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ORIGINAL ARTICLE

Evaluating heavy metal contamination and radiological effects in soil samples from Murree, Pakistan

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Abstract

Urbanization significantly contributes to soil contamination, and tourism-related activities may exacerbate the problem. Murree is a renowned tourist destination in Pakistan. In recent years, Murree's contamination levels have increased due to growing tourism and rapid urbanization. This study was designed to evaluate the contamination levels and measure the natural radioactivity in the urban soils of Murree. In this study, elemental analysis of soil samples from the urban areas of Murree was performed using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and an elemental analyzer, while the activities of naturally occurring radionuclides (NORMs) were measured using Gamma Spectrometry.. The concentrations of 26 elements were measured, and Ca (47,761 mg/kg) was found to have the highest concentration and while Sn (3 mg/kg) had the lowest. Various parameters, such as Enrichment factor, Geo-accumulation index, Pollution and Integrated pollution index, and Ecological risk factor were calculated to assess the soil contamination levels. These parameters revealed low to moderate contamination at most of the sites and high contamination levels at one site. Principal Component Analysis (PCA) and correlation matrix revealed various sources for these metals. Non-carcinogenic and carcinogenic health hazards related to Cu, Pb, As, Ni, Cr, Mn, Ba, Zn and Co, exposure via three pathways (inhalation, dermal contact, and ingestion) were calculated for both adults and children; namely Average Daily Dose (ADD), Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk for Lifetime Exposure (CRLE). The highest HI value observed in adults was 0.023 for Ni and in children 0.207 for Co. Cr exhibited a carcinogenic risk for both adults and children, whereas As posed a cancer risk only to children. The average specific activities of Ra-226, Th-232, K-40 and Cs-137 in Bq/kg were 26.8 ± 14.4, 17.4 ± 5, 495.9 ± 82, 8 ± 3.2 respectively. Health risks associated with exposure to radiation from radionuclides were also assessed. The spatial distribution of heavy metals and NORMs were studied using interpolation to quantify their distribution geographically in Murree. This study concludes that some urban areas of Murree, near the city center are highly contaminated and the radiological risk to the population and environment is low.

Keywords Elemental analysis · Pollution level assessment · Health risks · Interpolation · Principal component analysis · Natural radioactivity

Introduction

Pollution is increasing, globally due to anthropogenic activities (Prakash and Verma 2022). Urbanization is one of the primary contributors to soil pollution which is more widespread in urban areas (Vareda et al. 2019). The elemental profile of soil is an important factor for the assessment and source apportionment of pollutants in an area (Ali and Muhammad 2023; Din et al. 2023). The presence of heavy and toxic metals in soil poses a severe threat to human health as well as a potential danger to terrestrial ecosystems. Due to their long lasting and cumulative nature in soil, metals

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can increase their toxicity by reacting with organic and inorganic matter. Heavy metals can harm living things including microorganisms, plants, humans, and animals through the food chain. Metals interact differently with soil depending on the physicochemical characteristics of soil, which varies throughout the world (Sarkar 2002; Tyler 1981; Zaynab et al. 2022). High levels of heavy metals in soil can lower crop yield by reducing microbial activity, impeding nutrient uptake and accumulation, and inhibiting crop root growth (Burges et al. 2015).

In addition to harming the brain and central nervous system function, heavy metal toxicity can also affect vital organs such as liver, kidneys, lungs etc. (Kuo et al. 2006). Long-term exposure to heavy metals may also cause conditions like Alzheimer's disease, Parkinson's disease, and muscular dystrophy (Bakulski et al. 2020; Gilani et al. 2015; Mahurpawar 2015). High exposure to heavy metals has been related to lung cancer, lung disease, and to respiratory system damage. Various methodologies have been developed to estimate the health hazards posed by these metals on human health (Hassaan et al. 2016).

Generally, urban soil is heavily contaminated with metals. This is due to emissions from vehicles, industrial waste, residential pollutants, and weathering of pavements, buildings, and automotive surfaces (Irshad et al. 2019). These pollutants are both directly and indirectly deposited on the soil (Ferreira et al. 2016; Tong et al. 2020). Heavy metals are also found in soil as a result of natural processes such as complex physiochemical reactions caused by weathering of parent rocks, oxidation, and mineral dissolution (Ghani et al. 2022). The migration of heavy metals from soil to water bodies has the potential to cause significant harm to both human health and the environment (Bhatti et al. 2022; Ghani et al. 2023). Long-term exposure to urban soil pollution poses serious health hazards and has a negative impact on soil ecosystems (Yuan et al. 2021). Urban pollution has gained a lot of attention in recent decades due to its adverse impact on the environment and human health (Yao et al. 2021). The levels of contaminants such as heavy metals correspond to population size and population-related activities (Barsova et al. 2019). It is consequently essential to monitor the concentrations of toxicants in urban soils to determine the severity of pollution in and around a specific area, establish control and remediation strategies, and provide a baseline for future studies (Muhammad 2023).

Natural radiation originates from two sources: cosmic radiation and radionuclide decay. Naturally occurring radionuclides (NORMs) include primordial radioactive elements in the earth's crust, radioactive decay progenies, and radionuclides generated via cosmic-radiation interactions (Klement 2019). The half-life of primordial radionuclides is equivalent to earth's age. ^{238}U, ^{232}Th, and ^{40}K are radionuclides found naturally in soil. In general, NORMs contribute approximately 85 percent of the radiation dose to humans (Hendry et al. 2009). The activity concentrations of NORMs can be influenced by weathering, sedimentation, sorption, leaching, and subsurface water movement (Salbu 2006). ^{238}U decays to ^{226}Ra, which decays to radon gas ^{222}Rn. Inhaling radon causes lung cancer. Ingestion or inhalation of Radium can cause lung, bone, and nasal passage malignancies (Substances & Registry, 1999). To determine the health hazards associated with radiation, the activity of NORMs needs to be measured.

Murree is a district of the Punjab province located northeast of the capital city of Pakistan. It is the most famous tourist destination of Pakistan and is also famous among international tourists. Due to the increasing tourist influx, Murree is urbanizing rapidly. Satti et al. studied the spatial distribution of radionuclides in some areas of Murree and found that the levels of radionuclides and stable elements at different sites were quite distinct. This suggests that the soil may be sedimentary shale. The area had high levels of silicates and alumina. There was a weak to mild association between the concentrations of major elements and radionuclides (Satti et al. 2016). Salim et al. studied heavy metal concentrations in some areas of Murree of varying altitude and discovered that the concentrations of Cd and Mn in soil and plant samples vary with elevation, with most heavy metals (HMs) being found in the mid-elevation zones of the Himalayan slopes (Salim et al. 2020). Dust, soil, and plant samples that have HMs in them have many sources. Generally Pb and Cd are measured in higher amounts, while other HMs contribute much less to the total HMs content (Salim et al. 2020).

Evaluating pollution levels in urban areas of Murree is crucial due to the high number of tourists it attracts annually, and the potential impact of heavy metals on human health and the ecosystem in this popular tourist destination. There have been no reported studies on the pollution level, radionuclides activity, heavy metals assessment in the soil and the associated health hazards for the urban areas of Murree. The objective of this study is to address this gap by providing a detailed elemental profile along with pollution indices, source apportionment and assessment of health hazards for heavy metals. This work also examines the activity of radionuclides and their potential risks to human health. In this work, soil quality of Murree was also assessed for microbial activity and plant growth. Moreover, statistical analysis tools such as principal component analysis (PCA) and interpolation using ESRI ArcGIS have been used to determine the spatial distribution of pollutants while correlation of various pollutants was used to quantify their potential sources.

Materials and methods

Description of study area

Murree is a district of Punjab located at Latitude 33° 54′ 30.24″ and Longitude 73° 23′ 25.08″ with an average altitude of 2291 m. It is situated about 35 km northeast of Islamabad. According to the Koppen climate classification, Murree has a subtropical highland climate with relatively cool summers and cold frosty winters with heavy snowfall. The temperature varies from – 10 °C in winters to 32 °C in summers. Average precipitation annually is 1904 mm and Murree also receives ~ 1590 mm of snow in a calendar year. Although the local tribes have been living in this area for centuries, the construction of modern Murree began in 1853 by the British Raj. English officers found Murree's climate closer to their home because of its relatively cold meteorological conditions and established a permanent township here. Murree became a popular destination among British officers, and the trend continued after the Independence of Pakistan. Murree is the most visited tourist destination in Pakistan, and it is known as Malaka-e-Kohsar (Queen of Mountains). Due to its popularity as a tourist destination, Murree has seen a rapid rise in urbanization, which is more prominent in the city center and is spreading outwards with the construction of hotels, restaurants, and markets.

Sampling sites

Sixty soil samples were collected from Murree from fifteen sites, fourteen urban sites and one rural and relatively clean site at least 1km away from any population center. As can be seen from Table 1, the sampling sites are divided into three groups. Group-I includes samples from the urban sites situated away from the city center. Group-I sites are urban suburbs areas of Murree. These sites have hotels, restaurants, shops ranging from grocery shops to car repairs and some sites like S1 have seen a rapid rise in commercial apartments and residences. Group-II sites cover the major city center of Murree. Group-II includes all aspects of a vibrant city except an industrial area. To make a comparison, the sample in group-III was collected from a barren farm that is in a relatively unpolluted environment away from any road. Detailed sampling sites profiles are listed in Table 1. The study area map is given in Fig. 1.

Sample collection and pre-treatment

The soil samples were collected from a depth of 0–10 cm. To obtain uniformity in the samples, at each site 4 samples were collected within a radius of 10 m and mixed thoroughly. Each sample (~ 1 kg) was collected using latex gloves and a plastic scoop. The samples from each site were collected in labeled polyethylene zip bags to avoid any contamination. The samples were collected in March 2023, at the beginning of the spring season. The collected samples were then transported to the lab for pre-treatment and analysis. In the laboratory, the samples were air dried and then sieved using a vibrating sieve shaker. Homogenous samples were thus prepared for both elemental and radionuclide analysis. For natural radioactivity measurements ~ 100 g of each sample were sealed in identical bottles for 40 days to achieve secular equilibrium.

