Concentrations and Chemical Forms of Heavy Metals in Some Ultisols in Johore, Peninsular Malaysia

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ABSTRACT
The concentrations of heavy metals in soil are associated with biological and geochemical cycles and are influenced by anthropogenic activities such as agricultural practices, industrial activities and waste disposal. A total of 36 surface soil samples (Typic Kandiudult, Rengam Series) were collected from some major vegetable growing areas developed over granite. Twelve soils from areas not cultivated with vegetables but also developed over granite were also sampled for background values. The pseudo-total heavy metals, (Cu, Pb, Zn and Ni) were determined by the aqua-regia method. Chemical properties such as pH, organic carbon and CEC were also analysed. Some selected cultivated soil samples (24 of Ultisols and 12 of background soils) were analysed for chemical partitioning using a modified Tessier’s procedure (F1: exchangeable fraction, F2: fraction bound to organic matter, F3: fraction bound to amorphous iron oxides and F4: residual fraction). Mean values of the total heavy metals for the cultivated soils are Cu (23.3 mg kg⁻¹), Pb (18.0 mg kg⁻¹), Zn (49.4 mg kg⁻¹) and Ni (6.0 mg kg⁻¹). Comparison of these values to the contents in the background soils show that Cu and Zn have significantly increased. However, all these values are below the contaminated levels established for the country’s agricultural soil limits (95th percentile). From the partitioning study, the general trend in the Ultisols for Pb and Ni is residual > oxalate > exchangeable > organic. For Zn and Cu, the oxalate extractable phase is highest followed by the residual phase. Zinc and Pb contents in the soils are also positively correlated with the pH of the soil.

Keywords: Copper, zinc, vegetable soils, chemical fractionation

INTRODUCTION
Heavy metals in soils may be inherited from the parent materials or added through the use of organic and chemical fertilizers and pesticides. Knowledge of both the total concentrations and chemical forms or phase association of these metals is necessary to understand their behaviour in the soil system. Different sequential extraction techniques such as the five-step procedure of Tessier et al. (1979) are commonly applied to evaluate both the actual and potential mobility of metals in the environment. This extraction scheme allows the division of the total metal content into five fractions: exchangeable, carbonate bound, iron/manganese oxide bound and residual fraction. The scheme was developed for sediments but many studies have used these procedures for soils (Abollino et al. 2002; Lu et al. 2003, Lu et al. 2005). However, this scheme may not be suitable

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for soils which do not contain carbonate. Rauret (1998) also elaborated that the extractants used for the fraction of metals bound to carbonates (i.e. acetic acid and sodium acetate ) and the iron and manganese oxides (i.e. hydroxylamine in acid solution ) were not completely suitable. Both carbonates and oxides may not have completely reacted with the reagents. Shuman (1979) proposed a scheme to study microelements in acid soils that do not contain carbonates or sulphides. This scheme includes exchangeable, organic matter, Fe oxide, sand, silt and clay. Another speciation scheme was developed by the EC Standards, Measurement and Testing Programme formerly BCR (Bureau Community of Reference). This scheme (Rauret, 1998), proposes only four fractions: exchangeable (acetic acid), reducible (hydroxylamine hydrochloride), oxidisable species (hydrogen peroxide and nitric acid) and residual (aqua-regia). The BCR procedure had been tested for sediments (Thomas et al. 1994) and soils (Davidson et al. 1998).

In Peninsular Malaysia, studies on heavy metal concentrations in common agricultural soils have only started in the last decade or so and fractionation or phase association studies are still lacking. An earlier study on the assessment of contamination of agricultural soils and crops in Peninsular Malaysia (Zarcinas et al. 2004) showed that some of our soils already contain elevated values of Cd and Zn and that cabbages grown on these soils may show high values of Cu. The Malaysian soil investigative levels for heavy metals was also established by Zarcinas et al. (2004). The 95th percentile of heavy metal contents from 241 agricultural soils were proposed to be the investigative levels. Soils with values over this 95th percentile will be regarded as contaminated.

Soils developed from granite (Rengam Series) were chosen for this study. These soils are all located in vegetable farms. The main objectives of this study were to determine the concentration ranges of total heavy metals (Cu, Pb, Zn and Ni) and the chemical forms in four soil phases (i.e. exchangeable, amorphous Fe oxides, organic matter and residual).

