

Evaluation and Health Risk Assessment of Five Toxic Metals Concentration in Soil, Water and Seasonal Vegetables and Fruits from Pakistan-Afghanistan Border, Torkham

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Received: 28.06.2021; Revised: 30.08.2021; Accepted: 4.09.2021; Published: 30.10.2021

Abstract: Heavy metals are of serious concern for human health and food security. The risk to human health is directly related to soil and water pollution, which enter the food chain (vegetables and fruits). The current study was designed to investigate the heavy metals (Cr, Pb, Ni, Cd, and Zn) concentrations in five vegetables (Potato, Tomato, Turnip, Onion & Taro) and five fruits (Banana, Apple, Grapes, Pomegranate, and Guava) samples. We also estimated metal concentrations in water and soil samples. Torkham, a border region between Afghanistan and Pakistan, was selected for the purpose. The analysis was performed on Atomic Absorption Spectroscopy (AAS, Perkin- Elmer 700). In vegetables, the highest Pb and Ni were recorded in Potatoes (0.34 ± 0.066) and Onions (0.278 ± 0.021). While in tomatoes, the highest concentrations of Cd (0.90 ± 0.115), Zn (0.726 ± 0.008), and Cr (1.761 ± 0.028) were noted. While, in fruits the highest levels of Pb (0.32 ± 0.03), Cd (0.61 ± 0.0119), Zn (0.357 ± 0.0047) and Ni (0.111 ± 0.0128), while in apples we noted the highest Cr levels (0.789 ± 0.0452). We compared the metal concentrations with permissible limits set by World Health Organization/Food and Agricultural Organization (WHO/FAO). In the majority of the samples, the metal levels exceeded the permissible limits, while few were found within the safe limits. Based on heavy metals concentrations in soil, water, vegetables, and fruit samples. We calculated the health risk assessment, i.e., daily intake of metals (DIM) estimated daily intake (EDI), target hazard quotient (THQ), total target hazard quotient (TTHQ), carcinogenic risk (CR), health risk index (HRI) and contamination factor (CF). The EDI for Ni and Zn was in the safest region. While for Cd and Pb, the highest EDI was recorded in tomatoes (0.394) and guava (0.303), respectively. Similarly, Cr poses' serious risk with the highest EDI in tomatoes (0.771), apples (0.563), turnip (0.393), guava (0.282), and banana (0.263). If HRI, THQ, TTHQ, and CR are less than one (< 1), it means the exposed populations are not at risk. In the present HRI, THQ and TTHQ were found to be less than one. The contamination factor for Ni and Zn was found to be considerable ($CF < 6$), while Pb, Cd, and Cr presented the highest contamination degree ($CF > 6$). This study suggested that some samples may impose a certain degree of potential health risk. It is required that proper action should be taken to avoid chronic exposure and consequent adverse health effects.

Keywords: Torkham; heavy metals; AAS; DIM; EDI; HRI; THQ; TTHQ; CF and CR.

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1. Introduction

Heavy metal pollution is the key global eco-environmental issue, posing a serious health threat to plants, humans, and animals [1]. The underlying causes of heavy metal pollution include natural sources (erosion of soils, volcanic emissions, and weathering) and anthropogenic sources (agricultural burning, biomass activities, fossil fuel activities, and industrial burning) [2, 3]. The intensification of anthropic activities in developing countries with extremely high populations releases potentially harmful substances perturbing the environment [4, 5]. Heavy metals are a serious concern due to their toxicity, persistence, non-biodegradability, contamination, and bioaccumulation in the food chain. Additionally, the heavy metals contaminants are highly toxic, enter into water and food, eventually degrade their quality [6-8].

Water is the utmost widespread natural resource, and in most developing countries, freshwater availability remains a prime issue. Due to the unavailability of traditional water resources, treated or untreated wastewater is used for irrigation [9-11]. Furthermore, wastewater carries appreciable amounts of trace toxic metals. In the soil, the wastewater for irrigation leads to the accumulation of non-biodegradable heavy metals. The continued consumption of wastewater for irrigation leads to an increase in heavy metals and persists in soil increased the heavy metals concentrations in cultivated crops [12-14].

Soil functions as a sink and transport of substances to water and food [15]. At low pH, soil increases the mobility and bioavailability of heavy metals due to its effects on the solubility of heavy metals [16]. Heavy metals contamination with soil is normal, and to crops, it provides a crucial source of metals, and finally, living organisms are affected by these toxic metals [17].

Vegetables and fruits take up heavy metals from metal-polluted soils and accumulate them in higher quantities in edible and non-edible parts. Moreover, a higher concentration of these heavy metals badly affects the human body due to their non-biodegradable nature [18, 19]. Even though some metals are vital for plant growth and human nutrition, some metals (Cu, Cr, and Ni) are toxic at higher concentrations [20, 21]. Additionally, Cr, Co, Cu play an essential role in metabolism but are carcinogenic at elevated concentrations. A high level of Pb is highly toxic and causes chronic health risks, including lung cancer, stomach cancer, and nerve damage. Therefore, in the soil-plant-human system, it is important to investigate the HMs contamination and identify the health risks to heavy metals [22-24]. It is worthy to note that heavy metals above the permissible limit can cause serious health risks like gastrointestinal and renal toxicity, tumors, cardiovascular issues, tubular and glomerular dysfunctions, and osteoporosis.

