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Aqua regia and ethylenediaminetetracetic acid (EDTA) trace metal levels in agricultural soil

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Soil samples were collected from irrigation farmlands along the bank of Mada River and analysed for aqua regia and ethylenediaminetetracetic acid (EDTA) extractable trace metal (Cd, Cr, Cu, Pb, Zn Ni, Fe and Mn) concentrations. Water samples at source were also collected for analysis. Metal levels were quantified using atomic absorption spectrometry (AAS). Aqua regia and EDTA extractable Fe and Cd concentrations were the highest and lowest, respectively. The highest and lowest aqua regia and EDTA trace metal concentrations were recorded at sites 1 and 3, respectively. Aqua regia trace metal levels were generally higher than that of EDTA, but below the critical values for irrigation soil. Soils were extremely enriched with Cd (153 – 289), and deficient in Fe (0.5 – 1.0) contents. Fe Kd was generally the highest (21.45 – 44.35 kgl-1) and Zn (0.03 – 0.08 kgl-1) the lowest. Higher total metal contents result in a lower proportion of metal being sorbed, because potential absorption sites are filled in decreasing order of affinity. Strong and positive correlations existed for Cr/Zn (0.9879) and Cu/Ni (0.8077) at Site 1, Cu/Ni (0.9229) and Pb/Pb 0.9581) at Site 2, and Ni with Cr (0.9440) and Cu (0.8153) at Site 3. Significant correlations for soil-water indicated contributions of irrigation water to total metal contents in soil.

Key words: Trace metal, soil, aqua regia, ethylenediaminetetracetic acid (EDTA), enrichment factor, partition coefficient.

INTRODUCTION

Soil is a complex and heterogeneous mixture of organic and inorganic matter, as well as different components that determine the physical, chemical and biological properties of the soil (Friedlova, 2010; Ozba, 2011; Ponil et al., 2013). Long-term and extensive use of agricultural land with frequent application of growing practices and use of pesticides may cause heavy metals such as copper, nickel, zinc and cadmium to be strongly accumulated in the topsoil, a problem that affects agriculture and human health (Hector et al., 2011).

Metals cannot be synthesized or degraded by biological or chemical processes (Dekayir et al., 2010; Zovko and

Romic, 2011) and are chemically very reactive in the environment, which results in their mobility and bioavailability to living organisms (Tukura et al., 2012). Although, trace quantities of certain heavy metals are essential to animals and plant growth, they are of considerable environmental concern due to their toxicity and cumulative behaviour (Akpoveta et al., 2010; Ramesh et al., 2010). People can be exposed to high levels of toxic metals by breathing air, drinking water, or eating food that contains them. As a consequence, metals get into the human body by different routes - by inhaling, through skin, and via ingestion of contaminated

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food (Myung, 2008). Toxic trace metals entering the ecosystem may lead to geo-accumulation, bio-accumulation and bio-magnifications (Fagbote and Olanipekun, 2010; Kibria et al., 2012; Ponil et al., 2013). They get accumulated in time in soils and plants and would have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange and nutrient absorption) determining the reductions in plant growth, dry matter accumulation and yield (Adefila et al., 2010; Fagbote and Olanipekun, 2010; Jayashree and Sarma, 2012).

Trace metals are released into the environment by both natural and anthropogenic sources (Myung, 2008). Anthropogenic inputs are associated with industrialization and agricultural activates deposition, such as atmospheric deposition, waste disposal, waste incineration, urban effluent, traffic emissions, fertilizer application and long-term application of wastewater in agricultural land (Akan et al., 2010).

