Malaysian Journal of Soil Science Vol.11 : 81-95 (2007)
ISSN: 1394-7990
Malaysian Society of Soil Science

Domestic Sewage Sludge Application to an Acid Tropical Soil: Part III. Fractionation Study of Heavy Metals in Sewage Sludge and Soils Applied with Sewage Sludge

A. Rosazlin[1], I. Che Fauziah[2]*, A.B. Rosenani[2] & S. Zauyah[2]

[1]Forestry Division, Forest Research Institute of Malaysia (FRIM) 52109 Kepong, Selangor

[2]Department of Land Management, Faculty of Agriculture, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia

ABSTRACT

Soil fractionation studies of heavy metals can provide insight into their solubility and chemical reactivity in terms of labile and non-labile pools of these metals. The fractionation of cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in domestic sewage sludge, soil, soil applied with NH_4SO_4 and soil applied with sewage sludge was studied after the first and third maize cycles. The second cycle did not give significant yield results because of the dry period during this cycle. The correlation between different forms of heavy metals in the soil and content in maize grain was also investigated. Fractionation of heavy metals in sewage sludge showed that most soil metals were associated with the less soluble or non-labile soil moieties (carbonate, Fe-Mn oxides, organic and residual fraction). The dominant form of all heavy metals was the residual form (non-phytoavailable form) except for Cu. Leaving the residual fraction aside, Cd and Pb were dominant in exchangeable (labile pool) form, Ni in carbonate form and Zn in Fe-Mn oxide form. For the untreated and treated soils, the residual fraction was also the dominant fraction except for Cd and Pb. The organic form is the dominant form for Cu in sludge treated soil. In general, the percentage of water soluble content was less than 5%. Also, in general, there was no significant difference between the different metal fractions of the inorganic fertiliser treatment compared to the control, except for exchangeable Pb and Zn associated with Fe-Mn oxide fraction. The addition of sewage sludge tended to shift the solid phase forms of the metals away from the residual to the Fe-Mn oxide form. Significant correlations were only obtained between Cd content in maize grain and the organic forms in soil ($n=30$, $r=0.378$, and $p<0.05$), Ni content in grain with total metal in the soil ($n=30$, $r=0.406$, $p<0.05$) and between Cu content in maize grain and the carbonate, Fe-Mn oxide and organic forms in soils ($n=30$, $r=0.475$, $p<0.01$; $n=30$, $r=0.539$, $p<0.01$; and, $n=30$, $r=0.545$, $p<0.01$, respectively).

Keywords: Sewage sludge, fractionation study, geochemical forms, labile and non-labile pool, correlation study

* Corresponding author: Email:*fauziah@agri.upm.edu.my*

INTRODUCTION

Heavy metals in soils may be present in many forms. The fractionation of heavy metals in sludge-treated soils is important in order to evaluate their behaviour in the environment. Information on the distribution of these different chemical forms of heavy metals in soils can provide insight into their solubility, chemical reactivity, and the fractions that can serve as a pool of available forms for plant uptake (Stumm and Morgan 1981). However, knowledge of the total content of heavy metals present in soil only provides limited information on the mobility and availability. Identifying the chemical forms in which the metals are retained in soil is helpful to predict their potential mobility to water sources, plant availability and the amount of metal cycling through the food chain. Consequently, it is necessary to evaluate the ecotoxicological potential of these elements in a more accurate way. Compared to single extractants, multi-step extraction methods are found to furnish relatively more detailed information about heavy metals speciation in soils.

The application of sewage sludge to soils may alter the geochemical forms or metal fractions, which, in turn, may affect its availability to plants. Sewage sludge, with its organically bound nutrients and large fraction of organic matter, builds soil integrity and feeds plants over a longer period of time. Hence, this study was conducted to (i) investigate the different forms of Cd, Cu, Ni, Pb and Zn in sewage sludge using different chemical extractants; (ii) investigate whether there are any shifts in the metal fractions in soil applied with sewage sludge after the first and third maize cycles using different chemical extractants; and (iii) correlate between different forms of heavy metals in the soil with uptake by sweet maize.

MATERIALS AND METHODS

Sewage Sludge and Soil Samples

Sewage sludge was collected from Indah Water Konsortium (IWK) Sdn. Bhd. treatment plant at Taman Sri Gombak, Selangor. The sewage sludge was applied before planting of the first, second and third crop cycles. The second cycle was excluded in this study because of crop failure due to very dry weather. Soil samples used in this study were taken from 0-20 cm depth after maize harvest, from the plots of three treatments: T1- inorganic fertiliser (140 kg N/ha ammonium sulphate; T2- no inorganic fertiliser and sludge application; and T3 - 28 t ha^{-1} sewage sludge (560 kg N/ha) with five replicates (for details, please refer to Part I of the paper (Rosazlin *et al.* 2005).

Preparation of Soil Samples

In the laboratory, the soil samples were air-dried at room temperature. Each soil sample was sieved through a 2-mm sieve. About 10 g of each sample was finely ground to pass through the <250-mm sieve. The heavy metal concentrations were determined using the atomic absorption spectrophotometer (AAS).