**MATERIALS AND METHODS**

The soil samples (0-20 cm) were collected using a stainless steel auger. Thirty six soil samples developed over granite (Typic Kandudult, Rengam Series) were collected from some major vegetable growing areas in Johore. Twelve soils from areas not cultivated with vegetables but also developed over granite were also sampled for determination of background values. The soils were air-dried and analysed for chemical properties such as pH, organic C and cation exchange capacity (CEC). Soil pH was measured in a 1:2.5 (w/v) ratio of soil to water. Organic carbon was measured using the Walkley-Black method and cation exchange capacity was determined as described by Van Ranst et al. ((1999). The total heavy metal concentrations (Cu, Pb, Zn and Ni) were determined by the aqua-regia method (Van Ranst et al. 1999). Some selected soil samples (24 of cultivated and 12 of background soils) were analyzed for chemical partitioning. The sequential extraction procedures used was the modified schemes of Tessier et al. (1979) and Shuman (1979). The extraction was modified for our soils because these soils do not contain carbonates and appreciable amount of sulphides and manganese. The first two steps (for exchangeable and organic bound fractions)
are those from Tessier’s scheme, while the third step (for amorphous iron oxides) followed that of Shuman (1979). Step 4 is the determination of heavy metals in the residual fraction using aqua-regia instead of nitric, hydrofluoric and perchloric acid. All the analyses were performed in duplicates. Extractions were carried out on 1.0 g of soil and involved the following steps:

F1: Eight ml of 1 M MgCl2 were added to the sample and suspension was shaken for 1 hour and then centrifuged (20 min, 4000 rpm).

F2: Six ml of 0.02 M HNO3 and 10 ml of 30% H2O2 were added to the residue obtained from the first extraction, and the suspension was shaken for 5 hours at the temperature of 85±2°C. After cooling, 10 ml of 3.2 M CH3COONH4 were added and shaken for 30 minutes and centrifuged.

F3: The samples were extracted with 20 ml of solution 0.2 M ammonium oxalate and 0.2 M oxalic acid, shaken in the dark for 4 hours and centrifuged.

F4: The heavy metals contents in the residual fractions were determined by aqua-regia method.

Copper, Ni, Zn and Pb were determined by atomic absorption spectrophotometer (AAS).

RESULTS AND DISCUSSION

Chemical Properties and Total Heavy Metal Concentrations

Table 1 shows the mean of pH, cation exchange capacity and organic carbon for the cultivated Ultisols and the background soils. Included in this table are values for Ultisols and the 95th percentile for 241 agricultural soils from an earlier study by Zarcinas et al. (2004) in order to compare them with the results of the present study.

Table 1 shows that only soil pH in the cultivated soils is significantly higher than the background soils. This shows that this chemical property had increased due to the soil amendments such as application of chicken dung and lime.

Zinc content is the highest in both soil types, followed by Cu, Pb and Ni. Comparing the heavy metals between the cultivated and the background soils using T-test, Cu and Zinc have shown significant increase (p< 0.001) in the cultivated soils. The potential source of both these metals is the chicken dung which is added in large quantities to the soils for the production of vegetables.

Values of heavy metal concentrations in the cultivated Ultisols in the study area show values close to those of the Ultisols in other parts of the country as observed by Zarcinas et al. (2004). In general, all the heavy metal values are lower than the 95th percentiles established in an earlier study by Zarcinas et al (2004), thus indicating that these soils are still not considered contaminated.

Correlation studies (Table 2) of total heavy metal concentrations and soil chemical properties show that only total Zn and Pb is positively correlated with pH, Zn with organic carbon , while Cu is negatively correlated with CEC.
TABLE 1
Mean values for total heavy metal concentrations and chemical properties of Ultisols in Johore

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>O.C. (%)</th>
<th>CEC (cmol, kg⁻¹)</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cultivated Ultisols</td>
<td>5.62a</td>
<td>1.90</td>
<td>6.57</td>
<td>23.3a</td>
<td>18.0</td>
<td>49.4a</td>
<td>6.0</td>
</tr>
<tr>
<td>n=36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background Soils</td>
<td>4.42b</td>
<td>1.35</td>
<td>6.58</td>
<td>11.7b</td>
<td>14.5</td>
<td>25.1b</td>
<td>7.5</td>
</tr>
<tr>
<td>n=12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Ultisols</td>
<td>5.49</td>
<td>1.77</td>
<td>10.3</td>
<td>13.6</td>
<td>31.3</td>
<td>53.0</td>
<td>20.4</td>
</tr>
<tr>
<td>(n=58)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*95th percentile of 241 samples of agricultural soils</td>
<td>47.3</td>
<td>65.8</td>
<td>92.0</td>
<td>41.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*(Zarcinas et al. 2004)
Means with different letters show significant difference at level p<0.001.

Forms of Heavy Metals
The investigation on metal forms, particularly using sequential extractions, mainly concerns with surface soil horizons (Iyengar et al. 1981; He and Singh 1995; Chlopecka et al. 1996; Ma and Rao 1997; Ahumada et al. 1999). This study was, therefore, undertaken to investigate the distribution and chemical fractions of heavy metals in Rengam Series (Typic Kandiudult), because most of the vegetables collected from the study areas were cultivated on this soil type. The total metal concentrations in each fraction in the cultivated and background soils are shown in Table 3.

