Environmental Geochemistry of Surface and Subsurface Water from Dera Ismail Khan Division, Khyber Pakhtunkhwa, Pakistan

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Summary: The Dera Ismail Khan division is situated in the southern most part of the Khyber-Pakhtunkhwa province in Pakistan. Majority of population in this region obtain domestic water from tube wells, dug wells, ponds, stored run off of the Indus and Gomal rivers and perennial streams. This study is aimed to determine the physio-chemical contaminants in the surface and subsurface water which could cause environmental problem. For this purpose, representative water sample were collected from tube wells, dug wells, streams and rivers. These analyses were performed using Hach DR/2000 spectrophotometer and graphite furnace atomic absorption spectrometer. Chemically both surface and subsurface water samples of the area were classified as alkaline fresh water. The comparison of the data with standard limits set by Word Health Organization (WHO) for drinking water suggested that in certain areas of the division, the drinking water samples have high concentrations of Total Dissolved Solids, NO_3^{2-}, SO_4^{2-}, F^-, Cl^-, Fe^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, Ni^{2+} and Cd^{2+} while pH, EC, HCO_3^-, PO_4^{3-}, Na^+, Mn^{2+}, K^+, Cr^{3+} and Zn^{2+} were within the permissible limits. These contaminations could be attributed to the geogenic sources which might be responsible for the health related problems in certain areas of the division.

Introduction

Water quality can be evaluated by physical, chemical and biological parameters. It can be highly affected by wide range of geogenic and anthropogenic sources which indicates a complex variation over different spatial and temporal scales [1-3]. All over the populated part of the earth, the quality of natural fresh water is being disturbed by human activities. This is mainly due to the discharge of the municipal and industrial waste into the rivers. However, the addition of soluble matters from the catchment areas and from fertilizer of crop fields also play a role in contaminating the rivers and hence cause pollution in underground aquifers [4]. The excess of anions, cations and heavy and trace metals in the water because of their toxicity, especially in drinking water, may cause serious environmental health problems such as raising blood pressure, chronic anemia, stomach ramps, nausea, skin irritation, methemoglobinemia and carinogenisis etc. [4-6]. Water pollution in Pakistan, like other underdeveloped countries, is a widespread environmental problem which needs to be properly monitored. The water quality of Dera Ismail (D. I) Khan division has, therefore, been investigated during present study.

The Dera Ismail (D.I.) Khan division is situated in the southern-most part of the Khyber-Pakhtunkhwa (KP) province between latitude 31° 15′ and 32° 30′ N and longitude 70° 00′ and 71° 25′ E (Fig. 1). It contains two main physiographic units, 1) the alluvial lowlands, which include the structurally undisturbed Indus plains, and 2) the folded belt, which includes the Khisor, Murwat, Bhittanni, and Sulaiman ranges. These ranges and highlands form a nearly continuous mountain system between Salt Range and Potwar Plateau extending to the Balochistan province in the southwest. The climate of the region is sub-arid to subtropical continental lowland type. The average annual precipitation ranges from 290 mm in the hills in the north to 200 mm in Ramak in the south. More than 80% population of the D.I. Khan division is living in rural areas. These people obtain their domestic water from dug-wells and shallow drilled wells equipped with hand-pumps, ponds, stored runoff, the Indus and Gomal rivers and perennial streams. The public Health Engineering Department (PHED) drilled tube-wells for the supply of drinking water in major towns. Indus River forms the eastern boundary of the D.I. Khan division while the Gomal River flows through most parts of the division. The total surface covered by vegetation rarely exceeds ten percent as compared to the whole land [7].

