d	91.6 c	123 c	638 a	379 b
PEAT	10.1 c	35.6 b	26.7 b	31.7 b	638 a

Mean values followed by the same letter do not differ statistically by the Scott-Knott test at 5 % significance. The organic residues evaluated were: commercial compost (C.COM); garbage compost (G.COM); organic compost (O.COM); cattle manure (BOV); quail manure (QUAI); horse manure (HOR); chicken manure (CHIC); swine manure (SWI); sewage sludge 1 (SL1); sewage sludge 2 (SL2) and peat.

projections of the Organic Residues \times TE interactions were concentrated at the origin of the joint biplot related to the DMs. Thus, the DM/TE combinations, for the organic residues examined, do not contribute greatly to the triple interaction observed.

The semi-axes of the EPA 3050 and 3051 methods, presented on “opposite sides” of the biplot, show a negative interaction, i.e., the levels of TE from one EPA method has no similarity to the other, which is shown by the results in table 2. The data presented in figure 2b allow us to observe if the chemical elements have similar (or discrepant) levels when combining DMs and organic residues, as well as determine which combinations of residues and/or DMs are similar so we can determine which DM is most suitable for a given residue.

According to the results presented, the points related to SL1 \times EPA 3050 method (SL1 3050) and SL1 \times EPA 3051 method (SL1 3051) may be highlighted, given their opposite arrangement in the biplot. Thus, in accordance with the average levels of the six TEs analyzed for SL1, the EPA 3051A and

3050 methods present different recovery values, which are described in table 2. The points in proximity representing Cd, Fe and Zn lead us to conclude that in the average of the combinations of residues and DMs, the contents of these TEs exhibit a positive tendency, i.e., when the content of a given TE is increased, the others also rise. Likewise, Cr and Pb also show proximity of points, allowing interpretations similar to the aforementioned TEs. These elements are in quadrants opposite to Cr and Zn, thus showing a negative interaction, i.e., when the average of the combinations for one group is high, for the other it is low, and vice versa.

Figure 2c allows us to observe which residues have similar levels of a given TE, regardless of the DM, and for which TEs the DMs provide similar (or discrepant) recovery rates. This is evident from observing the points AR \times Cr and NP \times Cr, i.e., the levels of Cr by the AR and NP methods are discrepant from the averages of the different residues, which may be confirmed by the results shown in table 2. The same situation is observed for AR \times Cd and 3050 \times Cd. In addition, the proximity between the Cd \times MDA

