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Physico-chemical and Spectroscopic Elemental Analysis of Fresh Water in Villages near Chromium Mines of Khanozai, Balochistan Pakistan

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Abstract

The metal mining activities at northern areas of Province Balochistan like Khanozai and adjacent regions have been threatened the health of natural freshwater bodies. The present study predict the health risk related to the drinking water that are highly vulnerable to contamination and shows the physical parameters with heavy metal concentration in drinking water of the area that is closely situated to the chromite mining site. The investigated physical parameters are TDS, Total hardness, Turbidity, Alkalinity, pH, Conductivity, Color, Temperature, Taste and Odor. In chemical parameters, the concentration of Na, K and heavy metals like Pb, Cd, Zn, Cu, Ni, Co, Fe, Mn, and Cr were investigated. The obtained concentration results were compared with the standards of WHO and PNS. The determined values of heavy metals like Cr, Co, Ni, Cd and Pb in some samples were found exceeded from maximum concentration limit as shown by selected standards. Therefor the control and prevention methods of drinking water from contamination with heavy metals should be followed. The periodic monitoring of water resources in study area is recommended to save the public health in the affected area.

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Keywords: Heavy Metals, Atomic Absorption Spectroscopy, Flame Photometry

1. INTRODUCTION

The high-quality pure water has always been a basic need for maintenance of life on earth. It provides support to normal functioning of all biological activities. The quality preservation and protection of such natural mineral resource is a very important task for humans [1]. The fresh water is about 2.5% of all natural resources, out of which only 0.26% can be adapted for human economic use [2,3]. Only 20-30% of all fresh waters is provided by the groundwater [4,5]. The contaminated water has various damaging effects on a region or may extended throughout a country health. The diseases caused by drinking of contaminated water composes a huge burden on human health so the quality analysis of fresh water of a region has always been the first precedence to invalidate health problems [6]. If not monitored or regulated by any government institute, it causes serious concerns for the health of people [7].

The heavy metals contaminate the drinking water in those populated areas that are in vicinity of metal mines or industries. Although the metals like Cr, Mn and Cu exhibits beneficial properties for human health but their exceeded amount is toxic. Similarly, the metals like Pb, Hg, Cd and As shows very high toxic properties even at their lower concentrations with no beneficial importance for health of humans [8]. These metals get entered to water bodies by industrial and mining activities and sometimes by natural activities [9]. The contamination of drinking water in Pakistan with toxic metals have been reported in so many areas [10]. The toxicity and persistence of heavy metals gives them hazardous nature for health in contaminated region [11,12]. Pb, Cd and As are possibly more carcinogenic and causes diseases like nervous system, bladder, kidney, liver, cardiovascular and blood diseases [13].

The metal ore mines that are functional or abandoned, provides the main source for toxic and other rare earth elements to directly affect the each compartment of the environment so most of the waters in such areas are contaminated from moderate to high level with metals

like Pb, Co, Cd, As, Zn, Cr, Cu and U [14]. The flooding events causes ease to contamination of water bodies [15]. The untreated mine drainage also provides access for pollutants and contaminants to affect water resources [16]. The mining site in Victoria (Australia) have been contaminated the topsoil with Hg and Pb, that has determined as a risk for human health and aquatic life. With increased weather fluctuations, the contamination rate of toxic metals has mobilized with faster rate that poses environmental threat [17]. Due to no monitoring systems, this contamination is constantly happening [18].

The drinking of contaminated water with toxic metals cause adverse effects like, Pb accumulation causes neurocognitive problems, abnormal development, and intelligence problems [19]. Cd causes endocrine disruptions, and mutagenic activities. Zn contamination produces disease of respiratory system, also causes vomiting and nausea. Cr in higher concentration disturbs the sugar metabolism process [20]. Cu causes are kidney, brain damages and liver diseases. Ni contamination produces immune toxic and neuro toxic effects [21]. Excessive amount of Co produces severe hematologic, thyroid, cardiomyopathy and neurological abnormalities in humans. The exceeded amount of Fe causes changes in color, pH and taste of drinking water. Mn intake damages the nervous and cardiovascular systems.

