MANGANESE SPECIATION IN SELECTED AGRICULTURAL SOILS OF PENINSULAR MALAYSIA

Habibah, J., J. Khairiah, B.S. Ismail and M.D. Kadderi

School of Environmental and Natural Resource Sciences, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia,43600 UKM Bangi, Selangor, Malaysia

ABSTRACT

Manganese speciation in selected agricultural soils of Peninsular Malaysia is discussed in this study. Manganese concentration in the Easily Leacheable and Ion Exchangeable (ELFE), Acid Reducible (AR), Organic Oxidizable (OO) and Resistant (RR) fractions of soils developed on weathered rocks, soils of mixed nature, alluvium and peat deposits are described. The total manganese concentration in soils developed on weathered rocks was found to be higher than that in soils of mixed nature, alluvium and peat deposits because of the occurrence of resistant manganese oxide at the topsoils. Manganese speciation in paddy soils is influenced by the redox condition resulting from the alternate flooding and drying of the soils. Under reducing conditions, this metal tends to get dissolved and be available for plant uptake. Upon oxidation, manganese is precipitated into the acid reducible fraction as poorly crystalline manganese oxide and hydroxide and/or the resistant Fe-Mn mottles. In non-paddy cultivated alluvial soils, manganese speciation varies widely and is less understood. For the non-paddy cultivated peat soils, manganese is mainly associated with organic material, as indicated by the high manganese concentration in the OO fraction.

Keywords: Mangenese Speciation, Agricultural Soils, Peninsular Malaysia

1. INTRODUCTION

Manganese is a metal commonly found in soils and is likely to occur as oxides and hydroxides in the form of coatings on other particles and as nodules of different diameters. The Mn oxides are mostly amorphous, but crystalline varieties have also been identified in soils (Kabata-Pendias and Pendias, 1984). Most of the Mn oxides have strong specific adsorption to cations, leading to high accumulation of other heavy metals. Such metals can be adsorbed onto the surface of minerals like clay, as well as Fe and/or Mn oxy-hydroxides (Quemerais *et al.*, 1998). A study on serpentine soils of Ranau, Sabah indicated that over half of the soil Co is associated with Mn-oxide (Tashakor *et al.*, 2011). In Australia, zones rich in Mn oxy-hydroxides occur as coatings on fissure surfaces, contained large concentrations of Ce and U (Koppi *et al.*, 1996). Iron and manganese cycling has been observed

to have strong correlation with redox conditions, seasonal fluctuation of boundary conditions and quantity and reactivity of organic matter (Marchand *et al.*, 2006). Mn oxides also play an important role in the oxidation of Cr(III) to Cr(IV) in soils and the amounts of Cr(VI) produced through oxidation of Cr(III) by Mn oxides are related to the types of Mn oxides in the nodules, for example birnessite, lithiophorite, todorokite, lithiophorite and lithiophorite (Tan *et al.*, 2005). Mn oxides incorporate metal ions in their mineral structure and/or act as high-surface-area substrates favouring heavy metal adsorption (Decree *et al.*, 2010). The adsorption and desorption of heavy metals have been demonstrated to be associated with soil properties, including pH, organic matter content, Cation Exchange Capacity (CEC), oxidation-reduction status (Eh) and the contents of clay minerals, calcium carbonate, as well as Fe and Mn oxides (Zeng *et al.*, 2011).

Corresponding Author: Habibah, J., School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

Manganese compounds are important in soils because this metal is essential in plant nutrition and controls the behaviour of several other micronutrients (Kabata-Pendias and Pendias, 1984). The reduction and dissolution of Mn oxides increase the Mn mobility and bioavailability to organisms (Kämpf *et al.*, 2000). As a micronutrient, mangenese is required in microquantities but deficiency of this metal can cause serious crop production and animal health problems. Some crops like beans, oat, potato, sorghum, soya bean and wheat are highly sensitive to micronutrient deficiencies whereas barley, clover, corn, grass, sugar beet and turnip show medium sensitivity (Gupta *et al.*, 2008). Manganese deficiency generally occurs in soils with high pH (Clark, 1993). Response to manganese availability is most likely to occur in soils with high organic matter content, high-pH as well as in calcareous and sandy soils (Wiese, 1993). Excess manganese, for example in soils with high levels of water soluble or salt extractable Mn (Moraghan, 1979) may cause toxicity in plants. Manganese toxicity has been reported in crops grown on strongly acidic soils (Clark, 1993).