Organic matter and pH are the most important parameters controlling the accumulation and the availability of trace metals in soil environment (Ramesh et al., 2010; Eneje and Lemoha, 2012). Each change in pH alters the adsorption capacity of minerals and organic colloids. Positive charge prevails at low pH conditions under which anion exchange capacity is dominant, while at high, pH negative charge prevails and cation exchange capacity predominates (Tukura et al., 2013). Organic complexation may increase or decrease adsorption of trace metals affecting transport and fate (Yin et al., 2008). Methods used for the evaluation of the pool of soluble (available) trace metals in soils are based mainly on extractions by various solutions as single or sequential extraction (Amit and Sarita, 2006). Single extractants may broadly be divided into weak replacement of ion salts ($MgCl_2$, $CaCl_2$, NH_4NO_3), dilute solutions of either weak acids (acetic acid) or strong acids (HCl, HNO_3) and chelating agents (DTPA, EDTA) (ISO, 1995). The first type of extractants are able to release into solution metals which are associated with the exchange sites on the soil solid-phase and hence can be considered as bioavailable (Amit and Sarita, 2006). The chelating agents, such as DTPA, EDTA and NH_4AOC, form complexes with free metal ions in solution and thus reduce the activities of the free metal ions in solution, reflect mobilisable metals which can be used and metabolized by plants (Atun and Meja, 1998).

Intensive irrigation farming of vegetables was carried out in some farmlands along the bank of Mada River during the dry season. Research on physicochemical properties of irrigation water (Tukura et al., 2012) and soil (Tukura et al., 2013) has been reported. Information on trace metal contents of the soil is scarce. This research intends to evaluate aqua regia and EDTA trace metal levels of the soil, the impact of irrigation water on soil trace metal levels and to ascertain whether the agricultural soils were depleted, enriched or contaminated as a result of human activities.

MATERIALS AND METHODS

Sampling and sample preparation

Twenty sub-soil samples were collected at a depth of 1 to 10 cm using a hand trowel, from three irrigated farmlands along the bank of Mada River (Figure 1), and each combined to form a homogenized composite sample for each farmland. The homogenized samples were air dried for seven days, grind in a clean mortar and pestle and sieved to pass through a 2 mm alumina mesh, then preserved in washed clean plastic bottles for analysis. For the determination of aqua regia extractable trace metal concentrations, 28 cm^3 37% HCl:70% HNO_3 (3:1 v/v) was added to 1.00 g of the dried sieved (2 mm) sediment sample and left to stand for 24 h. The mixture was then heated on a hot plate at 140°C to near dryness. The residue was filtered through Whatman No. 41. The solution was then transferred into 50 cm^3 volumetric flask and made to mark with distilled water, then preserved for metal analysis.

The method used by Atun and Maja (1998) was adopted for EDTA extractable metal concentrations. 50 cm^3 of 0.05M EDTA was added to 10 g (5:1) of the sieved soil samples in 100 cm^3 conical flask. The mixture was shaken using an end to end shaker at 220 rpm for 60 min on a shaker, and then filtered through Whatman No. 41 filter paper. The filtrate was preserved for extractable metal analysis. Total metal concentrations in water samples from source were also determined. The irrigation water samples were collected in one litre polythene bottles properly washed, and 5 ml conc.HNO_3/L added to the sample for preservation (APHA, 1985). 50 cm^3 of acidified unfiltered water sample was mixed properly and transferred into a 250 cm^3 beaker. 3 cm^3 of concentrated HNO_3 acid was added and covered with a watch glass and heat gradually on hot plate. Concentrated HNO_3 acid was added continuously until digestion was completed. The solution was evaporated to near dryness and cooled. Small quantity of 1:1 concentrated HCl/HNO_3 acid was added and warmed. Watch glass and beaker walls were washed down with distilled water and filtered and volume adjusted to 25 cm^3 for total trace metal determination.

Statistical analysis

Aqua regia and EDTA trace metal concentrations in soil were presented as mean ± SD. Pearson's correlation coefficients (r) were estimated for trace metal levels in soil and water in order to determine water – soil trace metal relationship, their possible sources and mechanism of soil contamination, using SPSS statistics 17.0 software.

