Tropical Soil Labile Fractions of Copper in the Experimental Plots ±Ten Years after Application of Copper-Containing-Waste

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ABSTRACT

Copper is reported to be retained in soils for a quite long time particularly in soil treated with some amendments. This research was intended to evaluate the soil labile fractions of Cu ±10 years after application of Cu-containing industrial waste, lime, and cassava-leaf compost. Soil samples were taken from topsoils and subsoils of ±10 years old experimental plots set up in 1998 and factorially treated with a metal-spoon industrial waste at 0, 15, and 60 Mg ha⁻¹, lime at 0 and 5 Mg ha⁻¹, and cassava-leaf compost at 0 and 5 Mg ha⁻¹. The measured Cu labile fractions were compared to those in soils sampled at ±1.5 years and ±3 years after treatments. The results showed that the soil Cu labile fractions in waste treated soils were higher than those in the control treatments even though their concentrations decreased with the years of sampling. Lime showed a decreasing effect on soil labile Cu fractions, but the effect decreased with the years of sampling. The effect of cassava-leaf compost application on soil Cu labile fraction was in general not evidenced ±10 years after treatment.

Keywords: Cassava-leaf compost, copper, heavy metals, industrial waste, lime

INTRODUCTION

Heavy metals are by definition the elements with relatively high atomic density of > 6 g cm⁻³ or specific gravity of > 5 g cm⁻³. This category of elements is one of the research major focuses in soil science because the roles and effects of heavy metals are very important in the environment. Some heavy metals are needed by plants and animals at relatively small amounts. For example, Cu and Zn are considered as micro-elements for plant growth; therefore, they are needed by plants, even though only in relatively small amounts. On the contrary, some of the elements such as Cd and Pb are not needed by the living things. Both categories of these elements show similarity, they are toxic to the living things at concentrations relatively higher than their critical levels. For examples, the total concentrations of Cu in soils must not exceed 60 mg kg⁻¹; that of Zn must be below 70 mg kg⁻¹; while Cd and Pb must be < 9 and 100 mg kg⁻¹, respectively (Ross 1994a). These values are the toxic boundaries for plants.

However, the concentrations of heavy metals in soils are subject to natural and anthropogenic sources (Juracek and Ziegler 2006; Biasioli et al.)
Heavy metals in soil environment are distributed in several forms with decreasing bioavailability: free ions, complex ions, exchangeable forms, precipitates, and minerals (Salam 2017). Among these, free ions and to some extent complex ions and exchangeable forms, are the most mobile and potential to affect the living things because these forms are directly related to plant root absorption and heavy metal toxicities (Salam 2001; Daoust et al. 2006; Salam 2017). Therefore, the behaviors of these labile fractions of heavy metals in soils must be understood. This may include their behaviours related to the dynamics of some soil key properties such as soil cation exchange capacity (CEC), pH, and reaction time.

Soil adsorption capacity – part of it is expressed as CEC – is the most important soil property that influences heavy metal immobilization. This property may be improved by the addition of ameliorants. For examples, some researchers employed organic matters/biosolids (Salam et al. 2001; 2005; 2017; Tokunaga et al. 2003; Brown et al. 2004; Stehouwer et al. 2006; Schroder et al. 2008; Brown et al. 2009; Kukier et al. 2010; Mamindy-Pajany et al. 2014; Tang et al. 2014; Pukalchik et al. 2017) or P fertilizers such as TSP and rock phosphate (Brown et al. 2004; Kilgoutet al. 2008; Moseley et al. 2008). Organic matter is believed to provide functional groups such as phenolic and carboxyl in significant amounts and to increase soil CEC (Ross 1994b; Parfitt et al. 1995; Rodella et al. 1995; Salam 2001). The study of Lin et al. (2008) reported that Cu tended to be preferentially bound by Fe-oxides and organic matter. Some other ameliorants were also developed to immobilize heavy metals by precipitation, for examples by employing Na\textsubscript{2}HPO\textsubscript{4}, hydroxyapatite, or rock phosphate (Ma et al. 1990 1994 1995; Rabinowitz 1993; Ruby et al. 1994). As repeatedly reported by several researchers (Salam 1999 2001; Adams et al. 2004; Bang and Hesterberg 2004; Quaghebeur et al. 2005; He et al. 2006; Brown et al. 2009; Bolan et al. 2014; Malinowska 2017), the soil adsorption capacity or CEC is positively related to the changes in soil pH. In general, soil CEC increases with the increase of pH of soils with variable charges. The increase is due to the dehydogenation of soil particle surfaces in the presence of increased concentration of OH\textsuperscript{-}.

