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Estimation of Risk to the Eco-Environment and Human Health of Using Heavy Metals in the Uttarakhand Himalaya, India

Amit Kumar ¹, Marina Cabral-Pinto ^{2,*}, Amit Kumar ^{3,*}, Munesh Kumar ⁴ and Pedro A. Dinis ⁵

¹ School of Hydrology and Water Resources, Nanjing University of Information Science and Technology, Nanjing 210044, China; amitkdah@nuist.edu.cn or amit.agl09@gmail.com

² Geobiotec Research Centre, Department of Geosciences, University of Aveiro, 3810-193 Aveiro, Portugal

³ Central MugaEri Research and Training Institute, Central Silk Board, Jorhat, Assam 785000, India

⁴ Department of Forestry and Natural Resources, H.N.B. Garhwal University (A Central University), Srinagar Garhwal 249161, Uttarakhand, India; munesh.hnbgu@gmail.com

⁵ Marine and Environmental Sciences Centre (MARE), Department of Earth Sciences, University of Coimbra, Rua Sílvio Lima, 3030-790 Coimbra, Portugal; pdinis@dct.uc.pt

* Correspondence: marinacp@ua.pt (M.C.-P.); amitkumar.csb@gov.in (A.K.); Tel.: +351-964332189 (M.C.-P.); +91-8130952665 (A.K.)

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Abstract: In the modern era, due to the rapid increase in urbanization and industrialization in the vicinity of the Himalayas, heavy metals contamination in soil has become a key priority for researchers working globally; however, evaluation of the human and ecological risks mainly in hilly areas remains limited. In this study, we analyzed indices like the contamination factor (CF), degree of contamination (DC), enrichment factor (EF), geochemical index (I_{geo}), pollution ecological risk index (PERI), and pollution load index (PLI), along with cancer risk (CR) and hazard indices (HI), to ascertain the eco-environmental and human risks of using heavy metals in datasets collected from 168 sampling locations in Uttarakhand, India. The evaluation calculated of I_{geo} , EF, and CF suggests that represented soil samples were moderately contaminated and highly augmented with Rb, while PERI (75.56) advocates a low ecological risk. Further, PLI and DC (PLI: 1.26; DC: 36.66) show a possible health risk for the native population in the vicinity of the studied catchment. The hazard index (HI) is estimated greater than 1 ($HI > 1$) for Cr and Mn, representing a possible risk for cancer. However, adults are free from cancer risk, and other studied elements have been reported as noncarcinogenic. This assessment gives important information to policymakers, environmentalists, and foresters for taking mitigation measures in advance to mitigate the potential future risk of soil pollution on humans, ecology, and the environment.

Keywords: risk; heavy metal; human health; pollution indices; soil

1. Introduction

Due to the ubiquitous bioaccumulation of toxic heavy metals, even at the trace level, and the persistent concentration increase in soils and possible uptake through groundwater, atmosphere, crops, and the food chain, these elements are hazardous for human health [1–6]. Thus, heavy metals contamination in soil has been drawing much attention globally [7–10]. Generally, heavy metals in natural resources can be either natural (lithogenic inputs via weathering rocks) or anthropogenic in origin [11–14]. The change in climate conditions and socio-development features may amplify the inclusion of heavy metals in soils either by weathering or contaminant inputs such as surface

run-off, wastewater, sewage, and effluent, and has become a common but intense issue in various ecosystems [13,15–18]. These environmental problems are widespread in India [19–22]. Generally, long-term exposure to heavy metals profoundly creates health risks. Nonetheless, heavy metals do not show any adverse effect on human health and the environment if they are present at safe levels. If the concentrations of heavy metals exceed the safe limits, then they often cause acute health risks to mankind with severe consequences [9,10,16]. There are some trace elements that are essential for humans, such as iron, manganese, zinc, aluminum, lead, and cadmium; however, they may exert toxicity under pathological or artificially harsh conditions of exposure to excess levels [9–12,23,24], and references therein [25–29].

Soil characteristics are of considerable importance in holding the fertility of soil and balancing the nutrients requirements of different food chains [30]. The key information and mechanistic understanding of the outcome of various trace metals [31] and their dynamics are still under investigation in various ecosystems [32]. Furthermore, agriculture and the urban management of soil force change in the soil structure, function, and pedological properties [3,33,34]. In view of this, screening tools such as spectroscopic techniques (X-ray fluorescence (XRF)) and infrared diffuse reflectance techniques to understand the possible change in soil properties have been developed in recent years [35,36] and are used to investigate the elemental composition of the soil [37,38]. In this direction, important indices such as the cancer risk (CR), enrichment factor (EF), contamination factor (CF), geochemical index (I_{geo}), and hazard indices (HI) have also been used for quantifying the soil contamination and risk to the eco-environment and human health at regional and/or global levels [9,10,34,39–41]. Assessment of these important indices needs the existing background concentration (BC value) of individual heavy metals in the earth's crust. Thus, investigation for the assessment of the background concentration of these heavy metals in local/regional, national, continental, and global soils under different land-use systems was established [42–49]. However, the elemental concentration may vary in different land-use/regions due to variations in various controlling factors that contribute to soil formation and spatial distribution [43]. Therefore, it is of utmost importance to assess the local background concentration (BC) value of targeted heavy metal/metals in soil of specific region/land-use. This parameter is crucial to estimate the magnitude of contamination and its ameliorative measures for sustainable growth and development of the natural/anthropogenic ecosystem [11,12,44–52]. In India, the same trends have also been attempted by various researchers in different regions [19–22,53–59], but these studies are limited in the hills of the Indian Himalayas. Therefore, the present investigation was conducted to fill a knowledge gap that undermines the assessment of potential ecological and human health (carcinogenic) risks in the high hills of Uttarakhand, India. The results would be helpful for policy-makers and environmentalists to reduce the risk by making strategic mitigation plans in the future.

