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Original Research

Characterization of Heavy Metals in Soil as Affected by Different Land Uses in Northern Pakistan

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Abstract

Land use has a greater influence on the contamination of soils. The current research is conducted to study the effect of different land-use patterns and soil depth on heavy metal fractions in the soil. Significant differences among heavy metals (Cd, Cu, Fe, Ni, Pb, and Zn) in soils under various land use systems were observed. Variations in the soil heavy metals concentration were found dependent on land use patterns. Irrespective of the type of metal, Land uses differed for heavy metals concentrations in the order of fallow>pasture>crop>forest soils. Extracting reagents considerably varied for the concentrations of metals: HNO_3>Na_2EDTA>NaOH>KNO_3>H_2O. However, Ni concentration was found higher with NaOH than Na_2EDTA. Surface soil indicated a higher magnitude of heavy metals than sub-surface soil. This study will provide valuable information on heavy metal fractions associated with land use in the Abbottabad region of lesser Himalayas, Pakistan.

Keywords: heavy metals, fallow land, pastureland, crop land, forest land

Introduction

Soil hosts for all nutrients and plays a vitally important role of sink for heavy metals and pollutants. Heavy metal contamination of the environment has been reported as a world-wide matter of concern for scientists and planners. The environment is continuously being contaminated by various human activities that generate contaminants like heavy metals [1]. These activities in the environment gradually result in land use and land cover (LULC) changes. Arrangements, activities, and inputs people undertake in a land cover to produce, change, or maintain the land cover is called land use system. LULC changes play a significant role in ecosystem services [2]. Land use changes have strong influence and impact on the soil physio-chemical properties and its quality. One of the major impacts of such changes is decrease in land use value, vegetation, and soil fertility [3]. In mountainous area like lesser Himalayas the parent material also plays an important role in concentration of heavy metals because of topography that allows the transportation

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of heavy metals in various land uses of the area. Mountain soils are fragile ecosystems, and their high spatial variability originates from their strong dependency on factors such as parent material, climate, and relief [4]. Soil parent material is a primary source of trace elements particularly in weakly developed soils [5]. There are many factors which can have impact on land use. Among these factors land erosion, contamination due to human influence, parent rock mineral and establishment of the infrastructure as result of human development are significantly impacting factors. It is important to understand the influence of land uses on soil quality to have a better policy guideline and its subsequent implementation which ultimately yield in soil quality improvement.

Land utilization is an important factor which affects the heavy metals concentrations in the soils. Heavy metal pollution becomes part of the soil environment through various land uses mostly due to human influence. Therefore, land use pattern has always been associated with anthropogenic activities which could contribute substantial amount of metal into the soil [6-7]. Evolution of environment is mainly influenced by the land use land cover changes. This greatly affect the migration, distribution, and accumulation of the heavy metals in the environment. The anthropogenic activities trigger the contamination of heavy metals in soil. High spatial heterogeneity is found heavy metals acaccumulations in urban soils altered by many factors including land use pattern, soil properties, climatic conditions, and population [7-9]. There are many effects of changing land use patterns on soil heavy metal accumulation with long lasting impact on the environment. Therefore, it is globally viewed with concern as a common problem. This asks for sustainable soil management to continue the soil to provide the associated services [10]. Heavy metals are natural constituents of igneous rocks, sediments, and soils. In mountain regions some of the heavy metals may also be deposited due to environmental factors like wind and precipitation. Urbanization significantly modifies hydrological characteristics of an area [11]. The urban dust and heavy metals of nearby industrial areas and big cities cause pollution on soil surface and various land uses. They deposit excessive amounts of trace metal contaminants aerially across urban soil [12]. Atmospheric aerosols can travel long distances before redepositing, reaching remote areas such as the Arctic and high elevations such as the Himalayan Mountains [13-14]. Their deposition is especially influenced by precipitation and wind, particularly in regional convergence zones, such as mountain ranges, that trap atmospheric contaminants because of cold condensation and enhance atmospheric deposition [14]. Since precipitation tends to increase with altitude until a specific elevation limit and then tends to decrease [15], this factor may influence the distribution of heavy metals in he context of anthropogenic activities. Heavy metals are common persistent toxic pollutants in the environment [16]. Heavy metals have always occurred naturally in the environment, but their concentration has been changed significantly. Some changes, i.e., land usage, management, and deterioration, are the obvious product of human influences [17]. These metals have been known to cause environmental and health problems. Human activities such as industrial production, agricultural processes, mineral exploitation, food processing, commercial, social, and domestic activities generate contaminants like heavy metals [1]. Heavy metals from rubbish landfills also enter the soil after extensive urbanization and intensive agriculture. Therefore, the productivity of soil and its quality should be protected without affecting the ecological functioning of the soil. Heavy metal accumulation in land uses is a threat for soil environment, plants, and all consumers in chain. Therefore, heavy metals in agricultural soils have become a great concern around the world [18-19]. Heavy metal contaminants impact growers and consumers by entering the body through contaminated dust or the consumption of foods grown in the impacted soils [20]. Heavy metals accumulation was recorded higher in industrial land uses as compared to natural land use and under agricultural practices [21].

