

Major Ion Chemistry of Groundwaters From the Peshawar Intermontane Basin, NWFP, Pakistan

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(received April 21, 2008; revised June 12, 2008; accepted June 15, 2008)

Abstract. Investigation of spring and well waters of the Peshawar Intermontane basin and its surroundings in the Himalayan belt of Pakistan revealed that their temperature, pH, total dissolved solids and electrical conductivity values fall within the permissible range of drinking and irrigation water except the waters in vicinity of exposed faults. Minerals in the spring water are in the order of $Ca > Mg > (Na + K)$ with bicarbonate as the dominant anion, whereas in the well water, the order is reversed, with sulphate as the dominant anion.

Keywords: Peshawar hydrochemistry, ground water, minerals, Pakistan

Introduction

Investigation was carried out to determine the field characteristics and major ion chemistry of spring and well waters. The study site covered the Peshawar intermontane basin (PIB) and its surroundings in the Himalayan foreland fold-and-thrust belt of Pakistan (Fig. 1). The area, located between latitudes $33.5^{\circ}N$ - $34.7^{\circ}N$ and longitudes $71^{\circ}E$ - $73^{\circ}E$, is characterized by steep topography and V-shaped fluvial valleys in the north, which are drained by the river Indus entering from Indian Kashmir and the river Kabul entering from Afghanistan. Cold winters and warm, dry summers characterize the climate of the study area. June through August are the hot months, during which the daily mean maximum air temperature is about $40^{\circ}C$. The mean annual potential evaporation ranges from 85 cm in the northern part of the study area to 130 cm in the centre of the basin. Snowfall occurs in the mountainous north during the cold months of December to February, when monthly mean minimum temperatures are several degrees Celsius below the freezing point.

Peshawar valley is home to two million plus inhabitants with ever growing demand for water for drinking, industrial and irrigation purposes. Every water usage (human, industrial, irrigation etc.) requires a set of hydrochemical characteristics, suited for that particular consumption. The hydrogeological data for the region is scattered and scanty (Shah and Tariq, 2007; Tariq, 2001) and this research is the first attempt to fill this gap. The broader study conducted for this research is the first of its kind in that it synthesizes field, laboratory and simulation data to bracket the hydrochemical speciation in the PIB. This paper presents the field and laboratory data for groundwater in the study area.

General geology. Information on subsurface geology of the study area has been derived from the lithological logs of boreholes drilled by WAPDA, Pakistan, and made available through various information releases. These data indicate that the quaternary sediments vary in thickness from few meters to more than 150 m. However, the total thickness of quaternary sediments is not known because none of the boreholes penetrates the bedrock. The coarseness of these sediments increases from north to south in the basin (Tariq, 2001). In the central part of the basin, the alluvial sediments consist of a relatively large proportion of fine-grained material, where the sandy silt is interbedded with discontinuous alluvial sand and thin gravel layers of various thickness. The main rock types in this area are slates, phyllites, various types of schists, paragneisses, sandstones, and quartzitic crystalline conglomerates, all of which are intruded by basic-to-acidic igneous rocks.

Hydrogeology. The study area can be divided into two hydrogeological provinces. The basin is bordered by mountains of the Lesser Himalayas on three sides while the south-eastern side is a fluvial valley carved at the confluence of the Indus and Kabul rivers. In the mountainous region, the water table varies in depth in different intermontane valleys, suggesting hydraulic discontinuities. In fact, water table elevation varies considerably within the area, ranging from less than 100 m in the basin centre to more than 1600 m in the mountainous north in relation to mean sea level (Fig. 2). Abundant springs (both normal and high temperature) are present in this part of the study area, and locally they constitute an important source of drinking water in addition to dugwells. The outflow from these springs ranges from less than one l/sec to more than 2000 l/sec. The field investigations indicate that most of the springs have good quality water, and according to local authorities, there are no water-

borne diseases in these areas. Most of these springs flow from unconsolidated or semi-consolidated fluvial deposits or talus surrounded by various types of hard rocks. The PIB sediments consist of mainly sand and gravel formations that serve as productive aquifers in the north and south of the basin. The main sources of recharge to the aquifers are precipitation, seepage from rivers, surface storage reservoirs and irrigation networks. A large number of drilled wells and dug wells are present throughout the PIB. These wells are extensively used for irrigation, industrial and domestic purposes. Drilled wells range in depth from 50 to 150 m, whereas the wells dug are up to 20 m in maximum depth.

