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Trace Element Geochemistry of Groundwater of Winder, Balochistan, Pakistan and its Appraisal for Irrigation Water Quality

S. Naseem[1*], S. Hamza[2], E. Bashir[1], Tajnees Pirzada[3] and Mir Munsif Ali Talpur[3]

[1]Department of Geology, University of Karachi, Karachi 75270, Pakistan.
[2]Department of Geology, Federal Urdu University of Arts, Science and Technology, Karachi, Pakistan.
[3]Department of Chemistry, Shah Abdul Latif University Khairpur (Mir's) Sindh Pakistan.

Authors' contributions

This work was carried out in collaboration between all authors. Author SN designed the study and led the team in field work. Author SH prepared and analyzed the field samples. Author SN wrote draft of the manuscript. Author EB formatted and review the manuscript. Author TP helps in the analytical phase. Author MMAT managed the literature searches. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aims: The study is aimed to evaluate the concentration of trace elements and irrigation quality of the groundwater of Winder, Balochistan, Pakistan.
Study Design: The ophiolitic rocks of the study area upon weathering, contributed a large amount of certain trace elements to the groundwater. Samples of groundwater were collected and analyzed for trace elements.
Place and Duration of Study: The study area lays in the southern extremity of 450km long Bela Ophiolite, Balochistan, Pakistan. The work was carried out during 2011-2012.
Methodology: Sample collection and estimation of physical properties and chemical composition of water were carried out using standard procedures. The concentrations of trace elements were estimated by using Atomic Absorption Spectrophotometer.
Results: The trace elements concentration in the groundwater were found in the range of 8-800 for Zn, 14-107 for Cu, 13-103 for Cr, 32-1814 for Fe, 15-102 for Mn, 01-430 for Ni, 01-28 for Co, 16-139 for Pb and 1-30mg/kg for Cd.

**Corresponding author: E-mail: sngeo@yahoo.com;*

Conclusion: The present study revealed Fe>Ni>Zn>Pb>Cu>Cr>Mn>Cd>Co trend of abundance. Bivariate and ternary plots suggested alliance with the nearby exposed rocks. The statistical analysis of the trace elements data in form of correlation matrix and principal component analysis (PCA), further verify dissolution of trace elements from ophiolitic and sedimentary rocks.

The concentration of trace elements of the groundwater is discussed in relation to biological function in the plants and found within the safe range as compared to the permissible limit for irrigation purpose.

Keywords: Trace elements; irrigation water quality; geochemistry; Winder; Balochistan.

1. INTRODUCTION

Agriculture is the backbone of any country because it not only provides food stuff but also supplies raw material to industries and a main source of foreign exchange. The productivity of crops not only based on fertile soil, seed and fertilizers etc. but also on the quality of irrigation water. Major ions chemistry of groundwater is widely used for the assessment of irrigation water quality [1,2]. Little consideration has been paid on the trace elements on the quality of irrigation water, especially in Pakistan [3-5]. The toxic trace elements of groundwater are subsequently enriched in the edible parts of crops, which may be harmful for human beings, causing numerous medical problems [6]. Farming close to rock outcrops may provide certain trace elements in the supplied irrigation water [7]. In the vicinity of the study area, sedimentary rocks of Jurassic age (Ferozabad Group) and igneous rocks (Bela Ophiolite) of Cretaceous age are widely exposed. The dissolution of these rocks contributes a very discrete assemblage of ions in the soil [8,9]. The amount of trace elements in irrigation water may have dual characteristics. Some of these elements are essentially needed for the healthy growth of the crops. At higher concentration, these essentially required elements show toxicity. On the other hand some elements are hazardous even at very low concentration [10]. The trace element assemblage of irrigation water gradually enriches in the cultivating soils [11,12]. The trace elements are available to plants and continuous use of such water could result in accumulation of metals to such a concentration that may become phytotoxic and eventually hazardous to human health [13].

Winder River is the prominent river of the study area. It emerges from the hilly area of Pab and Mor ranges, flows through the narrow valley of Winder to the southern plain and finally enters into the Arabian Sea. These streams have low density and are dendritic in high relief areas and sub-parallel in the plain areas [14]. Small streams are ephemeral while, relatively large stream has restricted water flow throughout the year. A number of large tube-wells are present in the study area, used for irrigation purposes. The water bearing horizons are deep (>50m) and are confined at the contact of the sub-recent deposits with the overlying sand dunes. The aquifer is mainly composed of medium to coarse sand, pebbles and cobbles.