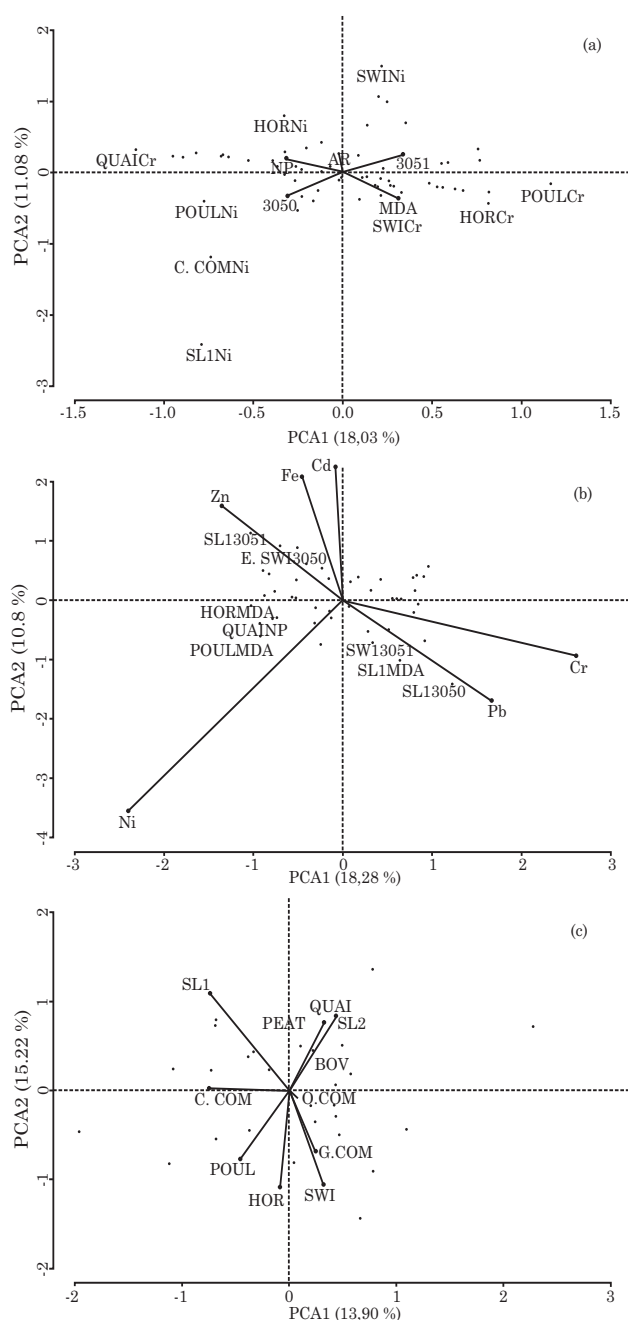


Figure 2 Conditional joint biplot in which (a) Organic residues × TEs is a function of DMs, (b) Organic residues × DMs is a function of TEs and (c) TEs × DMs is a function of Organic residues. The residues evaluated were commercial compost (C.COM), garbage compost (G.COM), organic compost (O.COM), cattle manure (BOV), quail manure (QUAI), horse manure (HOR), chicken manure (CHIC), swine manure (SWI), sewage sludge 1 (SL1), sewage sludge 2 (SL2) and peat (PEAT). The TEs analyzed were Cd, Cr, Fe, Ni, Pb and Zn by digestion methods EPA 3051A (3051), nitric-perchloric (NP), modified dry ashing (MDA), aqua regia (AR) and EPA 3050 (3050).

projection and the point corresponding to the HOR means that the recovery of Cd by the MDA method tends to be larger when the HOR is the digested sample. Furthermore, it is possible to observe which DMs are similar in relation to the recovery of TEs. This is possible due to the proximity, for example, between the AR x Cd and 3051 x Cd projections, which indicates that the AR and 3051 methods do not interact for determination of Cd, which is in agreement with the results shown in table 2.

In figure 2c, it is possible to observe which residues present similar behavior in relation to the average content of the different TEs after the use of the different DMs. PEAT, SL2 and QUAI showed similar levels of TEs for the different DMs. The SWI and G.COM residues are also present in the diagram in the same quadrant, showing that they have similar levels of TEs. However, the SL1 and O.COM appear in opposite quadrants; just as the CHIC, PEAT, SL2 and QUAI. Thus, these residues are evidence of different compositions in the average of the methods and TEs quantified.

From the results obtained, it is possible to verify that the recovery rates of TEs vary according to the DM employed and that the combinations of Residue/TE have an effect on the choice of the DM that provides the greatest efficiency in terms of chemical extraction. According to Zheljazkov & Warman (2002), recovery of TEs is regulated by the DM and depends on the chemical nature of the organic matrix. Although it was not the object of this study, data from PCA indicate that recovery rates of TEs vary with the chemical composition and origin of the organic residues evaluated. In fact, depending on the origin and mixtures of different matrices, as well as the presence of additives in their preparation, the organic residues may present various organic and inorganic constituents. Thus, the study of the composition/DM interaction should be investigated in future research.

Abreu et al. (1996) also verified variability in levels of recovery of TEs in different organic residues depending on the DM employed. Results obtained by García-Delgado et al. (2012) also support further research on this topic, as the authors noted that there is no polyvalent DM, i.e., a method that can be applied to all combinations of Residue/TEs found in nature. Based on this assumption, García-Delgado et al. (2012) proposed a decision support system in order to select the most effective digestion method. Among other factors, this decision support system included the presence or absence of CaCO_3 in the matrix, the organic matter content and the type of residue to be analyzed.

CONCLUSIONS

1. For most residues analyzed, the dry ashing method leads to the greatest recovery of Cd; however, the risk of volatilization and cross-contamination due

to the high vapor pressure of this chemical element makes the EPA 3050 method a viable alternative which is also effective in extracting Cd from organic residues. The dry ashing method should not be employed to determine Cr, Fe, Ni, Pb and Zn contents in digestion of organic matrices.

2. The NP and EPA 3050 methods lead to the greatest recovery of Cr and Fe for most of the residues; the *aqua regia* protocol presents the highest recovery of Ni for almost all residues.

3. The digestion methods-organic residue combination has an effect on recovery of Pb; however, for most residues, the microwave-assisted methods (EPA 3051 and 3050) lead to the highest extraction of Pb.