Heavy metal speciation has been successfully used as an indicator for heavy metal association in soil fractions (Iskandar and Kirkham, 2001), including the resistant and bioavailability forms, the acid reducible material and metal association with organic matter. For example, the sewage sludge amended soil contains high amounts of bioavailable Zn, Pb, Fe, Ce and Cu (Rajoo *et al.*, 2013). The understanding of heavy metal speciation could lead to the understanding of heavy metal behaviour and mobility in soils. Naturally, the bioavailable heavy metal will become a growing concern should its concentration exceed the threshold limit. In Peninsular Malaysia, heavy metal speciation studies have been carried out in selected agricultural soils (Habibah *et al.*, 2011; Khairiah *et al.*, 2006; Khairiah *et al.*, 2009a; 2009b; 2009c; 2012). However, a comprehensive understanding of manganese speciation in agricultural soils of different origins has never been compared. In the present study, manganese speciation in selected agricultural soils developed on weathered rocks, soils of mixed nature at hill slopes and on alluvial and peat deposits are compared.

2. MATERIALS AND METHODS

The speciation method introduced by Badri and Aston (1983) was applied to understand Mn speciation in agricultural soils. This method was used to quantify heavy metal concentrations in four geochemical phases, namely the Easily Leacheable and Ion Exchangeable (ELFE), Acid Reducible (AR), Organic Oxidizable (OO) and Resistant (RR) fractions. Metals extracted in the first fraction will be those that exist loosely bonded or adsorbed on exchangeable surfaces of clay minerals and organic matter. Metals combined with hydrous and amorphous Fe and Mn oxides, carbonates, sulphides and others (reducible phase) will be extracted in the second fraction. In the oxidizable organic fraction metals bonded strongly to various kinds of organic compounds will be extracted. Metals in the resistant fraction will constitute metals that still remain in the solid form or in silicate minerals. Metals in the first three fractions have the potential to leach out to the soil provided the soil pH is conducive enough for them to be in the available form in the soil water.

The current study was carried out at selected agricultural areas in Peninsular Malaysia on different types of soil of different origins. Soils developed on weathered rock were represented by the soils from Cameron Highlands and Cheras in the state of Pahang and Selangor respectively. The soils of mixed nature, developed on hill slopes were represented by soil samples from Kajang and Serdang in the state of Selangor. Samples of paddy soils were collected from Muda in the state of Kedah, Arau in the state of Perlis, Besut in the state of Terengganu and Bumbung Lima in the state of Penang. Alluvial soil from non-paddy cultivated areas was collected from Bangi, Sitiawan, Marang and Tumpat in the state of Selangor, Perak, Terengganu and Kelantan respectively.

Soils samples were collected from 0 to 30 cm depth at each sampling station. The soil samples were air-dried in the laboratory environment followed by grinding with mortar and pestle. 10 g samples were weighed into kartel bottles, followed by the addition of 50 mL of 1.0 M NH_4CH_3COO (pH 7). The samples were then shaken for 1-1½ h, followed by centrifuging at 3000 rpm for half an hour. This was followed by filtering through 0.45 µm pore size membrane filter paper. Then 50 mL of distilled-dionized water was used for the washing process following the same procedure to free it from the first ELFE reagent. The filtered samples were labelled as Easily Leachable and Ion Exchange fraction (ELFE). The second step in the extraction process was to add 50 mL of 0.25 M $NH_2OH.HCl$ followed by the same process of shaking,

