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ORIGINAL PAPER

Distribution of heavy metals in habitation land-use soils with high ecological risk in urban and peri-urban areas

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Abstract

The study investigated spatial distribution of heavy metals in soils of urban, peri-urban and rural habitation land-uses, and the ecological risks associated with them in the Indian Himalayan state of Himachal Pradesh. Soils of undisturbed forest were taken as control. A total of 72 soil samples were collected and assayed by atomic absorption spectrophotometer for cadmium, chromium, lead, manganese, nickel and zinc. Positive correlations were observed between cadmium–chromium, cadmium–manganese, cadmium–nickel, chromium–manganese, chromium–nickel and manganese–nickel. Higher concentrations (mg/kg) of cadmium (4.956 ± 0.031), chromium (17.299 ± 0.567), manganese (76.473 ± 0.031) and nickel (82.225 ± 7.342) were recorded in urban land-use soils. Lead (44.882 ± 3.202) and zinc (192.613 ± 34.180) reported maximum values in peri-urban and rural land-use soils, respectively. Peri-urban and urban land-use soils were extremely polluted with loads of lead and cadmium, respectively. However, control site was contamination-free. High values of contamination factor and geo-accumulation index in urban and peri-urban land-use indicated contamination in order of cadmium > nickel and > zinc. Degree of contamination and associated ecological risk index were also high in urban and peri-urban as compared to rural and control soils.

Keywords Contamination · Discriminant function analysis · Ecological risk index · Geo-accumulation · Himalaya

Introduction

Soil constitutes a major natural resource that not only sustains human livelihood but also provides goods for economic and ecological benefits (Skordas et al. 2013). Degradation of soil has led to breaking up of ecosystem processes that pose a serious ecological risk (Xu et al. 2016). Though contamination of soil is not a recent phenomenon, its pace has exponentially increased in recent times (Wagner and Hlatshwayo 2005).

The ecological risk posed by soil degradation and contamination varies along multiple gradients of which habitation land-use gradient is prime (Wagner and Hlatshwayo 2005). It is known that while physical disturbances due to natural influences on soil can be reversed with time (Giri and Singh 2017), toxic chemicals always have detrimental impacts on soil quality (Giri et al. 2017) and ecological characteristics of the region (Chowdhury and Maiti 2016). The presence of toxic heavy metals in soil can pose ecological risks with multifarious ramifications. Heavy metals like cadmium (Cd), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) are inorganic pollutants (Raj et al. 2017) having synergistic effects. Their trace concentrations are known to affect soil fertility (Giller and Witter 1998), reduce crop productivity (Nagajyoti et al. 2010) and influence ecological health (Chowdhury and Maiti 2016). Common sources of these heavy metals include industrial and mining activities, disposal of metalliferous waste (WHO 1981), use of chemical pesticides, fertilizers, herbicides (Ndungu and Bhardwaj 2016), vehicular emissions (Sharma and Uniyal 2016), emissions from process and coal burning (Kashyap et al. 2018) and developmental activities

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(Krishna and Govil 2007). These heavy metals are xenobiotic, highly mobile and persistent in soil (Kumar et al. 2014). From soils, they enter into the food chain and tend to biomagnify in trophic levels, thereby altering body metabolism in the humans (Aschale et al. 2017). Heavy metal concentrations across habitation land-use soils, which are altered by diverse kind of anthropogenic factors, call for analyzing the ecological risks associated with these using standard methodologies (Ngole-Jeme 2016). Ecological risk assessment is a highly preferred method to distinguish anthropogenic contamination of heavy metals from that of the background or uncontaminated soil (da Silva et al. 2017). At the same time, characterization of elemental pollution in soils based on contamination factors, degree of contamination and geo-accumulation index is important and much desired (Ngole-Jeme 2016).

In the hilly states of Himalaya such as Himachal Pradesh, based on similarities in morphometric features of habitations and anthropogenic practices, three major habitation land-uses namely urban, peri-urban and rural can be identified (Fig. 1). These land-uses differ with respect to their characteristics and exposure to levels of pollution (Sharma and Kuniyal 2016). As opposed to lowland areas where industries are the major source of soil pollution, here developmental activities, land clearing, dumping of waste, farm operations, vehicular traffic and congestion are prime sources of pollution (Sharma and Uniyal 2016). Recognizing this, the present study focused on (1) investigating concentrations and spatial distribution of heavy metals in urban, peri-urban and rural land-use soils and (2) assessing the potential ecological risks posed by these soils.

Date and location of research June 2016 to August 2018, Himachal Pradesh (32°14′46″–31°25′41″N and 77°11′30″–76°50′35″E).

Materials and methods

Study area

The study was conducted in Himachal Pradesh, a rich and diverse west Himalayan state. Detailed surveys were carried out in Kullu and Mandi districts of the state as they receive heavy influx of tourists, and changes in land-use characteristics are prominent here (Kuniyal 2002). It has been estimated that ~60 million tourists annually visit Kullu and its surroundings (HPTDC 2012; NGT 2014). This has resulted in a boom in construction activities around urban and peri-urban land-use to accommodate the increasing number of tourists. The National Green Tribunal (NGT), India, has taken note of this and imposed stringent regulations for minimizing the associated risks (SPCB 2013).

The identified habitation land-use types, i.e., urban ($n=4$), peri-urban ($n=4$) and rural ($n=4$) were sampled (supplementary Table 1S). Forest land-use that had minimal anthropogenic disturbance was taken as a control and used as a reference for comparison among the identified habitation land-uses. These habitation land-uses lie between coordinates 32°14′46″–31°25′41″N and 77°11′30″–76°50′35″E and altitude 500–2200 m amsl (Fig. 1).

Samples collection and storage

For soil sampling, at each site, surface litter, leaves, grass cover and other debris were removed. To ensure homogeneity in sampling; 8–10 discrete cores (subsamples) were collected from 0 to 15 cm depth (plow layer) with a conical hand auger and mixed to make one composite soil sample at each site. Each composite soil sample weighed around 1 kg and was packed in a 2-kg polyethylene thermoplastic bag to provide insulation and proper packaging. Sampling was done only on dry days and a total of 72 composite soil samples (3 habitation land-use × 4 sites of each habitation × 1 control × 6 replicates) were collected. Samples were labeled and brought to the laboratory for further processing and analyses. In the laboratory, soil samples were dried at room temperature (25–30 °C) and sieved through a 2-mm mesh screen. Quartering technique was used for mixing, rolling and turning of soil samples before weighing. Processed samples were kept in a desiccator in high-grade polyethylene containers (Tarson make) for heavy metal analyses. For sampling and handling of each soil sample, separate powder-free pair of gloves was used and discarded thereafter.

