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Geomorphic Significance on Distribution of Heavy Metals in Soils Affected by Pb-Zn Mining in a Limestone Karst, Western Thailand

P. Intamo[1], A. Suddhiprakarn[1,*], I. Kheoruenromne[1], S. Tawornpruek[1] and R.J. Gilkes[2]

[1]*Department of Soil Science, Faculty of Agriculture, Kasetsart University Bangkok 10900, Thailand*
[2]*School of Earth and Environment, Faculty of Natural and Agricultural Sciences University of Western Australia, Crawley, WA 6009, Australia*

**Corresponding author, Email: agrals@ku.ac.th*

Abstract

Soils in the Pb/Zn mineralized area derived from the limestone karst in Western Thailand, principally located in complicate mountainous/upland areas. The distributions of metals are influenced by the natural geomorphic processes and their translocation or by anthropogenic activities (Pb/Zn mine). The objective of this study was to evaluate contents of metals in soils relating to their geochemistry and geomorphic settings. Soil samples were collected at three depths including Ap, base of Ap-60 and 60-100 cm section. Total concentrations of metals in the soils were determined by extraction with *aqua regia*. Descriptive statistics, Pearson correlation coefficients and Principal Components Analysis (PCA) were carried out to interpret metal concentrations and distribution of metals in different geomorphic units on landscape.The average concentrations of Al, Si, Ti, Fe, Mn, Ca, K and Mg were high in all soil samples. In particular, concentrations of As, Ba, Cd, Cr, Cu, Pb and Zn exceed the limit for agriculture and habitation. The highest concentrations of As, Ba, Cd, Cr, Cu, Pb and Zn were 71 mg kg^{-1}, 1,611 mg kg^{-1}, 73 mg kg^{-1}, 71 mg kg^{-1}, 87 mg kg^{-1}, 8,177 mg $kg^{-1}$and 3,869 mg kg^{-1}, respectively. The distribution of Ag, Ba, Ca, Cd, Mg, Mn, Na, P, Pb, S, Sr and Zn were in the surface horizons whereas Al, As, Co, Cr, Cu, Fe, Mo, Ni, Sc, Th, V and Y increase with depth. Relationships of metals and some soil properties especially soil pH (pH $H_2O$and pH KCl) are strongly positive for Ag, Ba, Be, Ca, Mn, Mg, Pb, S, Sr, Y and Zn. Closed correlations among Ca, Ag, Ba, Cd, Pb, S, Sr, Mg and Zn and soil pH are associated with valley floor, lower footslope, lower midslope, and crest near to the Pb/Zn mines reflect the higher influence of anthropogenic activities than that of karst weathering processes. On the other hand, the high concentrations of Al, V, Cr, Fe, Ti, Sc, Ni, Mn, As, Cu, Bi, Co, Be, P, Y, Th, Ce, Rb, Mo, La, K and clay content are associated with upper and lower midslope positions. The overall results obtained therefore demonstrate that the distribution of high concentrations of As, Ba, Cd, Cr, Cu, Pb and Zn is mainly influenced by mining activities but general distribution of metal concentrations in these soils are clearly influenced by tropical karst weathering of the mineralized limestone.

Keywords: geomorphic setting, abandoned mine, lead-zinc mine, Western Thailand

Introduction

Western part of Thailand has been considered as a traditional mining region (DPIM, 2009). There are many abandoned and existing mines in mountainous areas. In the mineralized area, limestone is the dominant rock type and a typical karst topography has developed with steep sided limestone hills (Holdstock and Mlot, 2008). In karst corrosion landscapes weathering is concentrated along joints and bedding planes of the limestone producing a number of different sculptured features from the effects of solution and the surface landscape is complicate in the tropical climate (Butzer, 1976). Structure of landscape determines landscape functioning (Forman and Godron, 1986; Jordan and Szucs, 2011), that is, the relative position of landscape components inclusive of rock, soil, groundwater, surface water, biota, atmosphere and human structures determine the release, transport and deposition of chemical substances as contaminants. The spatial distribution pattern of chemical substances within and among landscape components reflects geochemical landscape structure (Korobova, 2010; Gayrabekov, 2012).

Mining operations pose the greatest potential risk to human health and the environment (Vega et al., 2004;Peplow and Edmond, 2005; Csavinaet al., 2012). The major origin for the release of high proportion of metals is dependent upon the geochemistry of that particular region. The environmental concern in mining areas is not only on damage of the landscape but also on the change of soil characteristics as the natural soil profile is destroyed. Besides, these sites are more likely to suffer from soil erosion by water. It is well known that soil characteristics are closely related to heavy metal holding in the soil, uptake of plants and mobility of metals (Li and Thornton, 2001). The nature of mining processes creates a potential negative impact on the environment both during the mining operations and for years after the mine is closed (Zobrist et al., 2009).

