Soil-plant relationship of *Pteropyrum olivieri*, a serpentine flora of Wadh, Balochistan, Pakistan and its use in mineral prospecting

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ABSTRACT. Biogeochemical investigation of *Pteropyrum olivieri*, a flora of Wadh area in perspective of plant-soil-rock relationship has been made. It is a native of Irano-Turanian region which extended into Saharo-Sindian region of Pakistan. The distribution of *P. olivieri* and some other co-ecological flora in relation to lithology was also discussed. Field observations showed its controlled population on the serpentine soil. The average abundance of Mg and Ca in soil was estimated to 2.43 and 5.46%, respectively. The Mg/Ca ratio of the soils of the study area was below unit (0.445), indicating pedogenesis from serpentinite. Quantitative estimation of Cr, Ni, Co, and Cu in soils and plant ash was made. Distribution of these elements has been discussed in context with soil chemistry, average abundance in plant ash and the exclusion mechanism of the flora. The concentration of Cr, Ni, and Co in the twigs of *P. olivieri* is more than the average abundance in the plant ash, while Cu concentration was less. Relationship among Cr, Ni, Co, and Cu has been established using scatter-grams to evaluate biogeochemistry of the *P. olivieri*. Bio-concentration factor (BCF) of the specie attributed Co>Cu>Ni>Cr trend. Present study outlines a number of anomalous zones which can be utilized for the exploration of new hidden mineral deposits in and around Wadh area. The rocks in the anomalous region served as good host for podiform chromite and associated mineralization.

Key-words: biogeochemistry, mineral prospecting, *P. olivieri*, Balochistan, Pakistan.

INTRODUCTION

In recent years there has been ever increasing interest in the study of plant-soil relationship for phytoremediation, phytoextraction, phytomining and mineral prospecting (Al-Farraj and Al-Wabel, 2007; Ebong et al., 2007; Ololade et al., 2007). In biogeochemical prospecting techniques, plants are used to indicate the presence of mineral deposits (Pratas et al., 2005; Ghaderian and Baker, 2007). Biogeochemical prospecting involves chemical analysis of plants, in order to detect the presence of mineralization beneath the earth surface (Brooks, 1972). Metallic ion composition of vegetation reflects the availability of elements in the vicinity of the root system, and the ability of the plant to absorb and accumulate these elements (Cohen et al., 1999).

The Bela Ophiolite (BO) of Balochistan, Pakistan is linked with Alpine-Himalayan Mesozoic Ophiolite Belt, which stretches from European Alps to Asia. It is a harzburgite sub-type ophiolite, which is common in Tethyan domain (Nicolas, 1989). It is characterized by mafics, tholeiitic basalts and ultramafics. Deposits and showings of Cr, Ni, Cu, and magnesite are reported at many places (Bashir et al., 2004). The ultramafics of Wadh area have been completely transformed to serpentinites and pedogenesis has produced soils containing high

concentrations of Mg, Fe, Ni, Cr, Co and Cu. Areas of serpentine soil facilitate better investigation for such elements for mineral prospecting (Freitas et al., 2004).

During the fieldwork in the Wadh area it is observed that *P. olivieri* has restricted population over the thin cover of serpentine soil. The plant is commonly associated with some known chromite quarries in the area. This idea provides the basis for current study. Present study elaborates soil-plant relationship and distribution of *P. olivieri* in framework of local geology. Variation in metal content of plant in relation to soil composition is discussed. The present study also focuses on the application of *P. olivieri* as biogeochemical indicator of Cr, Ni, Co, and Cu mineralization, associated with the BO in Khuzdar area.

GENERAL GEOLOGY

The study area lies within the Western Fold Belt of Pakistan forming the western margin of the Indian plate. The belt comprises of BO and sedimentary rocks ranging in age from Jurassic to Tertiary. The BO is the largest ophiolite in Pakistan and runs from Khuzdar to the Arabian Sea, west of Karachi. Globally it is linked with Alpine-Himalayan Mesozoic Ophiolite Belt, stretching eastward from European Alps to Zagros Mountains of Iran to the Himalayas.

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The study area is related to the upper unit of BO (Gnos et al., 1998) which comprised of true intact ophiolite sequence, exposed between Sonaro and Wadh. According to Nicolas (1989) it is a harzburgite sub-type ophiolite. It is characterized by thick (~2 km) mafics, tholeiitic basalts and abundant ultramafics and by the presence of chromite pods and magnesite deposits (Bashir et al., 2004).

