Physicochemical Study of Drinking Water from Dir Districts

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Summary: This paper presents a comprehensive picture of the quality of water of 51 different localities of upper Dir and lower Dir districts, NWFP, Pakistan. Samples of springs, wells, streams and rivers water were collected and investigated for both physical and chemical parameters like pH, conductance, total solids, total dissolved solids, total hardness, total alkalinity, chloride, sulphate, nitrate, iodide, fluoride, calcium, magnesium, sodium, potassium, zinc, iron and copper for quality assessment. The levels of these parameters were compared with the permissible levels recommended by international agencies. Most of the parameters were observed to be within the permissible limits but some have exceeded. The water of springs at Dir high school No. 1 and at road side near Muhansharif were found non-potable because of high level of total solids than that recommended by World Health Organization (WHO). The total hardness of water of well on road side at village Rani, of spring at road side near Muhansharif, of spring at front of high school No. 1 at Dir and of well at Khal bazaar was high than that permitted by American Public Health Association (APHA). The level of sulphat of Nehagdara stream at Wari bridge and of spring at Muhansharif, and the level of calcium of water of well at Khal bazaar exceed the limits recommended by the WHO. All the water samples were deficient in zinc, fluoride and iodide. The importance and implications of the levels of all the parameters investigated have been elaborated.

Introduction

Dir region has been bifurcated in 1969 into two districts namely lower Dir and upper Dir. The topography of the district is dominated by the mountains and hills, which are part of the ranges/branches of Hindukush and Hinduraj. The mountain ranges run from north to south and from northeast to southwest along the northern border with Chitral district. The important river is Punjkora, which enter the district from northeast and flows southwest along the boundary with Bajaur agency up to its confluence with Swat river. Its western bank is joined by two major streams (nallas or khawars) namely Kunai and Shanelai (Jandool) flowing from northwest. It is joined by the Asegai khawar, from the southeast. Finally, the Punjkora river joins the Swat river. The Swat river flows along the southern boundary of the district and is also joined by some streams flowing down from the southern and western slopes. The noteworthy is the Shewa khawar. The sources of drinking water in Dir districts are pipelines (nul), hand pumps, wells, streams and rivers. According to the 1998 census report, both rural and urban areas have 10.63% wells, 2.45% ponds, 32.67% pipes (nul), 0.1 % hand pumps and 28.10 % other sources like streams and rivers [1]. Gravity and artesian springs, deep and shallow wells and infiltration galleries under sandy riverbeds with a good depth of sand called zone of saturation, are common sources of ground water. It is generally pure when drawn from greater depths and possesses variable properties. The level to which water rises in free communication with soil voids is termed as water table. The water table remains constant so long as the withdrawn and recharge of the system is maintained in equilibrium. The water bearing strata, capable of yielding sufficiently large quantity of water for community is termed as aquifer. This aquifer is a big source of springs and is mostly used for drinking purpose, called potable water, which must be clear, odorless, neither too hard nor too soft and be free from microorganisms. While the non-potable water is mostly used in boilers, industries and other domestic activities.

Dir districts are hilly areas and the mineral contents of water may be enhanced when it passes through rocks. There is no any strict control on deforestation and hence the soil erosion is a big problem, which may render the water non-potable especially that of streams and rivers. Further the diffuse source pollution arises from a broad group of human activities, for which the pollutants have no

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obvious point of entry into receiving watercourses. In contrast, point source pollution represents those activities where wastewater is routed directly into receiving water bodies for example, discharge pipes. Non-point source pollutants, irrespective of source, are transported overland and through the soil by rainwater and melting snow. These pollutants ultimately find their way into groundwater, wetlands, rivers and lakes and finally to oceans in the form of sediment and chemical loads carried by rivers. Polluted water is a major cause of human diseases, misery and death. According to the World Health Organization (WHO) about 4 million children die every year as a result of diarrhea caused by water-borne infections. The bacteria most commonly found in polluted water are coliforms excreted by human beings. Surface runoff and consequently non-point source pollution contributes significantly to high level of pathogens in surface water bodies. Improperly designed rural sanitary facilities also contribute to contamination of groundwater [2].

The purpose of this research work was to investigate the quality of drinking water (springs, wells, streams and rivers) of Dir districts. It is necessary to examine the quality of water from time to time, in order to have a check upon the levels of inorganic, organic, microbial and bacterial pollutants. Many earlier research workers have also studied the drinking water of different areas with the aim to know the quality parameters and its contribution towards the health of human beings [3-10].

Results and Discussion

Table-1 and Fig. 1 indicate the locations of fifty-one drinking water samples collected from springs, wells, streams and rivers of Dir districts. They were studied to determine the levels of both physical and chemical parameters like pH, conductance, total solids, total dissolved solids, total hardness, alkalinity, chloride, sulphate, nitrate, free ammonia, iodide, fluoride, calcium, magnesium, sodium, potassium, zinc, iron and copper. The results obtained have been presented in Tables 2-4 and Figures 2-8. The WHO Guidelines [11] for drinking water have been given in Table-5.

Table-2 indicates that the level of pH of the water samples of Dir districts falls in the range of 6.76-8.82. The permissible range for pH recommended by WHO is 6.5-9.2. Many of the water samples are weakly alkaline. Sample No. 14 of Bibour spring and No. 48 of stream near Govt. College Dir have minimum and maximum pH respectively. All the water sources have pH level

Table-1: Code numbers of the drinking water samples collected at different locations of upper Dir and lower Dir districts.

Water Samples Locations	Sample Code No.	Water Samples Locations	Sample Code No.
Surbat **spring** at road side	1	**Well** on road side at Ouch Chawak.	27
Spring below new road at Dir	2	Barawal **river** at surbat village.	28
Rehankot Bala **spring** at Dir	3	Tape water at Rehankot Dir (source river)	29
Chenarcham **spring** at Dir	4	Tap water at Panakot (source river)	30
Tap water sample at Dir (Bekarae **spring**)	5	DIR **river** near Degree College Dir	31
Naow **spring** Girgat hills	6	Punjkora **river** near chokyatan bridge.	32
Spring near district council public school Dir.	7	Ousheri **river** at Darora bridge.	33
Spring near police station at Dir	8	Punjkora **river** near Nehag Stream.	34
Spring near military camp at Dir	9	Punjkora **river** at Muhansharif.	35
Spring near animal hospital at Dir	10	Punjkora **river** at Khal.	36
Spring near G.P. school Khan Shaheed at Dir	11	Punjkora **river** at sadu.	37
Spring in front of high school No.1 at Dir	12	Dir **river** at Dir Town	38
Gulabad **spring** at roadside.	13	Muhansharif **stream**	39
Bibour spring at roadside.	14	Nehagdara **stream** at Wari bridge	40
Spring near Darora bridge.	15	Karow dara **stream** at Akhagram bridge	41
Spring at roadside near Muhansharif.	16	**Stream** at Toormang bridge	42
Bibour **spring** near high school.	17	Timergara **stream** on road side	43
Chukyaton **spring** near forest check post.	18	Sadu **stream** on road side	44
Spring of Khakdar village.	19	Takhtabi canal (Punjkora river)	45
Care Dara **spring** sample	20	Dir **stream** at Dir	46
Well on road side at Rani, (tube well)	21	Gargo **khawar** near Govt. college Dir.	47
Well at Tari near P.S.O pump (tube well)	22	Ala **stream** near Govt. college Dir	48
Well at Khal bazaar (tube well).	23	Rabat **stream** on road side	49
Well at Timargara bazaar (tube well)	24	Rani **stream** on road side	50
Well at Talash bazaar (tube well)	25	Swat **river** at Chakadara bridge	51
Well at Gulabad (tube well)	26		