The heavy metal fractions in background and cultivated Ultisols, which were expressed as percentages of the sum of all the chemical fractions are presented in Figures 1 – 4. This analysis was performed to see whether there is transformation from one fraction to the other, within the background and cultivated soils.

Most of the Cu was present in the residual fraction (Fig. 1). The percentages of soil Cu in background soils followed the order of residual > organic > carbonate > Fe-Mn oxide > exchangeable with an average of 87.87%, 4.62%, 3.29% and 2.34%, 1.87%, respectively. The same pattern was also observed in the cultivated soils (Figure 1). The percentages of soil Cu in exchangeable, carbonate, Fe-Mn oxide, organic and residual fractions averaged 1.74%, 3.09%, 2.14%, 6.21%, and 86.81%. A substantial increase in the Cu percentages was observed when the H₂O₂ was used in the fourth step. This indicates that a substantial fraction of Cu was bound to the organic matter, after the residual fraction. According to Wong et al. (2002), Cu in natural soils was mainly associated with the residual fraction followed
TABLE 2
Correlation coefficients between total heavy metal contents and chemical properties of cultivated Ultisols.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEC</td>
<td>-0.35**</td>
<td>ns</td>
<td>ns</td>
<td>ns</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td>0.41**</td>
<td>0.27**</td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>ns</td>
<td>ns</td>
<td></td>
<td>0.30**</td>
</tr>
</tbody>
</table>

ns not significant
** significant at the 0.01 probability level

TABLE 3
Heavy metal fractions in cultivated and background soils

<table>
<thead>
<tr>
<th>Forms of Heavy Metals (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 Exchangeable</td>
</tr>
</tbody>
</table>

Cultivated soil (n=24)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.26</td>
<td>3.68</td>
<td>1.44</td>
<td>0.76</td>
</tr>
<tr>
<td>Pb</td>
<td>0.46</td>
<td>1.09</td>
<td>1.74</td>
<td>1.18</td>
</tr>
<tr>
<td>Zn</td>
<td>0.31</td>
<td>1.87</td>
<td>1.21</td>
<td>0.66</td>
</tr>
<tr>
<td>Ni</td>
<td>0.93</td>
<td>3.93</td>
<td>0.26</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Background soils (n=12)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.26</td>
<td>1.98</td>
<td>1.35</td>
<td>0.74</td>
</tr>
<tr>
<td>Pb</td>
<td>0.45</td>
<td>1.11</td>
<td>1.63</td>
<td>1.16</td>
</tr>
<tr>
<td>Zn</td>
<td>0.32</td>
<td>1.84</td>
<td>0.60</td>
<td>0.65</td>
</tr>
<tr>
<td>Ni</td>
<td>0.66</td>
<td>2.13</td>
<td>0.40</td>
<td>0.46</td>
</tr>
</tbody>
</table>

by the organic fraction. The high application of organic materials on cultivated soil resulted in an increase in the organic fraction (Lu et al. 2005). The association between soil Cu and the organic fraction was in agreement with the general finding that Cu forms the most stable complex with organic matter (Adriano, 1986). Grazebisz et al. (1997) and Ettler et al. (2005) have also found that the total fraction of Cu was bound to organic constituents. Copper is a very versatile trace cation in soils or depositional material and exhibits a great ability to chemically interact with mineral and organic components of soil.

The percentages of Pb fractions in the background soils were in the order of residual > organic > exchangeable > Fe-Mn oxide > carbonate with an average of 50.84%, 14.93%, 13.59%, 12.77% and 7.87%, respectively. The percentages of Pb in the cultivated soils presented in Fig. 2 followed the same order as the background soils with the mean percentages of 52.82%, 17.44%, 16.61%, 8.24% and 4.89%, respectively. Berti and Jacobs (1996) have reported that the majority of soil Pb was in the residual fraction in different soils prior to sludge amendments. The high percentages of non-residual fractions indicate that Pb has a strong affinity for organic matter, Mn oxides, Fe and Al hydroxides (Adriano 1986, Kabata-Pendias and Pendias 1993).

Soil organic matter has been recognized as a critical component in the retention of heavy metals in soils. An increase of organic matter content in soil would help to reduce metal ions from exchangeable sites and acidic conditions (Elliott et al. 1986; Weng et al. 2002) and then enhance the binding of metals to this fraction. Studies by Khairiah et al. (2004) in agricultural areas showed that Pb was high in
the organic fraction in soil cultivated with long bean. Increasing acidity may increase Pb solubility, but this mobilization is usually slower than the accumulation in the organic rich layer of soil. The typical localization of Pb near the soil surface in most soil profiles is primarily related to the surface accumulation of organic matter. High organic matter content in cultivated soils resulted in the increased organic-matter bound fraction.

