Environ Earth Sci (2010) 60:1091–1102
DOI 10.1007/s12665-009-0253-8

ORIGINAL ARTICLE

Pedo and biogeochemical studies of mafic and ultramfic rocks in the Mingora and Kabal areas, Swat, Pakistan

Mohammad Tahir Shah · Shaheen Begum ·
Sardar Khan

Received: 24 February 2009 / Accepted: 10 July 2009

Abstract This study highlights the heavy metals (HMs) distribution in soils and their uptake by wild plants grown in the soils derived from the mafic and ultramafic terrains. Plant and soil samples were analyzed for Cu, Pb, Zn, Cr, Ni and Cd using atomic absorption spectrophotometer. The data indicate that almost all the HMs in the soil samples collected from the study area exceeded the reference and normal agricultural soils. Greater variability was noticed in the uptake of HMs by various plants grown on the studied soils. High concentrations of Cu and Zn in *Cannabis sativa* L. (seft hemp), Pb in *Ailanthus altissima* (Mill.) (Ailanto), Ni and Cr in *Indigofrra gerardiana* Wall. ex Baker (sage), and *Saccharum griffihii* Munro ex Boiss. (plume grass) were noticed among the studied plants. The multifold enrichments of Cr and Ni in the *Indigofrra gerardiana* and *Saccharum griffihii* as compared to the other plants of the study area suggested that these plants have the ability to uptake and translocate high concentrations of Cr and Ni. The excessive concentrations of Cr and Ni in these plants can be used for mineral prospecting but their main concern could be of serious environmental problems and health risks in the inhabitants of the study areas.

Keywords Soils · Plants · Mafic ultramafic rocks · Heavy metals · Environmental impact

Introduction

Soil environment may be contaminated with high concentrations of heavy metals (HMs) naturally, as a result of proximity to mineral outcrops or weathering of parent rocks (Del Río et al. 2006). Environmental and human health problems are usually associated with soils contaminated with HMs and, therefore, much more attention has been given to these kinds of soils by the researchers from a wide range of disciplines. In order to reach to a better understanding of these metals as pollutants, it is important to understand their natural sources as well. In most cases the enrichment of HMs in soils is due to the hazardous waste pollution but there are many cases where soils derived form mineralized rocks are naturally enriched in HMs (Alloway 1990; McBride 1994; Del Río et al. 2002; Kifyatullah et al. 2001; Shah et al. 2004).

The geochemical characteristics of soils are helpful in identification of the existence of rocks of special characters in the uphill or underneath areas. The soils produced from the weathering of mafic and ultramafic rocks are of greater interest in regard to environmental and exploration studies. The mafic and ultramafic rocks are generally enriched in HMs such as Cu, Pb, Zn, Cr, Ni and Cd and similarly the weathered soils of these rocks especially the ultramafic rocks, often referred as serpentine soils, are also enriched in these metals (Brooks 1987; Dinelli et al. 1997; Lottermoser 1997). Many workers have suggested that Ni is highly accumulated in the thousands of plants growing on the serpentine soils (Brooks 1983; Robinson et al. 1997;

M. T. Shah (✉)
National Centre of Excellence in Geology,
University of Peshawar, Peshawar, Pakistan
e-mail: tahir_shah56@yahoo.com

S. Begum
Department of Environmental Sciences,
Fatima Jenah Women University,
Rawalpindi, Pakistan

S. Khan
Department of Environmental Sciences,
University of Peshawar, Peshawar, Pakistan

Baker et al. 2000; Pollard et al. 2002). The HMs dissolution in water and uptake by plants could result in the environmental problems of the area and also helps in the identification of pathfinders for the various types of mineral deposits (Brooks 1987; Adriano 1992; Adriano et al. 1994; Legittimo et al. 1995; Robinson et al. 1997; Brooks 1998; Kifyatullah et al. 2001; Shah et al. 2004).

The accumulation of HMs in the soil environment is of increasing concern because of the food safety and potential health risks. Food chain contamination is one of the important pathways for the entry of HMs into the human body (Zhu et al. 2004; Khan et al. 2008). Previously, numerous studies have demonstrated that wild plant species have accumulated high concentrations of HMs, grown on contaminated sites (Del Río et al. 2002; Del Río et al. 2006; Mills et al. 2006; Xio et al. 2008; Hernández and Pastor 2008; Dwivedi et al. 2008). However, more information are needed to identify the natural sources of HMs and their uptake by wild plants.

This research work was undertaken to study geochemical characteristics of the soils and plants of the Mingora and Kabal areas of the Swat region in the northern parts of Pakistan, where the mafic and ultramfic rocks are exposed (Begum 2008). This study will help in understanding the environmental impact of the HMs' enrichment in the soils and plants and their role in the geochemical exploration.

Geology of the study area

The present study area (Mingora and Kabal) is lying between latitude 30°44′ to 34°50′ north and longitude 72°15′ to 72°18′ east in the Swat region of northern Pakistan (Fig. 1). According to Afridi et al. (1995) the rocks exposed in the study area belong to the Indian plate, Mingora-Shangla mélange of the Indus Suture Zone and the Kohistan island arc. The Indian plate rocks are (1) Swat granite gneisses (Martin et al. 1962; Jan and Tahirkheli 1969; Di Pietro et al. 1999), (2) amphibolites with garnetifrrouces schist, biotite-schist hornblende and marbles of Marghazar Formation (Di Pietro 1991; Pogue et al. 1992) and (3) graphitic phyllites of the Saidu Formation (Kazmi et al. 1984; Treloar et al. 1989a, b; Lawrence et al. 1989; Di Pietro 1991, 1993). The Mingora-shangla mélange zone is composed of chaotic assemblages of mafic and ultramafic rocks such as serpentinite, greenschist, talc-carbonate schist and metabasalts (Kazmi et al. 1984; Jan and Jabeen 1990; Arif and Jan 1993). The Kohistan island arc rocks are mainly massive amphibolites of southern or Kamila amphibolite belt (Jan 1979, 1988; Bard et al. 1980; Treloar et al. 1990; Shah et al. 1992). Most part of the study area is covered by the Quaternary deposits mainly composed of stream channel deposits and also the weathering products of the aforementioned rocks in the area of study (Fig. 1).

