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Assessment of the Ecological and Health Risks of Potentially Toxic Metals in Agricultural Soils from the Drosh-Shishi Valley, Pakistan

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Abstract: Soil pollution is a highlighted concern of modern society, particularly in developing countries. The Drosh-Shishi valley, which is a hilly region near Afghanistan with a land area of around 15,000 km^2, is situated in the south of Chitral District (Pakistan) and has a population of approximately 450,000. Nowadays, this region is being explored for soil pollution, specifically heavy metals which pose a potential risk to human health. Therefore, our main goal was to investigate possible sources of heavy metals' spread and to assess the content levels in soil and the associated risks for human. We collected 34 representative samples from transported sediments and 31 from agricultural crops. We analyzed the soil samples for the contents of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn using ICP-OES analyzers. These values were used to obtain the contamination factor (CF) and to estimate the potential health risk caused by heavy metals according to the USEPA dose–response model. Our results suggest that the heavy metal pollution has a geogenic source, but it is also aggregated by chemical fertilizers used in farming. Regarding levels, most of the metals except Pb showed contents above the permissible level, with CF values from moderate to high. Overall, Cu and Ni showed a significant total cancer risk (TCR > 1×10^{-4}) in children. Therefore, we conclude that heavy metal pollution is causing a serious threat to humans in this area, and we recommend that authorities should make more efforts in monitoring the heavy metals content in soils to reduce potential health risks.

Keywords: environmental pollution; agricultural land; toxicity; atomic spectroscopy; human welfare; Chitral District

1. Introduction

The expansion of industrial activities [1] and agricultural intensification [2] in the world have provoked severe land degradation. Soil contamination by heavy metals is considered a serious threat in such areas [3]. Specifically, it increases toxicity in plants [4]; reduces water quality [5,6]; decreases soil health, crop yields [7], and food quality [8]; and threatens the health and well-being of humans and animals by the pollution of the food chain [9,10].

Heavy metals dispersed in soils, water, and the atmosphere and their levels in the biosphere increase due to anthropogenic activity [11]. Heavy metal sources might be natural, such as parent materials (rocks), or anthropogenic, such as industry, transportation, and household emissions [11,12].

Heavy metals may be released into the environment from industrial activities, fertilizers, pesticides, solid waste disposal, irrigation with effluents, sludge application, and automobile exhausts [13,14]. The soil environment is continually deteriorating due to improper waste disposal, chemical fertilizers, pesticides, industrial production, mineral exploitation, and food processing [15]. Due to heavy metals' non-biodegradability, these pollutants are accumulating in the soil environment to a considerable extent, where these pollutants can be bio-accumulated, bio-transferred, and biomagnified in food chains.

Vegetables grown on soils contaminated with heavy metals have been a major food chain channel for human exposure, posing a substantial health risk. Soil is the first route of accumulation of heavy metals in plant edible parts, and the second is through air deposition on exposed plant surfaces [16]. The health risk posed by a polluted food may be assessed by calculating daily metal intake, using a daily dietary index, and using a health risk index [17].

Heavy metal contamination has been increased in soils, urban road dusts, surface water, groundwater, wastewater, and air in Pakistan because of the fast population growth, industrialization, and urbanization [18]. Pakistan produces thousands of tons of different vegetables, but some of these products are seriously contaminated with heavy metals [19]. The lack of strict environmental controls in emerging nations such as Pakistan has led to an increase in the amount of heavy metals released into the environment [20].

Due to low socioeconomic status, vegetables are the most consumed food in these countries because of easy access; therefore, they could be the primary source of human exposure to heavy metals. In general, vegetable production has increased because of easily available resources such as wastewater irrigation, agrochemical fertilizers, and pesticides. In order to avoid or reduce hazards to human health, it is essential to recognize heavy metal primary sources, their dispersal, and exposure routes, as well as to establish safe threshold limits [21].

In the Drosh-Shishi valley (Pakistan), vein-type copper and lead have been reported in two sites along the Shishi fault in the eastern part [22]. In addition, a high mineral potential of copper, lead, and antimony was also reported [23]. Some rock units, such as talc carbonates associated with serpentine blocks in the northern suture zone along the Shishi and Mir Khani-Arandu valleys, are good host rocks for emeralds [24].

