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Ecotoxicological risk assessment of trace metals in humid subtropical soil

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Abstract In this work, several physicochemical properties of sub-tropical soil (up to 20 cm depth) like water holding capacity, organic carbon content, cation exchange capacity, texture, pH, and electrical conductivity were determined along with the trace metals, Co, Cr, Cu, Mn, Ni, Pb and Zn, in order to evaluate inter-relations among the trace metals and the soil properties. The contribution of the trace metals to ecotoxicological risk was assessed using various tools. Cr, Cu, Mn and Zn contents were found to be lower than the world average, but Co, Ni, and Pb had higher contents. The trace metal concentrations were utilized to obtain the pollution index and the potential ecotoxicological aspects. The trace metals were shown to have come from similar origin and their retention in the soil was contributed by properties like organic carbon, cation exchange capacity, clay content and water holding capacity of the soil. The pollution index showed that the trace metals had the sequence of Pb (considerably polluted) > Co, Ni (moderately polluted) > Cr, Cu, Mn and Zn (unpolluted). The composite ecological risk index was the highest in agricultural land with irrigation and fertilizer use, and was the lowest in the forest land.

Keywords Trace metals in soil · Ecotoxicology · Pollution index · Correlation matrix · Soil physic-chemical properties

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Introduction

Soil trace metals are sensitive indicators of environmental pollution levels (Pekey et al. 2004) as the metals have a role in determining chemical behavior, mineralogy, and fertility of the soil. Independent of the entry route, the trace metals in soil undergo biochemical, geochemical and chemical processes (chemical weathering, adsorption and ion exchange). There is growing concern throughout the world about the trace metals in soil, their toxicity levels, their entry into the food chain and the associated risks (Alfaro et al. 2015).

The soil gets naturally enriched with trace metals from the pedogenic biogeochemical cycles. The soil trace metal levels are mainly controlled by the chemical composition of the parent rock materials, but there are also contributions from peripheral anthropogenic activities such as dumping of industrial and municipal wastes, mining for minerals, use of fertilizers, insecticides, and other chemicals in agriculture. The presence of an iron-manganese layer is a common subtropical soil feature that acts as the source of various soil trace metals (Huang et al. 2008). Geochemical processes lead to the weathering of minerals and development of soil. The consequent feature of mineral weathering, release and translocation of the trace metals to soil varies to different extents based on the chemical behaviour of the trace metals (Galán et al. 2008). The pathways of the trace metals to the soil signify the relative distribution of the trace metals in different soil horizons and the related consequences to various segments of the environment. The trace metals themselves are sensitive to the changes in the environmental conditions and this factor determines their chemical speciation in the soil as well as their chemical behaviour in the ecosystem (N'gussan et al. 2009).

For the ecological risk assessment, the quantification of the available trace metals is considered to be a necessary

condition. It is known that various soil physic-chemical properties can influence the mobility of the trace metals leading to their enrichment or depletion in a particular location. If there is biomagnification of the trace metals in soil, they become much more detrimental to the ecology—the overall scenario being determined by the reactivity, magnification potential, human exposure and ecotoxicological aspects of the trace metals (Baize 2010).

Subtropical soils experiences three kinds of climate a year ranging from the hot dry to cold dry through the hot wet season with varied extent of humidity. The changes in climate conditions perturb the soil–water system and prevent the soil pore water from attaining equilibrium conditions when concentrations of the metal ions in solid soil phase and the pore water become well-defined. The climatological and anthropogenic activities, associated with the dry-wet cycles, induce stress in the form of shock to the soil microorganisms to release their body fluids that alter the trace metal equilibrium in soil. The body fluids of microorganisms accumulate trace metals by the process of passive diffusion and may mistakenly uptake the unwanted trace metal ions along with the nutrient metal ions (Driscoll and Akeiverfeldt 1994; Carrillo-Gonzãlez et al. 2006).

Soil trace metals are sensitive indicators of environmental pollution levels (Pekey et al. 2004) as the metals have a role in determining chemical behavior, mineralogy, and fertility of the soil. Independent of the entry route, the trace metals in soil undergo biochemical, geochemical and chemical processes (chemical weathering, adsorption and ion exchange). Chemical reactions in presence of available soil water includes hydration, hydrolysis and complexion processes. During these processes, the trace metals either get adhered to the soil particles or released to the environment. As a consequence, the mobility of the trace metals in the soil is affected. Hydration, complexation and intrusion of the metals into a fixed organic or inorganic constituent through exchange processes, reduce the mobility of the metals (Huang, 2008). On the other hand, soil microbes through their enzyme catalytic activities influence the dissolution, precipitation, adsorption and exchange properties of the metals and determine their composition ion the soil (Driscoll and Akeiverfeldt 1994). Plants utilize some of the trace metals as micro-nutrients and reduce their availability in soil. Higher uptake of trace metals by plants may create a situation of micronutrient deficiency and metabolic stress in the soil leading to constrains also in the input of organic matter through decomposition and transformation (Liang et al. 2009).

Adsorption of trace metals by the soil particles is affected by the soil pH (Green et al. 2003), cation exchange capacity (CEC) (Ziper et al. 1988) and soil organic matter (SOM) (Kashem and Singh, 2001). Organic matter in soil actively retains the metallic elements, usually by complexation reactions.

