Concentrations of Trace Metals in Selected Land Uses of a Dry Zone Soil Catena of Sri Lanka

F. Rosemary^{*}, U.W.A. Vitharana¹, S.P. Indraratne¹ and S.V.R.Weerasooriya¹

Postgraduate Institute of Agriculture University of Peradeniya Sri Lanka

ABSTRACT: Assessment of environmental risk associated with the pollution of trace metals is important for proper management of soils. This study was conducted to find out the present level of trace metals, their sources and the relationships among them in selected land uses. A Dry Zone soil catena consisting of uncultivated, paddy-cultivated and vegetablecultivated land uses was selected for this study. A total of 58 soil samples were collected on the basis of latin hypercube sampling approach. Soil samples were analyzed for the total concentrations of Cd, Cu, Pb, Ni and Zn. Exploratory data analysis, correlation analysis, mean comparison test and principal component analysis (PCA) were performed for the data. All the trace metals analyzed were below the maximum permissible levels in the soil catena studied. An accumulation of Cd was observed in paddy lands. The PCA confirmed the contribution of anthropogenic factors on Cd levels observed in this Dry Zone soil catena. Copper and Ni concentrations did not vary among the selected land uses while Zn, Cd and Pb concentrations varied with land uses. A strong and a significant relationship between Cu and Zn in all three land uses indicated a common origin of these metals. The PCA indicated that Cu, Zn and Pb would have originated from the mixed factor of natural and anthropogenic sources. The PCA also indicated the natural origin of Niin the tested soils.

Keywords: Paddy lands, PCA, trace metals concentrations, uncultivated lands, vegetable lands

INTRODUCTION

In present day agriculture, excessive application of inputs, such as fertilizers and pesticides are common practices. Some of these agrochemicals contain trace metals as an active ingredient (Rezania*et al.*, 1989). Excessive addition of such agrochemicals could lead to the contamination of agricultural soils. Elevated trace metal concentrations could cause phytotoxic effects and also could result in the trace metals contamination in edible crops (Cobb *et al.*, 2000). Soil ingestion and consumption of contaminated food are major pathways where human can be exposed to toxic trace metals. Accumulation of trace metals in the human body can cause diseases in the digestive system, anemia and chronic renal failure (Wanigasuriya*et al.*, 2008; Chandrajith*et al.*, 2010), etc. Therefore, public attention on soil contaminants has increased considerably in recent years.

Trace metals enter the soils from natural and anthropogenic sources. Burt *et al.*, (2003) reported that the quantity of trace metals that enter the ecosystem from anthropogenic sources is considerably higher than that of the natural sources. Anthropogenic sources, such

¹ Department of Soil Science, Faculty of Agriculture, University of Peradeniya, Sri Lanka

^{*} Corresponding author: rosemary.fernando@gmail.com

as chemical fertilizers, especially Triple Super Phosphate (TSP) contain considerable level of Cd as impurities (Pierzynski*et al.*, 2000) and Wijewardena&Gunarathne (2004) reported animal manures also contain some amount of trace metals. Excessive application of such chemical and animal fertilizers could lead to an accumulation of trace metals in agricultural fields. Premarathne*et al.* (2011) reported elevated levels of trace elements in soils of some parts of vegetable fields in Sri Lanka. Premarathna*et al.* (2005) also observed the total soil Cd concentration of 3.85 mg kg⁻¹ in vegetable growing soils in the upcountry wet zone of Sri Lanka. Previous studies by Bandara*et al.* (2008) showed 1.78 – 2.45 mg kg⁻¹ of Cd content in sediments collected from some reservoirs in the dry zone. However, there are onlyfew studies carried out in addressing the present level of trace metals content in soils of dry zone of Sri Lanka.