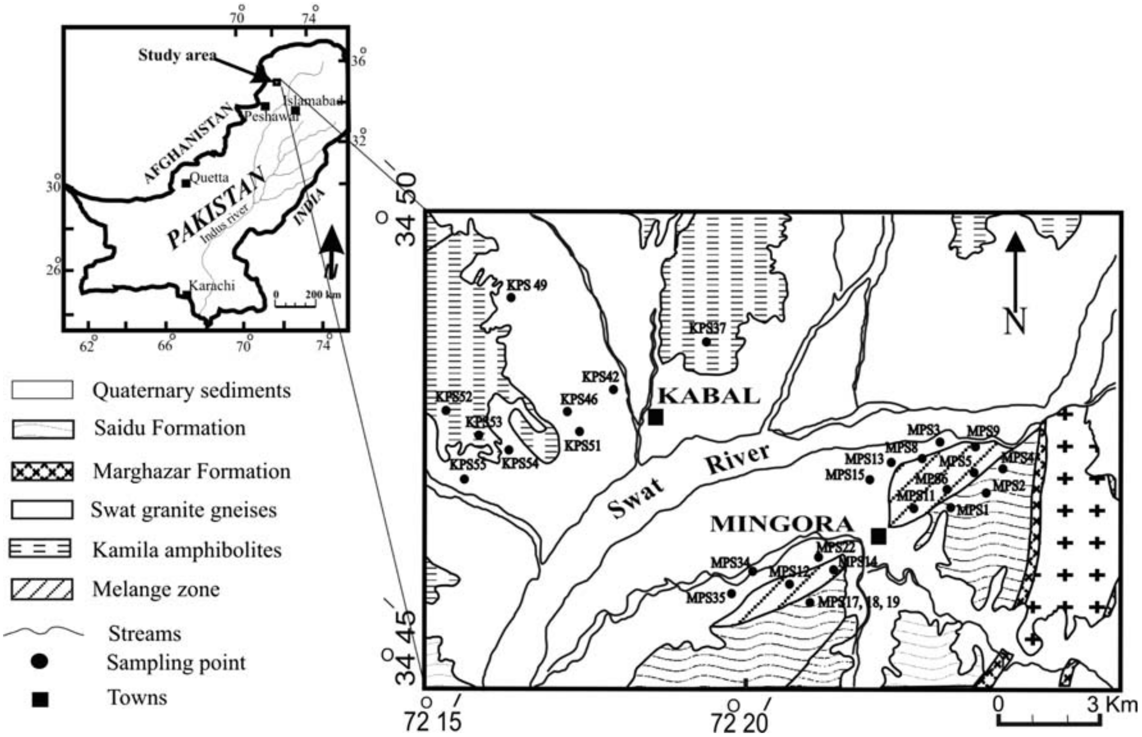

Fig. 1 Geological and samples location map of the Mingora and Kabal areas, Swat, Pakistan (modified after Afridi et al. 1995)

Materials and methods

Soil and plant sampling

Twenty-eight representative soil samples at various sites, shown in Fig. 1, were collected from the upper horizon (0–20 cm) with the help of an auger. Each sample was stored in kraft paper bags. The growing flora of the soils derived from mafic and ultramafic rocks in the Mingora and Kabal areas is very rich but nine prominent plant species including *Cannabis sativa* L. (seft hemp), *Ailanthus altissima* (Mill.) (Ailanto), *Indigofrra gerardiana* Wall. ex Baker (Dyer,s indigo), *Salvia moorcroftiana* Wall. Ex Bth. (sage), *Rumex hastatus* D. Don (Dock sorrel), *Xanthium strumarium* L. (Bur weed), *Dodonaea viscose* (L.) Jacq. (Switch sorrel), *Debergeasia sulicifolia* (D. Don) Rendle (Dutchman pipe) and *Saccharum griffihii* Munro ex Boiss. (plume grass) were also collected from the same site from where soil samples were collected (Fig. 1). All the plants were in seedling stage (<70 cm in height). After collection, the plants were identified and the botanical names were given to every plant with the help of a plant taxonomist of the Botany Department, University of Peshawar. Both the plant and soil samples were brought to the Geochemistry Laboratory of the National Centre of Excellence in Geology, University of Peshawar for further preparation and analysis.

The reference soil and plant samples were collected from an area (not shown on the map) about 50 km SW of the study area where meta-sediments and granite-gneisses were exposed. There was no input of the mafic and ultramafic rocks in the soils of this area. Therefore, in the following text, reference soils and plants samples will represent the background values for comparison purpose.

Samples' preparation and analyses

After transportation to the laboratory, each soil sample was air-dried and sieved through a <2 mm mesh, and then sealed in Kraft paper envelopes until analysis. Sub-samples were used to measure the physico-chemical properties according to standard procedures. For HM analyses, 0.5 g of each moisture-free powdered soil sample was taken in triplicate in a teflon beaker and treated with hydrofluoric acid (HF) and aqua regia (HNO_3:HCl ratio 3:1) and the final volume of 30 ml was prepared with 2 N HCl by following the method of Jeffery and Hutchison (1986) and Ryan et al. (2001). The extracts were analyzed using atomic absorption spectrometer, Perkin Elmer, Analyst 700, USA, (AAS-PEA-700).