The present study was designed to investigate the metal contents (Pb, Cd, Zn, Cr, and Ni) in water, soil, fruits, and vegetable samples. The sampling site plays a pivotal role in project designing, such as the mining infrastructure, industries, agricultural activities, minerals and fuel burring near storage houses, etc. We will specifically mention that various locations or sites have been explored in KP, such as Karak [25], D. I. Khan [26], Kohat [26, 27], Bannu, Hangu, Lakki Marwat [26], Swabi, Peshawar [28], Hazara [29], Haripur [30], Nowshera [31], River Kabul at Warsak Peshawar [32], Cherat [33], District Buner [34], Malakand [35], Kurram River [36], Chitral [37], River Siranat Khaki [38], Charsadda and Mardan [39] to name a few. However, to the best of our knowledge, there has been no major study about heavy metals estimation in soil, water and food crops in Torkham, KP. Although there are various sampling and/or analytical techniques such as Atomic Fluorescence Spectrometry (AFS), Atomic

Absorption Spectrometry (AAS), and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) used for analysis of heavy metals. However, we applied Atomic Absorption Spectrometry (AAS) technique.

2. Materials and Methods

2.1. Study site description.

Torkham (Urdu, Persian, and Pashto: تورخم Tūrkhām) is the border region between Pakistan and Afghanistan. It is located in District Khyber (Federally Administrated Tribal Areas), Pakistan. It is further connected to Jalalabad (75 Km) and Kabul (228 Km). On the Pakistani side, it connects to Peshawar (54 Km) in the east and further connects to Islamabad (243 Km). It lies 34° 1' 33.3012" north-latitude and 71° 33' 36.4860" east-longitude at Pakistan. The climate of Torkham is semi-arid, with an average temperature is 20.3°C, and the mean annual precipitation level is 407 mm. June is the hottest month with an average maximum temperature of 31.0 °C, and January is the coldest month with a minimum temperature of 8.4 °C.

2.2. Sampling and pre-treatment.

Soil samples containing 5 sub-samples of 1kg were collected from 10 cm in diameter and 20 cm deep. At a distance of every 10m from a different direction, each sample was collected. The samples were packed properly in polyethylene bags and brought to the laboratory. After properly air-dried, sieved through 2 mm mesh and stored in sealed polyethylene bags.

Vegetable and fruit samples were also collected from the same site and carried to the Institute of Chemical Sciences laboratory, University of Peshawar, Pakistan. All samples (Table 1) were washed with double deionized water to clean dust particles. At 60°C temperature for about 70 hours, the fruits and vegetables were dried in the oven and weighed constantly. The dried samples (of vegetables and fruits) were ground in a ball mill to fine powdered and then placed in a paper bag for further procedure.

Table 1. Description (botanical and vernacular names) of vegetables and fruits samples from Torkham.

S#	Plant species	Family	English Name	Vernacular Name	Part/s Used
1.	<i>Solanum Lycopersicum</i>	Solanaceae	Tomato	Tamator	Fruit
2.	<i>Solanum Tuberosum</i> L.	Solanaceae	Potato	Aalo	Tubers
3.	<i>Brassica Rapa Subsp. Rapa</i>	Brassicaceae	Turnip	Shaljum	Underground stem
4.	<i>Allium Cepa</i>	Amaryllidaceae	Onion	Peyaz	Underground stem
5.	<i>Colocasia Esculenta</i>	Araceae	Taro	Kachaloo	Underground stem
6.	<i>Malus Domestica</i>	Rosaceae	Apple	Apple	Fruit
7.	<i>Psidium Guajava</i>	Myrtaceae	guava	Amrod	Fruit
8.	<i>Musa Acuminata</i>	Musaceae	Banana	Kela	Fruit
9.	<i>Vitis Vinifera</i>	Vitaceae	Grapes	Angor	Fruit
10.	<i>Punica Granatum</i>	Punicaceae	Pomegranate	Anar	Fruit

2.3. Water, soil, vegetables, and fruit sampling.

Soil sample (1 g) in powdered form was placed in a beaker, and 15ml aqua regia (HNO₃: HCl at 1:3 ratio) was added to it and placed overnight. The next day samples were heated on a hot plate until they dried. HClO₄ (5 ml) was added and again heated slowly until close to dryness. The sample was then filtered through watt-man filter paper No. 42 into volumetric

flasks (50 ml) by adding diluted acid solution. In the end, 50ml of filtrates were diluted with deionized water and preserved for further analysis.

The pH of the water was measured and pre-washed with 20% HNO₃ and double distilled water and filtered. Few drops of HNO₃ were added and stored at refrigerator 4°C for further analysis.

Dried vegetable and fruit samples (2 g) in powdered form were weighed in beakers and 10 ml of HNO₃. The samples were kept overnight at room temperature. The next day samples were digested at 195°C for 1.5 h on a hot plate. We added 5ml of HClO₄ after cooling and gradually heated until the complete digestion. Samples were filtered and diluted with DDW in volumetric flasks to require volume (50 ml), washed with acidified water. Sealed samples were stored at room temperature for further analysis.

2.4. Analytical procedures.

The concentrations of Zn, Ni, Pb, Cd, and Cr in soils, water, vegetables, and fruits samples were analyzed by Atomic Absorption Spectrophotometry (AAS-700-Perkin-Elmer).

