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Full Length Research Paper

Speciation of heavy metals in paddy soils from selected areas in Kedah and Penang, Malaysia

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This study was carried out with the intention of evaluating heavy metal contamination in cultivated paddy areas. The speciation of heavy metals in paddy soils was determined in order to gain insight regarding their origin and distribution in soils. Five sampling sites were randomly selected from Kedah (Yan, Kota Setar, Kubang Pasu district) and Penang (Bumbung Lima district), where the soils constituted marine alluvial deposits. A site in Langkawi, where organic paddy farming is practised was used as the control. The sequential extraction method was adopted in order to obtain the four heavy metal fractions namely the easily leachable and ion exchange (ELFE), acid reducible (AR), oxidizable organic (OO) and resistant (RR) fractions. This study shows that the soil samples were clayey (82 to 96% of grain size <63 µm), fairly high in organic carbon (6.54 to 8.71%) and slightly acidic (pH 4.92 to 5.12). Heavy metal content in the soils varied widely and occurred in the following decreasing order of Fe>Mn>Cr>Cd>Pb>Zn>Cu. Heavy metals such as Pb, Cu, Cr and Zn predominantly occurred in the insoluble form (RR fraction), with the oxides of Fe and Mn incorporated into the clay minerals. Although, the fertilizers and pesticides studied contained low amounts of heavy metals, the elevated amount of amount of Mn and Cd in the soils (ELFE fraction) could possibly be attributed to the long-term and repeated application of these materials to the cultivated paddy areas.

Key words: Heavy metals, paddy soil, pesticide, fertilizer.

INTRODUCTION

Soils consist of heterogeneous media comprising decomposed rock fragments, clay minerals, oxides of Fe, Al and Mn, organic materials, organo-metallic complexes and soil solutions (Alloway, 1995). In cultivated paddy areas, the soils cannot be considered natural, as they have been highly modified by management practices including levelling, cultivation, puddling, submerging and fertilizing (Prakongkep et al., 2008). Apart from supplying micronutrients for the plant growth, some of the fertilizers and pesticides might introduce toxic heavy metals into the soils. According to Adriano (1986), phosphatic fertilizers contain varying amounts of Zn, Cd and other trace elements that originate in the phosphate rock. As for the manufactured fertilizers, the insufficiently purified product could contain several impurities including heavy metals (Gimeno-Garcia et al., 1996). Various types of fertilizers and pesticides that contribute to the heavy metals content in soils have been identified by McLaughlin et al. (2000). It was reported that the application of phosphate fertilizers in New Zealand and Australia contributed to the elevated levels of Cd in agricultural soils. Giuffré de López Camelo et al. (1997) reported that rock phosphate and NPK fertilizers contained heavy metal values several times higher than their natural levels in soils. More also, the application of rock phosphate to cultivated paddy areas in India caused an increase in the Cd content of the rice grain (Ramachandran et al., 1998), and in Malaysia, small amounts of Cd in the bioavailable form were found to be present in paddy soils at a few sites in Kedah (Khairiah et al., 2009a). However, the contribution from pesticides and fertilizers to the Cd contamination

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in these sites has yet to be determined.

Due to their cumulative behaviour and toxicity, heavy metals are potentially hazardous not only to crop productivity, but also to human health through food consumption (Das et al., 1997; Melamed et al., 2003; Kyuma, 2004). Heavy metals are also harmful to the environment because of their direct toxicity to biota and indirect threat to human health from groundwater contamination and accumulation in food crops (Martínez and Motto, 2000). The total metal concentration in soils cannot provide insight regarding their mobility and bioavailability (Powell et al., 2005). Thus, the sequential extraction technique has been adopted by many researchers for diverse types of soils including the upland soils (Khairiah et al., 2006) and paddy soils (Wong et al., 2002; Manceau et al., 2005; Khairiah et al., 2009a). Such procedures were proven to provide information on heavy metal speciation, including their origin, mode of occurrence, bioavailability, mobilization and transport in soils (Pérez-Cid et al., 1999).

At the northwest region of Peninsular Malaysia, paddy is cultivated in vast low lying plains consisting of the marine, fluvial and peat deposits. For decades, various types of fertilizers and pesticides have been applied to these areas to improve rice productivity and control pests. However, little effort has been done regarding the investigation of the effect of fertilizer and pesticide consumption to heavy metal contamination in paddy soils. In the current study, the sequential extraction method was adopted to determine heavy metal speciation in paddy soils. The objective of the study was to determine the status of heavy metal contamination in the paddy soils and factors that could influence their bioavailability to the paddy plants. The study will provide valuable insight regarding heavy metal contamination in paddy soils.

MATERIALS AND METHODS

The study area

The study was carried out at selected paddy cultivation areas at Yan, Kota Setar and Kubang Pasu, in Kedah and at Bumbung Lima in Penang. The soil from cultivated paddy area in Langkawi Island, where organic farming is practised, was used as the control. Five sampling sites were randomly chosen from each area. Consequently, five soil samples of 0 to 30 cm depth were collected at each site using a hand auger.