Enrichment factor (EF)

Enrichment factors (EF) were determined (Fagbote and Olanipekun, 2010; Shaila et al., 2010; Edward et al., 2011).

$$EF = (C_n/Fe) / (C_n/B_n)$$

C_n = measured content of elements, B_n = element's content in shale (Pb: 20, Cr: 90, Cu: 45, Cd: 0.20, Zn: 95, Fe: 95, Fe: 4700, Mn: 850, Ni: 68).

Partition coefficient (K_d)

Solid-solution partitioning is critical to assess the potential leaching of metals and their bioavailability in soils (Sauve et al., 2003). Metal partition coefficients (K_d) for soil-water system (Jerry and Terry,
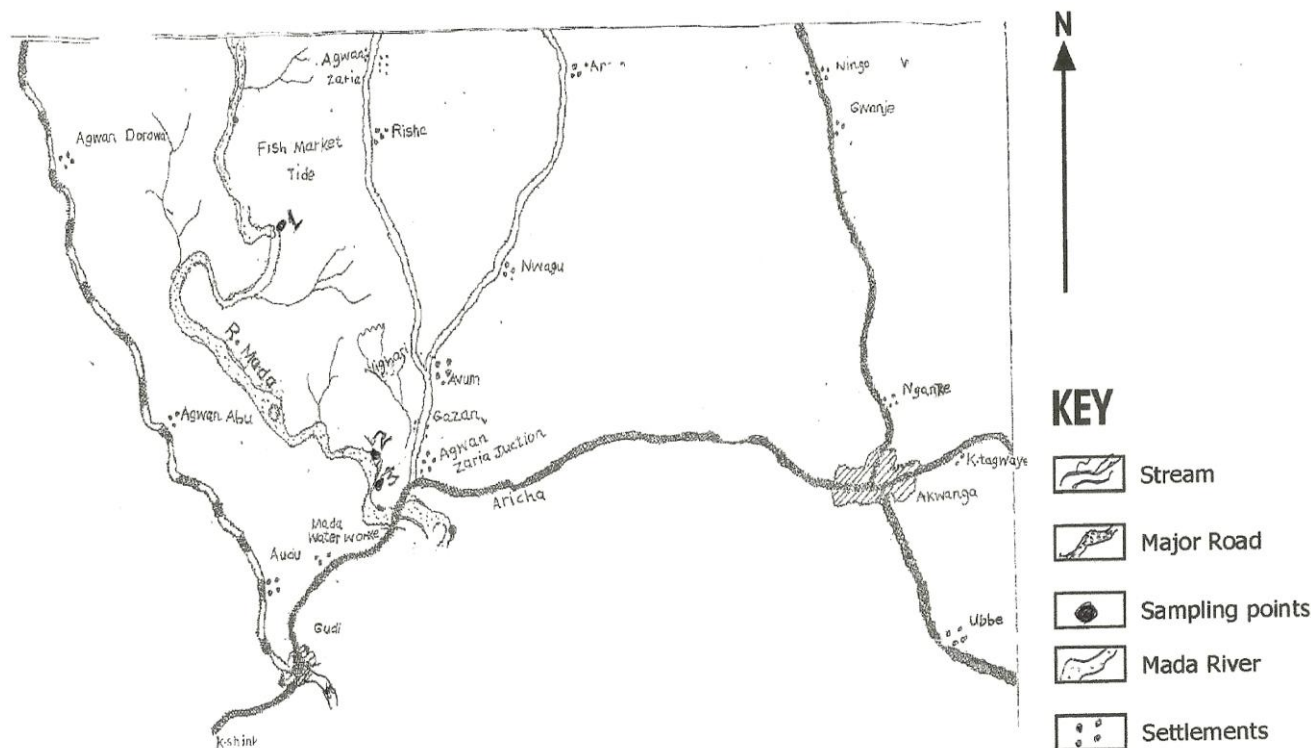
Figure 1. Map showing sampling sites.