Table 1 Sampling sites along with their co-ordinates and altitude

Sample ID	Name of the site	Location		Altitude (m)	Site description
		Latitude	Longitude		
S1	Kashmiri Bazar	33.9381	73.4467	2009	Group-I
S2	Kohsar Market	33.9716	73.4605	1770	
S3	Ausia	33.9935	73.4736	1525	
S4	Dewal Bazar	34.0077	73.4790	1342	
S5	Phagwari Bazar	33.9827	73.4967	1316	
S6	Aliyot Bazar	33.9490	73.4768	1543	
S7	Sehar Bagla	33.9195	73.4616	1772	
S8	Lower Topa	33.8963	73.4336	2000	
S9	GPO Murree	33.9071	73.3945	2191	Group-II
S10	Kashmir Point	33.9138	73.4044	2250	
S11	Kohsar University	33.9161	73.4062	2220	
S12	Jhika Gali	33.9150	73.4204	2086	
S13	Sunny Bank	33.9170	73.3924	1984	
S14	Company Bagh	33.8604	73.3270	1389	
S15	Bhurban	33.9656	73.4534	1758	Group-III

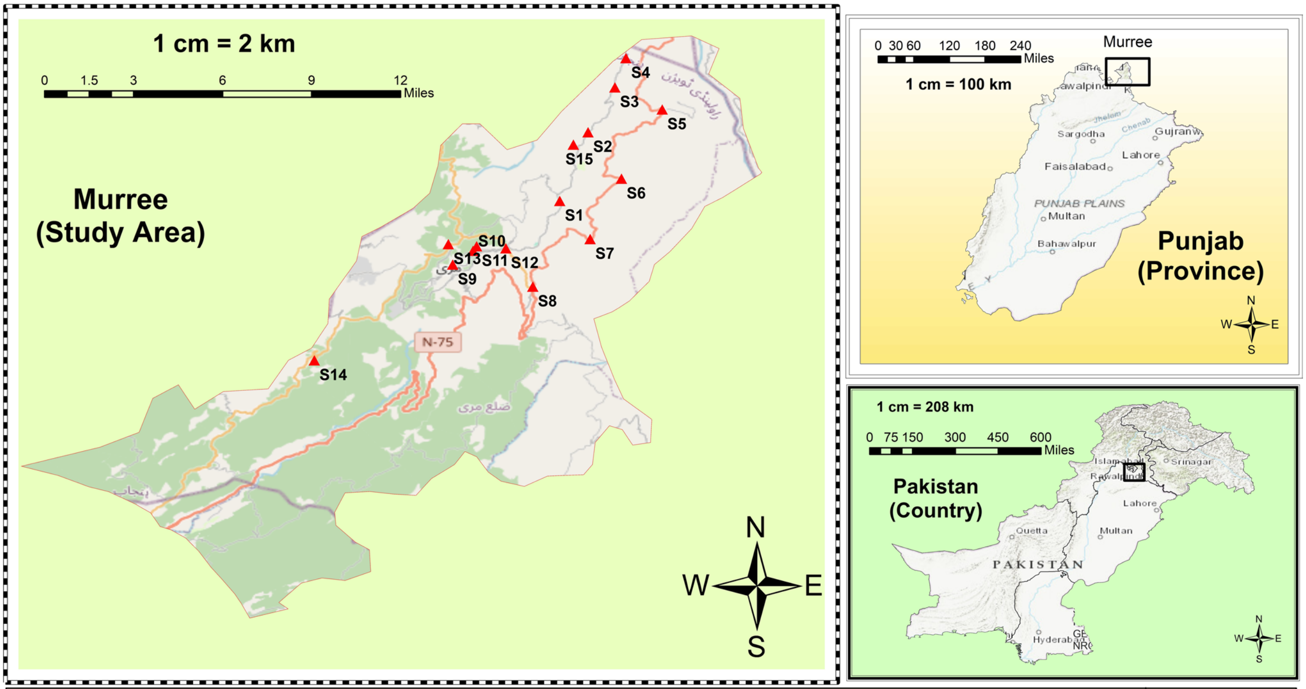

Fig. 1 Study area map

Sample digestion for ICP-OES

Before digestion, the glassware and plastic apparatus used in this study were soaked in 20% (v/v) HNO_3 solution and then washed with de-ionized water. Four-Acid digestion (Lichte et al. 1987) was used in this study to determine the elemental composition of soil samples. One gram of sample was directly weighed into a 125 mL Teflon beaker. After the addition of 1g of soil, 5 mL concentrated nitric acid (HNO_3), 5 mL concentrated hydrochloric acid (HCl), 15 mL concentrated hydrofluoric acid (HF) and 2.5 mL concentrated perchloric acid ($HClO_4$) were added into the beakers. The samples were then placed on a hotplate at 190–200 °C and evaporated near to dryness. The beakers were then half-filled with 10% HCl and placed on a hot plate at 100 °C. The solutions were then removed, cooled, and filtered into 50 mL flasks once the residue had dissolved. Each sample then received one mL of boric acid (H_3BO_3; 50 g/L) to complex any remaining hydrofluoric acid that could otherwise cause deterioration of the ICP glassware in the sample introduction system. Finally, each extracted solution was diluted up-to 50 mL using 10% HCl and transferred to clean plastic bottles. ICP-OES was performed at the Plasma Spectroscopy Lab of the Central Analytical Facility Division (CAFD) PINSTECH Islamabad. All chemical reagents used for digestion were of analytical grade.

Instrumentation and quality assurance

The present investigation involved utilization of ICP-OES for elemental analysis. The specific instrument employed for this purpose is the ICAP 6500, manufactured by Thermo-Scientific, United Kingdom. The experimental parameters for ICP-OES in the present study are presented in Table S1. For Quality Assurance (QA) purposes, NIST 2710a Standard Reference Material (Montana Soil) was also digested along with the samples, and subsequent elemental analysis was conducted on both the SRM and the samples. The results obtained for the SRM were compared with the certified values by calculating the z-scores as given below:

$$z - score = \frac{Value_{exp} - Value_{cer}}{\sigma_{cer}} \quad (1)$$

where $Value_{exp}$ is the experimental value for the SRM, $Value_{cer}$ is the certified value and σ_{cer} is the uncertainty at 1σ given in the NIST 2710a certificate.

Criteria for reliability of the results, using z-scores, are:
$|z_{score}| \leq 2$, performance is considered satisfactory,
$2 < |z_{score}| < 3$, performance is questionable and.
$3 \leq |z_{score}|$, performance is unsatisfactory.

The z-scores for NIST 2710a (Montana Soil) obtained during this work have been plotted in Fig. 2. All the elements showed satisfactory performance except for Na, Sr, Zr

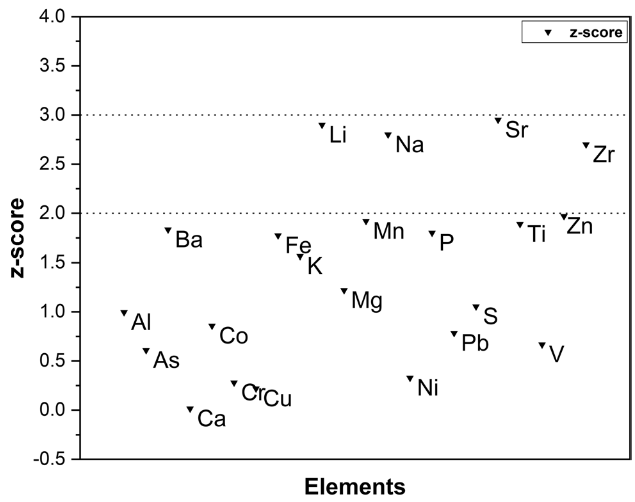

Fig. 2 Z-score values for elements

and Li, which showed questionable performance. Therefore, the results for these elements have not been used in calculation of pollution indices and other parameters. The plotted values of percentage recoveries for each element from NIST 2710a SRM are given in Fig S.

For quantification of carbon, nitrogen, and oxygen the Organic Elemental Analyzer (CHNSO Flash 2000 Thermo-Scientific) was used. The choice of carrier gas was helium (99%), whereas the oxidation process was carried out using oxygen (99%).

Activity concentrations measurements of NORMs in soil were conducted using a high purity germanium detector (HPGe), Canberra model (AL-30). The detector was connected to a PC-based multichannel analyzer (Inter-Technique type pro-286e) through a highly sensitive spectroscopic amplifier (Ortec model 2010). The data acquisition process utilizes Inter-gamma version 5.03 software. The resolution of the system is 1.9 keV for the peak corresponding to the energy of 1332.5 keV generated by Co-60. Soil standards SO0103, SO0309 and SO0303 were used to calculate the activity of NORMs in the soil samples by comparative method. These standards were provided during Quality Assurance Programme (QAP) conducted by the Department of Energy (DOE), USA from 1998 to 2004 (Siddique et al. 2006). These are matrix matched standards. Each sample and SRM was counted for 57,300 s.

Pollution study

Soil contamination levels can be determined by utilizing different pollution indices given in the literature. In this study contamination level was assessed by calculating Enrichment Factor (EF), Geo-accumulation Index (I_{geo}), Pollution Index (PI), Integrated Pollution Index (IPI) and Ecological Risk Factor(ERF), details of which are given in Table 2. The background values used in this study are given in Table S9, calculated by Wedepohl (1995).

Health hazards

Risk assessment is a systematic procedure aimed at evaluating the probability of adverse health outcomes within a specified timeframe for a particular anticipated quantity. Each contaminant's health risk assessment is often based on an estimation of the risk level and is categorized as posing either carcinogenic or non-carcinogenic health risks (Koller and Saleh 2018). The assessment of non-carcinogenic risks to human health involves evaluation of various factors, including the average daily dose (ADD) in mg/kg/day, hazard quotient (HQ), and hazard index (HI). These factors are considered for different types of exposure, namely ingestion, inhalation, and dermal contact (Zárate-Quiñones et al. 2021). The detailed profile for health hazards is given in Table 3.