The distributions of metals are affected by natural processes of landscape development and their transformation by natural-anthropogenic or anthropogenic activities. The main goal of this study was to assess the role of the landscape and soil geochemical factors on the spatial distribution of metals. Thus, the objectives of this research were (*i*) to analyze the total concentrations of heavy metals in limestone derived soils and (*ii*) to explore the relationships between heavy-metal concentrations in the soils and the geomorphic settings of mineralized limestone karst area, Western Thailand.

Materials and Methods

Study Area

This study was carried out in a Pb/Zn mineralized area in the Thong Pha Phum district, Kanchanaburi province, Thailand (UTM N 1645000/UTM S 1624000, zone 47P) where mines were in operation from in 1986 to 2002 (KEMCO, 1984). The mineralized area is situated in the Meklong Highlands, a jungle covered region in Kanchanaburi Province between the deeply incised valleys of Khwae Yai and Khwae Noi rivers, approximately 300 km northwest of Bangkok and 186 km from Kanchanaburi. The area is underlain by limestone with a typical karst topography of steep sided hills covered by thick tropical vegetation including bamboo jungle and rain forest (Holdstock and Mlot, 2008).

Geomorphic setting

The geomorphic settings are characterized into seven sections consisting of crest, shoulder, upper midslope, lower midslope, upper footslope, lower footslope and valley floor in a complicate mountainous landscape. The mountainous ridge elevation reaches over 800 m above mean sea level (MSL) and elevations of all geomorphic settings are in a range of approximately 200 and 750 m MSL. The research covered 128 km^2 area of soils in the derived limestone mineralized area. The majority of underground mines and mineral processing facilities of the Pb/Zn are shown in Figure 1. Within the study area, a primary school is located less than 2 km from the old mine.

Climate

The area is in tropical monsoonal climate with two distinct seasons. The dry season begins in October and ends in May, followed by a monsoon season between June and September. Annual rainfall ranges between 1,972 and 2,335 mm and temperature ranges between 26-27°C (TMD, 2015).

Field Work and Sampling

Soils of sixty sites were sampled at three depths including surface soil (Ap), surface soil-60 cm (Ap-60) and 60-100 cm, respectively along landscape

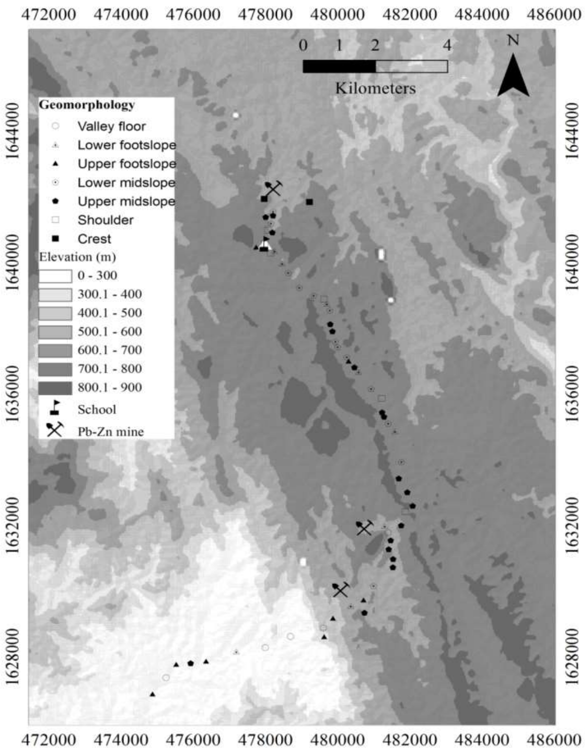

Figure 1 Location of the collected samples in Pb-Zn mining in a limestone karst, Western Thailand

traverses across geomorphic contrasting sites including crest, shoulder, upper midslope, lower midslope, upper footslope, lower footslope and valley floor in mineralized area in Kanchanaburi Province, Western Thailand. The sampling locations and topography of the study area are shown in Figure 1.

Soil Sample Analysis

A soil samples were air-dried, passed through a 2-mm stainless steel sieve to obtain the coarse fraction (>2 mm) and the fine earth (<2mm). The fine earth was analyzed for physical and chemical properties using standard methods. Particle size distribution was determined by the pipette method (Gee and Bauder, 1986). Soil pH was measured in 1:1 soil:solution using H_2O and 1M KCl (National Soil Survey Center, 1996). Cation exchange capacity (CEC) was measured using 1M NH_4OAc at pH 7.0 (Chapman, 1965). Organic carbon (OC) was determined by the Walkley and Black method (Nelson and Sommers, 1996).

Total metal concentrations by Aqua regia extraction

The *aqua regia* extraction was used for the strong acid extraction of metals from soils, and concentrations of 34 metals including Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, S, Sc, Si, Sr, Th, Ti, V, Y, Zn and Zr in solutions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Vega et al., 2006). The accuracy of the methods was verified by analyzing certified standard reference material (ASPAC 54). Certified analytical grade reagents were used throughout. Analytical grade HCl and HNO_3 (1:3 ratio) were used for digestion. Blanks were run through all experiments to detect any contamination.