4. The choice of the DM that leads to the highest recovery rate of Zn is conditioned on the organic residue analyzed.

ACKNOWLEDGMENTS

The authors acknowledge the financial support and scholarships provided by the CNPq, CAPES and FAPEMIG. We are also grateful to Dr. Leônidas Carrijo Azevedo Melo for providing part of the organic residue samples and to professors João José Marques and Luiz Roberto G. Guilherme for allowing quantification of the TEs in the Environmental Geochemistry Laboratory at UFLA and for providing the certified sewage sludge sample.

LITERATURE CITED

- ABREU JÚNIOR, C.H.; BOARETTO, A.E.; MURAOKA, T. & KIEHL, J.C. Uso agrícola de resíduos orgânicos potencialmente poluentes: Propriedades químicas do solo e produção vegetal. TORRADO-VIDAL, P.; ALLEONI, L.R.F.; COOPER, M. & SILVA, A.P., eds. Tópicos em ciência do solo. Viçosa, MG, Sociedade Brasileira de Ciência do Solo, 2005. v.4, p.345-390.
- ABREU, M.F.; BERTON, R.S.; ANDRADE, J.C. Comparison of methods to evaluate heavy metals in organic wastes. *Commun. Soil Sci. Plant Anal.*, 27:1125-1135, 1996.
- ATGIN, R.S.W.; EL-AGHA, O.; ZARARSIZ, A.; KOCATAS, A.; PARLAK, H. & TUNCEL, G. Investigation of the sediment pollution in Izmir Bay: Trace elements. *Spectrochim. Acta B*, 55:1151-1164, 2000.
- AZCUE, J. & MUDROCH, A. Comparison of different washing, ashing and digestion methods for the analysis of trace elements in vegetation. *Intern. J. Anal. Chem.*, 12:211-221, 1994.
- GARCÍA-DELGADO, C.; CALAB, V. & EYMARA, E. Influence of chemical and mineralogical properties of organic amendments on the selection of an adequate analytical procedure for trace elements determination. *Talanta*, 88:375-384, 2012.
- EUROPEAN FOOD SAFETY AUTHORITY - EFSA. Cadmium in food - Scientific opinion of the panel on contaminants in the food chain. Available at: <http://www.efsa.europa.eu/en/scdocs/doc/contam_op_ej980_cadmium_en_rev.1.pdf>. Accessed on Jul. 10, 2012.
- FERREIRA, D.F. SISVAR software: versão 4.6. Lavras, DEX/UFLA, 2003. 32p.
- HIGASHIKAWA, F.S.; SILVA, C.A. & BETTIOL, W. Chemical and physical properties of organic residues. *R. Bras. Ci. Solo*, 34:1743-1752, 2010.
- HSEU, Z.-Y.; CHEN, Z.-S.; TSAI, C.-C.; TSUI, C.-C.; CHENG, S.-F.; LIU, C.-L. & LIN, H.-T. Digestion methods for total heavy metals in sediments and soils. *Water Air Soil Pollut.*, 141:189-205, 2002.
- HSEU, Z.Y. Evaluating heavy metal contents in nine composts using four digestion methods. *Bioresour. Technol.*, 95:53-59, 2004.
- JURANOVIC, I.; BREINHOELDER, P. & STEFFAN, I. Determination of trace elements in pumpkin seed oils and pumpkin seeds by ICP-AES. *J. Anal. Atom. Spectrom.*, 18:54-58, 2003.
- KABATA-PENDIAS, A. Trace elements in soils and plants. 4.ed. Boca Raton, CRC Press, 2011. 505p.
- KROONENBERG, P.M. & DELEEUW, J. Principal component analysis of three-mode data by means of alternating least squares algorithms. *Psychometrika*, 45:69-67, 1980.
- LEIBOVICI, D. & SABATIER, R. A singular value decomposition of k-way array for a principal component analysis of multiway data, PTAk. *Linear Algebra Appl.*, 269:307-329, 1998.
- MARIN, B.; CHOPIN, E.I.B.; JUPINET, B. & GAUTHIER, D. Comparison of microwave-assisted digestion procedures for total trace element content determination in calcareous soils. *Talanta*, 77:282-288, 2008.
- MATTIAS, J.L.; CERETTA, C.A.; NESI, C.N.; GIROTTO, E.; TRENTIN, E.E.; LOURENZI, C.R. & VIEIRA, C.B. Copper, zinc and manganese in soils of two watersheds in Santa Catarina with intensive use of pig slurry. *R. Bras. Ci. Solo*, 34:1445-1454, 2010.
- McGRATH, S.P. & CUNLIFFE, C.H. A simplified method for the extraction of the metals in sewage sludge on soils, microorganisms and plants. *J. Ind. Microbiol.*, 14:94-104, 1995.
- MELO, L.C.A. & SILVA, C.A. Caracterização físico-química e comparação de métodos de digestão de resíduos orgânicos. *Quím. Nova*, 31:556-561, 2008.
- NEMATİ, K.; BAKAR, N.K.A.; ABAS, M.R.B.; SOBHANZADEH, E. & LOW, K.H. Comparative study of open system digestion and microwave assisted digestion methods for metal determination in shrimp sludge compost. *J. Hazard. Mater.*, 182:453-459, 2010.

