

Multivariate statistical analysis of heavy metals in soils of a Pb–Zn mining area, India

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Abstract Surface soil samples collected from a Pb and Zn mining area in India were subjected to multi-elemental analysis by using inductively coupled plasma–atomic emission spectrometry. Multivariate statistical methods such as principal component analysis and cluster analysis, coupled with correlation coefficient analysis, were used to analyze the data and to apportion the possible sources of elements in soils of a metal mining area. Soils in this area have elevated heavy metal concentrations especially Pb, Zn, Mn, Cu, As, and Tl. Using principal component (PC) analysis, six components were extracted, out of which two PCs explaining 50.12% of total variance are more important. The first principal component with a high contribution of Ag, As, Be, Cd, Co, Cu, Mg, Mn, Ni, Pb, and Zn was deemed to be technogenic/

anthropogenic component, and the second principal component, with high loadings for the five discerning variables (Al, Be, Cr, K, Li), was considered as lithogenic component. The third component having strong loadings of Ba, Ca, K, and Na is supposed to have a mixed origin (lithogenic as well as technogenic). Electrical conductivity and total organic matter were not correlated with any element and also have a strong loading in the fifth component which is probably the biomass and ions present in these soils. The findings of the principal component analysis were also substantiated by the cluster analysis. The present study would not only enhance our knowledge regarding the soil pollution status in the study area but would also provide us information to manage the sources of these elements in the study area.

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Introduction

Trace elements are ubiquitous in the environment, being present usually in small amounts in rocks, soils, air, water, and food (Thornton 1996). However, some geological parent materials, including black sedimentary sulfide-bearing shales (alum shales) and basic igneous rocks, often contain large amounts of trace elements. These elements originate

into the environment from a wide spectrum of natural and anthropogenic sources. Natural sources are weathering of mineral deposits, emissions from active volcanoes, sea salt sprays, forest fires, etc. The main anthropogenic sources are mining activities, metal processing industries, fossil fuel combustion, incineration of wastes and sludge, application of phosphate fertilizers, leaching from garbage dumps and some incidental sources, etc. Man's first use of metals for the manufacture of simple tools, weapons, and ornaments dates back to Bronze Age and during the period of Roman empire mining of Fe, Au, Ag, Sn, Cu, and Pb was active. Metalliferous mining associated with exploitation of non-ferrous metals has taken place on a massive global scale for several centuries. An increasing volume and range of heavy metals have been exploited with the growth of the world industry. In particular, lead, zinc, and copper have been mined extensively. Pb and Zn occur principally as sulfide minerals. Galena (PbS) and zinc blend (sphalerite, ZnS) usually occur together and have been mined in many regions. Cadmium is obtained as by-product of the smelting of ZnS, in which it has substituted for some of Zn and no ores are used primarily as source of Cd (Alloway 1990). Cd is closely related with Zn in its geochemistry; both elements have similar ionic structures and electronegativities. Although mines are classified on the basis of their predominant product, they may produce large quantities of other elements as co-products. It is well-known that metal ore processing is associated with contamination of the environment with a cocktail of contaminants rather than one metal. Metal mining, smelting, and processing throughout the world have contaminated soils with heavy metals in excess of natural soil background concentrations. These processes introduce metal contaminants into the environment through gaseous and particulate emissions, waste liquids, and solid wastes (Dudka and Adriano 1997).

The mining and smelting of the metals is a worldwide activity and indeed may be regarded as "global"—defined by the UK Inter-Agency Committee on Global Environmental Research to include matters of local or regional nature that are repeated with sufficient frequency to give them global significance. Investigations into environmental impact of mining activities have to date been largely limited to those in industrialized countries of the west (Verner et al. 1996; Li and

Thornton 2001; Rybicka 1996; Ullrich et al. 1999; Johnson et al. 1978; Alloway and Davies 1971; Stuben et al. 2001; Davies et al. 1985) with only a few in the developing countries (Jung and Thornton 1996; Lee et al. 2001). Priority in the future should be given to the investigations in developing countries where environmental considerations usually take second place to economic growth.

The heavy metal soil contamination from mining and smelting creates a wide spectrum of hazards under an equally wide spectrum of contexts. Adverse environmental impacts from contaminated mining sites include risk to human health, phytotoxicity, contamination of water and soil, and ecotoxicity.

The present investigation is centered on Zawar, a historical Zn–Pb mining community in Rajasthan (India). Zawar mines are the "earliest dated lead–zinc mines in the world." The world's oldest zinc mining district is littered throughout with ancient mines (old workings), slag heaps, and countless earthen retorts strewn all over the area; mute remnants of ancient mining and smelting activities indicate the presence of thriving zinc smelting industry in the past, which dates back to fourteenth century (Erskine 1908). Zawar group of mines comprises of three operating underground mines viz. Mochia, Balaria, Zawarmala, and one closed mine viz. Baroi. The lead–zinc ore mineralization is hosted by sheared metamorphosed dolomite in country rocks of greywackes, shales, and quartzites of Proterozoic age. The ore used for beneficiation is composed of galena (PbS), sphalerite (ZnS), and pyrite (FeS₂) in a gangue of dolomite and quartz. Native silver (Ag), chalcopyrite (CuFeS₂), arsenopyrite (FeAsS), pyrrhotite, and magnetite are also known to occur (Mookherjee 1964).

Over the years, these mining activities are liable to have contaminated the soil and biotic community with heavy metals, typically zinc, lead and cadmium, and other elements. In view of the above discussed facts, the primary objectives of the present study were (1) to study the physicochemical characteristics [viz. pH, electrical conductivity (EC), total organic matter (TOM)] of soils, (2) to determine elemental concentrations of some alkali and alkaline earth metals, metals, and metalloids (i.e., Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, and Zn) in the soils sampled from mining area, and (3) to find out interrelationship, interdependence, and

to define the natural or anthropogenic origin (source apportionment) of various physicochemical characteristics and elemental concentrations by using multivariate statistical analysis such as principal component analysis (PCA) and hierarchical cluster analysis (HCA) coupled with correlation analysis.