MJ of Soil Science 081-095.pmd 82 08-Apr-08, 10:49 AM

Chemical Analyses

The extraction procedure was carried out using 30 mL centrifuge tubes. The tubes were thoroughly cleaned and acid-washed (10% HCl) prior to use. The method of the sequential extraction procedure used in this study was that of Tessier *et al.* (1979) and followed by the modified version of Yang and Kimura (1995) and Chlopecka *et al*. (1996) as put forward by Salas *et al*. (1998). The five heavy metals (Cd, Cu, Ni, Pb and Zn) were partitioned into six operationally defined fractions. The forms of heavy metals are water soluble, exchangeable, carbonate bound, Fe-Mn oxides bound, organically bound and the residual form. Water soluble and exchangeable fraction is the plant available fraction. Carbonate, Fe-Mn oxides and organic fraction are considered as the 'inactive' and 'non-labile' pool, which will become available if soil condition changes. The residual fraction is part of the clay matrix and will not take part in the chemical reaction in the soil. The reagents employed and chemical forms solubilised with 5 g sample weights are listed below:

1. *Water Soluble Fraction* - extracted by adding 20 mL of distilled water to the tube containing 5 g of air-dried soil and then shaken for 2 hours at room temperature.
2. *Exchangeable Fraction* - extracted with 20 mL of 1.0 M magnesium chloride, followed by shaking for 2 hours at room temperature.
3. *Carbonate Fraction* - extracted with adding 20 mL of 1.0 M sodium acetate, adjusted to pH 5.0 using acetic acid, followed by shaking for 2 hours at room temperature.
4. *Fe-Mn Oxides Fraction* - residue from the carbonate fraction extraction was extracted using 20 mL of 0.04 M hydroxylamine hydrochloride in 25% acetic acid (v/v) for 8 hours at 65^{o}C with occasional agitation.
5. *Organic Fraction* - residue obtained from the extraction of the Fe-Mn oxides fraction was treated with 2 mL of 0.02 M nitric acid and 5 mL of 30% hydrogen peroxide. Then, the solution was adjusted to pH 2 with nitric acid. The mixture was heated up to 65^{o}C for 5 hours with occasional agitation. Three mL aliquot of 30% hydrogen peroxide was added and the mixture was adjusted to pH 2 with nitric acid. Then, the sample was heated again to 65^{o}C for 7 hours with agitation. After cooling, 5 mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid was added and the resulting solution was diluted to 20 mL with distilled water and agitated continuously for 30 minutes at room temperature.
6. *Residual Fraction* - final residue was transferred into a 250 mL beaker. Then, 50 mL aqua-regia (3:1 HCl : HNO_3) was added and left to react overnight after which the mixture was heated at 90°C for 2 hours, then made up to 100 mL.

MJ of Soil Science 081-095.pmd 83 08-Apr-08, 10:49 AM

RESULTS AND DISCUSSION

Forms of Heavy Metals in Sewage Sludge

All the domestic sewage sludge contained varying amounts of Cd, Pb, Zn, Ni and Cu. To understand the chemical form of the various metals in municipal sewage sludge, one must first determine the form these metals exist as after wastewater treatment processes. Each metal may be distributed between the soluble and solid phase depending upon which complex equilibrium controls the wastewater composition. However, in most cases, Cd, Pb, Zn, Ni and Cu have been found to be predominantly associated with the solid phase in wastewater influents (Page *et al.* 1981). The distribution of these metals among the various forms is dependent on properties of the specific metal and the characteristics of the sludge. The total metal concentrations in the Taman Sri Gombak sewage sludge sample were 2.68 mg kg^{-1} Cd, 73.29 mg kg^{-1} Pb, 2300 mg kg^{-1} Zn, 23.61 mg kg^{-1} Ni and 116 mg kg^{-1} Cu. However, the total concentrations of heavy metals in sewage sludge treated soil do not indicate the amounts that are available for plant uptake.

Overall, a higher percentage of all the heavy metals, except for Cu was obtained in the residual forms (*Fig.* 1). Sequential chemical fractionation of the sludge sample showed that extractable Cd occurred mainly in the residual form (34%), followed by the exchangeable form (24%), as well as in the carbonate, Fe-Mn oxides and organic form. Similarly, Pb occurred mainly in the residual form (84 %), followed by exchangeable form (9%). According to Silviera and Sommers (1977), higher exchangeable Pb was obtained in air-dried sewage sludge than in wet sewage sludge. High Zn content in the residual form (43%) was obtained and followed by Fe-Mn oxides (27%). As most of the Zn was adsorbed on the surfaces of hydrous oxides of Fe and Al, they would probably co-precipitate with these compounds during sewage treatment (Sommers, 1977). Nickel occurred in the residual form (55%), followed by carbonate form (22%). Copper (57%) occurred predominantly in the organic form. This is in agreement