Extraction of heavy metals from the soil

Prior to the analysis, the soil samples were air-dried in the laboratory and sieved through the 250 µm mesh before they were ground using a mortar and pestle. Heavy metal extraction from the soil samples was undertaken using the sequential extraction method of Badri (1984). The extraction process was divided into four fractions namely easily leachable and ion exchange (ELFE), acid reducible (AR), organic oxidation (OO) and resistant (RR) fractions. The ELFE fraction normally contained metals that were weakly bound to the clay surface area, secondary minerals and organic materials. Ten gram soil samples were put into Kartell bottles followed by the addition of 50 ml 1.0 M NH_4CH_3OO (pH 7). The samples were then shaken for 1½ h, and centrifuged at 3000 rpm for 30 min before being filtering through 0.45 µm millipore filter paper and made up to 50 ml with distilled water. Samples were washed with 50 ml distilled water, followed by further shaking and centrifugation as described earlier.

Consequently, a total of 50 ml $NH_2OH.HCl$ (pH 2) was added in order to extract the metals from the acid reducible (RA) fraction using the procedure earlier described. Metals extracted from this fraction mainly came from those which were strongly bound to secondary minerals. 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 to 1½ h, followed by the addition of 50 ml NH_4CH_3OO (pH 3.5), representing the metal bound to the organic matter. Samples were then digested using HNO_3:$HClO_4$ at 25:10 ratio in a sand bath at 100°C as in the RR extraction method. The digestion process was repeated until the samples turned whitish. The determination of heavy metal concentration was carried out using AAS (atomic absorption spectrophotometry) with the Perkin Elmer model (1100B). Organic carbon analysis and soil pH were also carried out by using the Walkey-Black (1934) and Duddridge and Wainright (1981) methods, respectively, while the <63 µm grain size was determined according to Badri (1984).

Extraction of heavy metals from fertilizers and pesticides

The most commonly used fertilizers and pesticides in the cultivated paddy areas of Kedah and Penang are N:P:K 13:13:17, N:P:K 12:12:17 and urea (N48%) fertilizers and pesticides containing active fenthion and carbaryl materials. Heavy metals from the samples were extracted by the wet extraction method (AOAC, 1984). A gram sample was placed in a 100 ml conical beaker to which 20 ml of 69% nitric acid was added. The digestion was performed on a sand bath at 60 to 80°C until the brown gas evaporated. Then, 3 ml of 60% perchloric acid was added, followed by heating on a sand bath until the mixture was clear. The cooled mixture was filtered through a 0.45 µm millipore filter paper assisted by vacuum pressure before being transferred into a volumetric flask and made up to 100 ml with distilled water. Heavy metals in the acid digest were determined by atomic absorption spectrometry (AAS) using the Perkin Elmer model.

RESULTS AND DISCUSSION

Heavy metal content in fertilizers and pesticides

It was found that all the fertilizers and pesticides studied contained low amounts of heavy metals compared to the heavy metal content of fertilizers used in Argentina (Giuffré de López Camelo et al., 1997). Among the heavy metals studied, the concentrations of Fe, Mn and Pb in the NPK fertilizers were higher than that found in the urea and pesticides (Table 1). On the other hand, Cu was undetected in all the samples and the Mn and Cr content were very low in the urea and pesticides.

Heavy metal content in paddy soils

Paddy soils in the studied areas constituted marine

Table 1. The concentration of heavy metals in selected fertilizers and pesticides.

Fertilizer and pesticide	Heavy metal (mg/kg)						
	Pb	Cd	Cr	Cu	Zn	Fe	Mn
Fenthion	0.195	0.012	0.007	ND	0.096	1.461	ND
Carbaryl	0.173	0.011	ND	ND	0.251	0.580	ND
Urea	0.154	0.010	ND	ND	0.136	0.356	ND
NPK 13:13:21	0.222	0.014	0.084	ND	0.414	8.710	0.726
NPK 12:12:17	0.235	0.017	0.562	ND	0.952	10.148	0.365

ND, Not detected.

Table 2. The organic carbon, pH values and grain size of the soil samples from cultivated paddy soils of Kedah and Penang.

Location	Percentage organic carbon	pH	Percentages grain size (<63 µm)
Yan	8.71 ± 0.70	4.92 ± 0.26	92.00 ± 3.24
Kota Setar	6.65 ± 1.36	5.20 ± 0.26	92.20 ± 2.59
Kubang Pasu	9.04 ± 2.20	5.10 ± 0.14	87.40 ± 5.94
Bumbung Lima	6.54 ± 1.01	5.12 ± 0.08	82.00 ± 7.00
Control (Langkawi)	5.53 ± 0.18	7.33 ± 0.06	96.33 ± 0.58

alluvial deposits. All the soil samples contained a high percentage of clay and silt (grain size <63 µm), indicating clayey soils (Table 2). The soils were slightly acidic (pH 4.92 to 5.12) and comparable to the Quaternary deposits in Kedah and Perlis (Khairiah et al., 2009a) and the marine alluvial soils in Setiawan, Perak (Khairiah et al., 2009b). The organic carbon content in these areas was fairly high ranging from 6.54 to 8.71%.

