# CONTAMINATION AND BIOACCUMULATION OF HEAVY METALS IN MEDICINAL PLANTS OF DISTRICT DIR UPPER, KHYBER PAKHTUNKHWA, PAKISTAN

# MARIA SHAHNAZ<sup>1</sup>, BUSHRA KHAN<sup>1\*</sup>, SARDAR KHAN<sup>1</sup>, JAVAID IQBAL<sup>1</sup>, ISHAQ AHMAD MIAN<sup>2</sup> AND MAMOONA WALI MUHAMMAD<sup>3</sup>

<sup>1</sup>Department of Environmental Science, University of Peshawar, 25120, Pakistan <sup>2</sup>Department of Soil and Environmental Sciences, The Agriculture University Peshawar, 25000, Pakistan <sup>3</sup>Pakistan Forest Institute Peshawar, 25000, Khyber Pakhtunkhwa, Pakistan \*Corresponding author's email: bushraasu@uop.edu.pk

#### Abstract

Environmental pollution caused by heavy metals (HMs) has gained more attention in recent decades due to their persistence, bioaccumulation and potentially toxic effects. This study was aimed to determine the heavy metals in soil and medicinal plant species sampled from District Upper Dir, Khyber Pakhtunkhwa (KP), Pakistan. The concentrations of HMs i.e. Cadmium (Cd), Chromium (Cr), Lead (Pb), Nickle (Ni) and Zinc (Zn) were measured in the soil (n =31) and medicinal plants (n= 31), by using graphite furnace atomic absorption spectrometry (AAS). Levels of HMs were used to estimate bioaccumulation factor (BAF). Mean concentrations of HMs in medicinal plants were 0.05 mg kg<sup>-1</sup>, 0.88 mg kg<sup>-1</sup>, 0.30 mg kg<sup>-1</sup> and 10.71 mg kg<sup>-1</sup> for Cd, Cr, Pb, Ni, and Zn respectively. The concentration of Cd (24 medicinal plant species) and Cr (6 species medicinal plant species) were above the permissible limits of World Health Organization (WHO) respectively. The highest mean Bioaccumulation Factor (BAF) value was found for *Mirabilis jalapa, Sagretia thea, Zenthoxylum armantum, Ajuga bracteosa,* and *Otostegia limbata* medicinal plant species. The bioaccumulation of HMs was in the order of root>shoot>leaves. While in the soil the mean concentrations of the selected HMs were in the order of Zn>Pb>Ni>Cr>Cd. In the conclusion the contamination in medicinal plants may contribute significantly to the exposure and health risks of the population. From the current study it is recommended that the medicinal plants should be tested for toxic heavy metals before use.

Key words: Heavy metals, Contamination, Bioaccumulation, Khyber Pakhtunkhwa.

#### Introduction

Heavy metals (HMs) are ubiquitous in the environment and present at small concentrations in soil due to the weathering of rocks and minerals (Hashmi *et al.*, 2007; Fergusson & Kim, 1991); however, anthropogenic activities have dramatically increased the concentrations of HMs in certain ecosystems especially concenteration of Pb, Fe, and Co in the fruit's plants (Sarma *et al.*, 2012; Parveen *et al.*, 2020).

The medicinal plants use for therapeutic applications has been on the rise worldwide, particularly in Asia (Abbasi *et al.*, 2011; Ahmed *et al.*, 2010; Chandrasekaran and Bahkali, 2013; Jaijoy *et al.*, 2010). The importance of medicinal plants is primarily due to their therapeutic effectiveness, ease of access, less costly compared to allopathic medicines and assumption that they are free from negative effects (Bohm, 2008; Huang *et al.*, 2010; Nathiya & Dorrcus, 2012). Mostly, population in developing countries relies on the unconventional medicine in their basic health care (Chan, 2003; Pandey *et al.*, 2010).

HMs contamination is of high concern due to their persistence, bioaccumulation and potentially toxic effects on living organisms (Censiet al., 2006; MacFarlane & Burchett, 2000). The problem of heavy metals entering the food chain requires systematic assessments to make timely decisions to avoid severe health effects because of the invisible mode of heavy metal toxicity (Chary et al., 2008). HMs can be accumulated in medicinal plants species and in the vegetables (Chan et al., 1993; Karri et al., 2008; Kabata-pendias, 2001; Gajalakshmi et al., 2012; Jarup, 2003), which is toxic to these plants species as well as to consumers (Memon et al., 2001; Houshmandfar &

Moraghebi, 2011; Siddhu *et al.*, 2008; Memon *et al.*, 2001). Some of HMs such as Zinc (Zn), Copper (Cu) and Nickel (Ni) are essential for the plants and humans; their excessive concentration is of great concern because of their toxicity to humans and animal (Zhuang *et al.*, 2009). However, metals such as lead (Pb) and Cadmium (Cd) are non-essential and are extremely toxic even at small concentrations (Khan *et al.*, 2008b; Korfali *et al.*, 2013; Gerendas *et al.*, 1999). The Lead and Cd are considered potential carcinogens which are associated with etiology of several diseases, especially cardiovascular, kidney, blood, nerves, and bone diseases (Jarup, 2003).

Use of plants for medicinal purposes has drawn high attention worldwide (Rates, 2000). According to World Health Organization (WHO), about 80% of the world's population consumes indigenous medicinal plants for various ailments (Rania *et al.*, 2015). Bioaccumulation of HMs in the medicinal plants is very toxic and have been reported in various studies (Qishlaqi & Moore, 2007; Ernst, 2002; Fabricant & Farnsworth, 2001; Sarma *et al.*, 2012). Poisoning associated with toxic metals in medicinal plants has been reported in Asia, Europe, and the United States (Olujohunge *et al.*, 1994; Kakosy *et al.*, 1996).