All the plant samples were properly washed with tap water and finally with double de-ionized water (DDW) to remove all visible soil particles. The washed plant samples were oven-dried at 70°C for 48 h to a constant weight and were ground with an electric grinder. About 2 g of each ground plant sample was taken in triplicate in Pyrex beakers separately and was digested with HNO_3–$HClO_4$ and aqua regia. The digestion procedure was adopted from Ryan et al. (2001). The extract was made to the final volume of 50 ml with DDW. Concentrations of HMs in the digested samples were determined using AAS-PEA-700. A reagent blank and standard reference plant and soil materials were included to verify the accuracy and precision of the digestion and subsequent analysis procedure. All the chemicals were of analytical grade. All the reagents and the calibration standards were prepared using the DDW. The results obtained were in triplicate.

The data were statistically analyzed using the statistical package SPSS 11.5. The measures were expressed in terms of mean, while the figures presented the mean values and standard deviation of triplicate. Statistical significance was computed using Duncan's multiple range test and Paired-samples *t* test, with a significance level of $P < 0.01$.

Results and discussion

Soil

Table 1 summarizes the results of HMs in the soil samples collected from the mafic and ultramafic rock terrains and reference sites. The concentration of Cu in the soils of Mingora and Kabal areas was ranged from 29 to 184 mg/kg with a mean value of 63 mg/kg (Table 1). Cu concentrations in the soil samples were significantly ($P < 0.01$) higher than the reference soil (Table 2). Cu in all the soil samples of Mingora and Kabal areas exceeded the normal agricultural soil value (20 mg/kg) of Bohn et al. (2001) and reference soil (Table 2). The occurrence of Cu in small amount (4–20 mg/kg) is generally beneficial for the normal growth of the plants while its amount less than 4 mg/kg is considered deficient and more than 20 mg/kg is considered toxic (Jones 1972; Adriano 1986, 2001). The high concentration (>20 mg/kg) of Cu in the soils of Mingora and Kabal areas could be hazardous as far as the normal growth of plants is concerned. The data indicate that the Cu concentrations in the soil samples were higher than the concentrations detected in the wastewater-contaminated soils (Mapanda et al. 2007). Furthermore, the concentrations of Cu were markedly high and generally similar to the values (83–162 mg/kg) detected in the soil contaminated with mine spill (Del Río et al. 2002).

Table 1 Physico-chemical characteristics of soils collected from Mingora and Kabal areas, Swat, Pakistan

Plant species	Cu		Pb		Zn		Cr		Ni		Cd	
	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil
Poaceae family												
S. griffihii (MPS-6)	19	49	5	60	12	104	358	1,245	289	1,929	0.23	3
S. griffihii (MPS-12)	30	62	7	49	19	15	289	1,425	256	1,440	0.24	3
S. griffihii (MPS-15)	7	75	5	53	4	63	63	372	37	259	0.09	3
S. griffihii (MPS-34)	12	48	5	57	8	135	87	324	45	253	0.13	2
S. griffihii (MPS-35)	23	47	3	49	33	106	118	349	77	270	0.40	3
S. griffihii (KPS-46)	18	73	5	52	30	63	102	299	63	177	0.38	3
S. griffihii (KPS-49)	29	49	7	46	18	78	71	363	57	242	0.24	3
S. griffihii (KPS-54)	14	32	5	46	21	38	56	261	49	143	0.25	3
Average	19	54	5	52	18	75	143	580	109	589	0.26	3
S. griffihii (reference)	6	21	3	11	6	16	5	10	4	12	0.09	0.8
Papilionaceae family												
I. gerardiana (MPS-11)	14	41	2	56	13	17	285	4,035	278	1,836	0.22	3
I. gerardiana (MPS-14)	9	34	2	67	8	18	256	5,647	269	2,341	0.18	4
Average	11	38	2	61	10	18	271	4,841	274	2,089	0.20	4
I. gerardiana (reference)	3	18	2	13	7	17	168	18	7	15	0.05	0.6
Polygonaceae family												
R. hastatus (MPS-9)	8	29	2	34	7	25	48	1,231	40	1,314	0.22	2
R. hastatus (KPS-37)	12	60	3	45	11	39	57	140	28	146	0.24	4
R. hastatus (KPS-52)	11	61	2	56	10	39	61	679	39	300	0.24	4
Average	10	50	2	45	9	34	55	683	36	587	0.23	3
R. hastatus (reference)	3	11	2	11	4	10	15	45	14	48	0.06	0.7
Labiateae family												
S. moorcroftiana (MPS-4)	24	65	5	90	22	50	45	457	70	360	0.26	3
S. moorcroftiana (MPS-17)	18	73	4	52	10	40	54	643	31	501	0.23	3
S. moorcroftiana (MPS-18)	15	48	5	47	14	44	40	554	27	421	0.21	3
S. moorcroftiana (MPS-19)	29	87	5	39	26	28	56	338	34	207	0.25	3
Average	22	68	5	57	16	41	49	498	40	372	0.24	3
S. moorcroftiana (reference)	4	7	3	5	5	2	10	56	8	42	0.03	0.6
Asteraceae family												
X. strumarium (MPS-5)	28	57	5	62	25	59	54	1,568	53	1,368	0.27	3
X. strumarium (KPS-55)	16	86	7	52	15	27	48	336	28	201	0.25	2
Average	22	72	6	57	20	43	51	952	40	785	0.26	3
X. strumarium (reference)	3	21	4	15	5	18	5	34	5	30	0.07	0.7
Sapindaceae family												
*D. viscos*e (MPS-3)	20	69	5	82	19	47	35	409	30	318	0.25	3
*D. viscos*e (MPS-8)	15	53	4	38	6	23	55	879	42	1,467	0.21	3
*D. viscos*e (KPS-51)	17	60	5	44	15	26	45	322	30	140	0.22	4
Average	17	60	5	55	11	32	45	537	34	642	0.23	3
*D. viscos*e (reference)	4	19	2	12	2	16	5	29	4	32	0.04	0.8
Ultricaceae family												
D. sulicifolia (MPS-13)	11	55	5	59	10	81	68	486	30	270	0.23	3
D. sulicifolia (MPS-2)	15	83	6	81	12	44	46	371	20	468	0.22	3
Average	13	69	6	70	11	63	57	429	25	369	0.22	3
D. sulicifolia (reference)	4	15	2	19	2	13	6	28	5	31	0.05	0.8
Cannabinaceae family												
C. sativa (MPS-22)	33	60	3	89	30	95	48	490	35	673	0.29	3