Activity calculations

The activity concentrations of ^{226}Ra and ^{232}Th were calculated using the photo-peaks of their daughters, i.e. for ^{214}Pb 351 keV, for ^{214}Bi 609 and 1120 keV and for ^{228}Ac, 911 keV. Photo-peaks at 662 keV and 1460.8 keV were chosen for ^{137} Cs and ^{40}K activity, respectively. The specific activities for ^{226}Ra, ^{232}Th, ^{137} Cs and ^{40}K were calculated using comparative method (Wasim et al. 2016), using the standards SO0303, SO0309 and SO0301 (Siddique et al. 2006) with 21-07-2023 being the reference date.

Radionuclide hazard calculations

Radionuclides present two types of hazards: external and internal. The external risks were quantified using Ra_{eq} (Radium equivalent activity), D_{out} (Outdoor external dose), and E_{out} (Annual outdoor effective dose). The indoor risks caused by radionuclides were measured using D_{in} (Indoor external dose) and E_{in} (Annual indoor effective dose). The carcinogenic risk of radionuclides was assessed using LCR_{in} (Lifetime Cancer Risk for indoor exposure) and LCR_{out} (Lifetime Cancer Risk for outdoor exposure), obtained using formulae given in Table 4 (Younis et al. 2021).

Results and discussion

The elemental composition of soil samples from 15 sites of Murree, obtained using ICP-OES and Organic Elemental Analyzer are given in Table S3. The average metal concentrations, in mg/kg, were found to be: Ca (47,761), Al

Table 2 Pollution indices parameters, formulae, and description

Parameter	Formulae	Description	Acceptance criteria	References
Enrichment factor (EF)	$EF = \left(\frac{C_n}{Al}\right)_{Sample} \Big/ \left(\frac{C_n}{Al}\right)_{Background}$	Enrichment factor (EF) identifies the variation of elemental concentrations with respect to background values. Background values here were taken from Wedepohl, and the formula used to calculate EF in this work is given by Taylor. Here, C_n is the concentration of a particular element and 'Al' is the concentration of Aluminum in the sample and background respectively	EF < 2 = minimum; EF 2–5 = moderate; Ef 5–20 = Significant; EF 20–40 = very high; EF > 40 = extreme	Wedepohl (1995), Taylor (1964), Jain et al. (1997a, b)
Geo accumulation Index (Igeo)	$I_{geo} = ln\left(\frac{C_n}{1.5} \times B\right)$	Geo accumulation index (I_{geo}) is used to identify the pollution level in an environmental sample. C_n is the concentration of an element in the sample and B is the background value	$I_{geo} \leq 0$ = not polluted; $0 < I_{geo} < 1$ = not polluted—moderately polluted; $1 < I_{geo} < 2$ = moderately polluted; $2 < I_{geo} < 3$ = moderate—strong pollution; $3 < I_{geo} < 4$ = Strong Pollution; $4 < I_{geo} < 5$ = Strong—very strong pollution	Nusrat, et al. (2021)
Pollution and Integrated Pollution Index (PI & IPI)	$PI = \frac{C_n}{B}$ $IPI = \sum PI$	Pollution Index (PI) shows the concentration w.r.t background value. The IPI for a site is calculated as the mean value of the pollution index for each element. For PI. C_n is the concentration of each element while B is the background value in mg/kg	PI ≤ 1, IPI ≤ 1 = Low; 1 < PI ≤ 3, 1 < IPI ≤ 2 = Moderate; PI > 3, IPI > 2 = High	Shah, et al. (2022a, b)
Ecological risk factor (ERF)	$ERF = \frac{C_n \times T}{B}$	The potential ecological risk of a metal is expressed quantitatively using an ecological risk factor (ERF). $\boldsymbol{C_n}$ is the concentration of a metal in mg/kg, B is its background value and **T** is its toxic response factor. Toxic response factor values for various metals are, Zn = 1; Pb = 5; Ba = 2; Cu = 5; Co = 5; Ni = 5; Cr = 2; Mn = 1; As = 10	ERF < 40 = Low; 40 < ERF < 80 = Moderate; 80 < ERF > 160 = Considerable; 160 < ERF > 320 = High; ERF > 320 = Very High	Kamani et al. (2017)
Carbon to nitrogen ratio (C/N)	$\frac{C}{N}$	Both carbon and nitrogen play vital roles in supporting plant growth, and evaluating their ratio can provide valuable insight into the quality of the soil. Rapid mineralization occurs when the carbon to nitrogen ratio falls within the range of 1 to 15, whereas microbial immobilization is observed when the carbon to nitrogen ratio exceeds 30	The ideal carbon to nitrogen ratio for soil microorganisms and subsequent plant growth is 24	Jain et al. (1997a, b)
Total organic matter (TOM)	$TOM = \%C \times 1.72$	Organic matter is typically present in smaller amounts in soil (1–6%) but plays a major role in improving soil quality. It helps in retention of essential nutrients in soil and makes the soil more fertile by enhancing microbial activity. %C is the percentage concentration of carbon, while 1.72 is the conversion factor assuming that Total Organic Matter (TOM) contains 58% organic carbon	A soil is considered to be of good quality if its organic matter percentage is 12–18%	Jain et al. (1997a, b)

Table 3 Health hazards indices from heavy metals

Parameters	Formulae	Description	References
Average daily dose ingestion Average daily dose inhalation Average daily dose dermal	$ADD_{ing} = \frac{C \times RIng \times EF \times ED \times 10^{-6}}{W \times AT}$ $ADD_{inh} = \frac{C \times Rinh \times EF \times ED}{PEF \times W \times AT}$ $ADD_{der} = \frac{C \times SA \times AF \times ABF \times EF \times ED \times 10^{-6}}{W \times AT}$	Here, 'C' is the concentration of a given metal in mg/kg. 'R_{Ing}' and 'R_{Inh}' are rate of ingestion and rate of inhalation respectively. 'EF' is the exposure frequency in days/year, 'ED' is the exposure duration in years, 'W' is the body weight in kg, 'AT' is the average time in days 'PEF' is particle emission factor, with unit m^3/kg, 'SA' is the surface area of the exposed skin in cm^2, 'AF' is the skin adherence factor expressed in mg/cm^2, 'ABF' is the unitless dermal absorption factor (Ahmad et al. 2021). The values of each of these parameters are, RING (mg/day) = 100 for adults, 200 for children; EF (days/year) = 180for both; RINH (mg/cm2) = 20 for both; SA (cm2) = 2145 for adults, 1150 for children; ED (Years) = 24 for adults, 6 for children; W (kg) = 70 for adults, 15 for children; PEF (m3/kg) = 1.3×10^9 for both; AT (days) = 8760 for adults, 2190 for children; ABF (As) = 0.03, ABF (other metals) = 0.001	Ahmad et al. (2021, Irshad et al. (2019)
Hazard quotient	$HQ = \frac{ADD(Ingestion,Inhalation,Dermal)}{RFD}$	Hazard Quotient (HQ), which is commonly used to quantify the possible non-carcinogenic risk of metals exposure to humans through three different pathways, is the ratio of ADD and RfD, which stands for chronic reference dose for each metal in mg/kg /day. Risk is regarded as minimal to low if the value of HQ is less than or equal to 1, and the exposed population of receptors will not experience any unfavorable consequences. The RFD values used in this work are given in Supplementary data	Ahmad et al. (2021), Irshad et al. (2019)
Hazard Index	$HI = \sum HQ = HQ_{Ing} + HQ_{Inh} + HQ_{Der}$	The sum of each pathway's hazard quotients is the hazard index (HI). Negative, non-carcinogenic health impacts are thought to be unlikely to arise for HI values < 1, whereas HI values > 1 suggests a possibility for such health effects	Ahmad et al. (2021), Bello et al. (2019)

Table 3 (continued)

Parameters	Formulae	Description	References
Cancer Risk For Lifetime Exposure	$CRLE = \left(\sum ADD\right) \times CSF$	This relation was used to calculate the Cancer Risk for Lifetime Exposure (CRLE) for cumulative exposure. The cancer slope factor, CSF, and the average daily dose, ADD, are used in the formula. RFD and CSF values for various metals are provided in Table S2	Ahmad et al. (2021), Koller and Saleh (2018)

Table 4 Radiation hazard indices formulae and description

Parameter	Formulae	Unit	Description	References
Radium equivalent	$Ra_{eq} = \left(\frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810}\right) \times 370$	Bq/kg	Radium Equivalent (Ra_{eq}) (Bq/kg) is used to estimate the risks related to materials containing Radium-226, Thorium-232 and Pottasium-40. ^{226}Ra, ^{232}Th and ^{40}K activity concentrations are A_{Ra}, A_{Th} and A_K respectively	Younis et al. (2021)
Outdoor external dose	$D_{out} = 0.462A_{Ra} + 0.604A_{Th} + 0.0417A_K$	nGy/h	It is used to quantify the risks associated with gamma radiations for outside exposure	Younis et al. (2021)
Annual outdoor effective dose	$E_{out} = D_{out} \times 1.22 \times 10^{-3}$	mSv/y	The goal of this evaluation is to quantitatively assess the annual risks associated with external exposure to gamma radiation	Younis et al. (2021)
Indoor external dose	$D_{in} = 0.92A_{Ra} + 1.1A_{Th} + 0.08A_K$	nG/h	It is used to quantify the risks associated with gamma radiations for internal exposure	Shah et al. (2022a, b)
Annual indoor effective dose	$E_{in} = D_{in} \times 4.905 \times 10^{-3}$	mSv/y	Annual Indoor External Dose is used to evaluate the potential risks associated with annual internal exposure to gamma radiation	Shah et al. (2022a, b)
Lifetime Cancer Risk	$LCR_{out} = E_{out} + L_E + R_F$ $LCR_{in} = E_{in} + L_E + R_F$	–	Lifetime cancer risk calculation describe the potential carcinogenic hazards linked to exposure to gamma radiation. Here, LCR_{out} and LCR_{in} are the lifetime cancer risks from outdoor and indoor exposure respectively. L_E is the life expectancy and it is taken as 66 years. R_F is the fatality risk factor per sievert, which is taken as 0.05 as per ICRP (1991) (James et al. 1991; UNSCEAR 2000)	Shah et al. (2022a, b)