There is a considerable increase in the concentration of heavy metals in soil due to atmospheric deposition in the central south China [22]. Some studies indicate contrasting results regarding heavy metals in soils of higher altitude, whose characteristics and pedogenic properties were less studied compared to lower altitude soils [23]. The urbanization impact was evaluated in relation to accumulation of heavy metals including Zn, Pb, Cd, and Cu. Their mean concentrations were 96.2, 27.3, 0.139, and 23.5 mg/kg, respectively. Certain urbanization indicators, including distance to city center, age of residential community, distance from sampling point and population density, were observed correlated significantly with contents of Zn, Pb, Cd, and Cu in residential soils [24]. The heavy metals concentration in garden land shows higher values as compared to the arable land [25].

Also, fractionation of heavy metals under the influence of various land use systems have been insufficiently reported earlier in the areas of lesser Himalayan region. Therefore, the study is aimed at characterizing heavy metals in the soils under various land uses in the Abbottabad region in lesser Himalayas.

Materials and Methods

The soil sampling area is land use systems in lesser Himalayan region in Abbottabad, Pakistan. The references of the area are 34°92′N latitude and 73°13′E longitude at an altitude of 4,120 feet above sea level. This area is situated on foothills of lesser Himalaya in Pakistan. Most of the study area comprises of moderately steep slopes. The temperature of the study

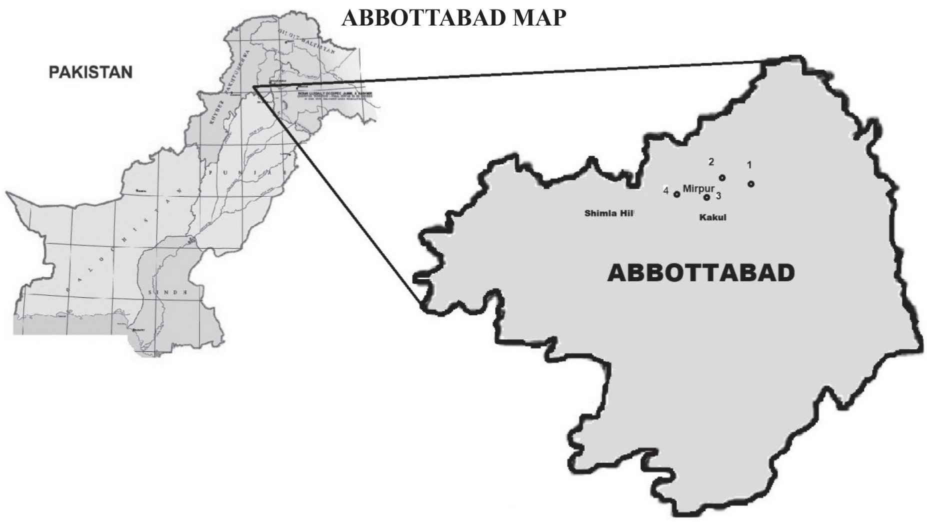

Fig. 1. (Source) Map of Pakistan, Surveyor General of Pakistan, 5th edition, 2020 (1,2,3,4 in Abbottabad representing forest land, pasture land, crop land and fallow land respectively).

area can rise as high as 38ºC (100ºF) during summer and receive appreciable precipitation especially in monsoon. On the other hand, temperature drops below -5ºC (23ºF) during the winters. Surrounding hills are covered with snow for a very short period in December and January.