Higher water holding capacity (WHC) results from a larger content of pore water in the soil that provides a medium for transporting the trace metals through the pores. Soil pH influences the trace metal mobility and it is known that acidic soils favor and alkaline soils lower their mobility across the soil matrix. Lack of oxygen in the soil can also trigger mobility of the metal ions (Gang et al. 2010). The lower the mobility of the metal ions, the higher is the chance to be retained by the soil maximizing their stay at a particular location and contributing to their role as soil contaminants. In agricultural soil, the extent of removal of nutrients from the soil cannot be counterbalanced by the post-harvest decomposition of the straws, leaving a negative balance (Whitbread et al. 2003). The trace metals may undergo redox reactions on clay mineral surface facilitating the involvement of these metals in the biological processes in soil.

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Soil trace metal analysis has a key role in arriving at a comparison with the natural background levels and in assessing the extent of weathering processes governing the association and dissociation of trace metals to soil (Wilson et al. 2008; Bini et al. 2011). The present work incorporates monitoring of Cr, Co, Cu, Mn, Ni, Pb, and Zn in tropical agricultural soil to establish their ecological hazard potential. The potent source of the trace metals in soil constitutes both the free and bound states. The bound metals might become bioavailable under appropriate unfavorable soil conditions. This work aims to determine the regional averages of the trace metals in the soil and to establish their correlation with soil physicochemical parameters.

Materials and methods

Soil sampling site description

Soil samples were collected from seven sites belonging to the tropical rainforest climate region subjected to humid
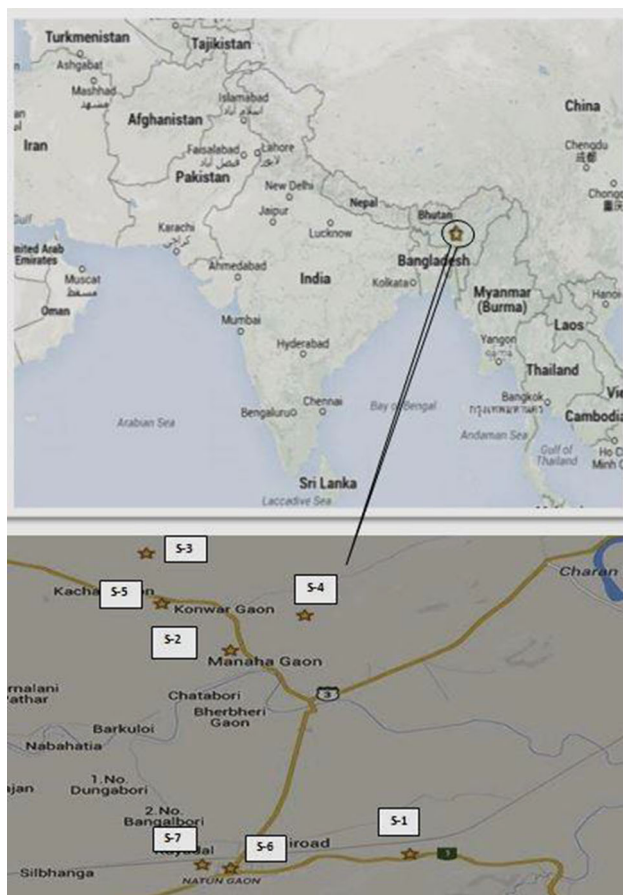
Fig. 1 The locations of the sampling sites (map not to scale)

subtropical climate in the state of Assam, India. The average rainfall in the area is 1530 mm, with temperatures of 25.5–32.9 °C (summer) and 19.8–24.8 °C (winter), the annual average being 9.0 –30.4 °C. The sampling locations are shown in Fig. 1 and the sample identities and brief description of the sites are given in Table 1. To incorporate the effects of various land use patterns on the abundance of soil trace metals, the sampling sites were selected from virgin forest land (S1), wetland (S2), paddy cultivated land affected by floods every season (S3), agricultural land having irrigation and fertilizer use facilities (S4) and without such facilities (S5), land experiencing urban (S6) and rural (S7) residential impacts.

Soil sampling and processing

Three samples were collected from 1 m^2 area, from A horizon, up to 20 cm depth (average conventional tillage depth) using a 5 cm corer. The collected soil samples were homogenized to form a composite sample, representing the specific soil type for a particular sampling location. The samples were air dried, passed through 2 mm sieve after which they were stored for laboratory analysis. The

samples were collected annually in three seasons viz. hot dry summer (April to June), wet hot summer (July to September) and cold dry winter (November to February) to take into account the impact of change in climate as well as the land use patterns over the rate of soil organic matter (SOM) decomposition and stabilization. The results described here are the seasonal averages' for a span of two years from April 2012 to November 2013.