Materials and methods

Sampling design

For this study, four important locations—(a) Balaria mine area: functioning mine ($n=8$), (b) Mochia mine area: functioning mine ($n=5$), (c) Zawarmala mine area: functioning mine ($n=5$), and (iv) Baroi Mine area: closed mine ($n=9$)—were selected. Topsoils (0–10 cm) were sampled as undisturbed core, by using a specially designed cylindrical stainless steel corer in the post-monsoon season of 2001. Soon after collection, the soil samples were carefully transferred to clean and dry self-sealing polyethylene bags for transport to laboratory. After being air-dried in paper-lined propylene trays at room temperature and disaggregated with a wooden roller, all samples were sieved through 2 mm sieve. The sample was thoroughly mixed and homogenized by coning and quartering and stored in tightly sealed polyethylene bags until further analysis.

Analytical techniques

The pH and EC of all the samples were determined in an aqueous suspension in the ratio (w/v), sample (1)/distilled water (2.5) (Okalebo et al. 1993). TOM was determined by Walkley–Black method, which involves oxidation by chromic acid (Jackson 1973). From the viewpoint of estimation of elemental concentrations, soils were digested by using microwave-assisted aqua regia digestion method (Chen and Ma 2001). The obtained suspension was filtered through an ashless Whatman 42 filter paper, diluted to 50 ml with 0.5 mol/l HNO_3 , and stored in polyethylene bottles at 4°C for elemental analysis. This method is considered adequate for extracting whole fraction of the element except the amounts that are bound with silicate minerals. Hence, the elements extracted by aqua regia represent the pseudototal concentrations.

All the vessels in contact with samples or reagents were cleaned by soaking in HNO_3 4 mol/l (overnight) and rinsed repeatedly with distilled water. All the extractions were conducted in triplicate. All chemicals used in this study were of analytical grade, and double-distilled or Milli-Q water was used throughout. The concentrations of major and trace elements in the extracts were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES). The analytical wavelengths (nanometers) used were Ag (328.068), Al (308.215), As (189.042), B (249.773), Ba (455.403), Be (313.042), Ca (317.933), Cd (228.802), Co (228.616), Cr (267.716), Cu (324.754), K (766.490), Li (670.784), Mg (279.806), Mn (257.610), Na (589.592), Ni (221.647), Pb (220.353), Sr (407.771), Tl (190.864), and Zn (213.856). Calibrants were prepared from 1,000 $\mu\text{g/ml}$ ICP standard solutions from Merck. Blanks were run simultaneously to reduce other sources of error.

Statistical analysis

To identify the relationships among heavy metals in soils and their possible sources, Pearson's correlation coefficient analysis, PCA, and HCA were performed using the statistical software package SPSS version 13.0 for windows. The correlation coefficient measures the strength of interrelationship between two elements, and PCA and HCA are the most common multivariate statistical methods used in environmental studies.

PCA is a statistical technique which is widely applied to a set of variables in order to reduce their dimensionality. PCA is used to extract a smaller number of independent factors (principal components) from a large set of intercorrelated variables, starts with the correlation matrix describing the dispersion of original variables and extracting the eigenvalues and eigenvectors. An eigenvector is a list of coefficients multiplying the original correlated variables to obtain new uncorrelated (orthogonal) principal components, which are weighted linear combinations of the original variables. Principal components are those whose original eigenvalues exceed 1 (Kaiser 1960). PCA has been widely applied to various environmental matrices, such as sediments (Tahri et al. 2005), soil (Fernandez-Caliani et al. 2009; Facchinelli et al. 2001; Bhuiyan et al. 2010; Qishlaqi

et al. 2009), dust (Anju and Banerjee 2003; Lu et al. 2010), and water (Tahri et al. 2005).

HCA is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behavior of dataset without making a priori assumption about the data, to classify the objects of the system into categories or clusters based on their nearness or similarity (Vega et al. 1998). HCA classifies a set of observations into two or more mutually exclusive unknown groups based on combination of internal variables. HCA is often coupled with PCA to check results and to group individual variables (Facchinelli et al. 2001). A dendrogram is the most commonly used method of representing hierarchical clustering. HCA has been widely applied to different matrices such as soils (Bhuiyan et al. 2010), sediments (Tack et al. 1993), dusts (Lu et al. 2010), and water (Gholami and Srikantaswamy 2009).

Results and discussion

pH, EC, and TOM

The pH of surface soils ($n=27$) varied between 6.41 and 8.47 with a median value of 7.58 (Table 1). It is concluded that the pH of soils from the Zavar mining area is either near neutral or alkaline. This finding contrasts with the other studies in similar type of metal mining areas, where the pH is usually acidic. In general, sulfide-rich and carbonate-poor materials produce acidic conditions in areas having metal sulfide as the ores. In contrast, alkaline-rich materials, even with significant sulfide concentrations, often produce alkaline conditions (Skousen et al. 2000). Electrical conductivity of surface soils varied between 0.04 and 0.24 mS/cm with a median value of 0.11 mS/cm (Table 1). The median levels of TOM in the surface soils were of the order of 1.74%, indicating that these soils are deficient in organic matter content.

Elemental concentrations in soils

As natural soil components, heavy metals are, as a rule, present in small amounts. These days soil is increasingly being polluted by heavy metals, whether from the air or by deliberate spreading of wastes.

High contents occur in some cases as a result of environmental pollution. Base metal mining is one of the most important point source of heavy metals in the environment. Mining and milling operations together with grinding, concentrating ores, and disposal of tailings, along with mine and mill waste water, provide obvious sources of contamination. Zavar area has a long history of metalliferous mining, and a number of mines are distributed along mineralized zones and most of old surface mines are abandoned due to a lack of ore minerals.

The total elemental data allowed us to elucidate the ranges of elemental contamination in the area (Table 1). The descriptive statistics of Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn, pH, EC, and TOM levels in these surface soils are summarized in Table 1. The data in Table 1 show that Al, B, Ba, Cr, K, Li, and Na have minimum values of coefficient of skewness and kurtosis, indicating that these elements have near normal/Gaussian frequency distribution and hence it is most probable that there is no significant anthropogenic/technogenic input of these elements and is predominantly lithogenic/geogenic in their origin. Also, aluminum is a conservative and natural element, contained predominantly in aluminosilicates (its anthropogenic origin is unknown) and participates in clay minerals (Vodyanitskii 2009). In many studies, the technogenic origin of heavy metals is revealed with the consideration of marker element (aluminum) content in the soil profile (Vodyanitskii 2009). Fernandez-Caliani et al. (2009) in their study on heavy metal pollution in soils around abandoned mine sites of Iberian Pyrite Belt (Spain) have also interpreted that Cr is a geogenic element. All other elements have high values of coefficient of skewness and kurtosis suggesting that their distribution is not normal and have a broad range of concentrations, which is the basis for concluding strong contamination of the study area with these elements. Also, therefore, arithmetic mean should not be considered as the best measure of central tendency. As a result, the median or geometric mean will provide more representative measure of central tendency and have been used to summarize the data.