The increase in soil CEC increases the adsorption of heavy metals. For example, it was reported that amendment of 5 Mg ha\textsuperscript{-1} CaCO\textsubscript{3} on soil contaminated with industrial waste significantly increased the soil pH and decreased the labile heavy metals extracted using several chemical extractants (Salam 2000; 2001; 2017). This behavior then increases the residence time of heavy metals in soils and decreases their availabilities to plants and mobilities in soil environment. The study of Daoust et al. (2006) lately reported that Cu partitioning and its toxicity were significantly affected by pH greater than by organic matter and clay content.

This research was intended to evaluate the soil labile fraction of Cu ±10 years after soil treatments with Cu-containing industrial waste, lime, and cassava-leaf compost.

**MATERIALS AND METHODS**

**Experimental Design**

Soil samples were taken from topsoils and subsoils in the experimental plots set up in July 1998, located in Sidosari, Natar, South Lampung. Treatments were previously set up in a randomized block design, consisting of 3 factors, namely industrial waste of metal spoon, lime (dolomite), and cassava-leaf compost, with 3 replications. The industrial waste of metal-spoon, which contained high amounts of Cu and Zn, was obtained from PT Star Metal Wares Jakarta. The pH of the industrial waste was 7.30 and the contents of Pb, Cd, Cu and Zn in the waste were 2.44 mg kg\textsuperscript{-1}, 0.12 mg kg\textsuperscript{-1}, 754 mg kg\textsuperscript{-1}, and 44.6 mg kg\textsuperscript{-1}, respectively (Salam et al. 2005).

The industrial waste was applied and thoroughly plowed to 30 cm soil depth at rates of 0, 15, and 60 Mg ha\textsuperscript{-1}. Lime and cassava-leaf compost were both applied and thoroughly mixed to the same soil depth one week later at rates of 0 and 5 Mg ha\textsuperscript{-1}. The lime used was CaCO\textsubscript{3}. The cassava-leaf compost was prepared as reported previously by Salam (2001). The rates of industrial waste, lime, and cassava-leaf compost were selected through a series of preliminary experiments reported previously.
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(Salam 2000). Each plot measured 4.5 m long and 4 m wide, 50 cm apart between plots and 100 cm apart between blocks. The complete experimental treatments are listed in Table 1. The experimental plots were set up in 1998 and planted with corn, dryland paddy, and left bare in between.

Soil Sampling and Data Analysis

Soil sampling was conducted on 15 February 2009 (±10 years after treatment). Composite topsoil (0-15 cm) and subsoil (15-30 cm) samples were taken diagonally from 5 points in each plot. Soil samples were air-dried, ground to pass a 2-mm sieve, and mixed thoroughly before analysis. The soil Cu labile fraction was determined using DTPA method (Baker and Amacher 1987) and the soil pH was measured using a pH electrode.

The data obtained in the current study were compared to those of ±1.5 years after treatment (Amirulloh 2000) and ±3 years after treatment (Prihatin 2002).

RESULTS AND DISCUSSION

Copper was chemically retained in the soil for more than 10 years since soil treatment with Cu-containing industrial waste in July 1998. Analysis of variance (Anova) shows that the industrial waste application significantly enhanced the soil labile factions of Cu (Table 2). Test of Least Significant Difference (LSD-Test) also shows the significance of this effect, particularly by the addition of the industrial waste at 60 Mg ha\(^{-1}\) (Table 3). The concentration of Cu at the addition of 60 Mg ha\(^{-1}\) was 3.93 times compared to that at Control at 0 – 15 cm, while that at 15- 30 cm was 2.55 times. The application of industrial waste at 15 Mg ha\(^{-1}\) also showed tendencies to increase the concentrations of Cu, i.e. 1.82 times and 1.49 times at 0 – 15 and 15 – 30 cm, respectively. The increases were clearly attributed to the fact that the industrial waste contained relatively high amount of Cu (Salam et al. 2005).