Table 1 continued

Plant species	Cu		Pb		Zn		Cr		Ni		Cd	
	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil
C. sativa (KPS-53)	27	184	4	41	25	28	53	274	39	184	0.28	3
Average	30	122	4	65	27	62	51	382	37	429	0.28	3
C. sativa (reference)	4	22	3	17	2	19	6	32	5	23	0.06	0.8
Simarubaceae family												
A. altissima (MPS-1)	25	64	6	62	22	40	43	446	64	436	0.29	2
A. altissima (KPS-42)	19	52	8	42	17	43	39	213	53	177	0.25	3
Average	22	58	7	52	20	41	41	330	59	307	0.27	3
A. altissima (reference)	4	18	3	15	3	10	6	29	5	23	0.06	0.8
Minimum (enriched soil)	7	29	2	34	4	10	35	140	20	140	0.09	2
Maximum (enriched soil)	33	184	8	90	33	135	358	5,647	289	2341	0.40	4
Average (enriched soil)	18	63	5	55	16	48	92	863	75	637	0.24	3

MPS and KPS indicate soil and plant samples from Mingora and Kabal areas, respectively; the numbers indicate the samples as shown on location map (Fig. 1)

Table 2 Concentration of heavy metals (mg/kg) in the plants and soils of the mafic and ultramafic terrains from Mingora and Kabal areas, Swat, Pakistan

	Enriched soils (this study)	Reference soils (this study)	Normal agriculture soil (Bohn et al. 2001)
pH	6.87–7.12	6.87–7.01	–
OM[a] (%)	2–6	2–5	–
Clay (>4 µm) (%)	9–22	10–12	–
Silt (4–5 µm) (%)	25–30	28–32	–
Sand (>4 µm) (%)	40–60	50–59	–
Cu (mg/kg)	63*	17	20
Pb (mg/kg)	55*	13	10
Zn (mg/kg)	48*	13	50
Cr (mg/kg)	863*	31	20
Ni (mg/kg)	637*	28	40
Cd (mg/kg)	3*	0.73	0.05

OM organic matters

* Significance at level $P < 0.01$

Pb concentrations were in the range of 34–90 mg/kg with an average amount of 55 mg/kg in the soil samples collected from Mingora and Kabal areas (Table 1). Pb in almost all the soil samples of Mingora and Kabal areas were many folds higher than that of the normal limit set for agricultural soils (10 mg/kg) and the reference soils (Table 2). Like Cu, Pb concentrations in the soil samples were significantly ($P < 0.01$) higher than the reference soil samples. The bioavailability of HMs from soil to plants depends on various factors including soil properties, climatic conditions, plant genotype and agronomic management (Kabata-Pendias and Pendias 2001). Pb occurs mainly as Pb^{2+} and its primary form in nature is galena (PbS). During weathering, it slowly oxidized and form carbonates which incorporate in the stable phases such as clay minerals, Fe-oxides, Mn and Al hydroxides, phosphates and organic matters (Kabata-Pendias and Pendias 2001). Therefore, phyto-availability of Pb in the studied soils seems to be very low. Obviously, total Pb concentrations in the soil samples are not a good indicator for phyto-availability because the plant uptake depends on the water soluble fraction of the metals (Adriano 2001; Khan et al. 2006). The findings of this study indicated that the Pb contamination level is lower than the Pb values detected in the soil samples collected from silver mine areas (Figueroa et al. 2008).

A wide range of Zn concentration was observed among the soils collected from the study areas. The concentrations of Zn were ranged from 10 to 135 mg/kg with an average concentration of 48 mg/kg in the soil samples of Mingor and Kabal areas (Table 1). Zn concentrations in the soil samples were significantly ($P < 0.01$) higher than the reference soils and in some samples have exceeded the normal limit (50 mg/kg) set for agricultural soils (Tables 1, 2). Zn is an essential metal for plant growth, and its high mobility within the plant is responsible for highest concentration of

Zn in wild plants (Bennetta et al. 2000). Zn deficiency can highly affect the nutrition quality of plants but its high concentration in the soils could be toxic for the plant growth and development (Adriano 2001). Therefore, it is suggested that the soils of Mingora and Kabal areas were generally safe, except at few places, and should have no toxic effects on plants.

