Asian Journal of Chemistry Vol. 19, No. 7 (2007), 5279-5304

Quality of Spring Water in the Catchment Areas of the Indus River

M. Aslam Mirza, M.Y. Khuhawar* and Rafee Arain
Dr. M.A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan
Fax: (92)(221)771372, Tel: (92)(221)771443
E-mail: kanwalseemi@yahoo.com; makashmiri2006@yahoo.com

A systematic and detailed study of the quality of spring water was conducted to assay the influence of rainfall, snow melt, deforestation, urban sewage and per se geochemical interactions. The area covered is at the foothills of Himalayas forming predominantly the catchments area of Indus river. 30 Springs were sampled over a period of two years on seasonal and hydrological cycle basis. The preliminary results indicate TDS for half of the water samples within 115-499 mg/L, for the remaining half it exceeds 500 mg/L. Inter sample, seasonal and hydrological cycle variance indicate no significant change in elemental composition and organic matter content but those contaminated with sewage of deforested locations show substantial variation both in elemental and organic matter content. Low rainfall also deters the dilution of pollutants occurring both naturally and through human activity. This study provides the database of the quality of water of Indus river.

Key Words: Spring water quality, Hydro-geochemistry, Chemical assay, Muzaffarabad.

INTRODUCTION

The present work covers a representative study of the catchments area of the Indus river in Kashmir at the foot hills of Himalayas with a population of more than 3.2 million (population density: 330 persons/km^2).The results of this preliminary study provide a credible guideline and a data base on spring water and variation in its quality. Three tributaries Neelum, Jhelum and Poonch across the studied area of more than 13000 km^2 with their stock of spring water, snow melt and surface run-off form the mother stream of Indus river.

Concurrently, human activities in the recharge area also bring about significant changes in spring water, affecting human health[1]. In urban areas like Muzaffarabad, Bagh, Bhimber, Mirpur and Kotli (Kashmir), the main source of spring water contamination are leaking sewage systems, gasoline stations, septic tanks, domestic and industrial effluents and leachate from waste disposal sites[2-8]. Rapid urbanization, level of industrial activity and population growth in the area have increased significantly the elemental composition of drinking and irrigation water because of the effluents from post redox industrial processes[9-15]. Saddle-shaped ridges where most of the towns have been developed also happen to be the recharge area of these springs. The domestic sewage of the towns is disposed off untreated through landfills and unlined open drains. In haphazardly growing towns of Authmuqam, Palandri, Trarkhal, Fatehpur, Rawalakot, Abaspur, Dhirkot, Charhoi, Hattian and Haveli, the pollution of surface water is obvious and is due to shallow soil column in the town areas for reverse osmosis of polluted surface water and the removal of its contaminants before being added as recharge to the subsoil water stock. The polluted subsoil water thus re-emanates with spring discharge.

Geology of area

The sampled area in Kashmir lies between longitude 73º-75º and latitude 33º- 36º and comprises of 13297 square Km area. It extends from the plains of Bhimber at northern edge of the Punjab through the outlying foothills of Himalayas, to the mountains in the north at 6325 m above sea level. The elevation ranges from 360 m in the south to 6325 m in the north. The average annual rainfall is of 1300 mm. It is a land strip in the shape of a crescent, 400 Km in length and varying width 15-60 Km. The snow line in winter is around 1200 m above sea level, while in summer it rises to 3300 m (Table-1)[16].

Geological study of the area was carried out by Meddlicott[17], Lydekker[18] and Middlemiss[19]. The area consists of Siwalik group of rocks in mostly the western part of the Poonch District along with the eastern bank of the Jhelum river. These rocks crop out between Kohala and Azad Pattan. The eastern contact runs in an irregular fashion from Hajeera through Rawalkot to Dhirkot. Wadia[20] carried out more detailed work on the targeted area and divided the Siwaliks of Kashmir into Lower Palandri, Middle Mang and Upper Sand Rock Stage. It may be pointed out here that both Palandri and Mang are located in Poonch District. The rocks between Titwal and Loat comprise of psammitic-pelitic sequence resembling tanol formation.The rocks found in the vicinity of Authmuqam have also been considered as a part of psammite pelite sequence. Kotli area indicates Precambrian rock formation[21]. The rocks consist of granite and crystalline groups and are mainly composed of chlorite, muscovite schists, mica granite, sand stone, quartzite, calcite, pyrite, *etc*. The geological formation of the area, *i.e.*, the fractured mica schists interbedded with thin bands of quartzite, granite gneiss and nonfoliated granitic rocks acting as barrier to the ground water flow and forming springs. Fractured mica schists covered with thin layer of top soil (0.15-1.50 m) provide a permeable recharge zone for groundwater[22].

TABLE-1
AREA, POPULATION* AND GEOGRAPHICAL FEATURES OF THE STUDY AREA

Longitude	73^0-75^0
Latitude	33^0-36^0
Area	13297 Sq.Km
Population	> 3.2 (million)
Topography	Mainly hilly and mountainous with valleys and plains at some places. Muzaffarabad, Poonch, Kotli fall in mountainous zone; Mirpur and Bhimber districts lie in the foot hills
Climate	Sub-tropical high land type
Rain fall (average)	1300 mm
Elevation from sea	Range from South: 360 meters Range from North: 6325 meters
Snowline	In winter: around 1200 meters In summer: around 3300 meters
Main Rivers	Neelum, Jehlum and Poonch; collect water from the study area and embrace Indus river in Pakistan
Population density (average)	330 persons/Km^2
Growth rate (average)	2.33 %
Urban rural ratio	12.5: 87.5
Villages	1646

Source: Population Census Organization-Islamabad, Pakistan.
*According to census 1998

Sampling: Prior to sampling a detailed survey of the area was undertaken. Spring location and *in situ* testing of physico-chemical parameters was carried out in order to plan proper sampling strategy (Table-2). The objective of the field survey was to locate and select the springs for the study. Since springs represent underground water[23], thirty perennial springs having sufficient discharge throughout the year were selected for the study (Tables 3a-e). The springs selected district wise were seven from Bhimber, six Kotli, five Sudhnoti, six Poonch, five Bagh and one Muzaffarabad. A total of 30 springs further classified into sub categories on the basis of their altitude, discharge, proximity to urban areas, level of forestation and precipitation records were targeted (Table-2).

The springs of group G_1 are located at higher altitude but in depressions with relatively higher population density (20000-30000) and the springs of group G_2 are perched on hillocks with medium population (10000-20000) intensity around the springs. The springs of group G_3 are present at high altitude with thin population (3000-15000). Springs of group G_4 lye within plains, but with thin population (2000-6000) (Table-2). A number

TABLE-2
CLASSIFICATION OF SPRINGS BASED ON POPULATION, ALTITUDE, GEOLOGY AND CLIMATE

Spring code	Description
G1	Altitude: 275-1626 m above sea level (springs present in depressions) Population: 20000-30000 Climate: High land subtropical type
G2	Altitude: 975-1982 m above sea level (springs situated on hillocks and slopes) Population: 10000-20000 Climate: High land subtropical type
G3	Altitude: 800-1676 m above sea level (springs present at high a altitudes in thin population) Population: 3000-15000 Climate: High land subtropical type
G4	Altitude: 700-1372 m above sea level (springs present in plains, slopes in thin population) Population: 2000-6000 Climate: High land subtropical type

G1 = S_4, S_{11}, S_{13}, S_{18}, S_{19}, S_{28}
G2 = S_2, S_5, S_{16}, S_{17}, $S_{25,}$ S_{26}
G3 = S_7, S_{12}, S_{14}, S_{15}, S_{20}, S_{21}, S_{22}, S_{23}, S_{24}, $S_{29,}$ S_{30}
G4 = S_1, S_3, S_6, S_8, S_9, S_{10}, S_{27}

of springs are present as cave type depressions within the mountains while others in artificial well type depressions. Most of the water consumed from the springs is recharged during the night. Some of the springs also indicate continuous flow of water, which is either stored in artificial reservoir or is reabsorbed in the bed.

Mode: The sampling mode was simple grab method. At least 2 samples were taken by 24 h, 12/4 months and 24 per hydrological year of 12 months. Pre-washed high density polythene bottles were suspended, at predetermined depths through a Secchi disc, from the surface and stopper removed by a sharp jerk through an attached line. Each spring was sampled laterally at the extremes, in the middle and vertically at varying depths at these points of the stream. Sub-samples thus taken were later integrated into a composite sample. Field measurements included pH, conductivity, dissolved oxygen (DO) and temperature of the stream and air. For elemental analysis each sample was acidified to pH < 2; for organic matter, fixed with $HgCl_2$. Separate samples were taken for specific analysis (Tables 3a-e).