The percentages of Zn in background soils (Fig. 3) follow the order of residual > carbonate > exchangeable > Fe-Mn oxide > organic with an average of 87.10%, 4.89%, 3.09%, 3.14% and 0.78%, respectively. In cultivated soils, the highest amount of Zn was also associated with the residual fraction with an average of 86.51% (Fig. 3). The means of non-residual fractions averaged 5.25%, 4.39%, 3.18%, and 0.68%, respectively. Wong et al. (2002) in their studies on agricultural soils have also found that soil Zn in the exchangeable and carbonate, specifically adsorbed fractions accounted for <10% of total soil Zn.

High proportion of Zn in carbonate fraction compared to other non-residual fractions was in agreement with the result reported by Tessier et al. (1979). The low percentage of Zn-organic bound was also similar to that reported by Kashem and Singh (1999) who found that the organic matter had little effect on Zn partitioning, although the contaminated soils contained higher amounts of organic matter. Lower percentages of soil Zn in organic fraction among the immobile fractions studied have indicated that the Zn-organic matter association may be relatively unstable.

The same trend as Zn was observed for Ni in this study. The percentages of Ni fractions in the background soil followed the decreasing order of residual > carbonate > exchangeable > Fe-Mn oxide > organic with an average of 79.53%, 7.71%, 5.04%, 4.54%, and 3.18%, respectively. Nickel in the cultivated soil showed the same fractionation order with averages of 82.31%, 6.23%, 4.67%, 3.96%, and 2.82%, respectively (Fig. 3).

Podlesakova et al. (2001) also indicated that high proportion of Ni was present in the residual form. Usually, it is present in soils derived from parent materials of mafic rocks. The highest concentration of Ni in the residual fraction may be those bound with silicate minerals, resistant sulphide and refractory organic materials (Li and Shuman 1996; Sims and Heckendorn 1991 and Emmerich et al. 1982). Metals in this fraction are expected to be chemically stable and biologically inactive.

Heavy metals in available fraction such as exchangeable and carbonate fraction may indicate the potential forms of metals that can be accumulated in the plant. However, the exchangeable fraction of the metals studied were very low indicating that under the present conditions, the availability of these metals to vegetables would be minimal. For Cd, Zn and Ni, all these trace elements in the first fraction extracted (exchangeable fraction) are usually dependent upon soil pH. Lim et al. (2002) investigated the changes of forms of Pb and Cd in soil at various pH values with different time and found that the changes of Pb and Cd in exchangeable fraction were pH-dependent. Generally, the change was small under acidic condition and larger decrease occurred at pH 7. Residence time also directly relates to the reactions between metal ions and soil. Studies done by previous researchers
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Fig. 1: Copper Fractions in Cultivated and Background Soil Expressed as Percentage of Sum of all Fractions (%)

Fig. 2: Lead Fractions in Cultivated and Background Soil Expressed as Percentage of Sum of all Fractions (%)

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Fig. 3: Zinc Fractions in Cultivated and Background Soil Expressed as Percentage of Sum of all Fractions (%)

Fig. 4: Nickel Fractions in Cultivated and Background Soil Expressed as Percentage of Sum of all Fractions (%)

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indicated that heavy metals in Fe-Mn oxides and organic compounds were very low in solubility and high stability for biological activity and would not have direct bearings on their uptake by plants (Xian 1989). Most of the heavy metals studied were found in the residual fractions.

The amounts of non-residual fractions (F1, F2 and F3) represents the amounts of active heavy metals, while those of the residual fractions may be considered to be the stable form and thus not available to plants for a reasonable period. In this study, the respective non-residual fractions of Cu, Pb, Zn and Ni in the Ultisols averaged 60.8%, 51.1%, 67.7% and 25.4%, which suggests that the mobility and bioavailability of the four metals are in the order: Zn > Cu > Pb > Ni.

CONCLUSION

Total heavy metal concentrations in cultivated Ultisols fall within the typical range for unpolluted soils. Heavy metal forms using a modified Tessier’s sequential extraction procedure showed that the general trend in Ultisols cultivated with vegetables for Pb and Ni is residual > oxalate > exchangeable > organic. For Zn and Cu, the oxalate extractable phase is highest followed by the residual phase. The amounts of non-residual fractions which represent the amounts of active heavy metals in the soils are in the order: Zn > Cu > Pb > Ni. Zinc and Pb contents in the soils are also positively correlated with soil pH.

REFERENCES


Chlopecka, A. 1993. Forms of trace metals from inorganic sources in soils and amounts found in spring barley. Water Air Soil Pollut. 69: 127-134.


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