- PELOZATO, M.; HUGEN, C.; CAMPOS, M.L.; ALMEIDA, J.A.; SILVEIRA, C.B.; MIQUELLUTI, D.J. & SOUZA, M.C. Comparação entre métodos de extração de cádmio, cobre e zinco de solos catarinenses derivados de basalto e granito-migmatito. *R. Ci. Agrovet.*, 10:54-61, 2011.
- R DEVELOPMENT CORE TEAM. *R: A Language and Environment for Statistical Computing*. Vienna, 2011. Available at: < <http://www.R-project.org/>>. Accessed on: May 18, 2012.
- REIS, C.F.; PEGORARO, T.; COELHO, S.R.M.; LUCAS, S.D.; LIMBERGER, C. & WATTHIER, E. Avaliação de quatro tipos de aberturas de amostras na determinação de cromo, cobre e zinco em águas residuárias. *Eng. Amb. Pesq. Tecnol.*, 8:17:25, 2011.
- SASTRE, J.; SAHUQUILLO, A.; VIDAL, M. & RAURET, G. Determination of Cd, Cu, Pb and Zn in environmental samples: Microwave assisted total digestion versus aqua regia and nitric acid extraction. *Anal. Chim. Acta*, 462:59-72, 2002.
- SILVA, C.A. Uso de resíduos orgânicos na agricultura. In: SANTOS, G.A.; SILVA, L.S.; CANELLAS, L.P. & CAMARGO, F.A.O., ed. *Fundamentos da matéria orgânica do solo; ecossistemas tropicais e subtropicais*. 2.ed., Porto Alegre, Metrópole, 2008. p.597-623.
- TEDESCO, M.J.; GIANELLO, C.; BISSANI, C.A.; BOHNEN, H. & VOLKWEISS, S.J. *Análise de solo, plantas e outros materiais*. 2.ed., Porto Alegre, Universidade Federal do Rio Grande do Sul, 1995. 174p. (Boletim Técnico, 5)
- TEDESCO, M.J.; SELBACH, P.A.; GIANELLO, C. & CAMARGO, F.A.O. Resíduos orgânicos no solo e os impactos no ambiente. In: SANTOS, G.A.; SILVA, L.S.; CANELLAS, L.P. & CAMARGO, F.A.O., eds. *Fundamentos da matéria orgânica do solo: Ecossistemas tropicais e subtropicais*. 2.ed. Porto Alegre, Metrópole, 2008. p.113-136.
- TIMMERMAN, M.E. & KIERS, H.A.L. Three-mode principal components analysis: Choosing the numbers of components and sensitivity to local optima. *Br. J. Math. Stat. Psychol.*, 53:1-16, 2000.
- UNITED STATES ENVIRONMENTAL PROTECTION AGENCY - USEPA. SW-846: Test methods for evaluating solid waste, physical and chemical methods. Washington, 1998.
- Yafa, C. & FARMER, J.G. A comparative study of acid-extractable and total digestion methods for the determination of inorganic elements in peat material by inductively coupled plasma-optical emission spectrometry. *Anal. Chim. Acta*, 557:296-303, 2006.
- YAWAR, W.; NAEEM, K.; AKHTER, P.; REHANA, I. & SAEED, M. Assessment of three digestion procedures for Zn contents in Pakistani soil by flame atomic absorption spectrometry. *J. Saudi Chem. Soc.*, 14:125-129, 2010.
- ZHELJAZKOV, V.D. & WARMAN, P.R. Comparison of three digestion methods for the recovery of 17 plant essential nutrients and trace elements from six composts. *Compost Sci. Util.*, 10:197-203, 2002.