EXPERIMENTAL

Dissolved oxygen (DO) in the samples was determined by Wrinkler method[24]. Chemical oxygen demand was estimated by micro-dichromate oxidation method[25]. Hardness, chloride and alkalinity were determined by

TABLE-3a
SAMPLING SITES OF SPRINGS OF THE STUDY AREA

Sample No.	Location of the Springs
S_1	Banwalian Painga spring Samahni District Bhimber
S_2	Baghsar Bluken spring District Bhimber)
S_3	Chowki Soona roadside spring District Bhimber
S_4	Bawli Bhimber city District Bhimber
S_5	Jandi Chountra spring District Bhimber
S_6	Paharshala spring District Bhimber
S_7	Charhoi Main Bazar spring Distric Kotli
S_8	Anoi Saroota spring District Kotli
S_9	Spring near boys degree college Pallandi Disrict Sudhnoti
S_{10}	Pehata spring District Sudhnoti
S_{11}	Housing Scheme spring Rawalakot District Poonch
S_{12}	Parat spring District Poonch
S_{13}	Main supply Bagh spring near lari adda District Bagh
S_{14}	Hari Ghail spring District Bagh
S_{15}	Dheer Kot Jamia Masjid spring District Bagh
S_{16}	Tatta Pani hot spring number 1 District Kotli
S_{17}	Tatta Pani hot spring number 2 Distict Kotli
S_{18}	Hajeera military zone spring District Poonch
S_{19}	Bawli Bazar Abbaspur spring District Poonch
S_{20}	Nakkar Nagni Abbaspur spring District Poonch
S_{21}	Spring below bridge Hajeera Town District Poonch
S_{22}	Kamal Nala Dheer Kot spring District Bagh
S_{23}	Ziarat spring Athmaqam spring District Mazaffarabad
S_{24}	Nihala spring Samahni District Bhimber
S_{25}	Spring near Jamia Masjid Tarar Khal District Sudhnoti
S_{26}	Rawalpindi road spring near Pilot High school Pallandri District Sudhnoti
S_{27}	Spring near the house of captain Sabir Farid Pallandri District Sudhnoti
S_{28}	Bawali spring Sensa District Kotli
S_{29}	Deegwar spring Forward Kahuta District Bagh
S_{30}	Parawa Chowk spring Fateh Pur District Kotli

titration with standard EDTA, silver nitrate and hydrochloric acid. Conductivity, salinity and total dissolved solids (TDS) were evaluated with Orion 115 conductivity meter. The pH was recorded with Orion 420 A pH meter. Kjeldahl nitrogen was determined by using standard procedure[24]. Orthophosphate, nitrate and nitrite were determined by spectrophotometery. Orthophosphate was determined by reducing phosphomolybdic acid formed with ascorbic acid to molybdenum blue. Total phosphate was estimated by persulphate acid hydrolysis, followed by determination as for orthophos-

TABLE-3b
MEAN VALUES OF PHYSICOCHEMICAL PARAMETERS IN THE SPRING WATER OF THE INDUS RIVER

Parameters	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
pH (25ºC)	6.750	7.630	6.910	6.930	7.230	7.080	7.020	6.780	6.980	6.720
EC (µS/cm)	776.0	780.0	779.0	1210	984.0	792.0	479.0	750.0	790.0	795.0
TDS (mg/L)	496.6	499.0	498.6	772.4	630.0	506.9	306.7	480.0	505.6	508.8
Salinity (g/L)	0.300	0.300	0.300	0.600	0.400	0.370	0.200	0.300	0.370	0.300
HCO_3 (mg/L)	391.3	380.8	376.6	280.0	348.1	438.2	244.9	301.3	250.0	240.0
TH (mg/L)	328.0	208.3	357.0	221.7	170.0	364.7	203.6	309.3	330.6	322.3
Cl^- (mg/L)	12.64	17.74	33.44	85.00	16.25	17.66	19.03	40.80	54.06	52.52
SO_4 (mg/L)	15.46	18.62	26.43	97.00	32.80	20.07	28.42	26.85	27.85	21.31
NO_2-N (mg/L)	0.006	0.003	0.007	0.470	0.009	0.014	0.005	0.005	0.005	0.056
NO_3-N (mg/L)	2.736	2.816	3.928	19.876	4.286	3.978	3.407	5.563	4.172	4.286
K.N. (mg/L)	0.800	1.045	5.91	0.855	0.811	1.098	1.060	0.890	1.650	0.950
O-PO_4 (mg/L)	0.188	0.202	0.208	0.163	0.177	0.197	0.266	0.251	0.190	0.217
T-PO_4 (mg/L)	0.233	0.266	0.228	0.184	0.193	0.221	0.269	0.334	0.226	0.251
DO (mg/L)	9.060	3.32	9.330	3.37	3.895	6.090	2.843	8.104	6.815	3.373
BOD (mg/L)	8.100	8.060	2.40	10.67	8.820	2.220	3.780	1.950	5.140	3.080
COD (mg/L)	8.160	25.00	18.00	40.00	21.00	28.00	32.00	38.00	24.48	26.00
Na (mg/L)	27.28	74.48	51.19	66.11	74.55	37.63	25.00	24.7	16.69	22.45
K (mg/L)	15.59	13.49	5.320	10.97	11.15	4.960	2.600	2.110	3.990	4.220
Ca (mg/L)	225.0	53.33	80.03	94.00	83.02	193.70	80.28	167.2	150.48	122.8
Mg (mg/L)	45.89	78.95	94.88	24.12	56.55	66.18	45.50	24.69	30.74	38.75
Fe (mg/L)	0.165	0.015	0.013	0.016	0.013	0.008	0.011	0.014	0.015	0.026
Cu (mg/L)	0.006	0.002	0.004	0.003	0.001	0.001	0.002	0.003	0.003	0.002
Zn (mg/L)	0.015	0.011	0.017	0.016	0.022	0.017	0.020	0.023	0.069	0.094
Ni (mg/L)	0.015	0.011	0.013	0.014	0.018	0.021	0.024	0.014	0.029	0.041
Pb (mg/L)	0.010	0.001	0.004	0.023	0.051	0.006	0.006	0.004	0.004	0.062
Cd (mg/L)	0.004	0.003	0.005	0.051	0.004	0.065	0.005	0.002	0.078	0.067
Co (mg/L)	0.041	0.042	0.056	0.063	0.058	0.060	0.078	0.061	0.046	0.107
SAR	0.613	2.132	1.299	2.220	2.185	0.844	0.785	0.666	0.458	0.615

phate. Nitrate was determined after derivatization with brucine sulphate. Nitrite was estimated using N-naphthyl ethylenediamine as derivatizing reagent as reported[24]. Sulphate was determined by turbidimetery as $BaSO_4$ using Hitachi 220 spectrophotometer. The metal ions Na, K, Ca, Mg, Fe, Pb, Cu, Zn, Ni, Cd and Co were determined with Varian Spectr AA-20 atomic absorption spectrometer with standard burner head and air acetylene flame as recommended by the manufacturer. The analysis was carried out in triplicate with integration and delay time 3 s each. Na, K, Ca and Mg were determined after appropriate dilution. Sample (250 mL) containing nitric acid (1 mL) was heated gently at 90-95ºC and was concentrated to

TABLE-3c
MEAN VALUES OF PHYSICOCHEMICAL PARAMETERS IN THE SPRING WATER OF THE INDUS RIVER

Parameters	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}	S_{17}	S_{18}	S_{19}	S_{20}
pH (25ºC)	7.150	6.990	7.330	7.240	6.940	6.960	6.870	8.060	7.050	7.410
EC (µS/cm)	898.4	792.3	1073	470.7	533.0	942.5	955.5	907.8	914.0	380.5
TDS (mg/L)	575.0	507.1	686.8	301.2	341.1	553.2	611.9	581.0	585.0	243.5
Salinity (g/L)	0.200	0.300	0.500	0.230	0.260	0.500	0.500	0.200	0.300	0.200
HCO_3 (mg/L)	201.3	220.0	130.0	190.0	172.5	230.7	235.5	220.4	24.3	160.5
TH (mg/L)	132.5	331.7	159.2	266.6	256.7	257.2	268.0	233.5	253.4	159.4
Cl^- (mg/L)	155.0	78.61	165.34	32.67	19.62	182.6	209.2	212.0	185.0	3.160
SO_4 (mg/L)	162.0	13.97	140.44	20.22	11.56	26.77	53.00	197.0	189.0	12.28
NO_2-N (mg/L)	0.070	0.010	0.075	0.090	0.007	0.314	0.219	0.120	0.220	0.123
NO_3-N (mg/L)	16.615	4.632	15.152	3.351	3.039	0.433	0.108	12.25	13.30	2.163
K.N. (mg/L)	0.944	1.145	1.275	1.059	3.989	0.975	0.854	0.589	0.986	0.459
O-PO_4 (mg/L)	0.275	0.194	0.212	0.190	0.040	0.049	0.013	0.026	BDL	0.033
T-PO_4 (mg/L)	0.318	0.222	0.221	0.214	0.046	0.056	0.025	0.034	0.001	0.46
DO (mg/L)	3.700	8.219	4.200	5.45	6.374	4.145	4.350	4.033	4.335	6.555
BOD (mg/L)	16.75	0.88	9.632	4.87	5.110	0.860	0.990	12.70	11.300	5.720
COD (mg/L)	42.50	13.20	28.00	12.00	8.000	16.00	16.50	22.00	24.00	6.120
Na (mg/L)	43.20	43.84	36.86	6.860	9.690	100.3	101.1	45.04	15.35	19.47
K (mg/L)	2.338	3.490	13.80	3.510	1.590	21.39	21.68	8.500	5.400	1.790
Ca (mg/L)	104.88	135.8	222.3	111.1	102.09	99.20	53.9	117.2	136.0	75.32
Mg (mg/L)	53.07	18.88	66.17	20.89	21.84	68.41	69.60	51.52	61.82	22.25
Fe (mg/L)	0.018	0.027	0.021	0.027	0.016	0.032	0.039	0.034	0.028	0.042
Cu (mg/L)	0.002	0.003	0.005	0.003	0.001	0.008	0.007	0.009	0.005	0.011
Zn (mg/L)	0.021	0.061	0.124	0.031	0.076	0.040	0.058	0.033	0.130	0.034
Ni (mg/L)	0.025	0.035	0.038	0.032	0.038	0.037	0.022	0.051	0.040	0.029
Pb (mg/L)	0.007	0.007	0.004	0.006	0.005	0.200	0.1680	0.170	0.150	0.158
Cd (mg/L)	BDL	0.076	0.064	0.003	0.002	0.053	0.081	0.075	0.004	0.101
Co (mg/L)	0.071	0.085	0.099	0.066	0.078	0.063	0.070	0.082	0.087	0.091
SAR	0.974	1.320	0.595	0.205	0.200	2.677	2.660	0.483	0.358	0.719

about 5-8 mL. The solution was transferred to volumetric flask and final volume adjusted to 10 mL. The solution was analyzed for the contents of Fe, Pb, Cu, Zn, Ni, Cd and Co by air acetylene flame atomic absorption spectrometer.