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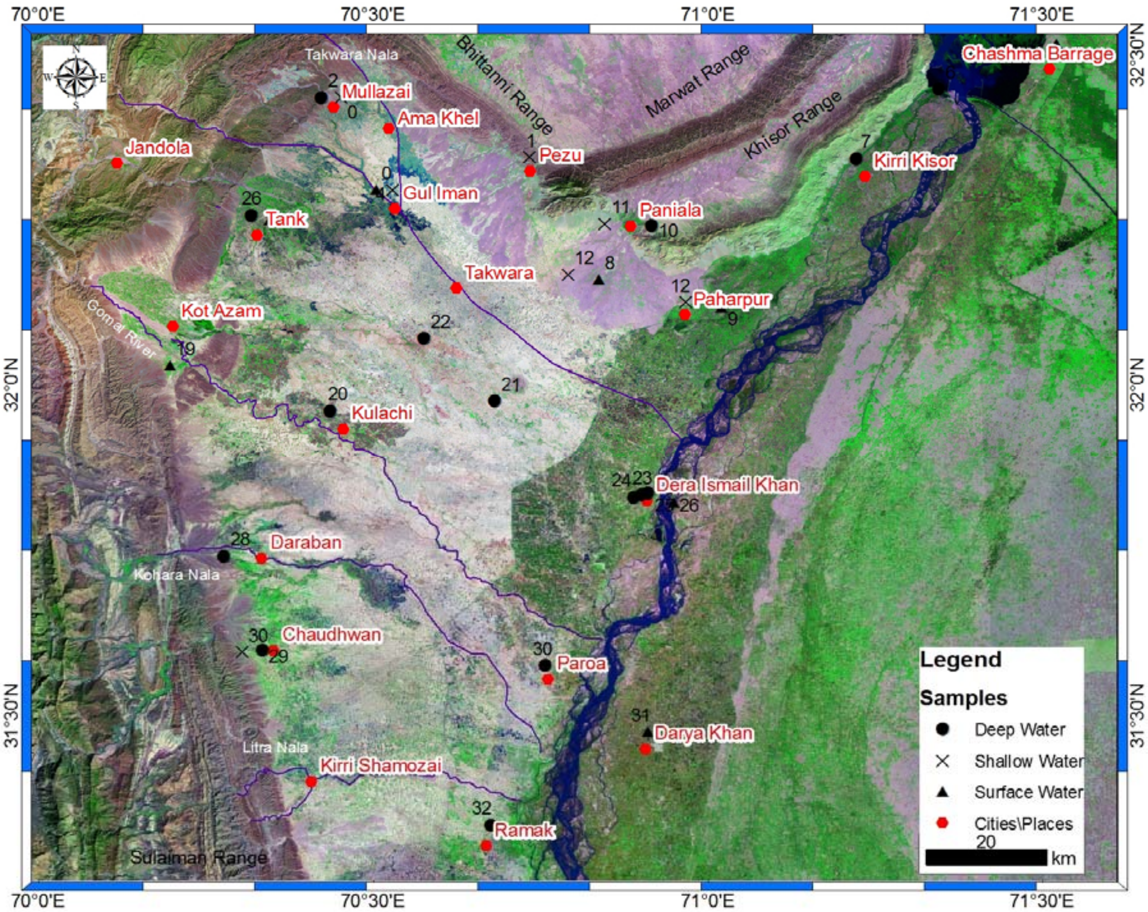

Fig. 1: Map of D. I. Khan division showing various localities and samples locations.

Several field surveys in this region revealed that numerous people complained about the increasing numbers of abdominal and skin diseases which are usually caused by the bacteriological and chemical contaminants in drinking water. The scarcity of drinking water in the region and the use of domestic water from different sources and the increasing trend of various diseases have made the basis for investigating the quality of water of the division. This study was, therefore, designed to determine the physio-chemical characteristics of surface and subsurface water in regard to their environmental impact in the area.

Results and Discussions

Average physio-chemical parameters of triplicate drinking water samples of both surface and subsurface water of the D.I. Khan division were statistically evaluated and the results are given in the Table-1. The surface water included samples collected from the streams and rivers while the subsurface water was divided into shallow water (<30 m) and deep water (>100 m). Deep water included water from tube wells and the shallow water included water from dug wells and springs.

The water samples were plotted in the Piper [8] diagram (Fig. 2). Majority of surface and subsurface water samples were plotted within the field of Na^+-K^+, Cl^--SO_4^{2-} type (normally called as alkaline earth fresh water) while some were plotted in the HCO_3^-, Ca^{2+}-Mg^{2+} type and Ca^{2+}-Mg^{2+}, HCO_3^- type (Fig. 2). This classification scheme suggests that the water from various sources in the D.I. Khan division is generally alkaline fresh water.

Physical Parameters

pH

pH in most of the samples was found less than 7.00, but in some samples collected from the northern part showed high pH. The highest pH value (9.07) was found in a dug well sample obtained from Gul Imam village while the lowest value (6.91) was found in the tube well sample of D.I. Khan colony. It was also observed that the pH in deep water was relatively lower than the surface and shallow water.

Table-1: Statistical summary of the water samples from D. I. Khan division.