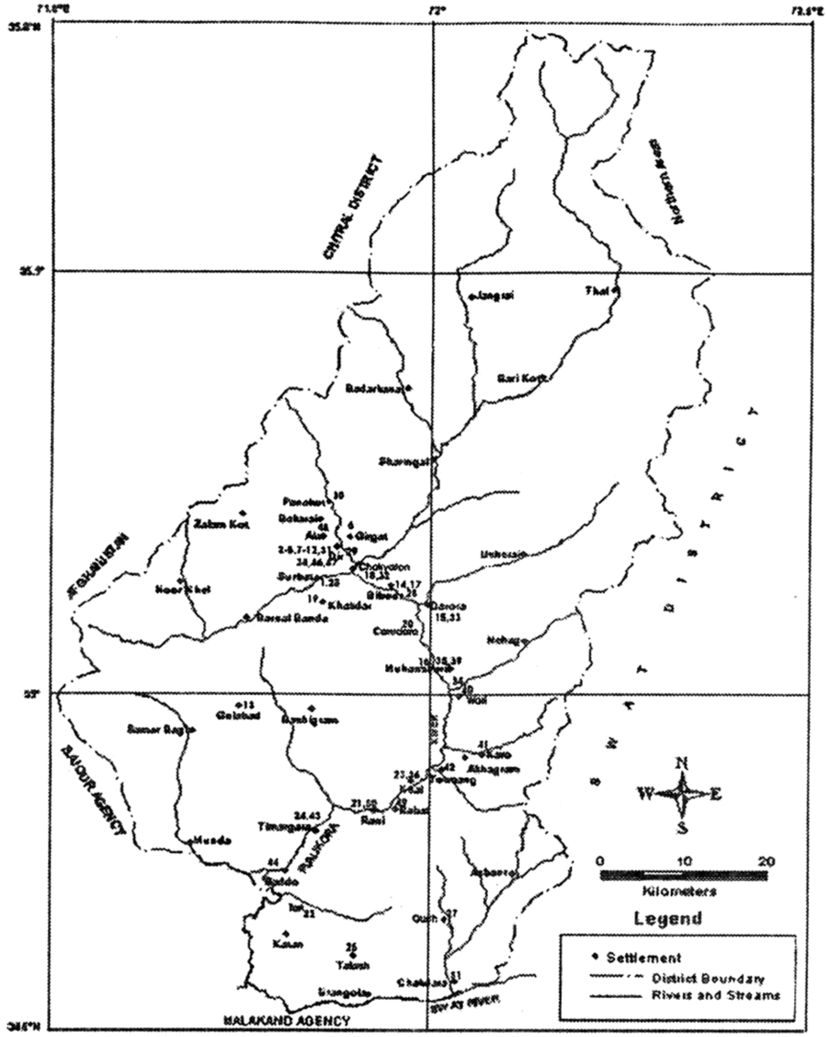

Fig. 1: Map of Dir Districts Showing Locations of Water Samples of Code No. 1-51.

within the limits recommended by WHO. Water with low pH (< 6.5) would be acidic, soft, and corrosive. This may leach metal ions such as iron, manganese, copper, lead, and zinc from the aquifer, plumbing fixtures and piping. Therefore it may contain elevated levels of toxic metals and may create aesthetic problems such as a metallic or sour taste and staining of laundry. It may also cause various acute and chronic diseases like esophagus and stomach irritation with pain and vomiting.

The level of total solids (TS) in the drinking water samples of Dir districts was observed to be in the range of 80-594mg dm^{-3}(Table 2). Many of the samples have total solids below the permissible limits of WHO (505 mg dm^{-3}) except those of springs at Dir high school No. 1 and on road side at Muhansharif. Several samples have total solids above 300 mg dm^{-3} which may be due to soil erosion and may have created the high turbidity observed in water of streams and rivers. The high amount of total solid mass may be controlled by extensive plantation in different regions of the districts and by preventing the deforestation.

Dissolved solids refer to any minerals, salts, metals, cations or anions frequently dissolved in water. Total dissolved solids (TDS) comprise mainly

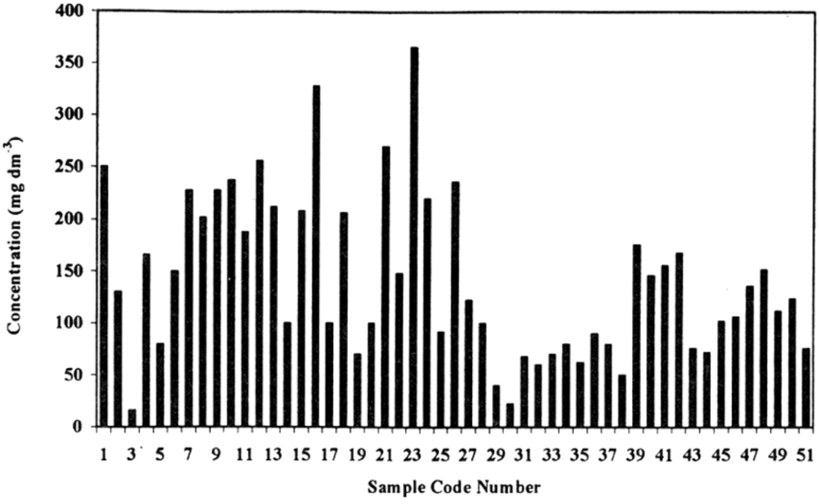

Fig. 2: Level of Total Hardness in the Water Samples Dir Districts.

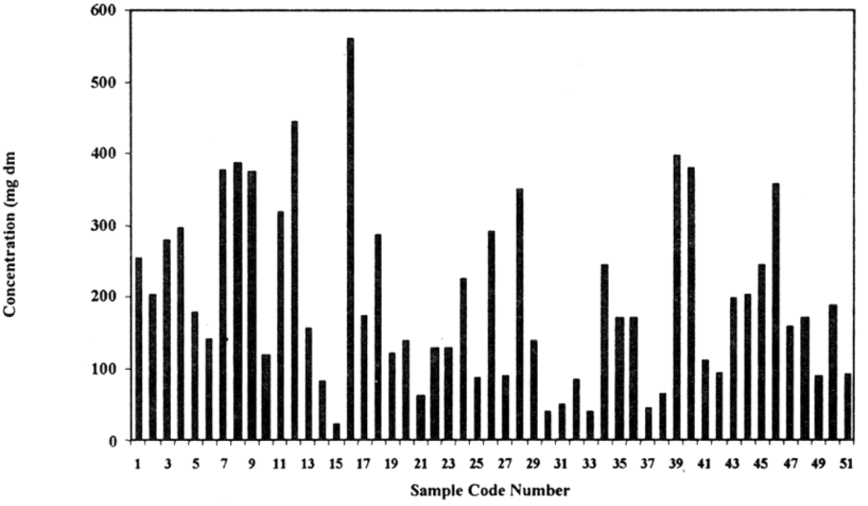

Fig. 3: Level of Total Dissolved Solids of Water Samples Dir Districts.

inorganic salts (bicarbonates, chlorides and sulfates of calcium, magnesium, potassium and sodium) and some small amounts of organic matter that are soluble in water. In other words, the total dissolved solids concentration is the sum of the cations and anions in the water. Therefore, the total dissolved solids test provides a measure of the amount of dissolved ions but does not tell us about the nature of ions. TDS in drinking-water originate from natural sources, sewage, urban run-off, industrial wastewater, and chemicals used in the water treatment process, and the nature of the piping or hardware used to convey the water, i.e., the plumbing. Table-2 shows the TDS values are in the range of 24-560 mg dm^{-3}. All the water samples have TDS within the permissible limits recommended by WHO (500 mg dm^{-3}) except that of spring near Muhansharif at road side. High level of TDS indicates high concentration of the dissolved ions, which render water non-potable, corrosive, and of salty or brackish taste.