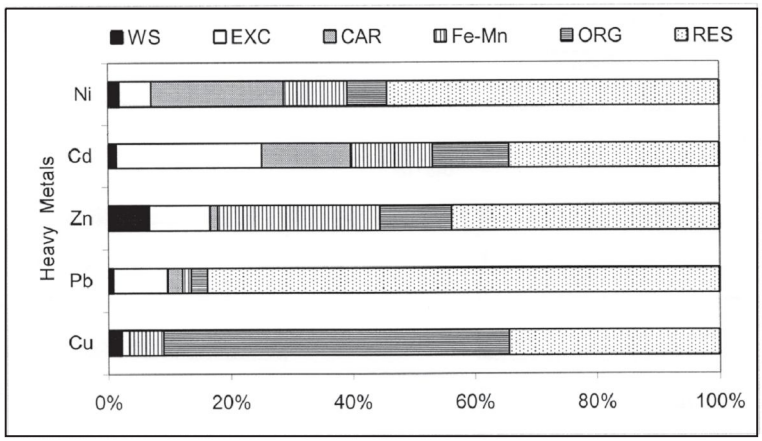


Fig. 1: Forms of Ni, Cd, Zn, Pb and Cu in sewage sludge

MJ of Soil Science 081-095.pmd 84 08-Apr-08, 10:49 AM

with the previous findings (Emmerich *et al*. 1982) where the major forms of Cu extracted were in the organically bound form. The order of Cu contents in the fraction is organic>residual>Fe-Mn oxide. It is similar to that reported by Schalscha *et al*. (1981) and is consistent with the known affinity of Cu for organic matter ligands. Generally, the percentage of water-soluble metals in sludge is approximately proportional to the total amount present (*Fig*. 1). This trend is especially apparent for Zn (7%), Cu (2 %) and Ni (2%) in the sludge studied. Water-soluble form of Cd and Pb made up only 1% of the total metal present as they might be attached to negatively-charged exchange sites or through relatively weak adsorption, and it is anticipated that this fraction would tend to be proportional to the total metal content present. Thus, the distribution of the metals in the sludge is variable, and this influences their behaviour after application to the soil.

Forms of Heavy Metals in Soil, Soil Applied with NH_4SO_4, and Soil Applied with Sewage Sludge

Table 1 shows the mean total heavy metals under investigation for the different treatments after the first and third maize cycles. Application of sewage sludge resulted in an increase in metal concentrations of the soil. The mean pH of the soil for the control treatment was 5.37 after the first maize cycle, increasing to 5.79 in the third cycle. For the soil applied with NH_4SO_4, the mean pH was 4.96 after the first cycle, remaining the same after the third cycle. Application of NH_4SO_4 resulted in increased soil acidity. This might have an effect on the water

TABLE 1
Mean total concentration of heavy metals (n=5) for the different treatments after the first and third maize cycle

Treatment	Cycle	Cd	Cu	Ni	Pb	Zn
		mg kg^{-1}				
T1 – Inorganic fertiliser (NH_4SO_4)	After 1st maize cycle	0.60	7.96	9.20	18.04	12.44
	After 3rd maize cycle	1.24	6.56	10.04	21.40	15.00
T2- control	After 1st maize cycle	0.64	7.82	9.76	20.52	13.68
	After 3rd maize cycle	1.24	7.04	10.48	21.40	14.65
T3- 560kg N/ha sewage sludge	After 1st maize cycle	0.72	7.72	8.60	18.28	16.24
	After 3rd maize cycle	2.19	9.52	11.12	24.04	33.00

MJ of Soil Science 081-095.pmd 85 08-Apr-08, 10:49 AM

soluble and exchangeable fraction, which can be seen for Pb. There also seemed to be higher amounts of Zn associated with Fe-Mn oxide fraction in the inorganic fertiliser treatment compared to the control. Otherwise, in general, there is no significant difference between the different metal fractions of the inorganic fertiliser treatment compared to the control. Application of sewage sludge resulted in a slight increase in soil pH from 5.68 (first cycle) to 5.86 (third cycle).

Cadmium

For Cd, the increased application rates of sewage sludge increased its content in the soil in both the water soluble and exchangeable forms, whereas the residual forms had decreased (*Fig. 2a*). However, there was no difference in the exchangeable form of the first cycle (38%) and third cycle (37 %) treated with sewage sludge. According to Brummer (1986), the exchangeable form can be categorised as mobile and can be used to estimate the total available heavy metals.

Cd content was also high in the carbonate form. There was a significant difference ($p<0.05$) between the two cycles treated with sewage sludge. The usage of sewage sludge may have influenced the increase in Cd associated with the carbonate fraction in the soil. However, no significant differences between the treatments were found in the percentage of Cd associated with the carbonate fraction and the range was 21 – 24 %. Chlopecka (1993) showed that Cd added to soil as carbonate is relatively mobile in acidic conditions and within a few years or less, may change to the exchangeable form.

Lowest Cd content was found in the organic form. As Cd is loosely bound to organic matter, it could have been extracted at the first level of extraction. This is consistent with the low adsorption constant of Cd to organic matter and provides evidence that Cd does not appear to form strong organic complexes (Sposito *et al.* 1982; Keefer *et al.* 1984). Salas *et al.* (1998) reported a low presence of Cd in the soil organic matter of Tanashi series which was treated with sewage sludge. In an acid soil, organic matter and sesquioxides are important in controlling the solubility of Cd (Kabata-Pendias and Pendias 2002).

