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Heavy Metals from Agricultural Soils from Cameron Highlands, Pahang, and Cheras, Kuala Lumpur, Malaysia

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Heavy metals have been well documented as they are amongst the most hazardous materials threatening the environment worldwide. Previous studies have found that vegetables grown in contaminated soils have increased uptake and accumulation of heavy metals in their various tissues (Cobb et al. 2000). The presence of heavy metals in vegetables may pose risks to human health, both directly and via potential contamination of the food chain, through the ingestion of contaminated vegetables (Pahlsson 1989).

Heavy metals in soils can be associated with several reactive materials and may exist in various forms that reflect their solubility and availability to plants (Zhang et al. 1997). Although the total metal concentrations may indicate the overall level of the metals in the soils, they provide no information regarding the chemical nature or potential mobility and bioavailability of a particular element (Powell et al. 2005). Sequential extraction has been adopted by researchers to study the mobility and bioavailability of heavy metals in various fractions of the soil (Hseu 2006). Such procedures produce information about the speciation of heavy metals and the origin, mode of occurrence, bioavailability, mobilization and transport of heavy metals.

Cameron Highlands is the centre for vegetable farming in Malaysia where farmers have been using heavy doses of various types of fertilizers and pesticides as regular agricultural practice whereas Kuala Lumpur is in the city centre where the main source of pollution would be the emission from motor vehicles. The objective of this study was to determine the speciation of heavy metals in Malaysian agricultural soils from the Cameron Highlands in Pahang and from Cheras in Kuala Lumpur.

MATERIALS AND METHODS

The study was carried out in two areas of Malaysia: Cameron Highlands, Pahang and Cheras, Kuala Lumpur. Cameron Highlands is situated in the highlands at 1070-1829 m above sea level. Its temperature ranges from 14-24°C. Cheras, on the other hand, is located near the city of Kuala Lumpur.

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Table 1. Average percentage of organic content, grain size and soil pH at each study area

Locations	Organic carbon (%)	Soil pH	Percentage fine grain (size <63µm)
Brinchang	1.36±0.08	7.02±0.07	36.07±6.55
Ringlet	2.89±0.08	6.97±0.07	46.23±0.08
Tanah Rata	2.43±0.08	6.26±0.42	44.69±2.09
Cheras	2.43±0.09	7.23±0.03	9.10±1.34

Soil samples were collected from three locations in the Cameron Highlands, namely, Brinchang, Tanah Rata and Ringlet, and from one location in Cheras. Three plots were chosen at each sampling area, and soil samples were taken at 0-30 cm depth using an auger.

Heavy metals were extracted by sequential extraction (Badri 1984). This extraction method yields four fractions: easily leachable and ion exchange fraction (EFLE), acid reducible fraction (RA), oxidation organic fraction (OO) and resistant fraction (RR). Soil samples were air-dried in the laboratory before being ground and sieved using a 250 µm mesh (Badri 1984). A 10 g soil sample was weighed into a Kartell bottle, and 50 mL 1.0 M NH_4CH_3OO (pH 7) was added to extract metals from the EFLE fraction. The samples were shaken for 1½ hr, then centrifuged at 3000 rpm for 30 min before being filtered through 0.45 µm millipore filter paper and then made up to 50 mL with distilled water. Samples were washed with 50 mL distilled water, followed by further shaking and centrifugation as described previously. Then 50 mL $NH_2OH.HCl$ (pH 2) was added to extract metals from the acid reducible (RA) fraction using the procedure described above. Metals in the organic oxidation (OO) fraction were extracted by adding 15 mL of H_2O_2 to the sample placed in a water bath for 1-1½ hr, followed by 50 mL NH_4CH_3OO (pH 3.5). Samples were then digested using HNO_3:$HClO_4$ at 25:10 ratio in a sand bath at 100°C as the RR extraction method. The digestion process was repeated until the samples turned whitish.