Table 1. The existing treatment units in the experimental plots at Sidosari, Natar, Lampung.

<table>
<thead>
<tr>
<th>Waste (W)</th>
<th>Lime (L)</th>
<th>Compost (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(_0)</td>
<td>L(_0)</td>
<td>W(_0)L(_0)C(_0) W(_0)L(_0)C(_1)</td>
</tr>
<tr>
<td>W(_1)</td>
<td>L(_1)</td>
<td>W(_1)L(_1)C(_0) W(_1)L(_0)C(_1)</td>
</tr>
<tr>
<td>W(_2)</td>
<td>L(_2)</td>
<td>W(_2)L(_2)C(_0) W(_2)L(_2)C(_1)</td>
</tr>
</tbody>
</table>

Notes: W = Waste (W\(_0\) = 0, W\(_1\) = 15, and W\(_2\) = 60 Mg ha\(^{-1}\)); L = Lime (L\(_0\) = 0 and L\(_1\) = 5 Mg ha\(^{-1}\)); and C = Compost (C\(_0\) = 0 and C\(_1\) = 5 Mg ha\(^{-1}\)).

Table 2. Analysis of variance of the changes in labile Cu concentration in a tropical soil treated with Cu-containing industrial waste, lime, and cassava-leaf compost after a particular period of time since treatment (Transformation of \(\sqrt{x}\)) (Ginanjar 2009).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Time (years)</th>
<th>0-15 cm</th>
<th>15-30 cm</th>
<th>0-15 cm</th>
<th>15-30 cm</th>
<th>0-15 cm</th>
<th>15-30 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>± 1.5(^{1})</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>C</td>
<td>± 3 (^{2})</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>L</td>
<td>± 10</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>WxC</td>
<td>± 1.5(^{1})</td>
<td>ns</td>
<td>ns</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>WxL</td>
<td>± 3 (^{2})</td>
<td>ns</td>
<td>ns</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>CxL</td>
<td>± 10</td>
<td>ns</td>
<td>ns</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>WxCxL</td>
<td>± 1.5(^{1})</td>
<td>ns</td>
<td>ns</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>± 3 (^{2})</td>
<td>ns</td>
<td>ns</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>± 10</td>
<td>ns</td>
<td>ns</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

Notes: W = Waste; C = Cassava-Leaf Compost; L = Lime; * = Significant at 5% significance level; ** = Significant at 1% significance level; ns = Not Significant at 5% and 1% significance levels; \(^{1}\)Amirulloh (2000); \(^{2}\)Prihatin (2002).
However, the concentrations of soil labile Cu in general decreased significantly with year of sampling, particularly at the addition level of 60 Mg waste ha\(^{-1}\). The concentrations of labile Cu at ±1.5 years were higher than those at ±3 years and those at ±3 years were higher than those at ±10 years (Figure 1, 2, and 3). The relative concentrations of labile Cu in the topsoils treated with 60 Mg waste ha\(^{-1}\) and 5 Mg lime ha\(^{-1}\) decreased from 0.67 at ±1.5 years to 0.54 at ±3 years and to 0.39 at ±10 years. The relative concentration of Cu is expressed as Cu/Cu\(_{0-1.5}\), \textit{i.e.} the ratio of the concentration of Cu at a particular time of sampling to that of the Control (No Compost and No Lime) at ±1.5 years. The relative concentrations of labile Cu at waste level of 60 Mg ha\(^{-1}\) are listed in Table 4.

The decreasing pattern of Cu was also observed with the application of industrial waste at 15 Mg ha\(^{-1}\) with a little rise at 10 years after waste application (Figure 2). This decreasing pattern was not observed in the subsoil (15-30 cm). The reasons are that the industrial waste was applied on topsoil (0-15 cm) and the Cu in the subsoil was originated from the topsoil moved downwards by leaching.

### Table 3. The effect of waste application on the concentrations of Cu labile fraction in a tropical soil ±10 years after treatment (Transformation of \(\sqrt{x}\)) (Ginanjar 2009).