Khyber, Attock-Cherat and Lower Swat-Bunner piedmont aquifers occur on the periphery of the basin, whereas flood plain and lacustrine aquifers occupy the central part of the basin. Depth to the water table is less than 5 m, except on the margins of the basin and in the southeast where it ranges from 5 to more than 30 m. Hydraulic conductivity ranges from 30-60 m/day and the average specific yield is 12% (Rathur, 1987); these values indicate a potentially high-yielding aquifer with substantial storage capacity. There is general groundwater flow from the margins of the basin towards the centre, with an average gradient of 0.004 (Bundschuh and Balke, 1991). Robberts (1988) estimated the total recharge to

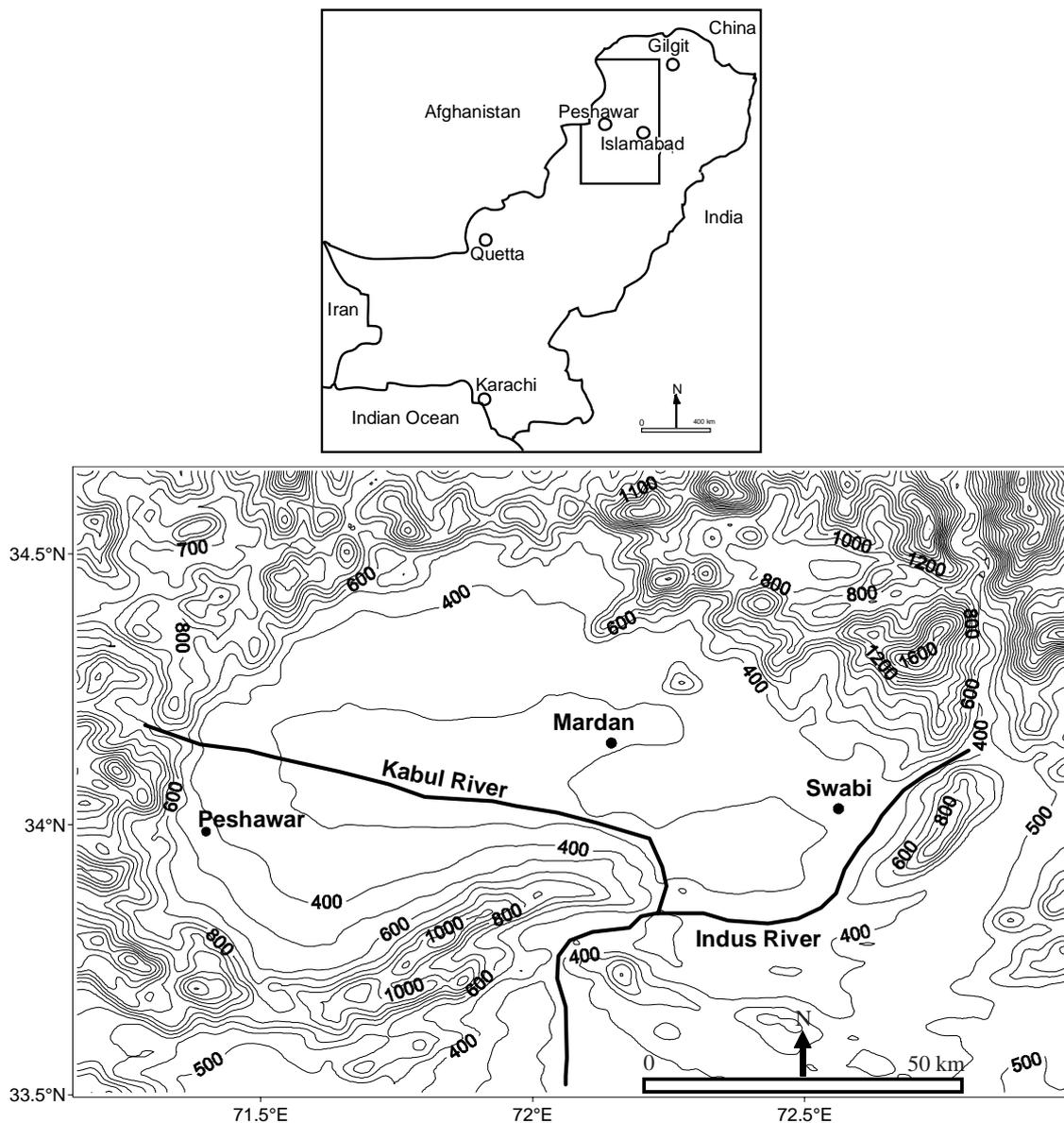


Fig. 1. Topographic map of the Peshawar Intermontane Basin (PIB) showing major localities and rivers. Contour elevations are shown in meters.

the basin as 923 Mm³/year over a 6270 km² area. The main contributors to this recharge are precipitation (151 Mm³/year), surface water irrigation (734 Mm³/year), groundwater-based irrigation (15 Mm³/year), and runoff water (23 Mm³/year). The discharge of the groundwater takes place mainly along the downstream part of the Kabul river and its tributaries (Fig. 2). Additional discharge occurs through subsurface outflow into the basin, pumping for irrigation, drainage, and water consumption for domestic and industrial purposes. The total estimated discharge from the basin is 891 Mm³/year, of which base flow constitutes 713 Mm³/year (Rathur, 1987).

Materials and Methods

A total of two sets of 71 water samples were collected from water wells, springs and seepages throughout the study area and data from 32 samples spanning the PIB are presented in this paper (Fig. 2). Each sampling site was mapped with a Garmin GPS V with a position accuracy of less than ± 3 m. General physicochemical parameters were determined in the field using Technika Water Quality Meter 850081 with dedicated sensor probes. All the water samples were filtered in the laboratory with a 0.45 μ m pore diameter filter, and the samples for cation analyses were acidified with nitric acid. Cations