Balochistan province has huge proved mineral resources like chromite, gypsum, coal, copper, lead, barite, gold, and others [22,23]. The chromite deposits are in Khanozai, Muslimbagh and Bela, it is the oxide ore of chromium with iron or sometimes with lead [(Fe, Mg or Al) Cr2O4]. The only source of chromium is chromite on commercial bases. The chromite deposits of Khanozai, Muslimbagh and Nasai are regarded the most extensive one in the country with total estimation of these reserves in millions of tonnes. Chromite mining in these regions has been started long ago. These deposits are being considered close to exhausting level. [24].

2. MATERIALS AND METHODS

2.1 Study area

Khanozai is the head quarter of Sub-Tehsil karezat of District Pishin at the distance of about 78Km North-East from provincial capital

Quetta (as shown in figure 1.1 and 1.2) with population of about more than 40,000 individuals according to 2017 census. Its location is at latitude 30.14 North and longitude 66.5 East.

Geochemical and petrological data shows that the alkalic impositions of the Khanozai and nearby regions have been enriched moderately with discordant compositions of trace elements as that of the basalts of ocean islands. The chromite deposits are associated with ophiolitic sequence in most cases. The observations explain that such intrusions take place due to the melting of subduction derived fluid with high amount of mainly lherzolite rocks (up to 5%) that are enriched and deep. Such processes occur by suffering of fractional crystallizations in the depth of about thirty (30) km in lithosphere. The constant variations have been found in trace elements such as Co, Ni, Cr and Sc with increasing Zr values most probably by olivine or chromite minerals accumulation which are not observable due to the alterations [25].

The underground water resources at north of Balochistan are on constant vanishing because of rapid increase in number of tube wells as the tariff of electricity has subsidized by the government and only groundwater source is available for utilization for the fruit farms. The rainfall in the study area and adjacent highlands is very low, the estimated annual rate of evaporation is higher than precipitation. The mining activities have been started in the study area on large scale in the beginning of 1st decade of present century with no precautionary measures to preserve the natural water bodies from contamination. The images of mining area are given in figure 1.3 and 1.4.

Fig. 1.1 Study area **Fig. 1.2 Chromite mines**

Figure 1.1 and 1.2 The study area and mines location

Fig. 1.3 Mining area

Fig. 1.4 Mined material

Figure 1.3 and 1.4 The Chromite mines of Khanozai

2.2 Sample collection and analysis

The samples were collected from tube wells, karezes and springs depending upon the availability of water from vulnerable sites which are situated in the close vicinity of mining area. Sample A was collected from tube well water of Zhadun village, sample B from spring in Sur-kach hill area, sample C from tube well water of Sur-kach village, sample D from karez water of Thora-khula village, sample E from tube well water of Zarghun village, sample F from stream of Khush-aab village, sample G and H were collected from water present inside two different mines, sample I from tube well water of Khanozai bazar, sample J from tube well water of Boys Degree College Khanozai, sample K from karez that is located close to mining area towards Thora-khula village and sample L was collected from standing flooded water, close to mining area. The samples were collected in bottles and transferred to the laboratory in coolers, so the temperature of the samples was maintained at 1-4C° [26]. The various parameters were investigated in laboratory like temperature, pH, salinity and conductivity by calibrated instruments and standard methods. Analysis of turbidity has determined via calibrated turbidimeter and total hardness was analyzed by complexometric titrations with EDTA. Total dissolved solids were analyzed by heating the sample at about 150-170C° in clean evaporating dish then the dried mass was weighed taking care to prevent any water hygroscopic activity by dried mass [27].

The estimation of Sodium and Potassium were carried out by the flame photometer. The toxic metals like Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb were investigated after digestion of water samples [28] with

conc. HNO3 by Atomic Absorption Spectrophotometer. The spectrophotometer was calibrated before analysis of samples.

3. RESULTS AND DISCUSSIONS

3.1 Analysis of physical parameters

The different investigated physicochemical parameters have been listed in table 1 along with their detected values of all 12 water samples. These detected values have been compared with the standard values of both national [29] and international standards [30]. The determined values of investigated properties in the water samples mainly depends on different factors like the amount of precipitation received and the depth from which the samples have collected. Lesser amount of precipitation causes lesser contamination as the less rainwater causes slower contamination and the water samples collected from deep resources are usually free from contamination due to the natural filtration of soil.