Soil sampling was one from topsoil (depth 0~25 cm) as well as sub-soil (25~50 cm) from fallow, pasture, crop, and forest land. Within each land use, soil was sampled randomly from three sites 100 meters apart. Samples were physically mixed homogenously, and samples were taken in four replications for laboratory analyses. These samples were air-dried, ground, and then sieved via 2 mm sieve. Total heavy metal concentration in the soil samples was determined after digestion the soil in a mixture of HNO_3-$HClO_4$ (1:5) on hot plate as adopted by [26] with an atomic absorption spectrophotometer. Modified version of sequential extraction procedure was followed to fractionate heavy metals (Cd, Cu, Fe, Ni, Pb and Zn). Sequential extraction was carried out for each soil sample of different land systems using 5 g of soil sample in 50 mL centrifuge tube. The heavy metals were fractionated into exchangeable, adsorbed, organically bound, carbonate precipitated and residual forms by sequential extraction with 0.5 *M* KNO_3, 16 hours; de-ionized water, 2 hours (extracted three times and combined); 0.5 *M* NaOH, 16 hours; 0.05 *M* Na_2 EDTA, 6 hours, and 4 *M* HNO_3 16 hours at 80ºC respectively. In extraction, the sample was centrifuged at 3000 rpm for 15 min. The supernatant was filtered by a 0.22-µm filter. The metal contents in the extract were determined with Atomic Absorption Spectrometer (AAS Perkin Elmer A Analyst 700 made in USA). The standards and patterns used in the tests are Barium (2%) HNO_3 1000 µg/L diluted with doubled deionized water. Statistical analysis of data was done with the help ANOVA.

Results and Discussion

Texture analyses of the soil suggested that generally the soil texture is loamy irrespective of the land use and soil depth. However, sand content further decreased in sub soil. The percentage of sand, silt and clay in fallow land was observed as 34%, 43% and 23%, respectively. The same pattern was observed in agricultural land with 38% sand, 30% silt and 32% of clay. In forest soil clay content was found maximum with 33% sand, 42% silt and 25% of clay. 40%, 33% and 27% of sand silt and clay content was noted in pasture soil. The values of SOC and total N were in the range 670-950 mg kg^{-1} and 430-580 mg kg^{-1} while CEC was noted as 180 mmol kg^{-1}-235 mmol kg^{-1}. In this study, heavy metals fractions with significantly different values were observed among various land uses. Land uses differed for heavy metals concentrations in the order of fallow land>pastureland>crop land>forest land. The variations in the heavy metal concentrations might be because of the differences in the land use, geological properties of parent material, and other soil characteristics as Land use and soil parent materials generally represent human activities and geological background factors [27-28]. In the process of extraction, the heavy metals concentration in the land uses remained highly dependent on the extraction method. The heavy metal fractions extracted by the reagents varied in the order HNO_3>EDTA>NaOH>KNO_3>H_2O. The concentration of Ni was observed higher after extraction with NaOH than Na_2EDTA (Table 2). Generally, heavy metals in different land systems have been found in various forms. The metal in water soluble form is readily leachable in soils and easily available for plants in the environment. However, metals in the residual fractions are tightly chemically bound and are not easily available under natural conditions. Regardless

Table 1. Cd, Cu and Fe concentrations (mg kg^{-1}) in soil under different land use systems.