Originally, water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and

Table-2: Levels* of different physico-chemical parameters of water samples of springs, wells, streams and rivers of upper Dir and lower Dir districts.

Sample Code	pH	Total Hardness (mg dm^{-3})	Total Alkalinity as $CaCO_3$ (mg dm^{-3})	Total Solids (mg dm^{-3})	Total Dissolved Solids (mg dm^{-3})
1	7.84	250 ±11	366 ± 15	262 ± 10	254 ± 16
2	7.48	130 ±5	207 ±9	270 ± 10	202 ±8
3	7.99	160 ±6	244 ±11	314 ± 13	280 ±11
4	7.73	166 ±7	109 ±5	332 ± 13	296 ±13
5	8.71	80 ±4	225 ±8	234 ± 13	178 ±7
6	8.60	150 ±6	293 ±12	236 ± 14	142 ±7
7	8.19	228 ±11	232 ±10	386 ± 16	378±15
8	8.01	202 ±9	292 ±12	474 ± 22	388 ±15
9	8.61	228 ±10	329 ±15	414 ± 20	376 ±14
10	7.91	238 ±13	256 ±11	332 ± 14	118 ±5
11	8.11	188 ±7	256 ±10	360 ± 15	320 ±12
12	7.87	256 ±12	341±14	594 ± 24	444 ±19
13	6.80	212 ±8	329 ±12	166 ± 7	156 ±7
14	6.76	100 ±4	158 ±6	154 ±6	82 ±4
15	8.39	208 ±9	225 ±10	428 ±19	24 ±1
16	7.82	328 ±14	427 ±20	566 ± 21	560 ±21
17	7.63	100 ±4	146 ±6	198 ±7	174 ±5
18	8.15	206 ±10	280 ±9	316 ± 12	288 ±11
19	8.59	70 ± 4	134 ±4	142 ± 6	122 ±6
20	8.04	100 ±5	152 ±5	162 ± 7	138 ±5
21	7.43	270 ±8	280 ±8	182 ± 7	62 ± 3
22	7.60	148 ±6	201 ±7	136 ± 6	128 ±6
23	7.56	366 ±13	457 ±21	258 ±9	130 ±7
24	7.62	220 ±11	329 ±13	400 ±16	224 ±9
25	8.28	92 ± 4	195 ±7	132 ±6	88 ±4
26	7.63	236 ±12	341 ±12	380 ±15	292 ±11
27	7.46	122 ±7	195 ±8	128 ±6	90 ±4
28	8.50	100 ±5	292 ±10	486 ±23	352 ±16
29	8.06	40 ±2	146 ±7	136 ±5	138 ±7
30	7.81	22 ±1	73 ±4	80 ± 4	40 ±2
31	7.87	68 ±3	79 ±4	144 ±6	50 ±2
32	8.00	60 ±3	97 ±4	94 ±3	84 ±4
33	8.15	70 ±4	201±8	200 ±10	40 ±2
34	8.21	80 ±4	109 ±4	260 ±11	244 ±10
35	8.55	62 ±3	97 ±4	194 ±6	172 ±8
36	7.89	90 ±4	122 ±5	242 ±11	170 ±7
37	8.28	80 ±4	127 ±5	192 ±9	46 ±2
38	8.38	50 ±3	122 ±5	98 ±4	64 ±3
39	8.65	176 ±7	219 ±8	444 ±17	398 ±12
40	8.80	146 ±5	194 ±7	440 ±16	380 ±10
41	8.75	156 ±6	194±7	210 ±8	112 ±5
42	8.55	168 ±6	151 ±6	262 ±12	94 ±4
43	8.20	76 ±4	244 ±10	310 ±14	198 ±8
44	7.62	72 ± 4	109 ±4	372 ±15	202 ±9
45	8.35	102 ±5	146 ±7	366 ±15	244 ±10
46	8.38	106 ±5	146 ±6	402 ±18	358 ±15
47	7.75	136 ±4	183 ±8	208 ±9	158±8
48	8.82	152 ±6	219 ±9	204 ±9	172 ±8
49	8.28	112 ±4	139 ±7	272 ±11	90 ±4
50	8.50	124 ±5	140 ±7	254 ±10	188 ±8
51	7.75	76 ±4	164 ±8	156 ±7	92 ±4

*Mean value ± Standard deviation.

magnesium ions present. Other polyvalent cations also may precipitate soap, but they often are in complex form, frequently with organic constituents and their role in water hardness may be minimal and difficult to define. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonates in milligrams per liter. The maximum limit of total hardness recommended by WHO and APHA (American Public Health Association) are 500mg dm^{-3} and 250 mg dm^{-3} respectively. Total hardness of the water samples was in the range 22-366 mg dm^{-3} (Table 2). All the water samples have hardness within the WHO and APHA limits except water samples No. 12 (spring at front of high school No.1 at DIR), No. 16 (spring near Muhansharif at road side), No. 21 (well on road side at Rani) and No.23 (well at Khal Bazaar), which are above the APHA limits (Table 1). High level of total hardness may cause diarrhea, gas trouble, kidney stone, heart problems, etc [12].

Table 2 shows that the level of total alkalinity of water samples of Dir districts varied in the range of 73-366mg dm^{-3} as $CaCO_3$ and therefore was below the limit of 500 mg dm^{-3}, recommended by WHO. Beyond the permissible limit, alkalinity cause many problems like hardness, kidney stone, gas trouble, damage of metallic pipes and severe irritation of the eyes, skin and mucous membrane [13].

Chloride in the water is present in combination with sodium, calcium and magnesium. Chloride makes its way to drinking water through

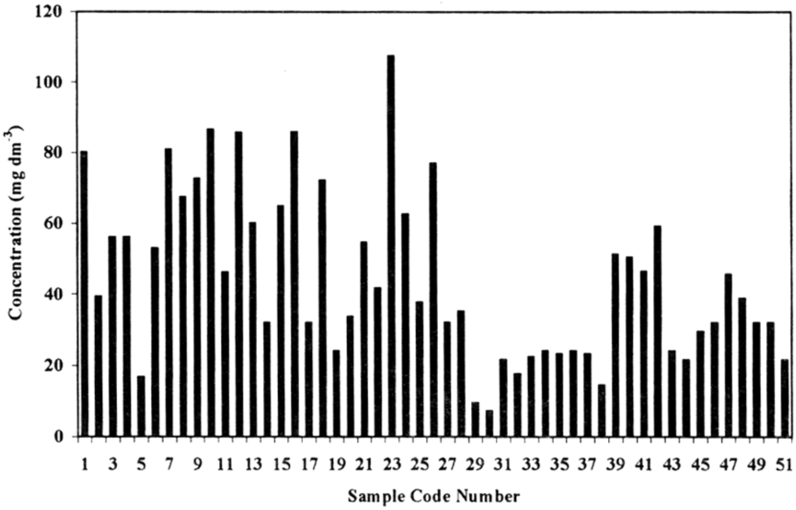

Fig. 4: Level of Calcium in the Water Samples Dir Districts.