Heavy metal analyses

Standard protocols of United States Environmental Protection Agency (USEPA) method 3050 were followed for digestion of the heavy metals in the soil samples (USEPA 1986; Edgell 1988; Kumar et al. 2014). After weighing 2 g each of soil samples on digital balance, the same were digested with addition of 10 ml HNO_3 (1:1) at 95 °C for 15 min in digestion tubes (specifications of tubes: FOSS make; material: glass; walls: straight; type: closed with a condenser at top; size: 40 × 300 mm; capacity: 250 ml volume) on an electric digester (KEL PLUS automatic 20 sample loader). After cooling the samples, 5 ml of concentrated HNO_3 was added and again heated for 30 min. This step was repeated to increase the solubility of metals present in the samples. After temperature reduction, 3 ml of H_2O_2 with 2 ml of deionized water was added. Ultrapure HCl (5 ml) was also added to the digestate, and samples were refluxed and heated for 15 min to ensure complete digestion and oxidation of metals.

At room temperature, the samples were filtered through Whatman filter paper (grade: 42; pore size: 2.5 μm) to

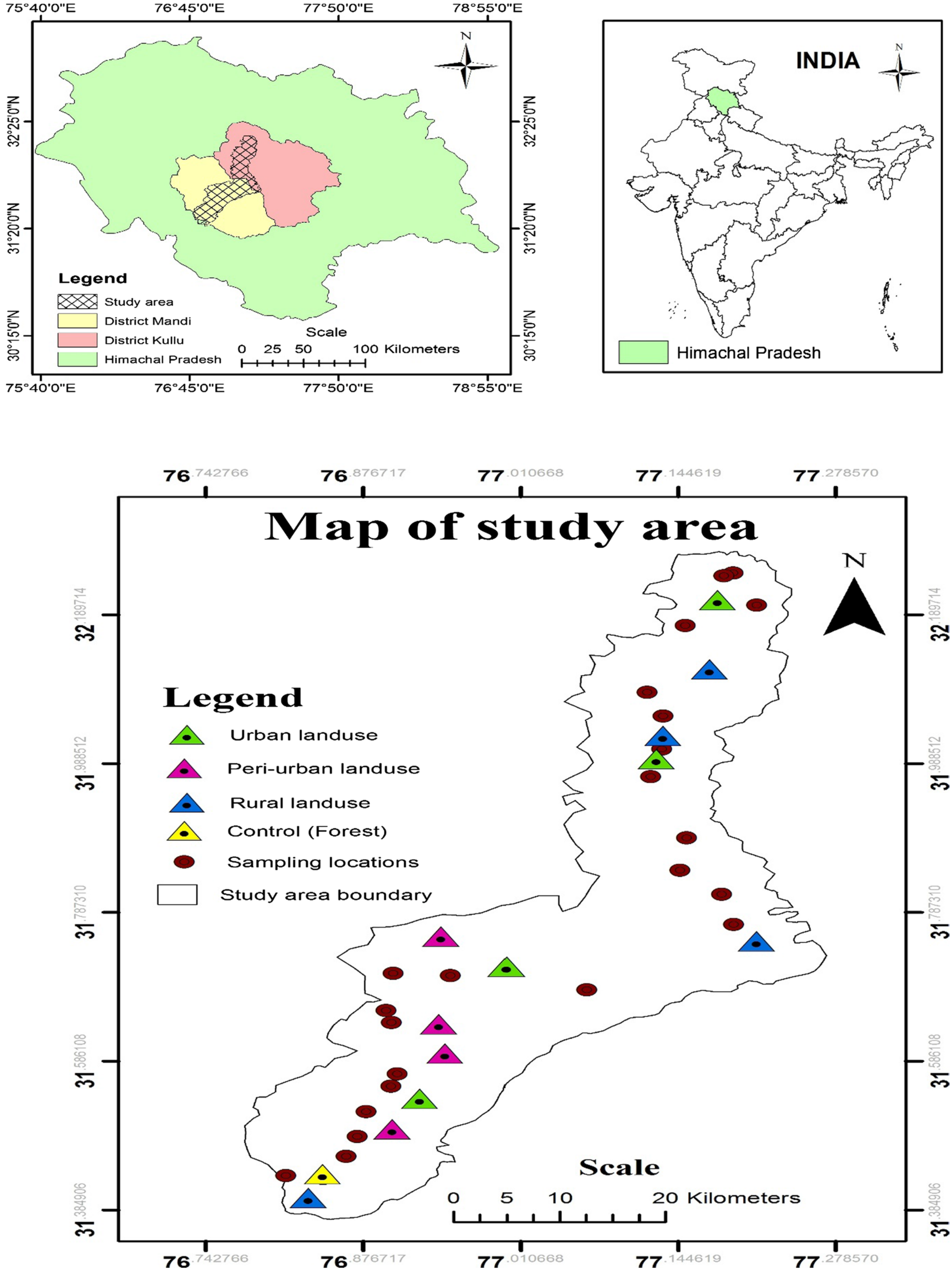


Fig. 1 Map of study area showing habitation land-uses in a Himalayan state of India

remove particulates in digestate to avoid clogging of the nebulizer. Finally, the volume of aliquots was made to the volume of 50 ml by adding double-distilled water.

Analyses for heavy metals (Cd, Cr, Pb, Mn, Ni and Zn) were done in AAS (atomic absorption spectrophotometer) (Perkin-Elmer Corporation 1996). All the samples were analyzed in duplicate. For ensuring calibration and precision of the instrument, standards were run after ten test sample determinations. A blank run was used to obtain correct readings of the instrument after analysis of every five successive test samples. Prior to analysis, the auto-sampler was programmed for regular rinsing of nebulizer with distilled water after every sample analysis. Operating parameters of AAS are given in supplementary Table 2S.

For the validation of analytical process, quality control and quality assurance (QC/QA) procedures were followed. Merk's Centipur® Standard reference material of each of the studied heavy metal was obtained from National Institute of Standards and Technology (USA, make) and analyzed. The percentage recovery of each metal was (≤5% standard deviation) determined by comparing the measured concentration with the certified values of standards.