The objective of the current study is to describe the trace element geochemistry of the groundwater and its suitability for irrigation purposes. The role of igneous and sedimentary rocks in contributing different trace elements is discussed. The trace element content is related with irrigation water standards and the biological role of each element is included. Possibly, present study helps to understand impact of rocks on irrigation water quality, thus creating awareness in the farmers of the area for better irrigation planning and mitigating environmental problems.

2. GENERAL GEOLOGY

The study area lies in the southern part of Mor Range, comprises of Cretaceous ophiolite and Jurassic sedimentary rocks. The Bela Ophiolite is linked with Neotethyan Suprasubduction Zone (SSZ) ophiolites that developed along the periphery of the Mesozoic Gondwanaland, represents the remnants of an anomalous oceanic crust produced in a proto-forearc setting [15]. The Bela Ophiolite is originated from obduction of Neotethyan oceanic plate on the rifted western margin of Indian plate Mid Oceanic Ridge (MOR), obducted floor of a back-arc basin (SSZ) and an associated island arc originated in a large oceanic fracture zone [16,17].

The rocks of Bela Ophiolite in the study area is represented by tholeiitic pillow basalt, bisected by a number of mafic sills/dykes and km size ultramafic blocks [18]. The mafic rocks are consists of fine grained basalt, olivine basalt, amygdaloidal and vesicular porphyritic basalt. In majority of the rocks, groundmass is composed of mixture of pyroxenes and plagioclase feldspars [19]. The ultramafic suite is composed of olivine, clinopyroxene and orthopyroxenes in variable proportions and shows variable degree of serpentinization [20]. These rocks have small deposits and showings of Mn, Cr, Fe, Ni and Cu [21].

Sedimentary rocks of the Mor Range consists of Ferozabad Group and were deposited on the shelf flank of a rift system resulting from the breakup of Gondwanaland [22]. The Ferozabad Group is comprised of Kharrari, Malikhore and Anjira formations [23] in which Mississippi Valley-type stratabound replacement (MVT) and sedimentary exhalative mineralization (Sedex) are confined. Sulphide mineralization comprises sphalerite, galena, pyrite and marcasite with minor chalcopyrite [24].

3. MATERIALS AND METHODS

Representative 48 groundwater samples were collected from Winder area (Fig. 1 and Table 1). The physical properties and chemical composition of water were estimated using standard methods [25]. Total Dissolved Solids (TDS) and pH were determined at the time of collection of samples by means of Denver Instrument, Model 50. Trace elements of water were measured by AAnalyst 700, PerkinElmer.