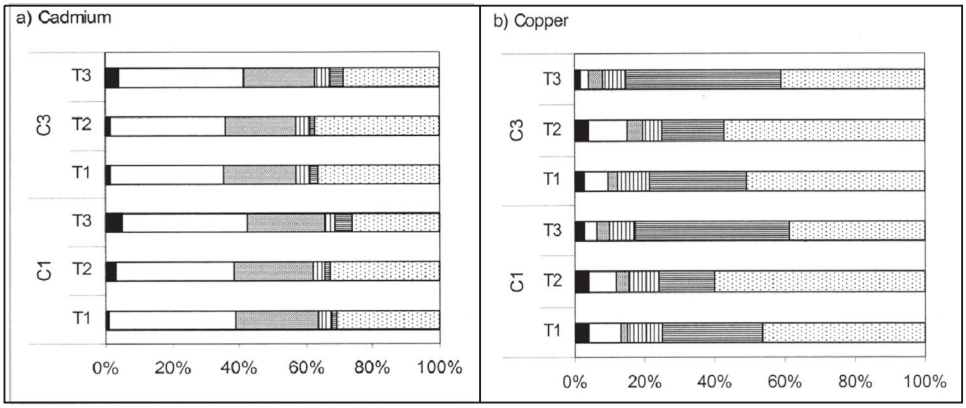
The exchangeable Cd was the dominant form in the sewage sludge. Furthermore, Cd was also dominant in exchangeable form in soils applied with sewage sludge. More Cd was in the exchangeable form than in the oxidised form, in which Cd was adsorbed on the surface of the clay and easily released (Hickey and Kittrick 1984; Tuin and Tels 1990). There was a significant difference ($p<0.05$) in exchangeable form between the inorganic fertiliser treatment and the control. Most of the soluble Cd might have shifted to other fractions and increased the percentage of exchangeable Cd. However, there was no geochemical change from sludge to soil amended with sludge between the first and third cycles. It also means that Cd is more easily available for plant uptake.

Copper

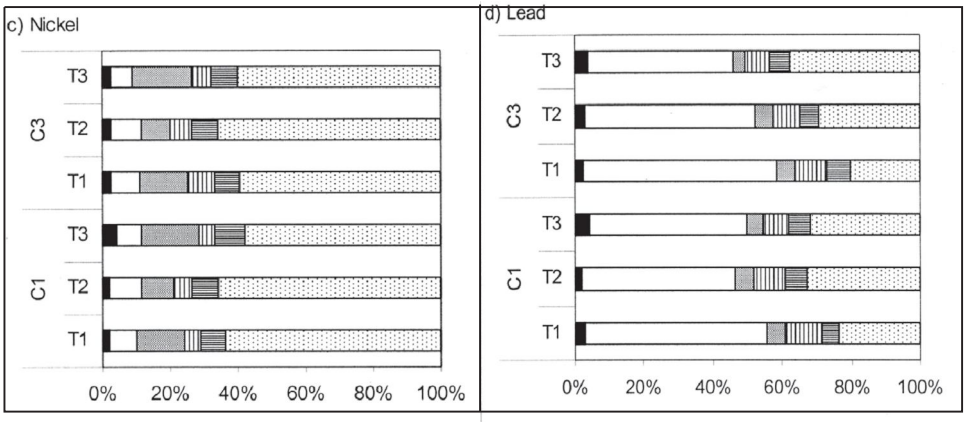
Overall, addition of the sludge increased with significant changes in all forms except for the residual fractions (*Fig. 2b*). A higher percentage of Cu in the

MJ of Soil Science 081-095.pmd 86 08-Apr-08, 10:49 AM

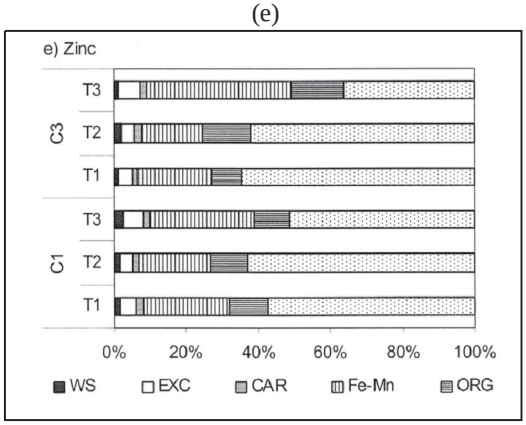
(a) (b)



(c) (d)



(e)



T1 - inorganic fertiliser , T2 – control (no fertilizer) , T3 – 28 t ha^{-1} sewage sludge

Fig. 2 (a-e): Forms of Cd, Cu, Ni, Pb and Zn in soil after first (C1) and third (C3) maize cycles

MJ of Soil Science 081-095.pmd 87 08-Apr-08, 10:49 AM

organic form was obtained in treatment with sewage sludge of both the first (43%) and third crop cycle (45%) compared to other forms. This might be attributed to the fact that soluble organics from the decomposition of the sludge solids had a greater affinity for Cu ions. The 2% increase in organic form between the crop cycles indicate that the distribution pattern of heavy metals extracted by sequential extraction procedure depended on heavy metal fractionation, the qualities and the application rates of sewage sludge. This is in agreement with previous findings (Salas *et al.* 1998; Robert *et al.* 1995) which also reported Cu associated with organic fraction to be the dominant form. Between the crop cycles, there were no difference in water-soluble Cu and no trend was found based on the different treatments. This suggests that these forms of Cu have been removed by plants and/or have leached from the surface soil profile, while that remaining behind have transformed to the less readily soluble form.

The sewage sludge treatment gave the highest concentration of Cu associated with the organic fraction and also increased after the third cycle. In the third cycle, there was no significant difference between the inorganic fertiliser treatment and the control. The contamination of control plots with sewage sludge through surface run-offs could have contributed to this situation. The most frequent chemical form of heavy metals in sewage sludge-treated soils was the organically bound form (Chang *et al.* 1984). However, this study showed that the organically bound form or of heavy metals in soil was relatively low, except for Cu. This result also shows that the chemical forms of heavy metals may depend on the soil characteristics and experimental conditions.