centrifuging and washing. This second fraction was labelled Acid Reducible fraction (AR). For the third fraction, 15 mL of H_2O_2 was added into the kartel bottles followed by placing them in a water bath for 2-2½ h. The samples were cooled off prior to adding 50 mL of 1.0M NH_4CH_3COO acidified with HCl to pH 3.5. The process was carried out in the same manner as described above. The filtered samples were labelled Organic Oxidation fraction (OO). For the extraction of heavy metals trapped in the mineral silicates or in the basic rock at each particular area, samples were digested using HNO_3: $HClO_4$ (in the ratio 20:10) and heated on a sand bath until the samples became whitish. They were then centrifuged and filtered using the procedure described and distilled-dionized water was added to make it up to 50 mL of the filtered sample and labelled as Resistant fraction (RR).

The determination of heavy metals in the soil was carried out using the ICP-Plasma. The other research parameters included in the study were soil pH (Duddridge and Wainright, 1981), organic matter content (Walkley and Black, 1934) and grain size (Badri and Aston, 1983). All the treatments were conducted in triplicate.

3. RESULTS

3.1. Total Mn Concentration in Agricultural Soils

In this study, the total Mn concentration in weathered soils was significantly higher than that of alluvial and peat deposits (**Fig. 1**). In the vegetable farming areas of Cameron Highlands and Cheras, the soil Mn concentration was 720.27 and 885 mg kg^{-1} respectively.

Manganese concentration in the alluvial soils of the study areas ranged from 10.11 to 158.89 mg kg^{-1} whereas in peat soils of Sepang, the total Mn concentration recorded was 87.97 mg kg^{-1}. Manganese concentration in alluvium deposited at the inland valleys (Bangi, Besut) was higher than that of the alluvium deposited in areas further from the source rocks (Marang, Tumpat, Sitiawan).

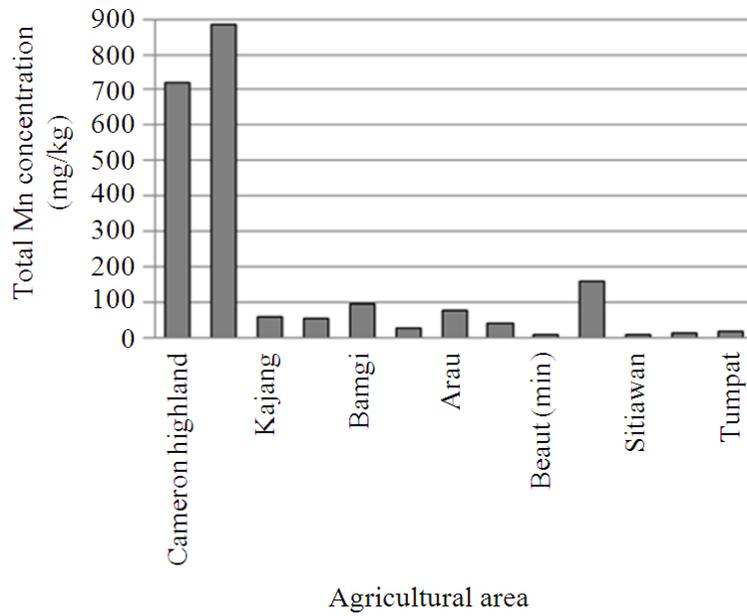## 3.2. Manganese Speciation in Agricultural Soils

Manganese speciation in agricultural soils of Peninsular Malaysia varied widely (**Table 1**). Generally, different speciation was observed in soils developed on weathered rocks, hill slopes, alluvium (paddy and non-paddy soils) and peat deposits. In soils developed on weathered rocks, Mn tended to occur in the resistant form. Nearly half of the soil Mn in Cameron Highlands and Cheras were concentrated in the RR fraction, indicating its presence in the resistant form. The Mn concentration in each fraction was in the following decreasing order: RR>OO~AR>ELFE (**Fig. 2**).

The agricultural soils of Kajang and Serdang constituted soils of mixed nature developed from eroded materials on hill slopes. The soils were acidic (pH 6.57 and 4.17 respectively), low in organic carbon content (1.28 and 0.13% respectively) and sandy. More than half of the soil Mn in Kajang and Serdang accumulated in the OO fraction (**Fig. 2**). It was followed by the ELFE, RR and AR fractions.