Heavy metal concentration in soil samples varied widely (Table 3). Among the heavy metals studied, the total Fe content was highest in all the soils, followed by Mn, Cr, Cd, Pb, Zn and Cu. Except for Fe, all the total heavy metal values were lower compared to the values recorded in the upland agricultural soils of Bangi and Cameron Highlands (Ismail et al., 2005). However, the content of heavy metals found in the studied soils was comparable to that of other agricultural soils developed on the marine, fluvial and peat deposits at Setiawan, Perak (Khairiah et al., 2009b), Kedah and Perlis (Khairiah et al., 2009a). In the current study, increased levels of bioavailable Mn and Cd were detected in the paddy soils, suggesting anthropogenic inputs into the soils.

Fe

Among the heavy metals studied, the concentration of iron was the highest in total (520.41 to 577.05 mg/kg) and in all soil fractions except for the Bumbung Lima soil. The values were higher than the Fe content of paddy soils of Kedah and Perlis (254 to 379.28 mg/kg) (Khairiah et al., 2009a), guava plantation soils in Setiawan, Perak (110.48 to 141.34 mg/kg) (Khairiah et al., 2009b) and the upland crop soils in Cameron Highlands (314 to 361 mg/kg) (Ismail et al., 2005). Normally, soils developed from marine alluvial deposits are low in Fe. The increased level of soil Fe in the studied soils could possibly be attributed to the fertilizers applied. According to Jäckel and Schnell (2000), ferric iron fertilization could suppress methane emission in paddy soils. In the current study, both the fertilizers used, namely N:P:K 13:13:21 and N:P:K 12:12:17 contained Fe, and after several years of usage, this agricultural practice could have contributed to the increased level of Fe in the paddy soils.

Most of the soil Fe was found in the OO, RR and AR fractions, accounting for approximately 39 to 40%, 29 to 34% and 24 to 29% of total Fe concentration, respectively. In comparison, low levels of ELFE Fe was observed in all the soil samples of less than one percent of the total Fe concentration (Figure 1). The affinity of Fe in the organic oxidizable (OO) fraction might possibly be attributed to the repeated accumulation of paddy straw in soils, thus promoting the formation of Fe-organic chelates. Furthermore, soils in the study areas were slightly acidic and exposed to the redox condition fluctuation. In such a condition, the insoluble hydrated iron oxide $Fe(OH)_3$, and the more stable dehydrated iron oxides such as goethite and lepidocrocite would develop (Alloway 1995; Manceau et al., 2005). Thus, the major Fe concentration in the RR and AR fractions can be explained by the occurrence of these insoluble forms of Fe in the soils, or low bioavailable Fe.

Mn

The concentration of total soil Mn in the studied areas ranged from 39.73 to 82.62 mg/kg. The highest Mn

Table 3. The average concentration of the heavy metal speciation of soils in the study areas (mg/kg).

Fraction	Area	Heavy metal						
		Pb	Cd	Cr	Cu	Zn	Fe	Mn
ELFE	Yan	ND	7.271^{a}	0.043^{a}	ND	ND	0.307^{a}	27.680^{ab}
	Kota Setar	ND	3.653^{a}	0.090^{a}	ND	ND	0.575^{a}	20.410^{bc}
	Kubang Pasu	ND	ND	0.072^{a}	ND	ND	0.503^{a}	42.620^{a}
	Bumbung Lima	ND	10.868^{a}	0.086^{a}	ND	0.193^{a}	0.423^{a}	18.260^{bc}
	Control	ND	12.350^{a}	0.010^{a}	ND	ND	0.018^{a}	5.017^{c}
AR	Yan	ND	0.001^{a}	0.154^{a}	ND	0.672^{ab}	150.220^{a}	11.300^{bc}
	Kota Setar	ND	0.058^{a}	0.309^{a}	ND	0.307^{b}	160.420^{a}	12.930^{bc}
	Kubang Pasu	ND	0.007^{a}	0.230^{a}	ND	0.912^{ab}	170.210^{a}	18.990^{b}
	Bumbung Lima	ND	0.015^{a}	0.245^{a}	ND	1.096^{a}	128.671^{a}	6.260^{c}
	Control	ND	ND	ND	ND	0.547^{ab}	89.498^{a}	36.267^{a}
OO	Yan	0.354b	0.037	7.624^{ab}	ND	ND	228.785^{a}	7.505^{b}
	Kota Setar	0.175b	0.001^{a}	6.241^{bc}	ND	ND	221.675^{ab}	8.315^{b}
	Kubang Pasu	0.409b	0.027^{a}	8.422^{a}	ND	ND	232.525^{a}	9.915^{b}
	Bumbung Lima	1.172b	0.026^{a}	5.221^{c}		ND	209.975^{bc}	5.065^{b}
	Control	20.865a	0.063^{a}	3.363^{d}	ND	ND	205.385^{c}	21.052^{a}
RR	Yan	5.692b	13.554^{a}	21.563^{ab}	2.327a	7.125^{a}	197.735^{a}	13.601^{b}
	Kota Setar	9.232b	6.801^{ab}	17.395^{ab}	2.078a	8.360^{a}	178.106^{a}	10.395^{b}
	Kubang Pasu	8.858b	3.506^{ab}	15.201^{b}	0.748a	8.684^{a}	170.834^{a}	11.098^{b}
	Bumbung Lima	23.237a	3.378^{ab}	16.653^{b}	2.599a	7.301^{a}	181.340^{a}	10.141^{b}
	Control	27.176a	0.320^{b}	24.371^{a}	ND	11.501^{a}	167.324^{a}	30.851^{a}