The mineral and agricultural resources of Pakistan have been exploited for economic growth. This exploitation has resulted in huge stress on the mining and agricultural sectors of the country and in environmental degradation [25]. Various studies have focused on the potentially toxic elements (PTEs) contamination along with the mining [26,27] and agricultural activities in Pakistan. Most recently, Ishaq et al. [28] reported the PTEs in the water and soil of Chitral city (Pakistan). It was reported that the mean concentration of heavy metals exceeded the permissible limits and was found to be much higher than their natural background values. These findings indicate that these zones are accumulating heavy metal pollution in soils, which poses potential risks to human health as the soil contamination ends up polluting food and water. A research gap exists about the spatial distribution, levels, and risk for humans. Therefore, this study has been conducted in the Shishi valley, which is located near the mineral-rich zone of Chitral District (northern Pakistan). To prevent the bioaccumulation of pollutants in plants and humans, agricultural soils must have their quality evaluated prior to crop cultivation. The main objectives of our present investigation were to assess the heavy metal contamination in the soil of the study area and evaluate the soil contamination level as well as to assess potential risks to humans.

2. Materials and Methods

2.1. Study Area

This research was carried out in the Drosh-Shishi valley, located in the south of Chitral District (35°35′ N, 71°49′ E—Pakistan), in 2018. The majority of soil samples were taken along the Shishi River, in the village of Shishi, which lends its name to the nearby valley and river. This river is located in the district of Chitral, which is bordered to the east by Gilgit-Baltistan, to the northwest by Afghanistan, and to the south by Dir District (Figure 1). The total population of Chitral District is 447,362 inhabitants, covering a surface area of 14,850 km^2 (District Census Report 2017). The total cultivated area is about 23,000 ha, with wheat, maize, barley, and rice and vegetables crops. The major water source is surface water, including irrigation channels, streams, and perennial springs used for drinking as well as irrigation purposes. From a geological point of view, the Drosh-Shishi valley is dominated by greenstones and amphibolites that present a high content of copper (Cu) associated with chalcopyrites [29]. Their mineralization is generally restricted along the shear zones and fractures of the Shishi fault [22].

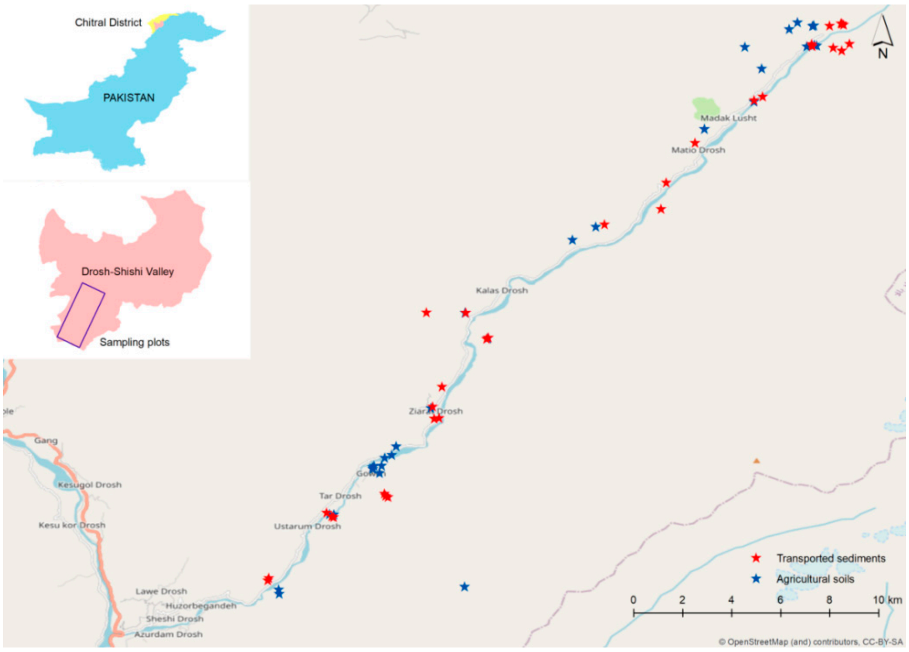

Figure 1. Map of study area showing location of sampling points.

2.2. Soil Sampling and Analysis

Two sampling plots were selected: transported sediments (n = 34 samples) and agricultural soils (n = 31 samples), in which random topsoil samples (0–30 cm in depth) were collected. Moreover, soil samples from different crops fields were collected, such as maize, wheat, beans, and vegetables, and transported sediments were collected from the main channel of mineralized zones in the area. Each sampling point was recorded with an accurate GPS (Figure 1).