Analysis of soil samples

The soil samples were analyzed as per standard methods, i.e. soil composition with respect to sand, clay and silt percentage by hydrometer method, soil texture using ISSS triangle (Sarkar and Halder 2010), water holding capacity (WHC) by perforated base cylinder method (Wilke 2005). Electrical conductivity (EC) (1:5 soil: water suspension, Elico CM 180) (Jackson 1958), pH (1:5 soil: water suspension, Elico LI 120), soil organic carbon (SOC) was determined by modified Walkley–Black method in which the organic carbon was oxidized by a mixture of $K_2Cr_2O_7$ and concentrated H_2SO_4 and nullifying the interferences of iron, chlorides, etc. (Sarkar and Halder 2010). The cation exchange capacity (CEC) was measured by ammonium acetate extraction method (Hasse 1994). To determine the total amounts of trace metals present in the soil samples, approximately 1 g of soil was digested with tri-acid mixture (concentrated hydrochloric, nitric and sulphuric acids in 1:2:4 proportions), the volume was made up to 100 ml and the trace metals were analysed in a Atomic Absorption Spectrophotometer (PerkinElmer AAnalyst 200) using air acetylene flame. The determined concentrations were converted to mg/kg using the formula: Trace metal (mg/kg) = (AAS reading in mg l^{-1} × volume of extract)/oven dry weight of soil.

All the chemicals used were of analytical grade and were procured from E. Merck. These were used without further purification. All the solutions were made in double distilled water. The analysis of each sample was done in triplicate and the mean of the three values is reported.

Calculations

Various indices have been computed and interpreted on the basis of world average trace metal concentrations and available literature (Hakanson 1980; Bhattacharya et al. 2006; Krupadam et al. 2006; Gong et al. 2008; Ogunkunle and Fatoba 2013; Jiang et al. 2014). The impact of environmental indicators is directly reflected through the single pollution index (Ogunkunle and Fatoba, 2013).This index most often indicates the trace metal pollution incorporating the land use practices or anthropogenic impacts on soil. It tries to correlate the average trace metal concentrations of a particular soil with the world reference values.

Table 1 Soil use type, GPS coordinates and description of the sampling locations

ID	Soil use type	Location	Description of the site
S1	Virgin forest land	N 26°05′57.2″ E 92°19′14.3″	Foothills of Karbi Hill range, Nellie, Morigaon District, Assam. Forest not harvested for last 60 years
S2	Wetland	N 26°11′49.6″ E 92°11′53.2″	Recipient of water overflows from vast paddy cultivated area, water locked for about eight months a year and moist almost the whole year
S3	Flood affected land	N 26°13′48.8″ E 92°10′38.8″	Located in Morigaon District of Assam, submerged by flooded water from the river Brahmaputra during hot-wet season
S4	Land used for paddy cultivation	N 26°12′32.8″ E 92°12′58.4″	Regular conventional tillage during the cold dry season with underground water irrigation. Experienced based application of fertiliser without any soil test
S5	Land used for paddy cultivation	N 26°12′46.9″ E 92°10′52.6″	Conventional tillage during the hot-wet season without application of irrigation and fertilizer
S6	Residential land	N 26°07′21.0″ E 92°11′53.0″	Urban area developed for last thirty years, without tillage activity on the soil. Water stagnation during heavy rainfall for a short duration
S7	Residential land	N 26°07′25.1″ E 92°11′28.5″	Rural area, no water stagnation, rare tillage activity

Table 2 Pollution risk level interpretation using pollution indices

Pollution index (PI)		Ecological risk index (E_r)		Potential ecological risk index (PERI)	
PI	Level	E_r	Risk potential	PERI	Risk potential
PI < 1	Unpolluted	$E_r < 30$	Low	PERI < 40	Slight
$1 \leq PI < 3$	Moderate pollution	$30 \leq E_r < 60$	Moderate	$40 \leq PERI < 80$	Medium
$3 \leq PI < 6$	Considerable pollution	$60 \leq E_r < 120$	High	$80 \leq PERI < 160$	Strong
$PI \geq 7$	Very high pollution	$E_r \geq 120$	Very high	$PERI \geq 160$	Very strong

The ecological risk index incorporates the total weighted values of trace metal concentrations of the soil in order to evaluate the total potential ecological risk. As this index includes the toxicity of different trace metals and their bioavailability in the soil, and nullifies the regional background levels (Horst, 1997), it serves as a good indicator of the risk factor to ecology. This index is used generally to assess the soil quality with respect to the trace metals.

The pollution Index (PI) is obtained from

$$PI = C_i / C_{ref} \tag{1}$$

where C_i is the mean trace metal concentration obtained by averaging values measured for six seasons for a particular sampling location and C_{ref} is the world average value (Co 11.3, Cr 59.6, Cu 38.9, Mn 488.0, Ni 29.0, Pb 27.0 and Zn 70.0; all values in mg/kg) for the particular trace metal (Kabata-Pendias 2011; Jiang et al. 2014). The Potential Ecological Risk Index for a single trace metal (E_r) and the overall Potential Ecological Risk Index (PERI) are calculated using the expressions:

$$E_r = T_r^i \times PI \tag{2}$$

$$PERI = \sum_r^i E_r^i \tag{3}$$

where T_r is toxicity response coefficient with a value of 5 for Co, Cu, Pb and Ni; 2 for Cr and 1 for Zn (Hakanson 1980; Krupadam et al. 2006). The basis of interpretation of the indices is given in Table 2.