We used pure and analytical-grade chemicals in the present study. Co, Zn, Ni, Pb, Cd, and Cr standard solution was prepared by diluting its 1000 mg L⁻¹ specified standard solutions (F. KamicaBusch, Switzerland). The recovery of Cd (101 ± 4.5%) and Pb (93 ± 7.3%) was satisfactory from these reference materials. For data quality assurance, each digested sample was analyzed in triplicate under standard conditions within the confidence level of 95%. All analyses were facilitated by the Centralized-Resource Laboratory (CRL), University of Peshawar, Pakistan.

2.5. Health risk assessment.

Details about various constants/parameters are described in table 2.

2.5.1. Daily intake of metals (DIMs).

The average daily intake of metals (DIMs) was calculated according to the following equation [54-56].

$$DIM = CM \times CF \times IR (\text{veg}) / Bw$$

Where CM is metal concentrations, CF is conversion factor (0.085) [55], IR is ingestion rate of vegetables, and BW is average body weight.

The average daily ingestion rate of food crops for adults (both male and female) was considered to be 0.345 kg-person₋₁-day₋₁, respectively [54, 55], while the average adult body weight was considered as 70 kg.

Table 2. Various constants. EFR=exposure frequency rate, ED=exposure duration, BW= body weight, ATn= averaged exposure time, CM= concentrations of metal, Cf= conversion factor, FIR= food ingestion rate, MAC= maximum allowed concentration.

Parameters	Sample (Value)	Reference	Vegetables (MAC= FAO/WHO, 2011)	mg/kg fw	Reference
Ef or EFR (days)	365	-	Pb	0.1	50
ED (years)	70	40	Cr	2.3	50
BW (kg)	70	41	Cd	0.05	50
ATn(days)	25550	-	Ni	10	50
CM (mg/kg dry weight) present study			Zn	Unknown	
Cf	0.085	42, 43	Fruits (MAC= FAO/WHO, 2002)		
Oral reference dose(RfD) (mg/kg/day)	Value		Cr	1.0	51

Parameters	Sample (Value)	Reference	Vegetables (MAC= FAO/WHO, 2011)	mg/kg fw	Reference
Pb	0.0035	44	Cd	0.05	51
Cd	0.001	45	Ni	0.8	51
Zn	0.3	46	Sample (Vegetable/Fruit)	FIR	
Cr	0.003	44	Tomato	30.66	45
Ni	0.02	46	Potato	35.51	45
Oral cancer slope factor (CPSo) (mg/kg/day)-1	Value		Turnip	22.85	45
Pb	0.0085	47	Onion	40.6	45
Cd	0.38	48	Kachalo	28.9	52
Cr	0.5	49	Apple	50	52
Ni	1.7	46	Amrood	66.3	52,53
			Banana	34.71	53
			Grapes	26.1	53
			Pomegranat	10	53

2.5.2. Health risk index (HRI).

To estimate the chronic health risk, the health risk index (HRI) for different metals was determined by the following formula [55, 56].

$$HRI = EDI/RfD,$$

Here, HRI and RfD, represent the human health risk index and reference dose of metal, respectively. If $HRI < 1$, it means the population is not at risk [54, 22].

2.5.3. Estimated daily intake.

The estimated daily intake (EDI) of all metals was calculated by applying the following equation.

$$EDI = C \times FIR / BW$$

Where C is the concentration of the element in the food type in mg/kg, FIR is the daily food ingestion rate in grams per day, and BW is the reference body weight (70 kg).

2.5.4. Target hazard quotient.

The target hazard quotient (THQ) is defined as the ratio of exposure to the toxic element and the reference dose.

The THQ describes the non-carcinogenic health risk posed by exposure to the respective toxic element. Suppose the THQ is < 1 then no cancer threat or vice versa. The following equation was used for this purpose.

$$THQ = EFR * Ed * FIR * C / RfD * Bw * TA \times 0.001$$

Where EFR is the exposure frequency to the trace element, Ed is the exposure duration (70 yrs), FIR is the food ingestion rate in grams per day for the respective food item, C is the concentration in a wet weight of the trace element in the given food item, RfD is the oral reference dose of the trace element in $\mu\text{g/g/day}$, BWa is the reference body weight of 70 kg, and ATn is the averaged exposure time (365 days*70yrs) and 10^{-3} is the unit conversion factor (see Table 2).

2.5.5. Hazard index or TTHQ.

The hazard index (HI) is the sum of the individual target hazard quotients of the elements assessed for each food type. If the HI is > 1 there is the potential for adverse non-carcinogenic health effects.

The equation for HI is:

$$HI = \sum_{N=1}^i THQ_n$$

2.5.6. Contamination factor.

Contamination factor (CF) is a ratio obtained from heavy metal concentrations in contaminated and background sites.

$$CF = C_m \text{ Sample} / C_m \text{ Background}$$

C_m is metal concentration as determined by AAS, and C_m background is constants for each metal, i.e., Bk for Pb is 0.0035, while for Cr, Zn, Cd, and Ni, the values are 0.003, 0.3, 0.001, and 0.04, respectively. Four contamination categories are documented based on the contamination factor (27). $CF < 1$ low contamination; $1 \leq CF \leq 3$ moderate contamination; $3 \leq CF < 6$ considerable contamination; $CF > 6$ very high contamination. While the degree of contamination (Cd) was defined as the sum of all contamination factors. The following terms are adopted to illustrate the degree of contamination: $Cd < 6$: low degree of contamination; $6 \leq Cd < 12$: moderate degree of contamination; $12 \leq Cd < 24$: considerable degree of contamination; $Cd > 24$: very high degree of contamination indicating serious anthropogenic pollution.