Parameters		Surface water samples (N = 9) (Rivers and streams)				Shallow water samples (N = 7) (Dug wells and springs)				Deep water Samples (N = 17) (Tube wells)				WHO limits
	Unit	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	
T	°C	19.5	33.2	24.7	4.8	22.8	27.9	25.3	2.3	21.3	33.4	25.4	3.5	--
pH	--	7.8	8.5	8.1	0.3	7.5	9.1	8.0	0.6	6.9	8.2	7.6	0.3	6.5-8.5
EC	μS/cm	310	1130	612	344	460	1600	976	365	500	3000	1246	697	--
TDS	mg/L	217	791	429	241	322	1120	683	255	350	2100	885	489	<1000
HCO_3^-	mg/L	75.0	362.5	166.9	98.1	125.0	445.0	264.3	108.6	125.0	460.0	225.6	97.3	--
NO_3^-	mg/L	0.4	2.6	1.1	0.7	0.1	90.0	16.9	32.8	0.1	3.2	1.0	1.0	50
SO_4^{-2}	mg/L	15.0	400.0	135.6	146.5	55.0	425.0	201.4	149.9	50.0	1600.0	447.9	398.4	250
PO_4^{-2}	mg/L	0.04	0.19	0.11	0.06	0.08	0.29	0.13	0.07	0.02	0.60	0.09	0.14	--
Cl	mg/L	24.4	269.1	97.8	93.4	40.0	333.0	173.4	121.6	45.0	618.0	191.9	142.5	250
F	mg/L	0.1	0.7	0.4	0.2	0.9	4.6	2.2	1.3	0.1	1.8	0.7	0.5	1.5
Ca^{+2}	mg/L	22.5	51.7	34.5	9.6	6.4	68.1	39.6	20.9	7.7	85.5	53.0	22.3	--
Mg^{+2}	mg/L	11.8	47.0	19.6	13.0	9.0	49.2	30.5	15.5	0.5	89.3	38.9	27.0	--
Fe^{+2}	mg/L	0.3	43.3	9.9	15.2	0.6	5.8	2.2	2.0	0.1	12.7	2.5	3.2	0.3
Mn^{+2}	mg/L	0.05	0.80	0.16	0.28	0.01	0.11	0.05	0.04	0.02	0.51	0.14	0.13	0.50
Na^+	mg/L	15.2	179.5	62.2	62.3	27.1	214.0	110.0	75.0	21.9	402.5	116.2	94.8	200
K^+	mg/L	3.4	9.5	4.8	2.2	1.7	11.4	5.8	3.5	2.5	33.9	8.6	7.4	--
Cu	μg/L	7.0	1000.0	140.9	375.0	6.0	26.0	11.3	7.1	<0.05	287.0	42.4	70.2	2000
Pb	μg/L	<0.05	287.0	44.3	106.5	1.0	13.0	5.6	5.1	<0.05	30.0	3.3	7.9	10
Zn	μg/L	<0.05	20.0	9.0	7.9	10.0	370.0	117.1	129.3	<0.05	50.0	20.6	14.8	3000
Cr	μg/L	<0.05	19.0	4.5	6.9	<0.05	16.0	2.9	5.9	<0.05	6.0	1.4	1.9	50
Ni	μg/L	<0.05	60.0	10.7	23.4	<0.05	<0.05	0.1	<0.05	<0.05	51.0	3.9	12.4	20
Cd	μg/L	<0.05	16.0	2.4	6.0	<0.05	12.0	2.8	4.8	<0.05	2.0	0.2	0.5	3

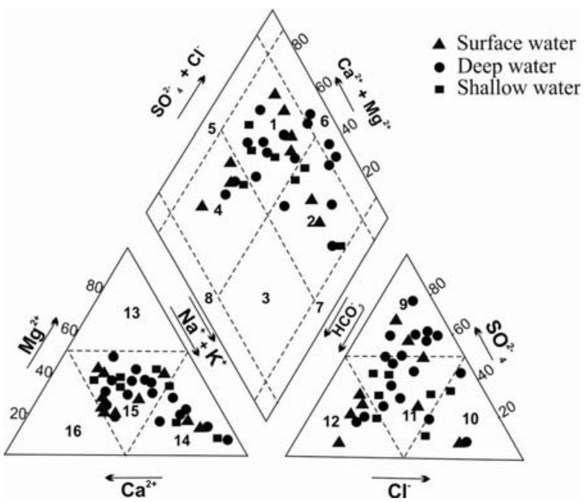

Fig. 2: Piper diagram [5] for the surface and subsurface water of the D. I. Khan division. Various fields are as: 1 = Na^+-K^+, Cl^--SO_4^{2-}; 2 = HCO_3^-, Ca^{2+}-Mg^{2+}; 3 = Cl^--SO_4^{2-}, Na^+-K^+; 4 = Ca^{2+}-Mg^{2+}, HCO_3^-; 5 = Ca^{2+}-Mg^{2+}; 6 = Cl^--SO_4^{2-}; 7 = Na^+-K^+; 8 = HCO_3^--CO_3; 9 = SO_4^{2-}; 10= Cl^-; 11 = No dominant ; HCO_3^-; 13 = Mg^{2+}; 14 = Na^+/K^+; 15 = No dominant; 16 = Ca^{2+}.