RESULTS AND DISCUSSION

During the pre-sampling field survey, it was noted that all the springs discharge water under gravity, suggesting that the aquifers in the studied area, are of unconfined nature. Such aquifers are more prone to contamination through direct percolation of contaminated surface waters[26,27]. The data

TABLE-3d
MEAN VALUES OF PHYSICOCHEMICAL PARAMETERS IN THE SPRING WATER OF THE INDUS RIVER

Parameters	S_{21}	S_{22}	S_{23}	S_{24}	S_{25}	S_{26}	S_{27}	S_{28}	S_{29}	S_{30}
pH (25°C)	7.380	7.400	7.050	7.460	7.310	7.210	7.000	6.920	7.760	7.840
EC (µS/cm)	457.5	687.0	179.0	472.5	845.0	867.0	772.0	874.0	226.0	468.7
TDS (mg/L)	268.8	439.6	114.6	302.4	541.0	584.8	494.08	529.36	145.0	300.0
Salinity (g/L)	0.200	0.200	0.200	0.200	0.100	0.300	0.300	0.300	0.100	0.100
HCO_3 (mg/L)	180.0	158.0	48.60	204.0	230.1	280.0	301.0	297.0	80.0	130.0
TH (mg/L)	195.0	169.0	60.00	221.0	219.0	26.00	321.0	308.0	84.00	280.0
Cl^- (mg/L)	63.8	3.66	3.091	15.66	67.17	85.00	95.70	172.0	42.08	0.258
SO_4 (mg/L)	15.81	23.69	42.32	13.66	17.88	23.94	22.02	144.0	18.89	27.98
NO_2-N (mg/L)	0.128	0.126	0.040	0.013	0.014	0.019	0.210	0.707	BDL	0.001
NO_3-N (mg/L)	1.903	2.458	2.429	2.113	0.381	1.358	2.855	10.871	BDL	0.189
K.N. (mg/L)	0.659	0.889	0.475	0.890	0.978	0.852	0.741	0.654	0.280	67.35
O-PO_4 (mg/L)	0.032	0.032	0.015	0.021	0.863	0.708	0.586	0.499	0.519	0.401
T-PO_4 (mg/L)	0.044	0.044	0.019	0.030	0.894	0.846	0.595	0.493	0.611	0.566
DO (mg/L)	7.050	9.105	7.095	7.260	4.830	6.207	3.103	1.724	6.900	6.154
BOD (mg/L)	2.070	6.770	2.140	1.190	6.920	4.770	13.11	6.150	1.350	1.760
COD (mg/L)	7.890	8.320	4.200	8.970	9.320	10.12	10.22	11.3	3.43	3.65
Na (mg/L)	17.42	36.45	7.808	14.00	30.05	52.79	45.30	71.00	16.56	40.10
K (mg/L)	2.620	2.280	4.190	6.400	4.620	2.840	3.800	4.500	3.650	2.620
Ca (mg/L)	105.3	103.4	32.90	118.0	135.0	162.9	176.0	197.0	50.81	78.00
Mg (mg/L)	27.38	52.40	8.690	33.30	47.70	48.49	21.20	12.50	12.68	27.50
Fe (mg/L)	0.024	0.036	0.025	0.021	0.102	0.046	0.057	0.045	0.044	0.032
Cu (mg/L)	0.007	0.005	0.003	0.009	0.019	0.010	0.039	0.010	0.009	0.008
Zn (mg/L)	0.027	0.047	0.162	0.036	0.037	0.009	0.014	0.010	0.006	0.003
Ni (mg/L)	0.026	0.026	0.010	0.020	0.037	0.022	0.019	0.016	0.031	0.027
Pb (mg/L)	0.172	0.237	0.086	0.165	0.109	0.083	0.095	0.082	0.005	BDL
Cd (mg/L)	0.072	0.099	0.045	0.067	0.191	0.080	0.089	0.176	0.010	1.062
Co (mg/L)	0.077	0.082	0.044	0.071	0.080	0.048	0.052	0.045	0.024	0.023
SAR	0.540	1.178	0.576	0.415	0.801	1.317	1.211	1.875	0.751	1.402

on mean values of physico-chemical characteristics of spring water are summarized in (Tables 3b-e) and reveal varying nature of the spring water. The difference in the quality of water is largely due to difference in the bed rock composition, variation in recharge environment of the zones and influence of human settlements[28].

pH of Spring water: The pH of all the springs varied within 6.72 to 8.06. The springs S_1, S_3, S_4, S_8, S_9 and S_{10}, lying in the plains or at the foothills, indicate pH < 7 because of leaching of acidic water by the decomposition of pine litters over the ground surface[22]. However, the springs S_2, S_7, S_{11}, S_{13}, S_{14}, S_{19}, S_{20}, S_{21}, S_{22}, S_{23}, S_{24}, S_{25}, S_{26}, S_{27}, S_{29} and S_{30} present

TABLE-3e
MINIMUM AND MAXIMUM VALUES OF PHYSICOCHEMICAL PARAMETERS OF SPRING WATER WITH STATISTICAL PARAMETERS

Parameters	Min.	Max.	Mean	Mode	Median	SD	SE
pH	6.72	8.06	7.1787	7.05	7.065	0.3299	0.060
EC (µS/cm)	179	1210	728.38	-	785	244.90	44.712
TDS (mg/L)	114.6	772.4	463.668	-	502.3	156.4897	28.571
Salinity (g/L)	0.1	0.6	0.2877	0.3	0.3	0.122	0.022
HCO_3 (mg/L)	24.3	438.2	231.5033	280	230.4	99.0775	18.089
TH (mg/L)	26	364.7	233.89	-	243.45	87.4298	15.962
Cl (mg/L)	0.258	212	71.3586	85	47.3	68.5336	12.512
SO_4 (mg/L)	11.56	197	49.708	-	25.185	56.2499	10.270
NO_2-N (mg/L)	0.00	0.707	0.1029	0.005	0.0295	0.1585	0.029
NO_3-N (mg/L)	0.00	19.876	5.022	4.286	3.195	5.284	0.965
K N (mg/L)	0.28	67.35	3.37	0.89	0.917	12.133	2.215
O-PO_4 (mg/L)	0.00	0.863	0.226	0.19	0.192	0.218	0.040
T-PO_4 (mg/L)	0.001	0.894	0.271	0.221	0.224	0.239	0.044
DO (mg/L)	1.724	9.33	5.566	-	5.77	2.074	0.379
BOD (mg/L)	0.86	16.75	5.642	-	4.99	4.237	0.774
COD (mg/L)	3.43	42.5	17.546	28	14.6	11.176	2.040
Na (mg/L)	6.86	101.1	39.109	-	36.655	25.701	4.692
K (mg/L)	1.59	21.68	6.514	2.62	4.205	5.585	1.020
Ca (mg/L)	32.9	225	118.898	-	108.2	50.316	9.186
Mg (mg/L)	8.69	94.88	41.751	-	42.125	22.066	4.029
Fe (mg/L)	0.008	0.165	0.034	0.015	0.027	0.031	0.006
Cu (mg/L)	0.001	0.039	0.007	0.003	0.005	0.007	0.001
Zn (mg/L)	0.003	0.162	0.042	0.017	0.029	0.04	0.007
Ni (mg/L)	0.01	0.051	0.026	0.014	0.026	0.01	0.002
Pb (mg/L)	0.00	0.237	0.069	0.004	0.037	0.075	0.014
Cd (mg/L)	0.00	1.062	0.088	0.004	0.065	0.191	0.035
Co (mg/L)	0.023	0.107	0.065	0.063	0.065	0.021	0.004

at a higher altitude indicated pH values 7.0-8.06 because of addition of calcium and magnesium due to rock erosion. However, seasonal changes are insignificant and fall within the WHO water quality standards[29].

Electrical conductivity, total dissolved solids, DO, BOD and COD: The electrical conductivity (EC) and total dissolved solids (TDS) indicated a significant variation among the springs. EC and TDS varied within the range 179-1210 µS/cm and 115-772 mg/L. An insignificant difference was observed in EC and TDS with seasonal variation for all the springs. The springs located within the depressions and higher population indicated EC within 845-1210 µS/cm and TDS 529-772 mg/L due to domestic waste-water. The springs present within plains with medium population density indicated EC 845-984 µS/cm corresponding to 541-630 mg/L. The springs at high altitude with thin population indicated EC within 179-792 µS/cm corresponding to 115-507 mg/L, while springs at the plains, but thinner in population indicated EC 750-795 µS/cm corresponding to 480-509 mg/L (Tables 3a-e).