To determine heavy metal concentrations, we used atomic absorption spectrometry (Perkin Elmer 1100B) with the following wavelengths (nm): Fe 248.9, Zn 213.9, Cd 228, Mn 213.9, Pb 283.3, Cu 324.8 and Cr 357.9. Organic carbon analysis and soil pH measurements were carried out using the Walkey-Black (Jackson 1958) and the Duddridge and Wainright (1981) methods, respectively, while grain size was determined by the method described by Badri (1984). The recovery study was carried out using the BCR sequential extraction procedure as described by Kartel et al. (2006). All analyses were replicated three times. The characteristics of the soils were as shown in Table 1. Data were subjected to an analysis of variance, and means were compared by the Tukey test at the 5% level of significance.

RESULTS AND DISCUSSION

Table 2 shows the levels of heavy metal concentration in the four fractions of the sequential extractions from soil samples taken from the four sites. The study showed that Mn was the most frequently detected metal in all the fractions of the four sites studied. In contrast, Pb was not detected in the soil samples from any of the four locations, and only in the Brinchang soil sample was Cd not detected at all. In the Ringlet and Tanah Rata soils, Cd was detected only in the OO and RR fractions, while in the Cheras soil Cd was detected in the OO, RR and RA fractions but not in the EFLE fraction. In general the percentage recovery of heavy metals extracted from the soils based on the certified value given by Kartel et al. (2006) was high for Mn and Cu. The percentage for the rest of the metals was quite low. This could be due to the fact that the total percentage of heavy metals detected from the entire area studied was low as compared to the certified values stipulated by Kartel et al. (2006) (Table 2).

Among the metals studied from the various fractions of sequential extraction in the soils, the lowest values of heavy metals (except for Cr) were discovered in the EFLE fraction. The highest heavy metal concentrations detected in the EFLE fraction were Mn, followed by Cu. This finding seems to imply that, in general, for the soils studied, the availability of heavy metals for plant uptake was low except for Mn and Cu. Therefore, low concentrations of heavy metals extracted in this fraction suggest that the potential for metal uptake by plants at the study areas was low. Relatively high Mn and Cu content in the EFLE fraction could be due to the agricultural application of pesticides and fertilizers containing these metals.

Studies by Stalikas et al. (1997) on agricultural areas in Greece showed that Mn and Fe were also relatively high in the soil as seen by extraction with DTPA (diethylenetriaminepentaacetic acid). It is not surprising, therefore, that these metals are commonly found in agricultural soils, especially in the EFLE fraction. Metals found in this fraction are readily available to plants. It can also be seen that the heavy usage of various pesticides and fertilizers for routine agricultural activities in these areas has not increased the levels of toxic metals in the EFLE fraction. According to McLaughlin et al. (2000), the use of fertilizers in agricultural areas can result in metal contamination of the soil. For instance, the usage of phosphate fertilizers has contributed to the Cd content in agricultural soils of New Zealand and Australia (McLaughlin et al. 1996). Pesticides like fungicidal sprays, usually containing the 'Bordeaux mixture' (copper sulphate) and copper oxychloride, have been found to induce considerable residual accumulation of As, Cu and Pb in the orchards of south Australia and New Zealand (McLaughlin et al. 2000). Kabata-Pendias and Pendias (1989) have reported that high concentrations of metals in agricultural soils could be due to the application of organic fertilizers, especially farmyard manure known to contain both Zn and Cu impurities. Farmers from all the study areas were known to use farmyard waste as fertilizer, which probably was the cause of the increased Cu concentration in the said soils.

In general, the acid reduction fraction in this study gave relatively higher concentrations of heavy metals than did the EFLE fraction. Heavy metals found in this fraction from the Ringlet and Tanah Rata soil samples showed the highest level of a single heavy metal, Mn, followed by Cu and Zn , while in the Brinchang soil Mn was the heavy metal most extractable in this fraction, followed by Fe, Cu and Zn. The

Cheras soil contained heavy metals like Mn, Zn, Cu, Fe and Cd in this fraction. Amongst the areas studied, the Cheras soil was observed to have the lowest Mn content in this fraction. This study showed variation in the acid reduction fraction of heavy metal concentrations in the soil samples studied.