Statistical analyses

Statistical analysis and principal component analysis (PCA) were performed using STATISTICA, version 10. The PCA, based on the correlation matrix, was conducted for the soil chemical data set. The aim of PCA was to ascertain any patterns in the soil samples in relation to these chemical characteristics and hence infer possible relationships between these and geomorphic settings of the soil.

Results and Discussion

Physicochemical Properties of Soils

Descriptive statistical parameters for physicochemical soil properties were categorized by surface soil, surface to 60 cm and 60-100 cm (Table 1). The particle size distribution shows that the soils have high clay content ranging from 350 to 546 g kg^{-1} followed by silt contents ranging from 295 to 441 g kg^{-1} and sand contents ranging between 86 to 276 g kg^{-1}. Soil texture includes clay loam, silty clay and clay. The textural class of soils on the crest is clay texture, on shoulder, upper and lower midslope positions are silty clay on the surface with clay accumulation in subsoils. In addition, soils on upper and lower footslopes and soils on valley floor positions have clay loam in Ap-60 cm section where both surface and deep subsoil section are clay. In all sites, the soils show clay content increases with depth indicating translocation of clay from the surface to

Table 1 Selected characteristics of the soils on different geomorphic settings in a limestone karst, Western Thailand. (n= Soil sampling sites).

Geomorphic	Soil horizon (cm)	Sand	Silt	Clay	Gravel (%)	pH		CEC	OC
		(------------gkg^{-1}---------)				H_2O	KCl	cmolkg^{-1}	g kg^{-1}
Crest *(n=2)*	Ap	239	327	435	0.8	6.7	5.3	19.0	2.9
	Ap-60	216	350	434	1.4	6.4	4.7	17.3	2.2
	60-100	181	295	524	0.8	6.1	4.4	11.5	0.5
Shoulder *(n=6)*	Ap	86	441	473	0.9	6.1	5.0	16.1	3.0
	Ap-60	106	425	469	0.5	5.1	4.5	14.3	1.1
	60-100	124	392	484	0.5	4.8	3.7	15.1	0.5
Upper midslope *(n =18)*	Ap	124	426	450	1.0	5.9	4.9	25.1	3.3
	Ap-60	126	396	478	2.1	5.3	4.4	14.8	1.4
	60-100	97	356	546	3.0	5.3	4.4	11.8	0.6
Lower midslope *(n =13)*	Ap	123	431	446	0.5	6.1	5.4	26.4	3.7
	Ap-60	118	438	444	1.3	5.7	4.8	14.3	1.1
	60-100	115	342	543	1.2	5.3	4.3	11.4	0.5
Upper footslope *(n =8)*	Ap	193	388	419	4.9	5.6	4.6	20.6	2.9
	Ap-60	247	381	372	6.8	5.0	3.8	10.4	1.0
	60-100	216	409	375	6.9	4.9	3.9	10.0	0.6
Lower footslope *(n =8)*	Ap	208	374	418	1.8	6.2	5.4	18.9	2.2
	Ap-60	200	437	362	3.7	6.1	5.3	13.1	1.0
	60-100	167	399	434	3.5	5.7	4.8	12.1	0.6
Valley floor *(n =5)*	Ap	276	347	377	2.0	6.3	5.6	15.6	2.2
	Ap-60	255	395	350	0.7	6.5	5.6	15.1	1.1
	60-100	208	340	452	4.5	6.4	5.5	11.9	0.8

subsoils. The gravel percentage (Table 1) was high in soils on the upper and lower footslope, and the valley floor soils have increasing gravel content with depth. The gravels were ferruginous nodules or ironstone fragments. The coarse fragments in soils can be formed by Fe cementation of fine earth materials. Thus, the soil on the three slope sections may have higher ferruginous nodules or ironstone gravels (Breward, 2007).

The pH (pH H_2O) varied between very strongly acid (pH 4.8) to neutral (pH 6.7) (Table 1). For all geomorphic settings, the pHH_2O decreased with depth except that of a valley floor soil wherepHH_2O increased with depth. The high pH H_2O value in subsoils on valley floor site was due to alkaline solution leached from Mg and Ca enriched soils upslope and low pH H_2O in surface soils reflected the effect of leaching.The CEC was medium to high for all soils and ranged from 10.0 cmol kg^{-1} to 26.4 cmol kg^{-1} (Table 1). The CEC values of soils decreased with depth. The CEC values were medium in subsoils. These indicate the influences of clay minerals, especially illite and vermiculite (Raheb and Heidari, 2012) and the high organic matter content (Reese and Moorhead, 1996). The organic carbon contents corresponded well with the trend of CEC in the soil profile. Organic carbon content in soils ranged from 0.5 to 3.7 g kg^{-1}. Organic carbon contents were low in all deep subsoil (0.5-0.8 g kg^{-1}), medium to high levels on Ap-60 cm (1.0-2.2 g kg^{-1}) and very high on surface horizons (2.2-3.7 g kg^{-1}) (Table 1). This is due to the higher accumulation of plant residue in the surface soils. The organic matter is a component of great importance because it tends to form soluble or insoluble complexes with the heavy metals. This is why they can migrate throughout the profile or be retained in the soils.