Concurrently a look at the BOD, COD, DO values also indicate a significant change in BOD and COD values of springs located in close proximity of urban settlements. Table-1b depicts data of two springs (S_3, S_4) one with a mix up of sewage water and the other without. There is significant increase in BOD and COD values and decrease in DO due to nutrients of organic matter brought in by the urban sewage (Fig. 1). The seasonal data on both the springs show marginal seasonal variations. The dissolved oxygen indicates the variation within 1.72-9.63 mg/L. Low oxygen contents have been observed for springs with little storage capacity and were sampled immediately after oozing. The springs with large storage capacity and greater surface area indicated higher DO contents, a contention supported by the absence of any odour of water.

Fig. 1. Effect of sewage on the quality of spring water

Nitrite, Nitrate and Kjeldahl nitrogen (K N): 24 Out of 30 springs assayed indicate nitrate concentration within the permissible limits of WHO[30,31]. However, water samples collected from the springs of group G1 with higher population indicate higher values within 10.87-19.88 mg/L compared to 0.19-4.6 mg/L for the springs at higher altitude with thinner population (Fig. 2, Table-4).

Nitrite is more toxic and Kjeldahl nitrogen indicates the recent pollution from wastewater. The nitrite and Kjeldahl nitrogen were also observed in higher concentration within 0.01-0.71 and 0.62-6.28 mg/L for springs surrounded by higher population compared to 0.001-0.13 and 0.26-1.15 mg/L, respectively from springs at high altitude with thinner population.

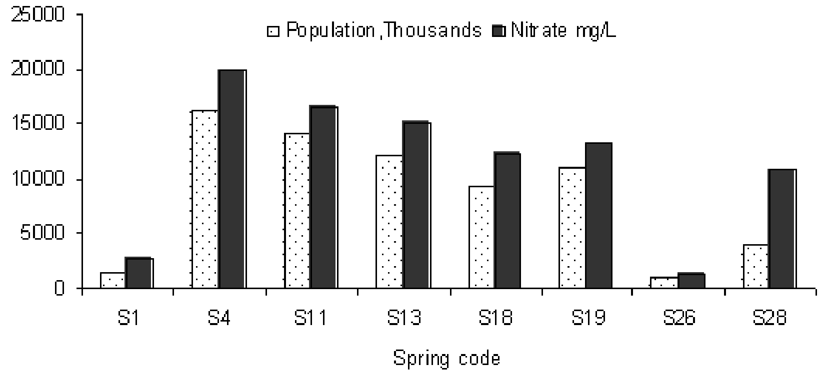

Fig. 2. Correlation between population and nitrate content

TABLE-4
CORRELATION BETWEEN POPULATION AND NITRATE OF THE STUDY AREA

Spring code	Population (Thousands)	Nitrate mg/L
S_1	0.987	2.736
S_4	16150	19.876
S_{11}	14211	16.615
S_{13}	12100	15.152
S_{18}	9500	12.25
S_{19}	7600	13.30
S_{26}	0.400	1.358
S_{28}	4000	10.871

The results indicate that Kjeldahl nitrogen exceeds the limits of WHO (Table-5). An increase in nitrogen content was generally observed in the springs S_2, S_3, S_6, S_7, S_9, S_{13}, S_{14} and S_{15} with increase in population. Kjeldahl nitrogen (K N), nitrite and nitrate are different forms of nitrogen and may be present in the water due to the decomposition of proteinous compounds that enter through waste water[32]]. Presence of nitrogen of mineral origin is rare in natural waters and presence of nitrogen compounds like Kjeldahl nitrogen, nitrite and nitrate in water indicate pollution by domestic waste water. Nitrate nitrogen is the highest oxidized form of nitrogen in water and WHO standards prescribe 10 mg/L as maximum permissible nitrate concentration of potable water[29]. The concentration of nitrogen in ground water is drawn from the biosphere[33]. Nitrogen is first fixed from the atmosphere and then mineralized by soil bacteria into ammonia. Under aerobic conditions nitrogen is finally converted into nitrate by nitrifying bacteria[34]. For nitrate nitrogen, six samples from the study area exceed the desirable limit of 10 mg/L as per WHO norms (Table-5) (Fig. 3). The consequences of high concentration of nitrogen in drinking water are toxic and cause blue baby disease, methaemoglobinaemia in children and gastric carcinomas[35,36].

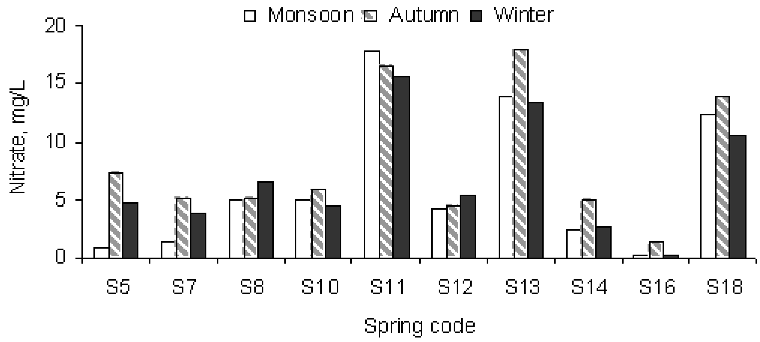

Fig. 3. Seasonal variations of nitrate in spring water

TABLE-5
SPRING WATER SAMPLES OF THE STUDY AREA EXCEEDING THE MOST DESIRABLE /PERMISSIBLE LIMITS OF WHO FOR DRINKING WATER AND THE RESULTING UNDESIRABLE EFFECTS ON HUMAN HEALTH

Parameters	Most desirable limit (1973)	Permissible limit (1973)	Springs exceeding desirable/ permissible limits	Undesirable effects
TDS (mg/L)	500	1500	S_4, S_5, S_6, S_9, S_{10}, S_{11}, S_{12}, S_{13}, S_{16}, S_{17}, S_{18}, S_{19}, S_{25}, S_{26}, S_{28} = 10	Gastrointestinal irritation
NO_3 (mg/L)	10	-	S_4, S_{11}, S_{13}, S_{18}, S_{19}, S_{28} =6	Blue baby
K (mg/L)	10	12	S_1, S_2, S_{13}, S_{16}, S_{17} = 5	Irregular heart beat, diarrhoea, nausea, vomiting, muscle weakness and fatigue
Ca (mg/L)	75	200	S_1, S_{13} = 2	Scale formation
Pb (mg/L)	-	0.01	S_5, S_{10}, S_{17}, S_{18}, S_{19}, S_{20}, S_{21}, S_{22}, S_{23}, S_{24}, S_{25}, S_{27}, S_{28} = 13	Mental retardation in children, lungs cancer, kidney failure, pregnancy disorder
Cd (mg/L)	-	0.005	S_4, S_6, S_9, S_{10}, S_{12}, S_{13}, S_{16}, S_{17}, S_{18}, S_{20}, S_{21}, S_{22}, S_{23}, S_{24}, S_{25}, S_{26}, S_{27}, S_{28}, S_{29}, S_{30} = 20	High blood pressure, hypertension, lungs cancer, prostrate enlargement, emphysema
Total Nitrogen (mg/L)	-	01	S_2, S_3, S_6, S_7, S_9, S_{12}, S_{13}, S_{14}, S_{15} = 9	Toxicity
DO (mg/L)	6.5	8.5	S_1, S_3, S_{22} = 3	Bad odor

Total chlorides and sulphates: Chlorides in spring water vary from 10.98 mg/L in S_5 to 211 mg/L in S_{18} (Fig. 4). The large variations in the chloride across springs suggest a difference in the input level of impurities that contaminate the ground water. The higher chloride level in springs located in densely populated areas (S_{11}, S_{13}, S_{18}) also indicate the influence of human activity in terms of increased pollution due to sewage and domestic waste. Lower concentration levels for springs S_5, S_7, S_8, S_{10}, S_{14}, S_{25}, of lower population density areas, also support the above assertion. Chloride content correlate inversely with the altitude, but linearly with population density. A similar correlation is observed for sulphates; 6.47 mg/L in S_{12} to 204 mg/L in S_{18}, fluctuating only due to urban effluents (Fig. 5).