In the study areas, Cr concentrations were ranged from 140 to 5,647 mg/kg with an average concentration of 863 mg/kg (Table 1). Cr concentrations in the soil samples were also significantly ($P < 0.01$) higher than the reference soil samples (Table 2). These highest concentrations of Cr suggest that this metal was highly enriched in the studied soils as compared to that of normal agricultural soil (20 mg/kg). The soil samples within the Mingora-Shangla mélange zone or in its vicinity in the Mingora area are having anomalous values (324–5,647 mg/kg) of Cr metal. This can be attributed to the formation of this soil, referred to as serpentine soil, due to the weathering of ultramafic rocks within the mélange zone where the Cr is generally associated with olivine, pyroxene and chromite (Arif and Jan 1993). Cr usually forms chromate ions (CrO_4 and $HCrO_4$) which are easily mobilized and sorbed by clays and hydrous oxides (Kabata-Pendias and Pendias 2001). Naturally occurring Cr compounds have principal valences of III (chromic) and VI (chromate). The Cr(VI) is much less stable than Cr(III) and can very easily be mobilized in both acid and alkaline soils. According to Bartlett and James (1979) and Gough et al. (1979), Cr in the soil is usually oxidized from Cr(III) to Cr(VI) and then it is available for plant uptake. However, the Cr(III) can only be mobilized in the acidic soils (Adriano 1986; Kabata-Pendias and Pendias 2001). Cr has stimulatory effects on the growth of the plants and could be toxic in these soils which are derived from the ultramafic rocks (Adriano 2001). The serpentine soils of the Mingora area, as having been derived from the ultramafic rocks, can produce toxicity in the plant species present in the study area. Furthermore, the concentrations of Cr in the soil samples were higher than the concentrations detected in the wastewater-contaminated soils (Khan et al. 2008). It means that the natural sources could equally be responsible for soil contamination with HMs.

A wide range of Ni concentrations were observed in the soil samples collected from Mingora and Kabal areas. Ni concentrations were ranged from 140 to 2,341 mg/kg with an average amount of 637 mg/kg (Table 1) and were significantly ($P < 0.01$) higher than the reference soil samples (Table 2). Ni concentrations in the soil samples of both Mingora and Kabal areas have shown the distribution patterns similar to Cr metal. Its concentration was many folds higher than the normal agricultural soil (40 mg/kg) and the reference soil samples (Table 2). This enrichment in the studied soils could also be due to the weathering of Cr–Ni bearing phases (i.e. olivine, pyroxene serpentine, etc.) in the ultramafic rocks of the mélange zone. However, the soils of Kabal area were less enriched as compared to that of Mingora area. Ni is beneficial for the plant growth if present in normal amount in soil; however, the soil with high concentration, especially derived from the ultramafic rocks, can produce toxicity symptoms in plants (Mishra and Kar 1974; Adriano 2001). The data indicate that the soils of Mingora area were highly contaminated with Ni and can be considered more toxic for the growth of plants.

Cd concentrations were ranged from 2 to 4 mg/kg in the soils of Mingora and Kabal areas (Table 1). Cd concentrations were significantly ($P < 0.01$) higher than the reference soil and exceeded the normal value set for agricultural soil (Table 2). Soil contamination with Cd is believed to be a most serious health risk. However, the Cd concentration (<4 mg/kg) in the studied soils was not considered as hazardous for the plant growth (Adriano 2001) and plants grown there had no symptoms of toxicity. The findings of this study indicated that the Cd concentrations in the soil samples were higher than the concentrations detected in the wastewater-contaminated soils and the soils contaminated with silver mine (Figueroa et al. 2008). However, the concentrations of Cd were lower than the values detected in some soil samples contaminated with mine spill (Del Río et al. 2002).

Plants

Table 1 summarizes the results of HMs in the plant samples collected from the mafic and ultramafic rock terrains and reference sites, while Fig. 2 indicates the enrichment values for various HMs in the plant samples. Cu concentrations were ranged from 7 to 33 mg/kg in the plant samples of Mingora and Kabal areas (Table 1). Cu concentrations in the plants grown on soils derived from mafic and ultramafic rocks were higher than the reference soil grown plants. Cu concentrations in the selected plant samples were in the order of *Cannabis sativa* > *Salvia moorcroftiana* > *Ailanthus altissima* > *Xanthium strumarium* > *Saccharum griffihii* > *Dodonaea viscose* > *Debergeasia sulicifolia* > *Rumex hastatus* > *Indigofrra gerardiana* (Table 2). However, the concentrations of Cu were lower than the values (27–65 mg/kg) detected in the wild plants (belong to the family Poaceae but different species) grown on soil contaminated with mine spill (Del Río et al. 2002). Cu concentration <5 mg/kg is considered inadequate for the growth of many of plant species (Kabata-Pendias and Pendias 2001). Cu in very small amount from 5 to 20 mg/kg in plant tissues are adequate for their normal growth, while more than 20 mg/kg is considered as toxic for numerous plant species (Jones 1972). It is mobile within the plant's body, which probably