Most of the previous studies on Pb/Zn mining areas are concentrated on Cd, Pb, and Zn contamination, and the results are reported as arithmetic means and standard deviations, although there are no

Table 1 Elemental concentrations (milligrams per kilogram), pH, EC (milli-Siemens per centimeter), and TOM (percent) in soils (n=27) from Zawar area

Element	Ag	Al	As	B	Ba	Bc	Ca	Cd	Co	Cr	Cu	K
Mean	6.00	25.31	44.96	272.56	498.89	1.22	13,785.37	8.93	15.96	41.74	29.52	18,368.30
Standard error of mean	1.05	0.55	14.99	28.68	36.58	0.08	6,238.94	1.66	1.85	2.44	3.95	1,237.54
Median	5.00	26.00	18.00	303.00	551.00	1.00	7,080.00	5.00	14.00	43.00	25.00	18,375.00
Mode	4.00	22.00 ^a	15.00	15.00 ^a	66.00 ^a	1.00	1,630.00 ^a	4.00	12.00 ^a	46.00	28.00	7,781.00 ^a
Geometric mean	0.00	25.16	25.10	201.40	445.41	1.17	7,494.23	6.43	14.22	39.89	25.54	17,282.20
Standard deviation	5.46	2.84	77.90	149.02	190.07	0.42	32,418.47	8.61	9.61	12.66	20.55	6,430.46
Variance	29.77	8.07	6,067.65	22,205.64	36,128.33	0.18	1,050,957,066	74.15	92.27	160.35	422.18	41,350,783.37
Skewness	1.59	-0.09	3.53	-0.41	-0.65	1.42	5.01	2.06	2.75	0.53	2.93	0.53
Standard error of skewness	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Kurtosis	3.44	-0.65	12.63	-1.04	-0.23	0.00	25.60	3.95	8.84	0.58	10.06	0.02
Standard error of kurtosis	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87
Minimum	BDL	20.00	9.00	15.00	66.00	1.00	1,630.00	2.00	6.00	20.00	9.00	7,781.00
Maximum	24.00	31.00	367.00	511.00	787.00	2.00	174,082.00	36.00	53.00	76.00	112.00	33,972.00

Element	Li	Mg	Mn	Na	Ni	Pb	Sr	Tl	Zn	pH	EC	TOM
Mean	42.89	1,375.89	1,798.07	10,403.04	41.07	1,435.26	43.15	3.16	1,442.59	7.55	0.11	2.36
Standard error of mean	2.97	369.00	583.80	1,147.70	2.65	697.01	3.87	0.38	265.41	0.11	0.01	0.30
Median	44.00	856.00	1,074.00	11,366.00	39.00	289.00	43.00	2.60	927.00	7.58	0.11	1.74
Mode	28.00 ^a	200.00 ^a	232.00 ^a	424.00 ^a	29.00 ^a	172.00	25.00 ^a	1.90 ^a	1,100.00	6.41 ^a	0.08	3.54
Geometric mean	39.83	857.11	1,040.14	7,630.06	39.23	404.45	39.52	2.72	1,075.83	7.53	0.10	1.95
Standard deviation	15.42	1,917.39	3,033.51	5,963.63	13.80	3,621.78	20.12	1.96	1,379.11	0.56	0.05	1.54
Variance	237.64	3,676,392.95	9,202,190.61	35,564,909.96	190.30	13,117,314.74	404.67	3.85	1,901,946.02	0.31	0.00	2.39
Skewness	0.22	4.01	4.50	0.11	1.78	4.03	2.14	1.54	2.41	-0.40	0.84	1.28
Standard error of skewness	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Kurtosis	0.15	18.50	21.93	-0.16	5.02	17.20	7.57	1.91	6.50	-0.53	0.52	1.50
Standard error of kurtosis	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87	0.87
Minimum	11.00	200.00	232.00	424.00	24.00	85.00	15.00	1.20	410.00	6.41	0.04	0.78
Maximum	76.00	10,207.00	16,295.00	23,335.00	90.00	17,773.00	120.00	9.00	6,521.00	8.47	0.24	6.94

BDL below detection limit

^a Multiple modes exist. The smallest value is shown

Table 2 Heavy metal levels in soils (micrograms per gram) of mining areas as reported in literature

Location	Pb		Zn		Cd		Cu		As		Reference
	Range	Mean (median)	Range	Mean (median)	Range	Mean (median)	Range	Mean (median)	Range	Mean (median)	
Pribram mining soils	416–2,070	1,032	599–3,890	1,790	4.5–33	11 (GM)	34–103	61.3	–	–	Rieuwerts et al. 2000
Bytom, Poland	69–5,260	(430)	41.7–12,100	(1,245)	0.75–106	(13)	–	–	16.9–138	(35.1)	Ullrich et al. 1999
Ystwyth alluvial, Wales	90–2,900	1,419	95–810	455	1.2–4.0	2.5	17–42	30	–	–	Alloway and Davies 1971
Wales (mine spoil)	–	14,000	–	34,000	–	435	–	–	–	–	Johnson et al. 1977
Sambo Pb–Zn mine, Korea	41–29,900	2,700	329–25,800	8,300	0.9–38.7	11.8	22–1,290	208	–	–	Jung and Thornton 1996
Bytom, Poland	129–2,290	–	193–12,592	–	2–85	–	–	–	–	–	Kucharski et al. 1992
Bukowno, Poland	46–1,520	–	90–9,200	–	1–42	–	–	–	–	–	Kucharski et al. 1992
Tarnowskie Gory, Poland	26–8,200	–	103–13,250	–	1–143	–	–	–	–	–	Kucharski et al. 1992
Katowice, Poland	20–1,050	–	61–2,110	–	X-20	–	–	–	–	–	Kucharski et al. 1992
Chrzanow, Poland	24–1,100	–	62–5,660	–	1–35	–	–	–	–	–	Kucharski et al. 1992
North Wales, UK	33–9,631	1,779	46–4,383	1,143	0.1–27	6.8	–	–	–	–	Davies et al. 1985
Leadville, CO, USA	46–49,000	1,098	204–12,100	1,516	3–110	17	–	–	–	–	Levy et al. 1992
Soria Province, Spain	<200–6.93%	–	<300–6.60%	–	4–90	18 mode	–	–	–	–	Garcia Sanchez et al. 1999
Derbyshire (mine area), USA	4,640–61,720	–	317–3,310	–	6.4–48.1	–	–	–	–	–	Li and Thornton 2001
Central and North-East Wales, UK	4,500–17,000	–	800–10,000	–	–	–	–	–	–	–	Johnson et al. 1978
Daduk, Korea	21–484	133	60–1,064	328	0.40–4.76	1.78	9.6–143.6	42.2	–	–	Lee et al. 2001
Iberian Pyrite Belt, Spain	59–6,500	640 (354)	22–6,890	621 (581)	<21.8	1.9 (0.5)	24–2,874	726 (417)	66–1,560	621 (581)	Fernandez-Caliani et al. 2009
Monica Mine, Madrid, Spain	–	–	92.4–2,243.6	845.7 (604.2)	1.78–34.98	16.35 (13.72)	17.3–605.3	308.7 (301.7)	–	–	Moreno-Jimenez et al. 2009
Wales and Cornwall (Mine), UK	6,150	–	1,590	–	3.6	–	–	–	–	–	Merrington and Alloway 1994