2.5.7. Carcinogenic risk.

Carcinogenic risk (CR) is used to determine the probability to develop cancer. . It can be calculated by the following equation as suggested by USPEA, 2000 [52]:

$$CR = CSF \times EDI$$

Where CSF is the carcinogenic slope factor for Pb and Cr was considered to be 0.0085 and $0.05 \text{ (mg/kg/day)}^{-1}$, respectively, as set by USPEA [57]. EDI is the estimated daily intake of heavy metals. If the risk level is 10^{-4} , it means the risk of cancer is 1 in 10000. If it is 10^{-6} , it means very low risk, i.e., 1 in 1000000. 3. Results and Discussion

3.1. Allowable limit of heavy metals.

In all samples, we calculated the lead, cadmium, zinc, chromium, and nickel concentrations. It was compared with the recommended limit as established by the FAO/WHO in 2011, 2002 to assess food contamination levels. The mean concentration with standard deviation is presented in table 3.

In vegetables, the highest lead was found in potato ($n=0.34$), followed by taro root ($n=0.33$) and turnip ($n=0.29$). Similarly, in fruits, the highest concentration was recorded in guava ($n=0.32$), followed by apple ($n=0.27$) and pomegranate ($n=0.22$). However, WHO/FAO in 2002 and 2011, recommended 0.1 mg/kg/fw levels for Pb. This confirms that the lead level in tested samples was comparatively higher and may pose a significant health threat. In vegetables, the highest cadmium was noted in tomato ($n=0.9$), followed by onion ($n=0.072$) and taro root ($n=0.064$). While in fruits, the highest Cd was found in guava ($n=0.061$), followed by apple ($n=0.038$) and grapes ($n=0.037$). WHO/FAO in 2002 and 2011 also described the recommended levels for cadmium, i.e., 0.05mg/kg fw. In the present study, the Cd levels in vegetables were higher than recommended levels, while in fruits, the Cd level was significantly lower than the permissible level. Similarly, In vegetables, the highest Zn was found in tomatoes ($n=0.726$), while in fruits, guava showed the highest levels in Zn, i.e. ($n=0.357$). The highest Cr was recorded in tomatoes ($n=1.761$), while in fruits, apple showed

the highest levels, i.e. (n=0.789). Similarly, onions (n=0.278) and guava (n=0.111) showed the highest Ni concentrations in the vegetables and fruits categories, respectively. The data about the water and soils samples are also described in table 3. The WHO/FAO in 2002 and 2011 recommended level for Cr in fruits and vegetables is 1.0 and 2.3 mg/kg fw, respectively. While, for Ni the recommended values for fruits and vegetables are 0.8 and 10 mg/kg fw, respectively. In our study, the recorded level for Cr and Ni were significantly lower than WHO/FAO recommended values.

3.2. Daily intake of heavy metals (DIM) through fruits and vegetables

The daily intake of heavy metals through the consumption of fruit and vegetables tested was calculated according to the formula mentioned above. The highest DIM was recorded for Cr, followed by Cd, Zn, Pb, and Ni, respectively. The values of DIM for the stated metals were found to be 0.00074 (in tomatoes), 0.0004 (in tomatoes), 0.0003 (in tomatoes), 0.00014 (in potatoes), and 0.00012 in onions. The details are described in table 4. We will mention that the formula's cf was (n=0.085), IR was 0.345, and BW was 70kg.

3.3. HRI.

The health risk index for heavy metals by consumption of vegetables and fruits for adults was also calculated, and the data is presented in table 5. HRI of Pb, Cd, Zn, Cr and Ni ranged from 0.002394-0.040696, 0.00796-0.377036, 0.000133-0.001014, 0-0.245911 and 0-0.002912, respectively. The highest HRI was found for Cd (n=0.377036), followed by Cr (n=0.245911), Pb (n=0.040696), Ni (n=0.002912) and Zn (n=0.001014). The reference doses for Pb, Cd, Cr, Zn, and Ni were kept constant, i.e., 0.0035, 0.001, 0.3, 0.003, and 0.04.

3.4. Estimate daily intake (EDI) of heavy metals.

The food chain is an essential pathway to determine the route of exposure of heavy metals to humans. The exposure of toxic metals to humans can be determined by their daily intake [1, 2]. Before calculations, it's worthy to note that FIR varies per sample. The list of FIR for vegetables and fruits is given in table 6. The tolerable daily intake recommended by IRIS of USEPA for Pb, Cd, Zn, Cr, and Ni is 0.002, 0.001, 0.3, 0.002, and 0.16 mg kg⁻¹ day⁻¹.