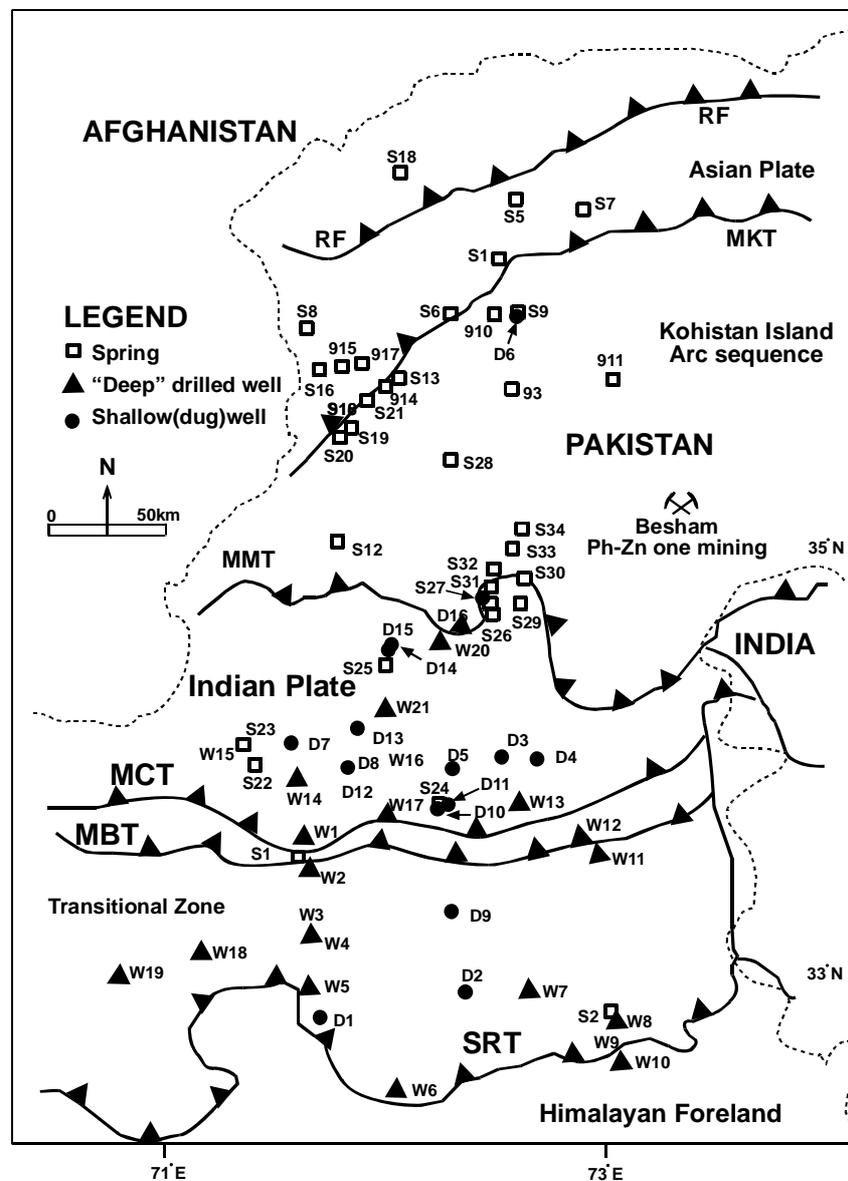


Fig. 2. Index map of sampling sites. Salt Range Thrust (SRT); Main Boundary Thrust (MBT); Kalabagh Fault (KF); Main Central Thrust (MCT); Main Mantle Thrust (MMT); Jhelum Fault (JF); Main Karakoram Thrust (MKT); Indus River (IR); Kabul River (KR); Kohistan Island Arc (KIA). PIB is located between MBT and MMT.

were analyzed using Perkin Elmer Optima 3300 DV ICP-OES with an AS90 plus autosampler. Precision errors were less than $\pm 6\%$ for trace elements and less than $\pm 3\%$ for the major cations (95% confidence). Multi-element stock solutions of 20 $\mu\text{g/ml}$ were used as standards for trace elements. Standard solutions for major elements consisted of 1000 mg/l of single-element solutions. Anion concentrations were determined using dionex DX 120 ion chromatograph with an AS50 autosampler. Precision errors were less than $\pm 3\%$ for all the anions (95% confidence). Anion standard solutions consisted of 1 mg/l , single-element solutions. Bicarbonate ion (HCO_3^-) was indirectly derived from total carbon analyzed by Shimadzu TOC 5000 instrument with precision error less than $\pm 2\%$ (95% confidence). The charge balance (cations-anions/cations + anions) was less than $\pm 5\%$ for all the samples.

Temperature, pH, total dissolved solids (TDS) and electrical conductivity (EC) were measured as part of the hydrochemical field work for this research.

Results and Discussion