Empirical methodologies of heavy metal contamination and geo-accumulation

For assessing the of extent and pollution loads of the studied heavy metals ($n=6$) in habitation land-use soils, contamination factor (Cf), degree of contamination (Cd), modified degree of contamination (mCd) and geo-accumulation index (Igeo) were worked out. These indices are useful in deciphering levels of heavy metal contamination in soils and have been used by various workers (Raj et al. 2017; Chowdhury and Maiti 2016; Ma et al. 2015; Islam et al. 2015).

Contamination factor (Cf): It is used to study heavy metal contamination of soils. Cf is the ratio between average content of metal in the studied soil sample and average shale value of the metal in the earth (Hakanson 1980).

$$\mathrm{Cf}i = [\mathrm{C}]\mathrm{soil}/[\mathrm{C}]\mathrm{shale}$$

where Cfi is contamination factor of ith metal, [C] soil is average content of metal in the studied soil (mg/kg) and [C] shale is average shale value of metal in earth (mg/kg). Average shale values used in calculations of Cf for Cd, Cr, Pb, Mn, Ni and Zn in soils were 0.3, 90, 20, 850, 68 and 95 mg/kg, respectively (Hakanson 1980). Categories of contamination are characterized as: $\mathrm{Cf} \leq 0$ (no), 1 (medium), 2 (moderate), 3 (moderate to strong), 4 (strongly polluted), 5 (strong to very strong) and 6 (very strong) contamination (Ma et al. 2015).

Degree of contamination (Cd): It determines the overall contamination potential of heavy metals at any location based on values of contamination factor computed for each heavy metal. Degree of contamination (Cd) was calculated using the formula given by Hakanson (1980).

$$\mathrm{Cd} = \sum_{i=1}^{n} Cfi$$

where Cfi is contamination factor of ith metal and n is the number of heavy metals studied (in this study, $n=6$). Contamination categories based on obtained values of Cd are characterized as: $\mathrm{Cd} < 8$ (low), $8 < 16$ (moderate), $16 < 32$ (high) and > 32 (very high) contamination (Hakanson 1980).

Modified degree of contamination (mCd): As in the name, it is a modified form of Cd that helps to understand even minimal levels of heavy metal contamination in polluted soils. It is a ratio of prior obtained Cd value to total number of pollutant elements. It was estimated as per formula given by Brady et al. (2015).

$$\mathrm{mCd} = \frac{\mathrm{Cd}}{n}$$

where mCd is the modified degree of contamination and n is 6.

Categories of contamination are graded as: [$\mathrm{mCd} < 1.5$ (very low), $1.5 \leq \mathrm{mCd} < 2$ (low), $2 \leq \mathrm{mCd} < 4$ (moderate), $4 \leq \mathrm{mCd} < 8$ (high), $8 \leq \mathrm{mCd} < 16$ (very high), $16 \leq \mathrm{mCd} < 32$ (extremely high), $\mathrm{mCd} \geq 32$ (ultrahigh) contamination] and taken from earlier study of Brady et al. (2015).

Geo-accumulation index (Igeo): Geo-accumulation index is used to determine heavy metal accumulation in soils. It compares the average concentration of each metal with its background concentration or with reference soils (Muller 1969).

$$\mathrm{Igeo} = \mathrm{Log2}(\mathrm{Csoil}/1.5\mathrm{Bn})$$

where Igeo is geo-accumulation, Csoil is average concentration of heavy metal in the soil sample and Bn is background concentration of heavy metal in reference soil (forest soils), and 1.5 is constant of lithogenic variability of metals in soils. Categories of geo-accumulation can be classified as: $\mathrm{Igeo} \leq 0$ (uncontaminated), $0 < \mathrm{Igeo} < 1$ (uncontaminated to moderately contaminated), $1 < \mathrm{Igeo} < 2$ (moderately contaminated), $2 < \mathrm{Igeo} < 3$ (moderately to heavily contaminated) and $3 < \mathrm{Igeo} < 4$ (heavily contaminated) (Aschale et al. 2017).

Ecological risk assessment

The same was developed by Hakanson (1980) to study the risks associated with enrichment of heavy metal in soils due to various anthropogenic practices.

Ecological risk factor: It deals with studying the effect of multiple heavy metals on soils at a specific place.

$$\mathrm{Er} = \mathrm{T}i \times \mathrm{Cf}i$$

where Er is the ecological risk factor, Ti is the toxic response factor of ith metal and Cfi is contamination factor of ith metal. For calculations of Er, toxic response factors (Cd—30, Cr—2, Pb—5, Mn—1, Ni—5 and Zn—1) as provided by Hakanson (1980) have been used. Categories of Er have been classified as: $\mathrm{Er} < 40$ (low), $40 < \mathrm{Er} < 80$ (moderate),

$80 < \text{Er} < 160$ (considerable) and $160 < \text{Er} < 320$ (high) ecological risk (Raj et al. 2017).

Ecological risk index: It is used determine the cumulative ecological risk associated with multiple heavy metals.

$$\text{ERI} = \sum_{i=1}^{n} \text{Er}i$$

where ERI is the ecological risk index, Er is ecological risk factor of ith metal and n is 6. Categories of ERI are classified as: $100 < \text{ERI}$ (low), $100 < \text{ERI} < 200$ (moderate), $200 < \text{ERI} < 400$ (high) and ≥ 400 (very high) ecological risk (Giri et al. 2017).

Statistical analyses

Analytical data sets were checked for outliers and normal distribution. Test statistics of Kolmogorov–Smirnov ($p > 0.05$) and Shapiro–Wilk test ($p > 0.05$) proved the statistical validity of the data (Frank and Massey 2012). Visual interpretation of Q–Q plots and histograms also suggested that data were normally distributed. Parametric multivariate analysis of variance (MANOVA) was then applied to test overall significant differences and also between individual studied heavy metals. For multiple comparisons among the studied heavy metals in each of the land-use soils, post hoc test was used (supplementary Table 3S). Correlation between the metals, irrespective of land-use soils, was analyzed using Pearson's correlation. Further, discriminant function analysis (DFA) was carried out to differentiate the three-habitation land-use and control soils based on overall heavy metal contents. (Test statistics of DFA are given in supplementary Table 4S.) Additionally, Wilk's lambda test was employed to decipher differences among the metal contents which could not be explained by DFA. (Results of test are given in supplementary Table 5S.) All statistical analyses have been carried out using SPSS (version 20.0). Spatial distribution maps were generated using ARC map (version 10.5).