The repeated alphabet in the same column indicates that the differences are not significant (p>0.05).
ND= Not detected

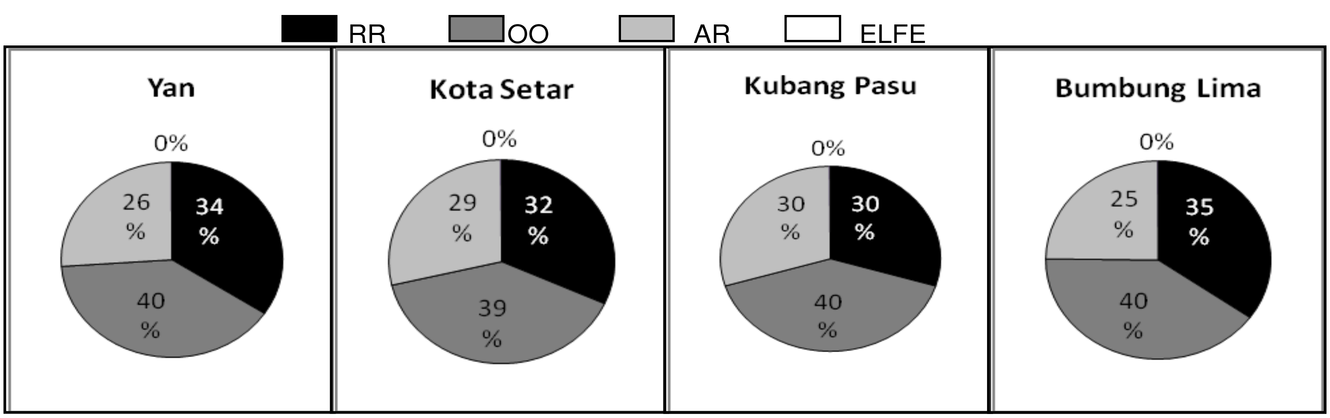

Figure 1. Speciation of Fe in paddy soils of Yan, Kota Setar, Kubang Pasu and Bumbung Lima.

concentration was detected in the ELFE fraction from the Kubang Pasu area. The rest of the studied areas also contained high amounts of Mn in all the soil fractions (Table 3). The values were higher than the total Mn values of the paddy soils from Kedah (3.57 to 13.2 mg/kg) (Khairiah et al., 2009a) and the guava plantation soils at Setiawan, Perak (7.00 to 11.92 mg/kg) (Khairiah et al., 2009b). However, these amounts were comparable to those found in the paddy soils of Arau, Perlis (76.14 mg/kg) (Khairiah et al., 2009a) and the Pearl River Delta (186 mg/kg) (Wong et al., 2002). The high Mn levels in the paddy soils studied could possibly be attributed to the

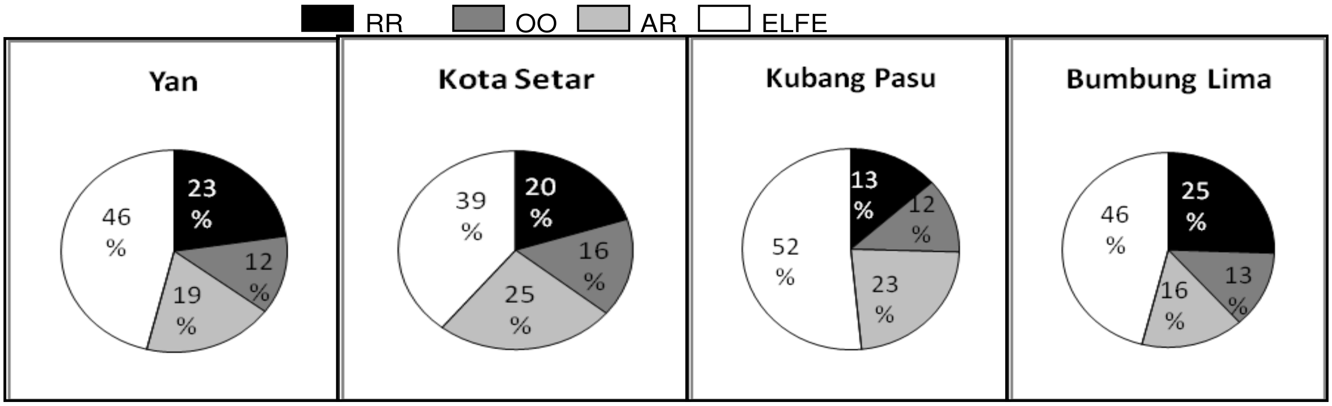

Figure 2. Speciation of Mn in paddy soils of Yan, Kota Setar, Kubang Pasu and Bumbung Lima.