3.4.1. Lead.

We will specifically state that the tolerable daily intake recommended by IRIS of USEPA for lead is 0.002 mg kg⁻¹ day⁻¹. Our analysis indicated that the consumption of lead is significantly higher than the tolerable daily intake. Precisely, the potato has higher EDI (n=0.17). The order of EDI for Pb in vegetables intake is as follow: turnip (0.0946 mg kg⁻¹ day⁻¹) < tomato (0.114 mg kg⁻¹ day⁻¹) < kachalo (0.136 mg kg⁻¹ day⁻¹) < onion (0.162 mg kg⁻¹ day⁻¹) < potato (0.172 mg kg⁻¹ day⁻¹). While, in fruits the highest value of Pb is found in Guava (0.303 mg kg⁻¹ day⁻¹) followed by apple (n=0.193), grapes (n=0.037), pomegranate (n=0.0314) and banana (n=0.0099). The toxicity of Pb affects various organs in humans, such as the kidney, spleen, lungs, and liver, triggering severe biochemical disorders.

Table 3. The observed mean \pm standard deviation of heavy metals (Pb, Cd, Zn, Ni, and Cr) in different vegetables, fruits, soil, and water samples from Torkham.

S#	Sample	Conc (Pb)	SD(Pb)	Conc (Cd)	SD (Cd)	Conc (Zn)	SD (Zn)	Conc (Cr)	SD (Cr)	Conc (Ni)	SD (Ni)
1.	Tomato	0.26	0.044	0.9	0.115	0.726	0.008	1.761	0.0285	0.225	0.0493
2.	Potato	0.34	0.066	0.04	0.008	0.303	0.0032	0	0.0106	0	0.0711
3.	Turnip	0.29	0.001	0.035	0.052	0.274	0.0028	1.206	0.0297	0.079	0.0131
4.	Onion	0.28	0.091	0.072	0.0112	0.543	0.007	0.053	0.0331	0.278	0.0201
5.	Kachalo	0.33	0.02	0.064	0.027	0.69	0.0096	0.319	0.0183	0.256	0.0126
6.	Apple	0.27	0.124	0.038	0.0108	0.095	0.0065	0.789	0.0452	0	0.074
7.	Amrood	0.32	0.03	0.061	0.0119	0.357	0.0047	0.298	0.0768	0.111	0.0128
8.	Banana	0.02	0.073	0.019	0.009	0.11	0.0065	0.532	0.0065	0	0.0365
9.	Grapes	0.1	0.049	0.037	0.037	0.351	0.103	0.351	0.0103	0.0687	0.0132
10.	Pomegranat	0.22	0.002	0.029	0.0228	0.105	0.0017	0	0.0123	0	0.459
11.	Water 1	1.01	0.074	0.65	0.113	0.076	0.0016	0	0.0275	0.042	0.0657
12.	Water 2	0.38	0.084	0.77	0.145	0.078	0.0026	0	0.0445	0.02	0.0367
13.	Soil 2	0.64	0.063	0.07	0.0043	0.902	0.007	0.117	0.0206	0.383	0.0523
14.	Soil 2	0.31	0.04	0.86	0.0089	0.423	0.009	0.047	0.0192	0.36	0.0719

Table 4. Daily intake of metals (DIM) ($\mu\text{g g}^{-1}$) in different vegetables, fruits, soil and water samples from Torkham.

Sample	DIM (Pb)	DIM (Cd)	DIM (Zn)	DIM (Cr)	DIM (Ni)
Tomato	0.00011	0.00038	0.00030	0.00074	9.4E-05
Potato	0.00014	0.00002	0.00013	0.00000	0.0E+00
Turnip	0.00012	0.00001	0.00011	0.00051	3.3E-05
Onion	0.00012	0.00003	0.00023	0.00002	1.2E-04
Kachalo	0.00014	0.00003	0.00029	0.00013	1.1E-04
Apple	0.00011	0.00002	0.00004	0.00033	0.0E+00
Amrood	0.00013	0.00003	0.00015	0.00012	4.7E-05
Banana	0.00001	0.00001	0.00005	0.00022	0.0E+00
Grapes	0.00004	0.00002	0.00015	0.00015	2.9E-05
Pomegranat	0.00009	0.00001	0.00004	0.00000	0.0E+00
Water 1	0.00042	0.00027	0.00003	0.00000	1.8E-05
Water 2	0.00016	0.00032	0.00003	0.00000	8.4E-06
Soil 2	0.00027	0.00003	0.00038	0.00005	1.6E-04
Soil 2	0.00013	0.00036	0.00018	0.00002	1.5E-04

3.4.2. Cadmium.

The dietary reference dosage for cadmium is $0.001 \text{ mg kg}^{-1} \text{ day}^{-1}$. The highest EDI value of Cd was found for tomato i.e. $0.39 \text{ mg kg}^{-1} \text{ day}^{-1}$, onion (0.041), kachalo (0.026), potato (0.0202) and turnip (0.0114). Furthermore, the order of EDI values for Cd in fruit samples is guava ($0.0578 \text{ mg kg}^{-1} \text{ day}^{-1}$) > apple ($0.027 \text{ mg kg}^{-1} \text{ day}^{-1}$) > grapes ($0.013 \text{ mg kg}^{-1} \text{ day}^{-1}$) > banana ($0.009 \text{ mg kg}^{-1} \text{ day}^{-1}$) > pomegranate ($0.004 \text{ mg kg}^{-1} \text{ day}^{-1}$). Cd is carcinogenic element cause lung cancer, kidney cancers and also damage kidney, lungs.