The physicochemical data for springs and deep and shallow water-wells are presented in Table 1 and 2 alongwith the hydrochemical data. These values fall within the accepted range of values recommended for water used for drinking and irrigation purposes.

Water surface temperature. Temperature ranges from 14 to 29.5 $^{\circ}\text{C}$ for the well waters and from 8 to 38 $^{\circ}\text{C}$ for

the spring waters. Groundwater temperature generally equilibrates itself with the mean annual air temperature for a particular locality. The mean annual air temperatures in the study area range from 13 to 25 $^{\circ}\text{C}$ (NASA, 2005). The regional distribution of differences between the water surface temperature and mean annual air temperature, designated here as ΔT $^{\circ}\text{C}$, is given in Table 1 and 2. It can be noticed that most groundwaters show some surplus over the mean annual air temperature. This surplus is a result of the deep circulation of the regional groundwaters to a depth of about 4 km (Yousafzai *et al.*, 2006).

pH distribution. The values of pH exhibit a rather narrow distribution in the study area, as shown in Table 1 and 2. In particular, the well waters range in pH from 7.1 to 8.6, whereas pH values of the spring waters range from 6.7 to 8.7. Moreover, the groundwater tends to be more acidic away from most major fault zones (except the MCT and MBT) and more alkaline groundwater in the vicinity of these fault zones (Yousafzai *et al.*, 2006). Also, higher values of pH are noticed in the centre of Peshawar basin (> 7.8) as compared to the low values on its margins (< 7.6).

