Analyzing Selected Heavy Metals Content of Compost used in Ethiopia

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Abstract:
The content of compost can potentially contaminate the environment with heavy metals. Therefore, this study aims to analyze heavy metal contents of compost using nitric acid, dry ashing, nitric– perchloric acid and sulfuric acid digestion methods. Atomic Absorption Spectrophotometer was used to determine the concentration of metals. Analytical results indicated that heavy metal recovered by nitric acid procedure was statistically significant (p<0.05) followed by Dry ashing and sulfuric acid methods. Nitric– perchloric acid procedure was not recommended because perchloric acid is potentially hazardous during digestion and it recovers relatively little heavy metal.

Key Words: Heavy metal; Compost; Acid Digestion method; Dry ashing.

1. Introduction
Composting is the biological decomposition of biodegradable solid waste under controlled predominantly aerobic conditions to a state that is sufficiently stable for nuisance-free storage and handling and is satisfactorily matured for safe use in agriculture. The production of compost from agricultural and industrial wastes, and municipal by-products is an important means of recovering organic matter and an essential method of disposal. Compost is applied to cropland to maintain and improve soil structure and plant nutrition [1]. However, the presence of heavy metals in composts is the main cause of adverse effects on animal and human health, transmitted through the food chain from soil, groundwater and plants [2]. Consequently, exactly analyzing the contents of heavy metal in composts is very important for the routine monitoring and risk assessment and regulation of environment.

Elemental analysis of a compost sample requires that the organic fraction of the sample be destroyed; leaving the heavy metals either in solution or in a form that is readily dissolved. The approaches for destroying organic material and dissolving heavy metals fall into two groups-wet digestion by acid mixtures prior to elemental analysis and dry ashing, followed by acid dissolution of the ash [3]. Various methods have been presented for digesting plant tissue and soil samples for metal analysis. However, composts have very different physical, chemical and biological properties from those of soils and plants [4, 5]. However, perchloric acid is potentially hazardous during the digestion of biological materials and can cause the loss of potassium and boron [6, 7]. Dry ashing may cause some elements to be lost by the volatilization or adsorption of elements on the walls of the furnace, such that As, Cr and Pb may be lost at ashing temperatures of 500–550°C [8].

Previous studies have established good procedures for measuring the total metal concentration in soil and sediment samples dissolved by concentrated mixtures of inorganic acids at high temperatures [9-14]. Less is known about the relative recovery of heavy metals from composts by the widely used digestion methods [15]. Many methods for digesting compost have been described in previous studies; they include concentrated nitric acid digestion, dry ashing, nitric– perchloric acid digestion and sulfuric acid digestion. These methods are considered to be appropriate for pseudo-total analysis. However, they do not completely dissolve silicate, but they are sufficiently good to attack and dissolve heavy metals bound to important compost constituents [15]. Heavy metals in the silicate mineral require digestion with hydrofluoric acid (HF) and strong acids. However, the use of HF in routine laboratories is not recommended, as it is highly corrosive and difficult to handle. Nitric acid digestion was an optimum method for estimating heavy metal content in soil samples with high organic matter content, being superior to microwave-assisted and aqua regia digestions [16-21].
The present study describes analysis of the contents of Cd, Cr, Cu, Ni, Pb and Zn in mixtures of dry plant materials used for preparing compost in Ethiopia employing four different digestion methods and to recommend the most appropriate digestion method for determining the six heavy metals in the compost.

2. METHODS

2.1. Compost samples
One mature compost sample from one source in Ethiopia was used in this study. It is Green plant materials. A compost was air dried and ground to pass through a 1 mm stainless sieve; it was then stored in the plastic bottle prior to analysis, pH of the compost/distilled water mixture (5:3) was determined using a glass electrode [22]; electrical conductivity (EC) was measured from the extract of a saturated paste of compost [23]. C/N ratio and organic matter content was estimated, too.

2.2. Methods of digestion
Before digestion to analyze heavy metals, the compost sample was dried at 70°C for 36h. Four digestion methods were applied here involving nitric acid, dry ashing, nitric– perchloric acid and sulfuric acid. All methods were performed in triplicate for sample.

2.2.1. Nitric acid digestion
One gram of sample was placed in a 250mL digestion tube and 10mL of concentrated HNO₃ was added [24]. The sample was heated for 45min at 90°C, and then the temperature was increased to 150°C at which the sample was boiled for at least 8h until a clear solution was obtained. Concentrated HNO₃ was added to the sample (5mL was added at least three times) and digestion occurred until the volume was reduced to about 1mL. The interior walls of the tube were washed down with a little distilled water and the tube was swirled throughout the digestion to keep the wall clean and prevent the loss of the sample. After cooling, 5mL of 1% HNO₃ was added to the sample. The solution was filtered with Whatman No. 42 filter paper and <0.45μm Millipore filter paper. It was then transferred quantitatively to a 25mL volumetric flask by adding distilled water.