The temperature of samples was in the range of 24-26 C°, it usually remains same. The pH of samples G and H were found to be 8.7, much exceeded from standard value while turbidity, conductivity, TDS, total hardness and alkalinity values were found below the standard values.

Table 1: The physical parameters

S. No.	Standards and Samples	Color	Taste	Odor	Temp. (C°)	pH	Conductivity (µS/cm)	Turbidity (NTU)	Alkalinity (mg/L)	TDS (mg/L)	Total hardness (mg/L)
01	*PNS	≤15TCU	***	***	***	6.5-8.5	***	<5	***	<1000	<500
02	**WHO	≤15 TCU	***	***	***	6.5-8.5	250	<5	<200	<1000	<200
03	Sample A	_	_	_	25	7.4	0.7	1.4	174	262	62
04	Sample B	_	_	_	26	7.9	0.4	0.9	178	494	66
05	Sample C	_	_	_	26	7.6	0.6	0.8	172	694	65
06	Sample D	_	_	_	24	8.2	0.9	1.8	187	520	79
07	Sample E	_	_	_	26	8.1	0.7	1.5	184	372	74
08	Sample F	_	_	_	25	7.2	0.3	1.2	171	278	66
09	Sample G	_	_	_	24	8.7	0.6	0.8	198	329	81
10	Sample H	_	_	_	25	8.7	0.4	0.8	196	320	78
11	Sample I	_	_	_	25	7.8	0.2	1.2	171	410	76
12	Sample J	_	_	_	26	7.9	0.4	1.4	181	389	74
13	Sample K	_	_	_	25	7.8	0.8	0.9	175	492	76
14	Sample L	_	_	_	26	7.6	0.5	1.3	188	280	71

*Pakistan National Standards 2010 (For the quality of drinking water)

**World Health Organization 2008 (Geneva, Switzerland)

***Not available

_ Not observed

3.2 Analysis of Chemical parameters

The chemical analysis of sodium, potassium and trace metals were performed, and the results obtained from the collected water samples are listed in table 2. The sodium concentrations in all samples have been found in the safe limits, similar is the case with the calculated concentrations of potassium. The different concentration of metals is due to nature of chemical composition and geological processes. The chromium concentration was found to be exceeded in some samples than the shown standards. Manganese and iron seem to be in lesser amount than the contamination level. There was found high concentration of cobalt in samples G, J and L as compared to international and national standards. Nickle showed a varied concentration analysis, the highest concentration was found in sample B and L even higher than WHO value, no any value detected in samples D and E while in other samples its values were found in the safe range. The next investigated metal was copper whose determined concentration is also lower than the mentioned standards in all samples. The zinc has given maximum allowed contamination value of 5 by PNS and 3 by WHO. Its maximum detected value is 2.0180 mg/L in sample H and thus, it also showed to be in safe limits. The determined concentration of cadmium indicates that it has contaminated water in some sites as the samples G, H and L shows exceeded value of concentrations than standards. The lead showed maximum concentration of 0.0208 mg/L in sample G, while B, H, J and L samples have also higher concentration values than WHO values of maximum concentration. The graphical representation of heavy metals concentration in each sample have been given in Figure 2.1 to Figure 2.9.