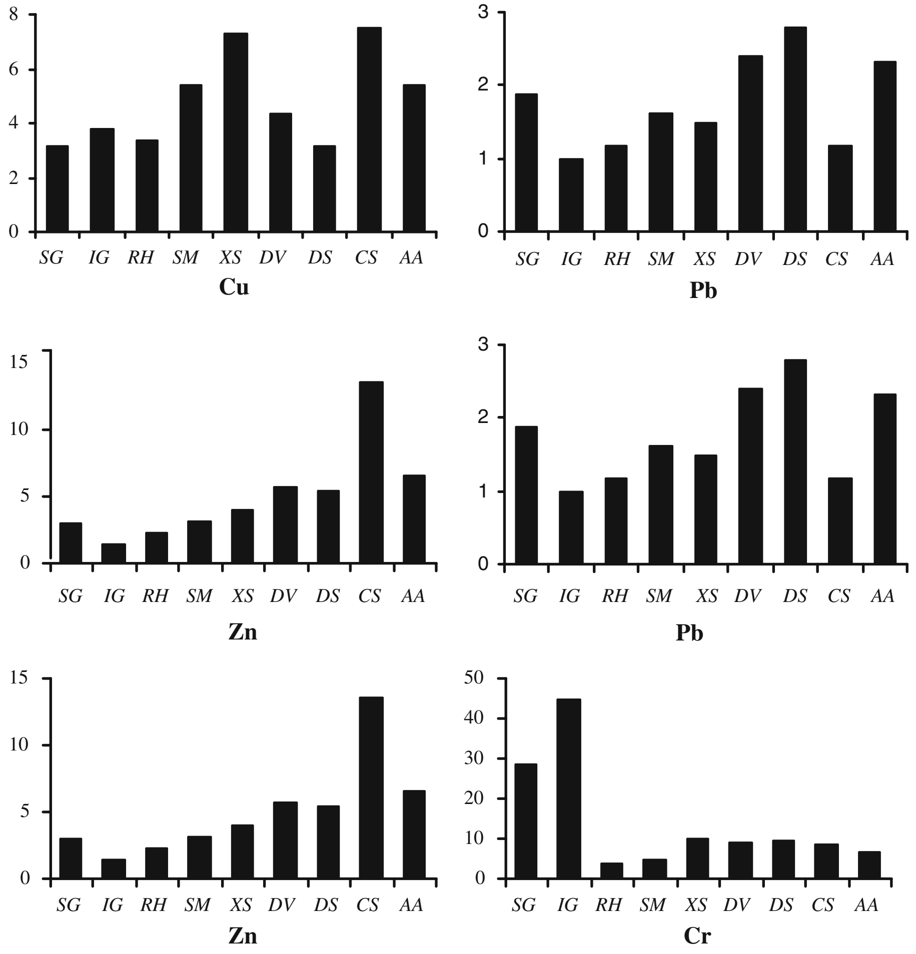

Fig. 2 Variable enrichment values of HMs in plant samples collected from Mingora and Kabal areas. Enrichment factor is calculated as HMs in plants of mafic-ultramafic terrain/HMs in reference plants. *SG*, *S. griffihii*; *IG*, *I. gerardiana*; *RH*, *R. hastatu*; *SM*, *S. moorcroftiana*; *XM*, *X. strumarium*; *DV*, *D. viscose*; *DS*, *D. sulicifolia*; *CS*, *C. sativa*; *AA*, *A. altissima*

explains its highest concentrations in wild plants (Bennetta et al. 2000). The data indicated that in some of the studied plants samples, the concentrations of Cu exceeded the limit causing phyotoxicity.

Pb concentrations in the plants grown in the study area ranged from 2 to 8 mg/kg. The highest Pb value (8 mg/kg) was detected in the samples of *Ailanthus altissima* (Table 1). Pb concentrations in the plants, except *Indigofrra gerardiana* and *Rumex hastatus*, grown on soils derived from mafic and ultramafic rocks were higher than the reference soil grown plants. Pb concentrations in the selected plant samples were in the order of *Ailanthus altissima* > *Debergeasia sulicifolia* > *Xanthium strumarium* > *Saccharum griffihii* > *Salvia moorcroftiana* > *Dodonaea viscose* > *Cannabis sativa* > *Rumex hastatus* > *Indigofrra gerardiana* (Table 1). In few cases, Pb contents in the studied plants were found >6 mg/kg (Table 1). As the whole plant, including roots, have been treated for the HMs concentration, therefore, it was not possible to find out that which parts of the plants have greater accumulation of Pb. However, previous studies (e.g. Zimdahl and Koeppe 1977; Kabata-Pendias and Pendias 2001) have shown that Pb is generally accumulated in the roots of many plants during the translocation of Pb in the plants. Pb concentrations in studied plant samples were inconsistent with the results in literature for both wild and domesticated plants (Del Río et al. 2002; Del Río et al. 2006). The concentrations of Pb ranging from 2 to 6 µg/kg are sufficient for the normal growth of plants while its background level in the forage plants is reported as 2.5 mg/kg (Broyer et al. 1972; Kabata-Pendias and Pendias 2001). Natural Pb concentration in plants grown in uncontaminated and unmineralized soils is generally ranging from 0.1 to 10 mg/kg with average amount of 2 mg/kg (Cannon 1976; Kabata-Pendias and Pendias 2001). Pb concentrations in the plant samples of Mingora and Kabal areas generally found within the permissible limit for the normal growth of various plants.

Highly variable concentrations of Zn, ranged from 4 to 33 mg/kg, were noticed in the plants of the study area (Table 1). Zn concentrations in the plants grown on soils derived from mafic and ultramafic rocks were many folds higher than the plants grown on the reference soils (Table 1). Zn contents in the studied plants were in the order of *Cannabis sativa* > *Ailanthus altissima* > *Xanthium strumarium* > *Saccharum griffihii* > *Salvia moorcroftiana* > *Dodonaea* *viscose* > *Debergeasia sulicifolia* > *Rumex hastatus* > *Indigofrra gerardiana*. Its accumulation in various plant species, especially in Calamine flora, has also been reported by many workers (Zalecka and Wierzbicka 2002; Kupper et al. 2000; Whiting et al. 2000; Hajiboland and Manafi 2007; Olko et al. 2008). Zn plays an important role in the plant metabolism and is not considered to be highly phytotoxic (Lindsay1972; Price et al. 1972). However, Zn toxicity limit depends on the plant species, physiology, genotypes and growth rate, and its uptake was different among the plant communities depending on their ability to accumulate and detoxify it like other HMs (Gupta et al. 2002; Jala and Goyal 2006). Upper toxic limit of Zn in most of the plants is ranged from 100 to 500 mg/kg (Brooks 1983; Macnicol and Beckett 1985). According to Jones (1972), the optimum requirement of Zn for plants varies greatly from species to species and, therefore, it is difficult to establish a single critical value. However, plants with Zn contents below 20 mg/kg are suspected of Zn deficiency with normal values ranging from 25 to 150 mg/kg of Zn (Jones 1972). Therefore, Zn contents of plants in Mingora and Kabal areas are generally low in Zn and, therefore, no environmental threats can be expected in the region in this regard.