universally accepted sampling and analytical procedures. The heavy metal concentrations in Zawar area soils are compared with data reported from other Pb/Zn mining areas. The observed mean concentrations in the surface soils as determined by aqua regia digestion were 8.93, 1,435, 1,442, and 1,798 $\mu\text{g/g}$, respectively, for Cd, Pb, Zn, and Mn (Table 1). Concentrations of all the metals ranged widely. The values are mostly within the usual range observed for similar kind of environmental settings (Table 2).

Although it is not possible to account for the metal contamination in individual samples, there are generally elevated levels around the mine sites, particularly in the vicinity of abandoned spoil heaps, old shafts, old workings, and recent activity centers. Verner et al. (1996) have also observed peaks of Pb, Zn, and Cd near abandoned mineral workings. Pb levels around 1–3% were observed immediately adjacent to old workings in Derbyshire, England (Coulbourne and Thornton 1978; Cotter-Howells and Thornton 1991).

In the present study, thallium concentrations varied from 1.20 to 9.00 $\mu\text{g/g}$ with a median concentration of 2.6 $\mu\text{g/g}$ and geometric mean 2.72 $\mu\text{g/g}$. Thallium is a rare but ubiquitous trace element with average concentrations of 0.49 ppm in continental crust and 0.013 ppm in oceanic crust (Delvalls et al. 1999; Peter and Viraraghavan 2005). Mean concentrations of thallium in the earth's crust are of the order of 0.1–1.7 mg/kg, mainly present in sulfide ores of zinc, copper, lead, and also in coal (Smith and Carson 1977). Thallium is normally associated with sulfide minerals and is often found in mineralized areas interspersed with sulfide deposits (Zitko et al. 1975). The most common anthropogenic sources of thallium are emissions and solid wastes from coal combustion and ferrous and non-ferrous smelting. According to Twidwell and Beam (2002), it is not unusual for thallium to be present in mined sulfide materials processed for recovery of gold, copper, lead, zinc, and uranium. The largest anthropogenic source of thallium is coal combustion, but some amounts of this element may be released by heavy metal smelting, cement industry, and refining processes (Kabata-Pendias and Pendias 2001). Heim et al. (2002) investigated thallium contents in soil and plants in the EuroRegion Neisse (includes Germany, the Czech Republic, and Poland) and found 0.5 mg/kg Tl in the median topsoil. Tl concentrations in the median French topsoils were 0.3 mg/kg (Tremel et al. 1997), and

soils from southeastern part of Silesian-Cracovian zinc–lead ore deposit region contained 0.44 $\mu\text{g/g}$ as median level of Tl (Jakubowska et al. 2007). A study of Asami et al. (1996) showed an average of 0.33 mg/kg in Japanese unpolluted surface soils. A concentration range of 0.17–0.22 $\mu\text{g/g}$ in garden soils in Canada and a range of 0.2–2.8 $\mu\text{g/g}$ on various soils in the USA were reported (Fergusson 1990; Pendias and Pendias 1992). Thallium concentration in soils from region of Kosovska Mitrovica varied between 0.10 and 5.06 $\mu\text{g/g}$ (Borgna et al. 2009). High concentrations of Tl in the Lanmuchang area of southwest Guizhou, China, where it ranged from 40 to 124 mg/kg in soils originating from the mining area and from 1.5 to 6.9 mg/kg in undisturbed natural soils, has been reported by Xiao et al. (2004). Yang et al. (2005) also analyzed thallium concentrations in Chinese soils. The concentration of Tl in the background soils ranged from 1.63 to 2.02 $\mu\text{g/g}$, while in the upper layer of soils which are spatially close to slag pile, high concentration of thallium (up to 15.4 $\mu\text{g/g}$) was observed.

The levels of Tl as observed in the present work are higher than the levels observed in background soils in most of the studies, but are within range as observed for similar kind of environmental conditions. According to Xiao et al. (2004), thallium contamination in soils and its ready assimilation by crops poses a menace to human health on account of its high toxicity. It has been reported that Tl is more acutely toxic than Hg, Cd, Pb, Zn, and Cu in mammals (Peter and Viraraghavan 2005; Cheam 2001).

Statistical pedogeochemical associations

Correlation coefficient

In order to establish inter-element relationships and to examine the sources of soil contamination by determining the statistical association between physicochemical characteristics and total elemental concentrations in soils, Pearson's correlation coefficients for all the analyzed elements and pH, EC, and TOM were calculated and are presented in Table 3. Of the correlations examined, pH, EC, and TOM were not significantly correlated with elemental data. Inter-element relationships provide interesting information on the sources and pathways of heavy metals.