After the third crop, the water-soluble and exchangeable forms in the soil treated with sewage sludge had decreased. Water soluble Cu decreased with time from 3 to 2% and 4 to 2% for the exchangeable form. Possible explanations for the decrease in water soluble and exchangeable Cu are (i) formation of stable complexes between Cu and soil organic matter, (ii) sorption by hydrous oxides in soil, and (iii) formation of precipitates (Silviera and Sommers, 1977). Thus, the mobility and bioavailability of Cu may be controlled by the binding of Cu to soluble organic matter (Kabata-Pendias and Pendias 2002).

Copper in the organic form was dominant in both sewage sludge and soils treated with sewage sludge. No transformation of Cu in the sludge to soil amended with sludge was obtained between first and third cycles. The dominant forms of Cu in both the crop cycles were the residual and organic forms (*Fig. 2b*). The residual forms played little role in the soil chemical reactions. The residual form is the heavy metals bound to mineral lattice and can be considered the inactive fraction in terms of chemical processes in the soil. The residual form is divided into two types: (a) heavy metal found in between the mineral layers; (or b) specifically adsorbed on the edge of the clays' layers and unable to be extracted by reagents (Calvet *et al.* 1989). According to Brummer (1986), the organic and residual forms are stable in the soils and not available to plants.

MJ of Soil Science 081-095.pmd 88 08-Apr-08, 10:49 AM

Nickel

The dominant form of nickel is residual, followed by carbonate form, exchangeable form, organic form and water-soluble form. There was significant increase in the concentration of the carbonate form and organic forms of Ni in the sludge-treated soils (*Fig. 2c*). Ni associated with the carbonate fraction is higher than Ni associated with the organic fraction. In terms of the total Ni (sum of all fractions), there was a decrease in the percentage of residual Ni but an increase in the organic and carbonate fractions as a result of sludge application. It appears that Ni carbonate and to some extent organic Ni, were the principal chemical forms of Ni that were formed after sludge application.

The concentration of exchangeable Ni of sewage sludge treatments in both the first and second treatments, were 8% and 7%, but there was no significant difference compared to the control treatment. It is possible that the sewage sludge did not influence the concentration of exchangeable Ni. Overall, the sewage sludge application had increased all the Ni forms in both the first and third cycles. Though Ni associated with the carbonate fraction is the dominant form, its percentage is not more than 20%. Nickel in the carbonate form was dominant in both the sewage sludge and soils treated with sewage sludge. Thus, there was no transformation of geochemical form from sludge to soil amended with sludge in the first and third cycles. This may suggest that liming did not strongly influence the increase of Ni in the carbonate form as sewage sludge contains a high concentration of Ni-CO_3.

Lead

Lead was surprisingly dominant in the exchangeable form in all the treatments for both crop cycles. This was followed by the residual form, Fe-Mn oxide, carbonate form and water soluble form (*Fig. 2d*). Normally, in highly weathered soils, Pb can form carbonates and is also incorporated into clay minerals, in Fe and Al hydroxides, Mn oxides and in organic matter (Kabata-Pendias and Pendias 2002). The content of Pb in exchangeable form has exceeded 50 %. However, there was no significant difference between the sewage sludge treatment compared to the inorganic and control treatment in the first cycle. In the third cycle, the organic treatment exhibited the highest exchangeable Pb. There was significant difference between sewage sludge treatment and control. This makes it difficult to explain why Pb extracted from sludge-treated or control soils were not taken up by the maize plants in sufficiently high amounts (for details, refer to Part II of the paper (Rosazlin *et al*. 2006)). Indeed, there is more general evidence to suggest that Pb is very immobile in the soil-plant pathway (Koeppe 1981). Pichtel and Anderson (1996) reported Pb in composted sewage sludge to be dominant in the carbonate form. Other findings reported Pb to be dominantly associated with the oxide fraction (Sposito *et al*. 1982; Dudka and Chlopecka 1990).

There was significant difference between the Pb water-soluble form in soil amended sludge compared to the control and inorganic fertiliser for the first and

MJ of Soil Science 081-095.pmd 89 08-Apr-08, 10:49 AM

third cycles. The results obtained suggest that the presence of Pb did not influence the forms of Pb in all treatments. The presence of Pb may not be due to the usage of sewage sludge. A factor such as parent material may have contributed to the Pb content in Oxisol or the red soil of the tropics. This is in agreement with previous studies (Wan Noridah 2000) where soils applied with sewage sludge showed no influence on the forms of Pb. The exchangeable form of Pb was dominant in both sewage sludge and soils amended with sewage sludge. However, no shift in the geochemical form from sludge to soil amended with sludge between the first and third cycles was observed in this study.

Zinc

Based on the results obtained (*Fig. 2e*), the dominant geochemical form of Zn is the residual form followed by Fe-Mn oxide after the first and third maize cycles. This is in agreement with previous findings (Iyenger *et al*. 1981). This may indicate the presence of a strong interaction between the metals derived from sludge and soil metal components which leached out of the soil. The Fe-Mn oxide bound Zn was higher than the other metals in the sludge treated plots. Several researchers also reported higher Zn in the form of Fe-Mn oxide (Tessier *et al*. 1979; Hickey and Kittrick *et al*. 1984; Tuin and Tels 1990; Krishnamurty *et al*. 1995). Zinc was also present in the forms of organic, exchangeable and water-soluble in the order: residual > Fe-Mn oxide > organic > exchangeable > water soluble.