Cr concentrations were ranged from 35 to 358 mg/kg in the plant samples collected from the study area (Table 1). The highest Cr concentration was detected in *Saccharum griffihii*, while lowest concentration in *Dodonaea viscose* (Table 1). Cr concentrations in the plants grown on soils derived from mafic and ultramafic rocks were higher than the reference soil grown plants. This can be attributed to the phyto- availability of Cr(VI) from the studied serpentine soils (Bartlett and James 1979; Gough et al. 1979). Cr on average was in the order of *Indigofrra gerardiana* > *Saccharum griffihii* > *Debergeasia sulicifolia* > *Rumex hastatus* > *Xanthium strumarium* > *Cannabis sativa* > *Salvia moorcroftiana* > *Dodonaea viscose* > *Ailanthus altissima.* Cr accumulation in the plants grown on the ultramafic terrains elsewhere has also been reported by Mertz et al. (1974), Petrunina (1974) and Kifyatullah et al. (2001). The toxicity limit of Cr in plants is generally reported from 1 to 10 mg/kg (Macnicol and Beckett 1985; Adriano 1992). In this regard, the Cr concentrations in all selected plants were manifolds higher than the recommended level for toxicity in plants. This high level of Cr could be hazardous for plant community in the study areas.

Ni concentrations were ranged from 20 to 289 mg/kg in the plant samples collected from the study areas. The highest Ni concentration was found in *Saccharum griffihii*, while lowest value was noticed in *Debergeasia sulicifolia* (Table 1). Like other HMs, variable concentrations of Ni were accumulated in these wild plants. Furthermore, Ni concentrations in the plants grown on soils derived from mafic and ultramafic rocks were higher than the reference soil grown plants. However, *Indigofrra gerardiana* and *Saccharum griffihii* showed greater accumulation of Ni among all the studied plants (Table 1). Ni concentrations were in the order of *Indigofrra gerardiana* > *Saccharum griffihii* > *Ailanthus altissima* > *Salvia moorcroftiana* > *Xanthium strumarium* > *Cannabis sativa* > *Rumex hastatus* > *Dodonaea viscose* > *Debergeasia sulicifolia* (Table 1). Ni accumulation in many plant species of serpentine flora has also been reported elsewhere (Brooks and Yang 1984; Reeves 1992; Robinson et al. 1997; Reeves et al. 1996; 1999; Brooks 1998; Kifyatullah et al. 2001; Hajiboland and Manafi 2007). The results indicated that the Ni concentrations were markedly higher and inconsistent with the values in the plants grown on wastewater-contaminated soils (Khan et al. 2008). The phytotoxic Ni concentrations are varied widely among plant species and are generally ranging from 40 to 246 mg/kg (Gough et al. 1979). It was noticed that the amount of Ni in all the studied plants was within the toxic range and could be hazardous for the plants growth.

This study shows that variable concentrations of Cd were accumulated in the wild plant samples and its concentrations were ranged from 0.09 to 0.40 mg/kg (Table 1). Cd concentrations in the plants grown on soils derived from mafic and ultramafic rocks were higher than the reference soil grown plants. However, the concentrations of Cd in plant samples were low as compared to other HMs and were not considered to cause toxicity (Adriano 2001; Kabata-Pendias and Pendias 2001). Del Río et al. (2002) reported the Cd concentrations higher than our values in the plants grown on site contaminated by mine spillage. The variable concentrations of various metals in the plant samples were due to their different uptake rates for these elements from the soils (Kifyatullah et al. 2001; Shah et al. 2004).

HMs' enrichment

Figure 2 shows the enrichment levels of the various HMs in the plants grown on the soils derived from mafic and ultramafic rocks of the Mingora and Kabal areas. The data showed the highest enrichment of Cu in *C. sativa*, Pb in *D. sulicifolia*, Zn in *C. sativa*, Cr and Ni in *I. gerardiana*, and Cd in *S. moorcroftiana*. However, the plant enrichment rates were highly varied from metal to metal and from species to species. Furthermore, it is suggested that the wild plants were highly contaminated with HMs and their enrichments were multifold.

Relationships between metals

Tables 3 and 4 showed the inter-elemental relationship for HMs in the studied soils and plants, respectively. No

Table 3 Inter-element correlation in the soils of Mingora and Kabal areas, Swat, Pakistan

Cu	Pb	Zn	Cr	Ni	Cd
1.00	−0.03	−0.15	−0.32	−0.36	0.11
	1.00	0.27	0.12	0.08	0.07
		1.00	−0.26	−0.15	−0.12
			1.00	0.83	0.30
				1.00	0.07
					0.31

Table 4 Inter-element correlation in the plants of Mingora and Kabal areas, Swat, Pakistan

Cu	Pb	Zn	Cr	Ni	Cd
1.00	0.36	0.73	−0.05	−0.02	0.50
	1.00	0.15	−0.05	−0.06	−0.03
		1.00	−0.08	−0.06	0.77
			1.00	0.97	−0.05
				1.00	−0.06
					0.33

significant inter-element correlation existed in the soils and plants. However, Ni and Cr showed good correlation in both the soils ($r = 0.83$) and plants ($r = 0.97$), while Zn and Cu ($r = 0.73$) and Zn and Cd ($r = 0.77$) also showed good correlation in plants (Tables 1, 2). Regression analysis was performed to identify the relationships between the metal concentrations in soil samples as well as in plant samples. The data indicated that these relationships were not strong, may be because of the different soil characteristics and plant physiologies (Khan et al. 2008; Xio et al. 2008). Linear regression analysis was used to examine the relationships between the concentrations in soils and plants (Fig. 3). The findings indicated that the weak positive correlations ($r < 0.33$) for Cu, Zn and Cd and a little stronger positive correlation for Cr ($r = 0.66$) and Ni ($r = 0.80$) existed in the studied soils and plants. The weak correlations of HMs in plants and soils can be attributed to the greater variation of these elements in the soils of the area and also the variable uptake rates of the different plants (Kifyatullah et al. 2001; Shah et al. 2004).