Most of the ultramafic rocks of the study area are partly to completely serpentinized equivalents of harzburgite, pyroxenite and dunite. These ultramafic rocks are highly altered into serpentinite. Possibly serpentines were formed by the alteration of olivines and orthopyroxene (Viti et al., 2005).

FLORA OF THE AREA

Phytogeographically, study area is the part of Saharo-Sindian region. The study area is a high altitude mountainous region (av. elevation 1,112 m), nearly barren and has very meagre vegetation. However, some wild, native and perennial floras are present. *Pteropryum olivieri*, *Nannorrhop ritchiana*, *Dodonaea viscosa*, *Fagonia bruguieri*, *F. indica*, *Withania cogalense*, *Leptadinia pyrotechnica*, and *Rhazya stricta* coexist in the study area. In the study area, *P. olivieri* mostly developed at the hill slope of ultramafic rocks.

Beside the phytogeographical (climate, altitude, etc.) control, lithological control is very powerful tool for the distribution of flora in the study area. Field studies of some selected flora reveal good relationship with the exposed rock-type (Fig. 1).

Collectively, *N. ritchiana*, *D. viscosa* and *P. olivieri* proved as a characteristic flora of ultramafic especially Mg-bearing rocks having chromium-nickel mineralization (Naseem et al., 2005). It is noteworthy that both species of *Pteropryum* do not coexist with each other reflecting control of lithology (Fig. 1).

SAMPLING AND ANALYTICAL METHOD

Both plants and related soils were collected from 21 different locations of Baran Lak and Ustam Butt areas (Fig. 1). In addition, 4 rock samples were also collected from Baran Lak (BL), Pahar Khan (PK), Ustam Butt east (UE), and west (UW) to demonstrate the nature of rocks which were responsible for the pedogenesis (Fig. 1). Dry twigs were ashed as recommended by Martin et al. (1996). Half gram of ash was digested with 5 ml concentrated nitric acid at 105°C in a 100ml beaker. The mixture was kept on hot plate when it was near to dryness a little hot water (5 ml) was added to dissolve salts. Finally 1% solution was prepared (Jones and Case, 1990). The solutions were analyzed by an Atomic Absorption Spectrophotometer (AAS) (Hitachi, Model Z5000) for trace elements.

Soil pH, Eh, and electrical conductivity (EC) were measured in distilled water extract after equilibrating 24 h, using Denver Instrument Model 50. Organic matter of the soil samples were determined by fusion method. Sieved soil samples (200 mesh) were digested in teflon crucibles using a mixture of 1:2 HF-HClO₄. The solution is prepared in a similar way as in ash and run on AAS.

Calcium and Mg of the soils were estimated by EDTA titration.

Fig. 1. Geological map of study area showing sampling sites and distribution of flora showing influence of rock-type (modified after Bashir et al., 2004).

RESULTS AND DISCUSSION

Edaphic Characters

Edaphic factors play an imperative role in the biogeochemical studies (Knight et al., 1997; Robinson et al., 1997a). Serpentine embraces a wide range of soils, differing in chemical and physical properties. Vegetation of serpentine soil has striking physiognomic contrast with that of other type of soil. The serpentine soils are characterized by high Cr, Co, Ni, Mg, and Fe and deficient in N, P, and K (Brooks, 1972, 1987). The serpentine soil may either promote plant diversity by enhancing opportunities for speciation or reduce diversity by increasing rates of extinction (Harrison et al., 2000). Most flora growing on serpentine soil is small in size (L'Huillier and Edighoffer, 1996). Texturally, serpentine soils are medium to fine grained and have low water-holding capacity (Nabais et al., 1996; Robinson et al., 1997b).

The soils of the study area have uniform characteristics and are light brown in colour. The serpentine soils generally possess Mg/Ca ratio <1 (Ghaderian and Baker, 2007). The average Mg/Ca ratio of the study area was found to be 0.445, reflecting more Ca in the soil (Table 1).

Important parameters of the collected soils are given in Table 1. The metal content of the soils of the study area shows fluctuating pattern of distribution. Copper and Co has

low abundance while Ni and Cr are high and their distribution pattern is nearly similar except in a few localities (Table 1). The Cr and Ni show positive relationship whereas Cr exhibits nearly inverse correspondence ($r = -0.402$) with total organic carbon (TOC) (Fig. 2). In alkaline conditions, the dissolved organic materials are capable to hold metal ions (Duke and Williams, 2008).