The solubility, mobility and bioavailability of trace metals in soils depend on their chemical species which are controlled by soil characteristics, such as pH, organic matter, clay content and secondary minerals (He *et al.*, 2004). Therefore, type of soils play a major role in the accumulation and persistence of soil trace metals. Further, land uses and management practices can affect the dynamics of trace metals concentrations in soils. Lu (2007) observed that As, Cd and Cr concentrations were greater in arable lands whereas in orchard lands, concentrations of Cu and Pb were high. Therefore, it is necessary to characterize trace metals in relation to different land uses to predict their behavior in soils.

Understanding the present level of concentration of trace metals in soils is necessary to detect trends of contamination of soils.Nevertheless, the implementation of mitigation strategies to minimize the exposure of trace metals to human, to reduce concentration in soil solution, to minimize food chain contamination and to reduce environmental risk for natural ecosystem are entirely dependent on the thorough understanding on the present level of heavy metal contaminations of soils. This study was conducted (i) to compare the concentrations of trace metals in different land uses (ii) to develop the relationship between trace metal concentrations and land uses (iii) to predict the sources of trace metal concentrations in a dry zone soil catena.

METHODOLOGY

Site description

A soil catena situated in Medawachchiya – Ranorawa – Elayapattuwa – Hurathgama -Nawagaththegama association (Mapa, 2010), in the dry zone of Sri Lanka was selected for this study. The selected catena covers an area of 94 ha and dominated with Ranorawa (in uplands) and Elayapattuwa (in lowlands) soil series. The central coordinates are 8° 7'57.07" N and 80° 7' 51.22" E and the average elevation is approximately 65 m from the sea level. Rainfall pattern is bimodal, consists of south west and north east monsoon rains, demarcating two major growing seasons namely, *Yala* and *Maha* seasons, respectively. Annual rainfall of the area is less than 1750 mm. Rainfed crop cultivation is practiced in *Maha* season and *Yala* season cultivation is practiced using the irrigation water from the Rajanganaya reservoir. Major soil great groups of the area are TypicRhodustalfs and OxyaquicPaleudalfs(USDA soil taxonomy). Major land uses of the area are uncultivated lands and agricultural land uses, namely rice fields and vegetable cultivations. Some of the uncultivated areas were previously cultivated but abandoned for more than two years. The selected catena is gently sloping towards the northern direction and paddy lands are mainly distributed at the northern part of the catena whereas vegetable and uncultivated lands are situated at the southern part of the catena.

Sampling method

Latin hypercube sampling technique (Budiman, 2006) was used to identify sample locationsrepresenting the spatial distribution of present land uses. Sampling was done at the end of April, 2012 and at each location, three samples were collected at the depth of 0-30 cm using a gouge auger then mixed to obtain a composite soil sample. Total of 58 samples were collected from paddy (27 samples), vegetable (16 samples) and uncultivated (15 samples) lands. All the sampling points were georeferenced using GPS receiver (Garmin GPS etrex10). Soil samples collected were air dried on clean polythene sheets, crushed and sieved using 2 mm sieve. Soil samples were stored in sealed transparent polythene bags, until analysis.

Laboratory analysis

Total trace metal concentrations were determined as the method described by Sposito*et al.* (1983), where 2g of air dried soil sample was digested with 20 ml of 4 M HNO₃ in a water bath at 80 °C for 4 hours. Xing &Veneman (1998) recommended the use of nitric acid in place ofhydrofluoric acid since it can be conveniently used as an extractant to solubilize metals from soils and from plant materials for environmental monitoring. Finally, the extracted soil sampleswere filtered using Whatman no 42 filter paper and total concentrations of cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) of filtrates were measured using atomic absorption spectrophotometer. A Standard Reference Material (SRM) no 2586 from National Institute of Standards and Technology (NIST), USA, was digested along with the samples to assure the accuracy of measurements. Satisfactory recoveries were found for Cd (86.8 %) and Pb (91.9 %) in SRM. To assure the accuracy and precision of analysis, standard quality control practices were adopted during the analysis and blank samples were included in each batch of analysis.