3.4.3. Zinc.

The average recommended daily intake of Zn is $0.3 \text{ mg kg}^{-1} \text{ day}^{-1}$, and all values for EDI calculated for Zn are lower than the tolerable daily intake recommended by IRIS of USEPA except tomatoes ($n=0.318$), onion ($n=0.314$), and guava ($n=0.338$). The details are provided in table 6. Zinc is an important metal for growth and development, and deficiency cause many defects in zinc metabolism.

3.4.4. Chromium.

The EDI of Chromium is $0.002 \text{ mg kg}^{-1} \text{ day}^{-1}$ recommended by IRIS of USEPA. Tomatoes, turnips, and apples exhibited higher values of EDI, i.e., 0.771 , 0.393 , and 0.563 , respectively. For other samples, the values (EDI) were below recommended levels. The toxic form of Cr compounds causes lung cancer and also leads to nose cancer and nasal sinuses.

3.4.5. Nickel.

The highest EDI for nickel was found in onions ($n=0.16$), followed by kachalo (0.106), tomato (0.099), turnip (0.025), and potato (0.00). While, in fruits, guava has the highest Ni value of EDI i.e., $0.105 \text{ mg kg}^{-1} \text{ day}^{-1}$ followed by grapes (0.026). Furthermore, no nickel is found in apple, banana, and pomegranate i.e., $0 \text{ mg kg}^{-1} \text{ day}^{-1}$.

3.5. Target hazard quotient (THQ).

Evaluation for risk assessment of daily intake values of heavy metals can be determined through the Target Hazard Quotient. The THQ values for Zn, Pb, Cr, Cd, and Ni in the majority of vegetables and fruits in the study area were found to be less than one. The highest THQ value in vegetables and fruits were noticed in cadmium (0.39) followed by Cr ($n=257$), Pb (0.0865), Zn ($n=0.00106$) and Ni ($n=0.0006$).

3.6. Total THQ or hazard index (HI).

Target hazard quotient can only determine the individual heavy metals in food, but more than one heavy metal is usually found in food items. Therefore, the total THQ or hazard index (HI) was calculated to determine all heavy metals in vegetables and fruits. The details are provided in table 7. When the HI exceeds unity, eating the contaminated food can cause serious health issues. The HI of Ni (1.018), Cd (1.295), Zn (3.554), and Cr (5.309) in the present study exceeded the unity, which can be interpreted as a health risk. Nonetheless, the lowest value of HI was found for Pb (0.358), i.e., lower than unity.

Table 5. Health risk index (HRI) for individual heavy metals in different vegetables, fruits, soil, and water samples from Torkham.

Sample	HRI (Pb)	HRI (Cd)	HRI (Zn)	HRI (Cr)	HRI (Ni)
Tomato	0.03112	0.377036	0.001014	0.245911	0.002356
Potato	0.040696	0.016757	0.000423	0	0
Turnip	0.034711	0.014663	0.000383	0.168409	0.000827
Onion	0.033514	0.030163	0.000758	0.007401	0.002912
Kachalo	0.039499	0.026811	0.000964	0.044546	0.002681
Apple	0.032317	0.015919	0.000133	0.110178	0
Amrood	0.038302	0.025555	0.000499	0.041614	0.001163
Banana	0.002394	0.00796	0.000154	0.07429	0
Grapes	0.011969	0.0155	0.00049	0.049015	0.00072
Pomegranat	0.026333	0.012149	0.000147	0	0
Water 1	0.120891	0.272304	0.000106	0	0.00044
Water 2	0.045484	0.322575	0.000109	0	0.000209
Soil 2	0.076604	0.029325	0.00126	0.016338	0.004011
Soil 2	0.037105	0.360279	0.000591	0.006563	0.00377

Table 6. Estimated daily intake (mg/kg bw/day) of heavy metals from fruits and vegetables for adults. MTDI stands for Maximum Tolerable Daily Intake (MTDI) (mg/day).

S#	Sample	FIIR	EDI (Pb)	MTDI	EDI Cd)	MTDI	EDI (Zn)	MTDI	EDI (Cr)	MTDI	EDI (Ni)	MTDI
1)	Tomato	30.66	0.11388	0.21	0.3942	0.02–0.07	0.317988	60–65	0.771318	0.035–0.2	0.09855	0.1–0.3
2)	Potato	35.51	0.172477	0.21	0.020291	0.02–0.07	0.153708	60–65	0	0.035–0.2	0	0.1–0.3
3)	Turnip	22.85	0.094664	0.21	0.011425	0.02–0.07	0.089441	60–65	0.393673	0.035–0.2	0.025788	0.1–0.3
4)	Onion	40.6	0.1624	0.21	0.04176	0.02–0.07	0.31494	60–65	0.03074	0.035–0.2	0.16124	0.1–0.3
5)	Kachalo	28.9	0.136243	0.21	0.026423	0.02–0.07	0.284871	60–65	0.131701	0.035–0.2	0.105691	0.1–0.3
6)	Apple	50	0.192857	0.21	0.027143	0.02–0.07	0.067857	60–65	0.563571	0.035–0.2	0	0.1–0.3
7)	Amrood	66.3	0.303086	0.21	0.057776	0.02–0.07	0.33813	60–65	0.282249	0.035–0.2	0.105133	0.1–0.3
8)	Banana	34.71	0.009917	0.21	0.009421	0.02–0.07	0.054544	60–65	0.263796	0.035–0.2	0	0.1–0.3
9)	Grapes	26.1	0.037286	0.21	0.013796	0.02–0.07	0.130873	60–65	0.130873	0.035–0.2	0.025615	0.1–0.3
10)	Pomegranat	10	0.031429	0.21	0.004143	0.02–0.07	0.015	60–65	0	0.035–0.2	0	0.1–0.3
11)	Water 1	0	0	0.21	0	0.02–0.07	0	60–65	0	0.035–0.2	0	0.1–0.3
12)	Water 2	0	0	0.21	0	0.02–0.07	0	60–65	0	0.035–0.2	0	0.1–0.3
13)	Soil 2	0	0	0.21	0	0.02–0.07	0	60–65	0	0.035–0.2	0	0.1–0.3
14)	Soil 2	0	0	0.21	0	0.02–0.07	0	60–65	0	0.035–0.2	0	0.1–0.3