The coastal plain of Peninsular Malaysia constitutes alluvial and peat deposits of the Quaternary era. Generally, the alluvium is comprised of clay, silt, sand and gravel deposited at marine and terrestrial environments, whereas peat deposits are accumulated locally at swampy areas (Bosch, 1988; Tjia and Sharifah Mastura, 2013). Manganese speciation in alluvial deposits varied, depending on the type of agricultural activities, which are identified as the waterlogged paddy cultivation method and the non-paddy cultivated areas. Paddy cultivation in the state of Kedah and other areas including Arau, Bumbung Lima and Besut is carried out on the alluvial deposits of marine and terrestrial origin, as well as on peat deposits. In these areas, Mn (in paddy soils) has always been highly concentrated in the ELFE fraction, indicating the bioavailable form. With the exception of Bumbung Lima (RR fraction), the Mn concentration in these paddy areas was also high in the AR fraction. The Mn speciation in the paddy soils of Kedah, Arau and Besut was in the following decreasing order: ELFE>AR>OO>RR whereas in Bumbung Lima the order was as follows: ELFE>RR>AR>OO (**Fig. 3**).

Manganese speciation in the alluvial deposits of non-paddy cultivated areas is widely varied. In Bangi area, the Mn speciation was in the following decreasing order: AR>OO>RR>ELFE. In Sitiawan, the concentration of Mn was highly associated with the RR fraction, followed by that in the AR, OO, ELFE fractions. In Marang, the Mn speciation was as follows: AR>ELFE>OO>RR, whereas in Tumpat, Mn concentration was higher in the AR fraction, followed by that in the OO, RR and ELFE fractions. In the peat soils of Sepang, more than half (55.16%) of the soil Mn was associated with organic carbon.

Fig. 1. Total manganese concentration in agricultural soils
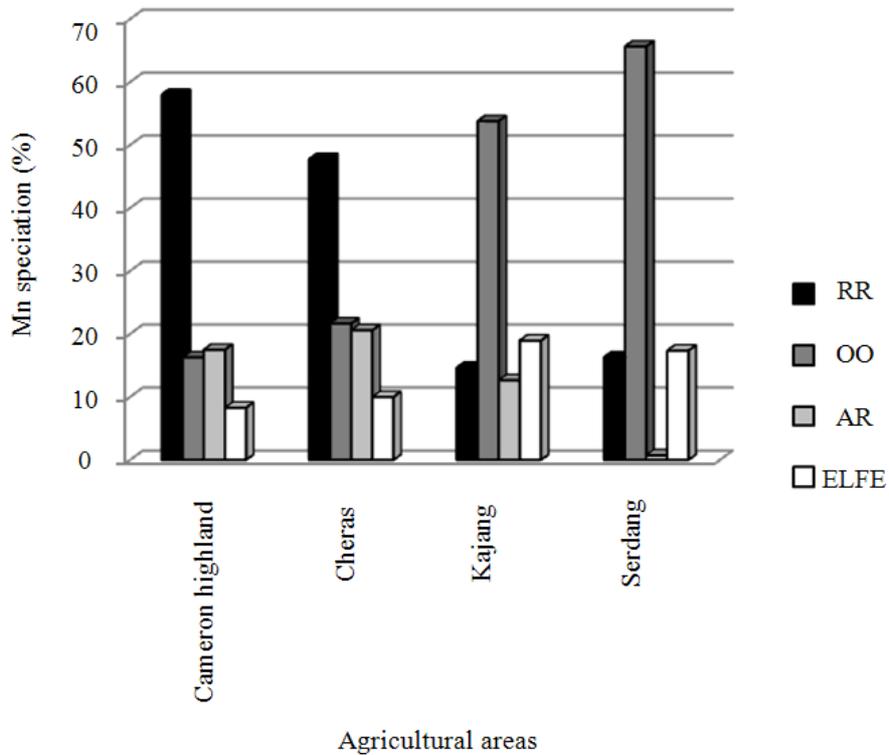
Fig. 2. Mn speciation in agricultural soils developed on the weathered rocks and the soils of mixed nature on hill slopes
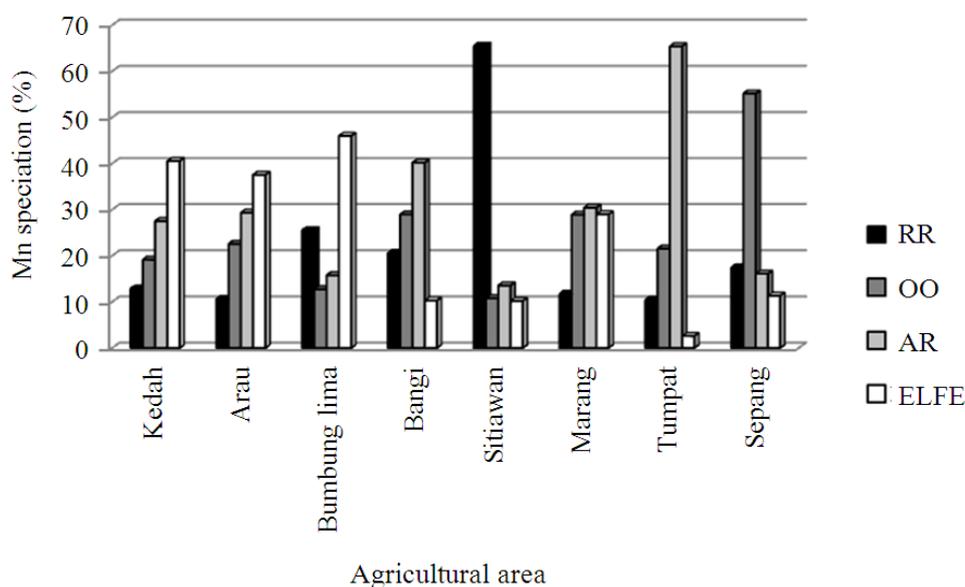
Fig. 3. Mn speciation in soils developed on alluvial and peat deposits (paddy and non-paddy cultivated areas)