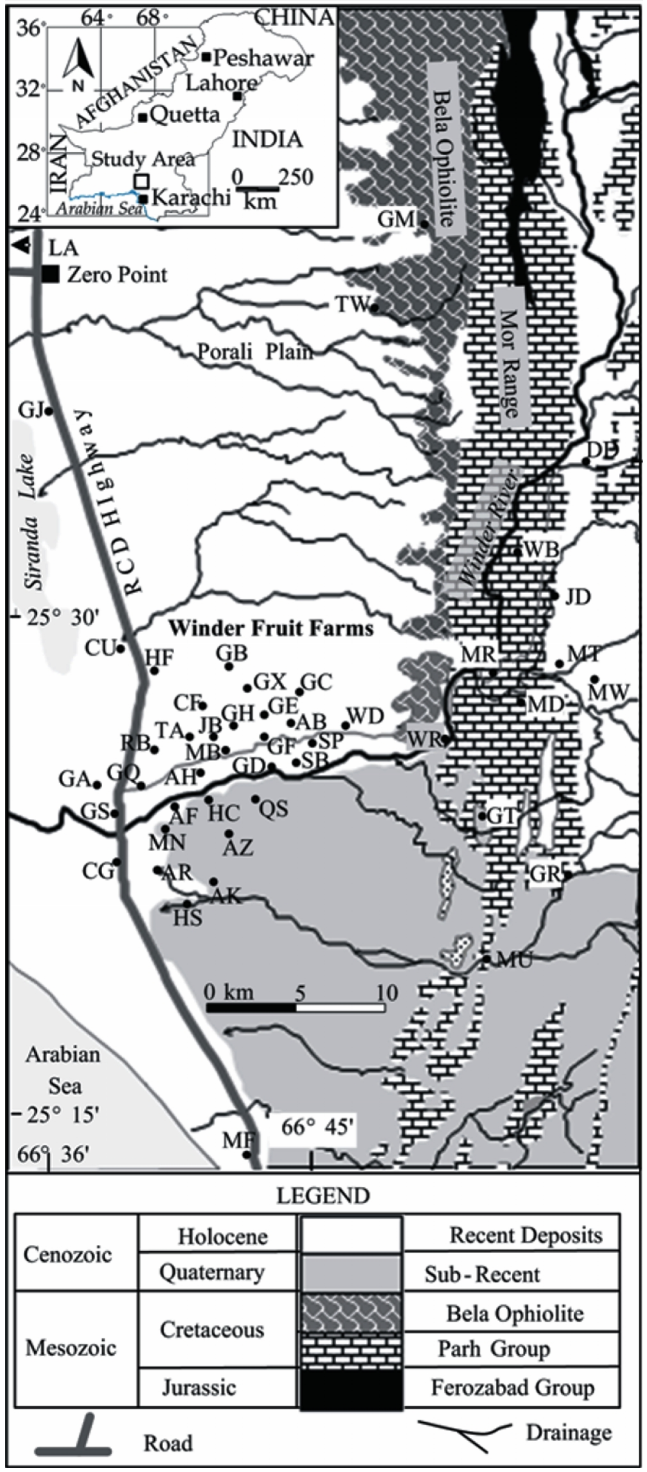

Fig. 1. Geological map of winder and adjoining areas of Balochistan, showing sampling sites

Table 1. Important trace elements composition of Winder area water samples (all are in µg/l)

Samples Sites	Zn (µg/l)	Cu	Cr	Fe	Mn	Ni	Co	Pb	Cd	pH	TDS (mg/l)
WD	19	15	22	764	64	32	9	58	2	7.64	1650
SP	15	14	13	147	16	34	10	59	11	7.73	2400
SB	11	38	14	126	16	47	4	57	2	7.06	1600
GH	25	31	14	181	17	35	4	57	6	7.71	1800
AF	100	61	49	1486	58	69	22	139	14	8.15	2230
HS	20	54	43	380	36	61	1	60	2	7.10	1000
AZ	15	47	34	346	30	60	9	99	9	7.19	3050
AK	11	46	29	161	21	57	17	108	17	7.14	4600
GS	13	44	26	302	55	54	3	67	5	7.18	1600
GA	15	45	25	239	20	52	1	61	3	6.92	900
HC	16	72	38	378	30	79	1	89	6	7.45	1000
AH	18	37	35	230	15	40	1	51	1	7.12	950
HF	38	79	82	1392	102	87	1	87	4	8.00	2790
GB	58	67	70	319	73	78	1	77	3	7.66	2000
GX	13	60	57	254	33	72	7	110	11	7.03	4120
GD	16	64	75	112	39	72	1	81	3	7.21	1180
QS	22	62	65	47	66	66	4	85	8	7.02	2230
GM	12	78	96	229	36	389	12	38	24	7.09	2400
MF	12	50	50	46	21	55	1	53	1	7.47	3200
CG	26	107	103	66	82	138	1	74	1	7.43	1800
AR	292	51	47	38	21	144	1	74	1	7.95	1200
GQ	14	47	45	32	22	151	5	74	1	6.71	3400
RB	800	60	59	43	38	59	2	59	1	7.65	1800
CU	8	48	48	1814	16	49	7	63	1	6.89	3800
GC	50	59	54	137	44	362	17	95	24	7.59	4800
AB	22	50	53	59	31	326	16	89	25	7.19	4000
GE	708	57	61	1108	54	364	16	87	16	6.82	5200
GF	11	50	57	1235	25	347	8	67	18	6.62	2900
WR	71	53	48	60	37	342	1	29	30	8.23	1000
MR	15	57	61	111	36	383	8	57	12	7.86	3600
MT	17	80	99	582	67	375	28	46	28	7.68	5400

Table 1 continues ….

DD	12	64	74	401	77	430	5	46	27	7.85	1900
WB	24	71	81	756	45	1	8	16	20	8.06	1250
CF	75	62	47	255	25	85	9	62	8	7.08	2650
TA	59	55	54	450	37	98	7	58	5	7.49	1500
JB	85	63	55	180	35	105	5	39	3	7.21	1925
MB	60	55	60	755	35	86	8	87	9	7.42	1150
MN	55	53	23	485	40	105	1	84	8	7.14	2025
MW	76	65	27	368	35	68	1	65	12	6.82	4030
GR	85	50	35	415	28	94	2	78	18	7.45	2040
GT	90	48	40	472	42	85	7	69	14	7.23	625
MU	75	65	45	510	22	74	4	36	10	7.47	1200
JD	105	75	41	462	32	96	2	95	15	7.81	2100
MD	91	45	50	450	34	88	2	97	18	7.36	1410
GJ	70	47	52	442	41	185	7	75	9	7.72	825
LA	68	40	75	95	75	305	13	70	4	7.94	1900
CS	65	52	88	432	65	358	18	75	8	7.75	2310
TW	80	55	94	387	72	405	12	67	4	8.18	1400
Min.	8	14	13	32	15	1	1	16	1	7.00	625
Max.	800	107	103	1814	102	430	28	139	30	8.00	5400
Av	76	55	52	411	41	149	7	70	10	7.00	2288
SD	151	16	23	401	21	131	6	23	8	0.41	1230
Median	26	54	50	332	36	86	5	68	8	7.00	1963