2005) was also determined as:

$$K_d = \frac{\text{Mental concentration in soil (mg/kg)}}{\text{Mental concentration in water (mg/l)}}$$

RESULTS

Results for aqua regia extractable trace metal concentrations are presented in Table 1. The concentration ranged from 0.010 ± 0.01 - 0.013 mg/kg for Cd, Cr: 0.0.45 ±0.01 - 0.05 0.00 mg/kg, Cu: 0.012 ± 0. 00 - 0.049 0.00 mg/kg, Pb: 0.090 ± 0.00 - 0.154 ± 0.03 mg/kg, Zn: 0.138 ± 0.0.01 - 0.242 ± 0.0.00 mg/kg, Ni: 0.066 ± 0.00 - 0.074 ± 0.00 mg/kg, Fe: 4.29 ± 0 0.01 - 8.646 1.55 mg/kg, and Mn: 5.086 ± 0.03 - 5.951 ± 0.0.01 mg/kg. Level of trace metal accumulation at the sites varied in the order Site 1 > Site 2 > Site 3. Results for EDTA (Table 2) indicated that the concentrations of trace metal varied from 0.001 ± 0.00 - 0.009 ± 0.00 mg/kg) for Cd, Cr : 0.001 ± 0.00 - 0.011 0.00 mg/kg, Cu: 0.022 ± 0.00 - 0.025 ± 0.00 mg/kg, Pb: 0.006 ± 0.00 - 0.054 ± 0.00 mg/kg, Zn: 0.085 ± 0.00 - 0.089 ± 0.02 mg/kg, Ni: 0.021 ± 0.00 - 0.042 ± 0.00 mg/kg, Fe: 1.154 ± 0.02 - 7.862 ± 0.02 mg/kg, and Mn: 0.216 ± 0.02 - 0.387 ± 0.05 mg/kg. Site 1 (1.03 ± 2.76 mg/kg) and Site 3 (0.28 ± 0.41 mg/kg) were the most and least accumulated,

respectively.

A comparison in the variations of aqua regia (total) and EDTA trace metal concentrations (mg/kg) in soil are shown in Figure 2. Concentrations of Cr at Sites 1 and 3 were similar and lowest at Site 1. Cu and Zn levels did not vary significantly at Sites 2 and 3. Total and EDTA concentrations of Pb and Ni were generally low, while that of Fe decreased in the order of Site 1 > Site > 2 > Site 3. Total Mn concentrations remained similar in all sites.