Table 2 Test statistics of MANOVA among habitation land-use and heavy metals

Variables	Test value	Hypothesis *df*	Error *df*	*p* value
Model	Pillai's trace 2.96	18	51	<0.001
Habitation land-uses	Wilk's lambda 0.00	18	42	<0.001
Heavy metals	Sum of Squares	*F* value	R^2 value	*p* value
Cd	86.24	15,037.69	0.99	<0.01
Cr	911.67	194.23	0.96	<0.01
Pb	738.11	299.56	0.97	<0.01
Mn	20,457.88	192.53	0.96	<0.01
Ni	34,352.49	132.75	0.95	<0.01
Zn	92,019.32	344.87	0.98	<0.01

df degree of freedom, R^2 coefficient of determination

Results and discussion

Spatial distribution of heavy metals in soils

The results of heavy metal contents (mean ± standard error) in soils of identified habitation land-uses are presented in Table 1. Concentrations of each heavy metal significantly differed ($p < 0.01$) among themselves and between the habitation land-use types (Tables 1, 2). Significant mean differences were revealed for Cd, Cr, Pb, Mn, Ni and Zn during their individual testing via MANOVA (Table 2) and multiple comparisons by post hoc analysis between each habitation land-use (supplementary Table 3S). Maximum significant Cd content (4.956 ± 0.031 mg/kg, $p < 0.01$) was found in urban followed by peri-urban (3.200 ± 0.019 mg/kg), rural (1.132 ± 0.003 mg/kg) and forest land-use soils (0.030 ± 0.003 mg/kg) (Table 1). Cd had significant positive correlations (Fig. 2) with Cr ($r = 0.96$, $p = 0.041$), Mn ($r = 0.99$, $p = 0.003$) and Ni ($r = 0.93$, $p = 0.05$). There were a weak positive correlation between Cd and Pb ($r = 0.41$, $p > 0.05$) and a negative relationship between Cd and Zn ($r = -0.09$, $p > 0.05$). However, both these relationships were nonsignificant (Fig. 2). Chromium and Mn had trends similar to that of Cd. Their highest concentration was in the urban land-use soils ($\text{Cr} = 17.299 \pm 0.567$ mg/

Table 1 Concentrations of heavy metals (mean ± SD) in studied habitation land-use soils (mg/kg)

Habitation land-use	Cd	Cr	Pb	Mn	Ni	Zn
Urban ($n = 4$)	4.956 ± 0.031	17.299 ± 0.567	2.257 ± 0.410	76.473 ± 3.357	82.225 ± 7.342	100.404 ± 6.217
Peri-urban ($n = 4$)	3.200 ± 0.019	8.172 ± 0.586	13.453 ± 0.615	44.882 ± 3.202	75.407 ± 1.803	94.167 ± 2.195
Rural ($n = 4$)	1.132 ± 0.003	6.349 ± 0.614	0.074 ± 0.007	13.294 ± 1.434	6.840 ± 0.571	192.613 ± 3.4180
Control ($n = 4$)	0.030 ± 0.003	0.079 ± 0.006	0.097 ± 0.021	1.467 ± 0.163	0.069 ± 0.007	64.617 ± 2.959

kg, $p < 0.01$ and Mn = 76.473 ± 3.342 mg/kg, $p < 0.01$). Chromium showed significant strong positive relationship with Mn ($r = 0.96$, $p = 0.043$) and moderate positive relationship with Ni ($r = 0.78$, $p = 0.05$). Correlation of Cr with Pb ($r = 0.17$) and Zn ($r = 0.11$) was weak and nonsignificant ($p < 0.05$). Nickel reported highest concentration (82.225 ± 7.342 mg/kg $p < 0.01$) in urban soils which was significantly higher in comparison with peri-urban and rural land-use soils (Table 2). While Ni had a strong positive correlation with Mn ($r = 0.92$, $p = 0.004$), it reported a negative correlation with Zn ($r = -0.38$, $p > 0.05$). Overall, concentration of Cd (1.120–5.021 mg/kg), Cr (4.521–19.124 mg/kg), Mn (9.541–88.457 mg/kg) and Ni (0.040–97.450 mg/kg) increased from rural to urban habitation land-use. Varied trends were seen in case of Pb and Zn. Significantly higher value of Pb was reported in peri-urban soils (13.453 ± 0.615 mg/kg $p < 0.01$) (Table 2), while Zn (192.613 ± 3.418 mg/kg, $p < 0.01$) reported higher values in rural soils. A weak nonsignificant positive correlation was observed between Pb and Mn ($r = 0.37$, $p > 0.05$), and Pb and Ni ($r = 0.65$, $p > 0.05$) (Fig. 2). On the other hand, Zn had a negative correlation with all the other heavy metals (Fig. 2). A comparative account of the results of the present study with other such studies done elsewhere is presented in Table 3.

Status of geo-accumulation, contamination and toxicity of heavy metals in soils

The geo-accumulation index for each metal is provided in Table 4. As expected, highest Igeo values for Cd (3.5), Cr (7.2), Mn (5.1) and Ni (3.0) were reported in the urban land-use soils followed by peri-urban land-use. On the other hand, highest Igeo values for Pb (6.5) and Zn (1.0) were observed in peri-urban and rural land-use soils, respectively. Contamination factor (Cf) measures were high for Zn in rural (2.028) and urban (1.057) land-use. Lead reported highest Cf (0.673) in peri-urban land-use soils. Cf values of Cd varied from 3.772 in rural to 16.519 in urban soils (Table 5). Estimates of Cf with reference to nickel were high in urban (1.209), peri-urban (1.109) and lowest in control forest soils (0.001). Degree of contamination (Cd) was 19.18 for urban and 13.58 for peri-urban land-use. For rural and control sites, Cd values were 5.89 and 0.89, respectively (supplementary Figure 1S). Equivalent results were obtained for modified degree of contamination (mCd), i.e., urban (3.20) followed by peri-urban (2.26), rural (0.98) and control (0.15) (supplementary Figure 4). Ecological risk factor (Er) values for each of the metals are given in Table 5. Er values of Cd ranged from 75.44 in rural soils to 330.39 in urban soils with the same being 213.33 in peri-urban soils. Minimum *Er* was noticed in the control forest soil (2.02). Overall, Er values for Cd were high when compared to other metals. Er values for Cr ranged from 0.14 in rural soils to 0.38 in urban land-use soils. In peri-urban soils, the same was 0.18. Risk factor associated with Mn and Ni increased from rural to urban land-use soils. Rural: 0.02, peri-urban: 0.05, urban: 0.09 and rural: 0.01, peri-urban: 5.54, urban: 6.05 were their respective values. Highest Er was noticed for Zn (2.03) in rural and for Pb (3.36) in peri-urban land-use soils when compared to control forest soils. Potential ecological risk index (*ERI*) was highest (338.53) in urban land-use soils and lowest (3.23) in the control (Fig. 3).