Results

Physico-chemical characteristics of the soil

The average values for a few physicochemical parameters (water holding capacity WHC, clay, sand and silt percentages, pH, electrical conductivity EC, soil organic carbon SOC and cation exchange capacity CEC) for the three seasons (hot-dry, hot-wet and cold-dry) are given in

Table 3 Mean and seasonal values of texture components and water holding capacity

Mean	S1	S2	S3	S4	S5	S6	S7
Clay %	16.15	45.02	21.18	40.75	20.82	13.50	19.67
Sand %	72.28	42.20	66.77	36.65	57.23	65.12	69.72
Silt %	11.62	12.78	11.95	22.60	21.98	21.42	10.63
Texture type	SL	Cl	SClL	Cl	SClL	SL	SClL
Seasonal values of water holding capacity (WHC %)							
Hot dry	31.58	54.43	43.70	60.96	42.71	36.24	32.91
Hot wet	25.61	53.46	39.19	58.64	33.61	37.01	30.27
Cold dry	23.67	52.53	40.05	56.68	50.87	40.81	33.13
Mean	26.95	53.47	40.98	58.76	42.40	38.02	32.10
Median	25.61	53.46	40.05	58.64	42.71	37.01	32.91
SD	4.12	0.95	2.39	2.14	8.63	2.45	1.59

SL sandy loam, *Cl* clay, *SClL* sandy clay loam

Tables 3 and 4. It is found that clay, silt and sand composition of the soil follows the sequence:

Clay: S2 > S4 > S3 > S5 > S7 > S1 > S6
Silt: S4 > S5 > S6 > S2 > S3 > S1 > S7
Sand: S1 > S7 > S3 > S6 > S5 > S2 > S4

and the soil texture is of three types: sandy loam (S1, S6), clayey (S2, S4; clay > 40 %), and sandy-clay-loam (S3, S5, S7). The water holding capacity, WHC, of the soil is in the order of S4 > S2 > S5 > S3 > S6 > S7 > S1 and it is observed generally that the clayey soil has the highest and the sandy-loam soil the least WHC.

Soil texture is an important factor for the retention and release of trace metals. Fine grained soils compared to their coarse counterparts are able to provide large surface area and net negative surface charge to contribute to the electrostatic sorption of the trace metals (Tack 2010). Heavy soils are characterized by higher soil aggregation and retention capacity of soil organic carbon. The soil aggregates acts as a barrier for solute transportation. Water and solutes are absorbed by soil aggregates through the action of capillary forces. These forces increase with the fineness of the soil texture, higher soil organic carbon and dry phase of the soil (Bachmann et al. 2003).

Metals are characterized by their well-known property of low ionization potential which make them prone to exist in the cationic form and to get associated with the soil available anions. Higher clay content and aggregation exert greater capillary force due to distribution of the solute metal ions in the vertical direction and this contributes to the localization of the trace metals in soil.

The pH does not follow any particular order, and the values are in the sequence of S6 > S5 > S4 > S7 > S1 ≈ S2 ≈ S3, the mean values varying from 6.6 to 8.0, mostly in the alkaline range. The soil electrical conductivity (EC) is from 125.8 to 196.2 µS/cm with large deviations from season to season. The mean EC is in the order of S5 > S4 > S2 > S3 > S6 > S1 > S7. The soil organic carbon, SOC, is highest in S2 and lowest in S1 (sequence S2 > S4 > S3 > S5 > S7 > S6 > S1) within the range of mean values from 2.41 to 6.88 % indicating wide variability among the sites. The cation exchange capacity has also a wide variance from 3.91 (S1) to 12.22 (S6) cmol/kg (order S6 > S4 > S2 > S3 > S5 > S7 > S1).

Trace metals

The average seasonal concentrations of 7 trace metals (Co, Cr, Cu, Mn, Ni, Pb, Zn) are given in Table 5. The mean trace metal concentrations are in the sequences of Co: S4 > S6 > S2 > S3 > S5 > S7 > S1; Cr: S4 > S1 > S5 > S3 > S2 > S7 > S6; Cu: S4 > S2 > S6 > S2 > S3 > S7 > S1; Mn: S6 > S7 > S4 > S5 > S3 > S2 > S1; Ni: S4 > S2 > S6 > S5 > S3 > S1 > S7; Pb: S4 > S2 > S6 > S5 > S3 > S7 > S1 and Zn: S2 > S5 > S4 > S3 > S6 > S7 > S1. No two sequences are similar, but the soil from the site S4, is found to be richest in the trace metals (except Mn and Zn) while the site S1 has the least concentration of the trace metals (except Cr and Ni). The mean concentrations of the trace metals are in the ranges of Co: 26.75–51.22 mg/kg, Cr: 5.10–52.94 mg/kg, Cu: 10.02–47.24 mg/kg, Mn: 129.55–445.81, 48.17–99.51 mg/kg, Pb: 100.9–145.3 mg/kg and Zn: 37.80–59.41 mg/kg. The soil thus has considerable contents of the trace metals.

Comparative study of the observed values of the soil trace metals with the world average (Kabata-Pendias 2011) values (Table 6) indicates that Cu, Cr, Mn and Zn are present below the world average while Co, Ni, and Pb have much higher concentrations in the present study sites.