From Table 3, total metal concentrations in water varied according to site. Concentration of Cd was relatively low at Sites 2 and 3 compared to Site 1 (0.009 mg/l). Cr varied from 0.10 to 0.17 mg/l, while concentration of Cu and Pb ranged from 0.06 to 0.09 mg/L and 0.23 to 0.28 mg/L, respectively. Zn varied from 1.63 to 1.69 mg/l, Ni: 0.03 - 0.09 mg/l, Fe: 0.13 to 0.39 mg/l and Mn: 4.01 to 4.27 mg/l. For EF results (Table 4), at Site 1, EF was in increasing order of Cr > Cd > Mn > Pb > Cu > Ni > Fe and Cd > Mn > Pb > Cu > Ni > Fe > Cd at Site 2. EF at Site 3 occurred in decreasing order of Cd > Mn > Pb > Cu > Ni > Cr > Fe. K_d results for soil-water trace metal concentrations are presented in Table 5. K_d for Cd at the sites varied from 0.09 to 1.43 kg^{-1}, Cr ranged from 0.05 to 0.38 kg^{-1} and Cu from 0.13 to 0.82 kg^{-1}, while K_d for Pb and Zn varied from 0.32 to 0.67 kg^{-1} and 0.03 to 0.08 kg^{-1}, respectively. Kd for Ni was in the range of 0.73 to 2.46, Fe from 21.45 to 44.35 kg^{-1} and Mn
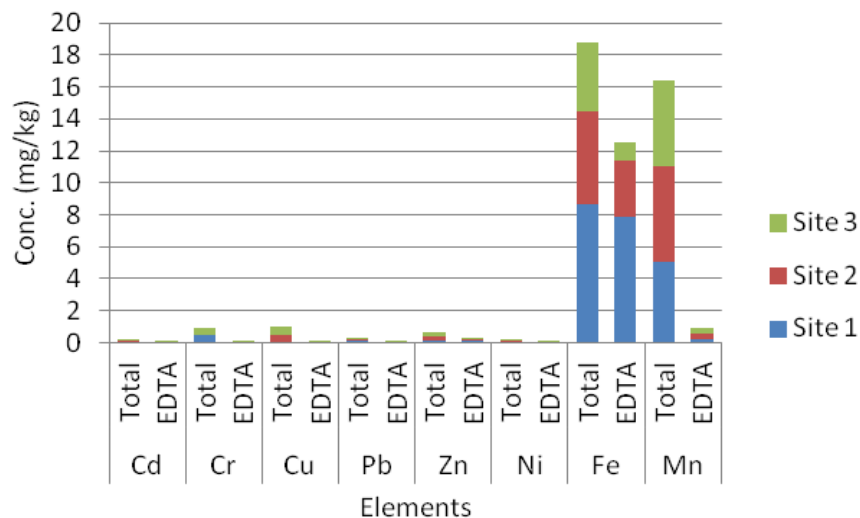
Figure 2. Sites variations in aqua regia and EDTA trace metal concentrations (mg/kg) in soil.

Table 1. Aqua regia extractable trace metal concentrations (mg/kg) in soil

Element	Sites		
	1	2	3
Cd	0.053±0.00	0.010±0.00	0.010±0.00
Cr	0.045±0.01	0.050±0.00	0.046±0.00
Cu	0.012±0.00	0.049±0.00	0.049±0.00
Pb	0.154±0.03	0.090±0.00	0.090±0.00
Zn	0.138±0.01	0.242±0.00	0.242±0.01
Ni	0.074±0.00	0.068±0.00	0.066±0.00
Fe	8.646±1.55	5.830±0.05	4.290±0.01
Mn	5.086±0.05	5.95±0 0.01	5.362±0.50
Mean	1.776±3.28	1.540±2.67	1.271±2.21

Table 2. EDTA extractable trace metal concentrations (mg/kg) in soil.

Element	Sites		
	1	2	3
Cd	0.001±0.00	0.009±0.00	0.009±0.00
Cr	0.006±0.00	0.011±0.00	0.001±0.00
Cu	0.025±0.00	0.022±0.00	0.022±0.00
Pb	0.006±0.00	0.054±0.03	0.054±0.00
Zn	0.089±0.03	0.085±0.00	0.085±0.00
Ni	0.042±0.00	0.021±0.00	0.027±0.00
Fe	7.862±0.20	3.520±0.04	1.154±0.02
Mn	0.216±0.02	0.343±0.00	0.387±0.05
Mean	1.03±2.76	0.51±1.22	0.28±0.41

from 1.26 to 1.46 kg^{-1}. Correlation coefficients for trace metal concentrations in soil-water system were determined (Tables 7 to 9).

At Site 1 (Table 6), Cd correlated moderately with Cu (0.6504). Correlations for Cr/Cr (0.6934), Cr/Mn (0.5547) was moderate, while Cr/Zn (0.9879) was positively

Table 3. Average trace metal levels (mg/l) in irrigation water.

Metal	Sites		
	1	2	3
Cd	0.009	0.007	0.007
Cr	0.12	0.10	0.17
Cu	0.09	0.06	0.09
Pb	0.23	0.28	0.25
Zn	1.69	1.63	1.63
Ni	0.03	0.06	0.09
Fe	0.39	0.13	0.20
Mn	4.01	4.08	4.27

Table 4. Enrichment factors (EF) for trace metal concentrations (mg/kg) in soil.