Discrimination function analysis

In DFA plot (Fig. 4), class centroids which are mean discriminant scores for heavy metal contents in each habitation land-use soils clearly showed significant differences and plotted in variable axis of two functions. The two discriminant functions showed a total 99.2% of discrimination among habitation land-use soils. Function 1 explained 96.3% of the variation, while function 2 explained 2.9% of the variation in the data sets (supplementary Table 4S). Test statistics of Wilk's lambda reported significant difference at $p < 0.01$ among (group means) all the studied heavy metals. Based on the values of Wilk's lambda, total accumulation of each metal followed an increasing order of Cd (0.000) > Zn (0.19) > Pb (0.033) > Cr (0.033) = Mn (0.033) > Ni (0.048) (supplementary Table 5S).

Discussion

Spatial variations in heavy metal contents around habitation land-uses are evident from the study (Fig. 5a–f). These variations can be explained on the basis of different anthropogenic and developmental pressures operating in the urban, peri-urban and rural land-use areas. Considering that there is no or minimal anthropogenic pressure on the soils of forest land-use (control site), the forest soil had lowest concentrations of the studied heavy metals as compared to the soils from other land-uses. Studies done elsewhere have also reported higher concentrations of metal in areas with high anthropogenic activities (Krishna and Govil 2007; Wagner and Hlatshwayo 2005).

In the present study, except Zn and Pb, all other metals reported their highest concentration in urban land-use (Table 2). Urban soils had 15% more Cd compared to peri-urban soils, while 18 times higher Cr assayed in urban soils in comparison with forest soils. Both these metals exhibited similar trends of increase in concentration from rural to urban land-use soils. A strong positive correlation among Cd–Cr is a testimony to this. Cd concentration in soils of urban, peri-urban and rural land-use was ~ 13, ~ 8 and ~ 2 times higher when compared with the world average content

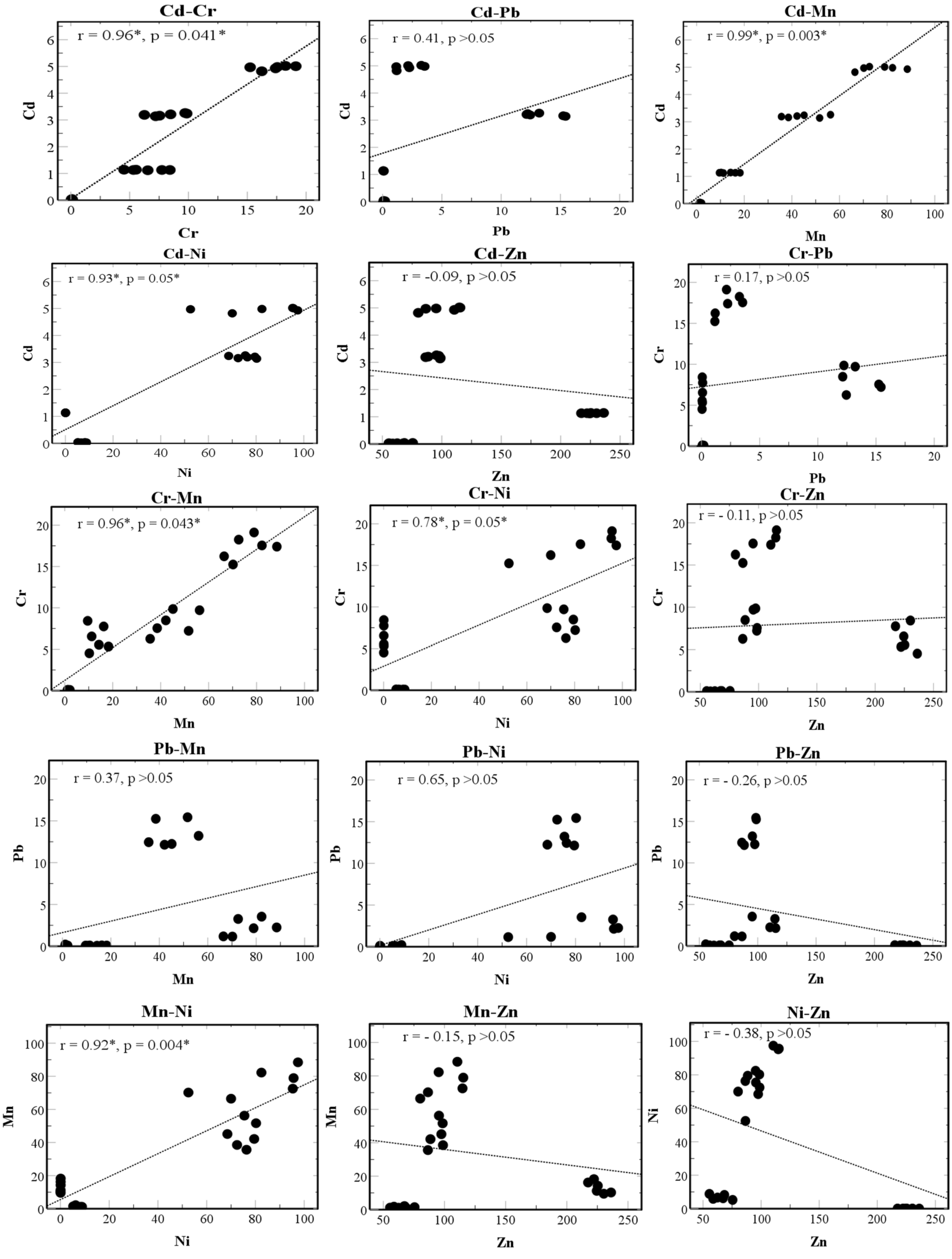


Fig. 2 Correlation scatter bi-plots among heavy metals in soils

Table 3 A comparative account of heavy metal contamination in soils (mg/kg) of present study with other studies, world and shale average