Heavy Metal Contents and Distribution in Soil Profile

Results on metals concentration were obtained through *aqua regia* digestion. Table 2 shows the concentration and distributions of metals in soil profile along the transverse across geomorphic settings and the critical values of metals in soils

Table 2 Contents and distributions of metals in the selected samples (soil samples<2 mm).

Geomorphic settings	Horizon	Al	Si	Ti	Fe	Mn	Ca	K	Mg	Ag	As	Ba	Be	Bi	Cd	Ce	Co	Cr	Cu	La
		(------ g kg^{-1} ------)								(------ mg kg^{-1} ------)										
Crest *(n=6)*	Ap	77	280	4.4	41	1.0	3.4	19	5.2	2.8	45	1611	0.5	2.4	1.6	80	8.3	38	54	28
	Ap-60	90	267	5.0	50	1.0	2.3	19	5.0	0.3	43	99	0.5	2.2	0.1	85	7.8	51	61	30
	60-100	100	261	5.3	56	0.9	1.5	20	5.4	0.3	48	110	0.5	2.6	0.2	94	9.4	71	72	36
Shoulder *(n=18)*	Ap	91	258	5.5	48	1.0	3.5	31	5.7	0.5	29	434	0.6	1.6	1.0	79	10.2	39	51	28
	Ap-60	103	272	5.7	53	0.8	1.6	35	6.3	0.3	29	165	0.6	1.7	0.3	81	10.7	35	53	28
	60-100	107	263	5.4	55	0.7	1.1	36	6.4	0.2	31	141	0.6	2.1	0.3	91	11.1	37	54	33
Upper midslope *(n=54)*	Ap	86	259	5.4	51	2.0	4.5	25	5.0	0.4	58	340	0.9	1.4	2.5	69	10.1	35	42	29
	Ap-60	102	255	5.6	60	1.7	1.6	29	5.4	0.1	64	145	1.0	1.4	0.1	77	11.2	42	45	31
	60-100	110	248	5.6	66	1.8	1.2	30	5.7	0.1	71	138	1.0	1.6	0.1	83	12.3	47	50	32
Lower midslope *(n=39)*	Ap	85	253	5.5	53	2.1	3.7	23	5.0	0.3	31	311	0.8	1.4	3.4	78	7.8	39	76	35
	Ap-60	101	256	5.7	63	1.9	1.9	27	5.6	0.1	34	152	0.9	1.7	0.2	85	9.3	44	87	35
	60-100	105	250	5.7	70	1.8	1.4	29	5.9	0.1	36	131	1.0	2.0	0.1	88	10.0	50	84	36
Upper footslope *(n=24)*	Ap	83	286	4.7	49	0.9	2.4	23	3.2	0.2	28	143	0.8	1.8	0.7	77	10.7	38	35	29
	Ap-60	96	284	4.8	56	0.8	1.1	26	3.4	0.1	28	110	0.8	2.0	0.1	80	12.0	37	37	29
	60-100	104	267	4.8	60	0.6	1.0	27	3.8	0.1	30	116	0.9	2.1	0.1	84	13.2	35	33	30
Lower footslope *(n=23)*	Ap	80	278	4.9	41	1.0	9.3	26	5.9	2.3	32	589	1.1	1.5	3.1	76	10.1	29	40	34
	Ap-60	88	286	5.0	45	0.9	5.9	29	5.6	3.1	37	315	1.2	1.5	2.6	87	12.4	31	39	37
	60-100	96	274	5.2	47	0.9	6.8	32	6.1	3.9	39	396	1.1	1.8	2.7	92	13.5	29	38	40
Valley Floor *(n=15)*	Ap	71	288	4.1	27	0.5	20.9	20	4.6	2.6	23	844	1.1	2.2	73.3	64	6.7	25	28	32
	Ap-60	79	307	4.5	28	0.4	11.5	23	3.8	5.0	19	140	1.41	1.5	4.2	61	7.2	28	24	31
	60-100	90	307	4.8	30	0.4	6.1	25	4.1	0.8	17	144	1.59	1.3	1.7	62	8.9	29	20	30
Critical value										20[2]	3.7[1]	750[2]	4[2]		1.4[1]		40[2]	64[2]	63[1]	