Table 3 Correlation matrix

	Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	K
Ag	1	0.126	0.129	0.076	0.030	0.001	0.370	0.007	0.000	0.230	0.000	0.063
Al	0.302	1	0.421	0.102	0.054	0.012	0.096	0.541	0.395	0.000	0.993	0.001
As	0.300	-0.161	1	0.279	0.904	0.578	0.761	0.129	0.201	0.549	0.094	0.738
B	0.347	0.322	-0.216	1	0.049	0.922	0.716	0.534	0.924	0.454	0.918	0.233
Ba	0.419 ^a	0.375	0.024	0.382 ^a	1	0.145	0.102	0.686	0.821	0.174	0.750	0.003
Be	0.582 ^b	0.474 ^a	0.112	-0.020	0.288	1	0.580	0.736	0.072	0.001	0.060	0.057
Ca	-0.180	-0.327	-0.061	-0.073	-0.321	-0.111	1	0.900	0.801	0.661	0.363	0.103
Cd	0.508 ^b	-0.123	0.299	0.125	0.082	0.068	0.025	1	0.000	0.436	0.000	0.724
Co	0.646 ^b	0.171	0.254	0.046	0.046	0.352	-0.051	0.758 ^b	1	0.259	0.000	0.457
Cr	0.239	0.706 ^b	-0.121	0.150	0.270	0.585 ^b	-0.088	-0.156	0.225	1	0.365	0.001
Cu	0.651 ^b	0.002	0.329	0.021	0.064	0.366	0.182	0.760 ^b	0.916 ^b	0.181	1	0.592
K	0.362	0.595 ^b	0.068	0.237	0.555 ^b	0.371	-0.321	0.071	0.149	0.586 ^b	0.108	1
Li	0.193	0.728 ^b	-0.347	0.408 ^a	0.212	0.269	-0.112	-0.294	0.072	0.707 ^b	-0.055	0.384 ^a
Mg	0.688 ^b	0.105	0.424 ^a	-0.122	0.094	0.503 ^b	-0.016	0.602 ^b	0.780 ^b	0.229	0.763 ^b	0.215
Mn	0.684 ^b	0.061	0.449 ^a	-0.147	0.090	0.473 ^a	-0.030	0.622 ^b	0.797 ^b	0.194	0.785 ^b	0.193
Na	0.241	0.210	-0.164	0.588 ^b	0.663 ^b	-0.007	-0.280	0.069	-0.132	0.088	-0.091	0.440 ^a
Ni	0.625 ^b	0.374	0.240	0.067	0.327	0.484 ^a	-0.179	0.624 ^b	0.838 ^b	0.516 ^b	0.795 ^b	0.451 ^a
Pb	0.737 ^b	0.019	0.465 ^b	-0.070	0.165	0.471 ^a	-0.069	0.626 ^b	0.712 ^b	0.073	0.729 ^b	0.163
Sr	0.110	0.185	-0.151	0.346	0.093	-0.185	0.177	0.352	0.340	-0.056	0.336	-0.239
Tl	-0.296	-0.081	0.147	-0.413 ^a	-0.145	-0.091	-0.035	-0.062	-0.109	-0.069	-0.038	-0.177
Zn	0.585 ^b	0.172	0.384 ^a	-0.078	0.136	0.363	-0.017	0.758 ^b	0.772 ^b	0.104	0.738 ^b	0.241
pH	0.088	0.112	-0.095	-0.176	-0.242	0.038	0.234	0.381 ^a	0.290	0.098	0.225	-0.030
EC	-0.073	0.171	-0.160	0.306	0.024	-0.019	0.200	0.216	0.044	0.198	0.037	-0.043
TOM	-0.068	0.218	-0.164	0.305	0.344	0.009	0.006	-0.091	-0.130	0.252	-0.147	0.128

	Li	Mg	Mn	Na	Ni	Pb	Sr	Tl	Zn	pH	EC	TOM
Ag	0.336	0.000	0.000	0.227	0.000	0.000	0.586	0.134	0.001	0.663	0.718	0.735
Al	0.000	0.601	0.762	0.293	0.055	0.925	0.355	0.687	0.390	0.578	0.395	0.274
As	0.076	0.028	0.019	0.413	0.229	0.014	0.451	0.464	0.048	0.636	0.426	0.414
B	0.035	0.546	0.463	0.001	0.741	0.729	0.077	0.032	0.698	0.380	0.121	0.122
Ba	0.289	0.641	0.654	0.000	0.096	0.412	0.644	0.471	0.499	0.225	0.904	0.079
Be	0.175	0.008	0.013	0.971	0.011	0.013	0.357	0.650	0.063	0.850	0.926	0.965
Ca	0.579	0.937	0.881	0.157	0.371	0.733	0.378	0.861	0.933	0.241	0.316	0.976
Cd	0.137	0.001	0.001	0.732	0.001	0.000	0.071	0.758	0.000	0.050	0.280	0.653
Co	0.721	0.000	0.000	0.511	0.000	0.000	0.083	0.590	0.000	0.143	0.827	0.518
Cr	0.000	0.252	0.332	0.661	0.006	0.718	0.781	0.732	0.605	0.627	0.322	0.205
Cu	0.785	0.000	0.000	0.651	0.000	0.000	0.087	0.850	0.000	0.258	0.853	0.465
K	0.048	0.282	0.334	0.022	0.018	0.416	0.229	0.377	0.225	0.881	0.829	0.526
Li	1	0.826	0.664	0.302	0.343	0.344	0.410	0.810	0.419	0.759	0.886	0.500

Table 3 (continued)

	Li	Mg	Mn	Na	Ni	Pb	Sr	Tl	Zn	pH	EC	TOM
Mg	-0.045	1	0.000	0.364	0.000	0.000	0.522	0.457	0.000	0.039	0.755	0.601
Mn	-0.088	0.994 ^b	1	0.405	0.000	0.000	0.554	0.523	0.000	0.049	0.796	0.626
Na	0.206	-0.182	-0.167	1	0.704	0.715	0.399	0.219	0.843	0.486	0.318	0.065
Ni	0.190	0.746 ^b	0.755 ^b	0.077	1	0.000	0.271	0.648	0.000	0.220	0.612	0.956
Pb	-0.189	0.868 ^b	0.891 ^b	-0.074	0.648 ^b	1	0.867	0.712	0.000	0.123	0.946	0.832
Sr	0.165	-0.129	-0.119	0.169	0.220	-0.034	1	0.532	0.440	0.696	0.149	0.594
Tl	-0.048	-0.149	-0.129	-0.244	-0.092	-0.074	0.126	1	0.727	0.675	0.631	0.116
Zn	-0.162	0.804 ^b	0.808 ^b	-0.040	0.757 ^b	0.714 ^b	0.155	-0.070	1	0.017	0.218	0.508
pH	0.062	0.399 ^a	0.382 ^a	-0.140	0.244	0.304	0.079	0.085	0.457 ^a	1	0.148	0.673
EC	0.029	-0.063	-0.052	0.200	0.102	-0.014	0.286	-0.097	0.245	0.286	1	0.002
TOM	0.136	-0.105	-0.098	0.360	-0.011	0.043	0.107	-0.310	-0.133	-0.085	0.564 ^b	1