Data analysis

Exploratory analysis was performedusing SPSS statistical package (SPSS Inc, USA) for all trace metals. The data was tested for the normality with Kolmogorov – Smirnov (K-S) test. Mean concentrations of trace metals across land uses were compared using the mean comparison test.Pearson correlation (r) analysis was performed for trace metals to find out the relationship among trace metals in different land uses. In this study, principal component analysis (PCA) with varimax rotation method was used with Kaiser normalization to identify the sources of trace metals.

RESULTS AND DISCUSSION

According to the K-S normality test, all trace metals showed normal distributions. Skewness and kurtosis coefficient of each trace metals also indicated the normal distribution (Table 1). According to the European community set standards (McGrath & McCormack, 1999), 3mgkg⁻¹ of Cd is the upper limit of the maximum allowable concentration in soils. The Cd contentsoffew samples showed elevated levels closer to the lower limit of the maximum allowable concentration (1 mg kg⁻¹) specified in the European community set standards (McGrath & McCormack, 1999). Moreover, all these samples were distributed in paddy and

vegetable lands. Therefore, the use of agricultural inputs could be suspected as the reason for the enrichment of Cd concentrations in some parts of the catena.Indraratne*et al.* (2011) observed Cd concentrations, ranging from 0.003mg kg⁻¹ to 0.09mg kg⁻¹ in the sediments of some selected tank bedsin Anuradhapura and Madirigiriya. The range of values observed in this catena was 0.01 to 0.65 mg kg⁻¹. The estimated upper limit of the geochemical baseline concentration for Cd in Medawachchiya – Ranorawa – Elayapattuwa – Hurathgama – Nawagaththegama map unit is 1.39 mg kg⁻¹ (Sanjeevani*et al.*, 2012). All the values observed in this catena were below this level. According to Ma *et al.* (1997) the estimated background concentrations of Cd in Florida soils is 0.21 mg kg⁻¹, for world soils it is 0.37 mg kg⁻¹ (Kabata-Pendias*et al.*, 1992). The Cd values obtained in this study were slightly higher than the values reported elsewhere. Differences could be due to the time frame of analysis, where in other places mentioned above determined their background concentrations about two decades ago.

The mean contents of Cd in paddy, vegetable and uncultivated lands were 0.35, 0.28 and 0.26 mg kg⁻¹, respectively. The mean comparison indicated that Cd content in paddy lands is significantly higher (p = 0.05) than that of the vegetable and uncultivated lands. Higher content of trace metals such as Cd, Pb, V, U and Cr were found in phosphate fertilizers (Dissanayake&Chandrajith, 2009). Further, Premarathna*et al.* (2011) reported TSPcontains 23.5 mg kg⁻¹ of Cd. The continuous use of Cd containing agrochemicals such as TSP could contribute to elevated levels of Cd in paddy lands. According to the information gathered from the farmers, most of the vegetable fields in the study area were not continuously cultivated whereas paddy lands were cultivated continuously. Further, Indraratne*et al.* (2011) found traces of Cd in irrigation water of Rajangana tank and its outlets. Therefore, the long-term use of irrigation of Cd in paddy growing lands.