Soil Depth	Land use	HM	KNO_3	H_2O	NaOH	EDTA	HNO_3	Total
Top Soil	Fallow	Cd	0.40±0.01^{A}	0.20±0.03^{A}	0.49±0.03^{A}	0.67±0.03^{A}	2.9±0.01^{A}	5.7±0.57^{A}
		Cu	0.32±0.01^{A}	0.25±0.03^{A}	1.85±0.03^{A}	3.35±0.03^{A}	24.05±0.01^{A}	40.3±0.28^{A}
		Fe	1.92±0.01^{A}	1.35±0.03^{A}	3.35±0.03^{A}	5.55±0.03^{A}	38.35±0.03^{A}	217.0±1.41^{A}
	Cropped	Cd	0.35±0.03^{B}	0.14±0.01^{B}	0.43±0.01^{B}	0.58±0.01^{B}	1.85±0.03^{C}	4.9±0.85^{A}
		Cu	0.28±0.0^{BC}	0.16±0.01^{B}	1.35±0.03^{C}	2.75±0.03^{C}	19.65±0.03^{C}	34.2±0.14^{C}
		Fe	1.34±0.03^{C}	0.90±0.01^{C}	2.92±0.03^{C}	4.97±0.03^{C}	31.25±0.04^{C}	200.1±0.14^{C}
	Pasture	Cd	0.37±0.03^{A}	0.17±0.03^{B}	0.47±0.03^{A}	0.63±0.01^{A}	2.39±0.04^{B}	5.4±0.28^{A}
		Cu	0.29±0.03^{AB}	0.19±0.03^{B}	1.51±0.03^{B}	3.15±0.01^{B}	22.05±0.03^{B}	38.0±0.41^{B}
		Fe	1.52±0.01^{B}	1.23±0.03^{B}	3.05±0.03^{B}	5.25±0.03^{B}	35.25±0.03^{B}	208.4±0.14^{B}
	Forest	Cd	0.29±0.03^{C}	0.05±0.03^{C}	0.32±0.01^{C}	0.48±0.01^{C}	1.15±0.01^{D}	4.1±0.14^{B}
		Cu	0.23±0.03^{D}	0.07±0.03^{C}	0.61±0.03^{D}	1.77±0.03^{D}	12.15±0.03^{D}	26.6±0.28^{D}
		Fe	0.92±0.01^{D}	0.32±0.01^{D}	2.15±0.03^{D}	3.91±0.01^{D}	19.75±0.03^{D}	188.8±0.14^{D}
Sub Soil	Fallow	Cd	0.38±0.01^{A}	0.18±0.03^{A}	0.47±0.03^{A}	0.66±0.01^{A}	2.65±0.03^{A}	5.5±0.28^{A}
		Cu	0.30±0.01 ^{A}	0.21±0.03^{A}	1.65±0.03 ^{A}	3.25±0.03^{A}	22.25±0.03^{A}	38.5±0.28^{A}
		Fe	1.71±0.03^{A}	1.15±0.03^{A}	3.15±0.03^{A}	5.35±0.03^{A}	36.15±0.03^{A}	211.1±0.14^{A}
	Cropped	Cd	0.34±0.03^{B}	0.12±0.01^{B}	0.40±0.01^{B}	0.57±0.03^{B}	1.75±0.03^{C}	4.8±0.14^{A}
		Cu	0.26±0.01^{BC}	0.14±0.03^{C}	1.15±0.01^{C}	2.55±0.03^{C}	18.05±0.03^{C}	33.1±0.028
		Fe	1.33±0.01^{C}	0.80±0.03^{C}	2.85±0.03^{C}	4.85±0.03^{C}	29.05±0.03^{C}	198.3±0.28^{C}
	Pasture	Cd	0.36±0.01^{A}	0.15±0.03^{B}	0.44±0.03^{A}	0.61±0.03^{A}	1.97±0.03^{B}	5.2±0.14^{A}
		Cu	0.29±0.03^{AB}	0.18±0.01^{B}	1.45±0.03^{B}	2.85±0.03^{B}	20.55±0.03^{B}	36.2±0.14^{C}
		Fe	1.41±0.01^{B}	0.92±0.01^{B}	2.97±0.03^{B}	5.12±0.03^{B}	33.15±0.03^{B}	205.5±0.28^{B}
	Forest	Cd	0.28±0.01^{C}	0.03±0.01^{C}	0.30±0.01^{C}	0.46±0.01^{C}	0.95±0.04^{D}	4.0±0.28^{B}
		Cu	0.15±0.0^{D}	0.05±0.03^{D}	0.315±0.01^{D}	1.46±0.03^{D}	10.25±0.03^{D}	24.3±0.28^{D}
		Fe	0.91±0.03^{D}	0.21±0.03^{D}	1.97±0.03^{D}	3.75±0.03^{D}	17.15±0.03^{D}	186.3±0.28^{D}
		LSD (0.05)	0.10	0.16	0.22	0.22	0.17	0.55

Note: Upper case letters in superscript indicate the significant differences among different land uses for the same heavy metal.

of the land use, the concentrations of metals varied in order Fe>Zn>Ni>Cu>Pb>Cd (Table 1, 2).