The left lower part is correlation coefficient; the right upper part is significance level

^aCorrelation is significant at the 0.05 level (two-tailed)

^bCorrelation is significant at the 0.01 level (two-tailed)

Ag levels were significantly correlated (0.01 level of significance) with Be (0.582), Cd (0.508), Co (0.646), Cu (0.651), Mg (0.688), Mn (0.684), Ni (0.625), Pb (0.737), and Zn (0.585). Aluminum was found to be strongly correlated with Cr (0.706), K (0.595), and Li (0.728). Statistically significant correlation at 0.01 level of significance was found between elemental pairs B–Na (0.588), Ba–K (0.555), Ba–Na (0.663), Be–Cr (0.585), Be–Mg (0.503), Cd–Co (0.758), Cd–Cu (0.760), Cd–Mg (0.602), Cd–Mn (0.622), Cd–Ni (0.624), Cd–Pb (0.626), Cd–Zn (0.758), Co–Cu (0.916), Co–Mg (0.780), Co–Mn (0.797), Co–Ni (0.838), Co–Pb (0.712), Co–Zn (0.772), Cr–K (0.586), Cr–Li (0.707), Cu–Mg (0.763), Cu–Mn (0.785), Cu–Ni (0.795), Cu–Pb (0.729) and Cu–Zn (0.738), Mg–Mn (0.994), Mg–Ni (0.746), Mg–Pb (0.868), Mg–Zn (0.808), Mn–Ni (0.755), Mn–Pb (0.891), Mn–Zn (0.808), Ni–Pb (0.645), Ni–Zn (0.757), and Pb–Zn (0.714). Significant correlation between Zn–Cd ($r=0.91$) and Pb–Zn ($r=0.77$) has also been observed by Ullrich et al. (1999). A strong positive correlation between Cd and Zn showed that the levels of Cd are dependent on Zn levels, which could be explained by strong geochemical associations between these two elements. Similar kind of correlation was also observed by Thornton et al. (1980) in Shipham soils. A strong correlation among elements (Ag, As, Be, Cd, Co, Cu, Mg, Mn, Ni, Pb, Zn) indicates their common technogenic origin, especially the mining of sulfide minerals. Al, Cr, K, and Li are also strongly correlated and have a lithogenic origin. In the present study, Ca, Tl, and Sr are not correlated with other elements, implying that different pedogenic processes are responsible for their levels in the study area.

The predominant form of occurrence of strontium in rocks, however, is substitution of Ca, K, and Ba in other minerals (feldspar, micas, calcite, aragonite, fluorite, barite, etc.); base metal sulfides, such as galena, may contain measurable amounts of Sr isotopes (Misra 2000). A significant correlation was found between EC–TOM (0.564). But no significant correlations were observed between elemental data and pH, EC, and TOM for the analyzed soils.

Principal component analysis

Principal component analysis was carried out to ascertain the possible contributing factors toward the

elemental concentrations and thereby determine which elements have a common origin in soils, by applying Varimax rotation with Kaiser normalization. By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors, the percent of variance explained by each of them was calculated by using SPSS 13 and is shown in Table 4. The results in Table 4 show that only six eigenvalues are >1 and are explaining 79.397% of variance. The first six eigenvalues were therefore selected for further analysis; other small but nonzero eigenvalues were discarded for the purpose of establishing a probable number of contributing source factors. The initial eigenvalues extracted were “cleaned up” by means of Varimax rotation. The comparison of initial and rotated eigenvalues and their corresponding contribution to-

ward explanation of % variance shows that both the eigenvalues and their corresponding contribution toward the explanation of cumulative % variance have not changed substantially. It is evident from the rotated component matrix (Table 5) that all the elemental data and physicochemical parameters are explained by six factors. The relations among the elements based on the first three principal components are illustrated in Fig. 1 in three-dimensional space.

The first principal component (PC1) spanning the greatest amount of variance (31.39%) includes Ag, As, Be, Cd, Co, Cu, Mg, Mn, Ni, Pb, and Zn. High loadings of these metals and metalloids in this component/factor/source clearly point to their technogenic/anthropogenic origin, which is beyond any doubt, because metals were mined and smelted in this area even in Middle ages and

Table 4 Total variance explained

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%
1	7.759	32.331	32.331	7.759	32.331	32.331	7.534	31.391	31.391
2	4.270	17.792	50.123	4.270	17.792	50.123	3.393	14.136	45.527
3	2.400	10.002	60.125	2.400	10.002	60.125	2.648	11.034	56.561
4	2.019	8.411	68.536	2.019	8.411	68.536	1.981	8.252	64.813
5	1.438	5.991	74.527	1.438	5.991	74.527	1.858	7.741	72.554
6	1.169	4.870	79.397	1.169	4.870	79.397	1.642	6.843	79.397
7	0.957	3.986	83.383						
8	0.729	3.038	86.422						
9	0.646	2.691	89.112						
10	0.616	2.566	91.678						
11	0.512	2.132	93.810						
12	0.405	1.689	95.499						
13	0.260	1.082	96.581						
14	0.240	1.001	97.582						
15	0.168	0.700	98.282						
16	0.128	0.532	98.814						
17	0.119	0.497	99.311						
18	0.052	0.218	99.530						
19	0.046	0.192	99.722						
20	0.030	0.124	99.846						
21	0.018	0.076	99.922						
22	0.015	0.063	99.985						
23	0.003	0.015	100.000						
24	8.55E-005	0.000	100.000						