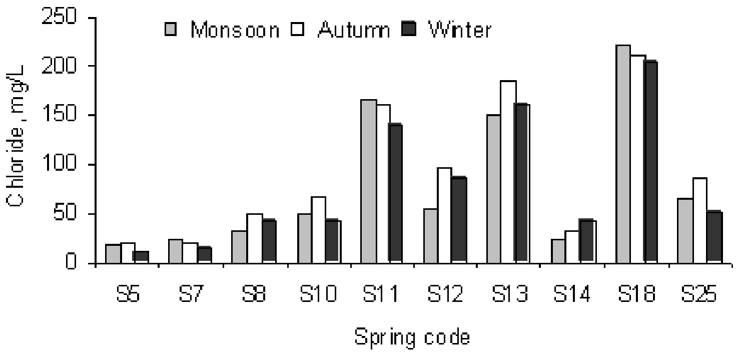

Fig. 4. Seasonal variations of total chlorides in spring water

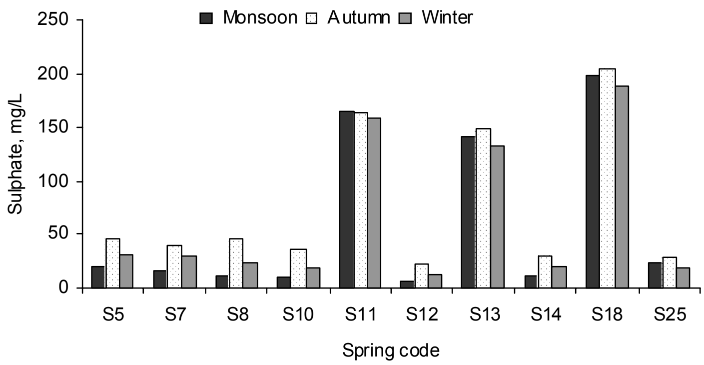

Fig. 5. Seasonal variations of sulphate in spring water

Phosphorous: The phosphorous content (orthophosphate and acid hydrolysable phosphate) of water is mainly due to the composition of the soil or waste generated by human activity, particularly of the detergents. Orthophosphate and acid hydrolyzable phosphate determined for springs with high population were orthophosphate 0.19-0.86 mg/L and total phosphate 0.2-0.9 mg/L and for the springs at high altitude with thin population orthophosphate 0.1-0.5 mg/L and 0.2-0.6 mg/L (Tables 3a-e). The difference between the two may solely be due to phosphate solubility in water.

Metal ion contents (MIC): The concentration of Na, K, Ca and Mg varied significantly within the inter-spring samples Ca being dominant throughout (Tables 3b-e) in the order: Ca > Mg > Na > K (Fig. 6). Ca was within 32.9-225 mg/L; Na 6.86-101.1 mg/L; Mg 8.96-94.9 mg/L and, K 1.59-21.7 mg/L. MIC found no correlation with population density and seasons (Fig. 7).

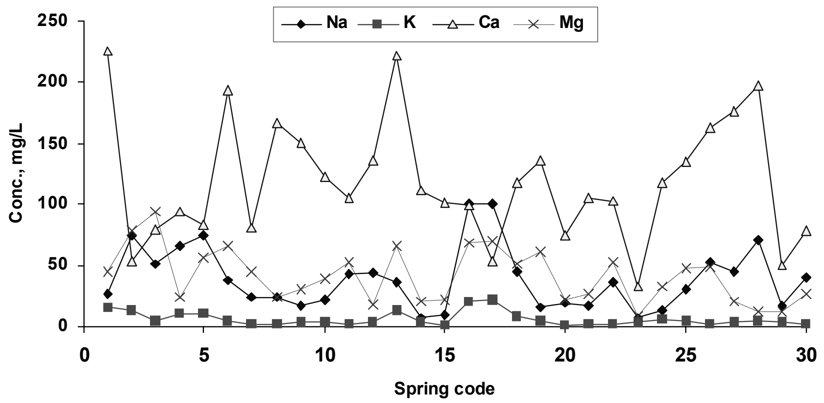

Fig. 6. Major cations in spring water

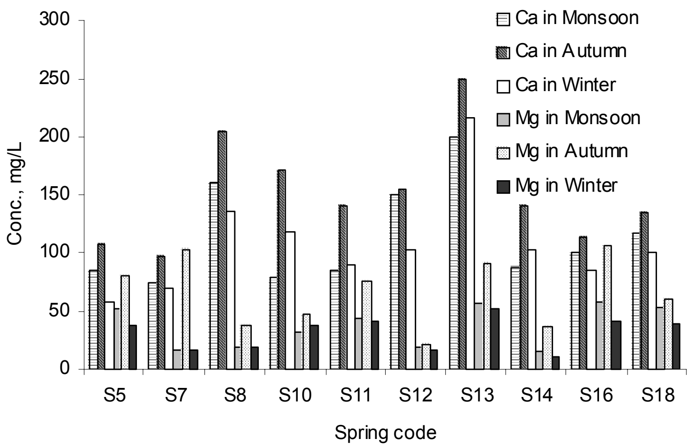

Fig. 7. Seasonal variations of Ca and Mg contents in spring water

Minor elements such as Cu, Ni, Zn, Fe and Co were also determined. Their presence was within the threshold values of WHO for metal ions but lead and cadmium (Pb, Cd) exceeded the permissible limits (0.01 mg/L) for springs S_4, S_5, S_{10}, S_{16}, S_{17}, S_{18}, S_{19}, S_{20}, S_{21}, S_{22} and S_{24} and (0.005 mg/L) for springs S_4, S_6, S_9, S_{10}, S_{12}, S_{13}, S_{16}, S_{17}, S_{18}, S_{19}, S_{22}, S_{25}, S_{26} and S_{27}, respectively. Fe amounted to 0.008-0.165 mg/L; Cu 0.0005-0.038 mg/L; Zn 0.003-0.38 mg/L; Ni 0.01-0.04 mg/L; Co 0.023-0.1 mg/L; Pb. 0046-0.17 mg/L and, Cd 0.009-0.19 µg/mL in the following order:

Zn > Cd > Pb > Fe > Co > Ni > Cu > Pb

Cluster analysis (CA): 15 Groups had correlation coefficients between 0.960-0.999 at 99 % confidence level implying that their aquifers possess same line of soil composition and lie within an average radius of 100 Km (Fig. 8) (Table-6).

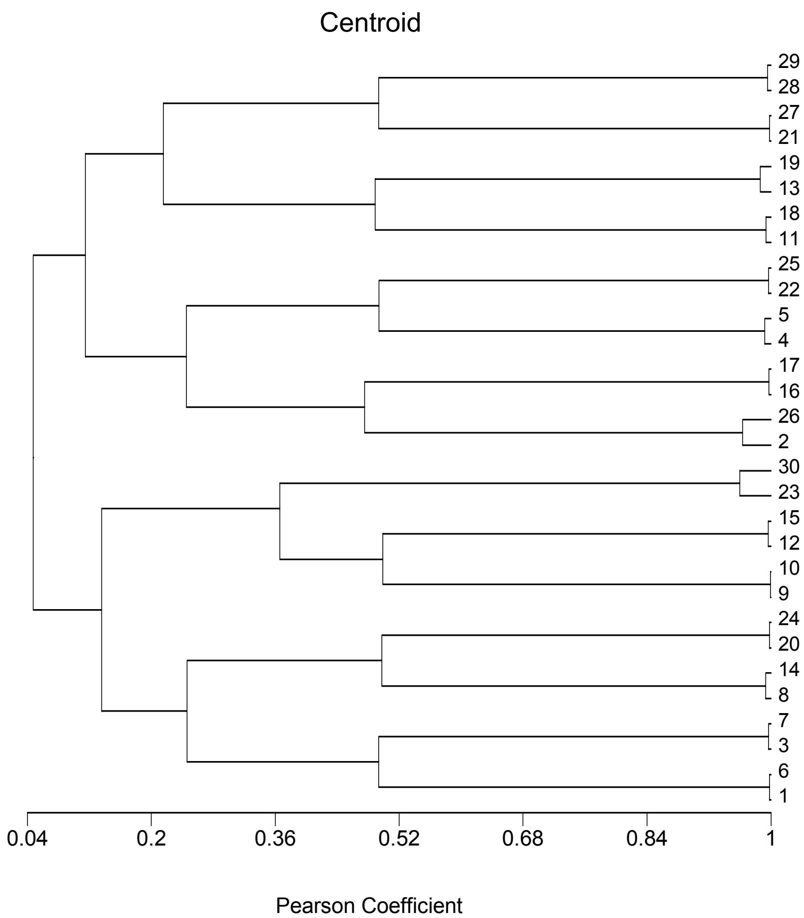

Fig. 8. Clustering of spring water in centroid diagram

TABLE-6
CLUSTER ANALYSIS; ANALYZING 27 VARIABLES × 30 CASES; CENTROID; PEARSON COEFFICIENT

Node	Group 1	Group 2	Simil.	Objects in group
1	9	10	0.999	2
2	21	27	0.998	2
3	20	24	0.998	2
4	1	6	0.998	2
5	16	17	0.998	2
6	3	7	0.997	2
7	22	25	0.997	2
8	12	15	0.996	2
9	28	29	0.996	2
10	11	18	0.994	2
11	8	14	0.993	2
12	4	5	0.992	2
13	13	19	0.986	2
14	2	26	0.963	2
15	23	30	0.960	2
16	Node 1	Node 8	0.499	4
17	Node 11	Node 3	0.498	4
18	Node 12	Node 7	0.494	4
19	Node 2	Node 9	0.494	4
20	Node 4	Node 6	0.493	4
21	Node 10	Node 13	0.489	4
22	Node 14	Node 5	0.475	4
23	Node 16	Node 15	0.366	6
24	Node 20	Node 17	0.246	8
25	Node 22	Node 18	0.245	8
26	Node 21	Node 19	0.216	8
27	Node 24	Node 23	0.136	14
28	Node 25	Node 26	0.114	16
29	Node 27	Node 28	0.048	30

Correlation matrix (CM): Correlation matrix of 27 mean variables was prepared for marked seasons (Table-7a,b). EC and TDS linearly correlate with salinity, HCO_3, Cl, SO_4, NO_3-N, BOD, COD, Na, K, Ca and Mg. EC-TDS, EC-salinity, EC-HCO_3, EC-Cl, EC-SO_4, EC-NO_3, EC-BOD, EC-COD, EC-Na, EC-K, EC-Mg, EC-Ca are also strongly correlated pair through the studied period: like an equally strong correlation can be established between pairs; SO_4-Cl, NO_2-Cl, NO_3-Cl, Na-Cl, NO_3-SO_4, *o*-PO_4-*t*-PO_4, BOD-SO_4, BOD-NO_3, COD-NO_3, Cu-*o*-PO_4-*t*-PO_4, Cd-KN, Na-K and Co-Ni. A strong negative correlation between Na and Ca indicates their mutual exchange in the soil/water matrix to maintain mass charge balance. Most of the variables are negatively correlated with pH and minor metal contents.