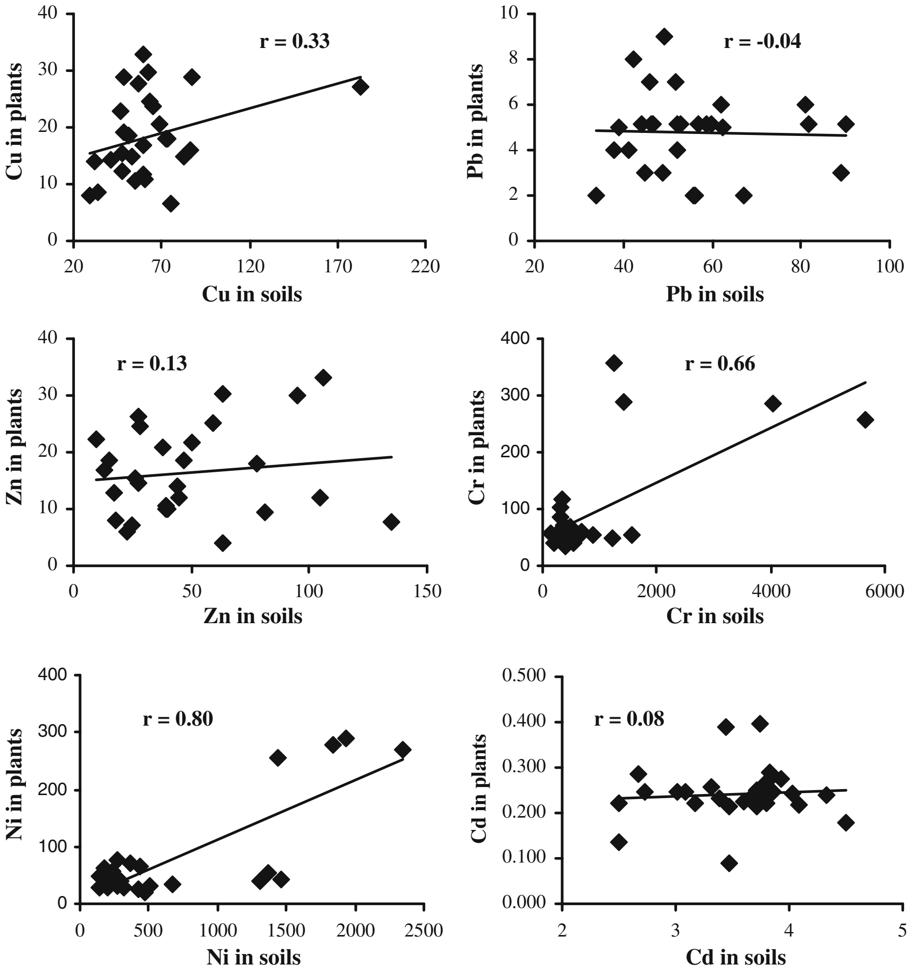

Fig. 3 Correlation between concentration of various HMs in the plants and associated soils of the Mingora and Kabal areas

Environmental perspectives

The biogeochemical studies show that the ability of various plants to uptake greater amount of various HMs from the soils has provided significant clues for both mineral prospecting and environmental degradation (Hawkes and Webb 1962; Levinson 1974; Rose et al. 1979; Brooks 1987; Robinson et al. 1997; Brooks 1998; Kabata-Pendias and Pendias 2001; Bohn et al. 2001; Kifyatullah et al. 2001; Shah et al. 2004; Hernández and Pastor 2008). It has been noticed during this study that most of the HMs were highly enriched in the soils but their toxicities on the plant species cannot be considered hazardous. However, the variable enrichment of Cr and Ni in the plant species, especially in *I. gerardiana* and *S. griffihii* grown on the soils derived from ultramafic rocks of the mélange zone in Mangora area can be applicable not only to mineral exploration but also to environmental and toxicological concerns. The Cr and Ni toxicity and their carcinogenic effects on both animals and human beings are well reported (Hernández and Pastor 2008; Xio et al. 2008; Khan et al. 2008).

The high concentrations of HMs in the soils and plants can be transferred directly (through inhalation of contaminated dusts and dermal contacts with contaminated soils) or from forage plants to animals and then to the inhabitants of the area through meat and milk of these animals. This food chain contamination is one of the major pathways through which HMs enter into the human beings. It has been found during discussion with the inhabitants and the physicians of the area that the cases of cancer, especially breast cancer in women and the intestinal and liver cancer in both genders, are increasing rapidly in the whole region. In this regard, a detailed study involving the biochemist, geochemist and epidemiologists is needed to be carried out in order to unravel the toxicity caused by these elements in the area of study.

Conclusions

It is concluded from this study that the lithologies of the area have played a major role in the enrichment of various HMs in the soils and plants. The high concentrations of Cr and Ni in soils and plants can be attributed to the mafic and ultramafic rocks of the Mingora-Shangla mélange zone and Kohistan island arc in the Mingora and Kabal areas. Furthermore, the elevated concentrations of HMs in soils and plants can cause serious health risks as these HMs reach to human beings through ingestion of contaminated food. This study suggests that detail investigations are needed to assess the level of daily intake of HMs by inhabitants through various pathways.

Acknowledgments The authors would like to thank Mr. Asadullah, taxonomist, Botany Department, University of Peshawar for plants identification and classification. This study was financially supported by the Director of NCE in Geology, University of Peshawar.

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