(43,757), Fe (27,224), Mg (8193), Ti (2974), Mn (520), Ba (157), Zn (122.3), Zr (111.3), V (90), Cr (80.62), Pb (36.75), Ni (27.55), Cu (19.50), Co (9.39), As (5.6), and Sn (3.01) while the mean concentrations of P, S, C, N and O in mg/kg were 861, 259, 41,280, 6080 and 72,626 respectively (Table S3). Spatial distributions of Cu, Cr, As, Pb, Zn, and Mn are given in Fig. 3, plotted using interpolation method in ESRI ArcGIS. The As content in soil ranged from 2.27 to 8.93 mg/kg. Copper concentration ranged from 3.36 to 51 mg/kg and has low to moderate values for Group I sites and moderate to high values for Group II sites. Chromium levels ranged from 55 to 107 mg/kg and had no consistent trend. High Cr values were observed at certain sites from both Groups I and II. The Pb concentrations were high for

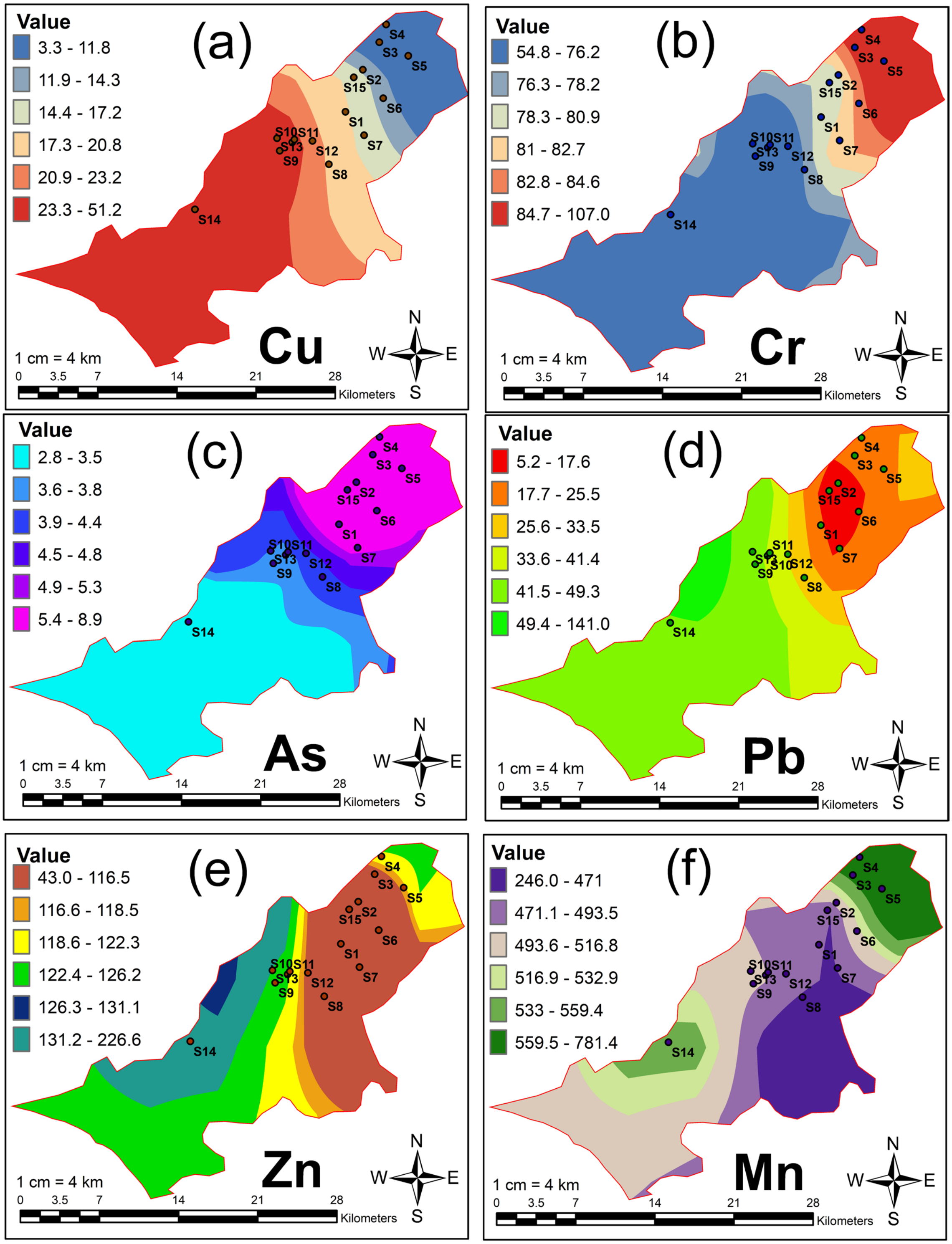

Fig. 3 Spatial variation of Cu (**a**), Cr (**b**), As (**c**), Pb (**d**), Zn (**e**), and Mn (**f**) in the soil of Murree

Group II sites S11 (93 mg/kg), S12 (64 mg/kg), and S13 (141 mg/kg) located near the city center, and low to moderate for Group I sites. Zinc is present in higher amounts at S1 (226 mg/kg) and S13 (188 mg/kg). Higher levels of V, Co, and Ni were observed at the group-II sites in comparison to the city center (Fig. 4).

For comparison, the average elemental composition of urban soils of Pakistan, Islamabad (Daud et al. 2009),

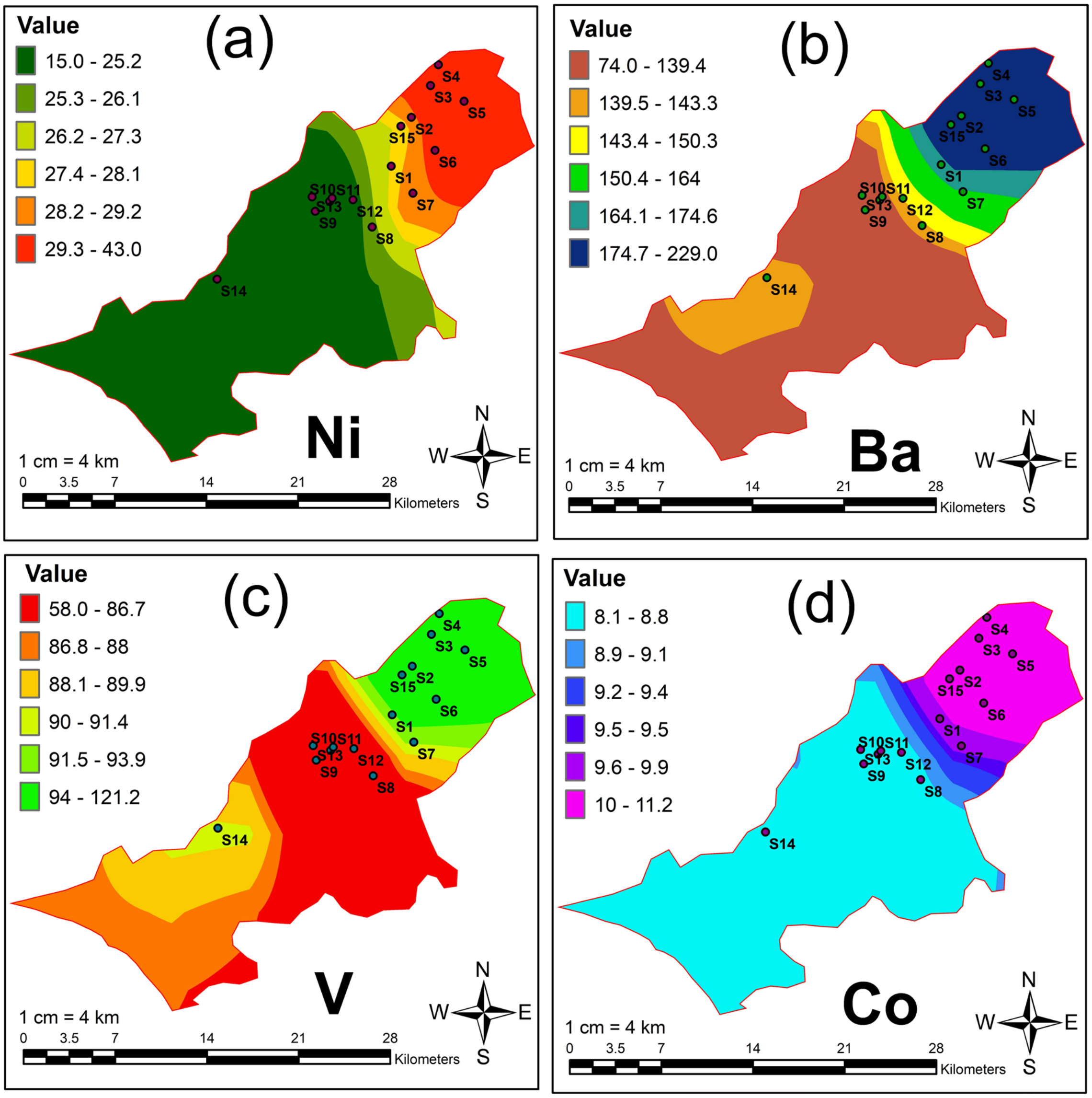

Fig. 4 Spatial distribution of Ni (**a**), Ba (**b**), Co (**c**) and V (**d**) in the soil of Murree

Gadoon Amazai (KPK) (Hussain et al. 2015), Hunza (Wasim et al. 2016), Sialkot (Malik et al. 2010), global average (Aleksonko 2014) and Murree (current study) are given in the Table 5. The mean concentration of Pb in the soil of Murree is comparatively higher than that of Islamabad, but lower than Sialkot, KPK, and the global average. The mean concentration of Chromium in (mg/kg) within the soil of Murree is found to be greater than the global average and Hunza, but comparatively lower than Sialkot, KPK, and Islamabad. The mean values of Zn in this work exhibit higher levels in comparison to Hunza, Islamabad, and Sialkot, although they are comparatively lower than those observed in KPK and the global average. The concentrations of Cu, As, Mn, Co, Ba, Ti, S, Sn, and P in the soils of Murree are comparatively lower than those found in other locations in Pakistan and the global average. Therefore, compared to the sites mentioned in Table 5. Murree appears to be a cleaner city for most elements.