4. RESULTS AND DISCUSSION

4.1 Zinc

Zinc has fairly high mobility with an average of 20µg/l in the water [26]. The collected samples of the Winder have 8-800, with an average of 76µg/l, which is much higher than average in groundwater. The high concentration probably contributed through ophiolites and Sedex/MVT mineralization [24] in the area (Table 2). The wide range of concentration of Zn is due to proximity of source and good mobility. Zinc is an essential micronutrient, required for the healthy growth of the plants. Zinc helps in chlorophyll formation and promotes formation of acetic acid in the root to prevent decaying. It motivates plant growth and prevents mottling and other disorders in the leaves [27]. Approximately 20mg/kg requires in its shoots for healthy growth. Low quantity of Zn may cause chlorosis i.e. appearance of yellow young leaves and diminutive growth of the plant (Table 3). The maximum permissible limit for Zn is 2000µg/l for irrigation water [28]. The maximum Zn noted in the water of Winder area is 800µg, indicating safe conditions.

4.2 Copper

Copper is capable to form complexes in the +1 to +4 valence states. $Copper^{+3}$ and Cu^{+4} complexes are uncommon and unstable in water. Cu^{+1} (cuprous) ions are form under reducing conditions but are highly insoluble in water. Cupric (Cu^{+2}) is the main soluble complexes of copper in aquatic environments [29]. In river water its concentration is about 3µg/l. In the samples of study area its concentration varies between 14-107µg/l (Table 1). Small scale Cu-mineralization is found with the rocks of Bela Ophiolite, however contribution from Sedex/MVT is also possible to some extent (Table 2). The Cu and Cr are associated with the lower most segment of an ophiolite. The binary plots signify their relationship with ophiolitic rocks of the study area (Fig. 2A), which is also evidenced from good correlation matrix (Fig. 3) of Cu with Cr ($r = 0.681$) and Mn ($r = 0.422$). Multivariate statistical techniques (Principal Component Analysis) are widely used to evaluate rock-water relationship [30-31]. The rotated space diagram (PCA) illustrates close affiliation of Mn, Cu and Cr indicating that the source of Cu is ophiolite (Fig. 4).

Copper as a micronutrient is essentially required in small quantities (5-10mg/kg) for metabolic processes in plants [32]. Mainly it is retains in Cu- proteins (plastocyanin), which is involved in the photosynthetic electron transport in the thylakoid lumen of chloroplasts. However, Cu >100mg/kg in the soil is lethal for most common plants due to its ability in the Fenton reaction [33]. The WHO recommended maximum concentration is 200µg/l, and toxic to a number of plants at concentration >1000µg/l [34]. The average Cu content of study area is 55µg/l, indicating safe condition.

Table 2. Comparison of trace elements of groundwater of Winder with average abundance [[1]26] and recommended values for irrigation [[2]34]

Element	[1]Average groundwater (µg/l)	Present study (Av.) (µg/l)	[2]WHO recommended (µg/l)	Inferred genetic affiliations
Zn	20.0	76	2000	Mainly related with Sedex/MVT with some contribution from Bela Ophiolite.
Cu	3.0	55	200	Mainly related with Bela Ophiolite with some contribution from MVS.
Cr	1.0	52	100	Entirely derived from lower most segment (ultramafic tectonite) of Bela Ophiolite.
Fe	100.0	411	5000	Contributed equally from different segments of Bela Ophiolite and Sedex/MVT.
Mn	15.0	41	200	Mainly derived from the upper unit of Bela Ophiolite (pillow basalts).
Ni	1.5	149	200	Derived from lower most segment (ultramafic tectonite) of Bela Ophiolite.
Co	0.1	07	50	Partially derived from cumulate gabbro and ultramafic tectonite of Bela Ophiolite.
Pb	3.0	70	5000	Mainly related with Sedex/MVT with some contribution from Bela Ophiolite.
Cd	1.0	10	10	Derived from upper massive volcanic sulphides (MVS) of Bela Ophiolite.