2. Materials and Methods

2.1. Study Site

Uttarakhand (28 44', 31 28' N to 77 35', 81 01' E) is administratively divided into 13 districts, having 71% (37,999.53 km²) of forest cover compared to the total geographical area (53,483 km² or 20,650 square miles), and shares its border as the international boundary with the northern region of China and eastern region of Nepal (Figure 1). The majority of the Uttarakhand population (10.11 million) lives in rural areas. Forest is the major asset of the state. The average annual precipitation is ~1550 mm. The climatic conditions are majorly temperate; however, tropical and subtropical climatic conditions exist only in plains and some of the foothills of the state. Chauhan et al. [60] classify the state into 2 high-altitude regions, i.e., lower (2400–4500 m above mean sea level and upper (>4500 m); 2 hilly regions, i.e., lower (300–600 m) and upper (600–2400 m); and a single terrain region (<300 m). The Uttarakhand climate is a cold, humid, and temperate type having altitude variation [60]. The soil fertility status in the state varies from low to medium among brown hill, mountain meadow, red

loamy, and sub-mountain soils. Most of the soils in the high-altitude region of Uttarakhand are acidic ($\text{pH} < 7$) in nature. Agricultural crops (e.g., rice, wheat, and sugarcane) and horticulture crops (tomato, cauliflower, cabbage, etc.) are the main crops in the high hills of the Himalayas. In the most populated altitudinal range (i.e., 1000–2000 m above MSL), there are oak (*Quercus spp.*), pine (*Pinus roxburghii*), banj (*Quercus leucotrichophora*), and buras (*Rhododendron arboreum*). Coniferous forests, e.g., deodar (*Cedrus deodara*) and Fir (*Abies species*), form the dominant forest vegetation at high altitudinal ranges (>2000 m) of the state [61–63].

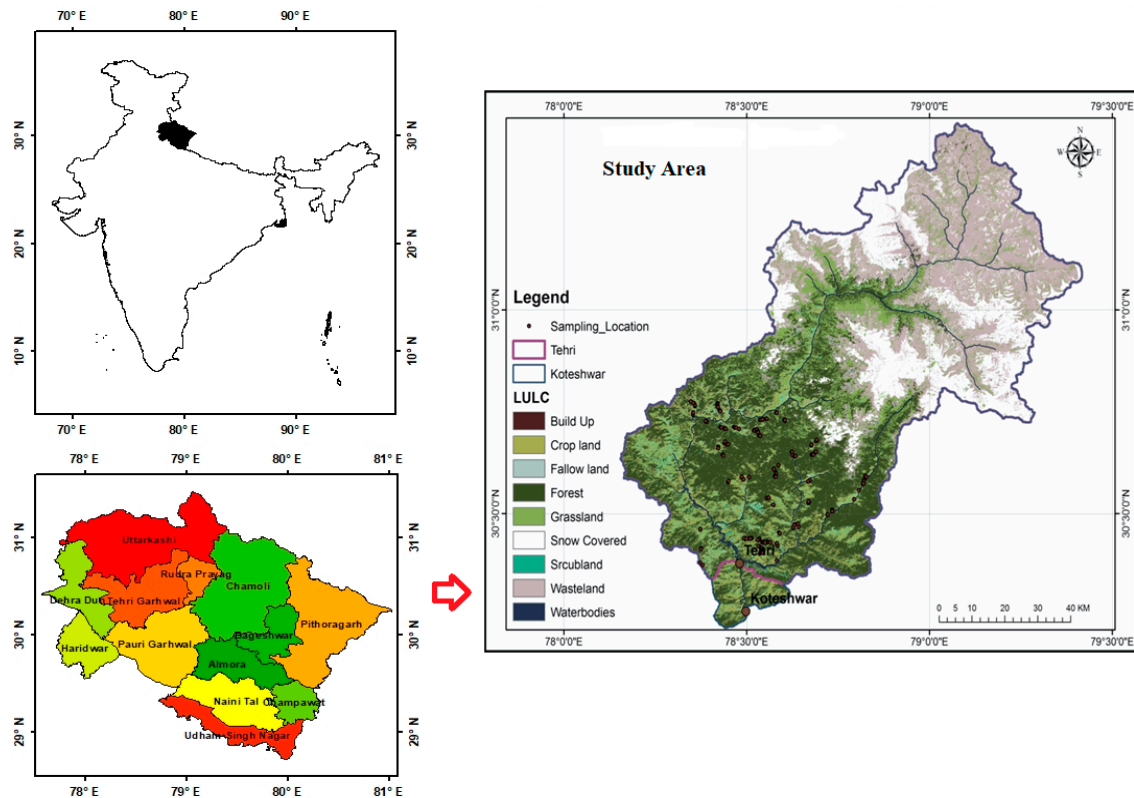


Figure 1. Study area in the high hills of Uttarakhand Himalaya, India.

2.2. Geology and Soils

From north to south (Figure 2a), the Himalaya in Uttarakhand includes four tectono-stratigraphic units [64,65]. (1) The Tethys, or Tibetan, Himalayan Zone comprising Palaeozoic to Eocene units deposited on the northern margin of the Indian plate [66,67]; (2) the Higher, or Greater, Himalaya Zone comprising Proterozoic crystalline rocks intruded by leucogranites [68,69]; (3) the Lesser Himalaya Zone with non-metamorphosed or weakly metamorphosed Indian continental crust and its sedimentary cover [69], intruded by Proterozoic plutons [70], along with Paleogene foreland deposits [71]; (4) the Outer Himalaya Zone comprising a thick Palaeocene to Quaternary sedimentary succession composed mainly of continental units derived from the Himalayan orogen [72–75].