		Mo	Na	Nd	Ni	P	Pb	Rb	S	Sc	Sr	Th	V	Y	Zn	Zr
		(------ mg kg^{-1} ------)														
Crest *(n=6)*	Ap	1.8	47	16	17	227	8177	49	607	8.6	27.4	12.2	54	17.4	290	472
	Ap-60	1.9	36	25	20	193	1008	60	248	10.4	6.2	15.2	70	18.3	140	569
	60-100	2.5	31	31	23	139	839	68	215	12.0	5.3	17.8	77	22.4	157	568
Shoulder *(n=18)*	Ap	0.8	34	22	16	284	448	59	314	8.4	13.5	13.1	36	10.6	126	273
	Ap-60	1.0	32	23	16	201	244	67	188	9.4	7.1	15.3	39	10.1	71	263
	60-100	0.9	27	27	17	144	205	62	179	10.6	5.8	17.1	39	12.4	78	265
Upper midslope *(n=54)*	Ap	1.7	36	23	21	344	1465	63	363	8.0	15.2	11.5	53	18.6	385	273
	Ap-60	2.0	33	27	25	230	876	74	220	10.1	9.5	15.4	62	20.1	260	270
	60-100	2.3	31	29	27	186	729	76	186	11.3	8.8	17.3	69	21.7	268	267
Lower midslope *(n=39)*	Ap	1.4	30	26	22	354	1293	69	379	7.5	10.9	12.6	59	21.9	331	292
	Ap-60	1.7	26	29	24	223	460	75	230	9.1	7.7	16.5	66	22.6	100	298
	60-100	1.8	25	31	25	162	524	77	192	9.7	7.1	18.1	67	24.3	98	296
Upper footslope *(n=24)*	Ap	0.5	40	26	19	300	444	41	262	7.9	7.8	12.6	38	16.9	130	269
	Ap-60	0.6	36	27	22	201	344	47	167	9.2	5.3	15.7	43	17.6	84	242
	60-100	0.6	36	28	22	194	224	46	146	9.7	6.0	16.9	43	18.7	82	227
Lower footslope *(n=23)*	Ap	0.7	34	24	20	341	1761	52	488	7.7	24.3	12.1	40	20.7	357	282
	Ap-60	0.9	32	27	23	240	1555	57	364	9.0	19.7	14.7	45	22.9	355	298
	60-100	1.0	31	29	22	177	1881	55	423	9.6	23.9	16.8	44	22.7	319	280
Valley Floor *(n=15)*	Ap	0.4	37	11	16	210	6577	44	628	6.0	35.1	11.9	34	20.3	3869	269
	Ap-60	0.3	36	19	18	156	5679	51	199	7.3	7.7	13.6	37	21.2	1168	303
	60-100	0.2	38	25	20	89	1560	49	144	8.3	6.1	15.2	37	23.8	500	319
Critical value			5[B]			50[B]		400[A]						130[B]		200[B]

[1]Soil quality standards for habitat and agriculture PCD: Pollution Control Department, Thailand (2004)
[2]Soil quality guidelines for the protection of environmental and human health: Canada and the European community (CCME, 2006)

allowed for agricultural and habitation. The quality standard of Canada and the European community (CCME) is used in this study because the limit of metals for contaminated soils of Thailand (PCD) does not include concentrations of some metals such as Ag, Ba, Be, Co, Cu, Mo, Ni, V and Zn. Therefore, of the combined CCME and PCD standards were used in this study (Table 2). The mean concentrations of 34 heavy metals in different sampling sites are shown in Table 2. Comparing among the seven geomorphic units, the average concentration of Al, Si, Ti, Fe, Mn, Ca, K and Mg are abundant in all soil samples. In particular, the concentrations of As, Ba, Cd, Cr, Cu, Pb and Zn exceed the limit of PCD (2004) and CCME (2006) for agricultural and residential use. The highest concentrations of As, Ba, Cd, Cr, Cu, Pb and Zn in soils were 71 mg kg^{-1}, 1,611 mg kg^{-1}, 73 mg kg^{-1}, 71 mg kg^{-1}, 87 mg kg^{-1}, 8,177 mg kg^{-1} and 3,869 mg kg^{-1}, respectively. In addition, the highest concentrations of Ba, Cr and Pb are in soils on the crest. The highest concentrations of As is on upper midslope and that of Cu on lower midslope. The highest concentrations of Cd and Zn are in the valley floor soils. Similar trends were observed in the results reported by Egashira et al. (1996) where the contents of V, Cr, Co, Ni, Cu, Zn and Sr in soils derived from limestone in the Central Region of the Mekong River, Laos, were higher than in soils derived from other parent materials and Yamasaki et al. (2013) reported that the contents of Cd, Mn, Sr, Pb and Zn were high in the limestone-derived soils.

The distribution of metals with depth varies according to the metals properties and geomorphic settings. The highest concentrations of Ag, Ba, Ca, Cd, Mg, Mn, Na, P, Pb, S, Sr and Zn are in the surface horizons (Table 2) reflecting their mobility and physical properties of the soils. In contrast, the concentrations of Al, As, Co, Cr, Cu, Fe, Mo, Ni, Sc, Th, V and Y increase with depths in most soil samples, except As, Cu and Mo on the valley floor where the surface horizons were enriched. The concentrations of Al, As, Co, Cr, Cu, Fe, Mo, Ni, Sc, Th, V and Y (Table 2) increase with depth could be affected by the parent rock.

In comparison the heavy metal concentrations in soils on shoulder and upper footslope are lower than on the other. The accumulation of heavy metals especially Cd, Pb and Zn increase on lower positions (lower footslope and valley floor) where crop practices are and habitation may have a high risk for Cd, Pb and Zn concentrations in the environment. The high concentrations of Cd, Pb and Zn in soils on lower positions are due to the influence from translocation of heavy metals from upper slopes. Luo et al. (2007) and Tuttle et al. (2014) reported that the content of heavy metals in soil and their impact upon ecosystems can be influenced by many factors including parent materials, climate, anthropogenic activities and transportation.