In Pakistan, there is no proper collection and processing system for the medicinal plants where people of the rural areas depend largely on traditionally prepared herbal medications (Shinwari & Khan, 2000; Wazir *et al.*, 2007; Abdul-Wahab *et al.*, 2008). The contamination of the medicinal plants with HMs could increase the toxicity chances (Boyd, 2009). Contamination of medicinal plants is mainly caused by the pollution of soil with toxic metals which may originate from polluted irrigation water, automobile/industrial emissions, atmospheric dusts,

pesticides and fertilizers (Baye & Hymete, 2010). The toxic metals interact with soil matrix and may persist for longer time creating long-term hazards. Their availability in soil is used as a key indicator of potential risks to the environment and human health (Barthwal *et al.*, 2008). Moreover, plants can also accumulate the metals for which no direct benefit and no significant physiological functions have been recognized. These metals may not be so harmful for the plants but are hazardous for human health as plants are part of the food chain (Razic *et al.*, 2006). Thus, it is of importance to evaluate the concentrations of essential and toxic metals in the plants and relevant soil.

The current study was aimed to 1) assess the contamination and bioaccumulation of selected HMs in soil and medicinal plants 2) To measure the bioaccumulation and transfer factors of HMs in selected medicinal plants. The novelty of this study is; no such investigation has been done previously to ensure the presence of HMs in soil and medicinal plants in Upper Dir, KP, Pakistan.

### **Materials and Methods**

**Study area:** The sample spots in the District Dir upper (Latitude 35 ° 10 N; Longitude 72 ° 54 E) is situated in the KP, Pakistan as shown in (Fig. 1 and Table 1).

The total area of the district is 3,699 square kilometers with a population of 575,858 (Barkatullah *et al.*, 2011). District Dir upper is rich in medicinal plants (Haider *et al.*, 2011) which are largely used by the local people as diuretic, blood purifier, tonic, carminative, expectorant and for the treatment of different diseases such as diarrhea, kidney problem, throat infection, constipation, gas trouble, hepatitis, hypertension, rheumatism, asthma, cough, diabetes, fever, and stomach problems (Qureshi *et al.*, 2009).

**Soil and plant samples collection:** Soil and medicinal plant samples were collected from different locations of the District Dir Upper as shown in Fig. 1. Samples of the medicinal plants (n=31) were collected and stored in polythene bags. Approximately 1 kg soil sample was collected to a depth of 30 cm from the base of each sample plant. The samples were cleaned from stones and twigs, packed in polyethylene bags and marked.

The medicinal plants were selected based on their significance and frequent utilization in preparation of traditional drug formulations, food supplements, and medicinal properties. Herbarium sheet of the different plant species was prepared, identified and taxonomically classified with the help of a plant taxonomist and available literature. The specimens of selected medicinal plants were deposited at Department of Botany, University of Peshawar. Details of the medicinal plants used in the present study are presented as supplemental information (Table 1).

Sample preparation and analysis: Soil samples were air-dried, homogenized and sieved through a 2 mm mesh. The samples were ground in a ball mill to less than 200  $\mu$ m mesh size and stored in polyethylene bags at room

temperature. About 0.5 g oven-dried soil was digested in the Teflon beaker using a mixture of hydrofluoric acid (HF) and hydrochloric acid (HCl) in a 3:1 ratio at 130– 140°C until complete digestion. The extracts were filtered through Whatman No. 41 filter paper, diluted to 50 ml and stored in the refrigerator before analysis on Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) (Perkin elmer A700).

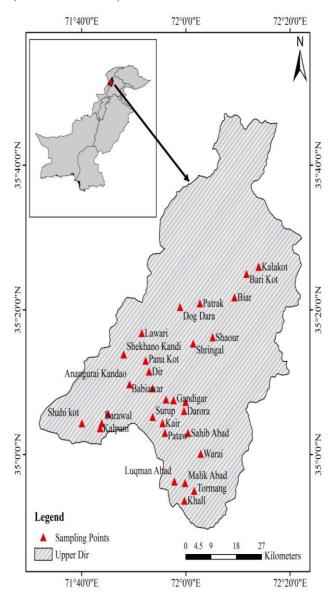


Fig. 1. GIS maps showing the sampling points in Upper Dir, KP, Pakistan.

Plant samples (root, shoot and leaves) were washed with deionized water, oven-dried at 70°C and powdered with an electric grinder. Plant samples (1.0 g) were taken in the Pyrex beaker and digested using analytical grade nitric acid (HNO<sub>3</sub>) for about 4 h at 120-130°C until complete digestion and disappearance of brown fumes. The solution was filtered into a centrifuge tube using Whatman No. 41 filter paper and the volume increased to 15 ml with deionized water. The extracts were used to quantify the concentration of selected heavy metals using GFAAS, (Perkin Elmer A700). All the samples were analyzed in triplicates.