The total Cd contents were affected by land use system with small variations. The soil samples of these land uses differed as fallow>pasture>cropped>forest. A similar pattern was noticed for other extractable forms of Cd and Cu among land uses (Table 1). Most of the Cd and Cu concentrations in the various land uses were present in the pool of residual and carbonate precipitated fractions. The study indicated that concentration of total Cu in the soil regulated the content of other forms of Cu. As the content of Cu in the land uses increased, more Cu was associated with the non-residual fractions which also increased the bioavailability of Cu in land uses. Complexity of metal ions occurs in the soil profiles which have different effects on metal precipitation and toxicity. The Cu and Cd have been found higher in the surface soil as compared to the sub-surface soil. Copper normally accumulates in the surface horizons, a phenomenon explained by the accumulation of metal from different sources [29]. In the sub soil the total Cd contents were affected by land use system with negligibly small variations. The soil samples of these land uses differed as fallow>pasture>cropped>forest irrespective of the extraction method (Table 1). However, Cd concentration in the sub soil was found lesser as compared with the topsoil. The same trend continued for the Cu in which concentration of Cu in subsoil was noticed lesser as compared with the u concentration in the topsoil (Table 1). Cu contents in the sub- soil also followed the same pattern i.e. fallow>pasture>cropped>forest.

Higher concentration of total Fe was found in the fallow land and the lower concentration was found

Table 2. Ni , Pb , Zn concentrations (mg kg^{-1}) in soil under different land use systems.

Soil Depth	Land use	HM	KNO_3	H_2O	NaOH	EDTA	HNO_3	Total
Top Soil	Fallow	Ni	2.35±0.03^{A}	0.75±0.03^{A}	3.65±0.03^{A}	4.25±0.03^{A}	9.55±0.03^{A}	49.5±0.28^{A}
		Pb	2.90±0.01^{A}	0.41±0.03^{A}	3.92±0.01^{A}	5.32±0.01^{A}	5.95±0.03^{A}	25.2±0.14^{A}
		Zn	0.38±0.01^{A}	0.18±0.01^{A}	0.56±0.01^{A}	1.92±0.01^{A}	36.65±0.03^{A}	123.2±0.14^{A}
	Cropped	Ni	1.87±0.03^{C}	0.43±0.03^{C}	3.15±0.01^{A}	3.55±0.03^{C}	8.75±0.03^{A}	40.7±0.28^{C}
		Pb	2.40±0.01^{C}	0.27±0.03^{C}	3.27±0.01^{C}	4.55±0.01^{C}	5.32±0.01^{C}	21.1±0.14^{C}
		Zn	0.27±0.03^{B}	0.13±0.01^{B}	0.38±0.01^{B}	1.42±0.01^{B}	32.45±0.03^{C}	101.7±0.28^{C}
	Pasture	Ni	2.15±0.01^{B}	0.55±0.03^{B}	3.55±0.03^{A}	3.95±0.03^{B}	9.15±0.03^{B}	46.4±0.28^{B}
		Pb	2.55±0.03^{B}	0.32±0.03^{B}	3.60±0.01^{B}	4.85±0.03^{B}	5.65±0.03^{B}	23.1±0.14^{B}
		Zn	0.29±0.01^{B}	0.17±0.03^{A}	0.43±0.03^{B}	1.60±0.01^{B}	34.87±0.03^{B}	110.1±0.14^{B}
	Forest	Ni	1.30±0.03^{D}	0.09±0.01^{D}	2.15±0.03^{B}	2.75±0.03^{D}	7.72±0.01^{C}	34.1±0.28^{D}
		Pb	1.70±0.01^{D}	0.12±0.03^{D}	2.25±0.03^{D}	3.45±0.03^{D}	4.35±0.03^{D}	15.8±0.14^{D}
		Zn	0.21±0.01^{C}	0.05±0.01^{C}	0.21±0.01^{D}	0.32±0.03^{BC}	25.11±0.01^{D}	71.2±0.14^{D}
Sub Soil	Fallow	Ni	2.15±0.01^{A}	0.65±0.01^{A}	3.35±0.03^{A}	4.13±0.03^{A}	9.25±0.03^{A}	47.2±0.1^{A}
		Pb	2.65±0.03^{A}	0.41±0.03^{A}	3.72±0.01^{A}	5.05±0.03^{A}	5.82±0.01^{A}	24.8±0.14^{A}
		Zn	0.33±0.03^{A}	0.17±0.03^{A}	0.52±0.03^{A}	1.70±0.01^{A}	35.05±0.03^{A}	113.6±0.14^{A}
	Cropped	Ni	1.85±0.03^{C}	0.32±0.01^{C}	2.91±0.03^{A}	3.52±0.03^{C}	8.65±0.03^{A}	40.1±0.28^{B}
		Pb	2.25±0.03^{C}	0.25±0.03^{C}	3.15±0.03^{C}	4.35±0.03^{C}	5.22±0.01^{C}	20.5±0.28^{C}
		Zn	0.25±0.03^{C}	0.10±0.01^{B}	0.31±0.01^{B}	1.25±0.03^{C}	31.15±0.03^{C}	95.1±0.14^{C}
	Pasture	Ni	2.05±0.03^{B}	0.45±0.03^{B}	3.25±0.03^{A}	3.75±0.03^{B}	9.23±0.03^{B}	44.1±0.28^{A}
		Pb	2.51±0.03^{B}	0.30±0.01^{B}	3.41±0.01^{B}	4.67±0.68^{B}	5.45±0.03^{B}	22.2±0.28^{B}
		Zn	0.27±0.03^{B}	0.15±0.03^{A}	0.40±0.03^{B}	1.59±2.11^{B}	33.25±0.03^{B}	103.1±0.14^{B}
	Forest	Ni	1.15±0.03^{D}	0.07±0.03^{D}	2.00±1.41^{B}	2.55±0.03^{D}	7.51±0.03^{C}	33.0±0.28^{C}
		Pb	1.55±0.03^{D}	0.11±0.03^{D}	2.11±0.01^{D}	3.25±0.03^{D}	4.11±0.01^{D}	14.5±0.28^{D}
		Zn	0.18±0.01^{C}	0.03±0.03^{C}	0.19±0.01^{D}	0.25±0.03^{BC}	21.77±0.03^{D}	62.3±0.28^{D}
		LSD (0.05)	0.05	0.04	0.05	0.07	0.13	0.38

