SOLID PHASE SPECIATION OF HEAVY METALS IN VERTICAL-FLOW CONSTRUCTED WETLANDS

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LIST OF ABBREVIATIONS

FAAS : Flammable atomic absorption spectrometer

FWS : Free water surface constructed wetlands

HFW : Horizontal-flow constructed wetlands

HRT : Hydraulic retention time

RC : Vertical-flow constructed wetlands for control purpose

RCP : Vertical-flow constructed wetlands spiked with the mixture of copper and lead

RCu : Vertical-flow constructed wetlands spiked with copper

RPb : Vertical-flow constructed wetlands spiked with lead

SSF : Subsurface flow constructed wetlands

VFW : Vertical-flow constructed wetlands

PENSPESIESAN LOGAM BERAT BAGI FASA PEPEJAL DALAM PAYA TIRUAN ALIRAN MENEGAK

ABSTRAK

Kajian ini bertujuan untuk mengkaji corak penspesiesan kuprum dan plumbum secara berasingan dan secara gabungan pada media sistem paya tiruan jenis aliran menegak. Empat unit paya tiruan berskala makmal yang berdimensi 64 cm (panjang) x 64 cm (lebar) x 82 cm (kedalaman) diisikan dengan batu kelikir (2.4 - 4.8 mm) sebagai media. Sistem paya tiruan ini yang ditanami dengan tumbuhan cattail (t*ypha latifolia*) terdedah kepada alam semula jadi dan menerima air buangan domestik dengan masa penahanan hidraulik 3 hari. Dua unit paya tiruan masing-masing diisikan dengan air buangan domestik yang mengandungi kuprum (10 mg/L pada peringkat pertama dan 15 mg/L pada peringkat kedua) dan plumbum (5 mg/L pada peringkat pertama dan 10 mg/L pada peringkat kedua). Paya tiruan yang ketiga diisikan dengan gabungan kedua-dua kuprum dan plumbum pada kepekatan yang sama dengan paya tiruan yang pertama dan kedua. Paya tiruan yang keempat digunakan sebagai kawalan. Kepekatan logam pada kedalaman media 0-15, 15-30, 30-45 dan 45-60 cm telah ditentukan melalui pengekstrakan secara langsung dengan menggunakan 65% HNO_3. Tatacara 5-peringkat berturutan digunakan untuk menentukan kepekatan logam sebagai pecahan tertukar ganti, karbonat, terturunkan, organik dan baki bagi kesemua paya tiruan. Keputusan menunjukkan bahawa kepekatan logam pada bahagian atas media sistem paya tiruan adalah lebih tinggi daripada bahagian bawah media. Didapati bahawa

SOLID PHASE SPECIATION OF HEAVY METALS IN VERTICAL-FLOW CONSTRUCTED WETLANDS

ABSTRACT

The objective of this study was to investigate the speciation patterns of copper and lead in the media of vertical-flow constructed wetlands treating the metals individually and in combination. Four laboratory-scaled constructed wetland units with dimensions 64 cm (length) x 64 cm (width) x 82 cm (depth) were filled with gravel (2.4 -4.8 mm) as the media and cattail (*Typha latifolia*) as the vegetation. The units were operated outdoors under batch conditions receiving domestic wastewater with a three-day hydraulic retention time. One unit was fed with domestic wastewater spiked with 10 mg/L copper during the initial stage and 15 mg/L copper during the later stage whereas the second unit was spiked with 5 mg/L lead initially and 10 mg/L later. The third unit was fed with domestic wastewater spiked with a combination of copper and lead with the same concentrations as the single-element units. The last unit was operated as a control. Metal concentrations of the media at 0-15, 15-30, 30-45, 45-60 cm depths were determined using direct extraction using 65% HNO_3 digestion. A five-stage sequential extraction procedure which identified the metals among five operationally defined fractions, namely, exchangeable, carbonate bound, reducible, organic bound and residual was used for all the wetland units.

The results showed that higher total concentrations of metals were obtained in the top layer of the media compared to the lower layer. Lower total metal concentrations were obtained for the media in the multi-element unit compared to those the single element reactor and this may indicate antagonistic effect. Based on the results of metal speciation, it was found that there was no depth effect on the metal speciation patterns. The reducible fraction was found to be the dominant fractions. However, at higher metal loading, there was an increase in the exchangeable and carbonate fractions indicated that the remobilization potential of the metals on the media has likewise increased.

1.0 INTRODUCTION

1.1 Constructed Wetlands

Constructed wetland (CW) system has been proven to be an effective low-cost treatment system which utilizes the interactive of emergent plants, microorganism and media in the removal of pollutants. It is capable of removing organic matter, nutrient and other pollutants simultaneously. For wastewater treatment, two types of CW, namely, free-water surface and subsurface flow, are generally used. In terms of flow format, horizontal flow is usually adopted though vertical-flow CW is gaining popularity. During the past few years, greater interest has been placed on constructed wetlands with vertical flow (Green *et al.*, 1998; Scholz and Xu, 2002).

1.2 Heavy Metals

Heavy metals are dangerous to living organisms because they possess a crucial property which differentiates them from other toxic components. They are not biodegradable in the environment (Tokalioglu *et al.*, 2000) and have the tendency to bio-accumulate in organisms. When it exceeds a certain level, it can become toxic or poisonous.

1.2.1 Residual and Non-residual Fractions

Dissolved metals from water that are transformed into solid state on the sediments are categorized as non-residual fractions whereas residual fractions on sediments refer to those solids containing trace metals that cannot be easily released except with the use of very strong acids such as hydrofluoric acid (HF). This is almost impossible under normal environmental conditions. Therefore, metals in non-residual fractions, which will dissolve again into the water body under various environment conditions, provide good study interest to environmental chemists and are important for the study of metal pollution in sediments.

There are a few techniques that can be applied to determine the concentration of the non-residual component. In an earlier research, the non-residual component was extracted using a single extraction. Both 0.5 M hydrochloric acid and 0.1 M hydrochloric acid were used to determine the non-residual heavy metals pollution in the biosphere (Nolting and Helder, 1991; Lim and Hooi, 1997). This extraction technique provides information on the basic theory of the quantity of metal trapped in the sediments. However, this is insufficient to explain the real situation i.e. how the metals came to be in the sediments and the factors that might have influenced the presence of these metals. Therefore, the non-residual fraction has been categorized according to their binding capability to the sediments, namely the speciation.

1.3 Metal Speciation

It has been widely recognized that the total dissolved metal concentration is a poor indicator of toxicity to aquatic and living organisms. The impacts of these metals are dependent on their speciation. Speciation is defined as different chemical and physical forms of an element existing in a sample. Different forms of the metal exhibit different toxicities, bioavailability and mobility in the environment and living organisms.

Metals are bound to different phases under different mechanisms, for example, metals that bind to the organic matter in the media are related to physical and chemical absorption, complexation and sedimentation. In order to differentiate the different phases, sequential extraction was recommended. Under this scheme, extractants are applied in order of increasing reactivity so that the successive fractions obtained correspond to metal association forms with lesser mobility (Hullebusch *et al.*, 2005). Practically, it is difficult to find one suitable reagent chemical that can release the theoretical fraction. In compromise, the metal fraction can be operationally defined as exchangeable, bound to carbonate, iron/manganese bound or reducible fraction and organic bound.

Capability for the metals in different fractions to be released to the environment is different. The following are the details for different fractions:

- Exchangeable fraction

In this fraction, the binding between metal and media is weak. Changes in ionic strength of the water are likely to affect the absorption-desorption resulting in the uptake or release of metals between the filter media and aqueous solution.

- Carbonate bound

Metals that are associated with filter media carbonates are sensitive to pH change. pH decrease caused metal carbonates to change into dissolved form.

- Iron/Manganese or reducible fraction

Metals in this fraction are unstable under reducing conditions and metal ions will be released to the dissolved form.

- Organic fraction

Metals that are bound to organic matter will degrade under oxidizing conditions. This results in the release of soluble metals.

The use of sequential extractions, although more time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals (Tessier *et al.*, 1979).

1.3.1 Sequential Extraction Method

There are a few types of sequential extraction procedures, including techniques recommended by Tessier *et al.* (1979), the Commission of the European Communities Bureau of Reference (BCR), based on techniques by Salomons and Forstner (1984), Towner (1984), Chester *et al.* (1985), Kersten and Forstner (1986) and Champanella *et al.* (1995). The differences between these techniques are the fraction stages, the chemical reagents used and the extraction conditions. As an example, the BCR scheme combines the carbonate and exchangeable fraction together into one fraction while Kersten and Forstner (1986) divide the Iron/manganese fraction into easily reducible and moderately reducible fractions.

Among these techniques, the most applied of the sequential extraction schemes were those recommended by BCR and the modified Tessier scheme. These two schemes are sufficiently repeatable and reproducible for application in fractionation studies. However, the BCR scheme seems to be of limited utilization to study anaerobic biofilms matrices (Hullebusch *et al.,* 2005). Therefore, the Tessier scheme is preferred.

These techniques present a series of different problems such as the low reproducibility especially with large particles and encapsulated pollutants

(Dahlin *et al.*, 2002), the error propagations (Koeckritz *et al.*, 2001), the strong influence of operative conditions (Ngiam and Lim, 2001), the effective selectivity of the extracting reagents (Nirel and Morel, 1990) and the re-adsorption of metals during extraction (Rendell *et al.*, 1980). However, this technique is still important for metal fractionation in order to predict metal mobility and bioavailability (Filgueiras *et al.,* 2004).