Element	Sites		
	1	2	3
Cd	153.1	289	289
Cr	260	0.3	3
Cu	13	5	5
Pb	16	9	9
Ni	6	5	5
Fe	1	0.7	0.5
Mn	31	36	33

Table 5. Soil/water trace metal partition coefficients (KgL^{-1}).

Element	Sites		
	1	2	3
Cd	0.09	1.43	1.43
Cr	0.38	0.05	0.27
Cu	0.13	0.82	0.56
Pb	0.67	0.32	0.36
Zn	0.08	0.03	0.03
Ni	2.46	1.13	0.73
Fe	22.18	44.35	21.45
Mn	1.27	1.46	1.26

strong. Strong correlations existed for Cu/Cu (0.7523), Cu/Pb (0.6934) and Cu/Ni (0.8077). Zn correlated weakly, except with Pb (0.5042) which was moderate. Mn correlated strongly with Cd (0.7740) and moderately with Ni (0.6154). From Table 7, Cd correlated moderately with Cu (0.673) and Zn (0.520), and strongly with Ni (0.9229), while Cr correlated moderately with Cu (0.5264) and positively strong with Ni (0.7170). Pb/Cu and Pb/Pb correlated moderately. Ni/Ni (0.9581), Fe/Fe (0.7845) and Fe/Mn (0.7308) relationships were significantly strong. Correlations for Ni/Cr (-0.8669) and Cr/Cr (-0.9221) were strongly negative. Fe related moderately with Pb (0.6644), weakly with Cd (0.0920). Results in Table 8 indicated that Cd/Cd (0.5099), Cd/Pb (0.6821), Cd/Ni (0.5989) and Cd/Mn (0.5303) correlated moderately. Positive and moderate correlations also existed for Pb/Cu (0.6541) and Fe/Pb (0.6644). Ni correlated very strongly with Pb (0'9940) and Cu (0.8035).

DISCUSSION

Accumulation of trace metals at Site 1 was in the order of Fe > Mn > Pb > Zn > Ni > Cu > Cd > Cr. A similar trend

Table 6. Correlation coefficients of trace metal concentrations in soil with water at Site 1.

Elements in soil	Elements in water							
	Cd	Cr	Cu	Pb	Zn	Ni	Fe	Mn
Cd	0.0661	-0.4660	0.6504	-0.3626	0.0234	-0.2069	-0.7979	-0.6504
Cr	-0.0651	0.6934	-3.67E-16	0.5670	0.9879	-0.9707	0.2611	0.5547
Cu	0.3568	-0.2735	0.7523	-0.9631	-0.4692	0.1596	0.3863	-0.5243
Pb	0.2171	-0.4160	0.6934	-0.1890	0.2195	-0.4160	-0.6093	-0.4160
Zn	0.2632	0.2354	-0.9420	0.5042	-0.1065	0.4372	0.3589	0.2691
Ni	0.2150	-0.7308	0.8077	-0.3669	-0.2131	-0.0385	-0.4587	-0.4231
Fe	0.2910	0.0289	-0.1157	0.1182	0.4120	-0.3181	-0.7078	-0.4627
Mn	0.7740	-0.0384	-0.8077	0.1048	-0.3196	0.6154	-0.2655	-0.3462

Significant at $p \leq 0.05$.

Table 7. Correlation coefficients of trace metal concentrations in soil with water of Site 2.