Relationships between Heavy Metal Content and the Physicochemical Properties of Soils Parameters

Understanding the relationship between the metals and soil parameters could help clarify the behavior of the metals in the soil. The relationships between the main soil parameters and metal concentration were assessed using Pearson correlation coefficient analysis (Table 3).Clay content, soil pH (pH H_2O and pH KCl), CEC and OC were strongly correlated with most metals. The lesser correlations are between sand, silt and gravel contents with metals. However, clay content is strongly correlated with Al, Ce, Cr, Fe, K, Mo, Rb, Sc, Th, Ti and V ($p \leq 0.01$), indicating that metal concentrations are controlled by minerals in clay fraction. Sand content is correlated with Ca and Si ($p \leq 0.01$). Silt content is correlated only with P while gravel content has no correlation with any metals in the soils. Soil pH is correlated positively with Ag, Ba, Be, Ca, Mn, Mg, Pb, S, Sr, Y and Zn ($p \leq 0.01$).Soil pH increase can induce metal immobilization through several processes including the increase of metal sorption onto negatives sites or the precipitation of metals in the form of oxides, hydroxides, carbonates and phosphates (Lindsay, 1979; Brad, 2004).Soil CEC exhibits a significant relationship with K, Mg, and P. The organic carbon content is correlated positively with Mn, P and S. To better quantify the relationships among the variables in this soil and to identify group of geochemically similar samples, Principal Component Analysis (PCA) was performed.

Table 3 The Pearson correlation matrix for metals and soil physicochemical characteristics. (n=179 samples)

	Sand	Silt	Clay	Gravel	pH H_20	pH_{KCl}	CEC	OC
	(------------------g kg^{-1}----------------)			(%)			($cmolkg^{-1}$)	g kg^{-1}
Ag	0.10	0.10	-0.16*	0.03	0.32**	0.39**	-0.11	-0.03
Al	-0.41**	-0.26**	0.54**	-0.21**	-0.16*	-0.19**	-0.06	-0.09
As	-0.03	0.03	0.00	0.03	0.03	0.08	-0.14	0.01
Ba	0.14	0.11	-0.20**	0.02	0.40**	0.42**	0.00	0.17*
Be	0.14	0.10	-0.19*	0.02	0.26**	0.31**	-0.15*	-0.09
Bi	0.04	-0.07	0.03	-0.02	0.03	0.06	-0.21**	-0.16*
Ca	0.25**	0.13	-0.30**	0.04	0.47**	0.52**	-0.01	0.14
Cd	0.16*	0.03	-0.15*	0.00	0.18*	0.22**	-0.02	0.08
Ce	-0.13	-0.16*	0.23**	-0.01	-0.15*	-0.17*	-0.22**	-0.27**
Co	0.01	0.06	-0.06	0.19*	0.14	0.17*	-0.26**	-0.19**
Cr	-0.29**	-0.29**	0.47**	-0.07	-0.13	-0.14	-0.17*	-0.13
Cu	-0.04	-0.06	0.08	-0.05	-0.03	0.01	-0.14*	-0.03
Fe	-0.16*	-0.11	0.22**	0.03	-0.07	-0.05	-0.28**	-0.14*
K	-0.54**	0.07	0.37**	-0.19**	-0.09	-0.17*	0.32**	0.04
La	0.07	-0.06	0.00	-0.04	0.02	-0.03	-0.06	-0.16*
Mg	-0.18*	0.00	0.14*	-0.22**	0.30**	0.27**	0.23**	0.18*
Mn	-0.21**	0.07	0.12	0.01	0.20**	0.20**	0.08	0.23**
Mo	-0.22**	-0.04	0.21**	-0.17*	-0.15*	-0.16*	0.02	0.02
Na	0.03	0.03	-0.05	0.01	-0.04	-0.04	0.09	0.13
Nd	0.01	-0.10	0.07	0.02	-0.19**	-0.26**	-0.06	-0.22**
Ni	-0.13	-0.02	0.12	-0.04	0.14*	0.17*	-0.14	-0.05
P	-0.11	0.19**	-0.07	-0.16*	0.13	0.15*	0.55**	0.64**
Pb	0.07	0.04	-0.09	-0.02	0.33**	0.36**	-0.03	0.13
Rb	-0.52**	-0.07	0.47**	-0.23**	-0.14	-0.21**	0.18*	0.00
S	0.13	0.13	-0.21**	-0.01	0.40**	0.48**	0.06	0.25**
Sc	-0.22**	-0.16*	0.31**	-0.02	-0.12	-0.07	-0.35**	-0.26**
Si	0.45**	0.07	-0.41**	0.06	-0.05	-0.05	0.00	-0.07
Sr	0.12	0.10	-0.18*	0.00	0.36**	0.39**	0.02	0.11
Th	-0.25**	-0.27**	0.42**	-0.03	-0.34**	-0.35**	-0.44**	-0.57**
Ti	-0.11	-0.23**	0.28**	-0.08	0.08	0.11	-0.12	-0.01
V	-0.33**	-0.27**	0.48**	-0.16*	-0.13	-0.13	-0.06	-0.05
Y	0.15	-0.14	0.00	0.02	0.25**	0.30**	-0.13	-0.07
Zn	0.15*	0.03	-0.14	-0.01	0.23**	0.28**	-0.01	0.09
Zr	0.16*	-0.10	-0.05	-0.06	0.13	0.02	0.03	0.02

* Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level

Metal Distributions in Different Geomorphic Settings

Multivariate statistical techniques of data analysis enable the evaluation of multi-metal geochemical data (Bellehumeur et al., 1994). These techniques were used in this study to determine metals with similar geochemical behaviors and to group soil samples on the basis of their geochemical affinity. The relationships between the PCs and environmental factors, such as pedological, biogeochemical and anthropogenic factors have been successful explored with PCA (Critto et al., 2003; Liu et al., 2006). The PCA of standardized raw data was used to identify affinity groups of metals and other soil properties particularly texture, CEC, OC, pH H_2O and pH KCl.

The PCA of soil properties and metal concentrations in soils of limestone karst area (Figures 2a, b) shows that the first two principal components of 34 metal concentrations account for 43.05% of the overall variability in the data (PC1-21.88% and PC2-21.17%). Three affinity groups of properties and the outliers are recognized. The first group consists of Ag, Ba, Ca, Cd, Mg, Pb, S, Sr and Zn and soil pH (pH H_2O and pH KCl) (Figure 2a), indicating that they are correlated with some soil

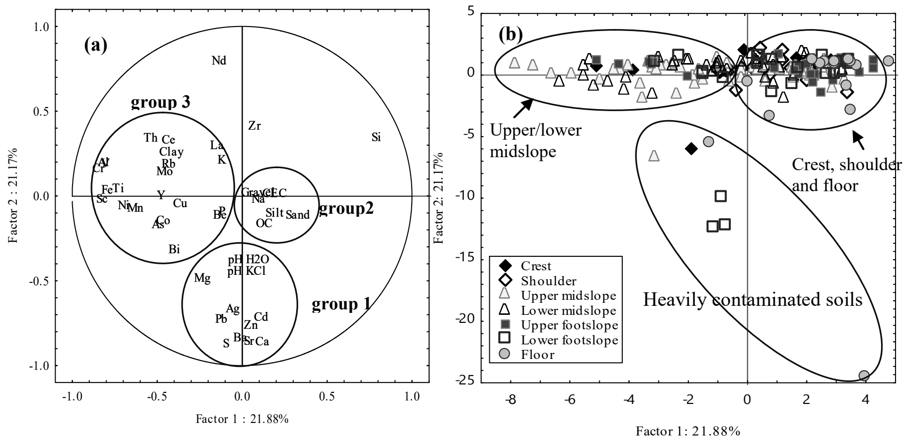

Figure 2 Graph of the PCA and their respective correlations with the variables studies (a) and plots of samples scores, identifying their respective geomorphic groups (b) for the first and the second principal component.

sample on the valley floor, lower footslope, lower midslope, and crest regions (Figure 2b). The association of these heavy metals can be defined as an anthropogenic component since the metals in this first group are high in only surface horizons on the four regionsclose to Pb/Zn mines. The second group Na, gravel, sand, silt, CEC and OC (Figure 2a) are correlated with soils on crest, shoulder, upper footslope, lower footslope and valley floor (Figure 2b). The third group consisting of large metals such as Al, As, Be, Bi, Ce, Co, Cu, Cr, Fe, K, La, Mn, Mo, Ni, P, Rb, Sc, Th, Ti, V, Y and clay content (Figure 2a) is mainly correlated with soils on upper and lower midslope (Figure 2b). The results of the third group can be defined as a natural component, as the variability of the metals is controlled by nature and weathering parent rocks. According to previous studies, it is well known that Ni, Co and Cr concentrations in soils are highly dependent on their contents in lithological units, and also in basic and ultrabasic rocks (Facchinelli et al., 2001) or the heavy metals may be immobilized through the coprecipitation process in the presence of Fe and Al oxyhydroxides and clay mineral (Kumpiene et al., 2008; Meng et al., 2014).

The PCA results have separated all metals in to three groups. In order to understand the inter-metal relationships on metals were analyzed by Pearson correlation coefficient. The metals in the first group of PCA results (Figure 2a), all metals (Ag, Ba, Ca, Cd, Mg, Pb, S, Sr and Zn) (Table 4) shows strong positive correlations ($p \leq 0.01$). There are significant positive correlations between the heavy metals themselves. This suggests a similar, if not identical, origin of the heavy metals, and indicates that anthropogenic activities could enhance the mobility of these heavy metals (Gil et al., 2004; Ramos-Miras et al., 2011). For the third group of the metals from PCA results (Figure 2a), the strong correlation among Al, Cr, Fe, Ti and V ($p \leq 0.01$) (Table 5) indicates that these metals have the same geochemical behavior.