TABLE-7a
CORRELATION MATRIX

	PH	EC	TDS	Salinity	HCO_3	TH	Cl	SO_4	NO_2-N	NO_3-N	K N	O-PO_4	T-PO_4	DO
PH	1.000													
EC	-.293	1.000												
TDS	-.284	.997	1.000											
Salinity	-.501	.724	.709	1.000										
HCO_3	-.316	.428	.430	.348	1.000									
TH	-.421	.271	.250	.235	.484	1.000								
Cl	-.043	.598	.573	.402	-.154	.034	1.000							
SO_4	.149	.470	.464	.170	-.262	-.099	.750	1.000						
NO_2-N	-.221	.386	.341	.411	-.002	.125	.552	.462	1.000					
NO_3-N	-.072	.574	.574	.383	-.067	-.016	.502	.831	.444	1.000				
K N	.354	-.195	-.192	-.283	-.173	.131	-.209	-.085	-.139	-.176	1.000			
O-PO_4	.056	.079	.099	-.272	.193	-.103	-.026	-.127	-.006	-.142	.143	1.000		
T-PO_4	.144	-.037	-.012	-.338	.138	-.177	-.127	-.197	-.059	-.206	.219	.939	1.000	
DO	-.009	-.409	-.391	-.283	-.046	.053	-.516	-.476	-.512	-.411	.082	-.203	-.120	1.000
BOD	.118	.476	.491	.088	.033	-.138	.360	.647	.211	.681	-.184	.101	.061	-.451
COD	-.286	.585	.590	.474	.303	.162	.280	.430	.075	.673	-.232	-.126	-.194	-.390
Na	-.092	.635	.609	.596	.438	.089	.480	.143	.458	.079	.005	.052	-.000	-.415
K	-.124	.508	.481	.671	.251	.097	.440	.116	.238	.039	-.140	-.264	-.323	-.245
Ca	-.313	.429	.431	.232	.337	.386	.214	.197	.150	.274	-.160	.286	.202	-.000
Mg	-.006	.513	.516	.341	.382	.121	.257	.162	-.161	.061	-.088	-.144	-.198	-.072
Fe	-.088	.024	.026	-.189	.136	.069	-.013	-.119	.008	-.225	-.030	.356	.358	.185
Cu	.113	-.007	-.009	-.175	.003	.042	.176	-.065	.208	-.196	.017	.523	.510	-.190

	PH	EC	TDS	Salinity	HCO_3	TH	Cl	SO_4	NO_2-N	NO_3-N	K N	O-PO_4	T-PO_4	DO
Zn	-.224	-.049	-.046	.147	-.584	-.137	.178	.253	-.067	.173	-.184	-.410	-.452	.021
Ni	.289	.081	.074	-.145	-.467	.027	.408	.303	-.082	.106	.013	-.077	-.074	-.158
Pb	.186	.009	-.017	-.041	-.301	-.202	.333	.121	.329	-.159	-.202	-.293	-.258	-.014
Cd	.386	-.156	-.157	-.299	-.191	.108	-.129	-.061	-.007	-.189	.956	.248	.326	.008
Co	-.152	.246	.245	.135	-.214	.055	.263	.234	.008	.292	-.382	-.346	-.332	-.142

TABLE-7b

	BOD	COD	Na	K	Ca	Mg	Fe	Cu	Zn	Ni	Pb	Cd	Co
BOD	1.000												
COD	.396	1.000											
Na	.067	.199	1.000										
K	.012	.125	.701	1.000									
Ca	.244	.149	-.092	-.006	1.000								
Mg	.142	.341	.488	.519	.001	1.000							
Fe	.143	-.419	-.044	.216	.377	-.073	1.000						
Cu	.245	-.376	.067	-.063	.220	-.198	.406	1.000					
Zn	-.015	-.008	-.318	.046	-.029	-.037	-.160	-.219	1.000				
Ni	.111	-.056	-.208	-.054	.084	.008	-.013	.021	.312	1.000			
Pb	-.014	-.341	.177	.187	-.152	.092	.107	.314	.151	.245	1.000		
Cd	-.179	-.311	.047	-.146	-.079	-.168	.058	.160	-.185	.059	-.050	1.000	
Co	.164	.271	-.160	-.041	.122	.167	-.175	-.118	.442	.570	.345	-.330	1.00

Hydrochemical profile: Major ion distribution through trilinear and ternary plots (Piper's diagram) indicates Ca as the predominant ion Ca-HCO_3 followed by Mg-HCO_3. The order being Ca-Mg-HCO_3 > Na-K-HCO_3; for chlorides the distribution is mixed Ca-Na-Mg-K-Cl. The nature of urban water is more of Ca-Mg-Cl/NO_3 type because of anthropogenic activity and thick forestation (Fig. 9). The SO_4 ions show minor presence because of lower level of industrialization and lack of sulphur deposits in the area. The water is suitable for drinking within maximum permissible limits of WHO. Mass-charge balance is maintained throughout the hydrological year but varies only slightly due to the composition of soil of sample area (Fig. 10).

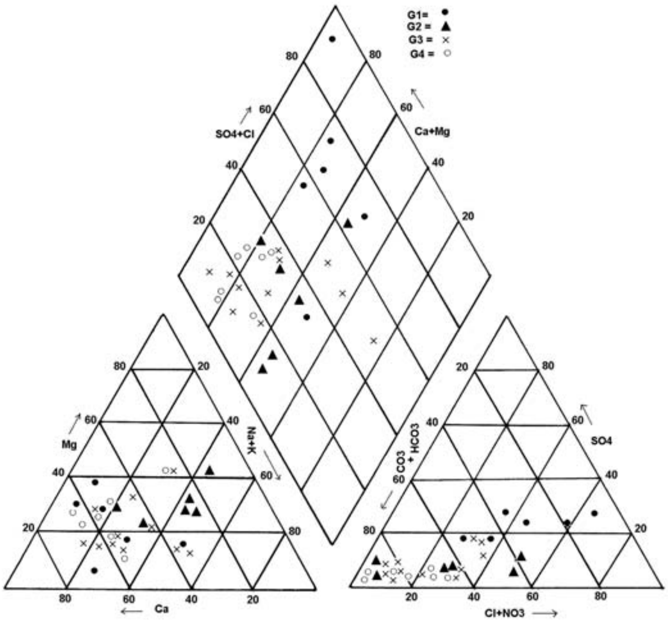

Fig. 9. Hydrochemical profile of spring water in Piper diagram

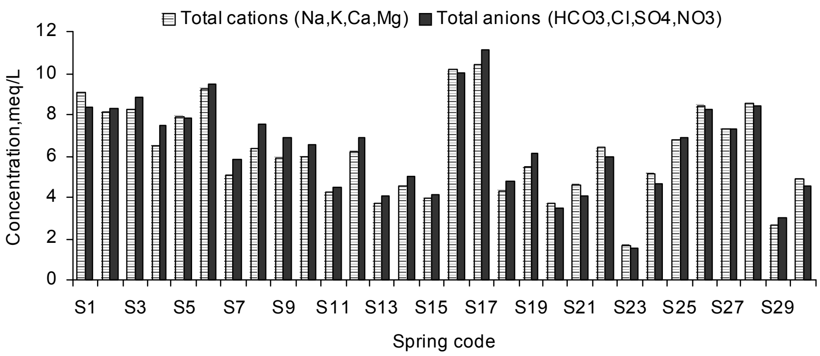

Fig. 10. Mass charge balance of cations and anions

Water suitability for irrigation

Hazards of alkalinity and salinity: The spring water samples were also tested regarding their suitability as irrigation water. Two parameters TDS, EC were specifically monitored as these are linearly correlated and are a measure of salinity hazard to crops. TDS values of all samples indicate that spring water is of fresh nature (Table-8) while EC based classification places 2 springs in excellent, 9 good and 19 in permissible class (Table-9). Since it reduces osmotic activity of plants and interferes with the absorption of nutrients[33], sodium adsorption ratio (SAR) was specifically calculated to determine the suitability of ground water for irrigation as follows[37]:

TABLE-8
NATURE OF SPRING WATER BASED ON TDS VALUES

TDS (mg/L)	Nature of water	Representing springs	No. of springs
< 1000	Fresh water	S_1-S_{30}	30
1000-10000	Brackish water	Nil	Nil
10000-100000	Saline water	Nil	Nil
> 100000	Brine water	Nil	Nil

$$SAR = \frac{Na^{+}}{(Ca^{2+} + Mg^{2+})^{½}/2}$$

where the concentrations are in meq/L. The SAR values range from 0.21-2.67 with an average value of 1.44 during one hydrological year. As spring water samples of the study area fall in the low sodium class A1 (Table-10) (Fig. 11), it implies that no alkali hazard is anticipated to the crops. If the SAR value is greater than 6-9, the irrigation will cause permeability problems on shrinking and swelling types of clays[33].