<table>
<thead>
<tr>
<th>Waste Levels (Mg ha(^{-1}))</th>
<th>Soil Depth (cm)</th>
<th>0-15</th>
<th>15-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>---------------</td>
<td>2.68 a</td>
<td>1.78 a</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>3.62 a</td>
<td>2.17 a</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>5.31 b</td>
<td>2.84 b</td>
</tr>
<tr>
<td>LSD 5%</td>
<td></td>
<td>1.01</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Note: The values followed by the same letters in the same column are not significantly different at 5% significance level.

### Table 4. The relative concentrations of Cu (Cu/Cu\(_{0-1.5}\)) in the topsoils treated with 60 Mg ha\(^{-1}\) of waste.

<table>
<thead>
<tr>
<th>Treatment Unit</th>
<th>± 1.5 years</th>
<th>± 3 years</th>
<th>± 10 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>No C, No L</td>
<td>1.00</td>
<td>0.77</td>
<td>0.19</td>
</tr>
<tr>
<td>No C, With L</td>
<td>0.67</td>
<td>0.54</td>
<td>0.39</td>
</tr>
<tr>
<td>With C, No L</td>
<td>0.80</td>
<td>0.60</td>
<td>0.21</td>
</tr>
<tr>
<td>With C, With L</td>
<td>0.55</td>
<td>0.64</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Figure 1. The effect of industrial waste, lime, and cassava-leaf compost on the concentration of a tropical soil labile fraction of Cu (Transformation of \(\sqrt{x}\)) at waste level 0 Mg ha\(^{-1}\) (compost 5 Mg ha\(^{-1}\) and lime 5 Mg ha\(^{-1}\)). Sources: Amirullah (2000); Prihatin (2002) and Ginanjar (2009). ■: 0-15 cm, □: 15-30 cm.
Figure 2. The effect of industrial waste, lime, and cassava-leaf compost on the concentration of labile fraction of Cu (Transformation of √x) at waste level of 15 Mg ha⁻¹ (compost 5 Mg ha⁻¹ and lime 5 Mg ha⁻¹). Sources: Amirullah (2000); Prihatin (2002) and Ginanjar (2009). ■: 0-15 cm, □: 15-30 cm.

Figure 3. The effect of industrial waste, lime, and cassava-leaf compost on the concentration of a tropical soil labile fraction of Cu (Transformation of √x) at waste level of 60 Mg ha⁻¹ (Compost 5 Mg ha⁻¹ and Lime 5 Mg ha⁻¹). Sources: Amirullah (2000); Prihatin (2002) and Ginanjar (2009). ■: 0-15 cm, □: 15-30 cm.
which were greatly depended on the grown crops, rainfall, and water percolation rates (Figure 4).

The decreasing trend in the concentration of Cu for the last ±10 years was due to several possibilities: (1) enhanced retainment by soil adsorption surfaces or by precipitation, (2) absorbed by plant roots, and (3) leached by percolating water to subsoil or groundwater, as described in Figure 4.

Based on the observation, the first possibility was unlikely. First, at ±10 years after treatment, the effect of lime had decreased significantly and, based on Anova, the effect on decreasing Cu labile fractions was not significant (Table 2). Second, the interaction of industrial waste of 15 Mg ha⁻¹ and lime tended to decrease the concentration of soil labile Cu. However, the effect was not significant. On the contrary, the interaction with industrial waste of 60 Mg ha⁻¹ in fact increased the concentration of soil labile Cu. The interaction of industrial waste and cassava-leaf compost also significantly decreased the soil labile Cu. However, the materials from compost were easily decomposed. Therefore, the logical possibility causing the decrease in the concentrations of labile Cu with time was Cu absorption by plant roots or Cu translocation into subsoil or groundwater (Figure 4). The complexation of Cu with soil humic substances may have mobilized Cu ions, so that it was more easily transported and/or absorbed by plant roots. In fact, Cu is more easily complexed by organic substances.

CONCLUSIONS

Copper of industrial-waste-origin was retained in soil for more than 10 years. The concentrations of labile Cu in general decreased with year of soil sampling. However, part of the Cu from industrial waste was translocated, probably absorbed by plant roots and/or moved into subsoil and/or groundwater through soil body.

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REFERENCES