1.4 Literature Survey

Studies have been carried out on the removal of heavy metals from wastewater using constructed wetlands. Cheng *et al.* (2002) constructed twin-shaped vertical flow constructed wetlands and found that these systems were able to decontaminate the toxic metal species with final concentrations far below WHO drinking-water standards. Metal species were found accumulating mainly on the top layer and root of the vegetations.

Scholz and Xu (2002) concluded that the vertical flow constructed wetlands were able to remove the copper and lead. However, different design control parameters including macrophytes and filter media did not enhance the metals reduction significantly after operation for 1 year.

Revitt *et al.* (1997) studied the relative efficiencies of pollutants removal including five metals, Cd, Co, Cu, Zn and Pb of airport runoff in three different designs of pilot scale reedbeed treatment systems located at Heahthrow airport. In general, raff systems showed poorer metals removal efficiency when compared with free water surface and subsurface constructed wetlands for the water samples. Zn showed negative average removal efficiency by the raff systems but positive removal efficiencies of 43.8 % and 46.9 % for free water surface and subsurface constructed wetlands, respectively. Cu and Cd demonstrated consistent positive removal efficiency by all reedbeed systems. 59.6% Cd and 65.6% Zn were absorbed by *Typha* particularly in the root and rhizome area.

Scholes *et al.* (1998) assessed the ability of two constructed wetlands in UK in treating urban runoff. One which comprised a horizontal subsurface flow system and a free water surface system had better removal efficiency for most heavy metals investigated in dry weather condition: Cu (68 %), Pb (65 %), Cr (51 %), Ni (48 %), Cd (25 %), Zn (13 %), whereas the other free water surface system showed good metal removal efficiency for Cd (53 %), Ni (52 %) and Cr (43 %). The result was based on the water sample analysis. Sediment samples showed the 2 systems were capable of retaining the heavy metals present in varying concentrations and decreasing in the following order Zn> Pb > Ni > Cu > Cr > Cd.

Mungur *et al.* (1997) concluded that laboratory scale subsurface flow constructed wetlands planted with *Typha latifolia, Phragmites australis, Schoenoplectus lacustris* and *Iris pseudacorus* is an efficient sink for heavy metals. The results obtained in treating the surface runoff dosed metals showed removal efficiency ranging from 81.7 % to 91.8 % for Cu, 75.8 % to 95.3 % for Pb and 82.8 % to 90.4 % for Zn. The removal efficiency was tested based on water samples collected from the outlet at timed intervals and their loadings calculated.

Song *et al.* (2001) assessed the lead and zinc removal efficiency in eight laboratory-scaled horizontal-flow constructed wetlands with different flow rates, substrate composition and temperature. There was little variation in the percentage removal for those two heavy metals under the different operational conditions and substrates of each constructed wetland. An average 90 % removal of lead and 72 % removal of zinc was observed.

Nelson *et al.* (2004) studied the removal efficiency of a surface flow constructed wetland on storm water, which had a retention time of approximately 48 hours. Copper and mercury removal efficiencies were still very high, both in excess of 80% removal from the water after passage through the wetland system. Lead removal from the water by the system was 83 %, zinc removal was 60 % and nickel was generally unaffected.

Demchak *et al.* (2001) used four vertical-flow constructed wetlands to treat acid mine drainage in Pennsylvania. The removal efficiency for Fe was found to be more than 60 % and 30 % for Al.

There have been studies done on the removal and speciation of heavy metals in horizontal-flow constructed wetlands. Lim *et al.* (2003) reported that metals removal efficiency of over 99 % was achievable for wetland units treating Zn, Pb, Cd singly or Zn, Pb, Cd and Cu in combination provided the sorption capacity of the media was not exceeded. When treating the metals in combination, an antagonistic effect occurred significantly for Pb and Cd. Based on the metal speciation pattern, the study concluded that the wetlands system was capable of maintaining the ASV-labile metal species at a low level (< 10 %) before media exhaustion.

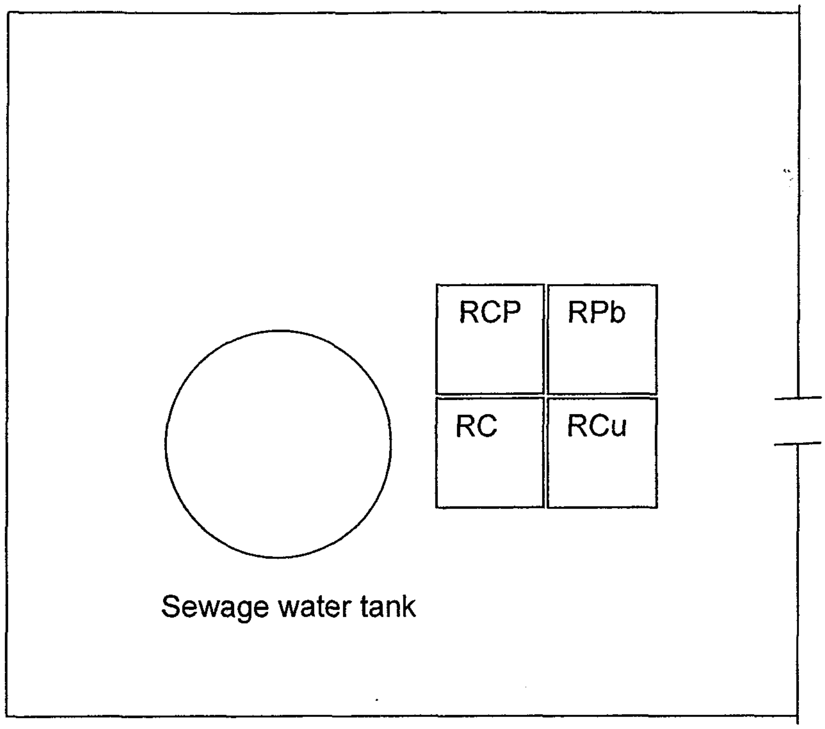

Figure 2.1 Layout Plan for the Experimental Set-up

Legend:

RCP	: VFW for mixture of copper and lead
RPb	: VFW for lead
RCu	: VFW for copper
RC	: VFW for control purpose

conditions. Four different depths of interest were studied for all the constructed wetlands. They were at 15, 30, 45 and 60 cm from the surface of the wetlands. Two heavy metals, copper and lead, were studied. Two VFW were reserved for copper and lead, respectively, another VFW for copper and lead in combination and the last VFW for control purpose. The experiment was divided into two operational stages, respectively, in order to investigate the effect of increasing metal concentrations on the metal speciation on the media.

Metal salts $Pb(C_2H_3O_2)_2$. $3H_2O$. and $CuSO_4.5H_2O$ were spiked into the domestic wastewater to give the concentrations of 5 mg/L lead and 10 mg/L copper, respectively, for the first stage and 10 mg/L lead and 15 mg/L copper, respectively, for the second stage.

2.2 Constructed Wetland Design

The VFW was made of fiber glass vessel with 0.5 cm thickness and was in a rectangular form with dimensions of 64 x 64 x 82 cm. Two PVC taps were installed on two opposite sides of the VFW at about 3.5 cm from the bottom of the VFW. These are used for the discharge of the wastewater. Five PVC tubes with a diameter of 6.5 cm and length of 75 cm were fixed vertically into each VFW. Holes with a diameter of 2 mm were bored randomly along the PVC tubes to ensure that the gravel inside the tubes was exposed to the wastewater just like the rest of the media. Figure 2.2 shows the top view and the cross-section of the VFW unit. The VFW was filled with gravel ranging in size from 2.4 to 4.8 mm. Cattail (*Typha latifolia*) plants used for this experiment were then planted. This cattail is commonly found and easily obtained from the marsh near Penang International Airport in Bayan Lepas.