TABLE-9
CLASSIFICATION OF IRRIGATION WATER BASED ON ELECTRICAL CONDUCTIVITY (EC)

EC (µS/cm)	Water class	Hydrological year (2004-2005) Representing springs	Total no. of springs
< 250	Excellent	S_{23}, S_{29}	2
250-750	Good	S_7, S_8, S_{14}, S_{15}, S_{20}, S_{21}, S_{22}, S_{24}, S_{30}	9
750-2000	Permissible	S_1, S_2, S_3, S_4, S_5, S_6, S_9, S_{10}, S_{11}, S_{12}, S_{13}, $S1_6$, S_{17}, S_{18}, S_{19}, S_{25}, S26, S_{27}, S_{28}	19
2000-3000	Doubtful	Nil	Nil
>3000	Unsuitable	Nil	Nil

TABLE-10
CLASSIFICATION OF GROUNDWATER BASED ON ALKALINITY HAZARD

SAR	Alkalinity hazard	Water class	Hydrological year (2004-2005) representing springs	Total no. of springs
< 10	A1	Excellent	S_1 - S_{30}	30
10 – 18	A2	Good	Nil	Nil
18 - 26	A3	Doubtful	Nil	Nil
> 26	A4	Unsuitable	Nil	Nil

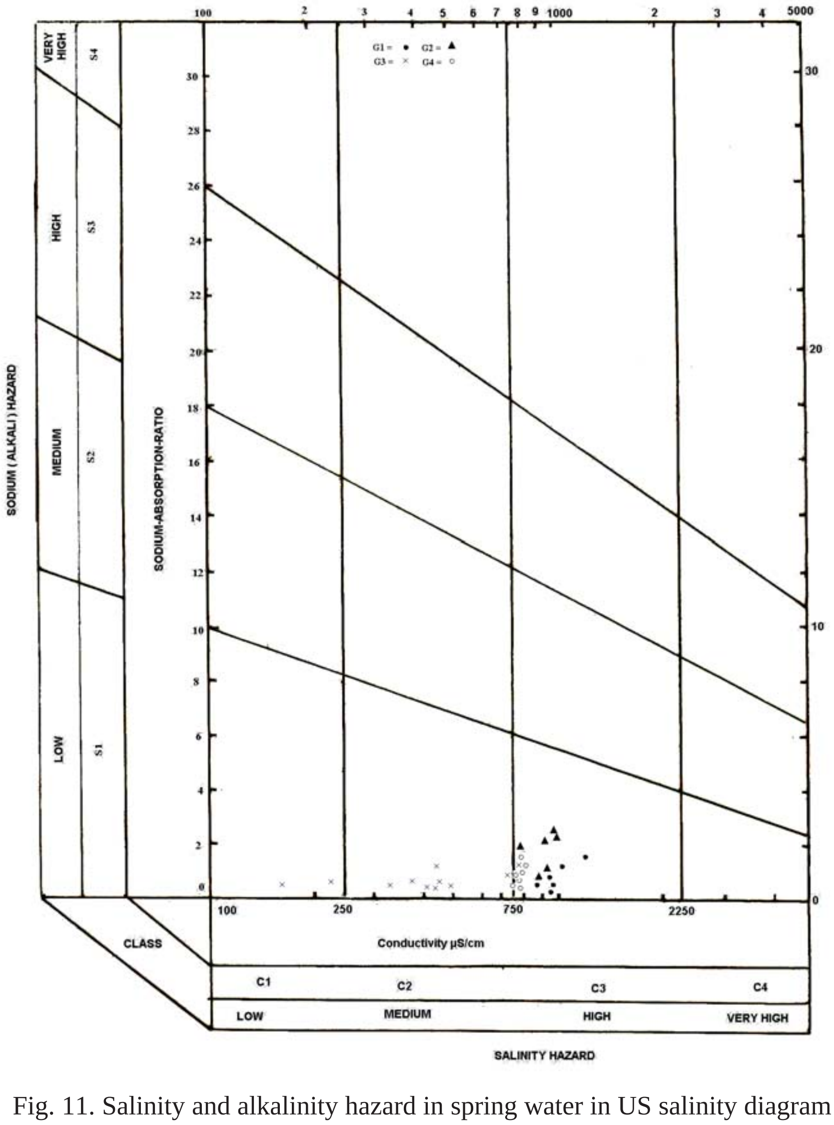

Fig. 11. Salinity and alkalinity hazard in spring water in US salinity diagram

Sodium concentration: The sodium percentage (Na %) is expressed as

$$Na\% = \frac{(Na^{+} + K^{+})100}{(Ca^{2+} + Mg^{2+} + K^{+} + Na^{+})}$$

where all the concentrations are in meq/L.

The sodium % (Table-11) indicates that the spring water is excellent for irrigation[38] and meets USDA standards (Fig. 12).

TABLE-11
QUALITY OF IRRIGATION WATER BASED ON % Na

Na (%)	Water class	Hydrological year (2004-2005) Representing springs	Total no. of springs
< 20	Excellent	S_1, S_6, S_8, S_9, S_{10}, S_{13}, S_{14}, S_{15}, S_{19}, S_{21}, S_{25}, S_{26},	12
20-40	Good	S_3, S_7, S_{11}, S_{12}, S_{20}, S_{22}, S_{23}, S_{24}, S_{27}, S_{28}, S_{29}, S_{30}	12
40-60	Permissible	S_2, S_4, S_5, S_{16}, S_{17}, S_{18}	6
60-80	Doubtful	Nil	Nil
> 80	Unsuitable	Nil	Nil

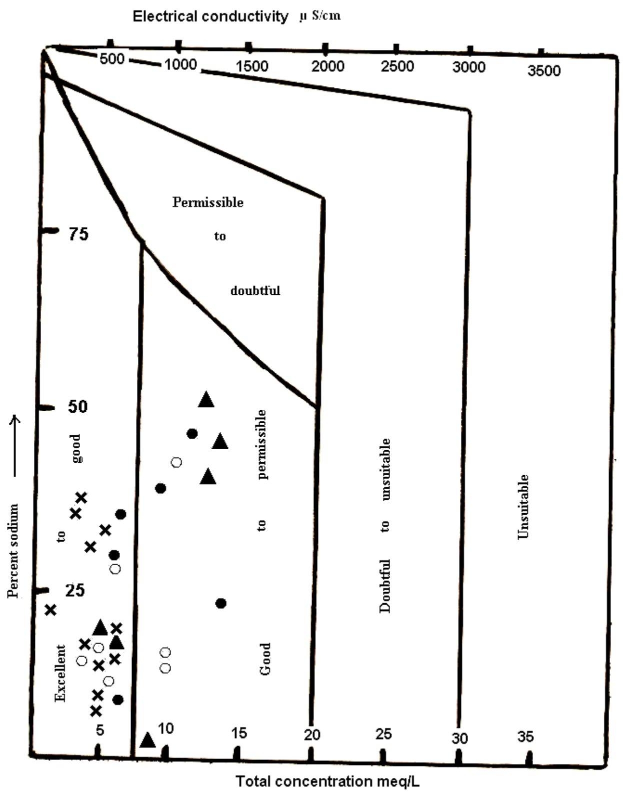

Fig. 12. Suitability of spring water for irrigation in Wilcox diagram

Permeability index (PI): If the concentration of sodium ions is high in irrigation water, they get absorbed by clay particles, displacing Ca^{2+} + Mg^{2+} ions (Fig. 13), reducing permeability[33,39] and eventually resulting in poor internal drainage.

The permeability index (PI) is calculated as per

$$PI = \frac{(Na^{+} + \sqrt{HCO_3^{-}})100}{(Ca^{2+} + Mg^{2+} + Na^{+})}$$

the concentrations are in meq/L.

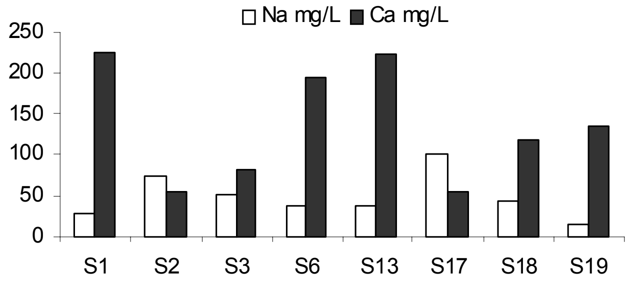

Fig. 13. Exchange of Na^{+} with Ca^{2+} ions

For samples in the present work PI ranges from 22.29 to 88.33 % in a hydrological year. The average value is 76.71 % that comes under class-1 of Donen's chart[40] making it excellent for cropping. While % Na categorizes 12 springs as excellent and equal number as good, six of satisfactory quality, none of them as doubtful (Table-11) (Fig. 12).

The application of these two parameters (Na % & PI) indicate that permeability index renders only one sample as unsuitable for irrigation but the % Na puts about six samples as border line indicating that the concentration of sodium is not high enough to render the water unsuitable for irrigation. Total hardness also indicates that hardness of water is mainly due to carbonates and bicarbonates of calcium and magnesium (2 samples soft, 2 moderate, 17 hard, 09 very hard) (Table-12).