After preparation of the samples in a laboratory, 0.10 g of each sample was used to estimate the total contents of metals by wet digestion (Anton Paar GmbH–Multiwave 3000). Nitric acid (65%), hydrochloric acid (36.5%), and hydrofluoric acid (48%) were utilized for digestion purposes. The concentrations of eight heavy metals (chromium (Cr), cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), manganese (Mn), copper (Cu), and cobalt (Co)) were determined by the CISRI laboratory (China Iron & Steel Research Institute Group) through inductively coupled plasma emission spectrometry (ICP-OES) methods (Agilent, 5110, USA) [30]. Each sample was analyzed three times, and the mean values were obtained. In this study, quality assurance and quality control (QA/QC) were rigorously maintained throughout the experiment by analyzing blanks and duplicates. Recovery rates for the heavy metals varied between 80 and 100%, indicating a high accuracy of the method used in this study, and the results are consistent with the quality control standard.

2.3. Contamination Factor and Assessment Model

Potential effects on the environment and humans were estimated from the calculation of the contamination factor (CF) and the human exposure and health risk assessment model, respectively. This model is based on the calculation of 12 equations that are shown and described below.

The contamination factor is considered a typical tool to assess heavy metal pollution in different environments. The CF was calculated using Equation (1) and interpreted according to the classes proposed by Hakanson [31]: CFi < 1, low contamination factor (indicating low sediment contamination of the substance in question); $1 \leq$ CFi < 3, moderate contamination factor; $3 \leq$ Cfi < 6, considerable contamination factor; CFi ≥ 6, very high contamination factor.

$$\mathrm{CFi} = \frac{\mathrm{C}m\ \mathrm{sample}}{\mathrm{C}m\ \mathrm{background}} \tag{1}$$

where CFi is the environmental contamination, C*m* sample is the concentration of the element in the soil samples, and C*m* background is the concentration of the metal in the upper continental crust. In Pakistan, there are still no local background concentrations or reference values for HMs in soils; for these reasons, as reference values (background), standard concentrations of the investigated metals in the Earth's crust were adopted as background concentrations [30]. The risk model was used to determine the total exposure of humans to the trace elements. In this model, the receptors are children and adults [32]. It enabled us to evaluate both non-carcinogenic (Equations (2)–(6)) and carcinogenic risks (Equations (7)–(11)) by three exposure pathways: ingestion (Equation (2)), dermal contact (Equation (3)), and inhalation (Equation (4)) [33]. For non-carcinogenic risk, the average daily intake (ADD) of heavy metals through each exposure pathway, namely oral ingestion (Equation (2)), dermal contact (Equation (3)), and air inhalation (Equation (4)), was calculated. The following equations were used:

$$\mathrm{ADD\_ing} = \frac{(\mathrm{C} \times \mathrm{IR_S} \times \mathrm{EF} \times \mathrm{ED})}{(\mathrm{BW} \times \mathrm{AT})} \times 10^{-6} \tag{2}$$

$$\mathrm{ADD\_dermal} = \frac{(\mathrm{C} \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED})}{(\mathrm{BW} \times \mathrm{AT})} \tag{3}$$

$$\mathrm{ADD\_inh} = \frac{(\mathrm{C} \times \mathrm{IR_i} \times \mathrm{EF} \times \mathrm{ED})}{(\mathrm{PEF} \times \mathrm{BW} \times \mathrm{AT})} \tag{4}$$

where ADD_ing, ADD_dermal, and ADD_inh represent the average daily exposure dose through the ingestion, dermal contact, and inhalation pathways (mg kg^{-1} day^{-1}), respectively; IR_s is the soil uptake rate (mg day^{-1}); IR_i is the soil suction rate (m^3 day^{-1}); EF is the frequency of contact (days per year); ED is the exposure duration (years); BW is the body weight (kg); AT is the time period of average doses (days); PEF is the emission factor (m^3 kg^{-1}); SA is the skin exposure surface area (cm^2); AF is the adhesion factor (kg cm^{-2} day^{-1}); ABS is the skin absorption factor; RfD is the reference dose (mg kg^{-1} day^{-1}); and LT is the average lifetime (days).