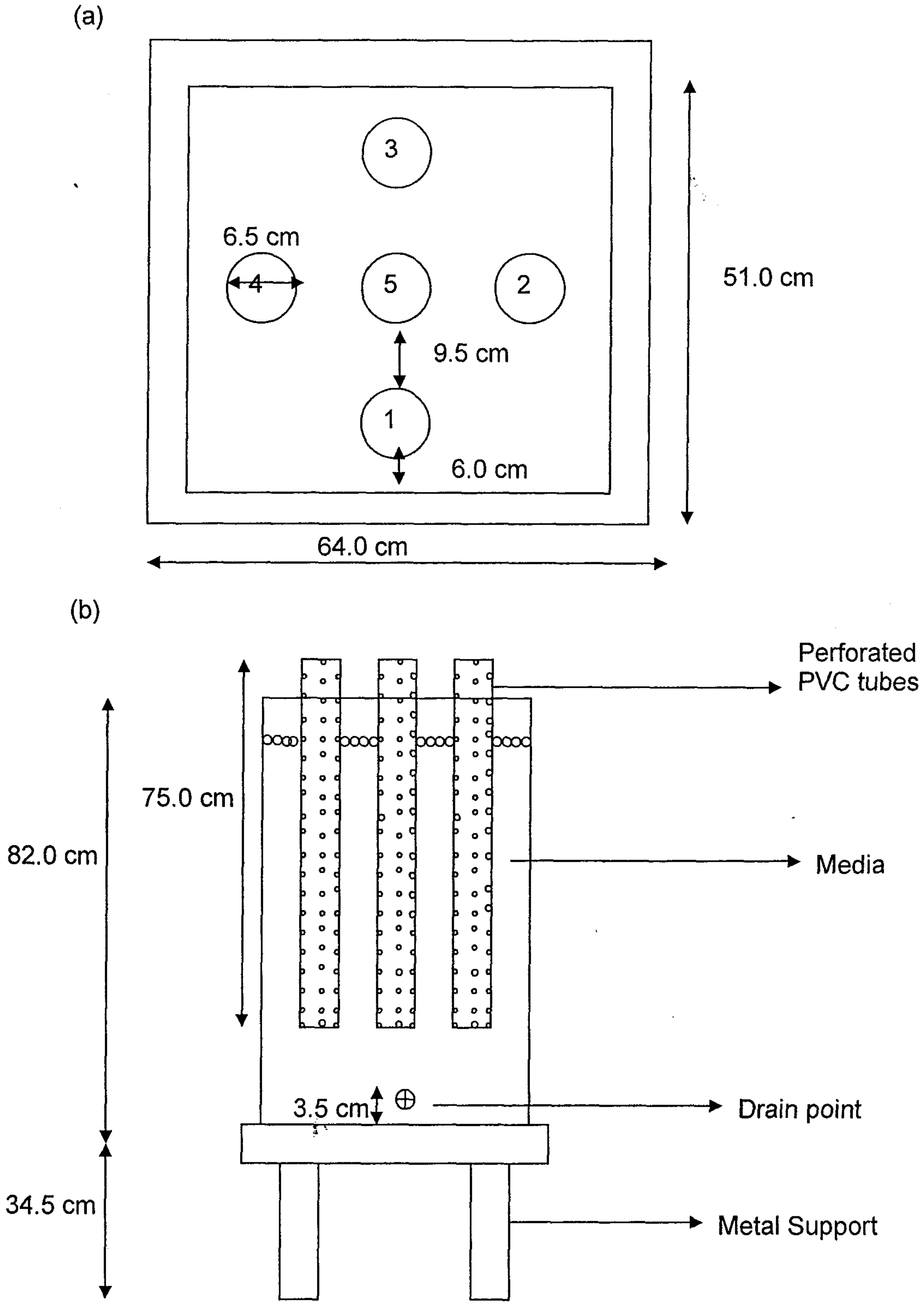

Figure 2.2: The VFW unit as viewed from (a) the top (b) the cross-section

2.3 Media Preparation

Gravels with size ranging from 2.4 mm to 4.8 mm were used. They were washed and soaked in 65% nitric acid overnight and cleaned twice with water. The gravels were then filled into the nylon net. The nylon net was cut and sewed with nylon rope and shaped into a long tube with a diameter of 4.5 cm and a length of 70 cm. When the cattail in the VFW had matured, the nylon net containing the gravels was inserted into the perforated PVC tube.

With the media and cattail plants in place, the porosity of the media was determined. This was done by filling up the VFW with tap water up to the media surface. The volume of tap water used was measured. The result showed that the volume of tap water needed was 65 L for all reactors.

2.4 Sample Collection and Preparation

After a period of two months, the gravels in the nylon netting from all the VFW units were collected. The nylon netting was pulled from the PVC tubes and the gravels were divided into four different segments, i.e. 0-15, 15-30, 30-45, 45-60 cm. The different segments were tied using plastic ropes. The nylon netting was then cut and the gravels from different segments were packed into labeled plastic bags. The plastic bags were sealed and stored inside the refrigerator. At the same time, nylon netting containing a new batch of gravels was put inside the PVC tubes.

Prior to the sequential extraction analysis, the gravels were dried at 100 ^0C overnight. Two 10.0 g replicate samples were weighted from each gravel sample. They were introduced into two different polystyrene containers. One was for sequential extraction and the other for total digestion. The sampling tube chosen for analysis was at position 2 and position 5 for every VFW unit (Figure 2.2a).

2.5 Sequential Extraction Procedure

The sequential extraction procedure was modified from Tessier *et al.* (1979) method. Heavy metals were extracted into 5 fractions. Figure 2.3 shows the flow diagram of this procedure.

2.6 Total Digestion

Exactly 20 mL of 65 % HNO_3 was added to the second set of dried weighted sample. The mixture was shaken at 250 rpm at room temperature for 8 h.

2.7 Heavy Metals Concentration Determination

The concentrations of copper and lead in the extracted samples were determined using flame atomic absorption spectrometer (Model: GBC 903). Prior to running the samples, standard solutions 1000 mg/L for calibration were prepared from the salts of $Pb(C_2H_3O_2)_2 . 3H_2O$ and $CuSO_4.5H_2O$, respectively, for lead and copper determinations.

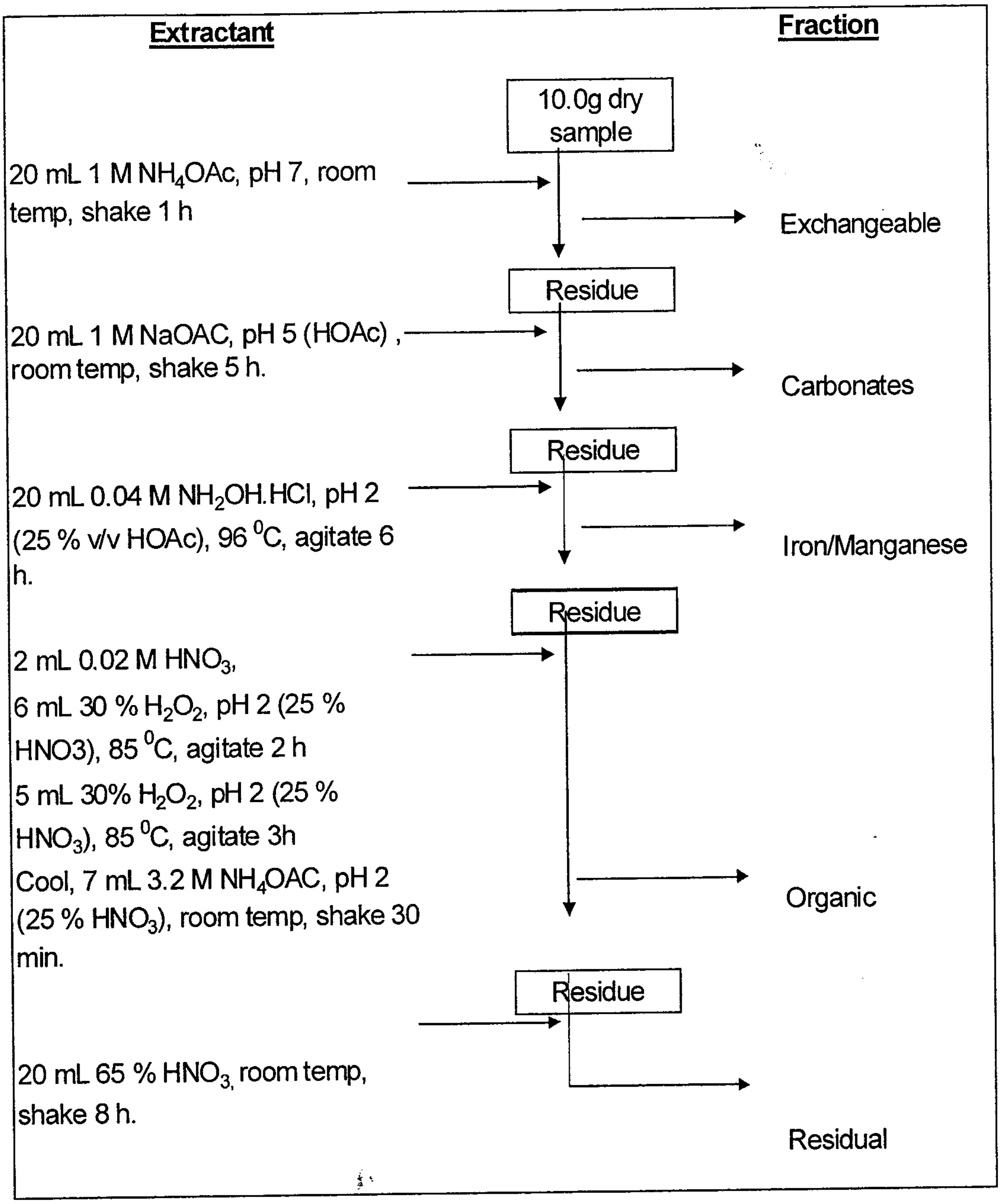

Figure 2.3 Flow diagram of the Sequential Extraction Procedure. (Tessier *et al.*, 1979)

the spiked Cu concentration was 10 mg/L and spiked Pb concentration was 5mg/L. CP5-2 denotes the media sample obtained from the sample tube at position 5 of the reactor RCP when the spiked Cu concentration was 15 mg/L and the spiked Pb concentration was 10 mg/L.

3.1.1 Copper

The wetland system, RCu, was fed with domestic wastewater spiked with Cu at 10 and 15 mg/L sequentially, each with a duration of two months. The total concentrations of Cu in the media C2 and C5 for lower and higher Cu concentrations are shown in Figure 3.1 The results for lower Cu concentrations in Figure 3.1 showed that a relatively higher total Cu concentration was observed in the top layer (0-15 cm) of the media at C5-1 as compared with other depths. In the top layer of the media, Cu concentration was found to be 45 μg/g and decreased to 30 μg/g in the bottom layer (45-60 cm).

For higher Cu concentrations, the same trend was observed. The Cu concentration for C2-2 and C5-2 in the top layer was found to be 80 μg/g and decreased to 50 μg/g in the bottom layer. The results indicated that the effect of media depth was more significant at high Cu concentration spiked into the wetland system.