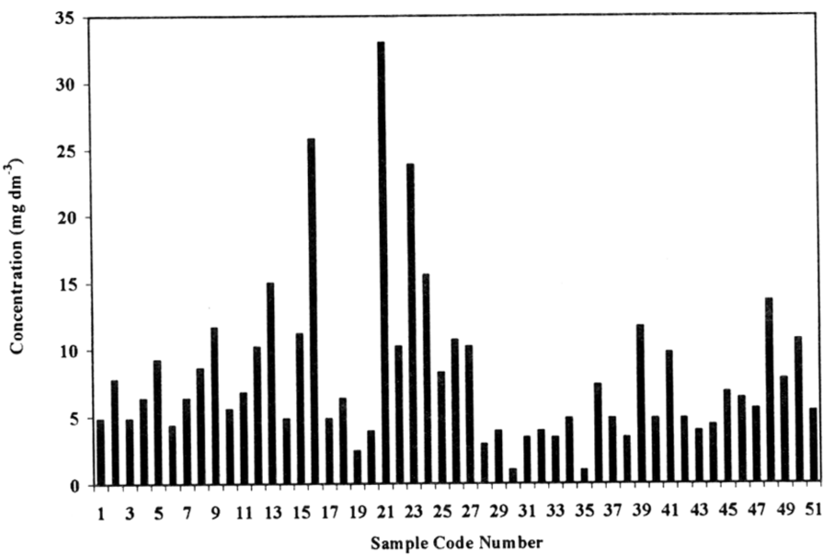

Fig. 5: Level of Magnesium in the Water Samples Dir Districts.

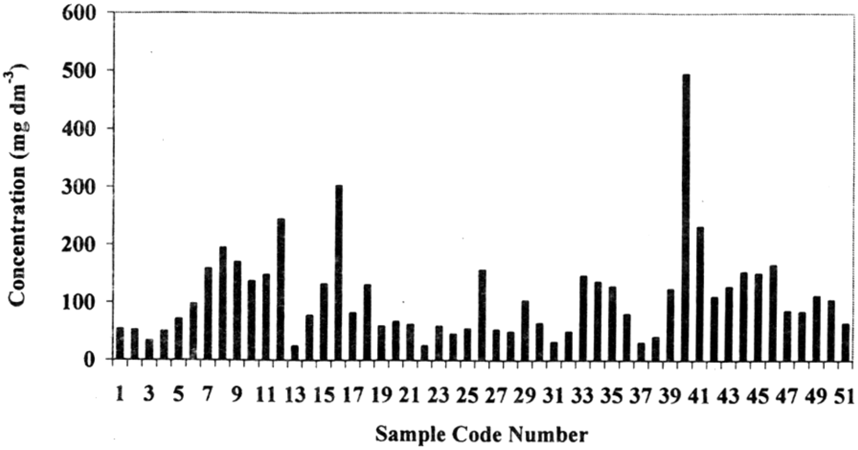

Fig. 6: Level of Sulphates in the Water Samples Dir Districts.

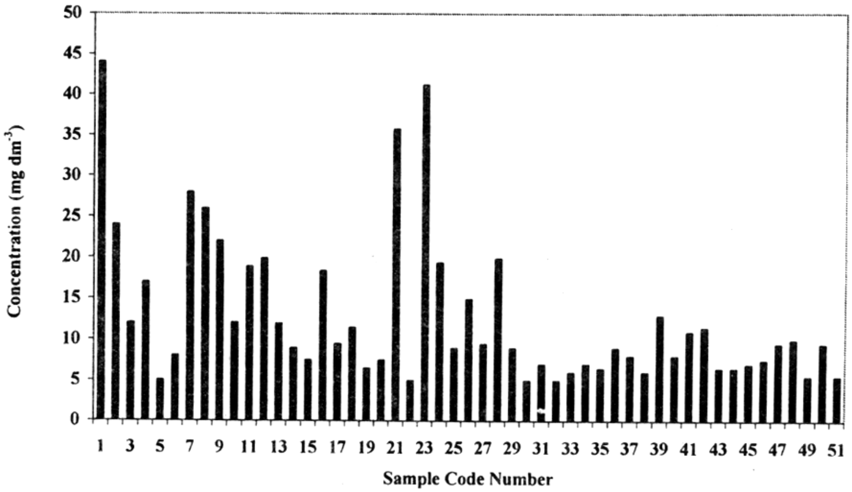

Fig. 7: Level of Chlorides in the Water Samples Dir Districts.

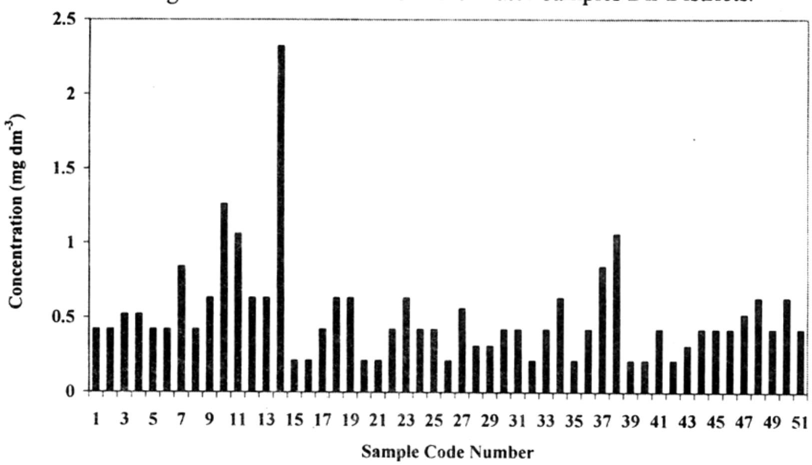

Fig. 8: Level of Iodides in the Water Samples Dir Districts.

Table-3: Levels* of different chemical parameters of water samples of springs, wells, streams and rivers of upper Dir and lower Dir districts.