The acquired data was examined using Principal Component Analysis (PCA). The sampling sites were divided into three groups (explained earlier), and PCA findings are nearly identical for each group as can be seen in the biplot in Fig. 5. Aside from S1 site sample, samples that were gathered outside of the city center are placed in PC1. Similarly, apart from S9 site sample, PC2 includes all the sampling locations inside or close to Murree City. S1 site, Kashmiri Bazar, is urbanizing rapidly, therefore its inclusion in PC2 is appropriate. However, S9 was obtained from GPO Murree,

Table 5 Comparison of elemental concentration in mg/kg of urban soils with current study

Elements	Islamabad	Gadoon Amazai (KPK)	Hunza	Sialkot	Murree (This Study)	World Average
Al	51,950	–	76,250	–	43,757	38,200
As	8.42	–	8	–	5.64	15.9
Ba	280.5	–	548	–	156	853.12
Ca	98,366.5	4088	86,250	6991	47,761	53,800
Co	29.5	32.5	13.8	35.50	9.40	14.1
Cr	101	301	48.2	155	80.63	80
Cu	22.67	144	–	26.85	19.5	39
Fe	31,554	1097	36,875	17,991	27,224	22,300
K	14,633.5	689	27,000	5515	13,502	13,400
Mg	11,816.5	786	28,000	6211	8193	7900
Mn	543.5	2508	613	-	519	729
Ni	–	59	–	85.46	27.5	33
P	–	–	–	–	861.8	1200
Pb	27.6	152	–	121.40	36.7	54
S	–	–	–	–	259.5	1200
Sn	19	–	–	–	3.02	6.8
Ti	5338	–	–	–	2974.2	4758
V	72.95	–	92	–	89.8	104.9
Zn	51.965	359	82.2	94.20	122.9	158
C	–	–	–	–	41,300	45,100
N	–	–	–	–	6100	10,000
O	–	–	–	–	72,600	490,000
References	Daud et al. (2009)	Hussain et al. (2015)	Wasim et al. (2016)	Malik et al. (2010)	This study	Alekseenko (2014)

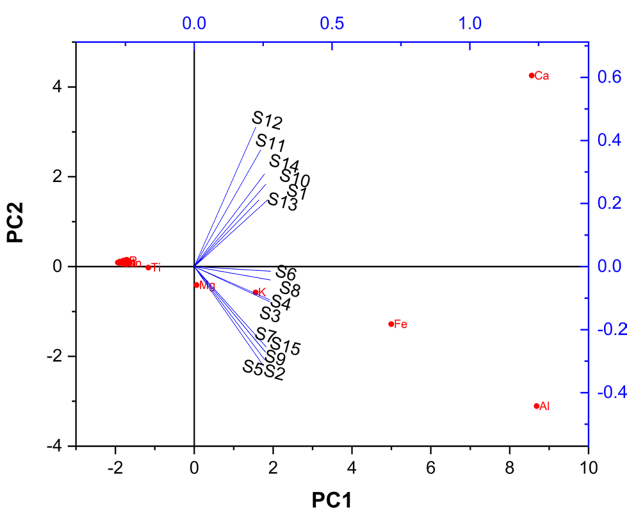

Fig. 5 Bi plot of samples and elements by calculating covariance matrix

the city center, but it was placed in PC1, so S9 can be viewed as an outlier. This may be due to the replacement of surface soil in the flower beds along the roadside near GPO for better flower growth. The classification is further supported by the fact that PC2 sites have significantly higher average concentrations of several elements, such as Pb, Zn, S, P, and Cu, than PC1 sites do. The biplot in Fig. 5 demonstrates that the three elements Ca, Fe, and Al are primarily responsible for the highest elemental variance between the two Groups.

A correlation matrix was also obtained to link the elements together and find their possible sources. The correlation matrix for elements is given in Table S5. From the matrix it was found that the following sets of elements highly co-relate with each other:

Set 1: Al, Ba, K, Fe, Mg.
Set 2: Co, As, Cr, Ni, Ti, V, Fe, K.
Set 3: Cu, Pb.
Set 4: Mn, Ti, V.
Set 5: Zn, P, S.

All the elements placed in the above sets co-relate with r = 0.6 or more which show a strong correlation between them. Set 1 and Set 4 components Al, Ba, K, Fe, Mg, Mn, Ti, and V are naturally occurring elements in the earth's crust and are classified as lithophiles, or "rock loving" elements. The weathering of rocks and minerals can cause the deposition of these elements in soil (Christy 2018).

The elements in set 2 are Co, As, Cr, Ni, Ti, V, Fe and K. These elements are grouped together because they are emitted during the burning of fossil fuels, particularly coal (Vouk and Piver 1983). Most of the people in Murree rely on burning wood and coal to heat their homes and for cooking during the chilly winters. Coal is also used in many commercial hotels. Since the advent of pipeline gas, this trend has been declining, but it will take decades for the government to fully supply the entire population with commercial pipeline gas, resources of which are also depleting. Therefore, the burning of coal and wood poses a significant environmental threat to Murree. Set 3 contains Pb and Cu. Leaded fuel is banned in Pakistan, but it has left an imprint on the soil combined with the fact that most of the vehicles use leaded paint which can be deposited on the soil via weathering (Del Rio-Salas et al. 2012; Mwai et al. 2022). Another source of lead is Pb acid batteries which are commonly used in most households, hotels and shops to supply backup power during electricity shutdowns and for storage. Cu is also released by automobiles and can be deposited on the soil via aerosol transport. It is also found in vehicle tires and in lubricating oil of motorcycles and cars (Ozaki et al. 2004). Pb and Cu strongly correlate with each other as their source is automobiles and vehicles. The grouping of Pb and Cu makes a lot of sense given that Murree is a well-known tourist destination and has overwhelming numbers of automobiles and vehicles passing through it every year. Zn, P and S are released during vehicular emissions and their grouping can trace their origin back to the tourist activities in the area.

EF, I_{geo}, Pollution and IPI, and ERF are all valuable indices for figuring out the pollution status of a site from anthropogenic activities. From Fig. 6a it is apparent that most of the elements have minimum enrichment. S1 (Kashmiri Bazar) has substantial Pb and Zn enrichment. Significant As

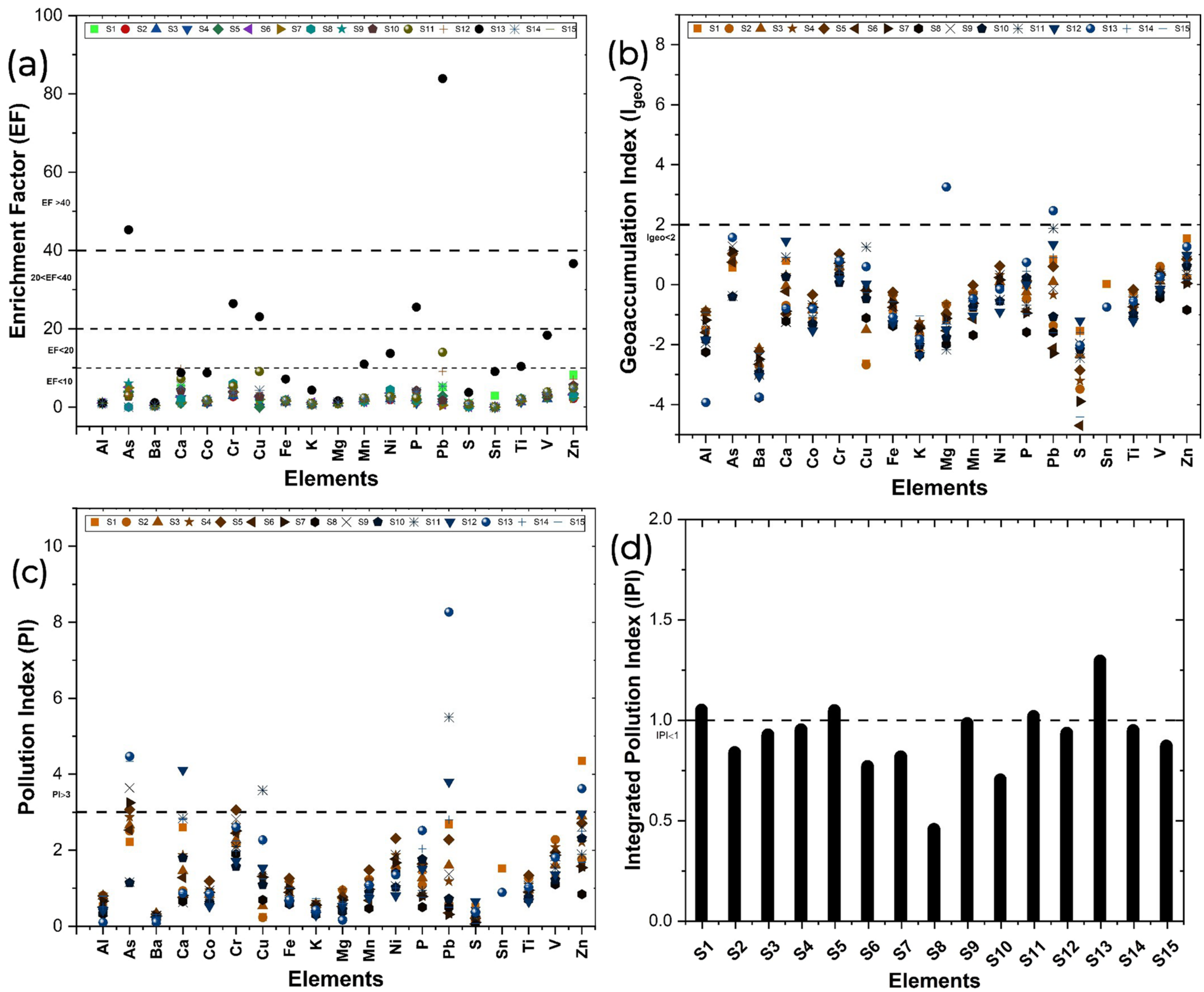

Fig. 6 Plotted values of Enrichment factor (**a**), Geo-accumulation Index (**b**), Pollution Index (**c**) and Integrated Pollution Index (**d**)