Trace element	Land uses	Min	Max	Mean \pm SD [*]	CV [#] %	Skewe -ness	Kur- -tosis
Cd	Paddy	0.01	0.63	0.35 ± 0.16^{a}	45.71	0.09	- 0.60
	Vegetable	0.01	0.65	0.28 ± 0.17^{b}	60.71	- 0.15	- 1.62
$(mg kg^{-1})$	Uncultivated	0.06	0.57	0.26 ± 0.18^{b}	69.23	0.48	- 1.37
Cu	Paddy	0.82	4.50	2.43 ± 0.85^{a}	34.97	0.39	0.59
Cu	Vegetable	0.78	8.54	2.97 ± 1.39^{a}	46.80	1.08	0.41
$(mg kg^{-1})$	Uncultivated	0.52	6.83	2.36 ± 1.91^{a}	80.93	1.46	1.99
Dh	Paddy	2.90	9.30	$6.05 \pm 1.71^{\circ}$	28.26	0.12	- 0.81
Pb	Vegetable	3.29	10.35	7.75 ± 2.36^{b}	30.45	- 0.86	- 0.68
$(mg kg^{-1})$	Uncultivated	7.19	9.69	8.63 ± 0.73^{a}	8.45	- 0.74	0.13
Ni	Paddy	0.04	13.45	4.95 ± 3.27^{a}	66.06	0.59	0.19
	Vegetable	3.26	15.27	7.22 ± 4.32^{a}	59.83	0.95	0.15
$(mg kg^{-1})$	Uncultivated	1.26	10.60	4.69 ± 2.73^{a}	58.20	0.85	1.06
Zn	Paddy	4.57	19.09	10.78 ± 3.38^{b}	31.35	0.13	0.12
$(mg kg^{-1})$	Vegetable	5.49	23.37	13.59 ± 5.20^{a}	38.26	0.31	- 0.49
	Uncultivated	9.33	19.52	14.48 ± 3.92^{ab}	27.07	- 0.12	- 1.65

 Table 1. Descriptive statistics of trace metals in different land uses in selected dry zone catena

*SD-Standard deviation #CV – Coefficient of variation

* Land uses followed by different letters are significantly different at the p < 0.05 level.

Copper is a micro-nutrient required in small quantities. This is an important nutrient for root metabolism and for reproductive growth in plants. The maximum permissible limit imposed for Cu in soils by the European community set standards (McGrath & McCormack, 1999) is 50 to 140 mg kg⁻¹. The mean contents of the Cu in paddy, vegetable and uncultivated lands were below the maximum permissible level set by European community set standards for Cu in soils (Table 1). The mean contents of Cu in paddy, vegetable and uncultivated areas were not significantly different. Jayewardene *et al.* (2012) documented 25, 23 and 57 mg kg⁻¹ of Cu contents in soils of agricultural areas of Madirigiriya, Talawa and Padaviya, respectively. The observed values for Cu were far below the estimated upper limit of the geochemical baseline concentration for Cu (26.51 mg kg⁻¹) by Sanjeevani*et al.* (2012) for the Medawachchiya – Ranorawa – Elayapattuwa – Hurathgama - Nawagaththegama map unit. The critical value and the range of optimum level of Cu content for paddy soils are 0.5 and 1 to 3 mg kg⁻¹ (Table 1).

Lead can be considered as least mobile heavy metal in the soil, out of metals studied. It can accumulate in the topsoil because usually it is not leached (Davies, 1984). The Pb content in all the samples were far below the lower permissible limit identified in the European community set standards (< 50 mg kg⁻¹). The mean contents of Pb were significantly different in different land uses. The average Pb content in uncultivated soils was higher than cultivated soils. Jayewardena*et al.* (2012) observed 21, 28 and 32 mg kg⁻¹ of Pb content in agricultural soils of Madirigiriya, Talawa and Padaviya areas, respectively. The values observed in this catena were below the upper limit of the geochemical baseline for Pbestablished for a dry zone map unit (Sanjeevani*et al.*, 2012). The Pb content in upper continental crust is 17 mg kg⁻¹ (Rudnick &Gao, 2005). Cultivation did not show any enrichment of Pb in the study area, indicating non-agricultural sources, such as parent material and atmospheric deposition of Pb.

Nickel is now considered as a micro and seventeenth plant nutrient (Liu, 2001) because it involves in translocation of nitrogen in plants. The optimum requirement of Ni for plants is less than 0.5 mg kg⁻¹ of dry weight (Liu, 2011). The mean contents of the Ni in paddy, vegetable and uncultivated lands in this catena were 4.98, 7.22 and 4.69 mg kg⁻¹ respectively, much less than the lower permissible limit (30 mg kg⁻¹) for Ni (McGrath & McCormack, 1999). No significant differences were observed among the different land uses in the Ni content. The established upper limit of the geochemical baseline concentration for Ni is 38.8 mg kg⁻¹ (Sanjeevani*et al.*, 2012) which is higher than the values observed for this catena.