Sample leastion	Plant species	GPS	Elemetican (m)	
Sample location		Latitude	Longitude	Elevation (m)
Shahi kot	Silybum marianum	35° 4'19.08"N	71°40'2.44"E	5865
Barawal	Punica granatum	35° 4'19.45"N	71°43'49.89"E	6504
Barawal bandai	Mirabilis jalapa	35° 5'37.40"N	71°45'3.07"E	6714
Anangurai Kandao	Ammi visnaga	35° 9'42.07"N	71°49'10.49"E	5357
Kalpani	Sagretia thea	35° 3'38.18"N	71°43'31.83"E	25950
Chutiatan	Pinus roxberghii	35° 9'8.75"N	71°53'36.34"E	7361
Babiawar	Olea ferruginea	35° 7'36.98"N	71°56'10.51"E	3241
Gandigar	Zanthoxylum armantum	35° 7'30.11"N	71°57'38.03"E	929
Chumra derai	Mentha longifolia	35° 7'14.89"N	71°59'56.42"E	8771
Darora	Adiantum venustum	35° 6'1.19"N	71°59'38.49"E	8771
Sahib Abad	Viola pilosa	35° 2'58.00"N	72° 0'23.34"E	10239
Pataw	Barberis lycium	35° 2'58.54"N	71°55'57.83"E	10235
Warai	Mentha arvensis	35° 0'5.29"N	72° 2'49.88"E	6243
Tomang	Verbascum thapsus	34°54'58.38"N	72° 1'35.06"E	22710
Malik Abad	Colocasia esculenta	34°56'3.28"N	71°59'49.73"E	22700
Luqman Abad	Portulaca oleracea	34°56'15.65"N	71°57'46.95"E	5442
Khall	Oryza sativa	34°53'37.22"N	71°59'42.40"E	30603
Kair	Solanum nigrum	35° 4'20.03"N	71°55'30.49"E	52739
Surup	Oxalis corniculata	35° 5'11.72"N	71°53'36.55"E	12762
Dir	Cichorium intybus	35°11'27.11"N	71°52'55.58"E	27164
Pana Kot	Ajuga bracteosa	35°12'58.29"N	71°52'16.16"E	27164
lawari	Otostegia limbata	35°16'46.97"N	71°51'30.90"E	51138
Shekhano Kandi	Ranunculus muricatus	35°13'49.68"N	71°48'3.99"E	74229
Sheringal S-1	chenopodium botrys	35°15'20.38"N	72° 1'23.45"E	74229
Sheringal S-2	Portulaca grandiflora	35°15'20.38"N	72° 1'23.45"E	74229
Shaour	Acrus calamus	35°16'12.20"N	72° 5'7.44"E	17608
Dog Dara	Teucrium stoksium	35°20'23.46"N	71°58'52.18"E	37182
Patrak	Talictrum foliolosum	35°20'54.04"N	72° 2'40.95"E	36733
Biar	Cedrela serrata	35°21'43.86"N	72° 9'19.32"E	56702
Bari Kot	Clematis grata	35°24'57.85"N	72°11'37.61"E	33098
Kalkot	Ziziphus mummularia	35°25'56.93"N	72°13'57.95"E	33098

Table 1. Localities from where the medicinal plant species were collected and their coordinates.

**Quality control:** Blank reagents and standard certified reference soil (GBW07406-GSS-6) and plant (GBW07603-GSV-2) materials were used with each sample batch preparation and analysis to verify the accuracy and precision of the digestion procedure and analysis. Reference soil and plants were obtained from the National Research Center (NRC) for Certified Reference Materials in China. All the apparatus and glassware used were acid-washed [5% HCl (v/v)] and rinsed with distilled water prior to use. The reagents used were of analytical grade.

**Bioaccumulation factor:** Bioaccumulation factor (BAF) is determined as the ratio of the concentration of HMs in a plant to the concentration in soil (Muhammad *et al.*, 2013). BAF value indicates the accumulation of metal in a plant from soil substrate (Ghosh & Singh, 2005). The BAF values were calculated by using Eq. (1).

 $BAF = \frac{Cplant}{Csoil}....(1)$ 

where  $C_{plant}$  and  $C_{soil}$  is the concentration of HMs in the medicinal plant and corresponding soil respectively.

### **Results and Discussion**

**HMs concentration in soil:** The concentrations of Cd, Cr, Pb, Ni and Zn in soil samples collected from different locations of the study area ranged from 1 - 1.52, 1 - 6.42, 9.34 - 11.93, 1.61 - 6.77 and 23.50 - 33.55 mg kg<sup>-1</sup> respectively. Mean concentrations of the selected HMs were in the order of Zn >Pb>Ni > Cr >Cd (Table 2).

Similar study was conducted by Ullah *et al.*, 2017, they reported that Cd concentration was in the range of 2.43 to 3.21 mg kg<sup>-1</sup> in soil samples collected from peach gardens of Khwazakhela area, Swat, KP, Pakistan. The possible contributors of HMs in the samples can be geological sources such as weathering, erosion of bedrocks and ore deposits (Ahmet *et al.*, 2006; Khan *et al.*, 2008a).

**Concentration of HMs in plants:** The concentrations of HMs in medicinal plants is given in Table 3. The concentration ranged from 0.01 - 0.13, 0.12 - 2.18, 0.09 - 0.61, 0.10 - 0.74 and 5.03 - 20.53 mg kg<sup>-1</sup> for Cd, Cr, Pb, Ni and Zn respectively (Table 2).