Sample Code	Chlorides (mg dm^{-3})	Ammonia (mg dm^{-3})	Sulphates (mg dm^{-3})	Nitrates (mg dm^{-3})	Fluorides (mg dm^{-3})	Iodides (μg dm^{-3})
1	44.00 ± 2	0.0000	52.67± 1.58	0.10±0.0053	0.1± 0.003	0.42±0.016
2	24 ±1.2	0.0000	51.02±1.02	0.10±0.004	0.1± 0.004	0.42±0.016
3	12 ±0.4	0.0000	32.92±1.31	2.70±0.081	0.1± 0.005	0.52±0.015
4	17 ±0.65	0.0000	49.38±2.4	0.50±0.015	0.1± 0. 004	0.52±0.020
5	5.0 ±0.15	0.0000	70.78±2.8	1.50±0.06	0.55± 0.016	0.42±0.021
6	8 ± 0.32	0.0000	97.11±5	8.20±0.41	0.48± 0.019	0.42±0.012
7	28 ±0.56	0.01± 0.001	158.84±4.76	5.10±0.204	0.20± 0.010	0.84±0.025
8	26 ±1.04	0.0000	195.05±3.90	4.40±0.13	0.28±0.005	0.42±0.012
9	22 ±0.66	0.0000	170.36±51	6.80±0.27	0.1±0.003	0.63±0.031
10	12 ±0.36	0.02± 0.002	136.62±6.83	6.41±0.19	0.1±0.004	1.26±0.054
11	18.86±0.75	0.0000	148.14±4.4	0.00±0.0	0.1±0.005	1.06±0.031
12	19.86±.59	0.0000	244.43±12.22	1.93±0.0772	0.1±0.004	0.63±0.052
13	11.91±0..6	0.0000	23.87±0.47	0.0000	1.0±0.03	0.63±0.018
14	8.93±0.35	0.0000	77.36±2.38	0.0000	0.28±0.005	2.32±0.092
15	7.45±0.22	0.0000	131.68±5.26	0.0000	0.55±0.016	0.21±0.006
16	18.37±0.73	0.040±0.003	302.04±9.06	0.0000	0.1±0.004	0.21±0.006
17	9.43± 0.70	0.0000	81.48±2.44	0.0000	0.1±0.0045	0.42±0.021
18	11.42±0.45	0.0000	130.03±4	0.0000	0.15±0.003	0.63±0.025
19	6.45±0.32	0.0000	58.43±2.92	0.0000	0.1±0.004	0.63±0.025
20	7.45±0.37	0.0000	66.66±2.92	0.0000	0.1±0.004	0.21±0.010
21	35.76±. 1.43	0.160±0.005	61.72±3.06	0.0000	1.85±0.074	0.21±0.010
22	4.96±0.24	0.06±0.002	24.69±0.74	1.81± 0.072	0.48±0.002	0.42±0.012
23	41.20±1.06	0.036±0.0015	58.43±2.92	0.0000	1.85±0.055	0.63±0.031
24	19.36±0.8	0.036±0.0016	45.27±2.26	1.30±0.026	0.1±0.004	0.42±0.016
25	8.93±0.34	0.016±0.005	54.32±2.17	1.95±0.078	0.1±0.0003	0.42±0.012
26	14.89±0.64	0.040±0.002	156.37±6.25	1.60±0.048	0.1±0.004	0.21±0.006
27	9.43±0.37	0.0000	52.67±1.58	0.0000	0.4±0.02	0.56±0.022
28	19.86±0.8	0.0000	49.38±11	0.0000	0.1±0.004	0.31±0.015
29	8.92±0.60	0.0000	103.03±5.15	0.30±0.015	0.48±0.044	0.31±0.009
30	4.96±0.20	0.0000	64.19±2.56	1.80±0.054	0.1±0.002	0.42±0.021
31	6.95±0.24	0.0000	31.27±0.93	0.0000	0.1±0.004	0.42±0.016
32	4.96±0.14	0.0000	49.26±1.47	0.0000	0.1±0.004	0.21±0.004
33	5.96±0.20	0.0000	146.49±5.85	0.0000	0.60±0.018	0.42±0.012
34	6.95±0.17	0.0000	135.79±6.79	0.0000	0.60±0.018	0.63±0.025
35	6.45±0.18	0.0000	127.57±5.10	0.0000	0.1±0.002	0.21±0.042
36	8.93±0.35	0.02±0.001	79.83±2.39	1.20±0.048	0.1±0.004	0.42±0.018
37	7.94±0.40	0.0000	30.45±1.21	0.10±0.005	0.1±0.005	0.84±0.016
38	5.96±0.18	0.0000	40.33±1.61	0.30±0.009	0.2±0.006	1.06±0.021
39	12.91±0.44	0.0000	123.45±6.17	0.0000	0.9±0.018	0.21±0.006
40	7.94±0.31	0.0000	495.44±14.86	0.30±0.009	0.9±0.036	0.21±0.008
41	10.92±0.43	0.0000	232.08±9.28	0.80±0.016	1.85±0.055	0.42±0.008
42	11.42±0.60	0.01±0.001	110.28±4.41	0.10±0.005	1.7±0.051	0.21±0.010
43	6.45±0.20	0.0000	127.57±3.82	0.0000	0.1±0.002	0.31±0.012
44	6.45±0.20	0.0000	153.08±6.12	0.0000	0.6±0.024	0.42±0.012
45	6.95±0.26	0.0000	150.91±6.03	0.10±0.002	0.15±0.004	0.42±0.016
46	7.45±0.37	0.040±0.002	165.42±3.30	0.0000	0.1±0.003	0.42±0.016
47	9.43±0.37	0.0000	85.59±2.57	7.18±0.359	0.1±0.004	0.52±0.020
48	9.93±0.37	0.0000	83.95± 3.35	10.10±0.404	0.1±0.005	0.63±0.012
49	5.46±0.20	0.0000	111.93±5.59	0.80±0.024	0.28±0.008	0.42±0.012
50	9.43±0.37	0.0000	104.52±4.18	1.93±0.077	1.0±0.02	0.63±0.025
51	5.46±0.16	0.016±0.005	64.19± 1.92	0.0000	0.1±0.004	0.42±0.021

*Mean value ± Standard deviation.

natural mineral rocks. Table 3, shows that the level of chloride of water samples of Dir districts was in the range of 4.96-44.68 mg dm^{-3}. All the samples had chloride level within the WHO limit i.e. 250mg dm^{-3}. A high level of chloride may cause gastrointestinal problems, irritation, diarrhea and dehydration [14].

Sulfates are a combination of sulfur and oxygen and are a part of naturally occurring minerals in some soil and rock formations that contain groundwater. The mineral dissolves over time and is released into groundwater. Sulfur-reducing bacteria, which use sulfur as an energy source, are the primary producers of large quantities of hydrogen sulfide. These bacteria chemically change natural sulfates in water to hydrogen sulfide. Sulfur-reducing bacteria live in oxygen-deficient environments such as deep wells, plumbing systems, water softeners and water heaters. These bacteria usually flourish on the hot water side of a water distribution system. Hydrogen sulfide gas also occurs naturally in some groundwater. It is formed from decomposing underground deposits of organic matter such as decaying plant material. It is found in deep or shallow wells and also can enter surface water through springs, although it quickly escapes to the atmosphere. Hydrogen sulfide often is present in those wells, which are drilled in shale or sandstone, or near coal or peat deposits or oil fields. Table 3 shows that the concentration of sulphate of water samples of Dir district varied in the range 120–794 mg dm^{-3}. The permissible level for sulphate recommended by WHO is 250 mg dm^{-3}. Two water samples having code No 16 (spring near Muhansharif at road side) and No. 40 (Nehagdara stream at Wari bridge) exceeded the limit of WHO. While that of water samples of code No. 12 and 41 was near to 250 $mgdm^{-3}$ and that of No. 7, 8, 9, 26, 44, 45 and 46 was more than 150 mg dm^{-3}. High concentration of sulphate imparts bad taste and when combined with sodium or magnesium becomes laxative and causes cathartic effects and corrosive mode of act. Fortunately, the level of magnesium of the aforementioned water samples was not high (Table 4), otherwise they would be highly laxative as the sulphates level was a little high [15].