2.2.2. Dry ashing
One gram of sample in a crucible was placed in a preheated muffle furnace at 200–250 °C for 30 min, and then ashed for 4h at 480°C. Then, the sample was removed from the furnace and cooled down; 2mL of 5MHNO₃ was added and evaporated to dryness on a sand bath. Next, the sample was placed in a cool furnace and heated to 400°C for 15min, before being removed (from the furnace, cooled and moistened with four drops of distilled water). Next, 2mL of concentrated HCl was added and the sample was evaporated to dryness, removed, and then 5mL of 2MHCl was added and the tube was again swirled. The solution was filtered through Whatman No.42 filter paper and <0.45μm Millipore filter paper, and then transferred quantitatively to a 25mL volumetric flask by adding distilled water [25].

2.2.3. Nitric– perchloric acid digestion
Nitric–perchloric acid digestion was performed, following the procedure recommended by the [26]. One gram of sample was placed in a 250mL digestion tube and 10mLof concentrated HNO₃ was added. The mixture was boiled gently for 30–45 min to oxidize all easily oxidizable matter. After cooling, 5mL of 70% HClO₄ was added and the mixture was boiled gently until dense white fumes appeared. After cooling, 20mL of distilled water was added and the mixture was boiled further to release any fumes. The solution was cooled, further filtered through Whatman No.42 filter paper and <0.45μm Millipore filter paper and transferred quantitatively to a 25mL volumetric flask by adding distilled water.

2.2.4. Sulfuric acid digestion
This method is the wet digestion procedure described by [27]. 0.5g of sample was placed in a 250mL digestion tube and 3.5mL of concentrated H₂SO₄ was added. The mixture was allowed to stand for 30 min at room temperature. About 3.5mL of 30% H₂O₂ was added to the digestion tube and the sample was then heated at 250°C for 30 min. Thereafter, the digestion tube was removed from the digestion block and cooled down. 1mL of 30% H₂O₂ was added until the digest was clear upon cooling. When the solution was clear following cooling, it was filtered through
Whatman No.42 filter paper and <0.45μm Millipore filter paper and transferred quantitatively to a 25mL volumetric flask by adding distilled water.

2.2.5. Heavy metal analysis
The concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the final solutions were determined by an atomic absorption spectrometer (AAS) (Hitachi Z-8100, Japan).

2.2.6. Statistical analysis
Significant differences between concentrations of heavy metals, following different digestion methods were analyzed by ANOVA (SAS Institute, 1982). Statistical significance was defined as p < 0.05.

3. RESULTS AND DISCUSSION

3.1. Characteristic of compost
Table 1 presents pH = 9.8 slightly alkaline. Such compost can be used in southwester parts of the country where the soil is acidic due to heavy rainfall and high temperature. The electrical conductivity (EC) values of the dry plant materials compost is high and shows that the compost has macro nutrients important for plant growth. The C/N ratio indicates the compost has optimum C and N which is a characteristic of Organic matter. This is in line with the findings cited in [30].

Table 1: Physiochemical Properties of the compost

<table>
<thead>
<tr>
<th>Compost</th>
<th>pH</th>
<th>Organic Matter</th>
<th>C/N</th>
<th>Electrical conductivity(dS/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry plant materials</td>
<td>9.8</td>
<td>52.7</td>
<td>20.5</td>
<td>149.4</td>
</tr>
</tbody>
</table>

4.2. Comparison of different digestion methods

4.2.1. Cadmium
The concentrations of Cd in the dry plant materials compost were detectable by any of the four digestion methods. Of the four digestion methods, nitric acid digestion was the most efficient in recovering Cd from compost. However, less Cd was recovered from compost digested by nitric–perchloric procedure was less than that recovered by nitric acid alone. Sulfuric acid digestion yields a similar recovery rate to nitric–perchloric acid for dry plant materials compost. The dry ashing procedure always recovered the least Cd from most compost samples. The concentration of Cd obtained by nitric acid digestion method is statistically significant when compared with other methods (P<0.05). This is in line with the findings cited in [30].

Table 2: Cadmium content (mg/kg) of compost by four digestion methods

<table>
<thead>
<tr>
<th>Compost</th>
<th>Nitric acid</th>
<th>Dry ashing</th>
<th>Nitric–perchloric acid</th>
<th>Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry plant materials</td>
<td>4.5</td>
<td>2.14</td>
<td>1.16</td>
<td>1.98</td>
</tr>
</tbody>
</table>

4.2.2. Chromium
The highest concentration of Cr was found in all digestion methods in the Nitric acid procedure (Table 3). The digestion power of dry ashing is related to the high temperature and the reactivity of free chlorine formed in the final solution; dry ashing is thus a better means of extracting refractory metals, such as Cr. The sulfuric acid procedure still recovered the least Cr from most compost samples. The dry ashing and nitric–perchloric acid procedures did not significantly differ in terms of recovering Cr from the dry plant materials [28]. The concentration of Cr recovered by nitric acid digestion method is statistically significant when compared with other methods (P<0.05). This is in line with the findings cited in [30].
Table 3: Chromium contents (mg/kg) in compost by four digestion methods