Table 2. Mean concentration of HMs (mg kg <sup>-1</sup> ) in soil.						
Sample location	Cd	Cr	Pb	Ni	Zn	
Shahikot	$1.08\pm0.01$	$1.17\pm0.03$	$9.55\pm0.01$	$3.56 \pm 0.08$	$25.98\pm0.02$	
Barawal	$1.07\pm0.03$	$2.25\pm0.03$	$10.05\pm0.01$	$4.79\pm0.11$	$27.57\pm0.04$	
Barawalbandai	$1.07\pm0.01$	$2.09\pm0.06$	$9.80\pm0.02$	$2.64\pm0.03$	$28.99\pm0.06$	
Ananguraikandao	$1.05\pm0.01$	$6.42\pm0.05$	$9.52\pm0.03$	$3.84 \pm 0.07$	$33.55\pm0.39$	
Kalpani	$1.06\pm0.02$	$3.71\pm0.05$	$9.34\pm0.04$	$3.44 \pm 0.05$	$33.32\pm0.72$	
Chutiatan	$1.04\pm0.02$	$3.41\pm0.03$	$9.62\pm0.03$	$3.56\pm0.05$	$23.60\pm0.03$	
Babiawar	$1.06\pm0.03$	$1.22\pm0.18$	$9.62\pm0.05$	$3.66\pm0.06$	$24.58\pm0.01$	
Gandigar	$1.06\pm0.02$	$1.19\pm0.04$	$9.55\pm0.08$	$3.52\pm0.06$	$25.10\pm0.01$	
Chumraderai	$1.02\pm0.02$	$1.63\pm0.17$	$9.51\pm0.04$	$2.65\pm0.20$	$23.99\pm0.04$	
Darora	$1.02\pm0.01$	$1.29\pm0.07$	$9.49\pm0.05$	$1.61\pm0.66$	$24.60\pm0.03$	
Sahib Abad	$1.06\pm0.03$	$1.46\pm0.12$	$9.49\pm0.03$	$3.67\pm0.10$	$23.58\pm0.01$	
Pataw	$1.04\pm0.02$	$3.38\pm0.03$	$10.54\pm0.10$	$3.56\pm0.07$	$31.87\pm0.13$	
Warai	$1.05\pm0.03$	$1.57\pm0.21$	$10.45\pm0.04$	$3.52\pm0.16$	$24.11\pm0.02$	
Tomang	$1.05\pm0.02$	$1.27\pm0.03$	$10.46\pm0.06$	$3.25\pm0.02$	$25.72\pm0.03$	
Malik Abad	$1.04\pm0.03$	$1.30\pm0.05$	$10.59\pm0.04$	$3.45\pm0.07$	$25.72\pm0.04$	
Luqman Abad	$1.06\pm0.01$	$2.45\pm0.05$	$11.92\pm0.07$	$6.59\pm0.09$	$29.45\pm0.28$	
Khall	$1.05\pm0.01$	$2.30\pm0.02$	$10.55\pm0.04$	$5.30\pm0.09$	$28.00\pm0.03$	
Kair	$1.01\pm0.01$	$1.99\pm0.02$	$10.42\pm0.03$	$6.02\pm0.08$	$28.70\pm0.05$	
Surup	$1.01\pm0.01$	$2.56\pm0.05$	$10.70\pm0.08$	$5.72\pm0.06$	$28.92\pm0.07$	
Dir	$1.02\pm0.02$	$2.92\pm0.06$	$10.72\pm0.06$	$6.77\pm0.10$	$29.00\pm0.07$	
PanaKot	$1.03\pm0.03$	$1.82\pm0.03$	$10.80\pm0.02$	$5.53\pm0.10$	$24.02\pm0.02$	
Lawari	$1.04\pm0.16$	$2.23\pm0.02$	$11.90\pm0.06$	$6.37\pm0.11$	$27.58\pm0.56$	
ShekhanoKandi	$1.03\pm0.02$	$2.38\pm0.05$	$11.93\pm0.08$	$5.64\pm0.07$	$27.46\pm0.53$	
Sheringal S-1	$1.01\pm0.02$	$2.26\pm0.01$	$10.65\pm0.04$	$4.44\pm0.01$	$28.84 \pm 0.13$	
Sheringal S-2	$1.03\pm0.02$	$2.41\pm0.02$	$10.83\pm0.03$	$5.79\pm0.02$	$29.14\pm0.12$	
Shaour	$1.00\pm0.01$	$2.54\pm0.02$	$10.82\pm0.02$	$5.83\pm0.14$	$29.20\pm0.37$	
Dog Dara	$1.03\pm0.01$	$2.22\pm0.03$	$10.75\pm0.06$	$6.25{\pm}0.06$	$30.24 \pm 0.80$	
Patrak	$1.04\pm0.02$	$2.21\pm0.01$	$10.73\pm0.02$	$6.43\pm0.09$	$28.91\pm0.14$	
Biar	$1.04\pm0.03$	$2.06\pm0.01$	$10.66\pm0.03$	$6.22\pm0.06$	$28.82 \pm 0.08$	
Bari Kot	$1.03\pm0.03$	$1.77\pm0.02$	$10.42\pm0.02$	$3.89 \pm 0.17$	$29.56\pm0.38$	
Kalkot	$1.03\pm0.01$	$4.02\pm0.04$	$10.81\pm0.02$	$5.87\pm0.09$	$29.65\pm0.28$	

-1. **—** . .

± Standard deviation

Highest metal concentrations were observed in the plant roots followed by the shoot. Whereas the leaf samples had the lowest metal concentrations for all the plants indicating that the uptake of metals in these plants was from the soil substrate only and low translocation to the upper parts of these plants. Mean concentration of the HMs in plant samples was found in order of Zn > Cr >Ni >Pb> Cd. The WHO recommended permissible limits of Cd, Cr, Pb, Ni and Zn for plant samples are 0.02, 1.3, 2.0, 10.0 and 50 mg kg<sup>-1</sup> respectively (Shah *et al.*, 2013; Nazir et al., 2015). The present study revealed that the concentration of Cd was higher than WHO permissible limits in 24 medicinal plants species (Table 2).

Plants are a good source for bioaccumulation of heavy metals. On one hand, this property has been used for phytoremediation (Kumar et al., 2019), on the other hand, it may prove to be hazardous when plants are consumed as food or therapeutic agent in traditional medicine. Although there is a great concern about heavy metal contamination of herbal raw materials, information regarding permissible limit is available only for Pb and Cd (Anon., 1998).

The high concentration/accumulation of Cd in plants may be due to the high mobility of the Cd in soil (Jarup, 2003). Likewise, the concentration of Cr was higher in 9 species (Mirabilis Jalapa, Sagretia thea, Zanthoxylum

armantum, Mentha longifolia, Viola pilosa, Colocasia esculenta, Cichorium intybus, Ajuga bracteosa and Otostegia limbata) (Table. 2). However, the concentration of Pb, Ni, and Zn were below the WHO permissible limits for all the plant species. To minimize the toxicity of metals in soils, organic amendments such as biochar and activated carbon are widely used to immobilize the contaminants (Puga, et al., 2015). Other methods adopted for reducing the mobility, availability, and toxicity of the heavy metals in soil were the application of phosphates and phytoremediation (Maria et al., 2014).

The lower concentrations of Ni and Zn observed in the present study showed a deficiency of these elements in the soil environment since both the metals are considered as essential micronutrients for the plants and the human body. Inadequate Zn diet and nutrition are estimated to affect one-third of the global human population (Hotz et al., 2004). The deficiency of Zn is affecting large areas of cultivated soils worldwide (Cakmak, 2008). Symptoms of Ni deficiency include interveinal chlorosis in young leaves resulting in necrosis of the plant tissue. Other symptoms include poor seed germination and decreased crop yield. In humans, Ni is found to be helpful for normal bone functioning and health (Gerendas et al., 1999).