Zinc is a micro-nutrient which is needed for the transformation of carbohydrates, regulate plant growth and consumption of sugars. When comparing paddy and vegetable cultivated soils, vegetable cultivated soils showed a significantly larger Zn content than that of paddy soils. Zinc deficiency has been reported in some parts of the dry zone of Sri Lanka. The critical value and optimum levels of Zn in soils for paddy cultivation in Sri Lanka are 1 mg kg⁻¹ and 2 to 4 mg kg⁻¹, respectively (Bandara*et al.*, 2005). The Zn content observed in the studied paddy soils was higher than the critical level. However, the Zn content in all three land uses was below the maximum permissible level set for environment pollution (300 mg kg⁻¹)(McGrath & McCormack, 1999). The values of Zn in this area were less than the established upper limit of the geochemical baseline concentration of 51.25 mg kg⁻¹ by Sanjeevani*et al.* (2012).

Correlations among trace metals and land uses

Copper showed a strong (r = 0.8, p = 0.01) (Table 2) correlation with Zn content in uncultivated soil, indicating that both are from the same origin. Strong relationship among trace metals explains the similar sources among them (Li *et al.*, 2009). None of other trace metals in uncultivated soils showed any relationship with others. Lead showed a positive correlation (r = 0.5, p = 0.01) with Cu, and with Ni (r = 0.5 p = 0.05) in paddy soils (Table 3). Copper showed significantly positive correlations with Zn (r = 0.8 p = 0.01) and Ni (r = 0.5, p = 0.01). Other trace metals in paddy lands did not show any relationship with other trace metals.

able 2. Pearson correlation matrix of trace metals concentrations in uncultivated lar	nds
(n = 15)	

Parameters	Cd	Cu	Pb	Ni
Pb	0.42	-0.38		
Ni	0.06	0.49	-0.41	
Zn	0.10	0.81**	-0.37	0.18

** Correlation is significant at the 0.01 probability level.

In vegetable cultivated soils, a strong and a positive correlation was observed between Cu and Ni (r = 0.8) at 0.01 probability level (Table 4). Zinc concentration showed positive correlations with Cu (r = 0.6) and also with Ni (r = 0.5) at the 0.05 probability level.

Table 3. Pearson's correlation matrix of trace metals concentrations in paddy (n=27) cultivated soils

Parameters	Cd	Cu	Pb	Ni
Cu	0.02			
Pb	0.11	0.49**		
Ni	0.08	0.54**	0.46*	
Zn	- 0.11	0.75**	0.35	0.38

** Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

Table 4. Pearson's correlation matrix of trace metals concentrations in vegetable (n=16) cultivated soils

Parameters	Cd	Cu	Pb	Ni
Cu	0.42			
Pb	-0.10	0.25		
Ni	0.27	0.81**	0.37	
Zn	0.13	0.56*	0.32	0.54*

** Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level.

Copper showed strong positive relationship with Zn in all three land uses (Table 2, 3 and 4) indicating a common source for both elements. However, the correlation analysis alone is not sufficient itself to explain the sources of trace metals.

Probable sources of trace metals in the selected dry zone catena

Principal component analysis can be used to identify the sources of trace metals as lithogenic, anthropogenic or mixed.

Table 5 shows the total variance explained by each component and component matrixes of trace metal contents. According to the PCA, trace metals could be grouped into two principal components which accounted for 61 % of total variation. The loading plot for two rotated component is shown in Fig. 2. First component is accounted for 39.9 % of the total variation which contributed greater positive factor loadings on Zn and Cu and a positive smaller factor loading on Pb. Second component is accounted for 21 % of the total variation which exhibited a positive factor loading on Ni and negative factor loading on Cd.