The total non-carcinogenic risk (THI) is therefore a sum of the hazard quotients (HQs, Equation (5)) that were estimated from the division of each ADD by its RfD, i.e., every metal $\times$ 3 pathways (Equation (6)).

$$\mathrm{THI} = \sum \mathrm{HQ} \tag{5}$$

$$HQ = \frac{\sum ADD}{Rfd} \quad (6)$$

Regarding the carcinogenic risk (CR), the average potential lifetime daily dose (LDD) was calculated for each exposure pathway by using Equation (7) (oral ingestion), (8) (dermal contact) and (9) (air inhalation). Subsequently, the CR for each case and the total CR (TCR) were calculated by using Equations (10) and (11), respectively.

$$LADD\_ing = \frac{(C \times IR_s \times EF \times ED)}{(BW \times LT)} \times 10^{-6} \quad (7)$$

$$LADD\_dermal = \frac{(C \times SA \times AF \times ABS \times EF \times ED)}{(BW \times LT)} \quad (8)$$

$$LADD\_inh = \frac{(C \times IR_i \times EF \times ED)}{(PEF \times BW \times LT)} \quad (9)$$

$$CR = \sum (LADD \times SF) \quad (10)$$

$$TCR = \sum CR \quad (11)$$

where LADD_ing, LADD_dermal, and LADD_inh represent the average daily carcinogenic risk exposure dose of the oral ingestion, dermal contact, and air inhalation pathways (mg kg^{-1} day^{-1}), respectively; IR_s is the soil uptake rate (mg day^{-1}); IR_i is the soil suction rate (m^3 day^{-1}); EF is the frequency contact (days per year); ED is the exposure duration (years); BW is the body weight (kg); AT is the time period of average doses (days); PEF is the emission factor (m^3 kg^{-1}); SA is the skin exposure surface area (cm^2); AF is the adhesion factor (kg cm^{-2} day^{-1}); ABS is the skin absorption factor; RfD is the reference dose (mg kg^{-1} day^{-1}); SF is the carcinogenic factor (mg kg^{-1} day^{-1}); and LT is the average lifetime (days). The RfD and SF values of each metal are shown in Table 1. The other parameters used in this model specifically for children and adults are summarized in Table 2.

Table 1. Reference values used for calculating the health risk assessment model for each heavy metal. RfD: reference dose; SF: carcinogenic factor. Both parameters are expressed in mg kg^{-1} day^{-1} [34].

Metals	RfD			SF		
	Ingestion	Dermal	Inhalation	Ingestion	Dermal	Inhalation
Cd	1.0×10^{-3}	2.5×10^{-5}	5.71×10^{-5}	6.1	6.1	6.3
Pb	3.5×10^{-3}	5.25×10^{-4}	3.52×10^{-3}	-	-	-
Cu	0.04	0.012	0.0402	-	-	-
Cr	3.0×10^{-3}	6.0×10^{-5}	2.86×10^{-5}	0.5	20	42
Zn	0.3	0.06	0.3	-	-	-
Ni	0.02	8×10^{-4}	0.026	-	-	-

Table 2. Parameters utilized for the health risk assessment model and their values for children and adults [34].

Parameter	Description	Unit	Children	Adults
IR_s	Ingestion rate of soil	mg day^{-1}	50	20
IR_i	Inhalation rate	m^3 day^{-1}	7.6	16
EF	Exposure frequency	days y^{-1}	350	350
ED	Exposure duration	years	6	24
BW	Average body weight	kg	24.7	57
AT	Average exposure time	days	ED × 365	ED × 365
SA	Surface area of skin	cm^2	2.800	5.700
AF	Adherence factor	kg cm^{-2} day^{-1}	2×10^{-6}	2×10^{-7}
ABS	Skin absorption factor	unit less	0.001	0.001
PEF	Emission factor	m^3 kg^{-1}	1.36×10^9	1.36×10^9
LT	Lifetime	days	76.49 × 365	76.49 × 365

2.4. Data Analysis

Most of the properties (heavy metals) were firstly described by using basic descriptive statistics parameters. Secondly, we explored sources by means of bi- and multivariate techniques such as correlation and principal component analysis (PCA) [35]. A correlation analysis was conducted to understand how the metals are related to each other and with other parameters studied. PCA was performed to identify those factors that explain the data variance of our dataset [36]. The effectiveness of the combination of both techniques for identifying potential sources of heavy metals has been already proven in other environments [37]. The statistical procedure was carried out using SPSS Statistics 20.0 (IBM).