Table 4 The Pearson correlation matrix for metal concentrations present in group 1 from PCA result (n=179 samples).

	Ag	Ba	Ca	Cd	Mg	Pb	S	Sr	Zn
Ag	1.00								
Ba	0.59**	1.00							
Ca	0.55**	0.78**	1.00						
Cd	0.22**	0.58**	0.74**	1.00					
Mg	0.31**	0.59**	0.52**	0.40**	1.00				
Pb	0.77**	0.62**	0.55**	0.52**	0.29**	1.00			
S	0.74**	0.88**	0.82**	0.53**	0.54**	0.62**	1.00		
Sr	0.64**	0.90**	0.85**	0.64**	0.66**	0.54**	0.89**	1.00	
Zn	0.38**	0.56**	0.73**	0.95**	0.38**	0.69**	0.56**	0.61**	1.00

* Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level.

Table 5 The Pearson correlation matrix for metal concentrations present in group 3 from PCA result (n= 179 samples).

	Al	As	Bi	Ce	Co	Cr	Fe	Mn	Mo	Ni	Rb	Sc	Th	Ti	V	Y
Al	1.00															
As	0.08	1.00														
Bi	0.24**	0.18*	1.00													
Ce	0.41**	-0.04	0.23**	1.00												
Co	0.25**	0.32**	0.40**	0.34**	1.00											
Cr	0.83**	0.23**	0.37**	0.41**	0.31**	1.00										
Fe	0.51**	0.46**	0.43**	0.23**	0.43**	0.66**	1.00									
Mn	0.44**	0.33**	0.13	0.13	0.40**	0.40**	0.64**	1.00								
Mo	0.30**	0.54**	-0.12	0.04	-0.08	0.34**	0.27**	0.23**	1.00							
Ni	0.40**	0.66**	0.18*	0.10	0.51**	0.41**	0.48**	0.51**	0.31**	1.00						
Rb	0.78**	-0.12	-0.06	0.29**	0.10	0.42**	0.04	0.26**	0.30**	0.17*	1.00					
Sc	0.60**	0.51**	0.46**	0.29**	0.44**	0.67**	0.73**	0.35**	0.24**	0.58**	0.11	1.00				
Th	0.48**	0.05	0.23**	0.56**	0.05	0.53**	0.38**	-0.09	0.24**	0.19**	0.22**	0.57**	1.00			
Ti	0.63**	0.20**	0.43**	0.28**	0.20**	0.73**	0.54**	0.38**	0.21**	0.39**	0.20**	0.52**	0.41**	1.00		
V	0.76**	0.35**	0.15*	0.29**	0.01	0.79**	0.50**	0.34**	0.64**	0.44**	0.48**	0.57**	0.56**	0.69**	1.00	
Y	0.21**	0.37**	0.08	0.14	0.35**	0.18*	0.30**	0.41**	0.09	0.69**	0.00	0.40**	0.12	0.28**	0.22**	1.00

* Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level.

Conclusions

Most soil samples on crest, shoulder, footslope and valley floor have low concentrations of metals. This indicates a weak dispersive distribution of the metals along these geomorphic units where soils have high gravel content sand and silt fractions that exhibit higher metal concentrations. The results also show that in area without contamination of metals natural geochemical processes which can be called karst corrosion is stony and controlling the distribution of metals in soils of all geomorphic units. The high values of CEC and OC which are essential factors for metal adsorption in soils show only minimal influence on metal distribution in soils on most of geomorphic units. High concentrations of As, Co, Cr, Cu and Mo exist in soils on upper and lower midslopes and in some soils on upper and lower footslopes. This indicates that differential erosion in some part of landscape can occur periodically during rainy season causing accumulation of different degrees in geomorphic units affected differentially by water flow. Collectively, the distribution of metals in soils does not show any marked difference among geomorphic units. The characteristic of the soils on midslope indicate the influence of Fe and Mn oxides (Thanachit et al., 2006). These oxides can play a major role on metal adsorption (Komárek et al., 2013) combining with adsorption of metals by clay minerals (Kumpiene et al., 2008) resulting in high accumulation of all heavy metals in soils on this geomorphic units. Also, the PCA analysis shows that in some soils on crest, upper midslope, lower footslope and valley floor are outliers (Figure 2b) the accumulation of heavy metals including Ag, Ba, Cd, Sr, Pb and Zn are affected by both geomorphic processes inclusive of weathering (karst corrosion) and erosion, and the proximity to contaminant sources.

The overall results on the distribution of heavy metals in soils affected by Pb-Zn mining of the limestone karst of the study clearly reveal the distinct geomorphic significance in tropical limestone karst development. This aspect of study in the effect of karst corrosion controlling the distribution of elements in soils on different geomorphic units of tropical karst landscape has not been reported in literature before. Due to the effect of humid tropical climate the intense weathering of limestone induces dispersive distribution of all metals in all part of karst landscape. The mining activities intensify their differential distribution.

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