Soil	Cd	Cr	Water					
			Cu	Pb	Zn	Ni	Fe	Mn
Cd	0.1307	-0.8054	0.6763	0.4631	0.5210	0.9229	0.2986	-0.4174
Cr	0.0041	-0.9224	0.5264	-4.69E-15	-0.3430	0.7120	-0.2256	0.2712
Cu	0.8387	-0.7560	-0.1387	-0.2774	-0.7906	0.2917	0.4160	0.5000
Pb	-0.3458	-0.6429	0.6290	0.6290	2.65E-15	0.7170	-0.1048	-0.3780
Zn	-0.6100	-0.3780	0.5547	-0.1387	0.3162	0.3647	-0.8321	0.3000
Ni	0.2226	-0.8669	0.7518	0.0289	-0.6594	0.9581	0.1157	-0.1043
Fe	0.4313	0.1336	0.1961	0.1961	-0.5590	0.3094	0.7845	-0.7071
Mn	0.8248	-0.6290	-0.3462	0.2308	-0.6580	0.1618	0.7308	0.1387

Significant at $p \leq 0.05$.

Table 8. Correlation coefficients of trace metal concentration in soil with water of Site 3.

Soil	Cd	Water						
		Cr	Cu	Pb	Zn	Ni	Fe	Mn
Cd	0.5099	-0.0837	-0.5105	0.6821	-0.8343	0.5959	0.1565	0.5303
Cr	-0.8776	0.4246	0.5918	-0.6621	0.5067	-0.2961	-0.2961	0.0758
Cu	0.3206	0.0938	0.0938	-0.6699	0.0034	-0.2945	-0.2945	-0.6976
Pb	-0.0463	0.6541	0.1635	-0.1369	-0.6363	0.0803	0.0803	0.2697
Zn	-0.1817	-0.5042	-0.0458	-0.2110	0.6370	-0.3988	-0.3988	-0.1890
Ni	-0.6142	0.9940	0.8135	-0.4919	0.1000	0.4313	0.4313	-0.1491
Fe	0.0920	-0.8479	-0.8480	0.6644	-0.3822	-0.15761	-0.15761	-1.69E-14
Mn	-0.7009	0.1833	0.4125	-0.6908	-0.2548	-0.4953	-0.4953	-1.01E-13

Significant at $p \leq 0.05$.

was observed for Fe and Mn at Site 3. Pb (0.090 ± 0.00 - 0.154 ± 0.02 mg/kg) and Zn (0.242 ± 0.01- 0.138 ± 0.01 mg/kg) were also high. Aqua extractable concentrations of Fe (5.83 ± 0 0.05 mg/kg) and Mn (5.951 ± 0.01 mg/kg) were generally high in all the sites, while Cd was the lowest (0.010 ± 0.00 - 0.013 ± 0.00 mg/kg). Trace metal levels were similar at Sites 2 and 3. Aqua regia extractable trace metal concentrations in all the sites were below the total values reported by Lindsay (1979) and the critical values for irrigation soil ((McLean and Bledsoe, 1992).

EDTA extractable concentrations of Fe (1.154 ± 0.02 - 7.862 ± 0.02 mg/kg) was highest in all the farms and Cd the least (0.001 ± 0.00 - 0.009 ± 0.00 mg/kg).

Concentrations of Mn (0.216 ± 0.02- 0.387 ± 0.05 mg/kg), Zn (0.085 ± 0.00 - 0.089 ± 0.00 mg/kg) and Pb (0.006 ± 0.00 - 0.054 ± 0.03 mg/kg) were relatively high. EDTA Mn levels were higher compared to EDTA levels of other metals. Total metal concentrations were higher than the EDTA levels in all the sites. The highest aqua regia and EDTA levels were recorded for Fe and Cd the lowest. Aqua regia extractable trace metal concentrations were generally higher than the EDTA extractable metal concentrations, since aqua regia is a stronger extraction reagent. Aqua regia (1.776 ± 3.28 mg/kg) and EDTA (1.030 ± 2.760 mg/kg) trace metal concentrations were generally highest at Site 1. Intensive agricultural activities and large deposits of debris occurred at the site due to flash flood usually experienced during rainy season.