Electrical Conductivity (EC)

EC was found in the range of 310-1130 μS/cm, 460-1600 μS/cm and 500-3000 μS/cm in surface, shallow and deep water respectively (Table-1). The highest value (3000 μS/cm) of EC was found in the water sample collected from a tube well in Ramak area. However, EC in the surface water was generally low.

Total Dissolved Solid (TDS)

TDS was found in the range of 217-791 mg/L, 322-1120 mg/L and 350-2100 mg/L in surface, shallow and deep water samples respectively (Table 1). The deep water samples collected from tube wells at Tank, Hathala, Potah, Poroa and Ramak and shallow water sample collected from dug well at Mullazai exceeded the permissible limit (1000 mg/L) of WHO [9].

Anions

HCO_3^-

The concentrations of bicarbonate were in the range of 75.0-362.5 mg/L, 125.0-445.0 mg/L and 125.0-460.0 mg/L in surface, shallow and deep water samples respectively (Table-1). The highest concentration (460.0 mg/L) of HCO_3^- was found in the tube well water at Chudhwan and the lowest concentration (75.0 mg/L) was found in the water sample collected from Indus River at Darya Khan.

NO_3^-

The concentration of nitrate in D.I. Khan area ranged from 0.4 to 2.6 mg/L, 0.2 to 90 mg/L and <0.10 to 3.2 mg/L in surface, shallow and deep water samples respectively (Table-1). Almost all the samples of water of D. I. Khan area, accept one sample of spring in Chadhwan, were having NO_3^{2-} within the permissible limit (<50 mg/L) of WHO [9]. The spring water at Chadhwan was, therefore, found unsafe for health.

SO_4^-

The sulphate contents in D I. Khan area were found in the range of 15-400 mg/L, 55-425 mg/L and 50-1600 mg/L in surface, shallow and deep water samples respectively (Table-1). The SO_4^{2-} contents of majority of the waters samples of surface and shallow water and some of the deep water are within the permissible limit (<250 mg/L) of WHO [9]. However, the SO_4^{2-} contents of water samples collected from Gomal River (400 mg/L), stream at Tank Zam (300 mg/L), dug well at Mullazai (375 mg/L) and spring at Chadhwan (425 mg/L) and tube wells at Tank (450 mg/L), Umer Ada (450 mg/L), Kullachi (700 mg/L), Hathala (775 mg/L) Potah (900 mg/L), D.I. Khan colony (275 mg/L), Daraban (450 mg/L), Chadhwan (450 mg/L), Poroa (1600 mg/L) and Ramak (675 mg/L) exceeded the permissible limit (<250 mg/L) of WHO [9]. Therefore, the drinking water of these areas, especially from tube wells, was found unsafe for health.

PO_4^{3-}

Phosphate contents generally varied from 0.04 to 0.17 mg/L, 0.08 to 0.29 mg/L and 0.02 to 0.13 mg/L in surface, shallow and deep water samples respectively (Table-1). All the water samples of D. I. Khan were, however, found safe as far as the PO_4^{3-} concentration is concerned.

Cl^-

Chloride concentrations ranged from 26 to 269 mg/L, 40 to 333 mg/L and 45 to 618 mg/L in surface, shallow and deep water samples respectively (Table-1). Chloride contents in the deep water at Kullachi (293 mg/L), Hathala (333 mg/L), Potah (314 mg/L) and Ramak (618 mg/L), shallow water at Mullazai (333 mg/L) and Yarik (312 mg/L) and stream water at panyala (269 mg/L) exceeded the permissible limit (<250 mg/L) of WHO [9]. However, Cl^- contents in both Indus and Gomal rivers were found low (<159 mg/L).

F^-

Fluoride concentrations ranged from 0.12 to 0.67 mg/L, 0.89 to 4.57 mg/L and 0.10 to 1.79 mg/L (Table-1). Fluoride contents at many places exceeded the permissible limit (<1.5 mg/L) of WHO [9]. These included the samples collected from shallow water at Pezu (4.57 mg/L), Mullazai (2.54 mg/L), Gul Imam (1.79 mg/L) and Yarik (2.72 mg/L) and deep water at Mullazai (1.62), Panyala (1.52 mg/L) and Ramak (1.79 mg/L). Rest of the samples of shallow and deep water and almost all the surface water samples were having F^- contents below the permissible limit.