Table 3. Deficiency and toxicity of trace elements on plants [27,35-36]

	Deficiency	Toxicity
Zn	Leaves display interveinal chlorosis or dusty brown spots, uneven plant growth, premature leaf fall and dicots shows drastic decrease in leaf size, loss of luster and shoots die off.	Leaves turning dark green, chlorosis, interveinal chlorosis and a reduction in root growth and leaf expansion.
Cu	Chlorosis or yellowing in younger leaves, stunted growth, delayed maturity.	Reduced growth, yellowing of the foliage, displaces Fe and other metals from important areas in the plant.
Cr	The function of Cr in the plant is not clear.	Reduced yield, effects on leaf and root growth, inhibition on enzymatic activities and mutagenesis.
Fe	Leaves turn white and eventually die (necrosis). chlorophyll production, Plant growth is slow, yellowing of the leaves and a general lack of vigour.	Excessive iron has reduced the uptake of manganese.
Mn	Yellowing of the leaves and a general lack of vigour, interveinal chlorosis in young leaves.	Blackish-brown or red spots on older leaves and an uneven distribution of chlorophyll, causing chlorosis and necrotic lesions on leaves.
Ni	Interveinal chlorosis in young leaves, poor seed germination.	Chlorosis and necrosis of leaves.
Co	Minor quantities of Co are required. No symptom is suspected due to Co deficiency.	Leaves exhibited brown spotting, mottling, curling and dark reddish-brown discolouration of veins.
Pb	Lead is injurious to plant.	Mimics Ca and inhibits many enzyme, stunted growth, chlorosis and blackening of root system.
Cd	*It is toxic; hence there is no question of deficiency.*	Chlorosis, leaf rolls and stunting. Cause P deficiency and reduce Mn transportation also reduce nitrate and its transport from roots to shoots.

4.3 Chromium

The average abundance of Cr in groundwater is approximately 1µg/l [26]. The water samples of Winder area contain Cr 13-103 (av. 52µg/l), which is much higher than average in water, but less than the maximum permissible limit of Cr in irrigation water (100µg/l).

The high content of Cr in the groundwater is the best reflection of ophiolitic rocks of the area because ultramafic rocks generally contain high (2980mg/kg) Cr [26]. The aqueous geochemistry of Cr is complex because it exists in two oxidation states, Cr^{+3} and Cr^{+6} and an oxyanion (CrO_4^{-2}). Chromium^{+3} are the predominant form in most water under reducing to moderately oxidizing conditions [37]. In aquatic systems Cr^{+6} is thermodynamically stable. Presence of oxygen with neutral-to-alkaline pH favors the persistence of Cr^{+6} and promotes its mobility [38]. Oxidation of Cr^{+3} to Cr^{+6} sorbed on mineral surfaces occurs in the presence of Mn oxides [39]. The assumption gets support from the correlation plots of Cr-Mn of the study area (Fig. 2B). Chromium shows good relationship (Fig. 3) with Cu (r = 0.681), Mn (r = 0.646) and Ni (r = 0.559).

Plants need Cr^{+3} in minor quantities and serve as a micronutrient. The Cr^{+3} is a non-hazardous species in contrast to Cr^{+6}, which shows toxic impact on plants [40]. The major part of the absorbed Cr is retained in the roots however it is relatively low in the leaves (5-30mg/kg). Organic matter reduces Cr^{+6} to Cr^{+3}, which is less bioavailable to plant, because Cr^{+3} become immobile at varying pH.