The studied soils cover geological units of the Lesser Himalaya and Greater Himalaya zones (Figure 2A,B). In the investigated region, the Greater Himalaya is mainly composed of micaceous schists, gneisses, calc-silicate gneiss, and locally metabasic rocks [69]. The Lesser Himalaya units are from its inner metasedimentary belt (diverse siliciclastic and carbonate metasedimentary and volcanic units) and outer sedimentary belt (diamictite, sandstone, slate, carbonates, chert/quartzite) [69,74].

Figure 2B presents the adapted soil cartography of Uttarakhand, according to the FAO/UNESCO [75]. The soil map reveals the strong link between geology, relief, and soil-type (Figure 2B). The higher-elevation areas with crystalline rocks of the Greater Himalaya are occupied

by lithosols, the lower Lesser Himalaya dominated by sedimentary units displays cambisols, and the transitional zone between these two geological units can be covered by either cambisols or lithosols.

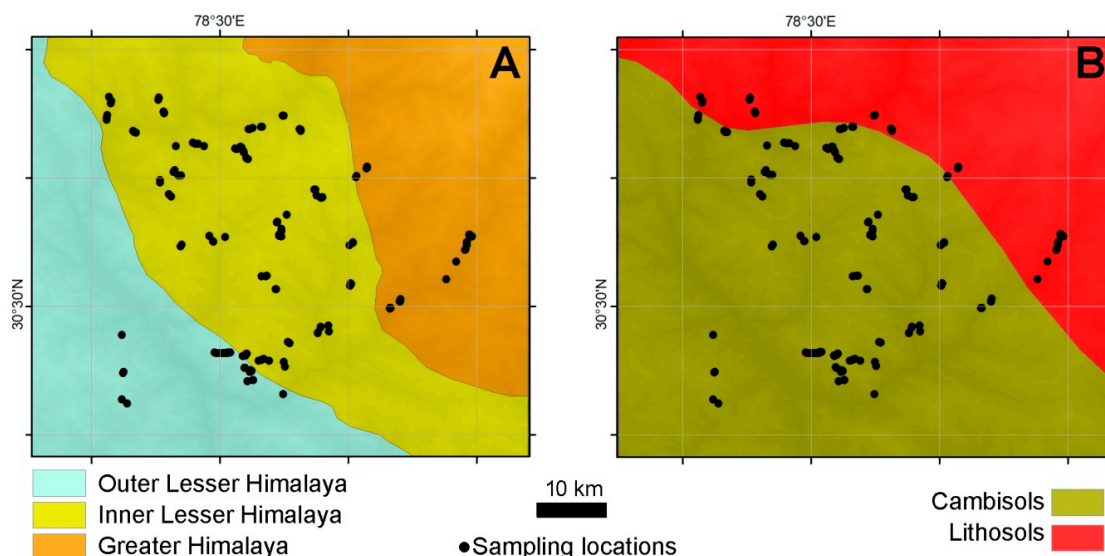


Figure 2. (A) Simplified geological (based on Mukherjee [76–79]) and (B) soil sketch of the studied area, based on FAO [75].

2.3. Soil Sampling and Analysis

Sampling of the soil was conducted in the Tehri Garhwal and Urrarkashi forest division of the Uttarakhand state of India in two stages (I-Tehri Garhwal; II-Urrarkashi forest division). A total of 168 randomized soil samples at a depth of 30 cm (1 in. = 2.54 cm) were collected following recommendations by the forest research institute (FRI, Dehradun, India) from different altitudinal ranges (Table 1) under the various forest species, as shown in Figure 1. Snow (18%) and wasteland (27%) of the catchment area were not considered for sampling, due to infeasibility conditions [62]. The coordinates and altitude of every individual sampling point were recorded by GPS (Garmin 76CSx, Garmin International Inc. Kansas, U.S.A). While collecting soil samples, a $0.50 \times 0.50 \text{ m}^2$ area of 30 cm depth was dug out using a soil auger at every location to collect soil (~500 g). Further, collected soil was mixed thoroughly; root debris, gravel, etc. were opted out from the samples; and then a composite sample was stored in polythene bags for further analysis in the laboratory with proper labeling to avoid errors. Individual soil samples along with the labeling were air-dried and then finely ground and sieved using a stainless-steel sieve of 100 mesh size. Further, elemental analyses, viz. Sr, Zn, Rb, Cu, Ni, Ca, Fe, Mn, Si, Al, Mg Cr, K, S, P, and Na, were analyzed using X-ray fluorescence (XRF, model: 54 pioneer, Bruker, 2008) [35]. The parametric statistical analysis (mean \pm SD) of individual heavy metals results was calculated and is listed in Table 1.

2.4. Eco-Environmental Risk Assessment

Eco-environmental risks were assessed using geostatistical indices to determine the degree and cause (e.g., anthropogenic or geogenic) of heavy metals contamination (Table 2). Indices like the degree of contamination (DC), contamination factor (CF), enrichment factor (EF), pollution load index (PLI), geo-accumulation index (I_{geo}), pollution ecological risk index (PERI), and potential contamination index (PCI) were estimated using recommended methods [34,39,63]. In India, region-specific background heavy metals composition values are not available for the studied regions; therefore, relevant values provided by Taylor and McLennan [61] were used to evaluate the indices followed by interpretation.

Table 1. Chemical elements concentration of soil (mean \pm SD) vs. altitudes.