Table 7. Calculation of Target Hazard Quotient (THQ) in vegetables and fruits samples.

Sample	THQ (Pb)	THQ (Cd)	THQ (Zn)	THQ (Cr)	THQ (Ni)
Tomato	0.032537	0.3942	0.00106	0.257106	0.002464
Potato	0.049279	0.020291	0.000512	0	0
Turnip	0.027047	0.011425	0.000298	0.131224	0.000645
Onion	0.0464	0.04176	0.00105	0.010247	0.004031
Kachalo	0.038927	0.026423	0.00095	0.0439	0.002642
Apple	0.055102	0.027143	0.000226	0.187857	0
Amrood	0.086596	0.057776	0.001127	0.094083	0.002628
Banana	0.002833	0.009421	0.000182	0.087932	0
Grapes	0.010653	0.013796	0.000436	0.043624	0.00064
Pomegranat	0.00898	0.004143	0.00005	0	0
Water 1	0	0	0	0	0
Water 2	0	0	0	0	0
Soil 2	0	0	0	0	0
Soil 2	0	0	0	0	0

The HI for the heavy metals analyzed for the fruits and vegetables ranged from 0.0358 for Cadmium to a high of 0.340 for Lead. The total HI is dominated by Cr, with a value of 5.309 higher than all other heavy metals. Evaluating the HI of Heavy metals in each vegetable and fruit examined for the five elements ranged from 0.143 for pomegranate to a high of 3.645 for tomato. We applied the following constants in the formula EFR (365 days), ED (70), FIR details are already provided in table 6, C is the concentration of each metal as determined by AAS, BW was 70, RfD for each metal is described above and Ta was constant i.e. 25550. While the total THQ or TTHQ is described in table 8. The oral toxicity RfDs given in US-EPA 2005 database are: for Cd = 5.00E-04; for Cr = 3.00E-03; for Ni = 2.00E-02; for Pb = 3.6E-03; and for Zn = 3.00E-01 mg/kg/day. The people exposed to $HQ < 1$ will be considered harmless from any chronic risks to happen [54, 58].

Table 8. Calculation of Total Target Hazard Quotient (TTHQ) of Pb, Cd, Zn, Ni and Cr in vegetables and fruits.

Sample	THQ (Pb)	THQ (Cd)	THQ (Zn)	THQ (Cr)	THQ (Ni)	Sum
Tomato	0.033	0.39	0.0011	0.257	0.0025	0.687
Potato	0.049	0.02	0.0005	0.000	0.0000	0.070
Turnip	0.027	0.01	0.0003	0.131	0.0006	0.171
Onion	0.046	0.04	0.0010	0.010	0.0040	0.103
Kachalo	0.039	0.03	0.0009	0.044	0.0026	0.113
Apple	0.055	0.03	0.0002	0.188	0.0000	0.270
Amrood	0.087	0.06	0.0011	0.094	0.0026	0.242
Banana	0.003	0.01	0.0002	0.088	0.0000	0.100
Grapes	0.011	0.01	0.0004	0.044	0.0006	0.069
Pomegranate	0.009	0.00	0.0001	0.000	0.0000	0.013

3.7. Contamination factor (CF).

The CF is a ratio of the concentration of elements found in samples to the background content. Based on contamination factor, four contamination levels are documented i.e., low contamination ($CF < 1$), moderate contamination ($CF \geq 3$), considerable contamination ($CF < 6$), very high contamination ($CF > 6$) [5]. In study site soil 1, CF values are 182.86, 70, 39, 9.575, and 3.01 for Pb, Cd, Cr, Ni, and Zn, respectively. CF order was found as $Pb > Cd > Cr > Ni > Zn$. Similarly, in study site soil-2, 860, 88.57, 15.66, 9, and 1.41 for Cd, Pb, Cr, Ni, and Zn. The order of CF values were found as $Cd > Pb > Cr > Ni > Zn$. Higher values of CF in the soil of study sites could be attributed to mining.

Furthermore, in water sample 1, CF values were 650, 288.57, 1.05, 0.25, and 0 for the Cd, Pb, Ni, Zn, and Cr, respectively. These CF values were found in order of $Cd > Pb > Ni > Zn > Cr$. In water sample 2, the metal values were 770, 108.57, 0.26, 0.5 and 0 for the Cd, Pb,

Zn, Ni and Cr. The CF values are described in Table 9. The background values for Pb, Cr, Zn, and Ni were kept constant, i.e., 0.0035, 0.003, 0.3, and 0.04. It is also noted that the CF for Cr, Pb, and Cd in vegetables and fruit samples was very high except Pb (5.71) in bananas and Cr (0) in potatoes. While CF for Zn and Ni in vegetables and fruits samples can be defined as moderately contaminated.