Correlation of trace metals with physicochemical properties

In order to correlate the trace metal concentrations to the major physicochemical characteristics of the soil, a linear regression analysis was done and the correlation coefficients are given in Table 7. A few significant correlations are found. The trace metal, Co, showed good positive correlation with CEC (77 %) and WHC (65 %), and also to some extent with silt (43 %) and clay (32 %) while fairly good negative correlation exists with sand (57 %), but it is very poorly related to SOC, pH and Electrical Conductivity, EC. The sequence at which Co occurs, i.e., S4 > S6 > S2 > S3 > S5 > S7 > S1, is very similar to the sequence of combined (WHC + CEC) except that in the latter, S2 precedes S6.

Table 4 Season-wise average values of soil chemical parameters

Season	S1	S2	S3	S4	S5	S6	S7
pH (1:5 soil:water)							
Hot dry	6.15	7.08	6.25	7.05	7.22	8.10	7.04
Hot wet	6.77	6.70	6.54	6.99	7.04	7.83	6.32
Cold dry	6.76	5.88	6.80	7.07	7.24	8.02	6.60
Mean	6.56	6.55	6.53	7.03	7.16	7.98	6.65
Median	6.76	6.70	6.54	7.05	7.22	8.02	6.60
SD	0.36	0.61	0.28	0.04	0.11	0.14	0.36
Electrical conductivity (1:5 soil:water) (µS/cm)							
Hot dry	151.35	193.65	225.50	193.30	235.25	166.10	152.45
Hot wet	162.30	207.50	133.00	174.40	210.00	167.15	103.15
Cold dry	80.45	127.75	147.55	167.30	143.40	146.80	121.80
Mean	131.37	176.30	168.68	178.33	196.22	160.02	125.80
Median	151.35	193.65	147.55	174.40	210.00	166.10	121.80
SD	44.43	42.61	49.74	13.44	47.45	11.46	24.89
Soil organic carbon %							
Hot dry	2.33	7.02	4.08	5.78	4.04	2.64	4.12
Hot wet	2.33	6.21	4.93	5.94	3.19	2.35	3.50
Cold dry	2.58	7.40	5.55	4.64	5.31	2.60	4.14
Mean	2.41	6.88	4.85	5.45	4.18	2.53	3.92
Median	2.33	7.02	4.93	5.78	4.04	2.60	4.12
SD	0.14	0.61	0.74	0.71	1.07	0.16	0.36
Cation exchange capacity (cmol/kg)							
Hot dry	3.53	8.51	8.78	11.35	6.14	13.91	3.99
Hot wet	3.52	8.90	5.99	11.45	5.03	12.36	4.17
Cold dry	4.67	7.97	6.88	12.09	4.70	10.38	4.26
Mean	3.91	8.46	7.22	11.63	5.29	12.22	4.14
Median	3.53	8.51	6.88	11.45	5.03	12.36	4.17
SD	0.66	0.47	1.43	0.40	0.75	1.77	0.14

Cr does not show strong correlation with any of the physicochemical properties taken for consideration, but its weak positive correlation to clay (25 %) and water holding capacity (26 %) as well as negative correlation to sand (33 %), cannot be ignored.

Cu is correlated with most physicochemical parameters except pH. It has strong or moderately strong positive correlation with WHC (91 %), clay (64 %), CEC (59 %), EC (48 %) and SOC (42 %) while it is negatively correlated with sand (88 %). In contrast, Mn is strongly and positively correlated to pH (77 %) and it has also weak, positive correlation with silt (31 %) and CEC (33 %). The soil containing the highest amount of Mn in this work was found to be alkaline (pH ~ 8.0) supporting the fact that Mn retention is favored by higher pH lowering the mobility of the trace metal.

The trace metal, Ni, has also strong or moderately strong correlation with several of the physicochemical properties of the soil, for example, with water holding capacity (74 %), silt (65 %), CEC (60 %), EC (47 %) and clay (34 %), electrical conductance (EC) (~ 47 %) while it has strong negative correlation with sand (70 %). It is observed that Ni-occurrence sequence (S4 > S2 > S6 > S5 > S3 > S1 > S7) is similar to the sequence in which WHC, silt and CEC together appear for the soil samples with a minor exception in the combined value for S1 and S7, i.e. towards the end of the sequence.

The toxic trace metal, Pb, is not dependent on the soil pH as observed from the correlation analysis, but is shows strong positive correlation with WHC (92 %) and moderately strong positive correlation with clay (58 %), CEC (57 %), SOC (47 %), EC (46 %) and silt (36 %). Pb has a very strong, negative correlation with sand (84 %) in the soil. It has again been found that the sequence of Pb-contents (S4 > S2 > S6 > S5 > S3 > S7 > S1) agree very closely with that of the sum of the two highly correlated properties of WHC and CEC with exceptions in S3 and S5.