Plant Name	Cd	Cr	Pb	Ni	Zn
Silybum marianum	$0.08 \pm 0.04$	$0.61 \pm 0.03$	$0.61 \pm 0.09$	$0.24 \pm 0.21$	$5.83 \pm 0.02$
Punica granatum	$0.01\pm0.02$	$0.43\pm0.05$	$0.15\pm0.03$	$0.20 \pm 0.15$	$7.28\pm0.03$
Mirabilis jalapa	$0.04\pm0.04$	$1.62\pm0.04$	$0.34\pm0.06$	$0.13\pm0.08$	$19.48\pm0.33$
Ammi visnaga	$0.03\pm0.05$	$0.33\pm0.02$	$0.13\pm0.02$	$0.11\pm0.03$	$5.03\pm0.09$
Sagretia thea	$0.12\pm0.57$	$1.59\pm0.03$	$0.29\pm0.08$	$0.30\pm0.05$	$19.20 \pm 1.50$
Pinus roxberghii	$0.03\pm0.08$	$0.38\pm0.03$	$0.12\pm0.04$	$0.28\pm0.07$	$5.70\pm0.03$
Olea ferruginea	$0.01\pm0.02$	$0.48\pm0.03$	$0.24\pm0.09$	$0.35\pm0.17$	$5.84\pm0.01$
Zanthoxylum armantum	$0.01\pm0.05$	$1.79\pm0.05$	$0.22\pm0.07$	$0.26\pm0.09$	$18.84\pm0.65$
Mentha longifolia	$0.06\pm0.03$	$2.00\pm0.04$	$0.40\pm0.14$	$0.38\pm0.20$	$20.54 \pm 1.14$
Adiantum venustum	$0.08\pm0.03$	$0.31\pm0.04$	$0.13\pm0.02$	$0.62\pm0.09$	$5.43\pm0.03$
Viola pilosa	$0.05\pm0.05$	$1.46\pm0.06$	$0.46\pm0.11$	$0.57\pm0.19$	$19.20\pm0.64$
Barberis lycium	$0.13\pm0.03$	$0.49\pm0.02$	$0.22\pm0.19$	$0.43\pm0.35$	$7.82\pm0.05$
Mentha arvensis	$0.08\pm0.06$	$0.37\pm0.03$	$0.19\pm0.04$	$0.38\pm0.04$	$6.76\pm0.04$
Verbascum thepsus	$0.06\pm0.03$	$0.34\pm0.01$	$0.09\pm0.04$	$0.27\pm0.04$	$5.48 \pm 0.04$
Colocasia esculenta	$0.03\pm0.03$	$1.38\pm0.01$	$0.21\pm0.09$	$0.34\pm0.11$	$18.09\pm0.65$
Portulaca oleracea	$0.05\pm0.02$	$0.87\pm0.04$	$0.22\pm0.09$	$0.61\pm0.12$	$6.64\pm0.03$
Oryza sativa	$0.07\pm0.02$	$0.37\pm0.01$	$0.20\pm0.14$	$0.75\pm0.06$	$5.39\pm0.04$
Solanum nigrum	$0.05\pm0.08$	$0.67\pm0.06$	$0.21\pm0.18$	$0.64\pm0.10$	$6.11\pm0.03$
Oxalis corniculata	$0.04\pm0.05$	$0.36\pm0.05$	$0.36\pm0.04$	$0.58\pm0.08$	$6.65\pm0.01$
Cichorium intybus	$0.03\pm0.05$	$1.31\pm0.03$	$0.32\pm0.12$	$0.46\pm0.01$	$9.48\pm0.02$
Ajuga bracteosa	$0.06\pm0.03$	$2.19\pm0.03$	$0.52\pm0.06$	$0.73\pm0.18$	$18.24\pm0.75$
Otostegia limbate	$0.03\pm0.02$	$1.71\pm0.02$	$0.31\pm0.06$	$0.52\pm0.04$	$18.59\pm0.74$
Ranunculus muricatus	$0.06\pm0.05$	$0.68\pm0.07$	$0.39\pm0.17$	$0.64\pm0.17$	$8.75\pm0.04$
Chenopodium botrys	$0.04\pm0.08$	$0.45\pm0.01$	$0.39\pm0.09$	$0.61\pm0.02$	$6.25\pm0.04$
Portulaca grandiflora	$0.01\pm0.05$	$0.46\pm0.03$	$0.26\pm0.06$	$0.21\pm0.07$	$14.72\pm0.03$
Acrus calamus	$0.02\pm0.05$	$0.56\pm0.04$	$0.29\pm0.18$	$0.48\pm0.08$	$11.80\pm0.04$
Tecurium stoksium	$0.03\pm0.03$	$0.69\pm0.06$	$0.11\pm0.06$	$0.35\pm0.22$	$7.32\pm0.05$
Talictrum foliolosum	$0.02\pm0.04$	$0.31\pm0.04$	$0.11\pm0.02$	$0.10\pm0.06$	$5.90\pm0.03$
Cedrela serrata	$0.07\pm0.04$	$0.59\pm0.06$	$0.49\pm0.08$	$0.28\pm0.08$	$7.06\pm0.08$
Clematis grata	$0.02\pm0.06$	$0.12\pm0.04$	$0.35\pm0.17$	$0.33{\pm}0.18$	$5.91\pm0.02$
Ziziphus mummularia	$0.05\pm0.06$	$0.63\pm0.03$	$0.44\pm0.20$	$0.70\pm0.24$	$5.99\pm0.01$

Table 3. Mean concentrations (mg/kg) of HMs in medicinal plants.

±Standard deviation

**Bioaccumulation factor:** The BAF is an important tool for estimating the soil to plant transfer of the heavy metals, contamination of the food chain and human exposure. The BAF values for the different medicinal plants are shown in Table 4.

The highest mean BAF value was found for *Mirabilis jalapa, Sagretia thea, Zanthoxylum armantum, Ajuga bracteosa* and *Otostegia limbata* (Table 4). The variation in the BAF values may be due to the difference in medicinal plants, sampling locations, and soil properties.