and Cr Enrichment is found in S9 (GPO), S6 (Aliyot Bazar), and S8 (Lower Topa), respectively. Sites S11 (Kohsar University) and S12 (Jhika Gali) have notable Ca, Cr, and Pb enhanced concentrations. Quick lime (CaO), which is frequently used to paint roadside walls, eventually mixes with the soil due to weathering, is probably the cause of the Ca enrichment (Li et al. 2019). S13 is significantly enriched in Ca, Mn, Ni and Ti and highly enriched in Cr, Cu, P and Zn. Only S13 (Sani-Bank) exhibits extremely high enrichment in As and Pb. Significant Enrichment of As, is observed in S15. The results of I_{geo} are presented in Fig. 6b and show that most of the sites are clean or have very low pollution levels. The sites S1 and S5, S7, S9, S15 are moderately polluted in Zn and As respectively. Moderate to low levels of pollution in Cu, Ca and Pb are observed at S11 and S12 sites. High levels of Pb pollution are observed at S13, while it is also moderately polluted in As and Zn. The results of PI and IPI are presented in Fig. 6c and d respectively. The majority of these sites display mild to minimal levels of contamination. S5, S7, S9, S13, and S15 exhibit significant As contamination based on PI values. Significant lead contamination is evident in S11, S12, and S13. Locations S13 and S1 show high levels of Zn pollution, whereas S5 and S12 are impacted by significant amounts of Ca and Cr contamination, respectively. Based on the IPI values, it’s evident that majority of the locations show moderate pollution levels, with the most significant pollution found at S13. Figure 7 displays the Ecological risk factor values. ERF values are generally low for most sites, suggesting a low ecological risk associated with heavy metals. At S13 and S15, there is a moderate ecological risk from As and Pb.

The results of Pollution indices show that most of the sites exhibit low pollution levels, with a few exceptions such as S13 (Sani Bank). The majority of the polluted sites are Group-II sites situated close to the city center of Murree. These sites show high levels of Pb and As pollution, along with moderate pollution of Cu, Cr, Ca, Ni, and Zn. The significant Pb pollution levels are due to the weathering of lead paints and the impact of leaded fuel historically used. Furthermore, yellow and white road markings also play a role in Pb pollution (Fuge 2012; Ozaki et al. 2004). High concentrations of As, Cu, Cr and Zn are linked with atmospheric deposition of these elements on soil due to the burning of coal and wood during the winter season in Murree, emissions from heavy traffic and deposition of waste by hotels and tourists alike (Fuge 2012).

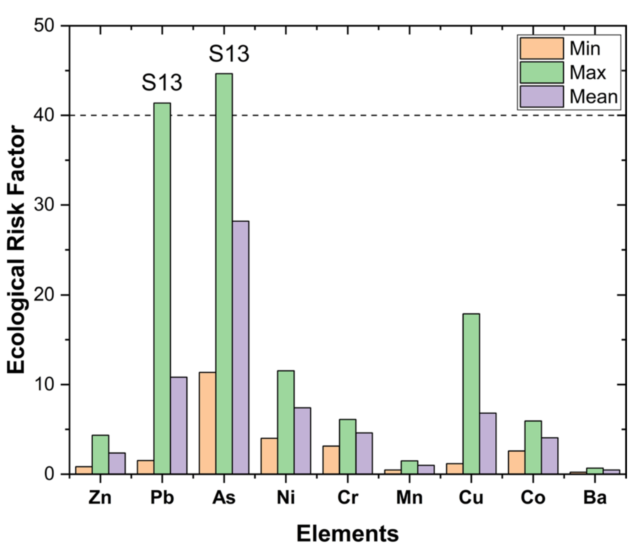

Fig. 7 Bar plot for Ecological Risk Factor (ERF) values

Diesel vehicles are widely used for the transport of goods as well as diesel buses are used as a means of public transport in Murree. Diesel soot contains elevated levels of Ni, Zn and As. The deposition of these metals from diesel soot to the soil explains their elevated levels at some sites (Vellingiri et al. 2022). Cr is found in large concentrations in peeling paintwork and anticorrosive treatments on automotive guardrails, which explains the high Cr values at S8, S11, and S13 (Oves et al. 2012). The moderate levels of Ca pollution can possibly be traced to the quick lime used to paint roadside walls, weathering, and erosion of which can elevate the levels of calcium in soil (Li et al. 2019). What is interesting here is that from Group-I, S1 (Kashmiri Bazar) showed elevated levels of pollution mostly in arsenic, lead, and zinc and S5 (Phagwari) has high levels of As, Cr, Pb and Zn because of transport related activities. Most of the Group-I sites are urbanizing rapidly to accommodate more and more tourists and tourism related activities which is apparent in Kashmiri Bazar’s case. At S1, leakage of sewage and dumping of waste near the road right in the center of the market is a cause for concern and is directly responsible for elevated levels of pollution at S1. The most striking result to emerge from the pollution indices is the presence of elevated levels of arsenic in S15. Since the soil from S15 was collected from an un-polluted site away from the road the presence of high levels of arsenic can have only one source namely poultry waste. Most of the local population near S15 site have domesticated chickens and use commercial chicken feed for their upkeep. Chicken feed contains arsenic, which can be deposited on the soil via chicken waste (Mondal 2020; Wallinga 2006). Hence, the high levels of arsenic at S15 can be explained by this argument. The above reasoning may also explain the high ERF due to Pb at S13 and As at S15. Sn was detected only at sites S1 and S13, possibly from burning of waste at both locations (Harper 2005).

Total organic matter (TOM) and carbon to nitrogen ratios were computed for the fifteen sites, and the results are presented in Fig. 8. Carbon to nitrogen ratios ranged from 2.6% to 15%, well below the 20–30% equilibrium range. The percentages of total organic matter ranged from 2% to 19.4%.

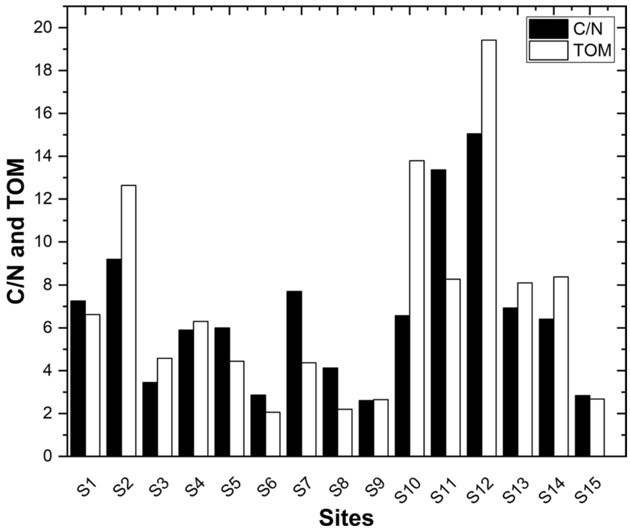

Fig. 8 Carbon–Nitrogen ratio (C/N) and Total Organic Matter (TOM) plotted values

Soil samples taken from locations S10 and S12 fall within the acceptable range for TOM. Most of the soil samples were found to be of low quality. Therefore, soil from these sites is not suitable for optimum crops or plant growth.

Health hazards associated with heavy and toxic metals

The mean concentrations of heavy and toxic metals in mg/kg are below the maximum allowed WHO values of these metals in soil (Ahmad et al. 2021). For both carcinogenic and non-carcinogenic risks, health hazards were assessed for adult and child exposure to these metals.

Average daily dose was calculated for Cu, Pb, As, Ni, Cr, Mn, Ba, Zn, and Co for three exposure pathways, ADD_{ING} (ingestion), ADD_{INH} (inhalation) and ADD_{DER} (dermal). Table 6 shows the calculated values of ADD for the three exposure pathways, both for children as well as adults. The values follow the pattern $ADD_{ING} > ADD_{DER} > ADD_{INH}$ for both adults and children. The highest dose for all metals in ADD of soil was found in ADD_{ING} and ADD_{INH} for children, whereas ADD_{DER} was greater for adults. Apart from Ba, it can be seen from Table 6 that all metals showed the following HQ trend in both adults and children $HQ_{ING} > HQ_{DER} > HQ_{INH}$. Barium followed $HQ_{ING} > HQ_{INH} > HQ_{DER}$ in both adults and children. The Hazard Index (HI) values for Cu, Pb, As, Ni, Cr, Mn, Ba, Zn and Co are 0.3 0$\times 10^{-3}$, 7.61 $\times 10^{-3}$, 13.9 $\times 10^{-3}$, 1.13 $\times 10^{-3}$, 23 $\times 10^{-3}$, 3.49 $\times 10^{-3}$, 2.27 $\times 10^{-3}$, 0.3 3$\times 10^{-3}$, 20.8 0$\times 10^{-3}$, for adults and 2.78 $\times 10^{-3}$, 69 $\times 10^{-3}$, 105 $\times 10^{-3}$, 9.20 $\times 10^{-3}$, 182 $\times 10^{-3}$, 25.2 0$\times 10^{-3}$, 15.4 0$\times 10^{-3}$, 2.70 $\times 10^{-3}$, 207 $\times 10^{-3}$, for children respectively. The highest observed HI value in adults is 0.02 for Cr and in children 0.20 for Co. In