Zn has very poor or no correlation with silt content of the soil, pH and CEC, but it shows moderately strong positive correlation with EC (67 %), SOC (58 %), clay (51 %) and WHC (54 %), and similar negative correlation with sand (58 %). The observed sequence of Zn contents

Table 5 Season-wise average trace metal concentration

Metal (mg/kg)	Season	S1	S2	S3	S4	S5	S6	S7
Co	Hot dry	23.91	21.40	33.57	30.36	26.18	37.66	29.17
	Hot wet	37.93	56.85	49.91	55.01	41.85	53.51	45.80
	Cold dry	18.40	31.44	18.57	68.28	28.15	30.02	19.45
	Mean	26.75	36.56	34.01	51.22	32.06	40.39	31.47
	Median	23.91	31.44	33.57	55.01	28.15	37.66	29.17
	SD	10.07	18.27	15.67	19.25	8.53	11.98	13.33
Cr	Hot dry	14.94	17.62	33.72	39.80	17.33	4.09	13.07
	Hot wet	38.71	20.24	BDL	67.72	67.18	3.12	13.84
	Cold dry	43.72	25.20	11.29	51.31	7.80	8.07	4.47
	Mean	32.46	21.02	22.51	52.94	30.77	5.10	10.46
	Median	38.71	20.24	22.51	51.31	17.33	4.09	13.07
	SD	15.37	2.67	6.47	14.03	31.89	2.62	5.20
Cu	Hot dry	10.87	13.49	12.34	41.06	25.98	17.02	7.40
	Hot wet	8.90	38.30	24.62	66.52	26.39	32.54	17.94
	Cold dry	10.29	22.19	19.21	34.14	29.45	31.22	12.12
	Mean	10.02	24.66	18.72	47.24	27.27	26.92	12.49
	Median	10.29	22.19	19.21	41.06	26.39	31.22	12.12
	SD	1.01	12.59	6.15	17.05	1.90	8.60	5.28
Mn	Hot dry	64.37	69.86	154.72	232.83	138.80	309.59	225.05
	Hot wet	118.69	213.25	225.84	230.80	348.24	481.78	156.19
	Cold Dry	205.61	138.89	197.90	334.71	212.07	546.06	475.61
	Mean	129.55	140.66	192.82	266.11	233.04	445.81	285.62
	Median	118.69	138.89	197.90	232.83	212.07	481.78	225.05
	SD	71.24	71.71	35.83	59.41	106.28	122.27	168.10
Ni	Hot dry	39.85	41.99	59.97	79.18	40.06	50.27	50.60
	Hot wet	49.98	118.20	65.23	131.98	90.18	95.04	55.97
	Cold dry	69.79	90.55	71.60	87.38	71.29	62.96	37.95
	Mean	53.20	83.58	65.60	99.51	67.18	69.42	48.17
	Median	49.98	90.55	65.23	87.38	71.29	62.96	50.60
	SD	15.23	38.58	5.82	28.41	25.31	23.07	9.25
Pb	Hot dry	101.0	139.8	129.5	143.3	124.9	119.8	122.3
	Hot wet	92.5	127.9	99.3	132.6	108.2	120.8	101.6
	Cold dry	109.0	127.6	127.3	160.1	134.1	129.0	117.7
	Mean	100.9	131.8	118.7	145.3	122.4	123.2	113.9
	Median	101.0	127.9	127.3	143.3	124.9	120.8	117.7
	SD	8.3	7.0	16.8	13.9	13.1	5.1	10.9
Zn	Hot dry	61.68	79.34	30.71	52.83	54.81	67.31	69.47
	Hot wet	31.31	59.70	42.59	48.87	49.50	27.75	8.87
	Cold dry	20.41	39.20	55.50	46.64	65.80	25.46	5.40
	Mean	37.80	59.41	42.93	49.44	56.70	40.17	39.17
	Median	31.31	59.70	42.59	48.87	54.81	27.75	8.87
	SD	21.39	20.07	12.40	3.14	8.31	23.53	36.03

BDL below detection limit

(S2 > S5 > S4 > S3 > S6 > S7 > S1) is identical to that of the combined SOC, clay and WHC with two exceptions in S5 and S6.

The spatial variation of the average contents of the trace metals, Co, Cr, Cu, Ni, Pb and Zn, for all the seasons is shown in Fig. 2. Since Mn is much more abundant than the other trace metals, it is excluded from this figure. On the basis of the average concentrations of the trace metals, the relative abundance of the trace metals is in the order of Mn > Pb > Cu > Zn (excepting S4) > Co in all the sites.

**Table 6** Trace metals in soil and the world averages (from Kabata-Pendias 2011)

Trace Metal	World soil average (mg/kg)	This work (mg/kg)		Comparison with the world average
		Minimum	Maximum	
Co	11.3	26.75 (S1)	51.2 (S4)	137.2–353.1 % Higher
Cr	59.6	5.1 (S6)	52.9 (S4)	12.8–91.4 % Lower
Cu	38.9	10.0 (S1)	47.2 (S4)	21.3–74.3 % Lower
Mn	488.0	129.6 (S1)	455.8 (S6)	6.6–73.4 % Lower
Ni	29.0	48.2 (S7)	99.5 (S4)	66.2–243.1 % Higher
Pb	27.0	100.9 (S1)	145.3 (S4)	273.7–438.2 % Higher
Zn	70.0	37.8 (S1)	59.4 (S2)	1.4–46.0 % Lower

Table 7 Correlations between mean trace metal concentration and soil physicochemical parameter