## Conclusion

The present study revealed that medicinal plants of the study area are bio-accumulated with heavy metals and the source may be geological inputs. The contamination of medicinal plants was in the order of Zn>Pb>Ni>Cr>Cd. The concentration of Cd and Cr was above the WHO permissible limits for some of the medicinal plants. The observed contamination in medicinal plants may contribute significantly to the exposure and health risks of the population. It is recommended that the medicinal plants should be evaluated for toxic heavy metals before use.

#### Acknowledgment

We would like to extend our utmost appreciation to Mr. Hashim Zahid and Engr. Amjad Ali for their volunteer support in sample collection, identification, and maps preparation.

 
 Table 4. Bioaccumulation factor of heavy metals in selected medicinal plants.

Plant name	Cd	Cr	Pb	Ni	Zn
Silybum marianum	0.07	0.52	0.06	0.07	0.22
Punica granatum	0.01	0.19	0.01	0.04	0.26
Mirabilis jalapa	0.04	0.77	0.03	0.05	0.67
Ammi visnaga	0.03	0.05	0.01	0.03	0.15
Sagretia thea	0.11	0.43	0.03	0.09	0.58
Pinus roxberghii	0.03	0.11	0.01	0.08	0.24
Olea ferruginea	0.01	0.39	0.02	0.10	0.24
Zanthoxylum armantum	0.01	1.50	0.02	0.07	0.75
Mentha longifolia	0.06	1.23	0.04	0.14	0.86
Adiantum venustum	0.08	0.24	0.01	0.38	0.22
Viola pilosa	0.05	1.00	0.05	0.15	0.81
Barberis lycium	0.13	0.14	0.02	0.12	0.25
Mentha arvensis	0.07	0.24	0.02	0.11	0.28
Verbascum thapsus	0.05	0.27	0.01	0.08	0.21
Colocasia esculenta	0.03	1.06	0.02	0.10	0.70
Portulaca oleracea	0.05	0.35	0.02	0.09	0.23
Oryza sativa	0.06	0.16	0.02	0.14	0.19
Solanum nigrum	0.04	0.33	0.02	0.11	0.21
Oxalis corniculata	0.04	0.14	0.03	0.10	0.23
Cichorium intybus	0.03	0.45	0.03	0.07	0.33
Ajuga bracteosa	0.06	1.20	0.05	0.13	0.76
Otostegia limbata	0.03	0.76	0.03	0.08	0.67
Ranunculus muricatus	0.06	0.28	0.03	0.11	0.32
Chenopodium botrys	0.03	0.20	0.04	0.14	0.22
Portulaca grandiflora	0.01	0.19	0.02	0.03	0.51
Acrus calamus	0.01	0.22	0.03	0.08	0.40
Teucirum stoksium	0.03	0.31	0.01	0.05	0.24
Talictrum foliolosum	0.02	0.14	0.01	0.02	0.20
Cedrela serrata	0.06	0.28	0.05	0.05	0.24
Clematis grata	0.02	0.07	0.03	0.08	0.20
Ziziphus mummularia	0.05	0.16	0.04	0.12	0.20

#### References

- Abbasi, A.M., M.A. Khan, M. Ahmad and M. Zafar. 2011. Medicinal plant biodiversity of lesser Himalayas-Pakistan. Springer Science & Business Media.
- Abdul-Wahab, O., E. Rjoob, A.M. Massadeh and M.N. Omari. 2008. Evaluation of Pb, Cu, Zn, Cd, Ni, and Fe levels in *Rosmarinus officinalislabaiatae* (Rosemary) medicinal plants and soils in selected zones in Jordan. *Environ. Monit.* & Assess., 140: 61-68.
- Abou-Arab, A.A.K., M.S.E. Kawther, M.E. Tantawy, R.I. Badeaa and N. Khayria. 1999. Quantity estimation of some contaminants in commonly used medicinal plants in the Egyptian market. *Food Chem.*, 67: 357-363.
- Ahmed, D., A. Waheed, M.A. Chaudhary, S.R. Khan, A. Hannan and M. Barkaat. 2010. Nutritional and antimicrobial studies on leaves and fruit of Carrisa opeca Stapf Ex haines. Elect. *J. Environ. Agric. Food Chem.*, 9(10): 1631-1640.
- Ahmet, D., Y. Fevzi, A.L. Tuna and O. Nedim. 2006. Heavy metals in water, sediment and tissues of Leuciscuscephalus

from a stream in southwestern Turkey. *Chemosphere*, 63: 1451-1458.