Table 1. Composition of soils of study area. TOC, Ca and Mg in %, Eh (mV) and trace elements are in mg/kg.

S.#	pH	Eh	TOC	Cu	Co	Ni	Cr	Ca	Mg
1	8.25	-76	1.34	48	62	877	262	10.04	9.6
2	8.75	-106	2.17	21	21	192	142	6.54	3.03
3	8.39	-84	1.44	45	21	281	169	7.61	3.24
4	8.39	-84	1.28	45	43	567	322	5.08	3.52
5	8.43	-87	0.98	48	50	594	520	3.86	0.46
6	8.76	-107	1.61	36	34	472	274	3.01	1.14
7	8.17	-71	1.02	66	48	329	257	5.52	4.68
8	8.54	-93	1.01	43	40	350	295	5.45	1.76
9	8.15	-68	1.68	42	55	233	290	5.12	1.12
10	8.66	-100	1.28	39	61	308	243	7.18	1.3
11	8.35	-81	1.61	40	16	237	235	4.02	1.09
12	8.62	-98	1.68	38	34	242	259	6.16	3.73
13	8.54	-93	0.9	42	31	200	537	0.74	1.12
14	8.39	-84	0.8	28	51	327	195	6.39	0.91
15	8.27	-77	0.87	37	31	489	799	2.73	1.42
16	8.48	-90	0.75	22	7	94	130	6.05	1.37
17	8.68	-103	1.66	27	15	213	159	6.92	2.56
18	8.11	-67	1.33	54	69	206	137	5.79	1.63
19	8.91	-115	2.79	48	23	312	112	5.44	3.77
20	8.15	-69	1.62	48	48	97	112	5.74	0.46
21	8.29	-73	0.78	48	26	140	125	5.24	3.18

Fig. 2. a) Cr vs. Ni; b) TOC vs. Cr plots of the soils of the study area.

Bio-Concentration Factor

Bio-concentration factor (BCF) is the ratio of the metals in plant to the metal concentration in the soil (Ebong et al., 2007). It is a convenient and reliable way to quantify the relative difference in the bio-availability of metals to plant. The calculated BCF of *P. olivieri* of the study area is illustrated in Fig. 3. It shows that the BCF of the majority of the samples is less than unity for different elements, except Co. The BCF trend shows $Co > Cu > Ni > Cr$, which implies that *P. olivieri* has the potential to accumulate more Co and less Cr. TOC contributes to the reduction of CrVI to CrIII and therefore reducing the concentration of the metal in soil, thus less available to plants.

Fig. 3. Statistics of bio-concentration factor of *P. olivieri* of Wadh area.

The influence of pH of the soil does not play much impressive role in the accumulation of trace metals. The correlation matrix between elements, pH, and Eh show that the Co has maximum influence of physicochemical condition (Fig. 4). The effect of pH and Eh was intermediate on Ni and Cu and less on Cr.

Fig. 4. Correlation matrix between trace metal content of *P. olivieri* and pH and Eh of the soils of study area.

Chromite and Ni-bearing minerals are the two important ores of the Wadh area. The mutual plots of BCF of Cr and Ni are important to examine biogeochemical response of *P. olivieri* in the study area for podiform Cr - Ni deposits (Fig. 5). The *P. olivieri* demonstrates inconsistency in the absorption of Cr and Ni because both of them are found in different horizons of ophiolite. The BCF values of Cr and Ni are plotted in all three zones. Some of them have absorbed low amount, in contrast to sample No. 5, 15, 16, 20, and 21 are in the Zone III. Majority of the species has transferred more Ni than Cr from the same soil. It is important to note that sample No. 21 has high Cr and low Ni and sample No 5 has reverse distribution (Fig. 5), although low concentration of Cr and Ni was noted in these localities.

Fig. 5. Cross-plot of bio-concentration factors (BCF) of Cr and Ni in *P. olivieri* of Wadh area.

Biogeochemistry

Chromium

The concentration of Cr in soils of the study area range between 112 to 799 mg/kg (Table 1) which is more than the average value (43 mg/kg) in soil (Rose et al., 1979). Bio-concentration factor of *P. olivieri* was found below unity in a range 0.084-0.893 with a mean of 0.372 (Fig. 3). The pilot reading recommends that twigs of *P. olivieri* are appropriate for biogeochemical study of Cr mineralization.