Trace metal	Correlation coefficient (R^2)							
	SOC	Clay	Sand	Silt	WHC	pH	EC	CEC
Co	0.16 (+)	0.32 (+)	0.57 (−)	0.43 (+)	0.65 (+)	0.18 (+)	0.20 (+)	0.77 (+)
Cr	0.10 (+)	0.25 (+)	0.33 (−)	0.12 (+)	0.26 (+)	0.07 (+)	0.01 (+)	0.01 (+)
Cu	0.42 (+)	0.64 (+)	0.88 (−)	0.34 (+)	0.91 (+)	0.04 (+)	0.48 (+)	0.59 (+)
Mn	0.17 (−)	0.14 (+)	0.01 (+)	0.31 (+)	0.00	0.78 (+)	0.00	0.33 (+)
Ni	0.19 (+)	0.34 (+)	0.70 (−)	0.65 (+)	0.74 (+)	0.18 (+)	0.47 (+)	0.59 (+)
Pb	0.47 (+)	0.58 (+)	0.84 (−)	0.36 (+)	0.92 (+)	0.07 (−)	0.46 (+)	0.57 (+)
Zn	0.58 (+)	0.51 (+)	0.58 (−)	0.11 (+)	0.54 (+)	0.01 (+)	0.67 (+)	0.03 (+)

(+) Positive and (−) negative correlation

Fig. 2 Spatial variation in the average concentrations of the trace metals (Co, Cr, Cu, Ni, Pb, Zn)
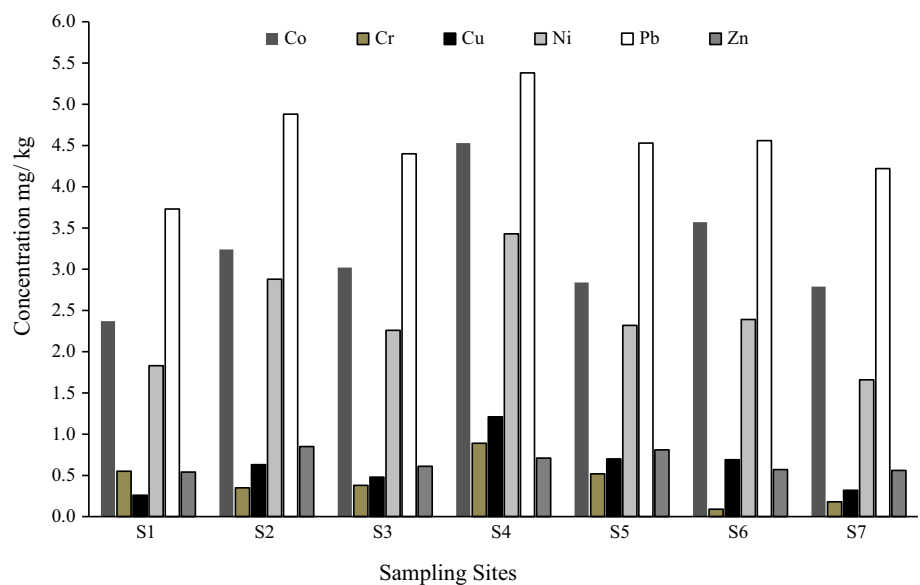
Differences occur mainly with respect to Cr and Ni. Kabata-Pendias (2011) has shown top soil mean contents in mineral soil to be in the sequence of Mn > Cr ≈ Zn > Pb > Cu > Ni > Co, which is different from the one obtained in this work. The observed sequence indicates a relative enrichment of Pb in the soil of the study area and depletion of Cr, Zn, Ni and Co.

Correlation among the soil trace metals

The correlation matrix for the trace metals (Table 8) shows very high positive correlation between Co and Cu ($R^2 = 0.87$), Co and Ni (0.93), Co and Pb (0.91), Cu and Ni (0.92), Cu and Pb (0.93), and Ni and Pb (0.93). The presence of these metals in the soil is thus interrelated

Table 8 Correlation matrix for the trace metals in the soil

Trace metal	Co	Cr	Cu	Mn	Ni	Pb	Zn
Co	1.00						
Cr	+0.42	1.00					
Cu	+0.87	+0.58	1.00				
Mn	+0.43	−0.43	+0.04	1.00			
Ni	+0.93	+0.58	+0.92	+0.30	1.00		
Pb	+0.91	+0.42	+0.93	+0.22	+0.93	1.00	
Zn	+0.25	+0.32	+0.61	−0.32	+0.49	+0.61	1.00

Table 9 Pollution indices (PI) for trace metals on a single metal basis

Sample ID	Co	Cr	Cu	Mn	Ni	Pb	Zn
S1	2.37	0.55	0.26	0.26	1.83	3.73	0.54
S2	3.24	0.35	0.63	0.29	2.88	4.88	0.85
S3	3.02	0.38	0.48	0.40	2.26	4.40	0.61
S4	4.53	0.89	1.21	0.55	3.43	5.38	0.71
S5	2.84	0.52	0.70	0.48	2.32	4.53	0.81
S6	3.57	0.09	0.69	0.91	2.39	4.56	0.57
S7	2.79	0.18	0.32	0.58	1.66	4.22	0.56

strongly suggesting a common origin of the metals. Relatively weak correlation is seen between Cu and Zn (0.61), Pb and Zn (0.61), Cr and Cu (0.58), Cr and Ni (0.58), and Ni and Zn (0.49). The correlation among the trace metals indicates that their enrichment in the soil has originated from a few common sources as observed in other similar work (e.g., Hu et al. 2013).