Conductivity and total dissolved solids. Conductivity, which is also known as electrical conductivity (EC), specific conductivity or conductance, is the reciprocal of the resistance in ohms between the opposite faces of a one cm cube of an aqueous solution at 25 $^{\circ}\text{C}$. The International Unit for conductivity is the Siemens, which is numerically equivalent to the

Table 1. Hydrochemical data for groundwater samples from drilled and dug wells (concentration in mg/l)

Sample ID	Ca	Mg	Na	K	Cl	NO_3	SO_4	HCO_3	pH	TDS	EC ($\mu\text{S/cm}$)	ΔT $^{\circ}\text{C}$	Balance
KPW-01	127.8	42.5	54.4	3.4	147.1	168.5	148.6	198.3	7.3	810	1210	6.3	-3.3
KPW-21	41.4	11.8	20.2	2.7	6.6	27.4	11.6	210	7.7	254	380	2.9	-4.0
PSW-51	57.6	25.1	34.6	3.8	50.6	39	87	230.1	7.6	423	632	6.9	-5.6
PSW-55	65.9	21.3	40.8	2.4	72.4	97.4	63.3	161.9	7.4	453	680	5.9	-3.9
PSW-57	38.1	16.2	56.3	4.3	14.2	16	32.3	285.4	7.5	353	530	6.6	-1.8
PSW-61	110.6	21.2	35.7	3.3	59.3	116.3	89.2	158.2	7.5	534	801	7.3	5.5
CSW-71	64.9	6.7	10.5	4.4	5.5	12.7	47.7	231.3	7.5	284	426	6	-4.3
PSW-22	75.6	22.3	23.7	4.2	27.9	57.4	129.3	203.6	7.6	441	431	5.1	-3.8
PSW-23	29	11.9	26.4	4.8	8.5	14.3	13.8	183	7.9	218	328	5.7	-0.7
PSW-24	18.3	10.3	27.6	5.7	11.2	10.2	15.2	152.3	7.7	198	297	4.7	-2.9
PSW-53	61.2	63.5	115.6	14.8	29.9	7.7	392.7	400.6	7.6	709	1061	1.3	-3.8
PSW-60	54	23.7	20.6	2.5	15.1	17.9	87.4	202.9	7.4	335	504	6.6	-2.1
PSW-62	23.6	3.4	6.3	3.2	5.5	4.3	40.4	60.1	8.1	101	151	8.1	-5.8
PSW-67	14.8	21.6	55	5.4	9.6	9.2	29.8	283.4	8	308	463	5.7	-5.9
CSW-69	70.6	7.3	7.3	2.4	12.6	6.2	10.4	205.3	7.7	345	522	6.4	5.6
CSW-70	62.9	8.9	3.3	2.1	4.6	5	38.3	228.4	7.5	272	408	6.8	-4.2
CSW-72	139.3	26.7	35.5	2.5	101.8	104.4	110.7	238.7	7.3	765	1148	6.6	0.0

Table 2. Hydrochemical data for groundwater samples from springs (concentration in mg/l)