Table 1. Mn speciation, pH, organic carbon content and grain size (less than 63 µm) of agricultural soils in Peninsular Malaysia

Agricultural area	Mn speciation (mg/kg)					pH	Organic carbon content (%)	Grain size less than 63 µm (%)	Sources
	RR	OO	RA	ELFE	Total				
Cameron highlands	417.73	117.07	125.90	59.57	720.27	6.75	2.23	42.33	Khairiah *et al.* (2006)
Cheras	422.70	191.70	182.30	88.40	885.10	7.23	2.43	9.10	Khairiah *et al.* (2006)
Kajang	8.52	31.36	7.38	11.04	58.30	6.57	1.28	15.72	Current study
Serdang	8.97	36.16	0.41	9.55	55.09	4.17	0.13	31.28	Current study
Kedah	3.31	4.93	7.08	10.44	25.76	4.94	5.67	80.82	Khairiah *et al.* (2009c)
Arau	8.08	17.17	22.31	28.58	76.14	4.63	5.53	73.15	Khairiah *et al.* (2009c)
Bumbung Lima	10.14	5.06	6.26	18.26	39.73	6.54	5.12	82.00	Habibah *et al.* (2011)
Besut	0.65-	0.42-	2.09-	3.45-	8.87-	5.45-	1.46-	67.37-	Khairiah *et al.* (2012)
	8.45	11.19	126.41	14.01	158.89	6.12	9.86	76.82	
Sitiawan	6.62	1.09	1.37	1.03	10.11	4.76	1.42	64.50	Khairiah *et al.*(2009a)
Bangi	19.95	28.05	38.93	9.96	96.89	6.83	1.24	17.54	Khairiah *et al.* (2009b)
Marang	1.54	3.79	3.99	3.80	13.12	6.03	2.56	32.40	Current study
Tumpat	1.72	3.55	10.77	0.43	16.47	5.78	1.78	13.67	Current study
Sepang	15.31	48.52	14.18	9.96	87.97	4.52	26.85	58.26	Khairiah *et al.* (2009b)