Table 9. Contamination factor of different heavy metals in vegetables, fruits, soil, and water samples from Torkham.

S#	Sample	CF (Pb)	CF (Cd)	CF (Zn)	CF (Cr)	CF (Ni)
1)	Tomato	74.29	900	2.42	587	5.625
2)	Potato	97.14	40	1.01	0	0
3)	Turnip	82.86	35	0.91	402	1.975
4)	Onion	80	72	1.81	17.66667	6.95
5)	Kachalo	94.29	64	2.3	106.3333	6.4
6)	Apple	77.14	38	0.32	263	0
7)	Amrood	91.43	61	1.19	99.33333	2.775
8)	Banana	5.71	19	0.37	177.3333	0
9)	Grapes	28.57	37	1.17	117	1.7175
10)	Pomegranat	62.86	29	0.35	0	0
11)	Water 1	288.57	650	0.25	0	1.05
12)	Water 2	108.57	770	0.26	0	0.5
13)	Soil 1	182.86	70	3.01	39	9.575
14)	Soil 2	88.57	860	1.41	15.66667	9

3.8. Carcinogenic risk.

According to US-EPA, by using the cancer slope factor (CSF), the carcinogenic risk is determined, i.e., developing risk by average lifetime dose of $1 \text{ mg kg}^{-1} \text{ day}^{-1}$ and is contaminant specific. The recommended safe limits by US-EPA for carcinogenic risk is defined as one additional case of cancer expected if one million people are exposed to these heavy metals. For regulatory purposes within the exposure range, the carcinogenic risk acceptance level is between 1×10^{-6} and 1×10^{-4} [59].

Data in table 10 (carcinogenic risk) illustrates the health risk to heavy metals like Pb and Cr. The data obtained revealed that CR for Cr exceeded its recommended safe limit that poses a significant carcinogenic health hazard. The highest carcinogenic risk (2.82×10^{-2}) for Cr was noted in apples and lowest (6.544×10^{-3}) in grapes. Moreover, among all the studied vegetables, the tomato has the highest carcinogenic risks (3.86×10^{-2}), and the onion has the lowest chances of carcinogenic risk (1.54×10^{-3}) associated with Cd. For Cd the order for CR is tomato > turnip > kachalo > onion > potato. For the fruits, CR for Cr was in the order of apple > guava > banana > grapes > pomegranate.

Table 10. Carcinogenic risk levels for heavy metals due to consumption of vegetables and fruits samples.

S#	Sample	CR (Pb)	CR (Cd)	CR (Cr)	CR (Ni)
1.	Tomato	0.00097	0.1498	0.3857	0.1675
2.	Potato	0.00147	0.0077	0.0000	0.0000
3.	Turnip	0.00080	0.0043	0.1968	0.0438
4.	Onion	0.00138	0.0159	0.0154	0.2741
5.	Kachalo	0.00116	0.0100	0.0659	0.1797
6.	Apple	0.00164	0.0103	0.2818	0.0000
7.	Amrood	0.00258	0.0220	0.1411	0.1787
8.	Banana	0.00008	0.0036	0.1319	0.0000
9.	Grapes	0.00032	0.0052	0.0654	0.0435
10.	Pomegranat	0.00027	0.0016	0.0000	0.0000
11.	Water 1	0.00000	0	0	0
12.	Water 2	0.00000	0	0	0

S#	Sample	CR (Pb)	CR (Cd)	CR (Cr)	CR (Ni)
13.	Soil 1	0.00000	0	0	0
14.	Soil 2	0.00000	0	0	0

Accordingly, the highest carcinogenic risk for Pb was noted in guava (2.576×10^{-3}) and the lowest in bananas (8.43×10^{-5}). Furthermore, in vegetables, the highest CR was calculated in potato (1.47×10^{-3}) and the lowest value in turnip (8.05×10^{-4}). The carcinogenic risk from exposure to Pb has exceeded the maximum recommended limit, i.e., 1×10^{-4} in most of the samples, which poses a serious effect on public health. Based on the data, it can be stated that the health risk tendency in fruits is higher in guava> apple> grapes> pomegranate> banana, while for vegetables, it is higher in potato> onion>kachalo> tomato> turnip. Further, it is noteworthy that CR for Cd surpassed the safe range in all fruits and vegetable samples.

4. Conclusions

In this study, we investigated the heavy metals (Cr, Pb, Ni, Cd, and Zn) concentrations in five vegetables (Potato, Tomato, Turnip, Onion & Taro) and five fruits (Banana, Apple, Grapes, Pomegranate, and Guava) samples, obtained from Torkham, a border region between Afghanistan and Pakistan. We also calculated daily intake of metals (DIM) estimated daily intake (EDI), target hazard quotient (THQ), total target hazard quotient (TTHQ), carcinogenic risk (CR), health risk index (HRI) and contamination factor (CF). In the majority of the samples, the metal levels exceeded the permissible levels, while few were found within the safe limits. This confirms that proper measures are needed to avoid adverse health effects.

Funding

This research received no external funding.

Acknowledgments

None.

Conflicts of Interest

The authors declare no conflict of interest.

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