Levels of metals extracted in the organic oxidation (OO) fraction were higher than in the EFLE and RA fractions, except for Cd where the level was very low in all the soils studied. The metal extracted at the highest level in this fraction was Mn, followed by Cu, Zn, Fe and Cr in the soils from all sites (Table 1). An earlier report on heavy metals in the peat soil (acidic) from Sepang, Selangor, showed that organic matter had great potential to retain heavy metals, especially Zn and Pb (Khairiah et al. 2004). However, the soils of this study were low in organic matter but had a high pH. Therefore, metals such as Zn were not retained as strongly as in acidic peat soil.

The results indicated that most heavy metals were found to be highest in the RR fraction of soils taken from all the sites studied. The exception was Cu, which was the highest in the OO fraction of the Brinchang soil, and Cr, which was highest in the EFLE fraction of the Cheras soil. The highest concentration of metals, especially of Mn and Fe, was discovered to be in the resistant fraction in all the soils studied. This indicates that most of these metals were strongly trapped within the silicate of clay minerals and were not available to plants (Badri 1984). Similar findings have been reported by Abbolino et al. (2002) for soils from the agricultural areas of north-eastern Italy. Their study found that most metals were present in the resistant fraction of the soil and therefore strongly bound to the soil matrix.

These results are also in line with previous studies by Khairiah et al. (2004), in which it was found that most metals were at their highest level in the resistant fraction in studies using the sandy soil from Bangi and the peat soil from Sepang. This finding would suggest that Mn, Fe and Zn were the more commonly occurring heavy metals present in the soils of the study areas.

The examined soils also can be considered as unpolluted, since the concentration of toxic metals like Pb and Cd were not detected in the EFLE fractions, the fractions which isolate metals that can easily be taken up by plants. At the same time the distribution of metals in the various fractions from sequential extraction were almost the same for all the studied soils. Levels of most metals were highest in the resistant fraction, followed by levels in the organic oxidation fraction, then the acid reduction fraction and finally they were at their lowest in the EFLE fraction.

The percentages of organic carbon in the soils ranged from 1.36- 2.89, and pH values from 6.26-7.23 (Table 2), indicating low organic content in the soils and neutral soil pH. The Ringlet soil samples showed the highest level of organic content whilst the Brinchang samples showed the lowest. The Cheras soil samples had the highest pH and the Tanah Rata soil the lowest (Table 2). Overall the organic content and pH values of the soils for the areas studied did not differ much. This lack of variation may be explained by the fact that these areas have been used for vegetable farming for a long time and have received similar types and levels of fertilizers for many years.

Table 2. Average heavy metal content in soils from the selected study areas

Fraction/ Location	Heavy metal (mg/kg)						
	Fe	Zn	Cd	Mn	Pb	Cu	Cr
Brinchang							
EFLE	0.5d	0.4d	ND	48.1c	ND	4.9c	2.2c
	±0.3	±0.3		±7.3		±5.4	±0.4
RA	10.0c	3.6c	ND	159.5b	ND	9.3c	1.0d
	±9.0	±1.9		±59.8		±0.5	±0.2
OO	28.4b	26.8b	ND	142.3b	ND	46.5a	3.8b
	±18.6	±6.4		±67.3		±46.6	±2.9
RR	361.6a	56.6a	ND	570.7a	ND	32.5b	11.1a
	±4.5	±11.4		±137.7		±4.9	±2.8
[a]Total	401.6	87.6	-	920.9	-	93.4	18.3
	±21.2	±13.2		±164.7		±47.2	±4.1
% recovery	1.4	25	-	144.3	-	82.2	-
Ringlet							
EFLE	1.0c	0.7d	ND	88.4c	ND	11.8c	1.6b
	±0.2	±0.3		±15.4		±5.7	±0.3
RA	0.5c	4.4c	ND	182.3b	ND	9.9c	0.7c
	±0.7	±1.5		±38.8		±0.1	±0.2
OO	5.9b	30.8b	0.1b	191.7b	ND	40.2b	2.1b
	±2.9	±3.7	±0.1	±27.0		±11.3	±0.7
RR	314.8a	54.1a	0.7a	422.7a	ND	54.5a	5.6a
	±3.9	±7.7	±0.2	±73.8		±15.3	±1.9
[a]Total	322.4	90.2	0.9	885.1	-	116.5	10.1
	±4.9	±8.7	±0.2	±89.0		±19.8	±2.1
% recovery	1.1	25.7	2.2	138.7	-	102.2	-
Tanah Rata							
EFLE	0.6d	0.45 d	ND	42.2c	ND	10.2c	2.3b
	±0.4	±0.5		±30.0		±0.1	±0.2

Table 2. (cont.).