Locations of study	Cd	Cr	Pb	Mn	Ni	Zn	References
Bogra (Bangladesh)	6.3	54	97	nr	83	nr	Islam et al. (2015)
Chenzhou (China)	2.14	70.1	204	nr	45.7	244	Ma et al. (2015)
East Singhbhum (India)	0.34	149.6	47	520.8	94.2	210.6	Giri et al. (2017)
Kombat (Namibia)	nr	20	119	760	9.4	45	Mileusnic et al. (2015)
Larissa (Greek)	0.5	245.6	15.2	nr	165.3	97.6	Skordas et al. (2013)
Miedzianka (Poland)	1.4	34.1	46	1334	19.4	82	Galuszka et al. (2015)
Qingdao (China)	0.29	82.2	250.2	nr	83.7	208.8	Xu et al. (2016)
Shahroud (Iran)	0.3	83.7	18.1	nr	33.3	80.4	Mirzaei et al. (2015)
Sukinda (India)	nr	11,336	nr	nr	nr	84.6	Kumar et al. (2014)
Zaheerabad (India)	nr	203.1	14.5	nr	31.5	99.3	Sakram et al. (2015)
Jharia (India)	2.61	48.73	13.77	212.4	nr	25	Raj et al. (2017)
Sunderban (India)	1.73	33.58	35.03	169.92	41.57	90.83	Chowdhury and Maiti (2016)
Urban ($n=4$)[a] Himachal (India)	*4.815–5.021*	*15.243–19.124*	*1.154–3.541*	*66.455–88.457*	*52.480–97.450*	*80.146–115.364*	Present Study
Peri-urban ($n=4$)[a] Himachal (India)	*3.140–3.260*	*6.245–9.845*	*12.142–15.426*	*35.620–56.214*	*68.480–80.240*	*86.410–98.750*	
Rural ($n=4$)[a] Himachal (India)	*1.120–1.140*	*4.521–8.421*	*0.049–0.095*	*9.541–18.241*	*5.240–8.840*	*22.150–236.120*	
Control ($n=4$)[ab] Himachal (India)	*0.022–0.042*	*0.055–0.095*	*0.060–0.200*	*1.140–2.130*	*0.040–0.085*	*55.479–75.481*	
World average	0.35	70	35	1000	50	90	Bowen (1979)
Shale average	0.3	70	20.0	850	68.0	95.0	Turekian and Wedepohl (1961)

Italicized values are range

[a] Habitation land-use of present study

[b] Forest (undisturbed) soils was taken as control

nr not reported

Table 4 Geo-accumulation index of heavy metals in studied habitation land-use soils

Habitation land-uses	Cd	Cr	Pb	Mn	Ni	Zn
Urban soil	3.5	7.2	3.9	5.1	3.0	0.1
Peri-urban soil	2.8	6.1	6.5	4.3	2.9	≤0[a]
Rural soil	1.3	5.7	≤0[a]	2.6	≤0[a]	1.0
Control soil[b]	≤0[a]	≤0[a]	≤0[a]	≤0[a]	≤0[a]	≤0[a]

[a] Practically uncontaminated soil

[b] Forest (undisturbed) soils was taken as control

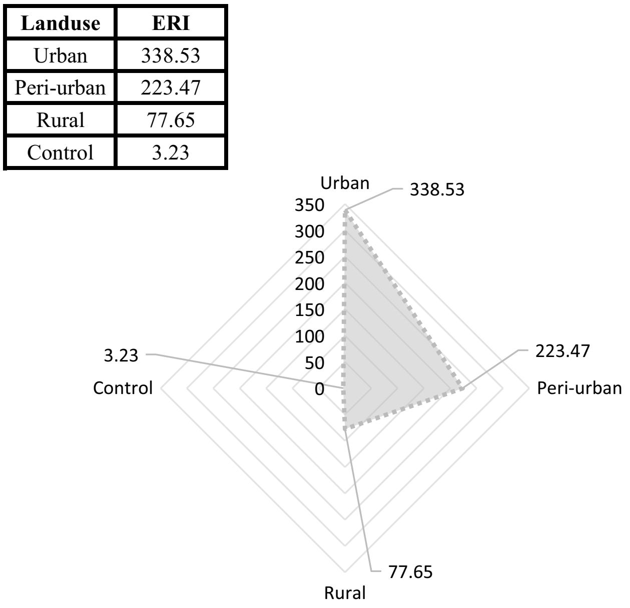
Table 5 Contamination factor (Cf) and ecological risk factor (Er) due to heavy metal accumulation in studied habitation land-use soils

Habitation land-uses	Cd		Cr		Pb		Mn		Ni		Zn	
	Cf	Er	Cf	Er	Cf	Er	Cf	Er	Cf	Er	Cf	Er
Urban soil	16.519	330.39	0.192	0.38	0.113	0.56	0.090	0.09	1.209	6.05	1.057	1.06
Peri-urban soil	10.667	213.33	0.091	0.18	0.673	3.36	0.053	0.05	1.109	5.54	0.991	0.99
Rural soil	3.772	75.44	0.071	0.14	0.004	0.02	0.016	0.02	0.101	0.01	2.028	2.03
Control soil[a]	0.101	2.02	0.001	0.00	0.005	0.02	0.002	0.00	0.001	0.50	0.680	0.68

[a] Forest (undisturbed) soils was taken as control

(Bowen 1979). Owing to heavy influx of tourists, widening of roads around urban locales of the study area is being carried out (Sharma et al. 2011). It has been documented that tunneling and widening of roads by heavy mechanized machinery can add significant Cd and Cr in terrestrial surface soils (Sharma and Kuniyal 2016). Further, anthropogenic pressures associated with mountain expeditions such as Raid de Himalaya (Kuniyal 2007) might be continuously adding Cd and Cr in urban environment(s). Similarly, Mn also had higher mean values in urban soils. Mixtures of manganese tricarbonyl used as a fuel additive in petroleum products (Pellizzari et al. 1999) after phasing out the use of Pb (WHO 1981), vehicles recycling units, junkyards, incineration of solid waste, situated in peripheral areas may account for this. Islam et al. (2015); Nagajyoti et al. (2010); Rahman et al. (2012) and Ma et al. (2015) have suggested the presence of multi-elemental contents in soils from mixed point and nonpoint sources of pollution around city areas. Other studies have suggested chemical similarities among heavy metals and interrelated concentrations based on highly positive significant correlations (Giri and Singh 2017; Raj et al. 2017).