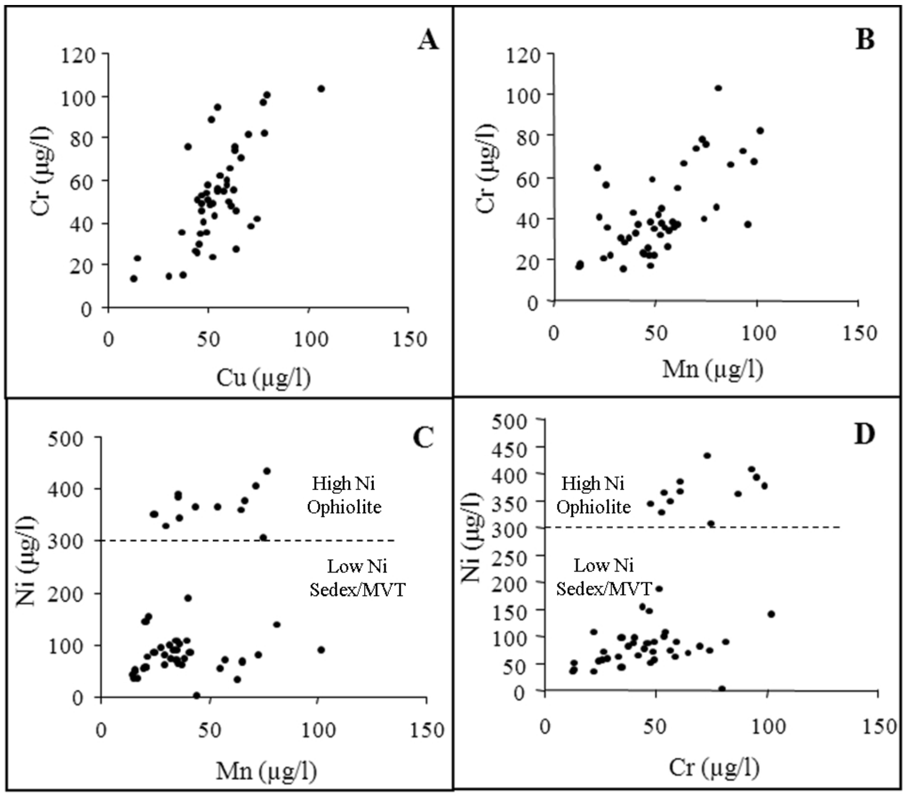

Fig. 2. Mutual relationships among important trace elements of Winder area

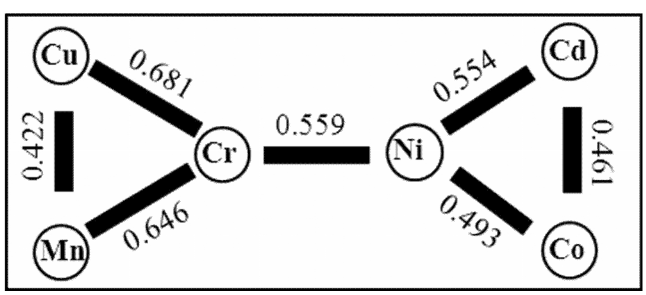

Fig. 3. Significant correlation matrix (*r* = > +0.4) of trace elements of groundwater of Winder area

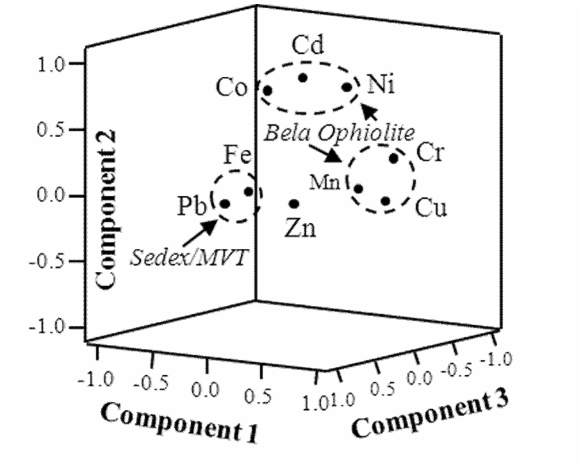

Fig. 4. Rotated space diagram (PCA) showing genetic affiliation of trace ions of the groundwater of the study area

4.4 Iron

The abundance of Fe in the groundwater is much influenced by the pH and Eh [26]. The concentration of Fe ranged from 32 to 1,840µg/l in the water samples of Winder area. The recommended maximum concentration of Fe for crop production is 5000µg/l and the present values are much below this level. Iron <100µg/l can cause blockages in micro-irrigation systems [41]. Water with high soluble Fe can discolour leaves and reduce the efficiency of transpiration and photosynthesis [42]. High content of Fe can precipitate the dissolved phosphate thus reducing the uptake of phosphorous in plants [43].

Iron is one of the major elements of Earth's crust and has variable geochemical characteristic. It is capable to concentrate in different segments of ophiolites and as well as sulphides in MVT or Sedex. The mutual relationship in form of ternary plots is valuable to infer genetic affiliation. The Fe-Cr-Cu plots are linear, indicating a common genetic source (Fig. 5A). The Fe-Cr-Mn plots are slightly wavy, reflecting diversified geochemical behaviour of Mn (Fig. 5B). All these elements are lithophile and have connection with Bela Ophiolite. In contrast, Zn and Pb are chalcophile but the linear trend is different.

4.5 Manganese

Manganese has been recorded in groundwater at concentrations between 15 and 102µg/l, less than the recommended 200µg/l for crop production. It is important to note that Mn mineralization is widespread in the vicinity of study area but also in the northern areas [44]. The process of spillitization of pillow basalt is responsible for accumulation of chrysocolla ($CuSiO_3.2H_2O$) and Mn minerals. The statistical analysis of Mn-Cr-Cu revealed genetic affiliation with ophiolite (Fig. 3 and Fig. 4).