application of agrochemical fertilizers in these areas. NPK fertilizers (with different ratio combinations) are frequently used in the cultivated paddy areas of Malaysia. The study found that N:P:K 13:13:21 and N:P:K 12:12:17 contained Mn, and the repeated usage of these fertilizers over several years possibly contributed to the accumulation of Mn in the paddy soils.

In all the soil samples, Mn was found to be highest in the ELFE fraction form (18.26 to 42.62 mg/kg), accounting for approximately 39 to 45% of total Mn concentration (Figure 2). It was followed by the AR (6.26 to 18.99 mg/kg), RR (10.14 to 13.60 mg/kg) and OO (5.06 to 9.92 mg/kg) fractions. According to Adriano (1986), the plant uptake of Mn increases in slightly acidic soils compared to that in strongly acidic or basic soil conditions. The easily leachable and ion exchange form of Mn represents the loosely bound metal species, which are easily taken up by plants (Kabata-Pendias and Pendias, 2001). In the current study, the paddy soils were slightly acidic (pH 4.92 to 5.20), thus being favourable to bioavailable Mn (ELFE fraction) in the soils. Being a micronutrient for plant growth, the major occurrence of Mn in the bioavailable form is not harmful to the plant. Manceau et al. (2005) discovered that Mn in paddy soils occurred as ferromanganiferous soft mottles, resulting from alternating oxidation and reduction cycles in the paddy field. This explained the comparable amount of Mn content in the RR and AR fractions, indicating the occurrence of insoluble Mn in the paddy soils. Repeated application of fertilizers in these areas could cause the accumulation of Mn in the insoluble as well as in the bioavailable forms.

Cd

The total Cd concentration in the soil samples ranged from 3.54 to 20.86 mg/kg. The values were higher than the Cd content in paddy soils of Thailand (<0.3 mg/kg) (Prakongkep et al., 2008), Pearl River Delta (<0.9 mg/kg) (Wong et al., 2002), Kedah and Perlis (0.07 to 2.35 mg/kg) (Khairiah et al., 2009a). The Cd concentration was highest in the RR fraction, especially from Yan, Kedah. This finding indicates that soils in Yan are naturally high in Cd. Except for Kubang Pasu, the ELFE fraction from all of the samples in the studied areas showed fairly high amount of Cd, followed by the RR, OO and AR fractions (Table 3 and Figure 3).

The high amount of Cd in paddy soils might possibly be attributed to the soil type, redox condition and repeated application of fertilizers and pesticides in the study areas. The study conducted by Shamshuddin and Paramananthan (1988) in Carey Island revealed that marine deposits contained high amounts of Al, basic cations and sulphate. According to Alloway (1995), Cd in the strongly gleyed soils occurred as sulphide mineral greenockite (CdS), hence, the low solubility of Cd in the flooded paddy soils. However, when the paddy soils return to the oxidizing state condition, the Cd^{2+} and SO_4^{2-} are formed, thus resulting in an increase in the mobility and bioavailability of Cd. Normally, the Cd content in soils is usually low. However, the presence of external Cd loading could increase its concentration in soils (McLaughlin et al., 2000; Kirkham, 2006).

In the current study, paddy soils consisted of marine alluvial deposits, thus providing a great supply of sulphate to the soils. The fluctuation of the redox condition as a result of the alternate flooding and draining in the paddy field would promote the formation of both the insoluble CdS (RR fraction) and the soluble Cd^{2+} ion (ELFE fraction). Apart from this factor, the fertilizers and pesticides added to the paddy soils could possibly contribute to the increased Cd levels in the soils. The study found that all of the fertilizers and pesticides commonly used contained a certain amount of Cd. Although, present in small quantities, Cd could accumulate in soils after several years of application of fertilizers and pesticides. The elevation of the