Major Cations

Ca^{2+}

Calcium contents ranged from 22.5 to 51.7 mg/L, 6.4 to 68.1 mg/L and 7.7 to 85.5 mg/L in surface, shallow and deep water samples respectively (Table-1). As WHO [9] did not define the permissible limit for Ca^{2+} in drinking water, therefore, comparison with the permissible limit was not made. However, relatively high amount (>80 mg/L) was found in the deep water samples collected at Potah, Daraban, Poroa and Ramak.

Mg^{2+}

Magnesium concentration ranged from 11.8 to 47.0 mg/L, 9.0 to 49.2 mg/L and 0.51 to 89.3mg/L in surface, shallow and deep water samples respectively (Table-1). It exceeded the permissible limit (<50 mg/L) of WHO [9] in the deep water samples at Hathala (60.7 mg/L), Potah (89.3 mg/L), Chadhwan (51.7 mg/L), Poroa (73.7 mg/L) and Ramak (72.3 mg/L). However, all the surface and shallow water samples showed Mg^{2+} concentration below the permissible limit.

Na^+

Sodium concentrations ranged from 15.2 to 179.5 mg/L, 43.7 to 188.5 mg/L and 30.3 to 402.5 mg/L in surface, shallow and deep water samples respectively (Table-1). Only one water sample, collected from Indus River at Chashma, exceeded the permissible limit (<200 mg/L) of WHO [9] while rest of the water samples were found below the permissible limit.

K^+

Potassium concentrations were found in the range of 3.44-9.5 mg/L, 1.65-7.4 mg/L and 2.45-33.9 mg/L in surface, shallow and deep water samples respectively (Table-1). Its concentration was generally found <12 mg/L in all types of deep, shallow and surface waters (Table-1). However, one sample collected from tube-well at Panyala showed relatively highest (33.9 mg/L) concentration of K^+.

Fe^{2+}

Iron ranged from 0.3 to 43.3 mg/L, 0.6 to 5.8 mg/L and 0.1 to 12.7 mg/L in surface, shallow and deep water samples respectively (Table-1). It was found lowest at Mullazai (0.1mg/L) and highest at Gomal river (12.7 mg/L). Iron exceeded the permissible limit (0.3 mg/L) of WHO [9] for drinking water in almost all the water samples.

Mn^{2+}

Manganese contents were found in the range of 0.05-0.80 mg/L, 0.01-0.11 mg/L and 0.02-0.51 mg/L in surface, shallow and deep water samples respectively (Table-1). In all the water samples Mn^{2+} concentration was found within the permissible limit (<0.5 mg/L) of WHO [9].

Heavy and Trace Metals

Cu^{2+}

Copper concentrations ranged from 7.0 to 1000.0 µg/L, 6.0 to 26.0 µg/L and <0.05 to 287.0 µg/L in surface, shallow and deep water samples respectively (Table-1). All the water samples were having Cu^{2+} within the permissible limits (<2000 µg/L) of WHO [9]. However, the Cu^{2+} concentration in the water sample of Gomal River was relatively high (1000 µg/L).

Pb^{2+}

Lead concentrations were found in the range of <0.05-287.0 µg/L, 1-13.0 µg/L and <0.05 to 16.0 µg/L in surface, shallow and deep water samples respectively (Table-1). It was noted that the Pb^{2+} concentration in most of the surface water and two of the deep water samples at Mullazai and Paharpur exceeded the permissible limit (<10 µg/L) of WHO [9]. However, the water sample from Indus River at Darya Khan showed alarming concentration (287.0 µg/L) of Pb^{2+}.

Zn^{2+}

Zinc concentrations were found in the range of <0.05-20.0 µg/L, 10.0 to 370.0 µg/L and <0.05 to 16.0 µg/L in surface, shallow and deep water samples respectively (Table-1). Zn^{2+} contents in all the water samples of D. I. Khan division were found within the permissible limit (<300 µg/L) of WHO [9].

Cr^{3+}

Chromium concentrations generally varied from <0.05 to 19.0 µg/L , <0.05 to 16.0 µg/L and <0.05 to 6.0 µg/L in surface, shallow and deep water samples respectively (Table-1). All the water samples showed Cr^{3+} within the permissible limit (<50 µg/L) of WHO [9]. Relatively high Cr^{3+} contents, but within the permissible limits, were noticed in the water samples collected from Gomal River and shallow water at Yarik.

Ni^{2+}

Nickel concentrations in most of the water samples of D.I. Khan were found below the detection limit (<0.05 µg/L) (Table 3.1). However, deep water at Hathala (51.0 µg/L), stream water at Pushapull (60.0 µg/L) and Indus river water at Cheshma (32.0 µg/L) were exceeded the permissible limit (<20 µg/L) of WHO [9].