Table 2: The chemical parameters

S. No	Standards and Samples mg/L	Na mg/L	K mg/L	Cr mg/L	Mn mg/L	Fe mg/L	Co mg/L	Ni mg/L	Cu mg/L	Zn mg/L	Cd mg/L	Pb mg/L
01	*PNS	***	***	≤0.05	≤0.5	***	***	≤0.02	2	5	0.01	≤0.05
02	**WHO	200	<50	0.05	0.5	0.5-50	0.001-0.01	0.02	2	3	0.003	0.01
03	Sample A	7.3	0.8	0.0457	0.1904	0.2295	0.0094	0.0133	0.0585	0.2134	0.0019	0.0054
04	Sample B	6.4	1.1	0.0721	0.1812	0.4428	0.0024	0.0231	0.0253	0.5964	0.0018	0.0139
05	Sample C	8.7	1.2	0.0340	0.2163	0.7128	0.0042	0.0175	0.0127	1.2237	0.0021	0.0074
06	Sample D	8.2	0.9	0.0339	0.1887	0.5209	0.0078	_	0.0353	0.8801	0.0020	0.0049
07	Sample E	7.9	0.7	0.0267	0.2151	0.2189	0.0124	_	0.0266	1.6139	0.0018	0.0058
08	Sample F	9.2	1.2	0.0121	0.2098	0.4242	0.0032	0.0123	0.0244	1.8965	0.0014	0.0068
09	Sample G	8.6	1.4	0.0715	0.2184	0.6692	0.0151	0.0117	0.0353	0.7853	0.0032	0.0208
10	Sample H	8.5	1.0	0.0780	0.1936	0.8118	0.0097	0.018	0.0351	2.0180	0.0037	0.0188

11	**Sample I**	7.3	0.8	0.0454	0.1842	0.1470	0.0041	0.0122	0.0377	1.4734	0.0019	0.0069
12	**Sample J**	8.9	1.2	0.0445	0.1968	0.3426	0.0142	0.0131	0.0384	0.4944	0.0028	0.0137
13	**Sample K**	8.1	0.7	0.0448	0.1900	0.4319	0.0026	0.0154	0.0495	0.3289	0.0027	0.0088
14	**Sample L**	7.4	0.9	0.0561	0.2014	0.3568	0.0181	0.04	0.0402	0.8606	0.0046	0.0126

*Pakistan National Standards 2010 (For the quality of drinking water)