3.1.2 Lead

In the wetland system fed with domestic wastewater spiked with Pb, RPb, the total concentrations of Pb in the media at P2 and P5 for lower and higher Pb concentrations are shown in Figure 3.2. The results showed that for lower Pb

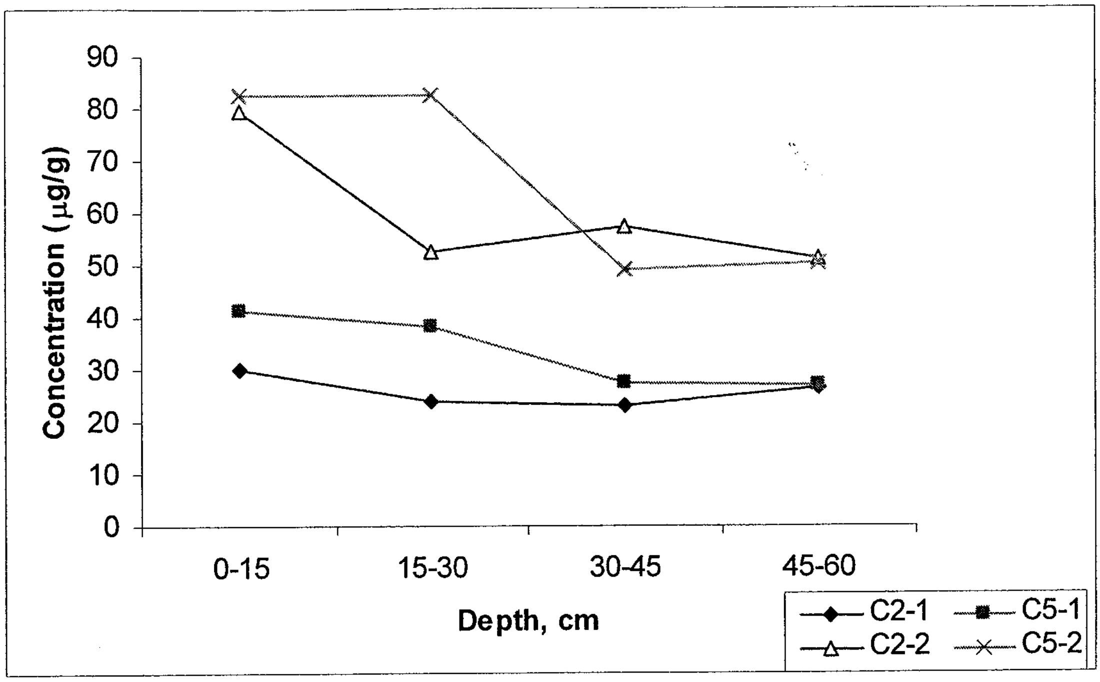

Figure 3.1 Total concentration of Cu at different media depth of RCu.

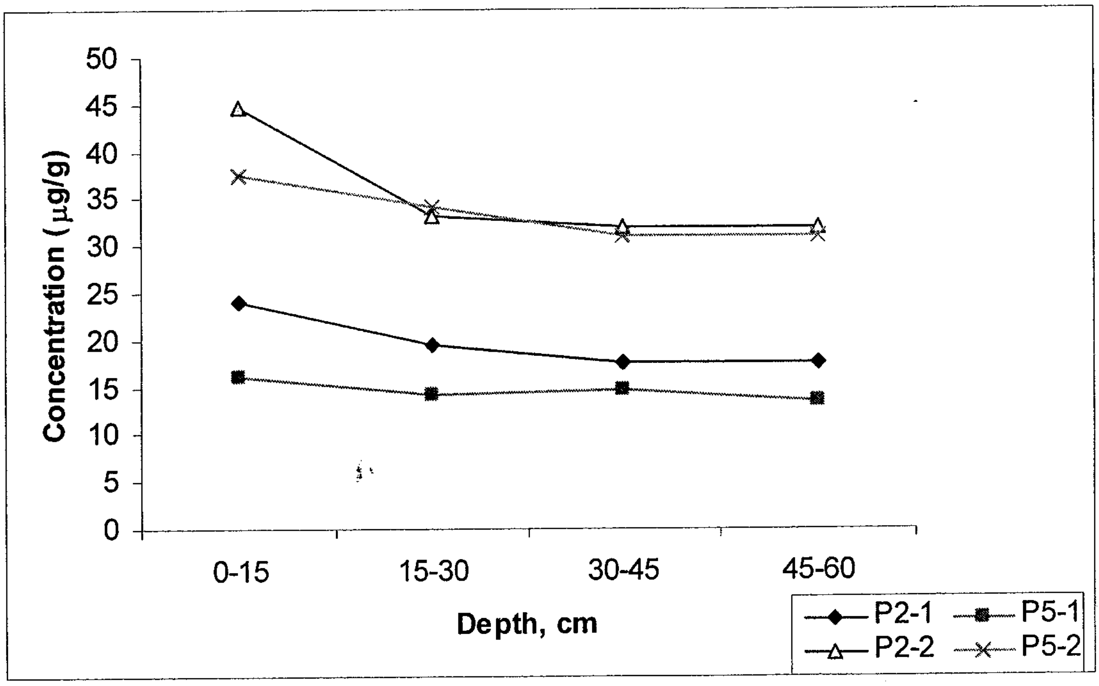

Figure 3.2 Total concentration of Pb at different media depth of RPb.

concentrations, the total concentration of Pb in the top layer of the media of P2-1 decreased from 25 μg/g to 17 μg/g. There was no change in total Pb concentration observed for P5-1.

For higher Pb concentrations, it was found that there was a decrease in the Pb concentration from the top layer to bottom layer of the media for both P2-2 and P5-2. The Pb concentrations for P2-2 and P5-2 in the top layer ranged from 38 – 45 μg/g and was found to be 30 μg/g in the bottom layer of the media.

3.1.3 Mixture of Copper and Lead

Figure 3.3 showed the total concentrations of Cu at different depths in the wetland unit RCP fed with domestic wastewater spiked with a mixture of Cu and Pb.

As can be seen in Figure 3.3, CP2-1 and CP5-1 showed neither an increase nor decrease in Cu concentration from the top layer to the bottom layer. The total Cu concentration at CP2-1 was found to be 15 μg/g and 25 μg/g at CP5-1, respectively. There was some variation observed for the Cu concentrations in CP2-2 and CP5-2. The results showed that higher Cu concentration was observed at CP5-2. It was found to be 90 μg/g at the top layer and decreased to 50 μg/g in the bottom layer whereas for CP2-2 the total Cu concentration was 60 μg/g in the top layer and decreased to 40 μg/g in the bottom layer of the media. Although some variation in concentration was observed for these 2 different sampling tubes, the same trend was observed.

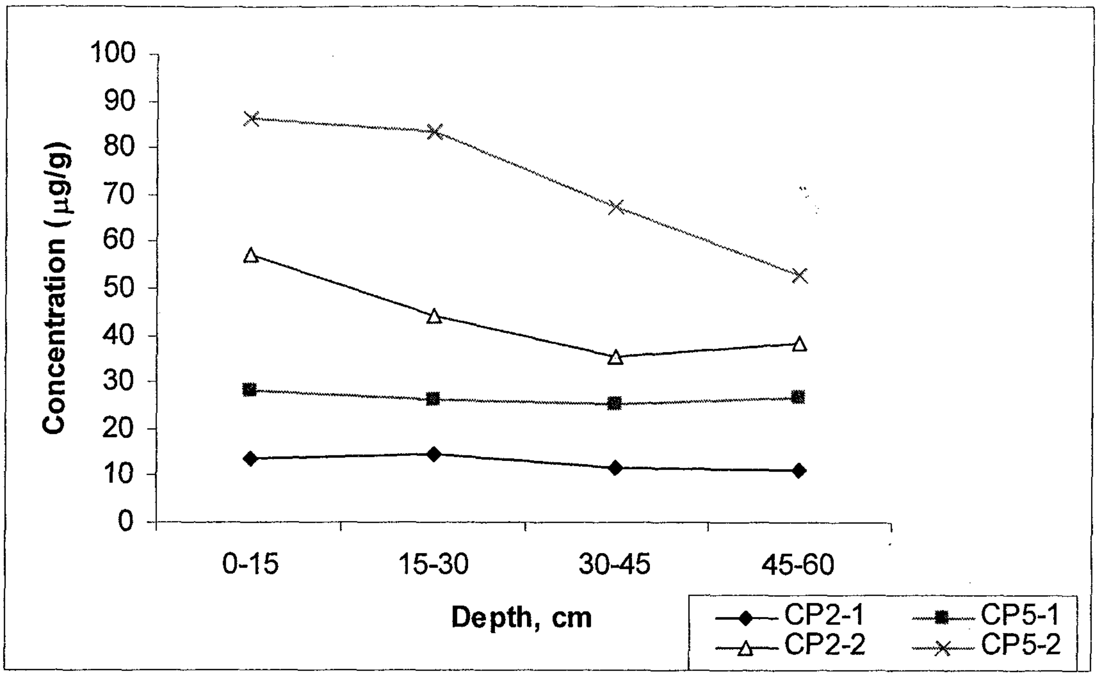

Figure 3.3 Total concentration of Cu at different depth of media in wetland units RCP.

The total concentrations of Pb at different depths in RCP are shown in Figure 3.4. The results showed the same trend as observed in Figure 3.3. It was found that the Pb concentrations at CP2-1 and CP5-1 ranged from15 µg/g to 20 µg/g regardless of the depths. A higher concentration of Pb at CP5-1 was observed. For lower metal concentration in RCu, RPb and RCP, no obvious trend in the total metal concentration was observed from the top to the bottom layer except for Cu, C2-1, C5-1 and P5-1. The effect of media depth was found to be significant when higher concentrations of Pb and Cu were spiked into the wetland systems.