The amount of Cr concentration in the plants is low and accumulation at hyper level is not common, even in the Cr-mineralized areas. The TOC also corresponds negative relation (Fig. 2) with Cr probably due to the fact that Cr VI is reduced to Cr III, which is less available to plants. The concentration of Cr in the twigs of *P. olivieri* ranges from 42 to 124 mg/kg with an average of 76 mg/kg (Fig. 6). All samples show high value as compared to the plant average value 6 mg/kg (Rose et al., 1979). In the study area, localities 2 and 4, Sonaro; 5, 6, 7, and 12, Baran Lak and 20, Ustam Butt areas have anomalously high values of Cr and these areas are promising for the podiform chromite deposits.

The association of Cr with other elements shows variable trend. Chromium does not show any sound relation with Ca and Mg although the two exhibit inverse relation with each other (Fig. 7a). The communal relation between Cr and Ni

in the *P. olivieri* is not impressive (Fig. 8a) but it is more significant in case of Cr/Ni and Ni plots, reflecting converse relation (Fig. 8d). However the association between Cr-Fe (Fig. 7b) is nearly positive. The diagram (7b) also exhibits negative relation in a few samples which suggest that Cr replaces Fe in the areas of high Cr and these locations apparently have no mineralization. The above statement is also true in case of Ni (Fig. 8a).

Fig. 6. Distribution of Cr, Ni, Co, and Cu in the *P. olivieri* of Wadh area. Average abundance of elements is given in the inset.

Fig. 7. Degree of correspondence between major and trace elements in the ash of *P. olivieri*.

Fig. 8. Degree of correspondence between trace elements in the ash of *P. olivieri*.

Nickel

Nickel is biogeochemically classified as a very toxic element, which is harmful to plants even at concentration <1 mg/kg (L'Huillier and Edighoffer, 1996). The average abundance of Ni in the native plants is about 65 mg/kg (Brooks, 1972). On the other hand, some plants may absorb high amount of Ni (>1000 mg/kg), such plant are termed as hyper-accumulator (Tilstone et al., 1997 and Roosens et al., 2003). The absorption level of *P. olivieri* is higher than average abundance but it may not classify as hyper-accumulator.

The range of concentration of Ni in the ash of *P. olivieri* is noted between 29 to 273 mg/kg (Fig. 6). L'Huillier and Edighoffer (1996) on the basis of experiment showed that Ni bioavailability in the ultramafic soil is very variable. The present result also proves the variability in the Ni uptake by the *P. olivieri*. Possibly in the areas of dunitic rocks Ni is more enriched, whilst in other areas with more harzburgite, it is low in abundance. The BCF (Fig. 3) also signifies low values (0.045 to 0.895); mean (0.403), which is less than world average (1.54). Probably this species has good exclusion mechanism that restricts the high intake of toxic nickel. Allaway (1968) proposed that the soil-plant system provides an effective barrier against toxicity of Ni. The graph plot between Mg and Ni in the ash of *P. olivieri* shows slightly positive linear relationship (Fig. 7c); on the contrary Ca shows negative behavior (Fig. 7d) reflecting more genetic affiliation with Mg-bearing rock.

Biogeochemical techniques are widely used for the exploration of Ni deposits in the world but they are not being applied in Pakistan (Naseem et al., 1995). The average abundance of nickel in the plant ash is 18 mg/kg (Rose et al., 1979), 20 mg/kg (Levinson, 1980) and 65 mg/kg (Brooks, 1972), and concentration beyond 65 mg/kg in the normal plants is considered anomalous for mineralization. In the study area high concentration of Ni is found in Baran Lak, Pahar Khan, and Ustam Butt areas. Probably the Ni-sulphide deposits are associated with chromite deposits which are common in the Baran Lak area. Ahmed (1992) also mentions the presence of Ni-mineralization in the study area.