3. Results

3.1. Heavy Metals

The descriptive statistical values of our dataset composed of 31 soil samples collected in agricultural soils and 34 in transported sediments are shown in Table 3. The mean concentration of every metal except Cr, Pb, Ni, Zn, and Mn was higher in the agricultural lands than their corresponding background values (crust value). Nonetheless, their high data variability showed fluctuating concentration levels in this context. Regarding transported sediments, their mean values were mostly lower than those in the agricultural areas but were also lower than those of the Earth crust except for Cd, Cu, and Co. Both environments showed a similar statistical pattern concerning data variability, pointing both to fluctuating conditions and to the possibility of random infiltrations from anthropogenic sources. Nevertheless, except for Pb, the rest of the parameters generally returned values of CV below 50%, which can be considered low or intermediate variability.

Table 3. Values of heavy metals' concentration (mg kg^{-1}) in agricultural soils and transported sediments. SE: standard error; SD: standard deviation; CV: coefficient of variation; BG: background value.

Agricultural Soils										
Metal	**Mean**	**Median**	**Min**	**Max**	**SE**	**SD**	**CV**	**Skewness**	**Kurtosis**	**BG**
Cr	55.48	55.50	30.89	92.53	2.98	16.85	30.38	0.29	−0.78	83
Cd	3.49	3.77	0.00	6.12	0.21	1.18	33.68	−0.47	0.96	0.098
Pb	9.13	8.94	0.00	21.65	1.08	6.12	67.03	0.34	−0.95	17
Ni	38.60	36.89	22.96	62.00	1.82	10.29	26.63	0.92	0.52	44
Zn	68.60	69.84	21.95	123.00	4.47	25.27	36.81	0.33	−0.26	71
Mn	568.00	555.20	246.77	830.40	28.43	160.82	28.28	−0.27	−0.64	600
Cu	69.30	64.33	38.90	123.40	4.27	24.18	34.88	0.73	−0.36	25
Co	34.00	34.85	22.23	41.00	0.89	5.04	14.80	−0.71	−0.05	17
Transported sediments										
Metal	Mean	Median	Min	Max	SE	SD	CV	Skewness	Kurtosis	BG
Cr	52.70	53.74	32.00	69.70	1.70	10.00	18.90	−0.30	−0.70	83
Cd	5.50	5.25	2.20	11.00	0.40	2.10	37.60	0.80	0.50	0.098
Pb	4.80	3.34	0.00	22.20	0.80	4.60	94.60	1.70	4.80	17
Ni	35.60	35.16	20.90	59.30	1.90	11.20	31.40	0.50	−0.40	44
Zn	40.50	39.50	29.00	61.00	1.50	8.50	21.00	0.70	−0.10	71
Mn	453.00	457.50	336.00	521.00	7.40	43.00	9.50	−1.00	1.30	600
Cu	35.40	32.00	13.00	80.00	2.80	16.20	45.80	1.10	1.50	25
Co	26.70	26.40	12.20	45.60	1.60	9.40	35.10	0.20	−0.80	17

3.2. Contamination Factor

The CF values obtained for each heavy metal are shown in Table 4. The degree of contamination ranged from no to moderate pollution, except for Cd which reached levels of very high as both agricultural soils and transported sediments were very highly contaminated with Cd. Curiously, Pb recorded the lowest degree of contamination in spite of its high values of concentration that were recorded (see Table 3 above).

Table 4. Contamination factors for agricultural soils and transported sediments.

Metal	Agricultural Soils	Contamination Degree	Transported Sediments	Contamination Degree
Cr	0.67	Low	0.63	Low
Cd	35.61	Very high	56.12	Very high
Pb	0.54	Low	0.28	Low
Ni	0.88	Low	0.81	Low
Zn	0.97	Low	0.57	Low
Mn	0.95	Low	0.76	Low
Cu	2.77	Moderate	1.42	Moderate
Co	2.00	Moderate	1.57	Moderate

3.3. Sources of Contamination

In order to identify potential sources, a correlation analysis between every heavy metal was performed (Table 5). Zn was positively correlated with Cd and Cr in agricultural soils, pointing towards their probable common source. In addition, strong positive correlations were found among various metal pairs from transportation sources, including Pb–Ni, Mn–Ni, etc. ($p < 0.05$). The results indicated a mixture of positive and negative correlations. Thus, it means the sources of contamination are not similar in all the cases.