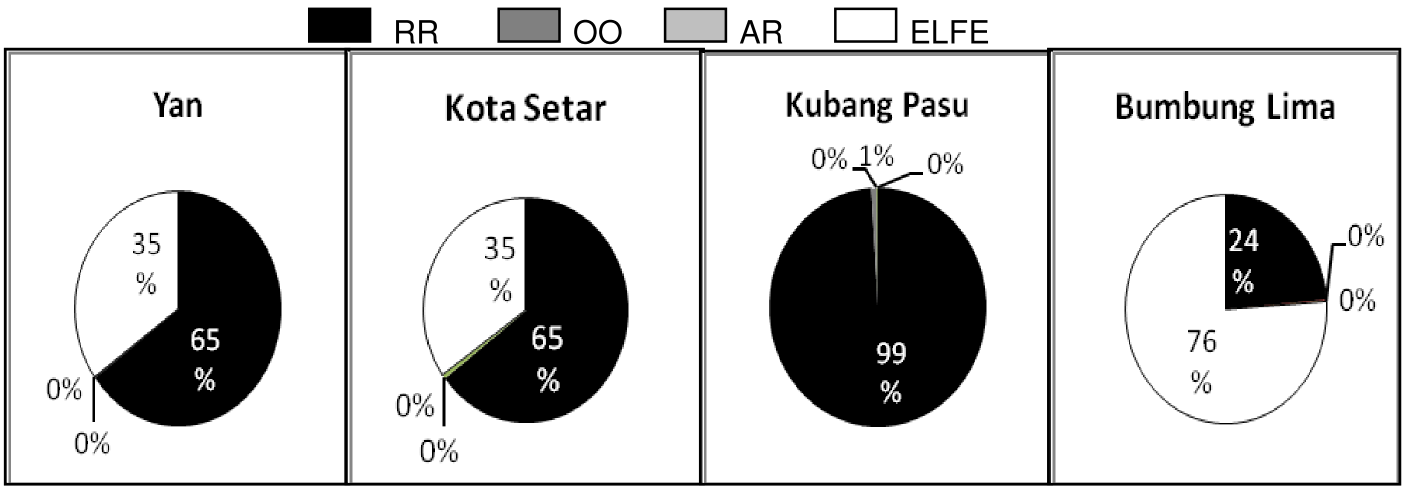

Figure 3. Speciation of Cd in paddy soils of Yan, Kota Setar, Kubang Pasu and Bumbung Lima.

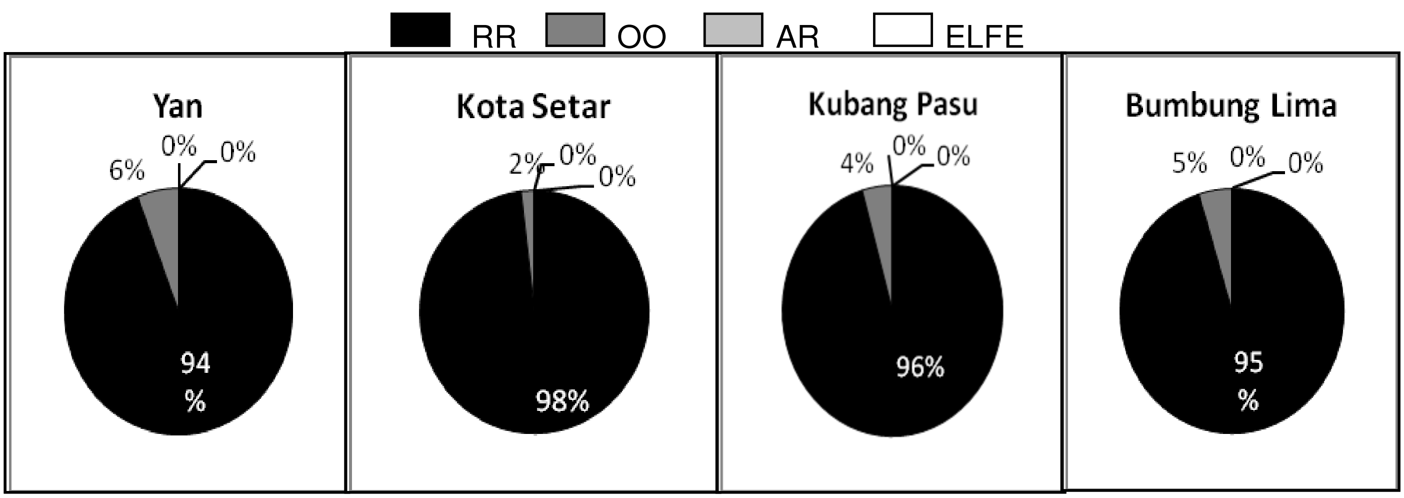

Figure 4. Speciation of Pb in paddy soils of Yan, Kota Setar, Kubang Pasu and Bumbung Lima.

bioavailable Cd in paddy soils poses some concern due to its toxicity and ability to hyper-accumulate in plants (Kirkham, 2006). Certain measures should be taken in order to solve the problem of cadmium accumulation.