Element (mg/kg)	Concentration in Upper Continental Crust (B) (mg/kg)	<1000 m	1001–1500 m	1501–2000 m	2001–2500 m	>2500 m
Sodium (Na)	28,900	3400 \pm 297	1746 \pm 695	2578 \pm 1443	2614 \pm 601	1767 \pm 736
Magnesium (Mg)	13,300	9780 \pm 1018	5600 \pm 1344	8141 \pm 3768	8036 \pm 2770	8230 \pm 2402
Aluminum (Al)	80,400	59,850 \pm 4596	62,181 \pm 8452	68,326 \pm 8116	65,887 \pm 7617	61,367 \pm 3099
Silicon (Si)	308,000	228,000 \pm 2828	214,667 \pm 27,390	205,894 \pm 27,718	196,875 \pm 28,175	213,666 \pm 20,502
Phosphorus (P)	700	882 \pm 157	790 \pm 345	974 \pm 515	1442 \pm 885	8912 \pm 89
Sulfur (S)	500	293 \pm 57	337 \pm 140	426 \pm 186	667 \pm 313	406 \pm 55
Potassium (K)	28,000	25,350 \pm 5303	25,819 \pm 6808	26,974 \pm 6739	23,525 \pm 4364	19,467 \pm 4196
Calcium (Ca)	30,000	7765 \pm 8676	10,860 \pm 16,511	8621 \pm 8314	11,051 \pm 6576	5703 \pm 3854
Chromium (Cr)	35	173 \pm 16	180 \pm 34	171 \pm 53	198 \pm 34	201 \pm 16
Manganese (Mn)	600	1342 \pm 1100	923 \pm 318	965 \pm 663	2069 \pm 2211	1087 \pm 643
Iron (Fe)	35,000	67,350 \pm 6717	54,233 \pm 16,734	62,716 \pm 27,569	67,181 \pm 22,068	55,633 \pm 13,250
Nickel (Ni)	20	99 \pm 22	106 \pm 37	104 \pm 31	128 \pm 23	112 \pm 6
Copper (Cu)	25	179 \pm 55	155 \pm 39	162 \pm 73	152 \pm 31	133 \pm 18
Zinc (Zn)	71	143 \pm 15	156 \pm 46	153 \pm 55	197 \pm 62	172 \pm 28
Rubidium (Rb)	112	564 \pm 300	729 \pm 390	956 \pm 1038	592 \pm 266	464 \pm 246
Strontium (Sr)	350	319 \pm 39	215 \pm 89	235 \pm 79	353 \pm 85	250 \pm 107
No. of samples collected		6	58	51	45	8

Table 2. Indices used to assess ecological risk for study area.

Indices	Information	Equations	Pollution Classification	Ref.
I _{geo}	Determines the extent of soil contamination from a comparison of the concentration of elements in the soil sample and the upper continental crust (UCC)	$I_{geo} = \log_2 \left[\frac{C_n}{1.5 \times B_n} \right]$	I _{geo} can be classified as: I _{geo} ≤ 0: Uncontaminated; 0 < I _{geo} ≤ 1: Uncontaminated to moderately contaminated; 1 < I _{geo} ≤ 2: Moderately contaminated; 2 < I _{geo} ≤ 3: Moderately to highly contaminated; 3 < I _{geo} ≤ 4: Highly to extremely contaminated; I _{geo} > 5: Extremely contaminated	[65,66]
EF	Standardizes the concentration of analyzed element against a reference element in the soil and the UCC	$EF = \left[\frac{C_n^{sample}/A_{sample}}{C_n^{crust}/A_{crust}} \right]$	EF classified as: 0 < EF < 1: No enrichment; 1 < EF < 3: Slight enrichment; 3 < EF < 5: Reasonable enrichment; 5 < EF < 10: Reasonably high enrichment; 10 < EF < 25: High enrichment; 25 < EF < 50: Very high enrichment; and EF > 50: Extremely high enrichment.	[63,80]
CF	Represents the effect or contribution of an individual element in soil contamination	$CF = \frac{C_n}{B_n}$	CF classified as: CF < 1: Low contamination; 1 < CF < 3: Reasonable contamination; 3 < CF < 6: Considerable contamination; and CF > 6: High or very high contamination	[60,80]
PLI	The product of CF in the soil sample	$PLI = (CF_1 \times CF_2 \times CF_3 \dots \dots CF_n)^{1/n}$	PLI classified as: PLI > 1 indicates the presence of pollution, whereas PLI < 1 indicates no elemental pollution	[80,81]
DC	The sum of CF of eight elements (Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr) considered for the study (i.e., cumulative effect of the heavy metals in soil contamination)	$DC = \sum_{i=1}^{i=n} CF$	DC classified as: DC < 8: Low contamination; 8 < DC < 16: Reasonable contamination; 16 < DC < 32: Considerable contamination; and DC > 32: High degree of contamination (i.e., serious anthropogenic impacts)	[82]
PCI	Used in forest ecosystems where heavy metals exist as complex mixtures with spatiotemporal variability.	$PCI = \frac{C_n^{max}}{B_n}$	PCI classified as: PCI < 1: Low contamination; 1 < PCI < 3: Reasonable contamination; and PCI > 3: Severe or very severe contamination	[80,83]
PERI	Provides an indication of major contamination agents and the identification of sites where studies could prioritize. Used to assess the degree of elemental contamination in response to their toxic effect or risk to the environment	$PERI = \sum P_n$ $P_n = T_n \times CF_n$	P _n classified as: P _n < 40: Low potential ecological risk; 40 < P _n < 80: Reasonable ecological risk; 80 < P _n < 160: Considerable ecological risk; 160 < P _n < 320: High ecological risk; and P _n > 320: Very high ecological risk. Moreover, PERI classified as: PERI < 95: Low potential ecological risk; 95 < PERI < 190: Moderate ecological risk; 190 < PERI < 380: Considerable ecological risk; and PERI > 380: Very high ecological risk	[80,82]

where C_n: Concentration of an analyzed nth element in the sample (C^{sample}) and upper continental crust (C^{crust}); B_n: BC value of nth element of continental crust; n: Number of elements considered for PLI evaluation; C_n(max): Maximum concentration of nth element found in all collected soil samples; P_n: Potential ecological risk factor of individual heavy metal, which can be evaluated using T_n (toxic response factor) and CF. The standardized value of T_n for metals like Cr, Mn, Ni, Cu, and Zn are 2, 1, 5, 5, and 1, respectively. T_n has been used to identify the toxic response of individual metal, while PERI gives the cumulative effect of five metals (Cr, Mn, Ni, Cu, and Zn) in the study catchment. For the calculation of EF, Al was chosen for normalization to a conservative geogenic element.