The amount of Zn in the form of water-soluble is not more than 1%. However, the water-soluble Zn in the sewage sludge treatment has increased in both crop cycles. Lindsay (1972) reported that the solubility of Zn in soil solutions increased 100-fold for each unit decrease in pH. Therefore, a unit decrease in pH after addition of the sludge could be responsible for the increase in water soluble Zn. Zinc may also have been released from organic complexes during the decomposition of organic matter in the sludge.

In the long-term, Zn in the form of Fe-Mn oxide increased with application of sewage sludge. A 10 % increase of Zn associated with Fe-Mn oxide fraction from 29% of total Zn after the first crop cycle to 39% after the second cycle was obtained. This increase was significant for both inorganic and control treatments. This shows that sewage sludge addition could greatly affect Zn concentration in the soil. It could be concluded that pollutant inputs of Zn may have been in both residual and Fe-Mn Oxide forms. Even though the trend is less clear compared with Cd and Pb, it is possible that mobilised Zn becomes more strongly associated when adsorbed onto Mn (Loganathan *et al*. 1977) or iron and aluminium hydrous oxide surfaces (Shuman 1977).

Zinc in the Fe-Mn oxide extractable form in the first cycle was 24% in the inorganic fertiliser treatment, 20% in the control and 29% in the sewage sludge treated soil. In the third cycle, the percentage was 21% in the soil with the inorganic fertiliser, 17% in the control soil and 39% in soil treated with sewage sludge. This increase was significant in sewage sludge treated soil. This indi-

MJ of Soil Science 081-095.pmd 90 08-Apr-08, 10:49 AM

cates that sewage sludge has a strong influence on Fe-Mn oxide form. According to Miller *et al*. (1986), organic matter and oxides of Fe and Mn are the main components that hold heavy metals. It appears that Fe-Mn oxide was the dominant form in both sewage sludge and soils treated with sewage sludge. Results showed a shift from residual form (first cycle) to Fe-Mn oxide form (third cycle) for the soil amended with sludge (*Fig. 2e*).

Correlation Study

Research on the possible adverse effects of heavy metal accumulation in agricultural soils amended with sewage sludge has focused on the available form of these heavy metals in relation to their uptake by plants (Silviera and Sommers 1977). The heavy metal contents of sludge constitute less than 1% of the dry weight of the sludge solids. But long-term applications may significantly increase the heavy metal contents of soils that could persist for several years (Kirkham 1975). Total heavy metals content of plants is influenced by many factors.

Significant correlation ($p<0.05$) was obtained between Cd in grains with the organically bound Cd in the soil (Table 2). No significant correlation was obtained between Cd in other forms with content in grains of maize. There was no significant difference between all forms of Zn and the content of maize crops. The types of extracting solutions might have contributed to this correlation. Previous findings suggest apositive correlation between Zn concentration in roots and Zn bound with Fe-Mn oxide. Furthermore, Zn in the form of Fe-Mn oxide is more available for plant uptake (Zhang *et al*. 1998). Positive correlations were found between water-soluble, exchangeable and organic Zn in the plant tissues. This is in agreement with previous findings (Rupa and Shukla 1999). However, Reneau *et al*. (1990) reported negative correlation because Zn in soils is not easily transported into the plant because of migration characteristics despite presence of a high content of heavy metals in soils.

TABLE 2
Correlation coefficient (r) between heavy metals in the soil after the first and third maize cycles and heavy metals content in the maize grain (n=30)

Element	Water soluble	Exchangeable	Carbonate bound	Fe-Mn Oxide	Organic bound	Residual	Total Metal
Cd	0.1515	0.2763	0.2690	0.1207	0.3779*	0.0005	0.0299ns
Pb	-0.0105	-0.0837	-0.2899	-0.1514	0.2350	-0.0394	0.1173ns
Zn	0.2356	0.1778	0.2783	0.2745	0.1051	0.0612	0.0814ns
Ni	0.3047	-0.0800	0.3091	-0.2849	0.0922	-0.0291	0.4059*
Cu	0.0565	-0.2354	0.4746**	0.5392**	0.5452**	0.2887	0.1402ns

ns - not significant
* - significant at $p<0.05$
** - significant at $p<0.01$

MJ of Soil Science 081-095.pmd 91 08-Apr-08, 10:49 AM

In the case of Cu, the organically bound forms in soils were positively correlated with the Cu concentration in the maize grains. A higher portion of organic form in the soils was also observed compared to other heavy metal fractions. Significant correlation ($p<0.01$) was obtained for Cu in grains with carbonate and Fe-Mn oxide forms.

The heavy metal concentration of Pb in the maize grains was negatively correlated with all the chemical forms of Pb in the soil, indicating non-availability of Pb for plant uptake.

There was significant correlation ($p<0.05$) between Ni in grain with total Ni in the soil. The total concentrations of heavy metals in soil do not indicate the amounts that are available for plant uptake (Srikanth and Reddy 1991). Chukuma (1993) observed that the total concentrations in the leaves of bilinga (*Nauclea popeeguinei L.*) and cogongrass (*Imperata cylinderica L.* Beauv.) did not reflect total concentrations of the elements in the soil, suggesting a gap between bioavailable forms and total soil concentrations of the elements.