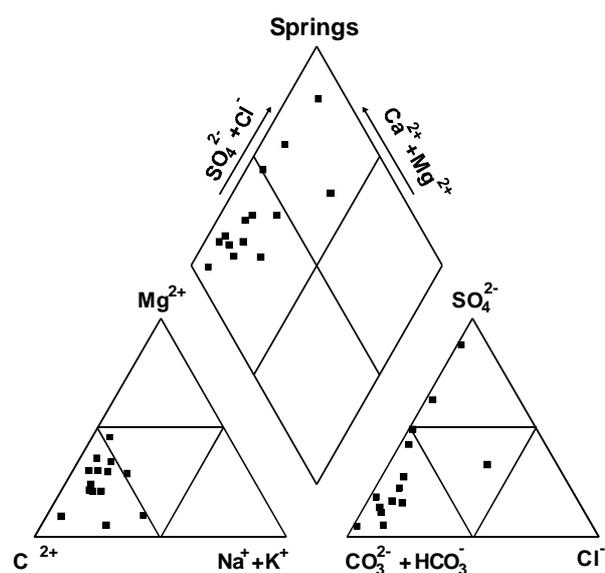
Sample ID	Ca	Mg	Na	K	Cl	NO ₃	SO ₄	HCO ₃	pH	TDS	EC (μS/cm)	ΔT °C	Balance
CSS-38	68	25.7	7.8	2.5	2.8	8.7	129.8	164.3	7.2	417	623	0.2	3.2
CSS-48	29.2	7.1	9	3.5	0.4	5.4	23.7	127.9	8.2	121	182	0.5	-4.2
PSS-54	59.3	23.5	15.8	1.8	17.3	36.2	74.1	219.4	7.3	351	527	7.7	-4.8
PSS-56	266.7	55	58.4	11.5	12.4	4.8	962	145.8	7.6	982	1475	5.7	-5.3
PSS-59	52	18.6	26.4	2.3	6.8	12.5	114.9	184.7	7.8	311	467	1.9	-4.2
CSS-68	95.4	29.1	14.8	3.4	8.5	7.8	252.1	178.3	7.6	372	559	2	-4.1
CSS-73	56.8	15.6	6.6	1.3	3.7	4.2	29.1	195.9	8.1	255	382	0.5	4.3
CSS-74	82.5	15.8	13.7	4.7	18.3	52.6	56.1	208.3	7.3	389	584	1.2	1.6
CSS-75	55.6	12.4	8.6	2.7	10.1	14.4	27.9	211.8	7.4	266	402	0.7	5.0
CSS-76	72.6	3.1	4.5	0.5	6.2	11.2	5.4	166.6	7.3	303	457	3.7	4.7
CSS-78	6.1	0.3	4.1	1	1.4	7.4	4.2	3.4	7.5	27	41	2.8	5.2
CSS-79	42.2	24.5	6.9	1.1	3.1	16.7	9.5	249.5	7.8	264	396	2.6	-2.0
CSS-80	27.8	6.1	6.2	1.4	6.6	4.8	13	84.1	6.7	124	182	1.1	5.7
CSS-81	30.4	9.8	7.8	2.2	6.3	17.3	12.5	113.3	7.2	152	227	1	2.8
CSS-82	10.2	0.9	2.9	1.4	3.3	4	4.6	26.3	8.1	27	40	0.6	4.7

mhos (Hounslow, 1995). The EC values indicate a general impression of the chemical behaviour and chemical quality of the groundwater in an area and are linked to the quantity of salts dissolved in the groundwater (Bundschuh, 1992). A usual rule for drinkable water is 10 mhos or 1000 micro Siemens per cm (μS/cm). The EC values range from 151 to 1210 μS/cm in the well waters, and from 40 to 584 μS/cm in the spring waters with the exception of one sample (S2, Fig. 2) which shows an EC value of 1475 μS/cm.

The highest values of EC are clustered around two centres in the Kohat-Pothohar basin. Groundwater in the vicinity of these centres is salty in taste and may cause longterm health problems. Generally, the distribution of EC values corresponds to the depth of groundwater levels; that is, the shallower the groundwater, the higher the conductivity (Bundschuh and Balke, 1991). No such correlation was observed in the groundwater of the studied area, however. The use of highly mineralized groundwater for irrigation purposes in some parts of the study area may lead to an increasing salt content of both the soil and groundwater (Bundschuh and Balke, 1991). Total Dissolved Solids (TDS) is calculated by adding the mass of ions to that of SiO₂. TDS ranges from 101 to 810 mg/l in the well waters and from 27 to 982 mg/l in the spring waters (Table 1-2).

Regional abundance of major elements in the groundwater samples are presented in Table 1-2, and the analyses are plotted on discriminant diagrams in Fig. 3 and 4. Conclusions can be drawn from these discriminant diagrams regarding water type, precipitation or solution, mixing and ion exchange

(Hounslow, 1995). The diamond part of the diagram may be used to characterize different water types. Most of the spring water is typically characterized by elemental abundance in the sequence Ca>Mg>(Na+K), with bicarbonate as the dominant anion, suggesting young and fresh recharge. However, two samples exhibit (Na+K)>Ca>Mg, with sulphate as the dominant anion (Fig. 3); both samples also show anomalous temperatures. The linear trend on the discriminate diagram for spring water- taken together with high TDS values indicate