2.5. Human Health Risk Assessment

The human health risk assessment was estimated with consideration of direct exposure of toxic heavy metals to adults and children through soils. The carcinogenic and noncarcinogenic risks were estimated as per the methodology of USEPA ([84]; Table 3). Chronic daily intake (CDI) was established for heavy metals exposure through ingestion (CDI_{ingest}), inhalation (CDI_{inha}) and dermal contact (CDI_{dermal}) by adopting the equations given below [84,85]:

$$CDI_{ingest} = \frac{C \times IR \times EF \times ED \times CF}{BW \times AT} \quad (1)$$

$$CDI_{inhalation} = \frac{C \times InhR \times ET \times EF \times ED}{PEF \times BW \times AT} \quad (2)$$

$$CDI_{dermal} = \frac{C \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

where C denotes the concentration of heavy metals available in soil ($mg\ kg^{-1}$). Noncancer risk is represented in terms of hazard index (HI) for multiple substances and/or exposure pathways [34]. HI is the sum of the hazard quotient (HQ), for each element and each pathway, and if $HI < 1$, there is a very low chance of noncarcinogenic risk. The other terms are explained in Table 3.

Table 3. Reference values adopted for the determination of chronic daily intake (CDI) based on USEPA [84].

Parameter	Units	Adult	Children
IR	$mg\ day^{-1}$	100	200
EF	$Days\ year^{-1}$	312	312
ED	Years	35	6
BW	kg	70	15
ATnc	Days	365×35	365×6
ATc	Days	365×70	365×70
CF	$mg\ day^{-1}$	10^{-6}	10^{-6}
SA	cm^2	6032	2373
AF	$mg\ cm^{-2}$	0.07	0.2
ABS	Unitless	0.001	0.001
InhR	$m^3\ h^{-1}$	1.56	1.2
ET	$h\ day^{-1}$	8	4
PEF	$m^3\ kg^{-1}$	1.36×10^9	1.36×10^9

where IR: Ingestion rate of soil; BW: Body weight; EF: Exposure frequency; ED: Exposure duration; ATc: Av. time for carcinogenic risk; ATnc: Av. time for noncarcinogenic risk; SA: Skin surface area available for contact; CF: Conversion factor; AF: Soil-to-skin adherence factor; ABS: Absorption factor; InhR: Inhalation rate; ET: Exposure time; PEF: Particle emission factor.

3. Results and Discussion

Heavy metals enter into the terrestrial environment through household wastes, agricultural and anthropogenic processes, the weathering of rocks, etc. where accumulation occurs in the air, soil, and water, while its excess concentration to ecological and human health is a more serious problem in the modern era than water and air pollution [19,34]. These problems are because heavy metals and/or metalloids are generally firmly bound by the organic components available in the topmost soil profile [20]. In general, heavy metals available in low or trace amounts are important for flora and fauna diversity, while high concentrations suppress its growth and finally cause plant decay.

Table 4. Background concentration of individual elements and calculation of eco-environmental indices.

Elements	PCI		CF	EF (Mean ± SD)		I _{geo} (Mean ± SD)		
Na	0.24	low contamination	0.08	low contamination	0.10 ± 0.05	no enrichment	−4.38 ± 0.63	uncontaminated
Mg	1.40	reasonable contamination	0.55	low contamination	0.68 ± 0.27	no enrichment	−1.55 ± 0.54	uncontaminated
Al	1.01	reasonable contamination	0.80	low contamination	1.00 ± 0.05	slight enrichment	−0.90 ± 0.18	uncontaminated
Si	0.84	low contamination	0.68	low contamination	0.85 ± 0.18	no enrichment	−1.17 ± 0.20	uncontaminated
P	4.11	severe or very severe contamination	1.41	reasonable contamination	1.84 ± 1.11	slight enrichment	−0.24 ± 0.76	uncontaminated
S	2.46	reasonable contamination	0.89	low contamination	1.15 ± 0.67	slight enrichment	−0.91 ± 0.73	uncontaminated
K	1.36	reasonable contamination	0.89	low contamination	1.12 ± 0.23	slight enrichment	−0.78 ± 0.37	uncontaminated
Ca	2.34	reasonable contamination	0.34	low contamination	0.42 ± 0.51	no enrichment	−2.71 ± 1.14	uncontaminated
Cr	8.34	severe contamination	5.34	considerable contamination	6.55 ± 1.49	reasonably high enrichment	0.39 ± 0.41	tends to moderately contaminated
Mn	14.83	very severe contamination	2.17	reasonable contamination	2.66 ± 2.85	slight enrichment	1.76 ± 0.34	moderately contaminated
Fe	4.09	severe contamination	1.75	reasonable contamination	2.15 ± 0.73	slight enrichment	0.12 ± 0.92	tends to moderately contaminated
Ni	8.55	severe contamination	5.68	considerable contamination	6.95 ± 1.93	reasonably high enrichment	0.11 ± 0.61	tends to moderately contaminated
Cu	16.60	very severe contamination	6.39	high or very high contamination	7.82 ± 2.50	reasonably high enrichment	1.86 ± 0.38	moderately contaminated
Zn	5.59	severe contamination	2.37	reasonable contamination	2.91 ± 0.89	slight enrichment	2.00 ± 0.38	tends to highly contaminated
Rb	42.95	very severe contamination	6.56	high or very high contamination	8.20 ± 6.95	reasonably high enrichment	0.57 ± 0.45	tends to moderately contaminate
Sr	1.48	reasonable contamination	0.76	low contamination	0.10 ± 0.05	no enrichment	1.82 ± 0.96	moderately contaminated
<p>Calculated DC = 36.66 (high degree of pollution) Calculated PLI = 1.26 (indicates presence of pollution)</p>								

3.1. Analysis and Indices Evaluation

Eco-environment and human health risks are being examined by heavy metal pollution index methods. These indices like DC, CF, EF, I_{geo} , PCI, PERI, and PLI play a vital role in knowing the overall risk with respect to individual heavy metals. The descriptive statistics (mean \pm SD) of soil elemental concentration for different altitudes and background concentrations (BCs) of elements are shown in Table 1. Eco-environmental indices with estimated contamination levels in the studied region are provided in Table 4 and a further ecological risk index (Table 5) has been also evaluated.