CONCLUSIONS

A fractionation study of sewage sludge showed that for all the heavy metals determined (Cd, Pb, Ni and Zn), the most dominant form was the residual form, except for Cu. The residual form is the heavy metals bound to mineral lattices that can be considered as the inactive fraction in terms of chemical processes in the soil. As for relatively more active fractions, Cd and Pb were mostly in the exchangeable form. Nickel was dominant in the carbonate form, Cu dominant in the organic form, while Zn was bound to the Fe-Mn oxides.

In general, there is no real difference between the different metal fractions of the inorganic fertiliser treatment compared to the control except for exchangeable Pb and Zn associated with the Fe-Mn oxide fraction. No shift in the geochemical forms of sludge to soil amended with sludge was observed for all the metals except for Zn. The application of sewage sludge tended to shift the solid phase forms of the metals away from those extractable with aqua-regia (residual fraction) to those extractable with hydroxylamine hydrochloride and acetic acid mixture (Fe-Mn oxide fraction). From the fractionation data and total elemental analyses from the first and third maize cycles, Cu and Zn increased with addition of sewage sludge. On the other hand, Cd, Pb and Ni did not show an increase in trend from the first to third cycles.

From the correlation study, relationships were found between Cu in grain and the carbonate, Fe-Mn oxide and organic bound Cu in soil. Meanwhile, Cd content in maize grain showed a positive correlation with organic bound form. Ni content in maize grain showed a positive correlation with total metal in soil. There was no correlation between Zn and Pb content in maize grain with these metal fractions in the soil. It can be concluded that the sequential extraction scheme that was used in this study revealed clear differences between the geochemical forms of metals in sludge-treated and inorganic fertiliser–treated soil and control.

MJ of Soil Science 081-095.pmd 92 08-Apr-08, 10:49 AM

ACKNOWLEDGEMENTS

We would like to express our sincere gratitude to Indah Water Konsortium Sdn. Berhad (IWK) for their generous funding of this project, UPM for giving us the permission to carry out this study and the staff of Soil and Plant Analytical Section, Department of Land Management, UPM for their assistance in the laboratory analyses.

REFERENCES

Brummer, G.W. 1986. Heavy metals species, mobility and availability in soils. In *The Importance of Chemical 'Speciation' in Environment Processes*, ed. M. Bernard, F.E. Brinckman and P.J. Sadler, pp. 169-192, Dahlem Konferenzen. Berlin, Heidelberg: Springer-Verlag,

Calvet, R., S. Bourgeois and J.J. Msaky. 1989. Some experiments on extraction of heavy metals present in soils. *J. Environ. Anal. Chem*. **39:** 31-45.

Chang, A.C., A.L. Page, J.E. Warneke and E. Grgurevic. 1984. Sequential extraction of soil heavy metals following a sludge application. *J. Environ. Qual*. **13:** 33-38.

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.

Chlopecka, A., J.R. Bacon, M.J. Wilson and J. Kay. 1996. Forms of cadmium, lead, and zinc in contaminated soils from Southwest Poland. *J. Environ. Qual*. **25:** 69-79.

Chukuma, C. 1993. Cadmium, lead and zinc form terrestrial plants in Enyogba-Abakaliki lead and zinc mine. Search for a monitoring plant species in trace element distribution. *Bull. Environ. Contam. Toxicol.* **51**: 665-671.

Dudka, S. and A. Chlopecka. 1990. Effect of solid-phase speciation on metal mobility and phytoavailability in sludge-amended soil. *Water Air Soil Pollut.* **51**: 153-160.

Emmerich, W.E., L.J. Lund, A. L. Page and A.C. Chang. 1982. Solid phase forms of heavy metals in sewage sludge-treated soil. *J. Environ. Qual.* **11**: 178-181.

Hickey, M.G. and J.A. Kittrick. 1984. Chemical partitioning of Cd, Cu, Ni and Zn in soil and sediment containing high level of heavy metals. *J. Environ. Qual.* **13**: 372-376.

Iyengar, S.S., D.C. Martens and W.P. Miller. 1981. Distribution and plant availability of soil zinc fractions. *Soil Sci. Soc. Am. J*. **45**: 735-739

Kabata-Pendias, A. and H. Pendias (eds.). 2002. *Trace Elements in Soils and Plant*. 3rd ed. Boca Raton, Florida, USA: CRC Press

Keefer, R.F., E.E. Codling and R.N. Singh. 1984. Fractionation of metal organic components extracted from a sludge-amended soil. *Soil Sci. Soc. Am. J.* **48:**1054-1059.

Kirkham, M.B. 1975. Trace elements in corn grain on long term sludge disposal site. *Environ. Sci. Technol.* **9**: 765-768.

Koeppe, D.E. 1981. Lead: Understanding the minimal toxicity of lead in plants. In *Effect of Heavy Metal Pollution on Plants,* Vol. 1: *Effect Trace Metals on Plant Function,* ed. N.W. Lepp, pp. 55-76. London: Applied Science Publishers.

MJ of Soil Science 081-095.pmd 93 08-Apr-08, 10:49 AM

Krishnamurti, G.S.R., P.M. Huang, K.C.J. Van Rees, L.M. Kozakand and H.P.W. Rostad. 1995. Speciation pf particulate-bound cadmium of soils and its bioavailability. *Analyst*. **120**: 659-665.