Note: Upper case letters in superscript indicate the significant differences among different land uses for the same heavy metal.

in the forest land (Table 1). However, many studies indicated that farmlands usually exhibited significantly higher heavy metal contents compared to other land use types due to the continuous application of agrochemicals [30-31]. The heavy metal fractions in various land systems varied in order of fallow>pasture >crop>forest. Most metals do not undergo microbial or chemical degradation, and the total concentration in the soil persists for a long time after their introduction [32-33]. The water-soluble concentration of Fe (mg kg^{-1}) was found as 1.35 in fallow land, 1.23 in pasture, 0.90 in cropped land and 0.32 in forest. Similarly, the other extractable fraction of Fe exhibited a similar pattern among land uses. Topsoil showed higher heavy metals content than sub-soils. This phenomenon could be due to transformation of nutrients and influenced by vegetation in the surface soil. [34] reported that the metal extractability was higher in the contaminated soil than uncontaminated soil not depending upon the extractant used which indicates a greater of heavy metals bioavailability from contaminated soils. Distribution of microelement in surface soil was controlled by the pH of soil and cation exchange capacity. Biological and human disturbances are more in the surface soil in the soil profile because of its vulnerability in the soil profile.

In comparison within topsoil, the total Ni concentration among different land uses was highest in the fallow land (49.5 mg kg^{-1}) and lowest in the forest land (34.1 mg kg^{-1}). Organically bound Ni was highest in fallow land (4.25 mg kg^{-1}) whereas lowest (2.75 mg kg^{-1}) in the forest land (Table 2). The greater Ni concentration was found in residual form, but its contents were also significant in both carbonates precipitated

Table 3. Pearson correlation coefficients for heavy metals in top and sub soils.

	Top Soil					Sub Soil				
HM	**Pb**	**Ni**	**Fe**	**Cu**	**Cd**	**Pb**	**Ni**	**Fe**	**Cu**	**Cd**
Zn	**-0.906**	0.979*	0.977*	0.994**	0.985*	0.998**	0.988*	0.983*	0.998**	0.992**
Pb	-	**-0.830**	**-0.797**	**-0.897**	-0.964*	-	0.993**	0.989*	0.996**	0.996**
Ni	-	-	0.992**	0.991**	**0.935**	-	-	0.999***	0.992**	0.999***
Fe	-	-	-	0.978*	**0.925**	-	-	-	0.989*	0.998**
Cu	-	-	-			-	-	-	-	0.996**

Note: The numbers in bold represent non- significant correlation, with n = 4 and p =<0.05 (*), p<0.01 (**), p<0.001 (***), (-) not applicable

and organically bound form. The pattern for Ni extraction among different extractants was observed in the following order HNO_3>NaOH>Na_2EDTA>KNO_3 >H_2O (Table 2). The nickel content was higher in the topsoil profile than sub-soil under all land uses (Table 2). Under acidic conditions mobility of organically bound Ni increases resulting into its bioavailability.