Table 1 reveals that the elevated concentration of Cu, Cr, Rb, and Zn is chiefly accountable for the soil pollution by an excess amount of heavy metals in the studied region of Uttarakhand Himalaya. The other elements such as Ca and S significantly contribute to soil contamination in some samples. The Al, Ca, Si, Mg, and Na were found to be less than their BC value. Moreover, Cu, Cr, Rb, and Zn were estimated to be more than their BC value. The maximum and mean values of Fe, Ni, and P were estimated at more than their BC value.

Table 5. Calculated potential ecological risk index.

S. No	Elements	Potential Ecological Risk Factor (Pn)	Ecological Risk
1.	Cr	10.69	Low
2.	Mn	2.17	Low
3.	Ni	28.38	Low
4.	Cu	31.95	Low
5.	Zn	2.37	Low
Net PERI		75.56	Low

The higher concentration of elements is an indication of the presence of contamination in the studied catchments and further risk to ecological life; contamination levels were classified based on the calculated values of the indices (DC, CF, EF, I_{geo} , PCI, PERI, and PLI). Further, a comparative analysis was done with an average estimated concentration of elements like Cr, Cu, Ni, Sr, and Zn with their threshold concentration in the soil sample of 100, 30, 80, 200, and 300 mg/kg, respectively [58,86,87]. The estimated average concentration of Cr and Cu was found higher than their corresponding threshold limit; however, Zn was found within its threshold limit. Moreover, mean concentrations of Sr and Ni were estimated more than their respective threshold limit. Geological indices like I_{geo} were estimated for individual elements as per the respective BC. The results reveal that the mean I_{geo} for elements such as Al, Ca, K, Mg, Na, P, S, and Si were found as $I_{geo} \leq 0$, indicating noncontamination of the studied catchment, which signifies no contamination with these elements, whereas elements like Cr, Cu, Fe, Mn, Ni, Rb, and Sr fall under moderately contaminated ($0 < I_{geo} \leq 1$) and/or tends toward moderately contaminated ($1 < I_{geo} \leq 2$) except Zn (which tends toward high contamination, i.e., $2 < I_{geo} \leq 3$). Overall, the I_{geo} analysis reveals that Ni and Rb to some extent, and Cu, Mn, and Cr have a considerable impact on ecological life and further risk to the health of the native population of the studied region of Uttarakhand Himalaya if these elements come into the food chain.

Therefore, regular monitoring of these metals in soils, food products, and vegetables are important to understand the potential health risk and further prevent accumulation of toxic metals in the food chain. Similarly, the EF of each element for the entire study was calculated and normalized against aluminum (Al) to a conservative geogenic element. The mean EF of elements Ca, Mg, Na, and Sr was estimated as 0.42, 0.68, 0.10, and 0.10, respectively, and no enrichment was found of these elements in the studied catchment, whereas Rb, Cu, Ni, and Cr fall under reasonably high enrichment ($Rb > Cu > Ni > Cr$). Al, Fe, K, Mn, P, S, and Zn that fall into the slight enrichment range ($1 < EF < 3$) might be an indication of the anthropogenic hindrance (e.g., construction of dams and roads) in the vicinity of the studied catchment.

The CF of each element was calculated, and the result reveals that Na, Mg, Si, Al, K, S, Sr, and Ca were found to be less than one (i.e., $CF < 1$), indicating no contamination in the soil of the studied

Himalayas catchment, while P, Mn, Fe, and Zn showed reasonable contamination ($1 < CF < 3$) in the studied samples. These elements are generally present in the natural ecosystem and also added to the food producing system as fertilizers, etc., and are beneficial for the growth and development at tracer levels [88]. Different species including humans in healthy conditions have been reported to have the intrinsic capacity to remove the excess elements without much damage. However, continuous exposure to certain elements either through occupation or through contaminated intake along with food, certain medical conditions, impairment of biochemical processes, and accidental intake could be problematic [3,89]. For example, neurotoxicity due to inhalation exposure to airborne Mn has been reported [24,90,91]. Fe toxicity has long been already established by Reissmann et al. [92]. The Zn is an essential element for many biochemically important enzymes in plants as well as animal systems. The permission limit of Zn in Indian soil is 600 $\mu\text{g/g}$ [93]. Over the permissible limits of these elements, they can be problematic/toxic to the living system through impairment of the various physiological, biochemical, growth, and development processes [3,94,95]. Moreover, Cr, Cu, Ni, and Rb fall under considerable contamination to high contamination levels, following the order $\text{Rb} > \text{Cu} > \text{Ni} > \text{Cr}$. Heavy metal toxicity involves oxidative and genotoxic mechanisms [96]. When the direct exposure of toxic elements is not present, these elements can have poisonous effects on the population of a particular region due to accumulation in the food chain [97]. The rubidium (Rb) is observed to be moderately toxic to human as it mimics potassium [26].