Lindsay, W.L. 1972. Inorganic phase equilibria of micronutrients in soils. In *Micronutrients in Agriculture*, ed. J.J. Mortvdt, P.M. Gioradano and W.L. Lindsay, pp. 41-57. Madison, Wisconsin: Soil Sci. Soc. Am.Proc.

Loganathan, P., R.G. Duran and D.W. Fuerstenan. 1977. Influence of pH on sorption of Co2+, Zn2+ and Ca2+ by a hydrous manganese oxide. *Soil Sci. Soc Am. J*. **41**: 57-62.

Miller, W.P., D.C. Martens and L.W. Zelazny. 1986. Effect of sequence in extraction of trace metals from soils. *Soil Sci. Soc. Am. J.* **50**: 598-601.

Page, A.L., A.C. Chang, G. Sposito and S. Mattigod. 1981. Trace elements in wastewater, their effects on plant growth and composition and their behavior in soils. In *Modelling Wastewater Renovation, Land Treatment*, ed. I.K. Iskander, pp. 182-222. New York: John Wiley & Sons.

Pichtel, J. and M. Anderson. 1996. Trace metal bioavailability in municipal solid waste and sewage sludge composts. *Biores. Technol*. **60**: 223-229.

Reneau, R.B., D.F. Berry and D.C, Martens. 1990. Fate and transport of selected pollutants in soil. *Interntl. Symp. Environ. Pollut. Aric.*, pp.14-44. Institute of Agricultural Science and Development, College of Agriculture, Seoul National University.

Robert W.T., He Xiu, A.M. Ahmed, J.W. Shuford and W. Tadesse. 1995. Fractionation of residual cadmium, copper, nickel, lead and zinc in previously sludge-amended soil. *J. Soil Sci. Plant Analysis.* **26 (13&14)**:2193-2204.

Rosazlin, A., I. Che Fauziah, A.B. Rosenani, and S. Zauyah. 2005. Domestic sewage sludge application to an acid tropical soil: Part I. Sludge as an N fertilizer for maize. *Malays. J. Soil Sci*. **9**: 39-52.

Rosazlin, A., I. Che Fauziah, A.B. Rosenani and S. Zauyah. 2006. Domestic sewage sludge application to an acid tropical soil. Part II. Heavy metals uptake by maize and accumulation in the soil. *Malays. J. Soil Sci*. **10**: 35-52

Rupa, T.R. and L.M. Shukla. 1999. Comparison of four extractants and chemical fractions for assessing available Zn and Cu in soils of India. Comm. *Soil Sci. Plant Anal.* **30 (19&20**):2579-2591.

Salas, F.M., M. Chino, S. Goto, T. Igarashi, H. Masujima and K. Kumazawa. 1998. Forms and distribution of heavy metals in soils long term applied with sewage sludge. J. ISSAAS. **4:** 64-98.

Schalsha, E.B., M. Morales, I. Vergara and A.C. Chang. 1981. Chemical fractionation of heavy metals in wastewater, solids and in soil. *Agrochimica*. **24**: 361-368.

Shuman, L.M. 1977. Adsorption of Zn by Fe and Al hydrous oxides as influenced by aging and pH. *Soil Soc. Am. J*. **41**:703-706.

Silviera, D.J. and L.E. Sommers. 1977. Extractability of copper, zinc, cadmium and lead in soils incubated with sewage sludge. *J. Environ. Qual*. **6**: 47-52.

MJ of Soil Science 081-095.pmd 94 08-Apr-08, 10:49 AM

Sommers, L.E. 1977. Chemical composition of sewage sludge and analysis of their potential use as fertilizers. *J. Environ. Quality*. **6**: 225.

Sposito, G., L.J. Lund and A.C. Chang. 1982. Trace metal chemistry in arid-zone fields amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd and Pb in solid phases. *Soil Sci. Am. J.* **46**: 260-264.

Srikanth, R. and S.R.P.Reddy. 1991. Lead, cadmium and chromium levels in vegetables grown in urban sewage sludge in India. *Food Chem.* **40**: 229-234.

Stumm, W. and J.J. Morgan. 1981. *Aquatic Chemistry*: *An Introduction Emphasizing Chemical Equilibria in Natural Waters.* 2nd ed. Town, Publisher????

Tessier, A., P.G.C. Campbell and M. Bissom. 1979. Sequently extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**: 38-44.

Tessier, A.P., G.C. Campbell and M. Biosson. 1979. Sequential extraction procedure for different soil clay fractions and goethite. *Geoderma* **34**: 17-35.

Tuin, B.J.W. and M. Tels. 1990. Distribution of six heavy metals in contaminated clay soils before and after extractive cleaning. *Environ. Tech.* **11**: 935-948.

Wan Noridah, W.A. 2000. Fractionation of heavy metals in sewage sludge treated soils. Final year project. Department of Soil Management, Faculty of Agriculture, Universiti Putra Malaysia, Malaysia

Yang, Z.Q. and M. Kimura. 1995. Solubility fractionation of Zn, Cu, and Cd in soils applied with sewage sludge and their potential availability to plant. *Environ. Sci*. **8 (4)**: 369-378.

Zhang, D., X. Shan and F. Li. 1998. Comparison of wo?? sequential extraction procedures for speciation analysis of metalsin soils and plant availability. *Soil Sci. Plant Anal.* **29(7&8)**: 1023-1034.

MJ of Soil Science 081-095.pmd 95 08-Apr-08, 10:49 AM