Table 5. Total variance explained and component matrixes for trace metals content

Component	Initial Eigen values			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	1.99	39.89	39.89	1.99	39.70	39.70
2	1.07	21.53	61.43	1.09	21.73	61.43
3	0.93	18.51	79.94			
4	0.81	16.11	96.04			
5	0.19	3.96	100.00			

Element	Componen	nt matrix
	PC1*	PC2*
Cu	0.88	-0.10
Pb	0.58	0.14
Ni	0.00	0.74
Cd	-0.07	-0.71
Zn	0.93	0.05

*PC1-Principal component one, PC2-Principal component 2

According to the correlation analysis, Cu and Zn must have a similar origin as both are highly correlated among them in all three land uses. In PCA, Cu, Zn and Pbwere clustered into a single group. Therefore, it can be stated that Cu, Zn and Pb could possibly be originated from a mixed source i.e., anthropogenic and natural sources. Copper could enter through Cu containing fungicides as anthropogenic sources. Anthropogenic source of Zn may be the Zn fertilizers and Zn containing minerals. Lead also originates from anthropogenic as well as natural sources.

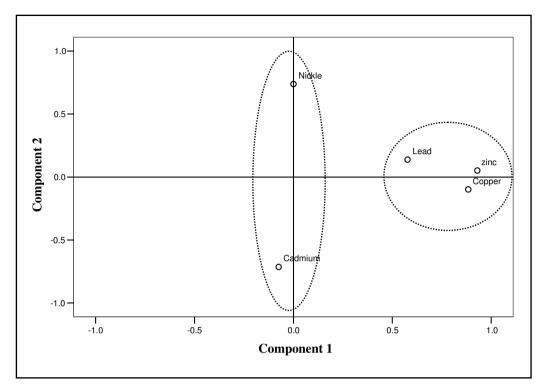


Fig. 2. Principal component analysis loading plot for the two rotated components

The observed concentrations of Cd were higher than the background value of 0.37 mg kg⁻¹ reported byKabata-Pendias (1992) for world soils. Therefore, the source of Cd has an anthropogenic origin. Positive relationships between Ni and Cu, Zn, Pb implied that Ni has a geogenic origin. In PCA analysis, Cd and Ni have been grouped into a same cluster but with a positive factor loading on Ni. Therefore, Ni could origin from natural source. However, it is difficult to conclude that sources of trace metals without analyzing soil properties. Because adsorption and retention of trace metals in soils are influenced by several factors such as organic matter, clay minerals, carbonates (Mico*et al.*, 2006) and cation exchange capacity (Aydinalp&Marinova, 2003).Lithogenic metals highly correlate with soil properties (Ma *et al.*, 1997) whereas anthropogenic metals have a weaker relationship with soil properties (Mico*et al.*, 2006). Therefore, further analysis has to be investigated to identify the sources of trace metals.

CONCLUSION

An assessment of the environmental risk due to environmental pollution such as trace metals is important for agricultural and non agricultural areas. The present study revealed that both agricultural and non agricultural soils of the studied catena were not contaminated to an environmental risk level for Cd, Cu, Pb, Ni and Zn. Observed total concentrations of Cd, Cu, Pb, Ni and Zn of the catena are below the maximum permissible limits reported in the literature. Land uses influence the trace metal concentrations of Cd, Pb and Zn whereas Cu and Ni concentrations are not different with different land uses. Copper shows positive relationships with Pb, Zn and Ni and Pb shows positive relationship with Ni in paddy cultivated soils. Copper shows positive relationships with Ni and Zn. Zinc also shows the relationship with Ni in vegetable growing lands. Based on the principal component and factor analysis Cu, Zn and Pb could have been originated from mixed component of natural and antropogenic sources and Cd possibly enters in to the soils through only anthropogenic sources. Nickel could enter from natural parent materials.

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