Pb

As for Pb, the total metal concentration in the paddy soils studied ranged from 6.05 to 24.41 mg/kg with the highest content in the AR followed by the OO fractions. However, its concentration is comparable to the Pb content in paddy soils of Kedah and Perlis (9.40 to 19.59 mg/kg) (Khairiah et al., 2009a) and in the alluvial soils of the guava plantation in Setiawan, Perak (7.32 to 19.61 mg/kg) (Khairiah et al., 2009b). Among the soils studied, paddy soils in Bumbung Lima contained the highest level of total Pb (24.41 mg/kg). Meanwhile, the total Pb concentration in soil samples from Yan, Kota Setar and Kubang Pasu were found to be less than 10 mg/kg. The higher level of Pb in the Bumbung Lima soil could possibly be due to its different origin.

Lead in all the soil samples was predominantly associated with the RR fraction (more than 94%), with a low level in the OO fraction (less than 6%). Although, a certain amount of Pb was present in the fertilizers and pesticides used, it tended to accumulate in the unavailable form. Lead was undetected in the AR and ELFE fractions (Figure 4). According to Li et al. (2007), Pb in paddy soils tends to accumulate with oxides of Fe and Mn. In the current study, the clayey nature of soils in the study areas, high amounts of insoluble Fe and fairly high amounts of organic matter could possibly be responsible for the fixation of Pb in the unavailable form.

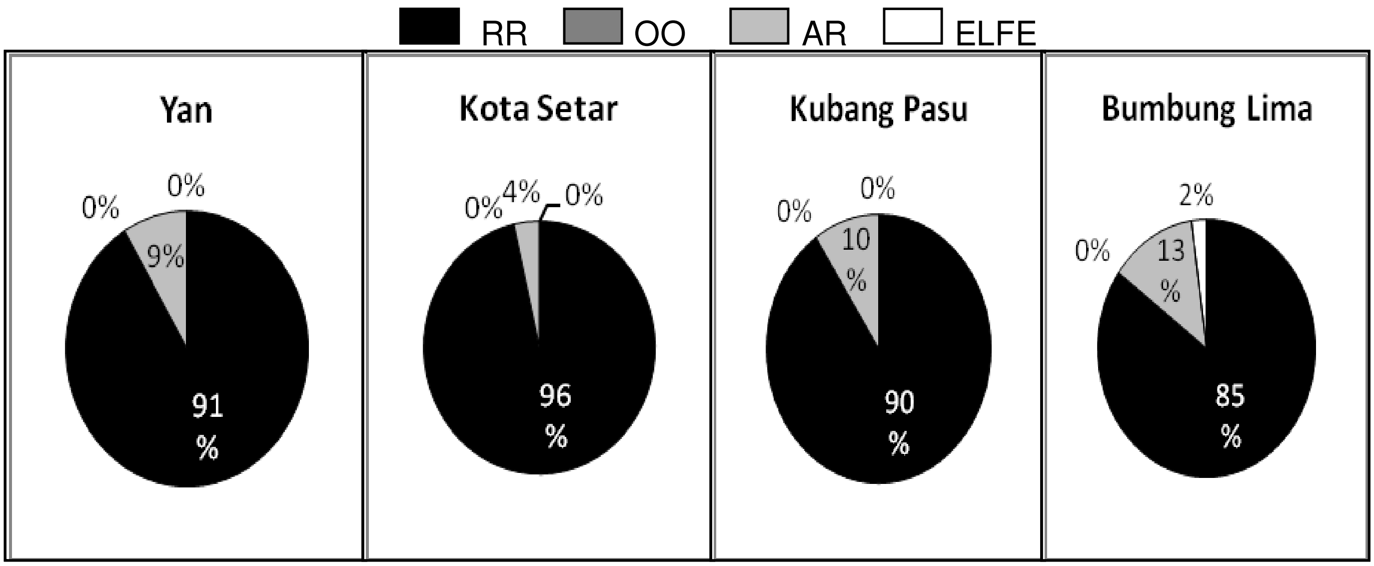

Figure 5. Speciation of Zn in paddy soils of Yan, Kota Setar, Kubang Pasu and Bumbung Lima.

Zn

Soil samples in the study areas contained low levels of total Zn (7.80 to 9.60 mg/kg) with the highest content in the RR fraction from all the areas. Zinc was predominantly associated with the RR fraction, which accounted for more than 90% of total Zn, with a small quantity of Zn in the AR fraction (Figure 5). Except for soil samples in Bumbung Lima, Zn was undetected in the ELFE fraction, indicating the low bioavailability of Zn in the soils. This result suggests that paddy soils in the study areas were deficient in Zn.

According to Adriano (1986), Zn deficiency was not uncommon in paddy fields throughout Asia particularly the neutral to alkaline calcareous soils containing more than 1% organic matter. In the current study, Zn was undetected in the OO fraction even though the paddy soils contained a fairly high amount of organic carbon. The study shows that both urea and NPK fertilizers contained a certain amount of Zn. However, their application to the soils could not result in an increase the Zn concentration. The higher level of Zn in the RR and AR fractions over the OO fraction in the paddy soils could be explained by the affinity of Zn for both Mn oxides and phyllosilicates in soils. Manceau et al. (2005) reported that in clayey paddy soil, Zn was predominantly bound to hydroxyl-Al interlayers sandwiched between 2:1 vermiculite layers in the fine soil matrix. It was also reported that Zn tended to associate with the ferromanganiferous mottles in paddy soils. According to Paramananthan (1989), paddy soils in the Kedah plain were abundant in phyllosilicate minerals constituting kaolinite, smectite and mica. Thus, the clayey nature of paddy soils in the study area would promote the formation of insoluble Zn in them.