Cd^{2+}

Cadmium concentrations were found in the range of <0.05-16.0 µg/L, <0.05-2.0 µg/L and <0.0-12.0 µg/L in surface, shallow and deep water samples respectively (Table 1). Cadmium in the deep water was found within the permissible limit (<3 µg/L) of WHO [9]. It exceeded the permissible limit in shallow water at Pezu (12.0 µg/L) and spring water at Chadhwan (7.0 µg/L) and in the water of Indus River at Chashma (16.0 µg/L).

The average contents of the selected anions, cations and heavy and trace metals in surface and sub-surface (shallow and deep) water were compared with the permissible limits of WHO [9] in Fig. 3. It was found that SO_4^{2-} in deep water and F^- in shallow water exceeded the permissible limit of WHO [9] while the SO_4^{2-} and Cl^- showed relatively high concentration in deep water. The NO_3^{2-} and F^-, however, showed relatively high concentration in shallow water (Fig. 3). Among the cations, the average Fe showed many fold high amount in all types of water samples. The Mn^{2+} and Na^+ showed low concentration as compared the permissible limit of WHO [9]. The average concentration of Pb^{2+} exceeded the permissible limit of WHO [9] while rest of the heavy and trace metals showed lower amount as compared to the WHO limits. Cu^{2+}, Pb^{2+}, Cr^{3+} and Ni^{2+} showed relatively high concentration in surface water while Zn^{2+} and Cd^{2+} showed relatively high concentration in shallow water (Fig. 3).

The statistical correlation among the physio-chemical parameters was performed by the statistical software (SPSS) and the results are given in Table-2. No significant correlation among most of the parameters was observed in the water of D.I. Khan division. However, some of the parameters having correlation coefficients with $p<0.05$ were: pH-EC (r = 0.997), pH-SO_4^{2-} (r = 0.748), pH-Cl^- (r = 0.886), pH-Ca^{2+} (r = 0.711), pH-Mg^{2+} (r = 0.784), pH-Na^+ (0.859), EC-SO_4^{2+} (r = 0.742), EC-Cl^- (r = 0.878), EC-Ca^{2+} (0.707), EC-Mg^{2+} (r = 0.791), EC-Na^+ (r = 0.853), SO_4^{2+}-Cl^- (r = 0.516), Ca^{2+}-SO_4^{2-} (r = 0.690), Mg^{2+}-SO_4^{2-} (r = 717), Na^+-SO_4^{2-} (r = 0.474), Na^+-Cl^- (r = 0.937), Ca^{2+}-Mg^{2+} (0.744), Mg^{2+}-Na^+ (r = 0.609), Fe^{2+}-Cu^{2+} (r = 0.926), Fe^{2+}-Cr^{3+} (r = 0.782) and Cu^{2+}-Cr^{3+} (r = 0.795). These correlations suggested that the heavy and trace metals behaved independently of physical parameters, anions and major cations in the water of D.I. Khan division while some of the major cations, anions and physical parameters were found interrelated. This could be due to the common source (i.e., halite and gypsum etc.) or similar geochemical behavior.

In the D.I. Khan division, the population is generally restricted to the main towns such as D.I. Khan and Tank and their premises. In most areas of these towns, the inhabitants are using tube well water for drinking and domestic purposes. In other areas of the D.I. Khan division the population is extremely scattered and is living in small densities in villages where the tube wells water has been provided to very limited areas. Most of the population living in these villages is generally using the water of Indus and Gomal rivers and their tributaries, streams, ponds and dug wells for drinking and domestic purposes. During this study water from all sorts of sources and places was studied qualitatively. It was found that the water of D.I. Khan division in certain areas may have health risk, as the concentrations of some of the chemical constituents are high. These areas are Tank, Hathala, Potah, Poroa and Ramak, Pezu, Tank Zam, Mullazai, Chadhwan, Umer Ada, Kullachi, D.I. Khan colony, Daraban and Chadhwan. It was noticed that among the various parameters such as TDS, NO_3^{2-}, SO_4^{2-}, F^-, Cl^-, Fe^{2+}, Pb^{2+}, Ni^{2+} and Cd^{2+}, not all but one or more parameters, were found exceeding the permissible limit of WHO [9] in the water samples of these areas. However, SO_4^{2-} and Fe^{2+} were found above the permissible limit in the water samples of many areas. Fluoride in few samples of shallow and deep water exceeded the permissible limit while the surface water has normal concentration of fluoride. Pb^{2+} and Ni^{2+} were found above the permissible limit in few samples of the surface water, however, very high concentration (287 μg/L) in the water of Indus River at Darya Khan and Ni^{2+} concentration (60 μg/L) in Pusha Pull was observed. These anomalies could be localized and need to be further investigated. The various types of diseases related with the toxicity of these elevated anions and heavy and trace metals may have drastic health effects on the inhabitants of the area if used for longer duration of time. Absence of major industries in the region support that the sources of contamination in the water of D.I. Khan may be geogenic and not the anthropogenic, however, this could be a localized phenomenon.