Nitrogen is the nutrient applied in the largest quantities for lawn and garden care and crop production. In addition to fertilizer, nitrogen passes naturally to the soil from decaying plant and animal residues. In the soil, bacteria convert various forms of nitrogen to nitrates. This is desirable as greater extent of the nitrogen used by plants is absorbed in the nitrate form. However, nitrate is highly leachable and readily moves with water through the soil profile. If there is excessive rainfall or over-irrigation, nitrate will be leached below the plants root zone and eventually reach groundwater. Nitrate-nitrogen in groundwater may result from point sources such as sewage disposal systems and livestock facilities as well as from non-point sources such as fertilized cropland, parks, golf courses, lawns, and gardens. Proper site selection for the location of domestic water well and proper well construction can reduce potential nitrate contamination of drinking water source. The concentration of nitrate in the water samples of Dir districts varied in the range of 0.00-10.10 mg dm^{-3} as can be seen from Table 3. The permissible limit recommended by WHO is 45mg dm^{-3} for nitrate. All the water samples show low level of nitrates. When the level of nitrate exceeds the permissible limit then the primary health hazard from drinking water with nitrate-nitrogen may occurs when nitrate is transformed to nitrite in the digestive system. The nitrite oxidizes iron in the hemoglobin of the red blood cells to form methemoglobin and causes methemoglobinemia or blue baby syndrome (a situation in which blood lacks the ability to carry sufficient oxygen to the individual body cells causing the veins and skin to appear blue). Most children over one year of age have the ability to rapidly convert methemoglobin back to oxyhemoglobin, hence the total amount of methemoglobin within red blood cells remains low in spite of relatively high levels of nitrate/nitrite uptake. However in infants under six months of age, the enzyme systems for reducing methemoglobin to oxyhemoglobin are incompletely developed and methemoglobinemia can occur. This also may happen in older individuals who have genetically impaired enzyme systems for metabolizing methaemoglobin [16].

The WHO Guideline for ammonia is 0.5 mg dm^{-3} and the spectrophotmetric nesslerisation method used in the present research work for investigation of ammonia can determine ammonia concentration as low as 20 μg dm^{-3}, and as high as 5 mg dm^{-3}. It is apparent from the table 3 that majority of the samples had undetectable level of ammonia. The water sample No. 21 of the tube well at village Rani had maximum content of ammonia (0.16 mg dm^{-3}) and the water samples No. 7, 10, 16, 22-26, 36, 42, 46 and 51 have showed the presence of traces in the range 0.01-0.06 mg dm^{-3}. Enhanced levels of ammonia are indicative of recent pollution. Sewage is a major source of ammonia, which results from the breakdown of urea, $CO(NH_2)_2$, by urease bacteria.

Table-3 shows that level of fluoride of the analyzed water samples varied in the range of 0.1-1.85 mg dm^{-3}. All water samples of Dir districts have fluoride level within the permissible range of WHO which is 2.0 mg dm^{-3}. Many of the water samples had very low level of fluoride (0.1mg dm^{-3}). Fluoride reduces the solubility of the enamel of teeth under acidic condition and there by provides protection

Table-4: Levels* of different metals in water samples of springs, wells, streams and rivers of upper Dir and lower Dir districts.

Sample Code	Ca (mg dm^{-3})	Mg (mg dm^{-3})	Na (mg dm^{-3})	K (mg dm^{-3})	Zn (mg dm^{-3})	Fe (mg dm^{-3})	Cu (mg dm^{-3})
1	80.20±. 01	4.86±0.19	9.0± 0.27	1.00± 0.05	1.00±0.04	0.01±. 0005	0.01±0.0005
2	39.30±1.5	7.77±0.02	13±0.65	2.00±0.08	2.00±0.08	0.07± 0.002	0.04±0.002
3	56.14±1.68	4.86±0.01	8.0±0.16	1.00±0.05	2.20±0.08	0.02±0.001	0.05±0.002
4	56.14±2.24	6.32±0.12	9.0±0.36	1.00±0.05	1.20±0.06	0.03±. 001	0.07±0.003
5	16.84±0.84	9.23±0.36	7.0±0.21	1.00±0.03	0.04±0.00	0.04±. 002	0.06±0.003
6	52.93±3	4.37±0.13	7.0±0.28	1.00±0.03	2.1±0. 10	0.06±0.002	0.03±0.001
7	81.00±2.64	6.32±0.12	23±0.46	3.00±0.12	1.1±0.05	0.08±0.003	0.01±0.0003
8	67.37±2.69	8.62±0.43	21±1.65	5.00±0.20	1.0±0.05	0.09±0.004	0.05±0.002
9	72.78±3.63	11.66±0.23	12±0.24	1.00±0.05	2.0±0.1	0.04±0.002	0.07±0.003
10	86.61±3.46	5.55±0.16	13±0.52	0.0000	2.2±0.11	0.01±0.005	0.06±0.003
11	46.16±2.30	6.80±0.27	20±0.20	3.00±0.15	2.3±1.09	0.01±0.001	0.03±0.001
12	85.81±3.43	10.21±0.20	21±0.63	1.00±0.04	1.1±0.05	0.02±0.001	0.05±0.002
13	60.15±1.80	15.0±0.75	7± 0.35	1.00±0.04	1.0±0.05	0.03±0.001	0.6±0.001
14	32.08±0.64	4.86±0.14	9± 0.76	1.00±0.05	1.0±0.04	0.04±0.002	0.02±0.002
15	64.96±1.94	11.18±0.44	7±0.40	0.0000	2.0±0.10	0.03±0.001	0.02±0.001
16	86.02±3.44	25.76±0.51	19±0.21	0.0000	3.0±0.15	0.06±0.015	0.01±0.0008
17	32.08±1.60	4.86± 0.14	6± 0.76	1.00±0.03	1.0±0.04	0.06±0.003	0.01±0.0005
18	72.18±2.88	6.32± 0.25	9± 0.45	1.00±0.04	2.0±0.10	0.02±0.0004	0.06±0.0005
19	24.06±0.72	2.43± 0.48	4±0.12	0.00±0.00	2.1±0.10	0.01±0.002	0.01±0.001
20	33.68±1.68	3.89± 0.19	5±0.20	1.00±0.04	2.3±0.09	0.03±0.002	0.01±0.0003
21	54.54±1.09	33.0± 0.66	11±0.33	1.00±0.05	2.5±0.12	0.06±0.003	0.01±0.0005
22	41.70±1.66	10.21±0.40	8±0.32	2.00±0.1	1.2±0.06	0.08±0.004	0.02±0.0005
23	107.47±3.22	23.81±0.71	24±1.20	6.00±0.3	1.3±0.06	0.7±0.003	0.01±0.001
24	62.55±1.25	15.55±0.77	14.0± 0.28	1.00±05	1.5±0.07	0.09±0.004	0.02±0.001
25	37.69±1.88	8.26± 0.16	11.0± 0.33	1.00±0.05	1.0±0.05	0.01±0.0004	0.03±0.001
26	76.99±3.07	10.69±0.32	9.00± 0.36	1.00±0.05	2.0±0.08	0.05±0.002	0.04±0.002
27	32.08±0.40	10.21±0.40	13± 0.65	1.00±0.03	2.00±0.1	0.03±0.001	0.05±0.002
28	35.28±1.41	2.92±0.14	6.00±0.3	1.00±.0.05	1.5±0.07	0.11±0.005	0.0000
29	9.62±0.28	3.89±0.15	3.00±0.15	1.00±0.04	1.4±0.07	0.22±0.008	0.07±0.002
30	7.22±0.36	1.0±0.05	3.00±0.12	1.00±0.04	1.0±0.05	0.11±0.0032	0.04±0.002
31	21.65±0.43	3.40±0.13	6.00±0.09	1.00±0.04	2.0±0.08	0.08±±0.016	0.02±0.001
32	17.64± 0.70	3.89±0.15	3.00±0.16	1.00±0.03	3.0±0.12	0.03±±0.001	0.05±0.002
33	22.45±0.67	3.40±0.13	4.00±0.20	1.00±0.04	1.0±0.04	0.08±±0.004	0.02±0.0001
34	24.06±1.20	4.86±0.20	4.00±0.16	1.00±0.05	2.0±0.08	0.03±0.001	0.06±0.002
35	23.26±0.46	0.97±0.02	4.00±0.25	1.00±0.05	3.0±0.09	0.05±0.002	0.03±0.001
36	24.06±0.72	7.29±0.21	4.00±0.20	1.00±0.03	2.3±0.09	0.06±0.002	0.05±0.002
37	23.26±1.16	4.86±0.20	5.00±0.25	1.00±0.03	2.3±0.06	0.04±0.001	0.03±0.001
38	14.44±0.28	3.40±0.13	5.00±0.20	0.0000	2.1±0.84	0.07±0.003	0.05±0.002
39	51.33±2.05	11.66±0.47	12.0±0.50	1.00±0.05	1.1±0.04	0.09±0.004	0.08±0.004
40	50.52±2.52	4.86±0.14	9.00±0.30	1.00±0.04	1.0±0.04	0.11±0.005	0.05±0.002
41	46.52±1.39	9.72±0.40	10.0±0.30	1.00±0.05	1.1±0.04	0.02±0.0008	0.02±0.001
42	59.35±1.18	4.86±0.20	10.0±0.50	1.00±0.05	1.2±0.03	0.06±0.002	0.01±0.0005
43	24.06±0.96	3.89±0.01	4.00±0.40	2.00±0.11	2.0±0.08	0.05±0.002	0.02±0.002
44	21.65±0.64	4.37±0.01	5.00±0.25	1.00±0.05	2.1±0.08	0.05±0.001	0.03±0.0015
45	29.67±1.48	6.80±0.27	8.00±0.32	1.00±0.05	2.2±0.08	0.02±0.0005	0.05±0.0015
46	32.08±0.64	6.32±0.25	8.00±0.40	2.00±0.08	2.0±0.09	0.01±0.002	0.06±0.002
47	45.71±1.37	5.55±0.28	7.00±0.35	1.00±0.05	3.0±0.05	0.04±0.002	0.01±0.002
48	38.96±1.55	13.61±0.54	10.0±0.40	2.00±0.06	1.0±0.05	0.05±0.002	0.11±0.002
49	32.08±1.60	7.77±0.48	8.00±0.32	2.00±0.06	1.0±0.04	0.06±0.003	0.04±0.002
50	32.08±0.64	10.69±0.42	11.00±0.55	3.00±0.15	1.0±0.04	0.08±0.004	0.09±0.003
51	21.65±0.64	5.35±0.25	4.00±0.20	1.00±0.04	2.0±0.06	0.09±0.003	0.03±0.001