Total Pb concentration was found highest in the soil of fallow land (25.2 mg kg^{-1}) (Table 2) whereas lowest was noticed in forest land (15.85 mg kg^{-1}). Other Pb fractions were higher in fallow land soil and lowest in the forest soil. Heavy metals occurred in relatively higher concentrations in urban, mineralized, and agricultural soils as compared to the forest soils indicating that the forest soils have suffered least anthropogenic inputs and the metal values in the forest soil could be used as 'present background values' in soil quality evaluation [35]. Table 2 shows greater concentration of Pb was found in the residual, carbonate precipitated and organically bound forms. Heavy metal in pasture, fallow, forest, and cropped land varied depending on the pattern of land use. Heavy metals distribution also differed with respect to soil profiles. Topsoil gave higher concentration of Pb than sub-soil. The heavy metal contents in the soil change slowly [36].

The Zn concentration under various land use systems was significantly different (Table 2). In surface soils, the higher amount of total Zn was observed in fallow (123.2 mg kg^{-1}) and the lowest content was observed in forest (71.2 mg kg^{-1}). [34] reported total metal concentration include all non-residual as well as metals present in silicate mineral matrix. In Table 2 water extractable Zn was higher in fallow land followed by pastureland and the least concentration was noticed under forest land use. The greater concentration of Zn was observed in the residual form. In comparison to it Zn contents were significantly lower in the carbonated precipitated and organically bound form. The exchangeable fraction is generally considered immediate nutrient reservoir for plants. Elements availability also depends upon soil pH values, and most of the elements are regarded as potentially phyto-available at normal pH. On the other hand, heavy metals present in some chemical forms are not available for plants under normal conditions. The total Zn was found higher in the topsoil than sub-soil irrespective of the land uses. A similar pattern was seen for other fractions of Zn. Important factors which affect heavy metal mobility are pH, sorbent nature, organic and inorganic ligands. Redox reactions (biotic and abiotic) also control the mobility and the toxicity of several elements. The main sources of Zn in soils have been associated with the use of liquid manure, composted materials, and agrochemicals [6, 37] associated heavy metals contamination in the soil environment to the land use pattern and these metals have been derived from industrial, traffic and natural sources.

Table 3 shows the Pearson correlation co-efficient among various selected heavy metals in total form in both top and sub soils. In top soils, significant relationship was found between all heavy metals except Zn and Pb which was negatively correlated (r^2 = -0.91, P = 0.09), Pb and Ni (r^2 = -0.83, P =0.17) , between Pb and Fe (r^2 = -0.79, P =0.20), Pb and Cu (r^2 = -0.89, P = 0.10) and Ni and Cd (r^2 = 0.94, P = 0.06), Fe and Cd (r^2 = 0.93, P = 0.08). Contrary to it in sub soils, the significant positive Pearson correlation co-efficient is observed among all the heavy metals in total form as indicated in Table 3. Highly significant relationship with p<0.001 was noted between Ni and Fe (r^2 = 0.99, P = 0.0006) and between Ni and Cd (r^2 = 0.99, P = 0.0007).

Conclusions

Many changes occur in the soil properties due to land-use and land cover change (LULC) which may also have impact on vegetation and livelihood of the inhabitants. This study indicated significant variations of heavy metals fractions as affected by soils of different land uses. Higher concentrations of heavy metals were observed in fallow land whereas lower concentrations were noticed in the forest land irrespective of vertical soil column. The land uses followed the order for heavy metals as fallow>pasture>crop>forest. The concentrations of heavy metals considerably varied among chemical reagents HNO_3>Na_2EDTA>NaOH> KNO_3>H_2O. Surface soil indicated comparatively higher concentration of heavy metals than sub-surface soil. This study will help in providing valuable information for further studies and will be useful for environmental quality management and rehabilitation of heavy metal polluted soils in various land uses.

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