Further, PLI was calculated by the conversion factors of each element, and the estimated PLI was found to be 1.26, indicating the presence of pollution in the studied catchment. Calculated PLI results were verified by the degree of contamination (DC) index (Table 4), with results showing a high degree of pollution (DC: 36.66; i.e., $\text{DC} > 32$) at the study site. This high value of DC is due to high anthropogenic activity in the studied catchment. The potential of contamination was calculated using PCI and the results reveal that the studied catchment has low contamination of Na and Si and reasonable contamination of Mg, Al, S, K, Ca, and Sr, whereas other parameters fall between severe to very severe contamination and follow the order $\text{Rb} > \text{Cu} > \text{Mn} > \text{Zn} > \text{P} > \text{Fe}$. After ascertaining the pollution contamination in the studied catchment, PERI was calculated (using CF and Tn values) to determine the potential ecological risk in the studied catchment (Table 5). The Pn of each element (Cr, Mn, Ni, Cu, Zn) was < 40 , where PERI was calculated as 75.56, indicating low ecological risk where Ni and Cu contribute a greater share compared to Cr, Mn, and Zn.

3.2. Health Implications of Soil Composition

The topsoil of Uttarakhand Himalaya, India, is well-augmented with Cr, Cu, Mn, Ni, and Zn to the upper crust concentration (UCC), taking into consideration the average BC calculated from the soil distribution values, and above Indian guidelines [98] (Table 6). This soil has Cr and Ni contents above the Indian [98], Canadian [99], and Dutch [100] guidelines for agricultural and construction uses. Cu is above the Canadian guideline for agricultural uses and also above Dutch guidelines (Table 6). The pathways of soil exposure chosen were ingestion, inhalation, and dermal contact, which are considered the same for both (children and adults). Alzheimer's and Parkinson's disease (neurodegenerative disorders) are considered due to the enhanced concentration of Cu, Fe, Mn, and Zn in tissue [101]. Manganese has been found to be a causing agent to induce Parkinsonism through environmental exposure; however, the medical assurance of this conclusion is unclear and needs further investigation [102]. Several elements are present in the natural ecosystem; however, their higher contamination/bioaccumulation than the permissible limits described them as being toxic/nontoxic based on the species (plants, animal, and human)-specific tolerance, which further depend on their interaction in the functioning of the living cells of different species. Most of the toxic elements studies are focused on Cu, Zn, Cr, Ni, Cd, Pb, Hg, As, and Se. However, the other metals might be having an important role to define toxic effects independently or in combination with other toxic metals. The mechanisms of the toxicity/residual/combined effects of these nonstudied metals also need to be understood. Therefore, in the present investigation, all the studied elements and their threshold in

light of the indices were evaluated for their hazards. However, for a clearer scenario, more studies are needed to investigate the effect of these reported elements in Himalayan mountainous ecosystems.

Table 6. Mean concentration of heavy metals in the studied site; composition of the upper continental crust and permissible limits (in mg kg⁻¹) as per Indian, Dutch, and Canadian soil.

	Mean Values	Concentration in Upper Continental Crust (B) * (mg/kg)	Indian Guidelines	Dutch Guidelines	Canadian Guidelines	
			Target Values	Target Values	Agricultural or Other Property Use	Parkland/Residential/Commercial/Community Property Use
Cr	173	35	35	100	67	70
Cu	99	25	25	36	62	92
Mn	1342	600	-	-	-	-
Ni	99	20	20	36	37	82
Zn	143	71	71	140	290	290

* Bold values indicated in the tables are the guideline values that are below the mean heavy metal content in Himalaya soils.

Geophagism (soil ingestion), dermal contact, and inhalation are the three key contact pathways of the human health risk from potentially toxic metals and/or elements. Geophagism is very common in children and rarely observed in few adults, while inhalation is related to the dusty composition of air and the dermal contact related to the play and profession in the near-surface environment [9,10,40,41,52]. Table 7 shows the hazard quotient (HQ) values for various pathways and elements resulting from exposure to soil elements.

Table 7. Hazard quotient (HQ) values for various pathways and elements resulting from exposure to soil elements, Uttarakhand, India.

	HQ Ingestion		HQ Dermal		HQ Inhalation	
	Children	Adult	Children	Adult	Children	Adult
Cr	$1.10 \times 10^{+00}$	1.18×10^{-01}	3.07×10^{-03}	4.69×10^{-04}	9.20×10^{-04}	5.19×10^{-04}
Ni	2.57×10^{-02}	2.75×10^{-03}	7.19×10^{-05}	1.10×10^{-05}	7.17×10^{-07}	4.04×10^{-07}
Cu	6.25×10^{-01}	6.70×10^{-02}	1.75×10^{-03}	2.67×10^{-04}	8.81×10^{-04}	4.97×10^{-04}
Mn	$1.10 \times 10^{+00}$	1.18×10^{-01}	3.07×10^{-03}	4.69×10^{-04}	1.47×10^{-02}	8.30×10^{-03}
Zn	8.40×10^{-03}	9.00×10^{-04}	2.35×10^{-05}	3.59×10^{-06}	2.35×10^{-07}	1.32×10^{-07}

For all elements, HQ ingestion is always the highest, while HQ inhalation is always the lowest (Figure 3). The noncarcinogenic HIs for all five elements are given in Table 7. For adults, the HIs were always less than 1, whereas for children, they were higher than 1 for Cr and Mn (Table 7). The HI values of these elements are mainly controlled by HQ ingestion, which are also greater than 1 for these two elements.

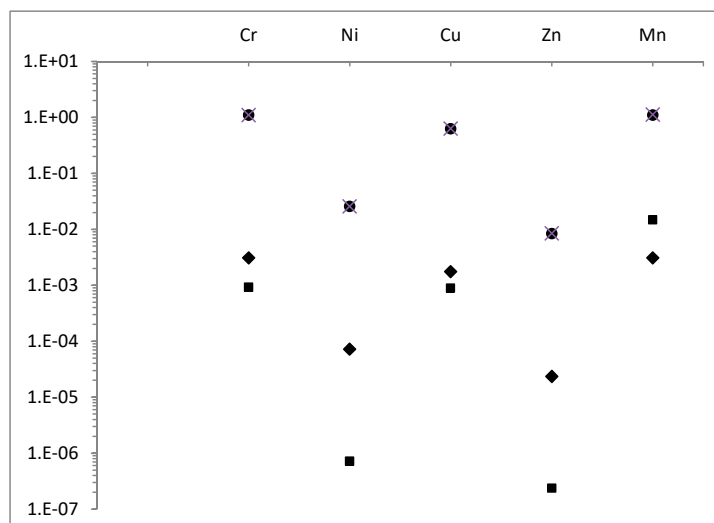


Figure 3. HQs for potentially toxic elements from Uttarakhand, India. Symbols: HQs for ingestion: Crosses; HQs for dermal contact: Diamonds; HQs for inhalation: Squares.