*Mean Value ± Standard Deviation.

against dental caries. The presence of fluoride in water results in a substantial reduction of dental caries in both children and adults. The incidences of caries decrease as the concentration of fluoride increases to about 1 mg dm^{-3}, although mottling of teeth may occur, when its level rises to 1.5-2 mg dm^{-3}. The inhabitants of Dir districts should be advised to use dental cream containing fluoride to overcome the shortage of fluoride. Above the permissible limit fluoride causes both acute and chronic effects such as muscular weakness, vomiting, nausea, gastrulae, collapse and myocardial failure and chronic toxicity including pain in legs and back, loss of weight and strength, mottling of teeth, and forward bending of vertebral column [17].

The level of iodide in the water samples of Dir districts varied in the range 0.2-2.32 μg dm^{-3} (table 3). Iodine, the 53rd element in the periodic table, is a key ingredient in thyroxin, a hormone produced in the thyroid gland. When a pregnant woman's diet lacks iodine, her fetus may suffer inadequate brain development because thyroxin production is inhibited. Thyroxin promotes complex brain development and thus directly affects an infant's intelligence. Although iodine is a critical nutritional supplement, very little of it i.e. about 0.001g (0.02 grain) daily is required to prevent iodine deficiency disorder. Persons born with below-normal brain development due to an absence of thyroxin may suffer severe mental retardation. The most extreme form of iodine deficiency disorder is cretinism, a condition characterized by severe mental retardation accompanied by physical deformities. If treated in early infancy, cretinism may be cured with lifelong iodine supplements. The level of iodide of waters of Dir districts is low. The people of these areas should be advised to use iodized salt in order to avoid diseases due to iodine deficiency like goiter, mental retardation, etc [18].

Calcium is present in all natural waters and its level depends upon the type of rocks through which the water passes. It is usually present in the form of carbonates, bicarbonates, sulphates, chlorides and nitrates. Calcium contributes to the hardness of water. Calcium is also an essential part of human diet. The concentration of calcium found in the water samples of Dir districts was in the range of 7.22-107.47 mg dm^{-3} (Table 4). All the water samples except No. 23 (well at Khal Bazaar) had calcium level below the recommended maximum level of WHO i.e. 100 mg dm^{-3}. Above the recommended limit of WHO, it may create the problems like deposition in water system and excessive scales formation. Various earlier investigators have studied the calcium in the drinking water and also reported its effects on living organisms.

Magnesium is one of the earth's most common elements and form highly soluble salts. High concentration of magnesium is undesirable in potable water, as it causes scale formation and cathartic and diuretic effects, especially when associated with sulphate. Many earlier research workers have studied magnesium in the drinking water and also reported its toxicity toward living things. The level of magnesium of the water samples analyzed was in the range of 1.0-25.76 mg dm^{-3} (Table 4) which is lower than the recommended limit of WHO for magnesium i.e. 36.45 mg dm^{-3}.

Zinc is an essential micronutrient of plants. It plays a significant role in the enzymatic system of human body, for example the enzymes like aldolase, alkaline phosphatase, etc depend totally on zinc. It is also essential for the normal functioning of the cells including protein synthesis, carbohydrate metabolism, cell growth and cell division. The recommended dietary intake of zinc is 15 mg per day. The zinc deficiency results into retardation of growth, anorexia, lesions of the skin and impaired development and function of reproductive organs. On the other side when the level of zinc is exceeded then it causes fever, depression, malaise, cough, vomiting, salivation and headache. However, its toxicity is less than that of Cd, As and Sb. The level of Zn in the drinking water samples of Dir districts was observed in the range of 0.04- 3.00 mg dm^{-3} (Table-4), which is lower than the recommended permissible limit of WHO (15 mg dm^{-3}). Therefore the inhabitants of these districts should be advised to fulfill the Zn requirement from other sources, as many of the water samples are deficient in Zn.