<table>
<thead>
<tr>
<th>Compost</th>
<th>Nitric acid</th>
<th>Dry ashing</th>
<th>Nitric–perchloric acid</th>
<th>Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry plant materials</td>
<td>4.57</td>
<td>1</td>
<td>1.04</td>
<td>3.16</td>
</tr>
</tbody>
</table>

4.2.3. Copper
The Cu content was highest in dry plant materials by the nitric acid digestion method used. However, nitric acid and dry ashing procedures were more efficient than the nitric–perchloric acid and sulfuric acid procedures in recovering Cu from compost sample (Table 4). During the nitric–perchloric acid procedure, adding HClO₄ accelerated the digestion. Copper has a high affinity for organic compounds [29], so using a digestion agent with a stronger oxidizing capacity results in the more complete decomposition the compost. Therefore, more Cu was recovered in digestion procedures in which stronger oxidants, such as HClO₄ and H₂SO₄ were involved. However, HClO₄, when hot, is a strong oxidant and can react with explosive force when brought into contact with easily oxidizable compounds, especially if the digestion mixture is almost dry. The concentration of Cu obtained by nitric acid digestion method is statistically significant when compared with other methods (P<0.05). This is in line with the findings cited in [30].

Table 4: Copper contents (mg/kg) in compost by four digestion methods

<table>
<thead>
<tr>
<th>Compost</th>
<th>Nitric acid</th>
<th>Dry ashing</th>
<th>Nitric–perchloric acid</th>
<th>Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry plant materials</td>
<td>3.17</td>
<td>2.69</td>
<td>1.10</td>
<td>1.19</td>
</tr>
</tbody>
</table>

4.2.4. Nickel
The four digestion methods did differ in terms of the recovery of Ni from the dry plant materials (Table 5). The nitric acid procedure showed more Ni in the compost than any other procedure. However, sulfuric acid was more efficient in recovering Ni than were nitric–perchloric acid and dry ashing procedures. Nitric acid exhibited the highest recovery only from the dry plant materials sample. The concentration of Ni obtained by nitric acid digestion method is statistically significant when compared with other methods (P<0.05). This is in line with the findings cited in [30].

Table 5: Nickel contents (mg/kg) in compost by four digestion methods

<table>
<thead>
<tr>
<th>Compost</th>
<th>Nitric acid</th>
<th>Dry ashing</th>
<th>Nitric–perchloric acid</th>
<th>Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry plant materials</td>
<td>4.66</td>
<td>1.55</td>
<td>2.21</td>
<td>2.41</td>
</tr>
</tbody>
</table>

4.2.5. Lead
The sulfuric acid procedure showed poor recovery from the compost with higher pH and EC values dry plant materials (Tables 1 and 6), probably because of the precipitation of Pb and the potential interference of PbSO₄ during the subsequent analysis. Relatively insoluble CaSO₄ may be formed, lowering Pb by coprecipitation from the compost sample with higher Ca content, as identified from pH and EC values. However, better dissolution is exhibited by the other methods, especially nitric acid digestion, which is associated with the lowest costs of reagents and equipment. The concentration of Pb obtained by nitric acid digestion method is statistically significant when compared with other methods (P<0.05). This is in line with the findings cited in [30].
Table 6: Lead contents (mg/kg) in compost by four digestion methods

<table>
<thead>
<tr>
<th>Compost</th>
<th>Nitric acid</th>
<th>Dry ashing</th>
<th>Nitric–perchloric acid</th>
<th>Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry plant materials</td>
<td>3.36</td>
<td>2.033</td>
<td>1.10</td>
<td>1.03</td>
</tr>
</tbody>
</table>

4.2.6. Zinc
Zinc was the most abundant heavy metal in dry plant materials according to all digestion methods. However, the methods clearly determined widely different Zn contents (Table 7). No digestion method recovered the most Zn from compost, but nitric acid and dry ashing procedures were recommended for recovering more Zn from compost sample than the other methods. The concentration of Zn obtained by nitric acid digestion method is statistically significant when compared with other methods (P<0.05). This is in line with the findings cited in [30].

Table 7: Zinc contents (mg/kg) in compost by four digestion methods

<table>
<thead>
<tr>
<th>Compost</th>
<th>Nitric acid</th>
<th>Dry ashing</th>
<th>Nitric–perchloric acid</th>
<th>Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry plant materials</td>
<td>4.94</td>
<td>3.15</td>
<td>1.56</td>
<td>1.69</td>
</tr>
</tbody>
</table>

5. Conclusion
The nitric acid digestion was the most efficient in terms of the recovery of the heavy metals in this study, especially for Cd, Zn, Cu, Cr and Ni. Based on cost and time effectiveness, the nitric acid procedure was recommended as the standard method for digesting compost in a traditional open-vessel digestion system. Dry ashing is recommended as a flexible method. The sulfuric acid procedure typically recovered least of the six heavy metals and should not be used to determine the Pb content in compost. Nitric–perchloric acid procedure is not recommended because perchloric acid is potentially hazardous during digestion and recovers relatively little heavy metal.

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References