- Anonymous. 1998. Quality control methods for medicinal plant materials. WHO Geneva, Switzerland.
- Athar, M. and S.B. Vohora. 1995. Heavy metals and environment. New Delhi, India: *Wiley Eastern Ltd.*
- Barkatullah and M. Ibrar. 2011. Plants profile of Malakand Pass Hills, District Malakand, Pakistan. African, J. Biotechn., 10(73): 16521-16535.
- Barthwal, J., S. Nair and P. Kakkar. 2008. Heavy metal accumulation in medicinal plants collected from environmentally different sites. Biomed. *Environ. Sci.*, 21: 319-324.
- Baye, H. and A. Hymete. 2010. Lead and cadmium accumulation in medicinal plants collected from environmentally different sites. *Bull. Environ. Contam. Toxicol.*, 84: 197-201.
- Bohm, H. 2008. 'Opuntia dillenii' an interesting and promising Cactaceae Taxon. J. Prof. Assoc. Cactus Dev., 10: 148-170.
- Boyd, R.S. 2009. High-nickel insects and nickel hyperaccumulator plants: A Review. *Insect Sci.*, 16: 19-31.
- Cakmak, I. 2008. Enrichment of cereal grains with zinc: Agronomic or genetic biofortificaion? *Plant Soil*, 302: 1-17.
- Censi, P., S.E. Spoto, F. Saiano, M. Sprovieri, S. Mazzola, G. Nardone, S.I. Di Geronimo, R. Punturo and D. Ottonello. 2006. Heavy metals in coastal water systems. A case study from the northwestern Gulf of Thailand. *Chemosphere*, 64: 1167-1176.
- Chan, K. 2003. Some aspects of toxic contaminants in herbal medicines. *Chemosphere*, 52: 1361-1371.
- Chan, T.Y., J.C. Chan, B. Tomlinson and J.A. Critchley. 1993. Chinese herbal medicines revisited: A Hong Kong perspective. *Lancet*, 342: 1532-1534.
- Chandrasekaran, M. and A.H. Bahkali. 2013. Valorization of date palm (Phoenix dactylifera) fruit processing byproducts and wastes using bioprocess technology – review. *Saudi J. Biol. Sci.*, 20: 105-120.
- Chary, N.S., C.T. Kamala and D.S.S. Raj. 2008. Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer. *Ecotoxicol. Environ. Saf.*, 69(3): 513-524.
- Choudhury, R.P., R. Acharya, A.G.C. Nair, A.V.R. Reddy and A.N. Garg. 2008. Availability of essential trace elements inmedicinal herbs used for diabetes mellitus and their possible correlations. *J. Radioanal. Nucl. Chem.*, 276(1): 85-93.
- Ernst, E. 2002. Toxic heavy metals and undeclared drugs in Asian herbal medicines. *Trends Pharmacol. Sci.*, 23(3): 136-139.
- Fabricant, D.S. and N.R. Farnsworth. 2001. The value of plants used in traditional medicine for drug discovery. *Environ. Health Perspect.*, 109(1): 69-75.
- Ferguson, J.E. and N. Kim. 1991. Trace elements in street and house dusts source and speciation. *Sci. Total Environ.*, 100: 125-150.
- Gajalakshmi, S., V. Iswarya, R. Ashwini, G. Divya and S. Mythili. 2012. Evaluation of heavy metals in medicinal plants growing in Vellore District, School of Bio Sciences and Technology, VIT University, Vellore- 632 014, TN. *Ind. Europ. J. Exp. Biol.*, 2(5): 1457-1461.
- Gerendas, J., J.C. Polacco, S.K. Freyermuth and S. Sattelmacher. 1999. Significance of nickel for plant growth and metabolism. J. Plant Nutri. & Soil Sci., 162(3): 241-256.

- Ghosh, M. and S.P. Singh. 2005. A comparative study of cadmium phytoextraction by accumulator and weed species. *Environ. Pollut.*, 133(2): 365-371.
- Haider, A., J. Sannai, H. Sher and A. Rashid. 2011. Ethnobotanical profile of some plant resources in MalamJabba Valley of Swat, Pakistan. J. Med. Plant Res., 5(18): 4676-4687.
- Hashmi, D.S., S. Ismail and G.H. Shaikh. 2007. Assessment of the level of trace metals in commonly edible vegetables locally available in the markets of Karachi city. *Pak. J. Bot.*, 39: 747-751.
- Hazrat, A., J. Shah, M. Ali and I. Iqbal. 2007. Medicinal value of Ranunculaceae of Dir valley. *Pak. J. Bot.*, 39(4): 1037-1044.
- Hotz, C. and K.H. Brown. 2004. Assessment of the risk of zinc deficiency in populations and options for its control. *Food Nutr. Bull.*, 25: 94-204.
- Houshmandfar, A. and F. Moraghebi. 2011. Effect of mixed cadmium, copper, nickel and zinc on seed germination and seedling growth of safflower. *Afr. J. Agri. Res.*, 6: 1463-1468.
- Huang, H.C., K.Y. Syu and J.K. Lin. 2010. Chemical composition of Solanum nigrumlinn extract and induction of autophagy by leaf water extract and its major flavonoids in AU565 breast cancer cells. J. Agric. Food Chem., 58(15): 8699-8708.
- Jaijoy, K., N. Soonthorncharennon, A. Panthong and S. Sireeratawong. 2010. Anti-inflammatory and analgesic activities of the water extract from the fruit of *Phyllanthus emblica* Linn. *Int. J. Appl. Res. Nat. Prod.*, 3(2): 28-35.
- Jarup, L. 2003. Hazards of heavy metal contamination. Br. Med. Bull., 68(1): 167-182.
- Jarup, L. 2003. Hazards of heavy metal contamination. British Council Medical Department.
- Kabata-Pendias, A. and H. Pendias. 2001. Trace Elements in Soils and Plants. *CRC Press*, Inc. Boca Raton, FL, USA.
- Kakosy, T., A. Hudak and M. Naray. 1996. Lead intoxication epidemic caused by ingestion of contaminated ground paprika. J. Toxicol. Clini. Toxicol., 34: 507-511.
- Karri, S.K., R.B. Saper and S.N. Kales. 2008. Lead encephalopathy due to traditional medicines. *Curr. Drug Safety*, 3: 54-59.
- Khan, S., A.E.L. Hesham, M. Qiao, S. Rehman and J.Z. He. 2010. Effects of Cd and Pb on soil microbial community structure and activities. *Environ. Sci. Pollut. Res.*, 17: 288-296.
- Khan, S., Q. Cao, Y.M. Zheng, Y.Z. Huangand Y.G. Zhu. 2008a. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing China. *Environ. Poll.*, 152: 686-692.
- Korfali, S.I., T. Hawi and M. Mroueh. 2013. Evaluation of heavy metals content in dietary supplements in Lebanon. *Chem. Cent. J*, 7(1): 1-13.
- Kumar, A., A.K. Chaturvedi, K. Yadav, K.P. Arunkumar, S.K. Malyan, P. Raja and A.N. Yadav. 2019. Fungal phytoremediation of heavy metal-contaminated resources: current scenario and future prospects. In Recent advancement in white biotechnology through fungi. *Springer, Cham.*, 437-461.
- MacFarlane, G.B. and M.D. Burchettt. 2000. Cellular distribution of Cu, BP, and Zn in the Grey Mangrove Avicemnia marine (Forsk.). *Vierh Aquatic Bot.*, 68: 45-59.
- Maria, L.F., M. Kede, I. Fabio, V. Correia, F. Paulo, S. Conceicao, F. Sidney, J. Salles, M. Marcia, C. Josino and

V. Moreira. 2014. Evaluation of mobility, bioavailability and toxicity of Pb and Cd in contaminated soil using TCLP, BCR and earthworms. *J. Environ. Res. Public Health*, 11(11): 11528-11540.