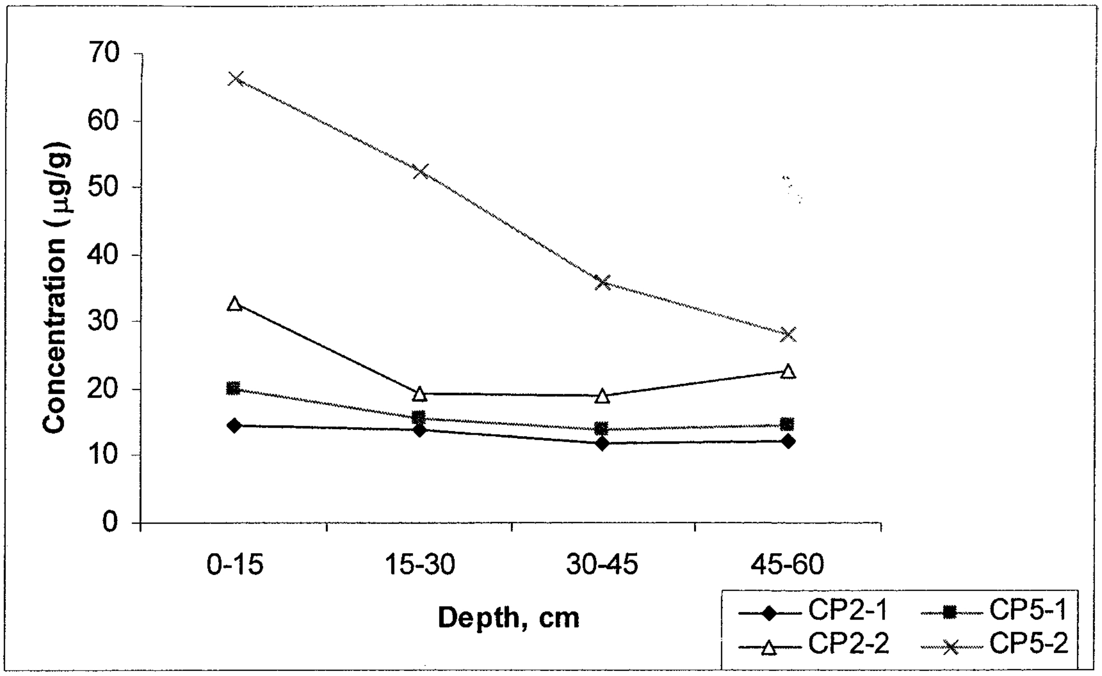

Figure 3.4 Total concentration of Pb at different depth of media in wetland unit RCP.

3.2 Speciation Patterns of Copper and Lead in Wetland Media

Metal speciation in the media was carried out using the sequential extraction technique. The speciation patterns of Cu at various depths for two different loadings are shown in Figures 3.5 and 3.6 whereas those of Pb are shown in Figures 3.7 and 3.8. The speciation patterns when the two metals were introduced simultaneously are shown in Figures 3.9 and 3.10.

3.2.1 Copper

Figure 3.5 showed that the Cu speciation patterns were similar at various depths for the two sampling positions with the reducible being the dominant

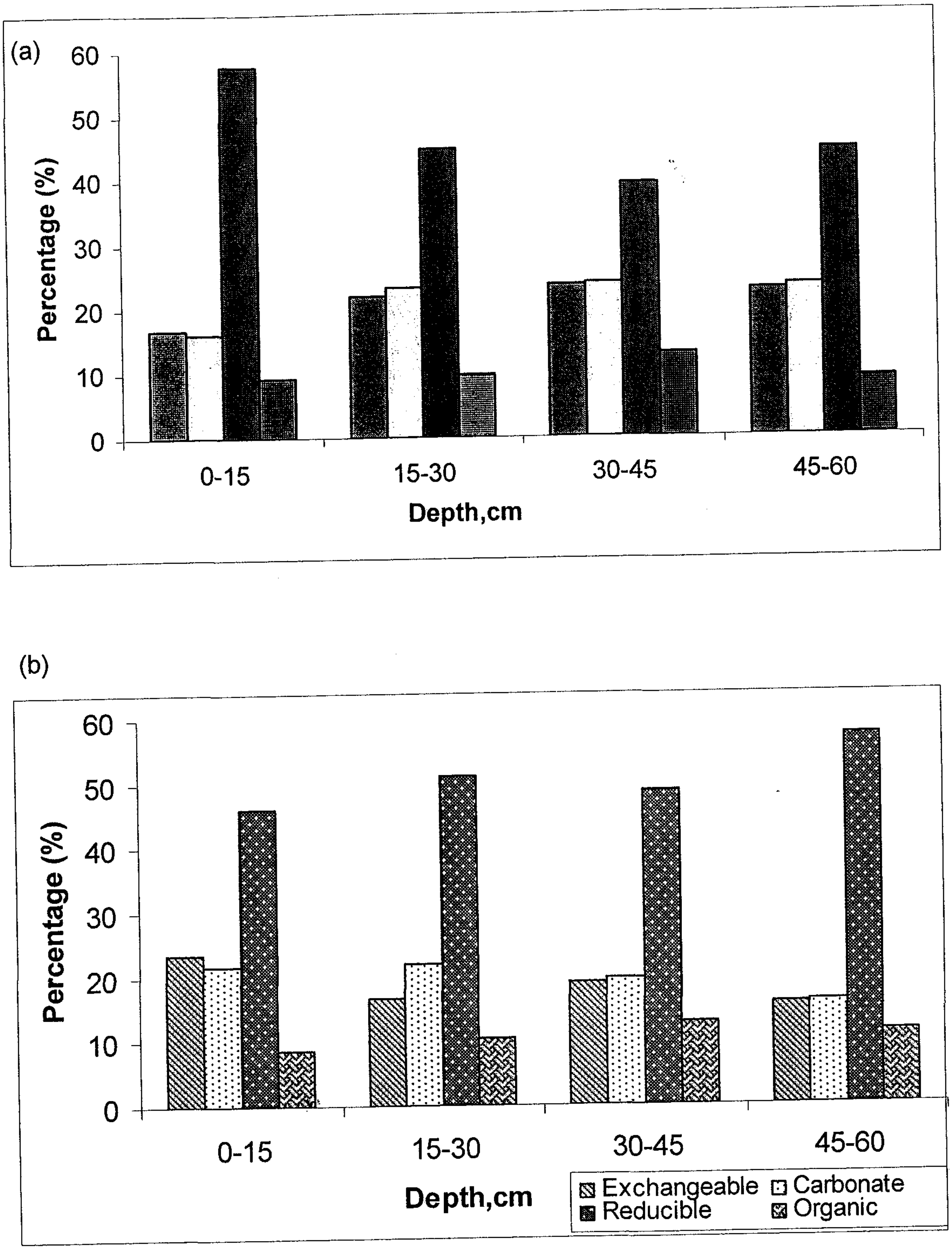

Figure 3.5 Cu speciation pattern at different depths in RCu spiked with 10 mg/L Cu at (a) sampling position 2 and (b) sampling position 5.

fraction. However, both the exchangeable and carbonate fractions seemed to have increased at higher metal loading (Figure 3.6).

3.2. 2 Lead

The results in Figure 3.7 showed that the Pb speciation patterns were similar except for the samples at 0-15 cm depth from position 2 and 45-60 cm depth from position 5. These may be due to experimental errors. The reducible and carbonate were the dominant fractions. The percentages of Pb associated with the reducible, carbonate, exchangeable and organic fractions were found to be 30-40, 30, 20-25 and 10 % respectively.

At higher Pb loading, a similar speciation pattern was also observed from the top to the bottom layer. The percentage of Pb associated with different fractions was as follows: carbonate (40 %), reducible (30 %), exchangeable (20-30 %) and organic bound (5-10 %).