Cu

Paddy soils in the study areas contained low levels of Cu (0.75 to 4.53mg/kg). The highest level was observed in the RR fraction of all the soils whereas in the rest of the fractions Cu was not detected (Table 3). Except for the Bumbung Lima soil, all of the soil Cu was found solely in the RR fraction. In Bumbung Lima, a small amount of Cu was present in the RR fraction (2.60 mg/kg) and the OO fraction (1.93 mg/kg), whereas Cu was undetected in the AR and ELFE fractions. The results suggest that the Cu found in soil samples was contributed by the natural marine alluvial deposits. The low Cu levels in marine alluvial soils were also reported by Khairiah et al. (2009b) for Setiawan, Perak. In the current study, Cu was undetected in all the fertilizer and pesticide samples used suggesting negligible anthropogenic input of Cu into paddy soils of the study areas. This finding was also supported by the fact that he paddy soils of Kedah and Penang were not contaminated with Cu.

Cr

The total Cr concentration in paddy soils of Kedah and Penang ranged from 22.20 to 29.38 mg/kg. In all the areas, most of the Cr was found in the RR fraction, followed by the OO fraction (Figure 6). The other two fractions were quite low in Cr concentration. According to Khairiah et al. (2009a), the clayey consistency, slightly acidic pH and high organic matter content of the soilwould promote the precipitation of insoluble Cr (III), hence the decrease in bioavailable Cr. In the current study, Cr was undetected in the pesticide carbaryl and the urea fertilizer, suggesting the low level of external Cr

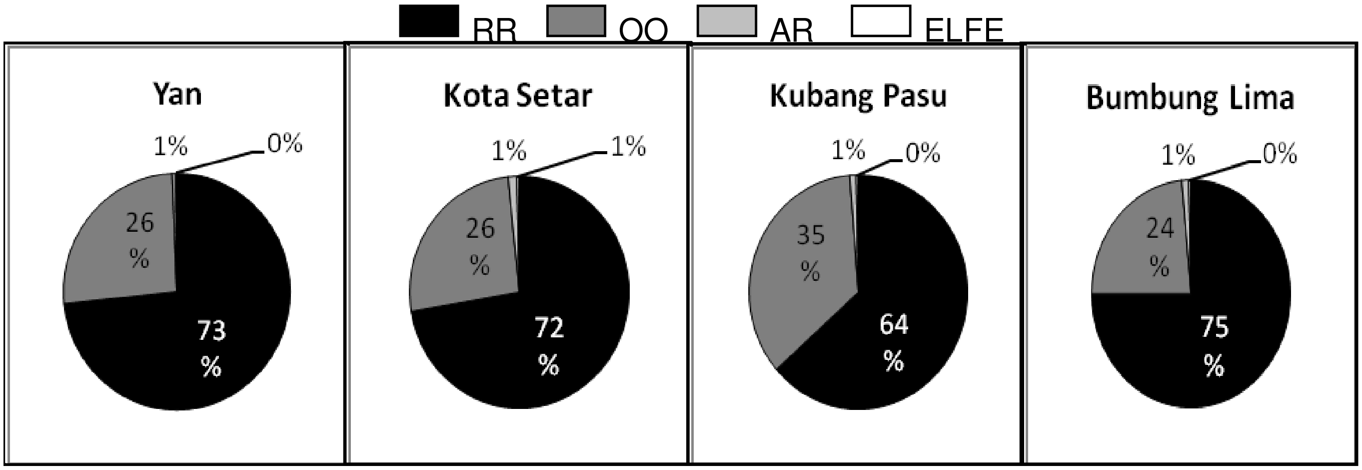

Figure 6. Speciation of Cr in paddy soils of Yan, Kota Setar, Kubang Pasu and Bumbung Lima.

loading in the soils. As in Kedah and Perlis, Cr in the study areas was also found in the unavailable form (RR fraction).

Conclusion

In the current study, speciation of heavy metals provide a valuable insight on the origin and distribution of heavy metals in paddy soils derived from marine alluvial deposits. Paddy soils from Kedah and Penang were characterized by their clayey nature, fairly high organic carbon content, slightly acidic pH and depleted content of total Pb, Zn and Cu. Most of the heavy metals such as Pb, Cu, Cr and Zn occurred predominantly in the insoluble form, possibly incorporated with the oxides of Fe and Mn and in the clay minerals. All the fertilizers and pesticides applied contained low levels of heavy metals. However, some of them contributed to the increased total Fe, Mn and Cd content in the paddy soils due to repeated application of the fertilizers and pesticides for crop production.

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