TABLE-12
HARDNESS BASED CLASSIFICATION OF THE SPRING WATER (GROUND WATER)

Total hardness as $CaCO_3$ (mg/L)	Water class	Representing springs
< 75	Soft	S_{23}, S_{26} = 2
75-150	Moderately hard	S_{11}, S_{29} = 2
150-300	Hard	S_2, S_4, S_5, S_7, S_{13}, S_{14}, S_{15}, S_{16}, S_{17}, S_{18}, S_{19}, S_{20}, S_{21}, S_{22}, S_{24}, S_{25}, S_{30} =17
> 300	Very hard	S_1, S_3, S_6, S_8, S_9, S_{10}, S_{12}, S_{27}, S_{28} = 9

Residual sodium carbonate (RSC): Residual sodium carbonate test[38] calculated as

$$RSC = (HCO_3^- + CO_3^{2-} - (Ca^{2+} + Mg^{2+})$$

places the samples in reasonably satisfactory category of spring water giving it a value of 0.279 *i.e.* < 1.25 for 25 springs; 4 springs fall in doubtful and 1 in unsuitable category (Table-13).

TABLE-13
CLASSIFICATION OF IRRIGATION WATER BASED ON RESIDUAL SODIUM CARBONATE

RSC (meq/L)	Water quality	Hydrological year (2004-2005) representing springs	Total no. of springs
< 1.25	Good	S_1, S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{13}, S_{14}, S_{15}, S_{16}, S_{17}, S_{19}, S_{20}, S_{21}, S_{22}, S_{23}, S_{24}, S_{25}, S_{26}, S_{27}, S_{28}, S_{29}, S_{30}	25
1.25-2.5	Doubtful	S_3, S_4, S_5, S_{18}	4
> 2.5	Unsuitable	S_2	1

Conclusion

The spring water in the encatchment areas of Indus river has substantial nutrition value with Ca dominating the major cation concentration. Minor elements Cu, Zn, Fe, Ni, Co fall within threshold values of WHO, only Pb and Cd go over this limit.

Hydrochemical analysis reveals that the spring water is fresh and abundance of major ions during a hydrological cycle follows the order: $Ca^{2+} > Mg^{2+} = Na^+ > K^+ = HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > CO_3^{2-}$. Alkali earth ($Ca^{2+} + Mg^{2+}$ = 4.654 meq/L) exceed alkalis ($Na^+ + K^+$ = 2.459 meq/L) and weak acids ($HCO_3^- + CO_3^{2-}$ = 4.624 meq/L) exceed strong acids ($Cl^- + SO_4^{2-}$ = 3.045 meq/L). This leads to Ca-Mg-HCO_3, Na-K-HCO_3 and Ca-Na-Mg-K-Cl type of spring water.

The overall mass charge is maintained throughout the hydrological year but at few locations the minor elemental concentration does alter due to the soil composition.

The seasonal variations amount to insignificant changes for many of the parameters studied mainly due to random error most likely due to bigger gaps in the number and frequency of sampling. Similarly, rainfall too does not affect the absolute value of these parameters but for diluting component.

Human activity is the main vehicle of deterioration in the quality of spring water; two springs with varying population density were especially focused to study this effect. The significant change takes place in chloride presence jumping from 10.98 to 211 mg/L, a ten fold increase; the sulphate concentration also inflates 30 fold from 6.47 to 204 mg/L, no sulphur deposits otherwise exist in the area. Nitrite, nitrate, Kjeldahl nitrogen and phosphate though present in traces correlate linearly with demographic changes.

Deforestation is also likewise linked to human activity. The springs with descending forestation indicate less availability of humic and fulvic acids delaying and lowering the release of nutrients from the soil thereby decreasing nutrient availability to recharging water and permeability of soil thus enhancing the recharge time.

The spring water in the absence of human activity is suitable for irrigation because of low sodium content, high permeability of soil and carbonate and bicarbonate nature of hardness of water.

REFERENCES

1. G. Veni, *Envirn. Geol. Water Sci.*, **16**, 63 (1990).
2. C. Barber, C.J. Otto and L.E. Bates, *J. Hydrogeol.*, **4**, 6 (1996).
3. C. Subbarao, N.V. Subbarao and S.N. Chandu, *Environ. Geol.*, **28**, 175 (1996).
4. M. Eiswirth and H. Hotzl, in ed.: J. Chilton, The Impact of Leaking Sewers on Urban Groundwater, Proceedings of the XXVII IAH Congress on Groundwater in Theurban Environment, Problems, Processes and Management, 21-27 September 1997. AA Balkema, Rotterdam/Brookfiled, Vol. 1, pp. 399-404 (1997).
5. T. J.R. Sharp, in ed.: J. Chilton, Groundwater Supply Issues in Urban and Urbanizing areas, Proceedings of the XXVII IAH Congress on Groundwater in the Urban Environment, Problems, Processes and Management, 21-27 September 1997, AA Balkema, Rotterdam/Brookfiled, Vol. 1, pp. 67-74 (1997).
6. R. Trauth and C. Xanthopoulos, *Water Res.*, **31**, 2711 (1997).
7. J. Niemczynowicz, *Urban Water*, **1**, 1 (1999).
8. D.N. Lerner, *Hydrogeol. J.*, **10**, 143 (2002).
9. D. Cain, D.R. Helsel and S.E. Ragone, *Ground Water*, **27**, 230 (1989).
10. H.W. Anderson, Effects of Agricultural and Residential Land Use on Groundwater Quality, Anoka Sand Plain Aquifer, East Central Minnesota, USGS Water Resour nvest Rep, pp. 93-4074 (1993).
11. D.A.V. Eckhardt and P.E. Stackelderg, *Ground Water*, **33**, 1019 (1995).
12. P.J. Squillace and C.V. Price, Urban Land-Use Study Plan for the National Water-Quality Assessmentprogram, US Geol Surv Open-File Rep, pp. 96-217 (1996).
13. M.H. Barrett, K.M. Hiscock, S. Pedley, D.N. Lerner, J.H. Tellam and M.J. French, *Water Res.*, **33**, 3083 (1999).
14. M.D. Trojan, J.S. Maloney, J.M. Stockinger and E.P. Eid, *Ground Water*, **41**, 482 (2003).
15. B.Y. Choi, S.T. Yun, S.Y. Yu, P.K. Lee, S.S. Park, G.T. Chae and B. Mayer, *Environ. Geol.*, **48**, 979 (2005).
16. www.ajk.gov.pk.com
17. C.S. Meddlicott, *Rec. Geol. Surv. India*, **9**, 49 (1896).
18. R. Lydekker, *Rec. Geol. Surv. India*, **9**, 155 (1876).
19. C.S. Mddlemiss, *Mem. Geol. Surv. India*, **26**, 302 (1896).
20. D.N. Wadia, *Mem. Geol. Surv. India*, **2**, 2 (1928).
21. M.N. Chaudhry and M. Ashraf, *Kashmir J. Geology*, **2**, 1 (1984).
22. K.D. Kumar, S. Rawat and R. Joshi, *Envirn. Geology*, **31**, 150 (1997).
23. M. Magaritz, I.B. Brenner and D. Ronon, *Appl. Geochem.*, **5**, 555 (1990).

24. APHA Standard Methods for Examination of Water and Wastewater, American Public Health Association, Washington DC, edn. 17, p. 1497 (1989).
25. S.E. Alen, Chemical Analysis of Ecological Materials Blach Well Scientific Publ., Oxford, edn. 2 (1989).
26. W.E. Walton, Groundwater Resources, New Yark, McGraw Hill, p. 347 (1970).
27. J.J. Fried, Groundwater Pollution, Amsterdam, Elsevier, p. 330 (1975).
28. L.L. Drever, The Geochemistry of Natural Waters, Prentice Hall, London, pp. 138-162 (1982).
29. W. Fresenius, K.E. Quentin and W. Schneider, Water Analysis, Berlin, Springer, pp. 725-726 (1988).
30. WHO International Standards for Drinking Water, World Health Organization, Geneva (1971).
31. WHO Guidelines to Drinking Water Quality, World Health Organization, Geneva, p. 186 (1983).
32. N.F. Voznaya. Chemistry of Water and Microbiology, Moscow, Mir Publishers, p. 347 (1981).
33. A. Saleh, F. Al-Ruwaih and M. Shehata, *J. Arid Environ.*, **42**, 195 (1999).
34. J.A. Tindall, R.L. Petrusak and P.B. McMohan, *J. Hydrol.*, **169**, 51 (1995).
35. H.H. Comly, *J. Am. Mwd. Asso.*, **129**, 12 (1945).
36. G. Gilly, G. Corrao and S. Favilli, *Sci. Total Environ.*, **34**, 35 (1984).
37. K.R. Karanth, Groundwater Asswssment, Development and Management, Tata McGraw Hill, New Delhi, pp. 720 (1987).
38. H.M. Ragunath, Groundwater, Wiley Eastern Ltd, New Delhi, p. 563 (1987).
39. R. Collins and A. Jenkins, *J. Hydrol.*, **185**, 71 (1996).
40. P.A. Domenico and F.W. Schwartz, Physical and Chemical Hydrogeology Wiley, New York, pp. 410-420 (1990).

(*Received*: 21 September 2006; *Accepted*: 16 June 2007) AJC-5703