Table 5. Coefficients of correlation between every metal in agricultural soils and transported sediments.

	Agricultural Soils						
	Cr	Cd	Pb	Ni	Zn	Mn	Cu
Cd	0.353						
Pb	−0.178	−0.102					
Ni	0.064	−0.077	−0.282				
Zn	0.411	0.472	−0.136	0.188			
Mn	0.128	0.260	0.026	−0.058	0.316		
Cu	0.020	0.262	0.226	−0.183	−0.066	−0.163	
Co	0.043	0.213	−0.019	−0.056	0.117	0.348	0.137
	Transported Sediments						
	Cr	Cd	Pb	Ni	Zn	Mn	Cu
Cd	0.274						
Pb	−0.463	−0.177					
Ni	−0.104	0.022	0.345				
Zn	−0.180	0.031	0.323	0.270			
Mn	0.234	0.161	−0.166	0.340	−0.147		
Cu	−0.043	−0.114	0.018	−0.256	−0.227	0.026	
Co	0.014	−0.278	0.031	−0.032	0.090	−0.277	0.005

Principal component analysis (PCA) was employed to understand the factors behind and trace the most probable sources of metals as well as their mutual relationships and variation in agricultural soils. The coefficients of correlation or loadings among the metals and the most important PCs are shown in Table 6. They are in consonance with the results obtained in the previous correlation analysis (Table 5). A total of 60% of variance was explained by the first three components in both environments: PC1 $\approx$ 25%, PC2 $\approx$ 20%, and PC3 $\approx$ 15%. In PC1, Cr, Cd, and Zn showed the highest loadings; meanwhile, Pb and Cu in PC2 and Co and Mn in PC3 showed a likely common source.

Table 6. Coefficients of correlation among metals and the three principal components.

Metals	**Agricultural Soils**			**Transported Sediments**		
	PC1	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**
Cr	0.761	−0.108	−0.079	−0.794	0.008	0.086
Cd	0.752	0.307	0.170	−0.497	0.253	0.360
Pb	−0.219	0.615	0.125	0.798	0.262	0.034
Ni	−0.017	−0.698	−0.191	0.324	0.581	0.483
Zn	0.746	−0.222	0.231	0.273	0.696	−0.154
Mn	0.148	−0.087	0.855	−0.169	−0.020	0.800
Cu	0.108	0.765	−0.261	0.237	−0.754	0.068
Co	0.046	0.172	0.694	0.020	0.119	−0.692
Eigenvalues	1.994	1.658	1.195	2.008	1.651	1.179
% of variance	24.925	20.725	14.933	22.249	19.241	18.981
Cumulative %	24.995	45.650	60.583	22.249	41.491	60.472

3.4. Health Risk

We also analyzed both non-carcinogenic and carcinogenic risk. In the first case, the total contents of heavy metals in agricultural soils were not absolutely bioaccessible (bioaccessibility < 1.0). Therefore, we suspect our results could suppose an overestimation of the health risk. Table 7 shows the adjusted values of bioaccessibility and exposure for the calculations.

Table 7. Values of non-carcinogenic and carcinogenic risk for children and adults by different pathways.