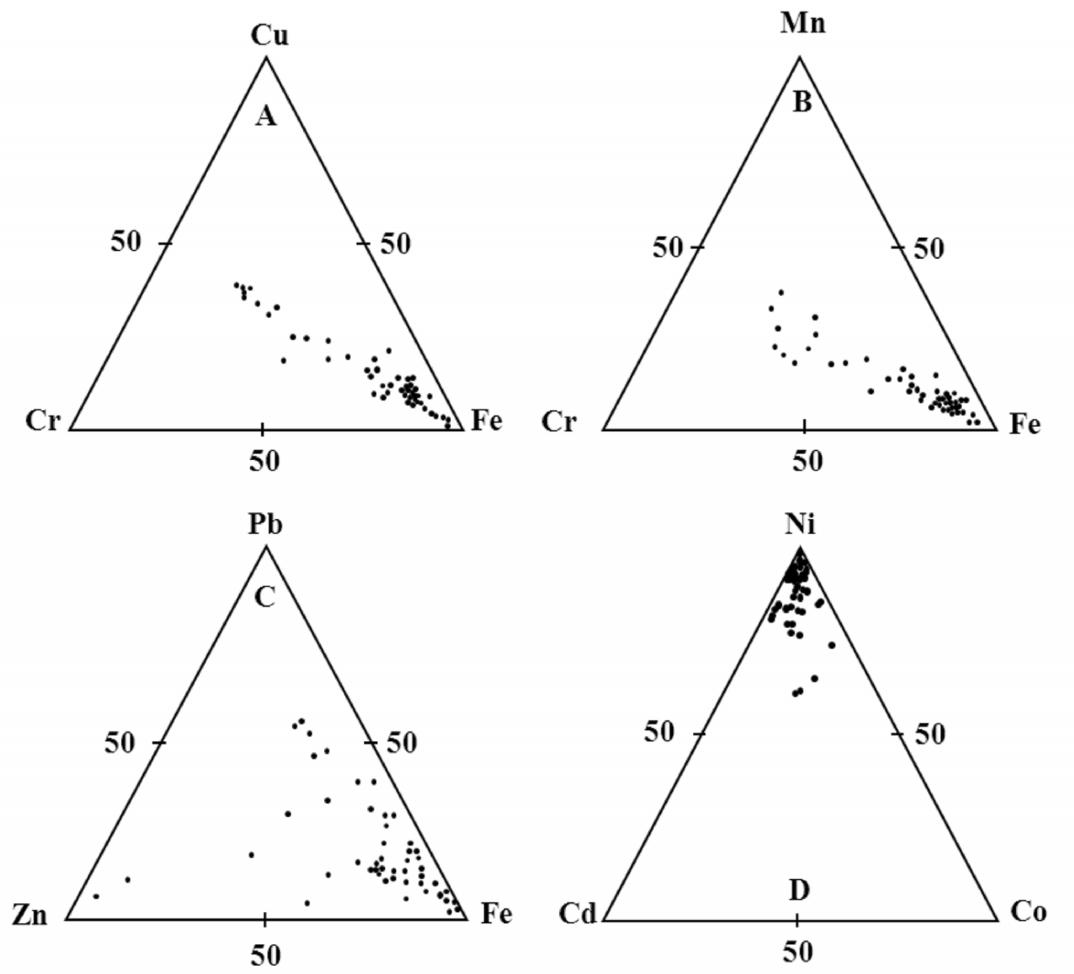

Fig. 5. Triangular variation diagrams of important trace elements of groundwater of study area

Manganese, like Fe, is not often deficient in soil but becomes insoluble under alkaline conditions. The deficiencies are more likely common in calcareous and alkaline soils [45]. The Mn concentration in the twigs of some of the selected wild and cultivated fruits is low as compared to average values in plants [46].

Manganese in plants is found at low levels and it is considered as essential micronutrients. The function of Mn in the plant is closely associated with the function of Fe, Cu and Zn as coenzymes. Manganese is needed for photosynthesis, respiration and nitrate assimilation [45]. It is involved in other cation-activated enzymes and photosynthetic oxygen evolution [47]. Manganese deficiency depresses oxygen production and phosphorylation. The deficiency of Mn leads to the accumulation of certain acids, such as citric acid, and is accompanied by a reduction in sugar and cellulose content of plants.