Alike Cd, Cr and Mn, higher content of Ni was reported in urban land-use soils. Manufacturers of thermostats, bulbs, tubes, wire and other electronic components use nickel due to its heat-resistant properties. It is also used in welding, soldering and repairing shops of home appliances (da Silva et al. 2017). There are various such units and shops in urban locals. Thus, high concentration of Ni in urban land-use soils could be attributed to long-term enrichment from these point sources of pollution. A positive correlation among these metals is reported to be related to anthropogenic activities like vehicular traffic, municipal waste disposal (Nagajyoti et al. 2010) and fossil fuel combustion (Sharma and Uniyal 2016) around urban areas (Fig. 2). Nickel with cadmium is used in formulations to construct electric batteries (Ngole-Jeme 2016), while with chrome Ni it is used in making outer shell (body) of buses and trucks (da Silva et al. 2017). Thus, second-highest concentrations of Cd and Ni in peri-urban land-use soils could be credited to the presence of several local vehicle revamping and mechanical shops near peri-urban areas (Wuana and Okieimen 2011). Their progressive decrease in rural and control soils can be ascribed to declining anthropogenic activities in these land-use systems.



Landuse	ERI
Urban	338.53
Peri-urban	223.47
Rural	77.65
Control	3.23

Fig. 3 Ecological risk index

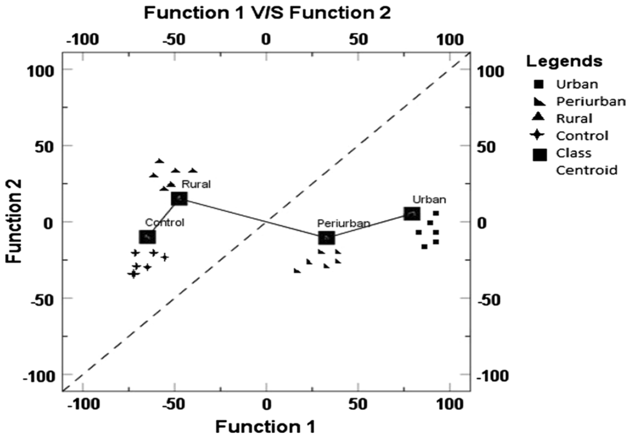


Fig. 4 Scatter plot of discriminant function analysis among habitation land-uses

As opposed to other metals, Pb reported its highest concentration in the soils of peri-urban land-use. Here, in the peri-urban areas, various units of brick kiln furnaces are active. These kilns use low-grade bituminous coal as a fuel, which may be one of the prime reasons for higher Pb in the soils of this land-use. Ash residues of low-grade coal burning contain significant amounts of Pb (Raj et al. 2017; Alloway 2013). Wagner and Hlatshwayo (2005) also reported that coal burning is a major source of Pb contamination in the environment. Present results are in line with the findings of Galuszka et al. (2015) who noticed high Pb (46 mg/kg) concentrations in urban areas of Poland that originated from burning of bituminous coal. Similarly, in the present study, highest concentration of Zn was observed in rural land-use soils. Here, Zn content was 30% higher in rural soils when compared to control soils. The respective mean content of Zn in rural, urban and peri-urban soils was 11, 1 and 5% higher than that of the world average (Bowen 1979). High concentrations of Zn in rural soils could be due to excessive use of fertilizers, pesticides and insecticides in the agricultural fields and apple orchards (Wuana and Okieimen 2011; Skordas et al. 2013). Zinc fertilizers such as zinc sulfate and zinc oxide are used in the apple orchards and agricultural fields in the study area. Negative correlations of Zn with all other metals also demonstrated the unique source of intrusion into natural environments of rural land-use soils (Fig. 2).

Thus, the degree of heavy metal contamination in soils around habitation land-uses varied from class 1 (practically uncontaminated) to class 6 (extremely contaminated), indicating spatial variations among heavy metals (Muller 1969). Owing to higher concentrations of Cd, Cr, Mn and Ni in urban environments, their geo-accumulation was also higher in urban land-use. Further, based on Igeo values, Cd contributed 5% in urban and 3% in peri-urban soils as compared to soils from rural land-use. Moderate to high pollution in urban and peri-urban soils is indicated by Igeo values of Cd followed by Ni. On the other hand, contribution for geo-accumulation by Cr, Mn and Pb in urban soils was negligible. However, in comparison with control soils, higher Pb and Zn contents promoted very high degree of geo-accumulation in peri-urban (167%) and rural (4%) soils, respectively. Lead in peri-urban soils was extremely polluting in nature, whereas control soil was practically uncontaminated. This, in turn, can alter metabolic processes of plants (Nagajyoti et al. 2010), reduce soil fertility (Giller and Witter 1998) and decrease crop productivity (Petrotou et al. 2012).

Contamination factor (Cf) for Cr and Mn posed a relatively lesser ecological risk in rural land-use that, however, increased toward urban land-use. Cd was very strongly polluting in urban land-use soils. Overall, moderate and high degree of heavy metal contamination was there in peri-urban and urban land-uses, respectively (supplementary Figure 1S). Low to high modified degree of contamination trend (supplementary Figure 2S) was observed with increased anthropogenic disturbance from rural to urban land-use. With respect to each of the quantified heavy metals, no contamination was there in control soils. Highly disturbed sites are reported to have a higher concentration of heavy metals in comparison with least disturbed sites (Sharma and Uniyal 2016). Ecological risk factors (Er) of other metals were lower than that of Cd and can be put under low ecological risk category. Urban and peri-urban land-use soils indicated high potential ecological risk, while soils of rural land-use showed moderate ecological risk especially due to