Table 6 ADD, HQ and HI values for adults and children

Metals	Adults			Children			Adults				Children			
	ADD_{ING} $\times 10^{-6}$	ADD_{INH} $\times 10^{-9}$	ADD_{DER} $\times 10^{-8}$	ADD_{ING} $\times 10^{-6}$	ADD_{INH} $\times 10^{-9}$	ADD_{DER} $\times 10^{-8}$	HQ_{ING} $\times 10^{-3}$	HQ_{INH} $\times 10^{-6}$	HQ_{DER} $\times 10^{-6}$	HI $\times 10^{-3}$	HQ_{ING} $\times 10^{-3}$	HQ_{INH} $\times 10^{-6}$	HQ_{DER} $\times 10^{-6}$	HI $\times 10^{-3}$
Cu	11.9	0.17	5.11	111	8.11	4.4	0.21	0.004	4.26	0.3	2.78	0.2	3.73	2.78
Pb	25.9	8.93	11.1	242	17.6	9	7.40	2.75	212	7.61	69	5.43	186	69
As	3.18	0.04	40.9	30	2.17	35.8	10.5	0.15	3333	13.9	102	7.22	2910	105
Ni	19.4	140	8.33	181	13.2	7.3	0.9	6.79	154	1.13	9.06	0.6	135	9.20
Cr	56.8	0.83	24.4	531	38.7	21.4	18.9	29.2	4062	23.0	177	1350	3560	182
Mn	366	5.39	157	3420	250	138	2.62	0.038	873	3.49	24	1.78	765	25.2
Ba	111	84.9	47.4	1030	75.3	41.6	1.58	594	96.8	2.27	14	527	84	15.4
Zn	86.6	1.27	37.2	809	59	32.6	0.28	0.0042	6.20	0.3	2.70	0.19	5.43	2.70
Co	6.23	0.009	2.84	60	4.51	2.4	20.8	17.1	1.78	20.8	206	790	1.56	207

both adults and children, the HI values for each metal were less than 1, indicating no appreciable health risk. However, children have HI values for each metal 8–10 times higher than adults. Higher hazard index values for children in Murree indicates an increased risk of non-carcinogenic health issues caused by heavy metals due to prolonged exposure. The carcinogenic risk to adults and children was calculated using cancer risk from lifetime exposure (CRLE) of metals and the values are given in Table 7. Cr posed cancer risk in both adults and children while As in children is above the limit of 1×10^{-6} set by US-EPA (Irshad et al. 2019). Carcinogenic metals, such as Cr and its compounds, induce oxidative stress and contribute to the development of cancer. Exposure to Cr(VI) results in DNA epigenetic modifications, which in turn lead to genetic changes in gene expression and consequently cancer (Iyer et al. 2023). The total cancer risk posed by Cr in children is 3×10^{-4} and in adults is 4×10^{-5}. However, it is unclear which oxidation state Cr exists in + 3 or the more toxic + 6. Therefore, the full extent of the danger to human health cannot be determined. This may be undertaken in future work given the higher amounts of Cr measured in Murree. The cancer risk value for As (4×10^{-5}) exceeded the threshold value for children only. Inorganic arsenic has a tendency to induce cancer, skin conditions, and neurological issues (Irshad et al. 2019; Mondal 2020). Children are therefore more vulnerable than adults

Table 7 Carcinogenic risk calculated for various metals for three exposure pathways

	Adults					Children				
	$CRLE_{Ing}$	$CRLE_{Inh}$	$CRLE_{Der}$	$CRLE_{Total}$	Cancer Risk	$CRLE_{Ing}$	$CRLE_{Inh}$	$CRLE_{Der}$	$CRLE_{Total}$	Cancer risk
Cu	–	–	–	–	–	–	–	–	–	–
Pb	2×10^{-7}	–	5×10^{-9}	2×10^{-7}	No	2×10^{-6}	–	4×10^{-9}	2×10^{-6}	No
As	4×10^{-6}	7×10^{-11}	6×10^{-7}	5×10^{-6}	No	5×10^{-5}	3×10^{-9}	5×10^{-7}	$\mathbf{4 \times 10^{-5}}$	**Yes**
Ni	–	1×10^{-6}	–	1×10^{-6}	No	–	1×10^{-7}	–	1×10^{-7}	No
Cr	$2 \times 10–^{5}$	–	9×10^{-6}	$\mathbf{4 \times 10^{-5}}$	**Yes**	3×10^{-4}	–	8×10^{-6}	$\mathbf{3 \times 10^{-4}}$	**Yes**
Mn	–	–	–	–	–	–	–	–	–	–
Ba	–	–	–	–	–	–	–	–	–	–
Zn	–	–	–	–	–	–	–	–	–	–
Li	–	–	–	–	–	–	–	–	–	–
Co	–	$9 \times 10^{-}$	–	9×10^{-10}	No	–	4×10^{-8}	–	4×10^{-8}	No

Table 8 Activities of Ra-226, Th-232, K-40 and Cs-137 in Bq/kg

Sites	Ra-226	Th-232	K-40	Cs-137
S1	21.6 ± 12.3	12. ± 3.9	426.7 ± 71	ND
S2	30 ± 17.7	18.8 ± 5.3	494.1 ± 82.6	ND
S3	26.1 ± 14.8	16.9 ± 4.7	499.5 ± 83	6.9 ± 2.8
S4	33.2 ± 18.7	18.2 ± 5	543.1 ± 90	ND
S5	22.2 ± 13.2	14.3 ± 4	509.8 ± 85	ND
S6	32.1 ± 16.2	17.7 ± 5.1	592.7 ± 99	ND
S7	26.9 ± 14	19.3 ± 5.4	538.6 ± 90	ND
S8	27.7 ± 17.1	16.3 ± 5.5	558.5 ± 93.4	ND
S9	26.1 ± 14.1	15.8 ± 4.5	484.3 ± 81	12.3 ± 5
S10	24.3 ± 15.6	14.9 ± 4.3	443.0 ± 74	ND
S11	30.5 ± 16.4	14.3 ± 4.1	443.9 ± 74.2	ND
S12	20.7 ± 11.7	12.6 ± 3.7	383.5 ± 64	ND
S13	25.4 ± 10.9	20 ± 6.2	466.6 ± 78	ND
S14	27.6 ± 10.6	22.9 ± 4.3	425.3 ± 71	ND
S15	28.3 ± 13	26.6 ± 7.2	629.4 ± 105	4.8 ± 1.9
Mean (This Study)	26.8 ± 14.4	17.4 ± 4.9	495.9 ± 82	8 ± 3.2
Previous Study (Satti et al., 2017)	25	53	368	13.6
World Average (UNSCEAR, 2000)	32	45	420	–

ND = Below detection limit, (Reference date: 27–07-23), values in Bq/kg to cancer risk, where ingestion, dermal and inhalation pathways respectively contribute to CRLE.

Radionuclides

Table 8 presents the measured activity values for Ra-226, Th-232, K-40, and Cs-137, expressed in (Bq/kg) for the reference date of 27-07-23. The measured activity concentrations of Ra-226 varied between 21.6 to 33.2 Bq/kg, with the lowest value observed at S1 site and the highest value observed at S4 site. The average value for Ra-226 is 26.8 Bq/kg, below the global average value of 32 Bq/kg for Radium. The maximum recorded activity concentration of Th-232 is 26 Bq/kg, at location S15, while the minimum recorded activity concentration is 12.1 Bq/kg, observed at location S1. The average activity concentration of Th-232 is lower than the global average. K-40 activities at the sites S15 and S12 are 629.4 Bq/kg and 383.4 Bq/kg, respectively, with S15 having the highest value and S12 the lowest. The mean activity concentration value of K-40 exceeds the world average, probably due to the higher altitude of these sites. Cesium-137 (Cs-137) is not naturally present in the environment, resulting in generally low concentrations in environmental samples. Cs-137 was detected at sampling sites S3, S9, and S15, with corresponding activity concentrations of 6.9, 12.3, and 4.8 Bq/kg, respectively.

PCA was again used for radionuclides. The biplot for radionuclides and sites using PCA can be seen in Fig. 9. A covariance matrix was established using the activities of radionuclides in soil samples. This matrix was then solved for eigen values and eigen vectors. The variance ratios for the newly formed variables (principal components) PC1, PC2, PC3, and PC4 are 0.51, 0.25, 0.13, and 0.09, respectively. Therefore, the first principal component (PC1) was found to correspond with the direction that exhibited the highest degree of variability within the dataset. The second major component, PC2, spans the direction of the second highest variance. Two principal components PC1 and PC2 were sufficient to describe the maximum variance. The linear combination of PC1 and PC2, with respect to the original variables, are given in the equations below.

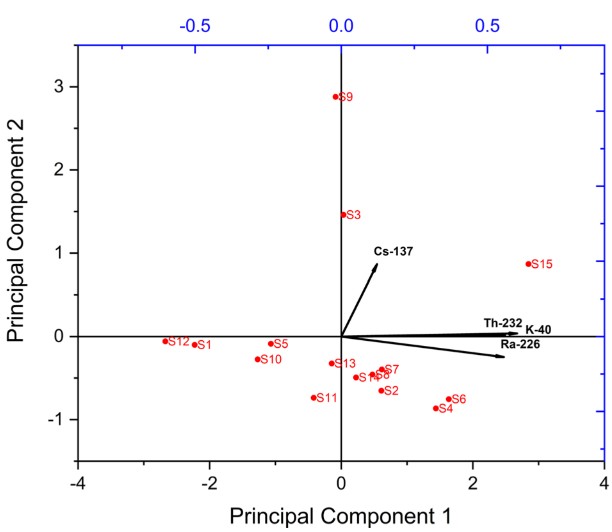

Fig. 9 Biplot for radionuclides using PCA

$$PC1 = 0.56A_{Th} + 0.55A_{Ra} + 0.60A_{K} + 0.12A_{Cs} \quad (2)$$

$$PC2 = 0.018A_{Th} - 0.27A_{Ra} + 0.040A_{K} + 0.96A_{Cs} \quad (3)$$

The loading values obtained from PCA reveal that the primary factors contributing significantly to the observed variation in PC1 are the activities of Ra-226, Th-232, and K-40. Similarly, PC2 exhibits a significant correlation with Cs-137, as seen by its highest loading value of 0.96. The NORMs correspond to PC1 and Cs-137 to PC2. The correlation matrix established between radionuclides can be seen in Table S7. A moderate correlation exists among Th-232, Ra-226, and K-40 due to their natural occurrence. However, Cs-137, being of anthropogenic origin, does not exhibit any correlation with other radionuclides.