- Memon, A.R., D. Aktorakligul, A. Zdemur, A. Vertii and T. Butak. 2001. Heavy metal accumulation and detoxication mechanisms in plants. *Turk. J. Bot.*, v.25, p. 111-121.
- Muhammad, S., T.M. Shah, S. Khan, M. Saddique, N. Gul, M.U. Khan, R.N. Malik, M. Farooq and A. Naz. 2013. Wild plant assessment for heavy metal phytoremediation potential along the mafic andultramafic terrain in northern Pakistan *Hindawi Publishing Corpor. Bio. Med. Res. Intern.*, Article ID 194765.
- Nabulo, G., C.R. Black, J. Craigon and S.D. Young. 2012. Does consumption of leafy vegetables grown in peri-urban agriculture pose a risk to human health?, *Environ. Pollu.*, 162: 389-398.
- Nanda Kumar, P.B.A., V. Dushenkov and H. Motto. 1995. Phytoextraction: The use of plants to remove heavy metals from soils. *Environ. Sci. Technol.*, 129(5): 1232-1238.
- Nathiya, M. and D. Dorrcus. 2012. Preliminary phytochemical and anti-bacterial studies on *Physalis minima* Linn. *Int. J. Curr. Sci.*, 24-30.
- Nazir, R., M. Khan, M. Masab, H.U. Rehman, N.U. Rauf, S. Shahab and Z. Shaheen. 2015. Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat. *J. Pharm. Sci.* & Res., 7(3): 89-97.
- Nordberg, G.F. 2010. Biomarkers of exposure, effects and susceptibility in humans and their application in studies of interactions among metals in China. *Toxicol. Lett.*, 192: 45-49.
- Olujohunge, A., P.A. Fields and A.F. Sandford. 1994. Heavy metal intoxication from homeopathic and herbal remedies. *Postgrad. Med. J.*, 70: 764-769.
- Pandey, A., R. Singh, J. Radhamani and D.C. Bhandari. 2010. Exploring the potential of *Ziziphus nummularia* (Burm. f.) Wightet Arn. from drier regions of India. *Genet. Resour*: *Crop Evol.*, 57: 929-936.
- Parveen, R., A.M. Abbasi, N. Shaheen and M.H. Shah. 2020. Accumulation of selected metals in the fruits of medicinal plants grown in urban environment of Islamabad, Pakistan. *Arab. J. Chem.*, 13(1): 308-317.
- Puga, A.P., C.A. Abreu, L.C. Melo, J. Paz-Ferreiro and L. Beesley. 2015. Cadmium, lead, and zinc mobility and plant uptake in a mine soil amended with sugarcane straw biochar. *Environ. Sci. Pollut. Res. Int.*, 2(22): 17606-14.
- Qishlaqi, A. and F. Farid Moore. 2007. Statistical analysis of accumulation and sources of heavy metals occurrence in agricultural soils of Khoshk River banks, Shiraz, Iran. American-Eurasian. J. Agri. & Environ. Sci., 2: 565-573.
- Qureshi, R.A., M.A. Ghufran, S.A. Gilani, Z. Yousaf, G. Abbas and A. Batool. 2009. Indigenous medicinal plants used by local women in southern Himalayan regions of Pakistan. *Pak. J. Bot.*, 41: 19-25.
- Rania, D., A.K. Safa, R. Husna and A.K. Munawwar. 2015. Determination of heavy metals concentration in traditional herbs commonly consumed in the United Arab Emirates. J. Environ. & Public Health, Article ID 973878.
- Rates, S.M.K. 2000. Review: Plants as a source of drugs. *Toxicon.*, 39: 603-613.
- Razic, S., S. Dogo and L. Slavkovic. 2006. Inorganic analysis of herbal drugs. Part II. Plant and soil analysis-diverse bioavailability and uptake of essential and toxic elements. J. Serb. Chem. Soc., 71(10): 1095-1105.

- Sarma, H., S. Deka, H. Deka and R.R. Saikia. 2012. Accumulation of heavy metals in selected medicinal plants. *Rev. Environ. Contam. & Toxicol.*, 214: 63-86.
- Shah, A., A. Niaz, N. Ullah, A. Rehman, M. Akhlaq, M. Zakir and M. Suleman Khan. 2013. Comparative study of heavy metals in soil and selected medicinal plants. J. Chem., 2013.
- Shailendra, K.D. and D. Sahabeb. 2002. Medicinal Herbs: A potential source of toxic metal exposure for man and animals in India. Arch. Environ. Health, 57(3): 229-231.
- Shinwari, M.I. and M.A. Khan. 2000. Folk use of medicinal herbs of Margalla Hills National Park, Islamabad, Pakistan. *J. Ethno Pharm.*, 69: 45-56.
- Siddhu, G., D.S. Sirohi, K. Kashyap, I. Ali Khan and M.A. Ali Khan. 2008. Toxicity of cadmium on the growth and yield of Solanummelongena L. J. Environ. Biol., 29: 853-857.

- Ullah, N., F. Hadi, F. Ullah, A. Ahmed, N. Ali and A.U. Jan. 2017. Analysis of heavy metals (Pb and Cd) in soil, peach fruit and its accumulation in human blood. *Int. J. Agron. & Agri. Res.*, 10 (4): 24-32.
- Waalkes. 2003. Effect of cadmium on DBA-(cytosine-5) methyltransferase activity and DNA methylation status during cadmium-induced cellular transformation. *Exp. Cell Res.*, 4: 355-365.
- Wazir, S.M., S. Saima, A.A. Dasti and M. Subhan. 2007. Ethnobotanical importance of salt range species of District Karak. *Pak. J. Plant Sci.*, 13(1): 29-31.
- Zhuang, P., B. Zou, N.Y. Li and Z.A. Li. 2009. Heavy metal contamination in soils and food crops around Dabaoshan mine in Guangdong, China: implication for human health. *Environ. Geochem. Health*, 31(6): 707-715.

(Received for publication 2 March 2020)