Cobalt

Cobalt and Cr have similar genetic affiliation and are common in the lower most segment of ophiolite. The mean abundance of Co in plant ash is 5 mg/kg (Reedman, 1979). The Co content of the *P. olivieri* varies between 5 to 39 mg/kg. Naseem et al. (1995) show slightly low content of Co in the twigs of *Tamarix aphylla*, collected in the south of study area, where pillow basalts are exposed. The specific difference in the level of Co absorption in the north and south is possibly due to the influence of bed-rock. The contrast behavior between Co and Cr is possibly due to redox conditions. Cobalt and Cr respond diverse relation in response to pH and Eh of the soil to uptake the metal (Fig. 4).

The rocks of Wadh area have good potential for Co mineralization along with Cr. The liaison is supported by the mutual plot (Fig. 8c), which exhibits two distinctive trends. Trend 1 shows nearly positive linear relation. The second trend exhibits inverse relation. It is recorded high in the 4, 7, 10, 12, 13, 15, and 19 localities (Fig. 6). It is important to note that BCF was high in comparison to Cr, Ni, and Cu (Fig. 3). Deposits of Co mineral are not yet discovered in Pakistan; however a collaborative programme along with Cr mining may put Co mineralization on the mineral map of Pakistan.

Copper

Biogeochemically, Cu is classified as micronutrients necessary for healthy plant growth. Concentration pattern of Cu in samples shows little fluctuations (Fig. 6). According to Rose et al. (1979) anomalous areas are those where concentrations of Cu is greater than 130 mg/kg. The twigs of *P. olivieri* have low Cu proportion (11 to 26 mg/kg), which

is much below the anomalous value. The relatively low concentration of Cu can be explained on the basis of host rocks, exclusion mechanism of the specie and redox behaviour of Cu. Massive Cu-sulphides are associated with pillow basalt, which is missing in the area. Additionally, the alkaline and serpentine derived soil has low sorption and fixation of Cu (Brooks, 1987). Copper is sensitive to redox environment because it can easily transform into $\text{Cu}^+/\text{Cu}^{2+}$ ions. The correlation between Cu and Eh is not encouraging (Fig. 4), because the alkaline soil restrict the ion exchange capacities of the soil (Duke and Williams, 2008). Al-Farraj and Al-Wabel (2007) also shows low bioavailability of Cu even in the mining area of Saudi Arabia.

CONCLUSIONS

A small shrub *Pteropryum olivieri*, of family Polygonacea has limited population over the thin cover of serpentine soil, mostly developed at the hill slope of ultramafic rocks of Wadh area. These rocks are mostly serpentinites derived from the alteration of harzburgite, pyroxenite and dunite. The average composition of soil of the study area displays more Ca (5.46%) and less Mg (2.43%). The average soil composition reflects low Cu and Co and high Ni and Cr.

P. olivieri of the study area shows $\text{BCF} < 1$ for different elements and exhibits $\text{Co} > \text{Cu} > \text{Ni} > \text{Cr}$, trend. The correlation matrix between elements, pH and Eh show that the Co has maximum influence of physicochemical condition. Nickel and Cu shows intermediate while the effect of pH and Eh was less on Cr. The concentration of Cr in the *P. olivieri* ranges from 42 to 124 mg/kg with an average of 76 mg/kg. All samples show high value as compared to the plant average of 6 mg/kg. The accumulation of Cr at hyper level is not achieved, even in the Cr-mineralized areas due to the fact that CrVI is reduced to CrIII, which is less available to plants due to high amount of TOC. The range of concentration of Ni in the ash of *P. olivieri* is noted between 29 to 273 mg/kg. Bioavailability of Ni in the soil of the study area is variable, possibly due to variation in bed rock composition and good exclusion mechanism of the plant. Relatively high concentration of Ni in Baran Lak, Pahar Khan and Ustam Butt areas reflects the presence of Ni-mineralization in the study area. The Co content of the *P. olivieri* varies between 5 to 39 mg/kg, and is suitable of mineralization. The plant has absorbed more Co from the soil, probably due to redox conditions which favours its accumulation. The high BCF of the species can be adopted as an alternative method of exploration of Co in the study area. The concentration level of Cu in the twigs of *P. olivieri* was much below than the anomalous value (11 to 26 mg/kg). The low abundance of Cu can be explained on the basis of reducing alkaline soil and strong exclusion mechanism of the plant.

Several deposits and showings of chromite and magnesite are known in the study area. The present study revealed other possible zones of Cr, Ni and Co mineralization in the Wadh area. These possible zones can be further evaluated with the aid of other exploration techniques such as geochemistry, geophysics and drilling.

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