4. DISCUSSION

In this study, it was found that total Mn concentration in agricultural soils depended on the soil composition, which reflected their origin. Soils that originated from weathered rocks naturally reflected the constituents of their parent material. According to Uren (2013), the concentration of Mn in soil derived from rocks which contained high proportions of ferromagnesian minerals (1300-2200 mg kg^{-1}) was higher than that of felsic igneous rocks

(500 mg kg^{-1}). The concentration of Mn oxy-hydroxide is also high in lateritic soil on serpentine bedrock (Tashakor *et al.*, 2011). Cameron Highlands and Cheras agricultural areas constituted weathered felsic igneous rocks and the total Mn concentration in both areas reflected the natural origin of this metal. The sandy natured soils of Marang, Tumpat and Sitiawan could also have contributed to the lower Mn content. The lower amount of manganese in sandy soil was due to the manganese occurrence as coated Mn oxides on the sediment surface (Kämpf *et al.*, 2000).

In this study, Mn speciation was widely varied according to the soil composition, which in turn reflected their parent materials. In soils originated from weathered igneous rocks, Mn was highly concentrated in the Resistant (RR) form. Conversely, its concentration in the available form (ELFE) was almost non-existence.

In igneous rocks, Mn^{2+} primarily replaced Fe^{2+}, Mg^{2+} and ions of similar size in silicates. Upon weathering, the minerals or rocks disintegrated and manganese ions were released into the environment. Mechanical decomposition of granite, accompanied by some leaching of biotite, can be connected locally with the loss of two thirds of the primary manganese content (Wedepohl *et al*., 1970). The fate of Mn depended substantially upon the leaching of the divalent manganese (Mn^{2+}) in solution, mainly as the bicarbonate ($Mn(HCO_3)_2$) and the precipitation of very insoluble hydroxides and oxides of trivalent (Mn^{3+}) or quadrivalent manganese (Mn^{4+}). The Mn^{2+} released from minerals was immediately reprecipitated as insoluble MnO_2, if conditions permitted. Only a minor proportion was lost in the surface run-off (Kämpf *et al*., 2000). A study on weathered schist associated with U mineralisation showed strong enrichment of REEs in Mn oxide accumulation zones. The deposition of Mn-phases, appear to have led to the enrichment of Ce relative to the other REEs. This differential enrichment suggests a redox mediated process involving Mn oxy-hydroxide surfaces (Koppi *et al*., 1996).

The soil pH in Cameron Highlands and Cheras was 6.75 and 7.23 respectively. In such conditions, the solubility of Mn will be affected by the redox conditions (Kyuma, 2004). In a humid tropical country like Malaysia, the weathering processes is dominated by oxidation (Shamshuddin and Ishak, 2010), resulting in the formation of MnO_2. Similarly, in the present study, the soils that were developed on weathered rocks contained high amounts of resistant MnO_2 as indicated by the high level of Mn in the RR fraction.

In the present study, even though the organic carbon content in agricultural soils of Kajang and Serdang was low, Mn tend to accumulate with the soil organic carbon. According to Adriano (1986), organic soils act as an effective sorbent compared to mineral soils in an acidic environment. This is consistent with the results of a study on paddy soil which showed that the EDTA-extractable content of Cr, Cu, Fe, Mn, Pb and Zn were negatively correlated with the soil pH, but positively correlated with the organic matter content (Zeng *et al*., 2011).