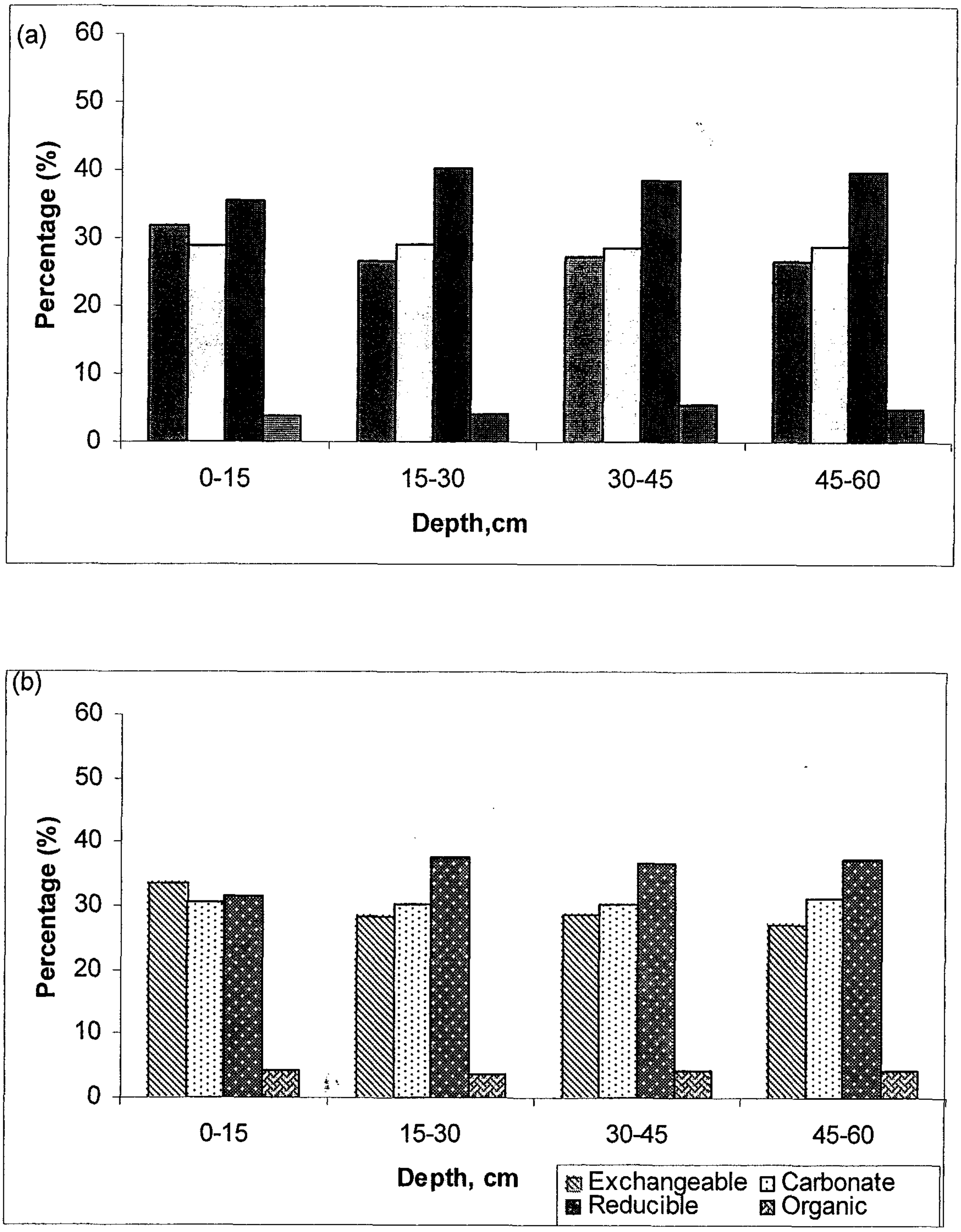

Figure 3.6 Cu speciation pattern at different depths in RCu spiked with 15 mg/L Cu at (a) sampling position 2 and (b) sampling position 5.

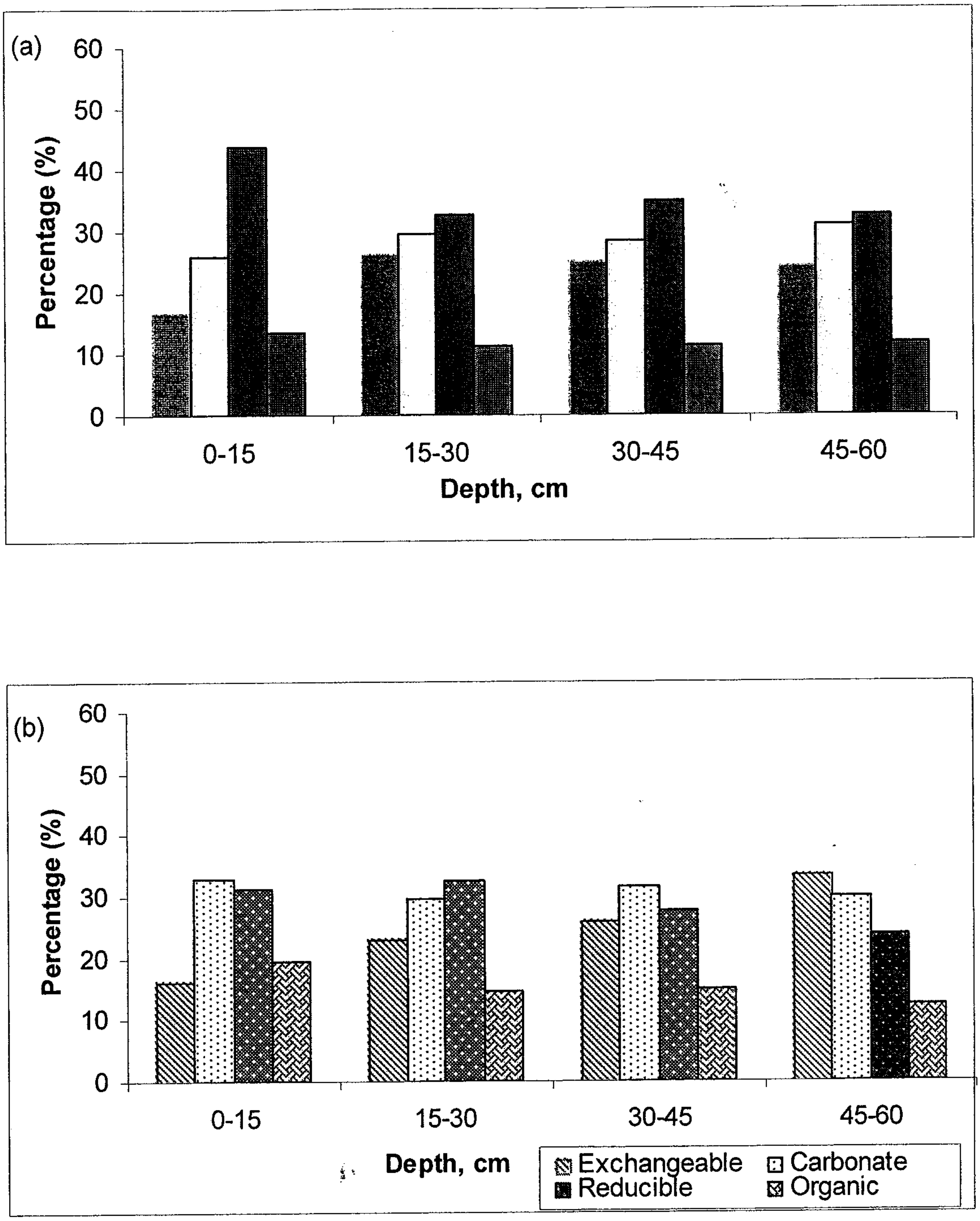

Figure 3.7 Pb speciation pattern at different depths in RPb spiked with 5 mg/L Pb at (a) sampling position 2 and (b) sampling position 5.

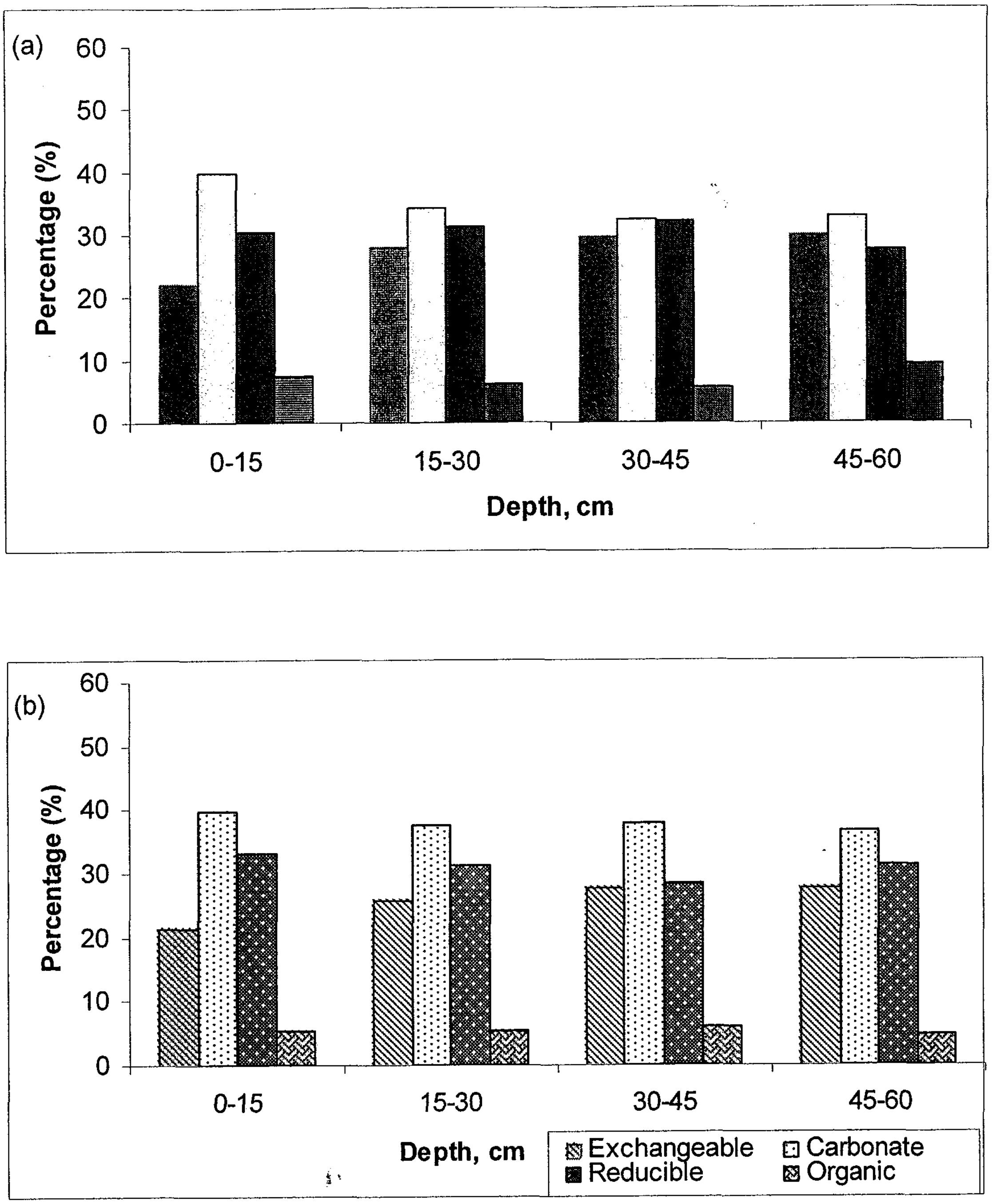

Figure 3.8 Pb speciation pattern at different depths in RPb spiked with 10 mg/L Pb at (a) sampling position 2 and (b) sampling position 5.