Table-2: Linear correlation matrix for physic-chemical parameters in the water of D. I. Khan Division (N = 33)

	pH	EC	TDS	HCO3	NO3	SO4	PO4	Cl	Ca	Mg	Na	K	Fe	Mn	Cu	Pb	Zn	Cr	Ni	Cd
pH	1	.997	*-.352*	0.246	-0.028	.748	-0.156	.886	.711	.784	.859	0.092	0.036	0.142	0.045	-0.269	0.013	-0.01	-0.076	-0.306
EC		1	*-.380*	0.266	-0.032	.742	-0.168	.878	.707	.791	.853	0.103	0.028	0.137	0.039	-0.272	0.011	-0.019	-0.081	-0.308
TDS			1	-0.282	0.011	*-.369*	0.13	-0.049	-.634	-.453	-0.053	-0.061	.339	0.06	0.318	0.132	-0.092	*.391*	0.063	0.26
HCO3				1	*.421*	0.26	-0.048	0.088	0.331	*.432*	0.11	-0.129	-0.081	-0.259	0.001	-0.31	0.261	-0.094	-0.24	-0.053
NO3					1	0.051	0.024	-0.077	0.05	0.059	-0.055	-0.131	-0.04	-0.111	-0.069	-0.054	0.085	-0.072	-0.075	0.253
SO4						1	-0.261	.516	.690	.717	.474	0.027	0.017	0.018	0.054	-0.189	-0.098	-0.1	-0.016	-0.202
PO4							1	0.004	-0.231	-0.143	0.045	-0.028	-0.09	-0.079	-0.055	0.126	0.245	-0.111	-0.02	-0.104
Cl								1	*.339*	.508	.937	0.13	-0.033	0.19	-0.004	-0.224	0.005	0.036	-0.075	-0.326
Ca									1	.744	*.386*	-0.057	0.122	0.073	0.077	-0.26	0.121	-0.103	-0.088	-0.158
Mg										1	.609	0.048	0.116	-0.183	0.162	-0.219	0.015	0.021	-0.024	-0.173
Na											1	0.179	0.001	0.044	0.009	-0.21	0.026	0.053	-0.056	-0.292
K												1	-0.103	-0.136	-0.065	-0.09	-0.009	-0.106	-0.038	-0.116
Fe													1	0.261	.926	-0.078	-0.186	.782	0.102	0.061
Mn														1	0.157	-0.079	-0.198	0.232	-0.136	-0.183
Cu															1	-0.041	-0.135	.795	0.005	0.013
Pb																1	-0.049	-0.021	-0.018	0.117
Zn																	1	-0.189	-0.104	-0.04
Cr																		1	0.01	-0.005
Ni																			1	0.188
Cd																				1

Bold correlation is significant at the 0.05 level (2-tailed)
Italic correlation is significant at the 0.01 level (2-tailed)

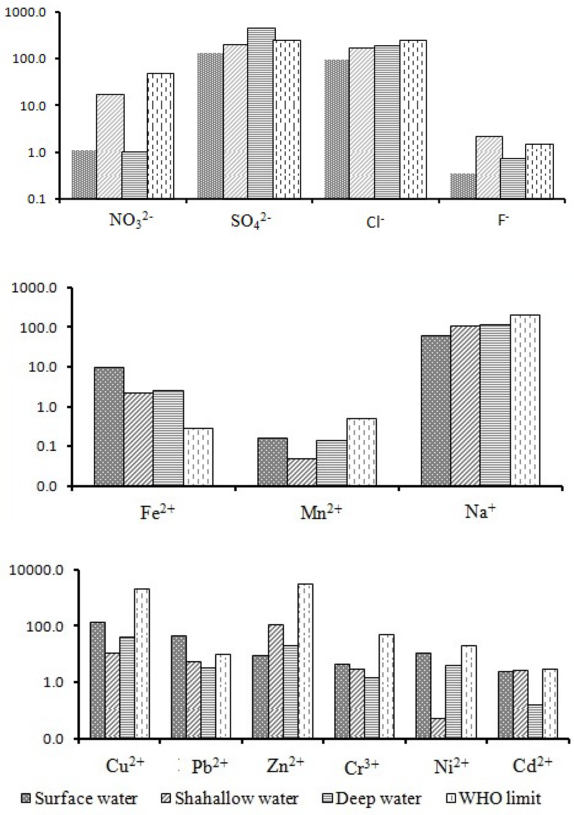

Fig. 3: Comparison of the average contents of selected chemical parameters of surface and subsurface water and WHO limit.