4.6 Nickel

The collected water samples of the Winder area show variability from 1-430μg/l (Table 1). It is in good agreement with the ophiolitic rocks of the area. Nickel is associated with podiform chromite and massive volcanic sulphides (MVS), in different segments of ophiolite [48]. The diverse character of Ni is best demonstrated on Ni vs. Cr and Mn plots, exhibiting two level of Ni concentration (Fig. 2C and Fig. 2D). All elevated values >300μg/l are confined in the closely collected samples GC to DD (Table 1). The high concentration probably reflects dominance of Ni in the area and subsequent enrichment in the groundwater of Winder River. The Ni values (<300μg/l) are probably related to Sedex/MVT mineralization or can be indicative of background concentration in the study area. The Co-Ni-Cd ternary plot (Fig. 5D) shows clustering at the corner of Ni, except few which relatively contains high Co and Cd.

The concentration level of Ni in the water samples of Winder area are high (av. 149μg/l) as compared to average abundance (1.5μg/l) in the water [26]. Majority of the samples are within the maximum allowed value (200μg/l) for irrigation purposes [34], however 12 samples have higher values. All samples possess very high Ni in the irrigation water (Table 1). Nickel is biogeochemically recommended as a very lethal element, which is harmful to the plants even at <1mg/kg concentration [49].

4.7 Cobalt

The abundance of Co in the groundwater is low (av. 7μg/l). Nearly 33% samples have concentration below 1μg/l, exceptionally it is high in samples AF and MT (Table 1). Genetically, Co is mainly derived from the dissolution of ophiolitic rocks of the study area. The correlation matrix of Co-Ni is 0.493 and Co-Cd is 0.461, indicating their mutual alliance with Bela Ophiolite (Fig. 3), which is also demonstrated from Principal Component Analysis (Fig. 4). The maximum recommended value of Co in irrigation water is 50μg/l. Biological function of Co is not very clearly understood but it is considered essential for the plants in minor quantities. Excess Co may hinder in the plant growth causing mottling, curling and brown spotting in the leaf area (Table 3). Jayakumar and Jaleel [50] showed negligible effect on Soybean (Glycine max) plants, experimentally grown on soil having Co <50mg/kg.

4.8 Lead

Lead is chalcophile element and enriched in sulphide deposits. The abundance of Pb in groundwater is 3μg/l and has low mobility [51]; in the Winder area Pb vary from 16-139 with a mean of 70μg/l (Table 1). In the study area, Pb is more closely associated with Fe (Fig. 5C). Probably, the Fe-Pb alliance is the reflection of sedimentary origin, which is also supported from rotated space diagram (Fig. 4).

The allowable limit in irrigation water is 5000μg/l, and the samples of the Winder area are much beyond the upper limit. The Pb is phytotoxic element and has no known biological functions in plants, but it may accumulate in some plant species known as hyperaccumulators for Pb [52]. However, in normal plants, excess Pb causes stunted growth, blackening of root system and chlorosis. High Pb interfere with Fe may cause upsets in minerals nutrition and water balance, which ultimately change hormonal status and affects membrane structure and permeability [53].

4.9 Cadmium

The abundance of Cd in the Earth's crust is about 100µg/l and commonly found in association of Zn and other sulphides as greenockite (CdS) and cadmium selenide (CdSe). Since there is no input suspected from anthropogenic sources in the area, it is mainly related with sulphide phase of Bela Ophiolite. During weathering Cd is releases into water which is generally soluble and mobile in water [54]. The pH has main control on its abundance in groundwater [55]. The range of Cd in the groundwater of Winder area is 1-30 with an average of 10µg/l, which is nearly same as the maximum allowable limit of Cd (10µg/l) in irrigation water but relatively elevated as compared to average groundwater (1µg/l). Cadmium is phytotoxic element; it can be absorb through root and can be store in the range of 5-30mg/kg in the leaves at sub-toxic level, but it can accumulate less in the edible parts of the plant [56]. It is important to note that high Cd is associated with Co and Ni (Fig. 4), reflecting contribution from lower sulphide segment of ophiolite.

5. CONCLUSION

Groundwater samples of Winder area are mainly used for irrigation purposes. The trace elements assemblage of groundwater revealed Fe>Ni>Zn>Pb>Cu>Cr>Mn>Cd>Co trend. The concentration of Zn, Cr, Ni and Cd found much higher than the permissible limit for irrigation purpose in some samples. Copper and Pb were within the safe range, while Fe, Mn and Co were less. The communal conduct of Cr, Mn and Cu signifies their common genetic affiliation with ophiolitic rocks which is also verified by Principal Component Analysis (PCA). On the other hand, Pb shows relationships with Fe, probably indicating alliance with carbonate rocks of Ferozabad Group. Nickel showed two separate populations, values >300 µg/l are related to ophiolite. The Ni values (<300µg/l) are probably related to Sedex/MVT mineralization or can be indicative of background concentration in the study area.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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