Manganese speciation in paddy soils of the study areas was observed to have been influenced by redox conditions. The seasonal wetting and drying cycles throughout the paddy cultivation controlled the dissolution and precipitation of Mn-oxyhydroxides. Manganese was mobilized by reduction and then precipitated upon oxidation into various forms, such as pore infillings, mottles and concretions (Adriano, 1986; Kyuma, 2004; Mancheau *et al*., 2005). The presence of both iron and Mn mottles and concretions were reported in paddy soils of the Kemubu Plain (Paramananthan, 1989). In flooded soils, Mn(IV) was reduced to Mn(II) thus increasing the water-soluble Mn^{2+} ions in paddy soils. Upon drying, Mn was oxidized into the resistant Fe-Mn mottles and occluded as oxides and hydroxides. Mancheau *et al*. (2005) reported that ferromanganiferous (FeMnMot) mottles in clayey paddy soils were enriched with both Fe and Mn, whereby, Mn occurred as resistant lepidocrocite and birnessite. Manganese in the background mass occurred as Mn-oxyhydroxides. Upon flooding, the reducing condition recurred, rendering the dissolution of the Mn-oxyhydroxides and Mn^{2+} was liberated. This condition explains the high percentage of Mn in the bioavailable form (ELFE), followed next in the Acid Reducible (AR) and unavailable Resistant (RR) forms.The changes of Mn oxidation state was also observed at the oxic-anoxic interface of the continental slope sediments (Anschutz *et al*., 2005).

Apart from the redox condition, the high percentage of bioavailable Mn in paddy soils might be attributed to the application of fertilizers containing Mn during paddy cultivation. Anthropogenic heavy metals tend to occur in the bioavailable form. However, Mn toxicity has not been observed in the paddy soils of Peninsular Malaysia because the amount of bioavailable Mn is well below the threshold level. The threshold level for Mn toxicity is >300 mg kg^{-1} of readily reducible Mn (Kyuma, 2004). Furthermore, this metal is an essential micronutrient.

Manganese speciation in the alluvial deposits of non-paddy cultivated areas varied widely and is less understood. The inconsistent Mn speciation in soils could be related to the grain size sediments and its present environmental condition. According to Schulte and Kelling (1999), the acidic sandy soils are likely to contain high manganese levels. Excess manganese levels tend to occur in acidic soils (pH) especially when these soils are low in organic matter and temporarily waterlogged. Generally, the non-paddy cultivated areas of Peninsular Malaysia were highly exposed to oxidizing conditions. The soils were occasionally submerged by shallow water table during the rainy season. The seasonal

moisture change and the presence of interfering organic and inorganic components in the soil solution could possibly be related to the occurrence of fine grain size and poor crystallinity of Mn oxides in soils (Kämpf *et al.*, 2000). In the current study, Mn oxides could reflect the occurrence of Mn in the RR and AR fractions. Apart from that, Mn speciation in the agricultural soils of alluvial deposits might be attributed to the soil composition due to the distance from the source materials and grain size distribution. More detailed studies are needed to understand Mn speciation in soils with respect to both parameters.

In peat soil, Mn tends to be associate with soil organic matter. According to Adriano (1986), high accumulation of Mn in organic matter was attributed to organic matter complexation, particularly, humic acid. Organic matter is widely known for its ability to absorb heavy metals and is less pH-dependent than sorption by mineral soils. Hence, the high Mn concentration in the OO fraction was not surprising since soils in the Sepang area were rich in organic carbon content (26.85%). The factors that determine the available fraction for some elements are their physicochemical and biological properties, such as soil pH, the prevailing redox conditions, extent of organic matter degradation, grain size distribution, water content and microbial activity that could change with time (Tagami and Uchida, 1998).

5. CONCLUSION

The total Mn concentration was significantly higher in soils developed on weathered rocks compared to those from the eroded materials, alluvium and peat deposits. Most of the soil Mn in weathered rocks was concentrated as the resistant manganese oxides at the topsoils. In the soils of mixed nature, formed from eroded materials on the hill slopes, Mn tended to be associated with the organic carbon. Manganese speciation in the waterlogged paddy soils was influenced by the redox conditions caused by alternate seasonal wetting and drying conditions. In paddy soils, Mn concentration is highest in the bioavailable form, followed by the AR and RR forms. In the non-paddy cultivated alluvial soils, Mn speciation was more varied and less predictable. Manganese in peat soils was highly associated with the organic matter, as indicated by the high Mn concentration in the OO fraction.

6. ACKNOWLEDGEMENT

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