The spatial distribution of K-40, Th-232, Ra-226 and Cs-137 is given in Fig. 10. The assessment of the risk associated with radionuclides in soil involves the computation of radiation indices, which are presented in Table 9. The radium equivalent values exhibit a below-average trend as compared to the global values, with a mean value of 38.29 Bq/kg. The values of the outdoor hazard indices are also below the global average. The mean values for D_{out}, E_{out}, and $ECLR_{out}$ have been calculated as 43.58 nG/h, 0.05 mSv/y, and 0.18, respectively. The indoor hazard indices, D_{in}, E_{in}, and $ECLR_{in}$, have mean values of 83.5 nG/h, 0.41 mSv/y, and 1.35, respectively, which surpass the global average. Therefore, Indoor exposure presents a greater risk in the soil of Murree. The annual effective dose is lower than the standard limit of 1 mSv/y proposed by International Committee of Radiation Protection (ICRP) for general public (Ahmad et al. 2015; Eckerman et al. 2012). Overall, the hazards posed by exposure to the natural radiation from the soil of Murree are low, but constant radionuclide monitoring in the soil is suggested.

Conclusion

In this study, the pollution level assessment of urban areas of Murree was carried out along with the health hazards associated with exposure to heavy metals Moreover natural radioactivity was measured along with the health hazards

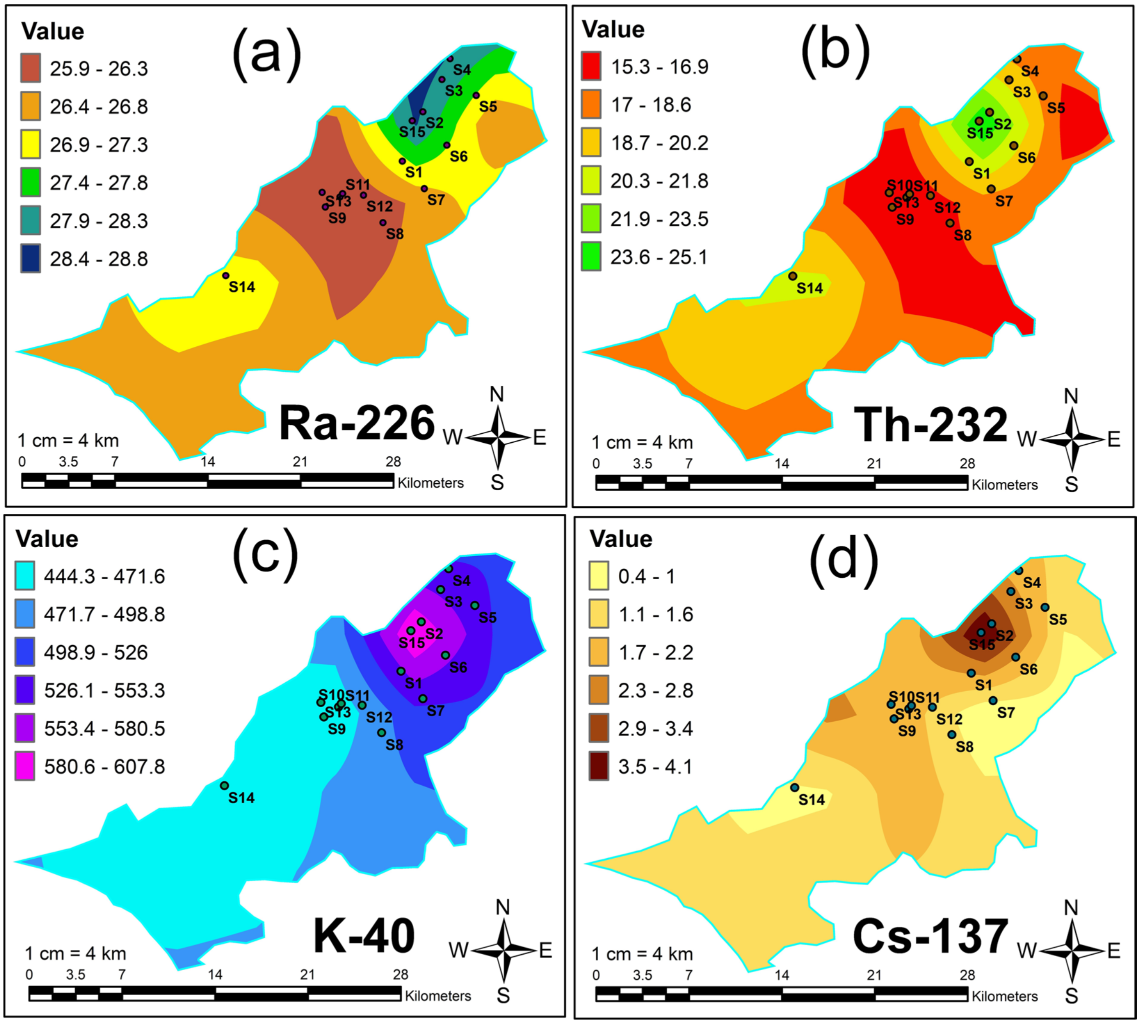

Fig. 10 Spatial variation of specific activity of K-40 (**a**), Th-232 (**b**), Ra-226 (**c**) and Cs-137 (**d**)

associated with natural radionuclides. The possible sources of heavy metal were identified as the combustion of coal, automotive emissions, leaded paints, tourist activities, and natural sources. Pollution indices revealed that the sites near the city center are more polluted than the sites away from it. Ecological risk factor was low for most of the sites with moderate risk at S13 and S15 (Bhurban) posed by Pb and As respectively. It was found that the soils in Murree are of low quality unsuitable for optimal crop or plant growth as their carbon to nitrogen ratios ranged from 2.6 to 15, and total organic matter ranged from 2% to 19.4%. The highest calculated average daily doses for various metals in soil through three exposure pathways: ingestion, inhalation, and dermal was found in children's ADD_{ING} and ADD_{INH}, while ADD_{DER} was high for adults. Children had higher HI values for each metal (8–10 times higher) than adults. It was found that only Cr in children posed a carcinogenic risk. The average specific activities of Ra-226, Th-232, K-40 and Cs-137 in Bq/kg were 26.8 ± 14.4, 17.4 ± 4.9, 495.9 ± 82, 8 ± 3.2 respectively. Health hazards posed by exposure from radionuclides were low and the effective dose per year was well below the standard limit of 1 mSv/y. The overall finding of this study showed that urbanization is leading to pollution of Muree's environment. The exposure to Cr constitutes the primary source of health risks, with children being particularly susceptible to the occurrence of non-carcinogenic and carcinogenic disorders. Further research is needed to assess the long-term effects of urbanization on the health of the population in Murree.

Recommendations

Given the potential for bioaccumulation of heavy and toxic metals, it is recommended to government agencies and the tourism department to implement further measures

Table 9 Health hazard indices for exposure from radionuclides

Sites	Ra_{eq} (Bq/kg)	D_{out} (nGy /h)	D_{in} (nGy/h)	E_{out} (mSv/y)	E_{in} (mSv/y)	$E_{out}+E_{in}$ (mSv/y)	$LCR_{out}\times10^{-3}$	$LCR_{in}\times10^{-3}$	$LCR_{total}\times10^{-3}$
S1	32.9	35	67.3	0.04	0.33	0.37	0.14	1.09	1.23
S2	38.6	45.8	87.8	0.06	0.43	0.49	0.18	1.42	1.61
S3	38.6	43.1	82.6	0.05	0.41	0.46	0.17	1.34	1.51
S4	41.9	48.9	94	0.06	0.46	0.52	0.2	1.52	1.72
S5	39.3	40.1	77	0.05	0.38	0.43	0.16	1.25	1.41
S6	45.4	50.1	96.3	0.06	0.47	0.53	0.2	1.56	1.76
S7	41.5	46.7	89.1	0.06	0.44	0.49	0.19	1.44	1.63
S8	43.1	45.4	88.1	0.06	0.43	0.49	0.18	1.43	1.61
S9	37.9	41.8	80.1	0.05	0.39	0.44	0.17	1.30	1.46
S10	34.2	38.7	74.1	0.05	0.36	0.41	0.16	1.20	1.36
S11	34.2	41.2	79.2	0.05	0.39	0.44	0.17	1.28	1.45
S12	29.6	33.7	63.6	0.04	0.31	0.35	0.13	1.03	1.16
S13	36.4	43.3	82.7	0.05	0.41	0.46	0.17	1.34	1.51
S14	32.8	44.2	84.5	0.05	0.41	0.47	0.18	1.37	1.55
S15	48.5	55.3	105.3	0.07	0.52	0.59	0.22	1.71	1.93
Mean	38.2	43.5	83	0.05	0.41	0.46	0.18	1.35	1.53
World Average (UNSCEAR, 2000)	129	84	59	0.07	0.41	0.52	0.29	1.16	1.45

to restrict vehicular movement in Murree. This can be achieved by imposing further limitations on the number of tourists allowed to enter the area and by introducing environmentally sustainable transportation options for both tourists and residents. Moreover, it is imperative to raise awareness regarding the proper disposal and burning of waste materials. The government should actively support the reduction of pollution resulting from the combustion of coal and wood through the provision of alternative solutions such as renewable energy. It is necessary to conduct a thorough investigation of cancer cases in the urban areas of Murree and determine the extent to which they may be linked to the consumption or exposure to heavy and toxic metals.

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Data availability Data is available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors have not disclosed any competing interests.

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