Extraction method: principal component analysis

Table 5 Rotated component matrix

Variables	Principal component						Communality
	1	2	3	4	5	6	
Ag	0.744	0.212	0.300	0.060	-0.188	0.348	0.849
Al	0.068	0.845	0.287	0.106	0.124	-0.051	0.830
As	0.465	-0.324	0.195	-0.303	-0.167	-0.214	0.525
B	-0.050	0.184	0.375	0.499	0.148	0.587	0.792
Ba	0.131	0.199	0.804	0.042	0.113	0.161	0.743
Be	0.447	0.559	0.090	-0.330	-0.084	0.113	0.649
Ca	-0.005	-0.128	-0.662	0.131	0.204	0.220	0.562
Cd	0.805	-0.283	0.059	0.335	0.158	-0.038	0.869
Co	0.896	0.147	-0.080	0.257	-0.081	0.003	0.903
Cr	0.141	0.896	0.073	-0.121	0.161	0.013	0.868
Cu	0.900	0.032	-0.109	0.248	-0.084	0.052	0.893
K	0.198	0.527	0.579	-0.212	0.051	0.037	0.701
Li	-0.136	0.871	0.058	0.246	-0.060	0.122	0.859
Mg	0.925	0.112	-0.079	-0.249	-0.031	0.057	0.941
Mn	0.939	0.061	-0.060	-0.242	-0.024	0.035	0.949
Na	-0.092	0.045	0.741	0.255	0.260	0.281	0.771
Ni	0.826	0.358	0.179	0.114	0.041	-0.070	0.862
Pb	0.890	-0.061	0.070	-0.202	0.034	0.058	0.846
Sr	0.126	0.014	-0.016	0.911	0.123	-0.068	0.866
Tl	-0.101	-0.032	-0.039	0.116	-0.134	-0.860	0.784
Zn	0.893	0.009	0.030	0.028	0.190	-0.145	0.857
pH	0.373	0.146	-0.420	0.041	0.409	-0.261	0.574
EC	0.044	0.060	-0.056	0.221	0.882	0.025	0.837
TOM	-0.132	0.102	0.245	-0.060	0.734	0.308	0.724

Extraction method: principal component analysis; rotation method: Varimax with Kaiser normalization. Rotation converged in seven iterations

presently also zinc and lead mining and beneficiation in this area is known worldwide. Fernandez-Caliani et al. (2009) in their study of heavy metal pollution in soils around the abandoned mine sites of the Iberian Pyrite belt (Southwest Spain) have also strong loadings of Cd, Pb, Zn, Cu, and As in single factor, which is interpreted as mining related anthropogenic factor. Asami (1988a, b) have also observed areas with soil contamination by As, Be, Zn, and Pb from mining/smelting in Japan.

The second principal component (PC2) accounts for 14.136% of the variance and has high loadings for Al, Be, Cr, K, and Li and indicates the dominance of lithogenic elements. K and Al are out of the eight abundant rock forming elements found in biosphere (Adriano 1986). Also, aluminum acts as a natural

marker element (its anthropogenic origin is unknown). Aluminum is the conservative element and is contained predominantly in aluminosilicates (Vodyanitskii 2009). Cr is a ferrofamilly transition element and is known to be added geogenically (Hanesch et al. 2001). So, this factor is principally lithogenic.

The third principal component (PC3) represented 11.034% of variance and high positive loadings of basic cations such Ba, K, Na, and negative loadings of Ca and pH. Ca, Na, and K are out of the eight abundant rock forming elements found in biosphere (Adriano 1986). Also, these elements would have been added to the soils from wind dispersion of dust from mine tailings and wastes tips, which are frequently encountered materials in the study area. The mine tailings and wastes are having calcareous

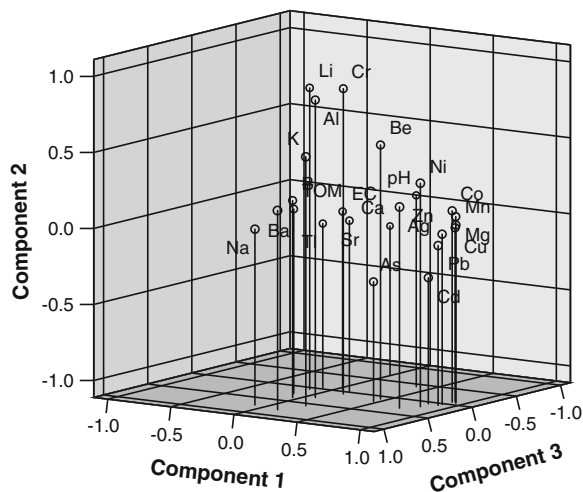


Fig. 1 Principal component analysis results in the three-dimensional space showing loadings of first three principal components

minerals (dolomite, ankerite) as indicated by X-ray diffraction analysis. This indicates the obvious addition of these elements, particularly Ca to the soils from technogenic activities. Cations such as Ca^{2+} , Mg^{2+} , K^+ , and Al^{3+} may accumulate in minesoils because of sulfuricization. Sulfuricization is the process by which sulfide minerals such as pyrite are oxidized, minerals are weathered by sulfuric acid produced, and new mineral phases are formed from the dissolution process (Fanning and Fanning 1989). Sulfuricization produces cations such as Ca^{2+} , Mg^{2+} , and K^+ . These ions may accumulate faster than they can be leached (Sencindiver and Ammons 2000). Association of pH with Ca, K, and Na indicates that these elements and their compounds are playing role in maintaining the pH of these soils. It should be noted that this component has high loadings of typical lithogenic elements (Na, K, Ca); this

Table 6 Rotated component matrix

Element	Principal component				Communality
	1	2	3	4	
As	0.436	0.026	-0.203	-0.427	0.414
Ag	0.751	0.369	-0.066	0.285	0.786
Be	0.477	0.269	-0.458	0.123	0.525
Cd	0.780	0.004	0.395	-0.017	0.765
Co	0.918	-0.026	0.197	0.010	0.882
Cu	0.918	-0.084	0.221	0.029	0.899
Mg	0.926	-0.022	-0.281	0.009	0.936
Mn	0.936	-0.022	-0.258	-0.027	0.944
Ni	0.843	0.296	0.076	-0.023	0.805
Pb	0.878	0.059	-0.180	-0.043	0.809
Zn	0.879	0.059	0.047	-0.083	0.785
Sr	0.155	-0.019	0.909	0.052	0.853
Tl	-0.113	-0.049	0.199	-0.848	0.773
Ba	0.118	0.836	0.061	0.135	0.734
Ca	0.020	-0.650	0.155	0.296	0.535
K	0.198	0.729	-0.266	0.106	0.653
Na	-0.118	0.762	0.281	0.321	0.777
B	-0.031	0.427	0.399	0.645	0.758
Eigenvalue	7.367	2.731	1.888	1.647	
% of variance	40.928	15.173	10.489	9.151	
Cumulative%	40.928	56.101	66.590	75.741	

Extraction method: principal component analysis.