Fig. 5 Spatial distribution of heavy metals in habitation land-use soils

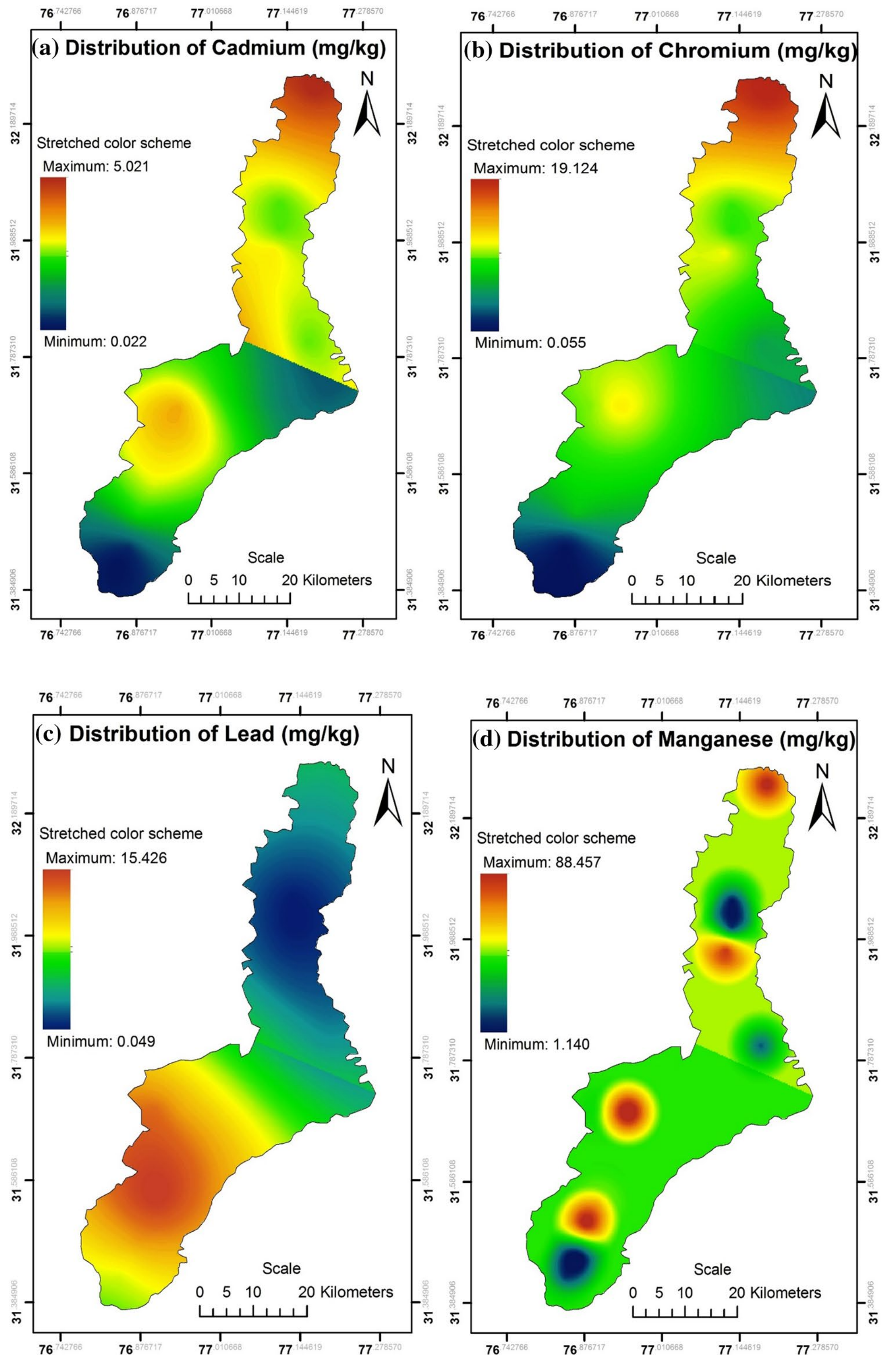
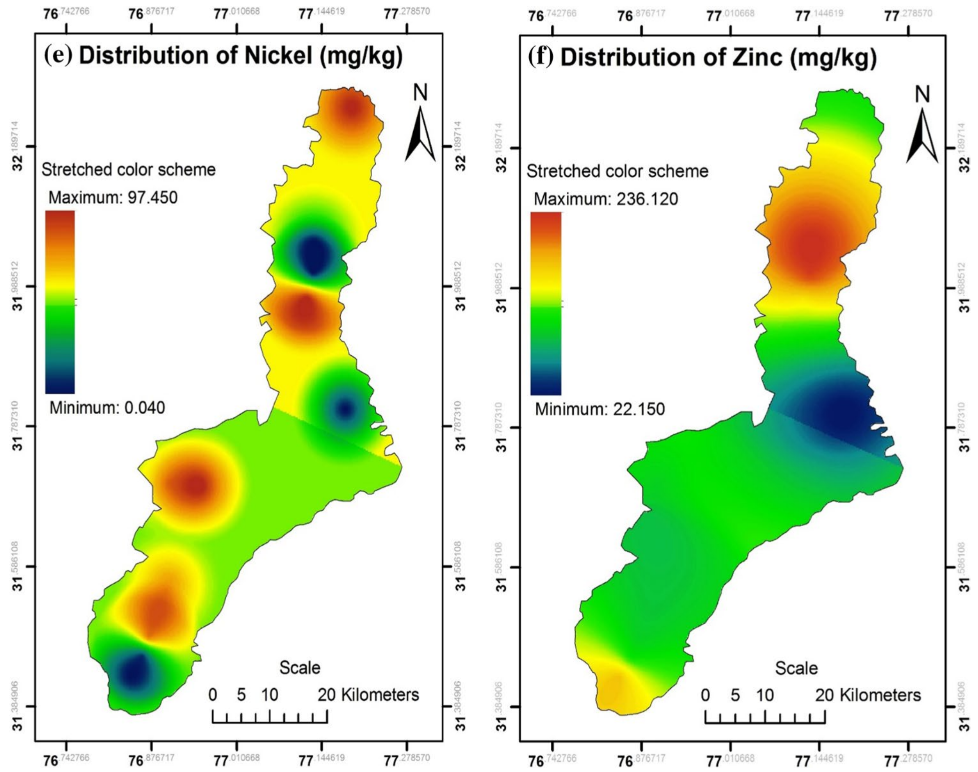


Fig. 5 (continued)



the accumulation of Zn. Zinc could get accumulated in fodder plants in rural areas and may prove toxic to livestock. It is to be kept in mind that a slight increase in metal accumulation often leads to higher potential ecological risk.

Conclusion

The study concludes that heavy metal accumulation in soils varies around habitation land-uses. Higher metal concentrations accounted for higher geo-accumulation in urban land-use soils. The ecological risk index was higher in urban soils followed by peri-urban, rural and control soils. Thus, mechanisms to limit dispersion of metals in the urban environment need to be worked out. The study is a pioneering effort in carrying ecological risk assessment in the Himalayan region and more of these are desired.

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Compliance with ethical standards

Conflict of interest The authors of the manuscript declare they have no conflict of interest.

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