The noncarcinogenic HIs for all five elements are given in Table 8. For adults, the HIs were always less than 1, whereas for children, they were higher than 1 for Cr and Mn. The HI values of these elements are mainly controlled by HQ ingestion, which are also greater than 1 for these two elements. For all elements also, HQ ingestion is always highest, while HQ inhalation is always lowest, except for Mn (Figure 3).

Table 8 shows that the hazard indices (HI) of Cu, Ni, and Zn were below 1; hence, they do not pose a noncarcinogenic risk. For Cr and Mn for children, HI is observed as 1.3 and 4.2, respectively, showing a potential noncarcinogenic risk. The findings of this study were in good agreement with other studies [49]. The case percentage with HI > 1 is 5% and 11% for Cr and Mn, respectively. These findings suggest that children playing should be free from soil exposure, and also, the chance of hand-to-mouth intake should be completely avoided.

Table 8. Maximum and minimum range of hazard indexes and cancer risks due to soil exposure for potentially toxic elements, in Uttarakhand, India.

Element	Hazard Indexes		Cancer Risks	
	Children	Adult	Children	Adult
Cr	0.4–1.3	0.0–0.1	1×10^{-07} to 4×10^{-07}	1×10^{-07} to 1×10^{-06}
Cu	0.0–0.1	0.0–0.0		
Mn	0.2–4.2	0.0–0.6		
Ni	0.0–0.1	0.0–0.0	0 to 5×10^{-09}	0 to 2×10^{-08}
Zn	0.0–0.0	0.0–0.0		

Cr and Ni pose a significant carcinogenic risk as per the International Agency for Research on Cancer (IARC) guidelines [103] in the current investigation. The cancer risk (CR) data for exposure to soil with potentially toxic elements categorized from carcinogenic to possibly carcinogenic to humans [103] indicated that the Cr and Ni cancer risk was up to the standard of carcinogenic risk of 1×10^{-4} to 1×10^{-6} [84] in all the locations of soil sampling.

Indian Himalayan having a rich diversity of flora and fauna, and in recent decades, due to the rapid exploitation of resources, weathering and deforestation, has caused vulnerability to climate change. For the sustainable environmental management and pollution remediation in this region, it is necessary to analyze the concentration of heavy metal and physico-chemical characteristics of the soil together so that its potential risk and its key factor affecting pollution can be determined fruitfully.

The Greater Himalaya includes basic rocks, which are rich in Cr, Ni, Mn, and Cu. Lithosols covering these units are incipient and particularly affected by physical weathering, with their heavy metals contents possibly inherited from parent rocks. Cultivated Cambisols can also explain an anthropogenic origin for contaminants.

All anthropogenic activities underway in the vicinity of the Himalayas with some natural factors are mainly responsible for the soil contamination in the Himalayan region [104,105]. As Uttarakhand Himalaya is vulnerable to climate change, it is highly important to conserve biodiversity, which will further help in socio-economic developments. Preventive measures such as seasonal remediation must be given priority by environmentalists, foresters, and decision-makers to minimize the environmental damages in the coming future. In this study, we suggest that researchers of the different domains conduct a comprehensive investigation on bioavailability, concentration, and transfer of the potential of trace elements in different areas such as agricultural and aquatic in the vicinity of Uttarakhand Himalaya to examine the contamination level and its risk so that its impact on public health and biodiversity (flora and fauna) can be minimized. The environmental standards made by the Ministry of Environment, Forest and Climate Change (MoEF & CC, India) could be helpful for encouraging ecology, and reduced public health risk can enhance the pace of socio-economic developments and limit the human health risks to a great extent. Considering the possible impacts of studied toxic elements on the human health of the native population directly or indirectly through ecosystem consequences, the outcome of this investigation recommends putting forward preventive measures for environmental protection and socio-economic development in the region.

4. Conclusions

This study was conducted in the Uttarakhand Himalaya of India to evaluate the eco-environmental risk and health hazard (carcinogenic or noncarcinogenic risk) to humans using sixteen different soil elements. The elemental concentrations of Cr and Cu were found above their background concentration and threshold limits. The contamination indices (I_{geo} , EF, and CF) evaluated showed that Cu, Cr, and to some extent, Ni and Rb have a considerable impact on soil contamination. The evaluation of DC and PLI obtained values of 36.66 and 1.26, respectively, suggesting that soil of the studied Himalaya catchment is polluted with heavy metals, whereas the calculated PERI was 75.56, indicating low ecological risk. The overall results show no significant ecological risk associated with the heavy metal contents in the soils. Observed elemental contaminations can be ascribed to both geogenic anthropogenic causes and the studied catchment. The health risk assessments for selected heavy metals, whose content was above the Indian, Canadian, and Dutch guidelines, suggest that no major carcinogenic risks for adults were evaluated, due to soil intake, but Cr and Mn concentrations indicate potential carcinogenic risk for children. Therefore, regular monitoring of the reported metals in soils, food products, and vegetables are obligatory to prevent accumulation of metals in the food chain. These key findings will be highly useful for the water resource planners, managers, and environmentalists to make strategic planning in advance to take care of the ecology and human health for people living in the vicinity of the Himalaya catchment.

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