	Non-Carcinogenic Risk							
	Children				**Adults**			
	$HQ_{ingestion}$	HQ_{dermal}	$HQ_{inhalation}$	THI	$HQ_{ingestion}$	HQ_{dermal}	$HQ_{inhalation}$	THI
Cd	6.97×10^{-6}	7.81×10^{-8}	7.79×10^{-10}	0.01	1.21×10^{-6}	6.89×10^{-8}	7.11×10^{-10}	4.0×10^{-3}
Pb	1.73×10^{-5}	8.0×10^{-7}	1.94×10^{-9}	6×10^{-3}	3.01×10^{-6}	1.71×10^{-7}	1.77×10^{-9}	1.0×10^{-3}
Cr	1.0×10^{-4}	1.22×10^{-6}	1.21×10^{-8}	0.06	1.88×10^{-5}	1.07×10^{-6}	1.11×10^{-8}	0.024
Cu	1.73×10^{-5}	1.94×10^{-7}	1.94×10^{-9}	5×10^{-4}	3.01×10^{-6}	1.71×10^{-6}	1.77×10^{-9}	8.96×10^{-5}
Ni	1.74×10^{-5}	1.94×10^{-7}	1.94×10^{-9}	4×10^{-4}	1.31×10^{-5}	7.49×10^{-7}	7.74×10^{-9}	2.0×10^{-3}
Zn	1.74×10^{-5}	1.94×10^{-7}	1.94×10^{-9}	6.11×10^{-5}	2.34×10^{-5}	1.33×10^{-6}	1.37×10^{-8}	1.0×10^{-4}
	Carcinogenic Risk							
	Children				**Adults**			
	$CR_{ingestion}$	CR_{dermal}	$CR_{inhalation}$	TCR	$CR_{ingestion}$	CR_{dermal}	$CR_{inhalation}$	TCR
Cd	5.47×10^{-7}	6.13×10^{-9}	6.11×10^{-11}	3.3×10^{-6}	3.79×10^{-7}	2.16×10^{-8}	2.23×10^{-10}	2.44×10^{-6}
Pb	1.36×10^{-6}	1.53×10^{-8}	1.52×10^{-10}	8.40×10^{-6}	9.44×10^{-7}	5.38×10^{-8}	5.55×10^{-10}	6.09×10^{-6}
Cr	8.52×10^{-6}	9.55×10^{-8}	9.53×10^{-10}	6.21×10^{-6}	5.91×10^{-6}	3.37×10^{-7}	3.48×10^{-9}	9.84×10^{-6}
Cu	2.36×10^{-5}	1.35×10^{-6}	1.39×10^{-8}	7.04×10^{-4}	7.42×10^{-6}	4.23×10^{-7}	4.36×10^{-9}	4.79×10^{-5}
Ni	3.01×10^{-6}	1.72×10^{-7}	1.77×10^{-9}	3.0×10^{-4}	4.13×10^{-6}	2.357×10^{-7}	2.43×10^{-9}	6.87×10^{-6}
Zn	1.36×10^{-6}	1.53×10^{-8}	1.52×10^{-10}	9.92×10^{-7}	7.35×10^{-6}	4.186×10^{-7}	4.32×10^{-9}	1.22×10^{-5}

For children, ingestion HQ values ranged from 6.97×10^{-6} (Cd) to 0.00001 (Cr), while these values were lower for dermal contact and air inhalation. The values in adults were also relatively lower than those in children. The HQ values of all exposure pathways in agricultural soils were lower than one.

Regarding carcinogenic risk, the values showed some risk for heavy metals such as Cu and Ni, particularly in children (TCR > 1×10^{-4}). In adults, the highest risk was observed from the contents of Cu and Zn, usually provided from agriculture through the application of manures. The significant difference found between the values of TCR for Zn in children and adults is also remarkable, particularly due to the low impact of air inhalation in children in comparison to adults.

4. Discussion

Our investigation depicts that the average HM concentrations are relatively high, particularly in the agricultural lands. Nonetheless, their data patterns revealed a varying pattern that may prompt us to consider punctual sources of contamination associated with anthropogenic sources. This finding would be in consonance with the ideas expressed by Wang et al. [38] in their work conducted in apple orchards. Of course, the concentrations of heavy metals recorded here are above background values. In addition, their variability suggests their being a consequence of anthropogenic activities since low variability should be interpreted as an adequate content to be considered a natural resource. In other words, only humans can alter the natural spatial homogeneity of these properties in soils and sediments.

The sources of these metals are often identified through a correlation analysis between them that shows identical behaviors and/or mutual dependence [39]. According to Wang et al. [40], a significant positive correlation between metals can be interpreted as them coming from a similar source, having comparable behavior, and transferring under physico-chemical environments. For instance, we suspect that industrial seepages can be an important source since some industries, such as food processing and paint factories as well as leather tanning, electroplating, plastic, etc., are located nearby in the study area. Another plausible hypothesis is the use of pesticides and fertilizers since agricultural lands recorded higher concentrations on average.

Some sources appeared to be identified by the PCA, with conclusions that are comparable to those from the correlation analysis. PC1 is probably associated with anthropogenic factors because the average contents of some metals were relatively high.

The influence of human activities on the content of cadmium in soil has already been proven by Loganathan et al. [41]. Thus, in this case, the possibility of industrial and chemical activities being the main source for transported sediments and intensive farming being the main source for agricultural soils can be assumed [42]. In fact, heavy metals such as Zn and Cd are commonly found in organic fertilizers, particularly phosphates, and also chemical pesticides [43]. In this line, Atafar et al. [44] also identified overuse of chemical fertilizers and pesticides as the most plausible source. Concerns about the accumulation of Cd in soils have led some producers of fertilizers, following the suggestions of the European Union (EU), to change fertilization methods [45] and sources [46].