**World Health Organization 2008 (Geneva, Switzerland)

***Not available

_ Below detection limit

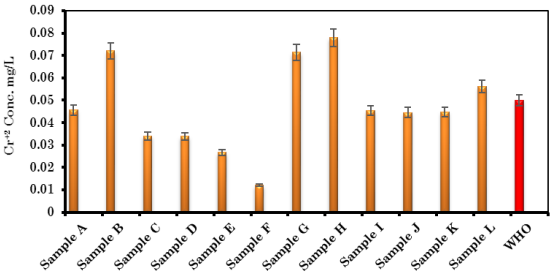

Fig. 2.1 Cr concentration

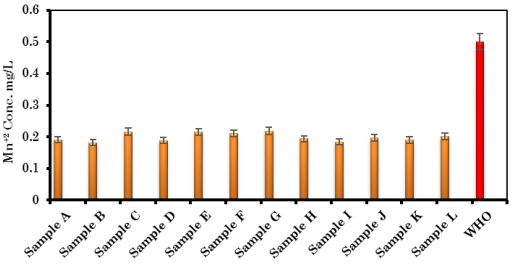

Fig 2.2 Mn concentration

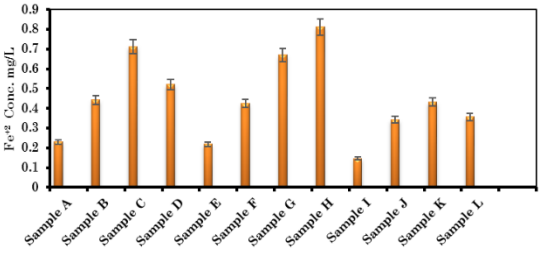

Fig 2.3 Fe concentration

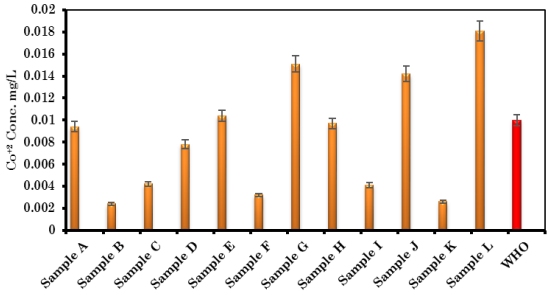

Fig 2.4 Co concentration

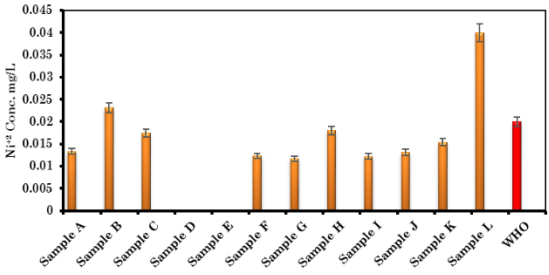

Fig 2.5 Ni concentration

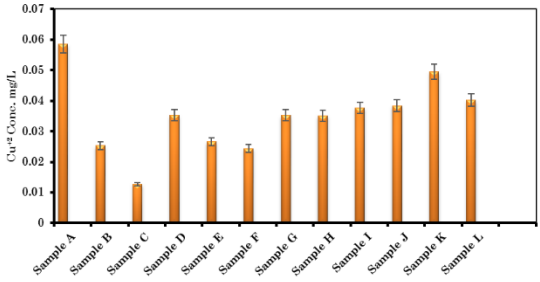

Fig. 2.6 Cu concentration

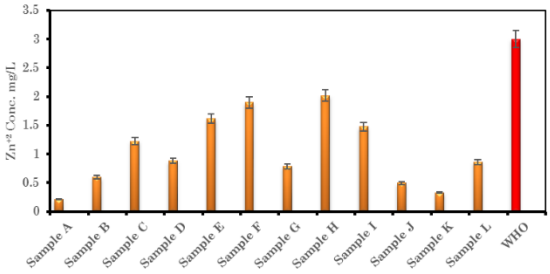

Fig. 2.7 Zn concentration

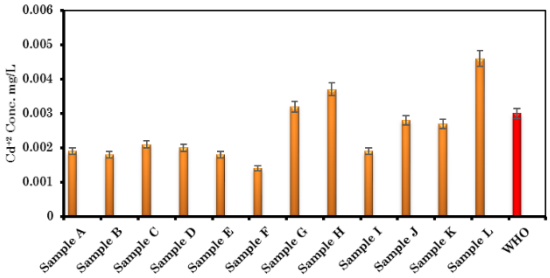

Fig. 2.8 Cd concentration

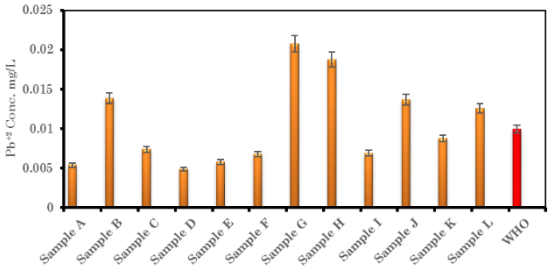

Fig. 2.9: Pb concentration

Fig. 2.1-2.9: The heavy metals concentration in water samples along with WHO standard values (metals for which standard value of maximum concentration was found). In figure 2.5, metal concentration in sample D and E was below detection limit.

4. CONCLUSION

This work links the community with their health concerns which is very important to overcome challenges related to a healthier environment.

It also helps to overcome the need to improve water quality as the obtained results may use to compare with those which will be studied in future research works. In physical parameters, pH values were found mostly alkaline. In determination of chemical parameters, the contamination of water with meals were observed in some samples. This higher concentration level of heavy metals can cause damaging effect on the human health as the contaminated water is on constant use by people. As the raining water in study area in summers flow towards west in the form of flood, so the heavy metals have found an easy access to water bodies of all villages that are situated along the mineral rich block. The composition of water is controlled by the interaction of mineral rocks and soil with running water. Therefor the mining activities for nearly two decades have been caused exceeded concentration of heavy metals from safe limit in freshwater bodies of the study area. The present study shows the higher level of Cd, Pb, Cr, Ni and Co from local and international standards in some samples. This determined data provides important information about the health of drinking water of the region. The accumulated toxic metals in the water bodies and their consequent reach into human body causes increased health risk in the region, so it is necessary to make the water bodies free of metals contamination by the legislation and implementation of strict control policy by the provincial and federal government to ensure safe and healthier future for the people of the region.

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