RA	26.4c	2.5 c	ND	35.9b	ND	7.6c	1.1c
	±18.7	±2.4		±18.5		±3.9	±0.1
OO	84.7 b	14.5b	ND	17.2b	ND	13.4b	2.0b
	±40.1	±7.5		±12.5		±2.3	±0.2
RR	357.2a	20.7a	0.1a	259.8a	ND	27.3a	6.2a
	±3.2	±4.1	±0.1	±30.0		±1.1	±2.2
[a]Total	469.1	38.1	0.1	355.0	-	58.5	11.6
	±44.3	±8.9	±0.1	±47.9		±4.7	±2.2
% recovery	1.6	10.9	0.3	55.6	-	51.3	-
Cheras							
EFLE	0.2d	2.3d	ND	15.5d	ND	11.5c	2.0a
	±0.2	±0.7		±4.1		±0.7	±0.1
RA	5.3c	13.5c	0.2b	79.5c	ND	11.2c	0.9b
	±3.2	±2.7	±0.1	±12.7		±0.5	±0.1
OO	16.0b	31.1b	0.4a	163.1b	ND	31.9b	0.7c
	±4.5	±3.1	±0.1	±80.9		±8.5	±0.1
RR	280.0a	55.2a	0.5a	550.7a	ND	37.6a	0.4d
	±3.2	±5.9	±0.1	±69.6		±5.2	±0.3
[a]Total	301.6	102.1	1.2	808.9	-	92.2	4.2
	±6.4	±7.2	±0.2	±107.5		±10.0	±0.3
% recovery	1.0	29.1	2.9	126.8	-	80.8	-
[b]Certified value	28900	350.4	-	638	-	114	-
	±600	±4.8		±28		±2	

ND = not detected; Means followed by the same letter within a column are not significantly different at the 5% level. [a]Total (EFLE + RA + OO + RR); [b]Source: Kartel et al. (2006).

He and Singh (1993) found from their investigation that areas under long-term cultivation in south eastern Norway had lower organic content and higher pH than newly cultivated fields despite the use of farmyard waste and fertilizers containing phosphate. They proposed that the lower organic content discovered in the soil from their study sites also could have been due to long-term farming activities as well as to the application of phosphate fertilizer and farmyard manure. The areas of the present study have similarly been used for vegetable farming for a few decades and show similar soil characteristics.

He and Singh (1993) also noted that soil pH appears to be an important factor regulating the solubility of heavy metals. Solubility of Pb, Cr, Zn and Mn decreased when soil pH increased (Harter 1983). Organic material was shown to form complexes with and reduce the availability of metals to the soil (Khairiah et al. 2004). Therefore, the higher the organic content in the studied soil, the lower the availability of metals in the easily leachable and ion exchange fraction as shown in this study. But the results of this study showed that higher levels of metals were still found in the RR fraction.

In terms of grain size, approximately 9.10% and 46.23% consisted of grains <63 µm – the degree of grain fineness identified by Margui et al. (2004) as containing relatively higher metal concentrations than the larger soil grains. The higher percentage of fine-grained particles contributed to the higher heavy metal content in the soil or sediments because of its high surface area-to-particle size ratio (Horowitz and Elrick 1987).

In general pH, organic matter content and grain size play a very important role in the availability of heavy metals in the soil to plants. In this study these factors seem to have enhanced the binding of heavy metals to various components; consequently reducing the availability of heavy metals to plants. The heavy metals found in the soils studied were in their highest concentrations in the resistant fraction, followed by oxidation organic fraction and acid reducible fraction. Relatively low concentrations of heavy metals were found in the easily leachable and ion exchange fraction, indicating that they might not be easily absorbed by plants, thus keeping low the level of contamination by heavy metals in the vegetables produced from these areas.

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