Copper rarely occurs in natural water. Most copper contamination in drinking water happens in the water delivery system, as a result of corrosion of the copper pipes or fittings. Table 4 shows that the concentration of copper in the water sample analyzed varied in the range of 0.00-0.09 mg dm^{-3}. The maximum permissible limit for copper recommended by WHO is 3 mg dm^{-3}. Thus the level of copper in all the samples is below the WHO limit. Copper level above the permissible limit of WHO can cause a bitter metallic taste in water and result in blue-green stains on plumbing fixtures. Stomach-intestinal distress such as nausea, vomiting, diarrhea and stomach cramps are the health problems associated with copper contamination in water. Copper is also an essential micronutrient and is required by the body in very small amount. People with Wilson's disease, are more sensitive to copper deficiency.

Iron is one of the most troublesome elements in water supplies. Rainwater as it infiltrates the soil and underlying geologic formations dissolves iron, causing it to seep into aquifers that serve as sources

Table-5: WHO recommended Guidelines for drinking water [11].

Parameters	WHO Guidelines	Parameters	WHO Guidelines
Color	Colorless	Chlorides	250 mg dm^{-3}
Odor	Odorless	Iodide [18]	0.001 g daily
Taste	Tasteless	Fluoride	2.0 mg dm^{-3}
Temperature	12°C	Nitrates	45 mg dm^{-3}
pH	6.5-9.2	Nitrites	0.1 mg dm^{-3}
Specific Conductance	400 μS cm^{-1}	Free Ammonia	0.5 mg dm^{-3}
Total solids	505 mg dm^{-3}	Sulphates	250 mg dm^{-3}
Total suspended solids	5.0 mg dm^{-3}	Calcium	100 mg dm^{-3}
Total dissolved solids	500 mg dm^{-3}	Magnesium[15]	36.45 mg dm^{-3}
Total hardness (as $CaCO_3$)	500 mg dm^{-3}	Copper	3 mg dm^{-3}
Total Alkalinity (as $CaCO_3$)	500 mg dm^{-3}	Iron	1.0 mg dm^{-3}
BOD	6.0 mg dm^{-3}	Potassium	12 mg dm^{-3}
COD	10 mg dm^{-3}	Sodium	250 mg dm^{-3}
Dissolved Oxygen	≥ 3 mg dm^{-3}	Zinc	15 mg dm^{-3}

of groundwater for wells. Iron is mainly present in water in two forms, either the soluble ferrous iron or the insoluble ferric iron. Water containing ferrous iron is clear and colorless. When exposed to air in the pressure tank or atmosphere, the water turns cloudy and a reddish brown substance begins to form. This sediment is the oxidized or ferric form of iron that will not dissolve in water. Iron is not hazardous to health, but it is considered a secondary or aesthetic contaminant. Essential for good health, iron helps to transport oxygen in the blood. Dissolved ferrous iron gives water a disagreeable taste. When the iron combines with tea, coffee and other beverages, it produces an inky, black appearance and a harsh, unacceptable taste. The iron in the water samples of Dir districts was found in the range of 0.01-0.11 mg dm^{-3} (Table 4) which is below the maximum limits of WHO i.e. 1.0 mg dm^{-3}. Iron limits for drinking water are based on aesthetic parameters rather than on toxicity.

Potassium ranks seventh among the elements in order of abundance, yet its concentration in most drinking waters reaches 20 mg dm^{-3}. Occasionally brines may contain more than 100 mg dm^{-3} of potassium. The level of potassium in the water samples of Dir districts is in the range of 0.0-6.0 mg dm^{-3}. The maximum WHO recommended limit for potassium is 12 mg dm^{-3}. Among the water samples, the samples coded No. 10, 15, 16, 19 and 38 had undetectable amount of potassium, while sample No. 6 had maximum level i.e. 6.00 mg dm^{-3}. But as apparent from Table 4 many of the samples had level of potassium of about 1.00 mg dm^{-3}, which is well below the WHO recommended limit.

Sodium was found in water samples of Dir districts in the range of 3.0-24.0 mg dm^{-3} (Table 4), which is lower than the WHO maximum acceptable concentration i.e. 250 mg dm^{-3}. Sodium in drinking water is not of a health concern for most people, but may be an issue for someone with heart disease, hypertension, kidney disease, circulatory illness or on sodium controlled diet. Studies have shown that reducing salt intake will lower blood pressure in people with hypertension, but it can not be conclusively inferred that increased sodium intake will cause hypertension [19].

Experimental

Water samples of springs, wells, streams and rivers were collected from fifty one different locations of upper Dir and lower Dir districts, in clean polyethylene bottles in the shinny days of the month of January. Before sampling each bottle was rinsed to be pre-concentrated with the sample of water. The bottles were caped and carried to the laboratory immediately for analysis. The water samples were coded and their locations have been shown in the Fig 1 and Table-1.

All the stock solutions were prepared with distilled water. All the reagents used were of analytical grade (Merck & BDH) and were not subjected to any further purification. The instruments used were calibrated before each analysis. pH of water samples was determined by pH meter [HI 8428, Hana]. The levels of total hardness, calcium and magnesium were determined by using 0.01 M EDTA as titrant and Muroxide and Erichrome black T as indicators [19, 20]. The levels of total alkalinity, total solid, total dissolved solid, chlorides, sulphates, iodide and fluorides were determined by standards methods of American Public Health Association [21]. The levels of total solid and total dissolved solid were determined by gravimetric methods. Total alkalinity was determined by titration method. The level of ammonia was determined by nesslerisation method using spectronic 20 [Milton Ray Spectronic 20D]. Nitrate was determined by hydrazine reduction method. Chloride was investigated by mercuric nitrate method. Sulphate was determined by gravimetric method using barium chloride as a precipitant. The levels of fluoride and iodide were determined by complexone method and catalytic reduction method respectively. The levels of metals like Fe, Cu, Zn, Na and K were determined by atomic absorption spectrophotometer [Perkin Elmer 3300, equipped with HGA-600 graphite furnace]. The mean values of the results along with standard deviations have been presented in Tables 2-4.

Conclusions

From the investigation of the levels of the physiochemical parameters of water samples obtained from fifty one different locations of Dir districts, it may be inferred that many of the water samples are suitable for drinking purposes and domestic uses but some have objectionable levels of certain parameters, The water of springs at Dir High school No.1 (sample No.12) and at road side near Muhansharif (sample No. 16) may be considered unsuitable for domestic uses and drinking purposes because of high level of total solids. Total hardness of water samples No. 12, 16, 21 and 23 are higher than APHA limit. The water sample of well at Khal bazaar has level of calcium higher than recommended by WHO. Some of the samples have high amount of total solids, therefore for its control extensive plantation in different regions of the districts and prevention of deforestation must be encouraged. The water sample No. 7, 8, 9, 12, 16, 26, 40, 44, 45 and 46 have high level of sulphate which may be due to leaching of rocks. All the water samples have very low levels of zinc, fluoride and iodide. The inhabitants of theses districts should be advised to use iodised salt and dental cream rich with fluoride. In the present investigation it has been observed that a few water samples have levels of metals (such as calcium and magnesium) which do not correspond with the levels of cations (like sulphates and chlorides) with which they are generally combined. This may be due to the occurrence of these metals in other forms (such as bicarbonates, phosphates, etc.), because Dir is a hilly area and leaching of different minerals by water may occur. The potable water of the hilly areas like Dir districts should be regularly examined in order to have a check upon the increase of water pollution, due to human activities and soil erosion because of deforestation.

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