Experimental

Samples Collection and Preparation

Two sets of triplicate drinking water samples were collected from different sources such as tube wells, dug wells, springs, streams and rivers in preconditioned polyethylene bottles in the densely populated areas of D.I. Khan division (Fig. 1). Precautionary measures were taken to avoid any possible contamination during sampling. The newly purchased unused polyethylene bottles were cleaned with the ultrapure distilled water collected from the Elga Purelab water purification plant. During collection of each water sample, the bottle was again washed with the same water and every possible care was taken to avoid contamination during collection and transportation of the sample. One set of samples was collected in 500 ml bottles and were filtered through 0.45 μm filter paper. The filtrates were immediately acidified with 0.1 N HNO_3 [10] and stored at 4 °C until major cation and heavy and trace metals analysis in the Geochemistry laboratory of the NCE in Geology, University of Peshawar, Pakistan. Another set of samples was collected in 500 ml bottles and analyzed on spot for temperature (T), pH, electrical conductivity (EC) and anions such as chloride (Cl^-) sulfates (SO_4^{2-}), nitrates (NO_3^{2-}) and phosphates (PO_4^{3-}) by using various instruments.

Instrumentation and Chemical Analysis

Temperature were determined by thermometer and pH and EC by Hach pH and conductivity meter. pH meter was calibrated with the known buffer solutions and the EC was calibrated with the 0.01M KCl. SO_4^{2-}, NO_3^{2-}, Cl^- and PO_4^{3-} were determined on Hach DR/2000 spectrophotometer by using the Hach reagents powder pillows of SulfaVer 4, NitraVer 5, Mercuric thiocynide and PhosVer 3 respectively as recommended by the American Public Health Association (APHA) [11]. Fluoride was determined by SPANDS method as recommended by APHA [11]. In this method the water was first passed through the Hach distillation apparatus and then run on Hach DR/2000 spectrophotometer by using the Hach SPANDS reagent solution. Major cations (i.e., Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, Mn^{2+}) were measured by flame while heavy and trace metals (i.e., Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Ni^{2+}, Cd^{2+}) by the graphite-furnace atomic absorption spectrometer (Perkin Elmer 3300, HGA600) under the standard instrumental conditions recommended by the manufacturer and with background correction. Hollow cathode lamps were used for respective elements. Air-acetylene was used as fuel for flame atomic absorption spectrometer (FAAS) while graphite tube with platform was used in the graphite furnace atomic absorption spectrometer GF-AAS. Certified stock standard solutions purchased from Perkin Elmer PVT (Ltd) were used for calibration purpose. Calibration curves from the working standards of 0.2, 0.5, 1.0, 2.0, 5.0 and 10 mg/L of Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, Mn^{2+} and 0.05, 0.1, 0.2, 0.5 and 1.00 mg/L of Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Ni^{2+}, Cd^{2+} were prepared. The detection limits of various elements are Ca: 1.5 μg/L , Mg: 0.15 μg/L, Na: 0.3 μg/L, K: 3.0 μg/L, Fe: 5 μg/L, Mn: 1.5 μg/L, Cu: 0.014 μg/L , Pb: 0.05 μg/L, Zn: 0.02 μg/L, Cr: 0.004 μg/L, Ni: 0.07 μg/L, Cd: 0.002 μg/L. The accuracy of the method was determined by running the triplicate samples, collected during field, having standard deviation of $<0.1\%$ and also by preparing the acid mixture blanks and by spiking the samples with known concentrations of all cations determined with mean recoveries of 90.5±1.2%.

All the reagents, chemicals and acids used were of analytical grade (Merck, Germany). All the glassware used were thoroughly washed in ultrasonic bath and cleaned with the ultrapure distilled water and kept for 3 hours in an oven at 110 ºC prior to use.

Conclusions

The water samples from the surface water (i.e., rivers and streams) and subsurface water (i.e., tube wells, dug wells and springs) used for drinking and domestic purposes by majority of the inhabitants of D.I. Khan, were analyzed for the physio-chemical parameters. The surface water is relatively rich in both major cations and heavy and trace metals while shallow water is rich in anions. Deep water showed relatively lesser contents of analyzed contaminants. It was found that the concentrations of TDS, NO_3^{2-}, SO_4^{2-}, F^-, Cl^-, Fe^{2+}, Pb^{2+}, Ni^{2+} and Cd^{2+} in certain areas of the D.I. Khan division were reaching to toxicity level and may cause health related problems. The source of this contamination could be geogenic rather than anthropogenic [12-14].

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