3. 2.3 Copper and Lead in Multi-element Wetland RCP

Figures 3.9 and 3.10 showed that the speciation patterns of Cu in the presence of Pb and vice versa. The results showed that the Cu speciation patterns when Pb was present were similar to those when Pb was not present. The exchangeable fraction increased at higher Cu loading especially at upper media (Figure 3.10).

In the case of Pb, a similar speciation pattern was observed from the top layer to the bottom layer. At lower loading, the percentage of Pb bound to different fractions was as follows: reducible (40-50 %), carbonate (30-40 %), exchangeable (10-20 %) and organic (10 %) (Figure 3.9).

At higher metal loading, there was a substantial increase in the percentage of exchangeable fraction from 10-20 % to 30-40 % for all depths.

3.3 Comparison of Copper and Lead in Single Element and Multi-Element Wetlands

3.3.1 Total Metal Concentrations

Figures 3.1 and 3.3 showed that the total concentrations of Cu in RCu were higher than RCP except at CP5-2. The total Cu concentration in CP5-2 was found to be 80 μg/g in the top layer of the media and 60 μg/g in the bottom layer Cu loading, it was observed that the total concentration of Cu was higher in RCu than RCP with a difference of 10 μg/g to 20 μg/g whereas for higher Cu loading, the difference in total Cu concentration was found to be 20 μg/g.

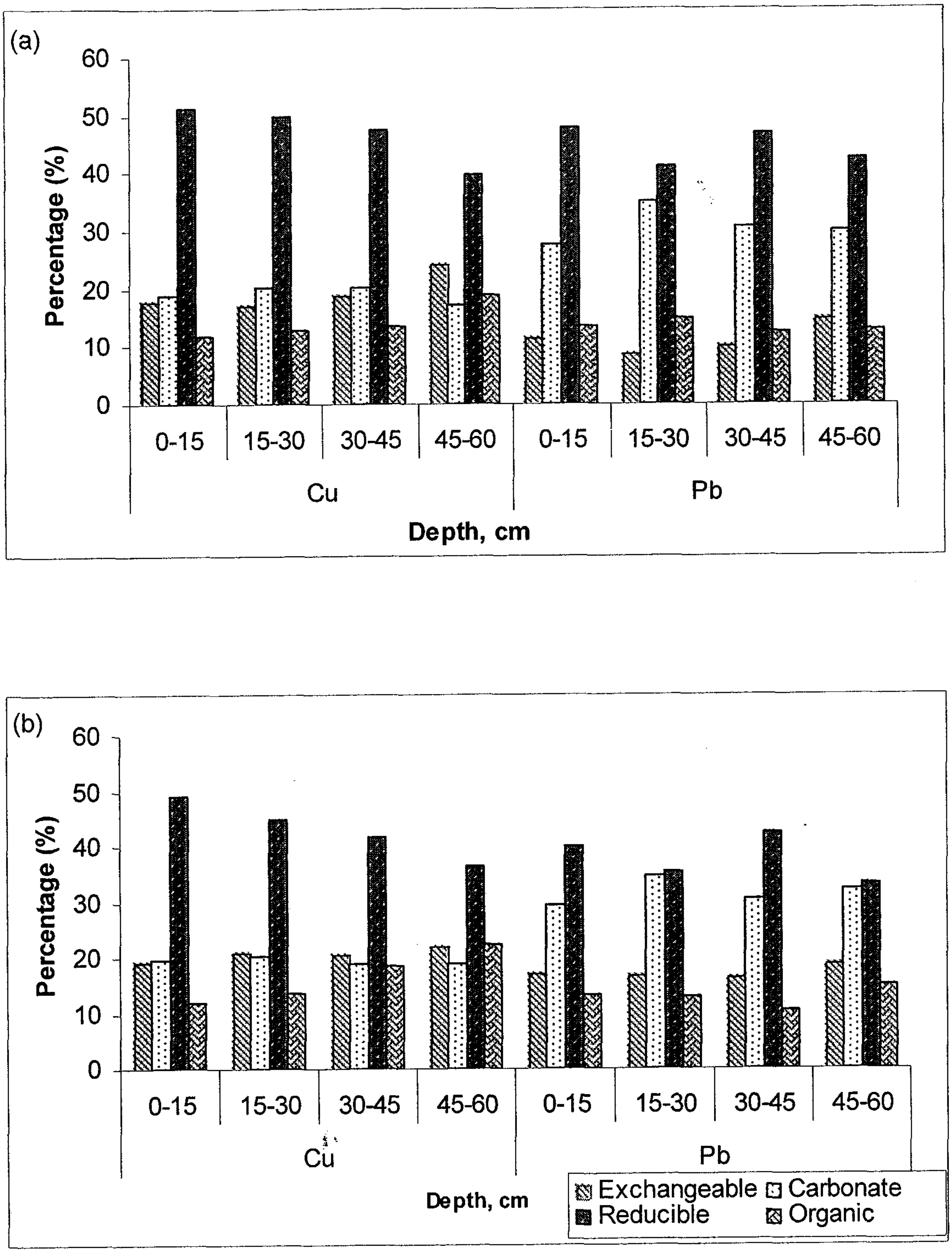

Figure 3.9 Cu and Pb speciation patterns at different depths in RCP spiked with 10 mg/L Cu and 5 mg/L Pb at (a) sampling position 2 and (b) sampling position 5.

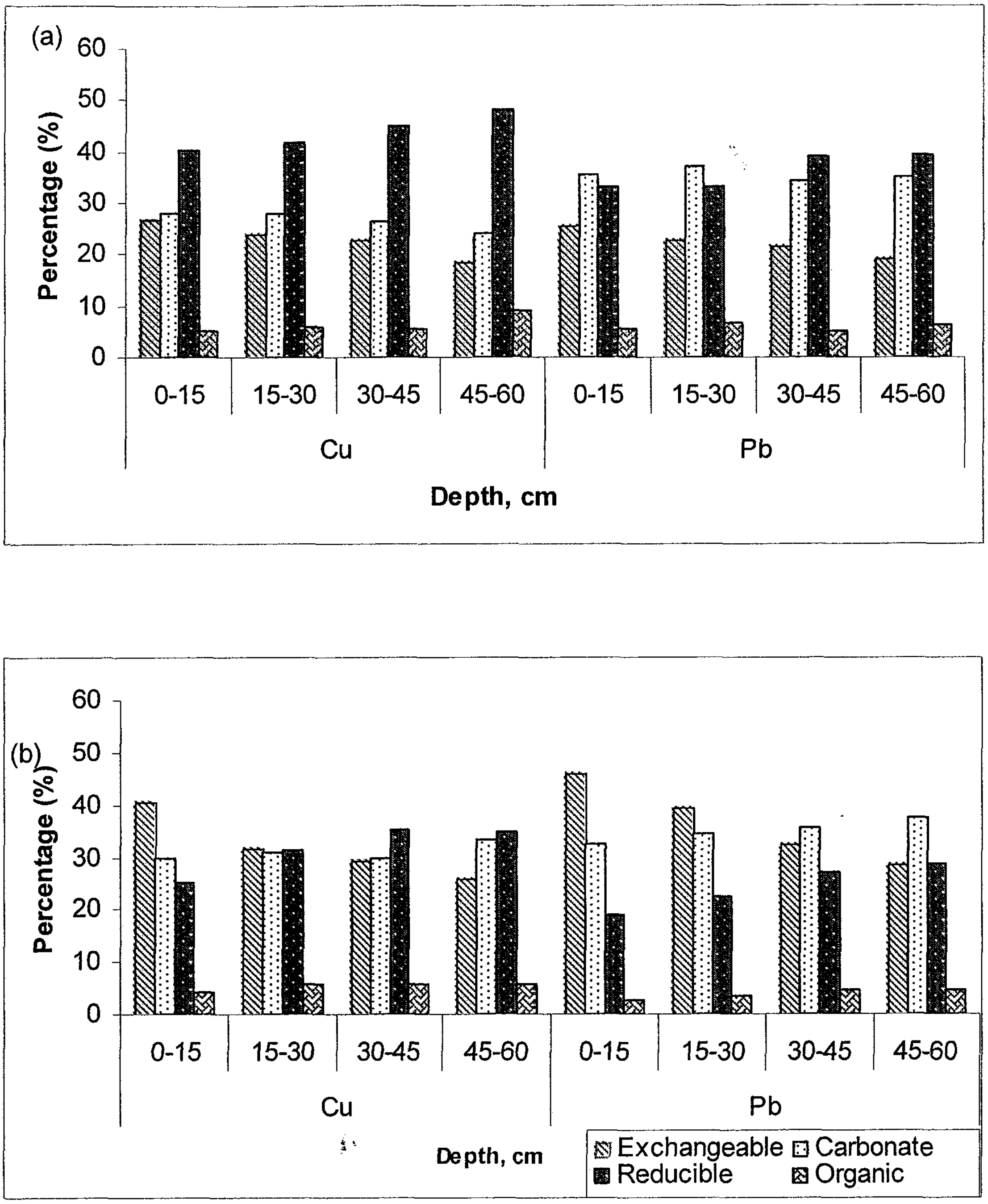

Figure 3.10 Cu and Pb speciation patterns at different depths in RCP spiked with 15 mg/L Cu and 10 mg/L Pb at (a) sampling position 2 and (b) sampling position 5.

The same trend was observed for lead. Figures 3.2 and 3.4 showed that the total concentrations of Pb in RPb were higher than RCP except at CP5-2. The inhomogeneity of the media sample could have resulted in the extremely high total lead concentration observed at CP5-2. The lead concentration was found to be 65 μg/g at the top layer of CP5-2 and 30 μg/g at the bottom of the media. For lower Pb loading, the Pb concentration ranged from 15 μg/g to 25 μg/g in RPb whereas in RCP, lower concentrations of lead ranging from 10 μg/g to 20 μg/g were obtained. For higher Pb loading, the concentration of lead in RPb was found to be 10 to 15 μg/g higher than the concentration of lead in RCP.