EF can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure, and to assess the degree of anthropogenic influence. Five contamination categories (Sutherland, 2000) are recognized on the basis of the enrichment factor as follows:

i. EF < 2 is deficiency to minimal enrichment,
ii. EF 2 - 5 is moderate enrichment,
iii. EF 5 - 20 is significant enrichment,
iv. EF 20 – 40 is very high enrichment,
v. EF > 40 is extremely high enrichment.

Soils were generally extremely enriched with Cd (153 - 289), very high enrichment for Mn (31 - 36) and deficient for Fe (0.5 - 1.0). Trace metals EF were highest at Site 1, except for Cd and Mn. Site 1 was extremely enriched with Cr (260) and significant enrichment for Mn (31), Pb (16), Cu (13) and Ni (6). Soil at Site 2 was significantly enriched with Pb (9), moderately enriched with Cu (5) and Ni (5), and deficient in Cr (0.3) and Fe (0.7). As the EF values increase, the contributions of the anthropogenic origins also increase. Human activities may account for the enrichment of soil by Cd, Cu and Pb, while Fe in soil may exist in nature.

Trace metal partition coefficients varied according to sites. K_d for Ni were greater than unity at Sites 1 (2.46 kgl^{-1}) and 2 (1.13 kgl^{-1}). Fe and Mn have the highest K_d at Site 2 and the lowest at Site 3. K_d for Fe was generally the highest (21.45 – 44.35 kgl^{-1}) in all the sites. Lower log K_d values suggest lower affinity of organic soils to sorb metals (Kucuksezgin et al., 2008). In most situation, a higher total metal content results in a lower proportion of metal being sorbed because potential absorption sites are filled in decreasing order of affinity (Sauve et al., 2003; Jerry and Terry, 2005). The more a soil becomes saturated with cations, the lower the metal affinity of the remaining sites (Sauve et al., 2003). K_d values obtained in this research were lower than the values reported by Sauve et al. (2003) in organic horizons of a forest soil. Correlation study of trace metals cannot only provide assessment of the relationship among metals but also

provides the basis for prediction of pollution sources of trace metals (Tukura et al., 2007). Correlations of Cr/Zn (0.9879) and Cu/Cu (0.7523) at Site 1 were positively strong. Cd/Ni (0.9229), Cd/Cu (0.8387) and Cd/Mn (0.8248) correlations were positively significant at Site 2, while Ni/Cr (0.9940) and Ni/Cu (0.8135) exhibited high and positive correlations at Site 3. Significant correlations between some metals in soil and water indicated that trace metal contents in irrigation water contributed to the total concentration of the metals in the soil.

Conclusion

Aqua regia (total) and EDTA (available) extractable Fe and Cd concentrations were the highest and lowest, respectively. Aqua regia trace metal levels were generally higher than that of EDTA, aqua regia being a stronger extracting reagent. The highest and lowest aqua regia and EDTA trace metal concentrations were recorded at Sites 1 and 3, respectively, attributed to intensive agricultural activities and large deposit of debris from flood at Site 1. Total metal concentrations were below the critical values for irrigation soil. Soils were extremely enriched with Cd (153 – 289), and deficient in Fe (0.5 – 1.0) contents. Anthropogenic sources might be responsible for the relative Cd, Cu and Pb enrichment of soil. Fe in soil may exist in nature. K_d for metals were below 1, except for Ni at Sites 1 and 2. Fe K_d was generally the highest (21.45 – 44.35 kgl^{-1}) and Zn (0.03 – 0.08 kgl^{-1}) the lowest. Higher total metal contents result in a lower proportion of metal being sorbed because potential absorption sites are filled in decreasing order of affinity. Correlations of soil-water trace metal levels indicated that at Site 1, Cr/Zn, Cu/Cu correlated strongly. Positive and strong correlations were recorded for Cu/Ni (0.9229) and Pb/Pb 0.9581) at Site 2. At Site 3, Ni correlated significantly with Cr (0.9440) and Cu (0.8153). Significant correlations for soil-water indicated contributions of irrigation water to total metal contents in soil.

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