Rotation method: Varimax with Kaiser normalization. Rotation converged in six iterations

suggests that the parent material, technogenic addition of these elements, and subsequent pedogenic processes are major factors in the amount and distribution of these elements.

Principal components 4 (8.25% variance) and 6 (6.843% of variance) contain B, Sr and B, Tl, respectively. pH, EC, and TOM are represented independently by PC5, which is consistent with those obtained by Bhuiyan et al. (2010) for coal mine affected agricultural soils of Bangladesh, characterized by high loadings of pH and EC in a separate principal component.

As discerned from the PCA, it is very distinctive that Sr and Tl along with B have high independent loadings in PC4 and PC6, respectively. To investigate the possible sources of Sr and Tl, the data for all the variables except lithogenic elements (Al, Cr, Li) and soil characteristics (pH, EC, and TOM) were further

subjected to PCA, and from the rotated component matrix (Table 6), it was found that pedogeochemical associations have not changed at all except the minor changes in loadings. So, it is interpreted that certainly some different pedogeochemical processes/sources are there for Sr and Tl, which could be the mineralization of these elements along with other minerals in this area.

Hierarchical cluster analysis

Variables are grouped into clusters using hierarchical cluster analysis with average linkage between groups and the absolute values of correlation matrix as a similarity measure (Fig. 2). This way, strongly interrelated variables are clustered, irrespective of the positive or negative sign of the relationship. The results of HCA are shown in Fig. 2 as a dendrogram.

Fig. 2 Dendrogram using average linkage (between groups) obtained by hierarchical cluster analysis

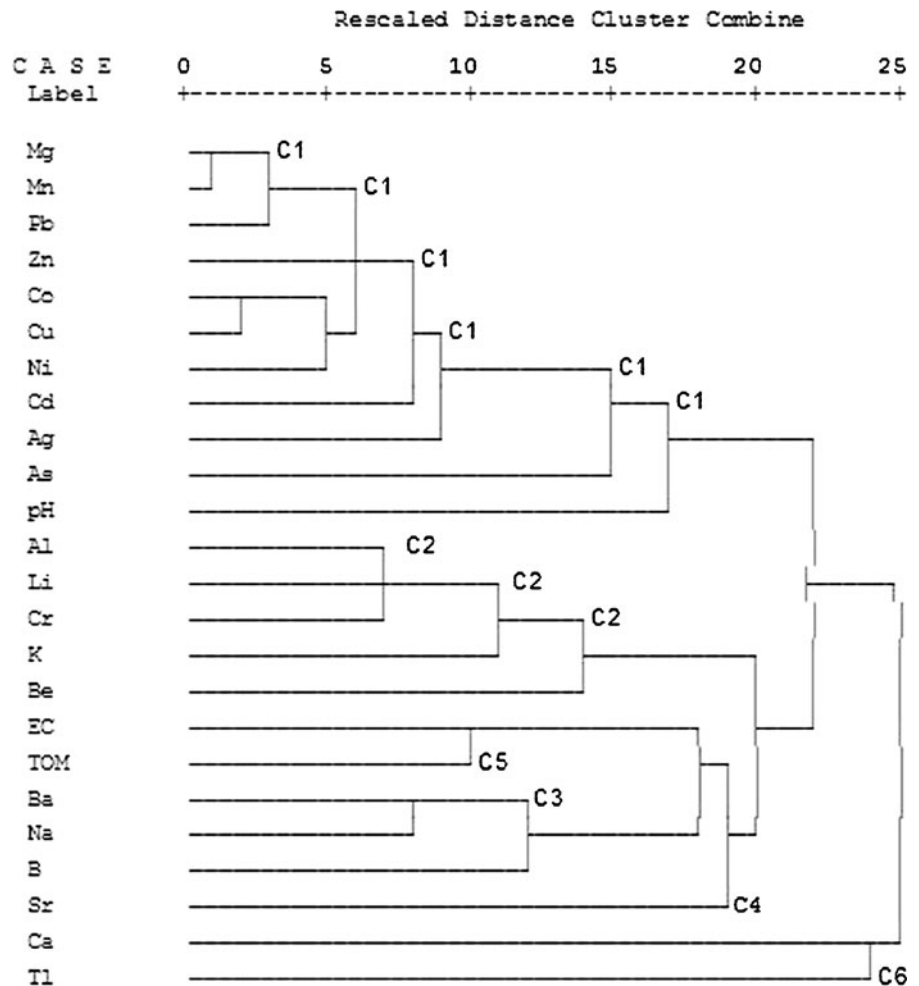


Figure 2 displays six clusters: (C1) Mg–Mn–Pb–Zn–Co–Cu–Ni–Cd–Ag–As–pH, (C2) Al–Li–Ca–K–Be, (C3) Ba–Na–B; (C4) Sr–B–Na–Ba, (C5) EC–TOM, and (C6) Ca–Tl. However, it is observed that clusters 3, 4, and 5 join together at a relatively higher level, possibly implying a common source.

Conclusion

The results obtained in this study add to our knowledge of elemental contents and their possible sources in soils of a Pb–Zn mining area. This study also demonstrates that multivariate analysis (PCA, HCA) and correlation matrix methods can provide important and valid (useful) tools for source apportionment and dynamics of elements in polluted soils. PCA identified six components, among them PC1 is loaded with Ag, As, Be, Cd, Co, Cu, Mg, Mn, Ni, Pb, and Zn, which have anthropogenic origin, and PC2 is loaded with elements viz. Al, Be, Cr, K, and Li, having lithogenic origin. The observations of PCA are further substantiated by hierarchical cluster analysis.

Thallium has relatively higher levels in the study area. Considering the high levels of Tl and its known toxicity, thallium speciation and uptake by plants should be investigated in this area. Also, further research efforts should be addressed to enhance our understanding of processes controlling metal speciation and bioavailability in soils.

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