**Fig. 3.** Discriminate diagram for spring water samples.

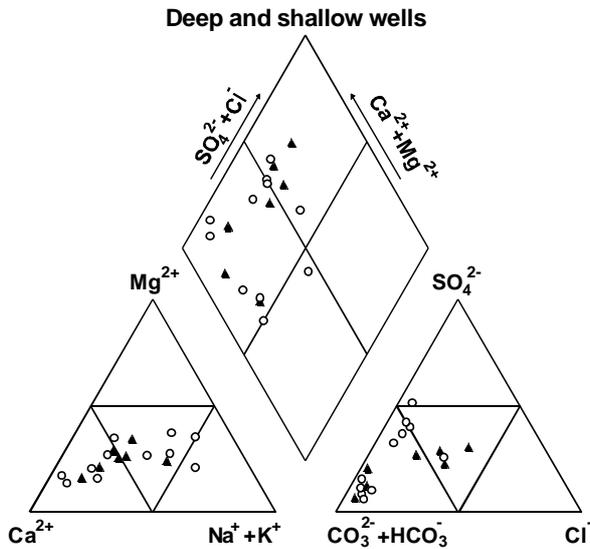


Fig. 4. Discriminate diagram for well water samples. Open circles represent shallow wells while deep wells are shown by triangles.

dissolution of Ca^{2+} , Mg and sulphate (Fig. 3). Examination of Table 2 indicates that Ca^{2+} is the dominant cation in these samples, suggesting dissolution of chlorites and related rocks which are abundant in the region. The linear trend stretches all along the left axis of the plot, indicating mixing of two types of waters.

The trends for both the shallow and deep water samples exhibit ion exchange in which calcium and magnesium in solution are being replaced by sodium. The trends start parallel to constant magnesium and then curve towards the sodium apex, suggesting that more calcium is being exchanged than magnesium (Hounslow, 1995). Most significantly, water samples from one shallow well and three deep wells, all located in an immediate vicinity of the major thrust zones (MBT and MMT), demonstrate clear imprints of admixture of oil-brines. All of these samples also show a significant surplus temperature over the local mean annual ground surface temperature (Table 1-2). The surplus temperature over the local mean annual ground surface temperature (ΔT °C) shows several positive anomalies. One such anomaly is located along the MKT, and another is located along MCT and MBT. All of these samples exhibit temperatures of at least 6 °C above the local mean annual temperature (Table 1-2). Furthermore, all samples with such significant excess temperature over the local mean annual air temperature also have anomalously high concentrations of SiO_2 , whereas those along the MKT are also characterized by anomalously high concentrations of boron and strontium (Yousafzai *et al.*, 2008).

Conclusion

Most of the Peshawar Basin aquifers are unconfined. Temperature, pH, total dissolved solids (TDS), and electrical conductivity (EC) values of the groundwaters fall within the normal range for water used for drinking and irrigation purposes with the exception of a few samples (KPW-01, PSW-53, CSW-72, PSS-56). These samples represent waters which are in the vicinity of exposed or blind faults and may indicate thermal waters which have excessively dissolved materials while ascending to shallow levels. Results from water chemistry indicate that the spring water is dominated by the sequence $\text{Ca} > \text{Mg} > (\text{Na} + \text{K})$, with bicarbonate as the dominant anion, suggesting young and fresh recharge. However, the well water exhibits the reverse order of preference for these cations indicating the process of ion exchange. Cation exchange processes play an important role in controlling the chemical composition of groundwater in addition to dissolution processes (Grasby *et al.*, 1999; Cerling *et al.*, 1989). There are several possible explanations for the variation in the groundwater chemistry such as the mixing of waters of different origins, dissolution of the clastic sediments composing the aquifer systems, precipitation of minerals from the water and cation exchange with clay etc.

Acknowledgement

The manuscript was revised according to the suggestions of Drs. Yoram Eckstein and Peter S. Dahl of Kent State University, USA. Financial support from Geological Society of America and Sigma Xi Research Society in conducting fieldwork is gratefully acknowledged. Department of Geology at Kent State University facilitated analytical and computational procedures. I am indebted to Dr. Ksenija Dejanovic of Department of Geology at Kent State University for her priceless help in carrying out the chemical analyses. Last, but not least, I thank Mr. Ghafar Khan, a local geologist, for his support in the fieldwork.

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