Contamination and risk indices

The pollution indices, PI (C_i/C_{ref}) computed for each metal separately for each site (Table 9) suggest that the concentrations of Cr, Cu, Mn and Zn represent the uncontaminated state of the soil (PI < 1.0) with respect to these trace metals. However, the soil is moderately polluted with respect to Co and Ni ($1 \leq PI < 3$) and considerably polluted with Pb ($3 \leq PI < 6$). The situation is more or less similar in all the sites.

Ecological risks due to individual trace metal and the overall risk are summarized in Table 10. The data show a low level of ecological risk due to individual trace metals, but the cumulative potential ecological risk index (PERI) is considerable to put the sites under the medium potential ecological risk category.

Discussion

Higher concentrations of Pb, Cu, and Zn are of ecological concern. These metals might have originated from two industrial sources, a pulp and paper industry (close to S1, S6 and S7) and a cement industry (close to S2, S3, S4 and S5). The probability of deposition from air also cannot be ruled out. The region has been experiencing rapid development works in recent times involving blasting, crushing and transportation of granite rocks among others, and these activities might have contributed to the trace metal contents of the soil in the area. Natural weathering processes are also likely to release some of the trace elements present in the rock. Reports of industrial contributions to trace metal composition of soil are abundant (e.g. Ogunkunle and Fatoba 2013).

In the present study, it is observed that physicochemical properties of the soil such as WHC, SOC, CEC and clay content are correlated to the soil trace metal concentration. In general, higher retention capacity for the trace elements lowers their mobility resulting in local enrichment of the trace elements. It has been suggested that amorphous or

Table 10 Soil trace metal individual ecological risk (E_r) and composite risk (PERI) values for the sampling sites

Sample ID	Ecological risk of individual trace metal (E_r)						Composite risk (PERI)
	Co	Cr	Cu	Ni	Pb	Zn	
S1	11.84	1.09	1.29	9.15	18.69	0.54	42.60
S2	16.16	0.71	3.16	14.40	24.41	0.85	59.69
S3	15.09	0.76	2.41	11.31	21.98	0.61	52.16
S4	22.66	1.78	6.07	17.15	26.90	0.71	75.27
S5	14.19	1.03	3.51	11.58	22.67	0.81	53.79
S6	17.87	0.17	3.46	11.96	22.80	0.57	56.83
S7	13.92	0.35	1.61	8.30	21.20	0.56	45.94

particulate soil organic matter increases the effective surface area of the soil particles which helps in retaining more of the trace metals on their surface (Adrino 2001). Further, high molecular weight organic compounds in the SOM can provide sufficient space to entrap the trace metals (Schmitt et al. 2002). Significant correlation of SOM to Co, Mn, Zn and Cu has been known for a long time (Haynes and Swift 1984). It is also known that trace metals, particularly Cu and Pb, are capable of forming insoluble complexes with the organic matter making them less mobile (Battaillard et al. 2003). All these factors lead to accumulation of the trace metals in the soil.

The trace metals can also be retained on the soil particles by a cation exchange mechanism (Martinez and Mottor 2000) when the CEC is considerable. Irrespective of the nature of the soil clay, higher clay content supports higher retention of soil trace elements (Murray et al. 2004). Again solubility of trace metals in soil is a pH regulated phenomenon (Henry 2000) and it has been observed that high soil pH contributes to greater retention of the metals (Basta et al. 1993; Ghosh and Singh 2005). This work has indicated a higher correlation between water holding capacity and trace metal contents which might have resulted from interactions among several soil physicochemical characteristics. For example, CEC is regulated by soil pH and both these properties are influenced by the presence of soil water in the form of WHC providing a medium to support soil chemical processes contributing to higher retention of the trace metals.

This work assesses the enrichment of trace metals without taking into consideration their intrusion into the food chain and consequent biomagnifications that are governed by antagonistic and synergistic interactions of other elements present in the soil. Soil microorganisms with their complex structures can also act as excellent biosorbents for the trace metals retaining them through cell surface adsorption/desorption, intercellular accumulation and metabolism. The presence of the trace metals in the present study should be considered in the context of all these mutually interactive forces.

Conclusion

The trace metals, Co, Cr, Cu, Mn, Ni, Pb, and Zn, were found to follow the same order in which the cumulative (WHC + CEC) existed. Similarly, close correspondence was observed between the sequence in which Ni occurred in the sampling sites and the cumulative (WHC + silt + CEC) and also for Zn and the cumulative (WHC + SOC + clay). The other trace metals, Cu, Cr and Mn, the sequences of their occurrence do not show such relationship with the bulk physicochemical properties.

Regressional analysis show significant correlation between Cu and WHC, Clay, CEC, EC and SOC, Mn is related to pH only and Cr does not show any correlation with soil physicochemical properties.

Correlation studies exploring soil trace metal origin suggests a common origin of soil trace metals. Individual pollution indices for Zn, Cu, Cr and Mn suggest uncontaminated state, Ni, Co and Pb values suggest contamination to considerable extent. Though there is no individual potential ecological risk for all the trace metals, when the cumulative potential ecological risk indices (PERI) are evaluated, it is seen that all the sites fall under the medium potential ecological risk category.

Conflict of interest The authors declare that they have no conflict of interest.

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