The lower concentration of metals observed in multi-element wetlands as compared to single element wetlands showed the occurrence of an antagonistic effect. This can be explained by the competition among metals to adsorb to the media in the multi-element wetland.

3.3.2 Metal Speciation Patterns

It was found that the Cu speciation patterns in the single element and multi-element situations at lower loading were similar. The predominant fraction was found to be the reducible fraction. At higher loading, Cu in reducible fraction decreased in percentage even though this fraction was still the predominant fraction. The same trend was observed for Cu in the organic fraction. The Cu in the organic fraction at higher loading decreased as compared to lower loading. In contrast, the Cu in carbonate bound and exchangeable fractions increased from lower loading to higher loading.

Pb in RPb and RCP showed similar speciation patterns. The highest percentage of Pb was bound to the reducible fraction. At higher loading, Pb in the reducible and organic fractions were reduced when compared to lower loading. The predominant fraction was the carbonate bound fraction at higher loading. This indicated that metal removal treatment either in single element or multi-element situations would not affect the metal speciation patterns but the metal itself would have different speciation patterns at different concentrations loading.

3.4 Comparison of the Total Metal Concentrations` with the Sum of Metal Concentrations in the Sequential Extraction Steps.

The total concentrations of Cu obtained by direct digestion of the media and from the sum of the Cu concentrations in the sequential extraction steps are shown in Table 3.1. Comparison of these two values of Cu concentration showed a good agreement except for a few samples at different depths. The recovery values ranged from 111-173 % for C2-1 and C5-1 and 85-135 % for C2-2 and C5-2.

The total concentrations of Pb by direct digestion of the media and from the sum of the Pb concentrations in the sequential extraction steps are compared in Table 3.2. Higher recovery values were observed in P2-1 and P5-1 which ranged from 123-147% whereas in P2-2 and P5-2, the values ranged from 110-131 %. This may be related to the lower concentration of Pb at P2-1 and P5-1

Table 3.1 Comparison of the total concentration of Cu in RCu by direct digestion method and the sequential extraction procedure.

Sample	Depth (cm)	Direct digestion of the media (μg/g)	Sum of the sequential extraction steps (μg/g)	Recovery (%) (extraction /digestion)
C2-1	0-15	30.2	33.7	111
	15-30	23.9	33.5	140
	30-45	23.2	26.6	115
	45-60	26.3	32.6	124
C5-1	0-15	41.2	46.1	112
	15-30	38.3	46.2	121
	30-45	29.3	40.9	140
	45-60	27.1	46.8	173
C2-2	0-15	79.8	90.7	114
	15-30	52.5	69.5	132
	30-45	57.3	68.3	119
	45-60	51.3	69.2	135
C5-2	0-15	82.6	101.9	123
	15-30	82.5	70.4	85
	30-45	49.0	51.5	105
	45-60	50.4	51.9	103

Table 3.2 Comparison of the total concentration of Pb in RPb by direct digestion method and the sequential extraction procedure.

Sample	Depth (cm)	Direct dissolution of the media (μg/g)	Sum of the sequential extraction steps (μg/g)	Recovery (%) (extraction /digestion)
P2-1	0-15	24.2	32.6	134
	15-30	19.5	25.6	131
	30-45	17.6	22.6	128
	45-60	17.6	21.7	123
P5-1	0-15	16.2	23.9	148
	15-30	14.1	22.4	159
	30-45	14.6	19.4	133
	45-60	13.6	20.0	147
P2-2	0-15	44.6	58.4	131
	15-30	33.2	43.7	131
	30-45	31.9	40.0	125
	45-60	32.0	41.5	130
P5-2	0-15	37.4	42.7	114
	15-30	34.1	37.6	110
	30-45	31.0	34.2	110
	45-60	31.0	34.9	113

Table 3.3 Comparison of the total concentration of Cu in RCP by direct digestion method and the sequential extraction procedure.

Sample	Depth (cm)	Direct dissolution of the media (μg/g)	Sum of the sequential extraction steps (μg/g)	Recovery (%) (extraction /digestion)
CP2-1	0-15	13.7	18.4	134
	15-30	14.4	19.0	132
	30-45	11.7	16.2	139
	45-60	11.1	15.7	141
CP5-1	0-15	28.3	39.1	138
	15-30	26.1	41.8	160
	30-45	25.2	44.2	173
	45-60	26.6	36.9	138
CP2-2	0-15	57.3	63.1	110
	15-30	44.1	47.5	108
	30-45	32.3	51.9	161
	45-60	38.4	54.6	142
CP5-2	0-15	86.6	90.4	104
	15-30	83.5	90.7	109
	30-45	67.3	78.7	117
	45-60	53.0	72.1	136

Table 3.4 Comparison of the total concentration of Pb in RCP by direct digestion method and the sequential extraction procedure.

Sample	Depth (cm)	Direct dissolution of the media (μg/g)	Sum of the sequential extraction steps (μg/g)	Recovery (%) (extraction /digestion)
CP2-1	0-15	14.6	20.8	142
	15-30	13.8	17.5	129
	30-45	11.8	17.2	146
	45-60	12.0	14.9	124
CP5-1	0-15	19.9	25.3	127
	15-30	15.4	24.6	160
	30-45	13.8	23.7	172
	45-60	14.4	20.0	139
CP2-2	0-15	32.8	35.8	109
	15-30	19.2	27.2	142
	30-45	18.9	27.7	147
	45-60	22.5	28.3	126
CP5-2	0-15	66.4	69.0	104
	15-30	52.5	55.6	106
	30-45	35.8	44.0	123
	45-60	28.1	35.5	126

increase in the potentially remobilizable fractions such as the exchangeable and the carbonate fractions.

The Pb speciation patterns reported in Lim *et al.* (2003) were also different from those found in this study. In the earlier study, the exchangeable fraction was the dominant fraction for Pb which constituted 68 % in the single-element reactor and more than 90 % in the multi-elements reactor. In this research, the dominant fraction of Pb was found to be in the reducible and carbonate fractions which constituted 30-50 % and 25-30 % respectively at lower Pb concentration loading. With higher concentration loading, there was a significant increase of Pb in the carbonate fraction indicating the possibility of media exhaustion.

However, the sequential extraction procedure applied in Lim *et al.* (2003) was from the Commission of the European Communities Bureau of Reference (BCR). This three-stage scheme involved the extraction of the exchangeable, reducible and organic fractions and combined the exchangeable and carbonate fraction together into one fraction. Combining the percentage of lead in the exchangeable and carbonate fraction in this study, it was found that the sum of these two fractions ranged from 45-55 % in the single element reactor and for the multi-elements reactor, it ranged from 60-75 %. Comparing these values with the results reported by Lim *et al.* (2003), the value for the multi-elements reactor was found to be different.

It was observed that plants did not play any significant role in the speciation of Cu because similar speciation patterns were obtained regardless of the different depths in the wetland systems. This seems to be in agreement with the observation by Lim *et al.* (2001). Similar Cu speciation patterns were obtained for the subsurface wetlands unit with and without cattail as the wetland vegetation.

3.6 Experimental Implication

Information on metal speciation patterns is important in assessing the suitability of the constructed wetlands for metal removal as certain fractions may be easily remobilized and returned to the environment if there are changes in the environmental conditions. Based on the Cu and Pb speciation patterns of this study, it was found that the reducible fraction was the predominant fraction for both metals. These two metals were not easily remobilized when low metal concentrations were spiked into the wetland system. However, at higher loading, there was a tendency of increased metal percentage in the exchangeable and carbonate fractions which are recognized as the more easily remobilizable or environmentally available forms. This would result in negative impacts to the environment.

4.0 CONCLUSIONS

Based on the results of this study, conclusions were made on the total concentration of Cu and Pb in the media, the speciation patterns of Cu and Pb and the comparison of the total metal concentrations using direct digestion method and from the sum of the metal concentration using sequential extraction procedure.

4.1 Total Concentrations of Copper and Lead in Wetland Media.

Overall, higher concentrations of metals were observed at the upper layer of the media in all wetland systems. This was especially significant with higher concentration of metals spiked into the wetland systems. The presence of plants in the upper layer can indirectly influence metals storage through their effect on oxygenation, buffering pH and the addition of organic matter.

In general, lower total metal concentrations on the media were observed in wetland unit RCP compared to those in RCu and RPb when lower concentrations of metals were introduced into the wetland systems. This was found to be the antagonistic effect. However, variation in the total metal concentrations observed in different positions within the same wetland system when higher concentrations of metals were introduced precludes the same conclusion to be made.

4.2 Speciation Patterns of Copper and Lead in Wetland Media.

The percentage of Cu in the reducible fraction was found to be dominant in the media from the upper layer to the bottom layer. However, at higher copper concentration, the percentages of Cu in the reducible and organic fraction were lower. In contrast, the percentages of Cu in the exchangeable and carbonate fractions increased.

Pb in the RPb showed similar speciation patterns as Cu except that at higher concentrations of lead the percentage of Pb in the carbonate fraction was found to be predominant. Similar speciation patterns for Cu and Pb were observed for

RCP. This indicated that at higher metal loading, the remobilization potential of the metals on the media increased.

4.3 Comparison of the Total Metal Concentrations from Total Digestion with the Sum of Metal Concentrations in the Sequential Extraction Steps.

The recovery value was determined by comparing the total concentrations from the direct digestion method with the sum of the metal concentration for the sequential extraction procedure. The recovery value obtained ranged from 85-173 % for Cu and Pb. Higher recovery value was observed at low concentrations.

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