In PC2, the average content of Pb was very similar to the background value, i.e., from a geogenic source. For instance, Navarro-Pedreño et al. [47] suggested that metals such as Cu are controlled by the geochemical composition of the parent material and geogenic processes. Potentially, it can be a consequence of specific agronomic practices (e.g., manure) [36].

Livestock manures are important sources of soil pollution due to excesses of Zn and Cu. High levels of Cu can be due to some specific agrochemicals and also traffic density due to proximity between roads and plots. This finding is consistent with Chen et al. [37], who reported that Cu and Pb are the main heavy metals derived from anthropogenic sources in agricultural soils. Additionally, Tahirkheli et al. [22] noticed vein-type copper and lead along the Shishi valley, so it can be considered that PC2 could be a nature–human compound source factor.

Co and Mn dominated PC3, and Mn showed values much higher than its background values. It can be speculated that the origin of these could be the regular weathering of the parent material. In fact, Micó et al. [46] found high levels of Co, Cr, and Ni in calcareous and alluvial areas. In this regard, PC3 can be interpreted as a lithological influence factor. The association of Co with the cluster composed of Cr, Cd, and Zn as well as the positive correlations between them can point out that it can be a geogenic source. The results obtained in the transported sediments and agricultural soils show prevailing similarities. However, confirmation of the identity of the exact source of changes in this region needs further in-depth studies.

Regarding human health, the values obtained here did not indicate a serious risk of cancer and diseases in spite of having recorded values much higher than the usual background values for every HM. According to the USEPA [33], HQ values lower than one for a given metal should be interpreted as a safe level. Our results suggest that ingestion and dermal contact are the main ways of entrance. This result is consistent with comparable findings from earlier research [9]. Our concerns, however, stem from the fact that all of these exposure paths could result in non-carcinogenic risk because of the area's growing urbanization and agricultural practices for economic expansion.

The cancer risk associated with Cu and Ni in children is the most concerning finding from our research. According to the USEPA [33], TCR values below 1×10^{-6} should be regarded as inconsequential and show that the relevant element is non-carcinogenic. The measured TCR levels exceeded 1×10^{-4}. It can be considered that the model utilized in this work is an effective tool for risk assessment. Nonetheless, the calculation of these risks (carcinogenic and non-carcinogenic) is influenced by several uncertainty factors. Additionally, Pakistan and/or other countries may not be able to fully utilize the USEPA [33] values. As a result, we support performing this kind of research in many more study scenarios. This study draws the attention of local farmers and policymakers about the convenience of maintaining and supporting a sustainable food production system in which the use of fertilizers is progressively reduced through precision farming and/or other techniques [48]. Therefore, this research could help policymakers sustainably regulate agricultural activities and adopt measures for improving crop production and protecting agricultural lands from environmental pollution.

5. Conclusions

This study analyzed the HM concentrations (levels, sources, and health risk) in a developing area of Pakistan. Their contents were sorted as Mn > Cu > Zn > Cr > Ni > Co > Pb > Cd in agricultural soils and as Mn > Cr > Zn > Ni > Cu > Co > Cd > Pb in transported sediments. Our results suggest that this area has three sources of heavy metals: anthropogenic (PC1), mixed (PC2), and geogenic (PC3). Regarding human influence, apart from industrial activities nearby, agriculture should perhaps reduce the consumption of chemical fertilizers and pesticides, and a rethinking of the current application of manure could also be useful. Concerning health hazards, the values obtained here showed concerning levels of Cu and Ni for childhood cancer rather than non-carcinogenic risk. The rapid urban growth of this area and the consequently higher demand for food products can cause agricultural intensification, and cancer risk could perhaps start to be a serious problem for local authorities. Nevertheless, further in-depth research in this area and many others abroad is still needed. Several soil remediation strategies and management approaches, including physical remediation, chemical remediation, bioremediation, and agro-ecological engineering techniques, are being explored with the potential to reduce heavy metal contents in soils. However, the implications of these sustainable solutions which are both technically and economically feasible are needed to bring in practices at the field level by enforcing the execution of policies.

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