ISSN-1680-9955

Pak. J. Anal. Chem. Vol. 6, No. 2, (2005) 72 – 79

Quality of Rain Water and its Suitability for Drinking and Agricultural use in District Bhimber Azad Kashmir, Pakistan

M. Aslam Mirza*, M. Y. Khuhawar and A. J. Kandhro
Dr. M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan
E-mail addresser: kanwalseemi@yahoo.com (M. Y. Khuhawar)

Received: 28-08-2006 , Revised: 20-09-2006 , Accepted: 30-10-2006

Abstract

District Bhimber shares its borders with Gujrat and Jhelum Districts of the Punjab Province of Pakistan and is situated at the foothills of mountain series of Himalayas. The area falls in subtropical highland type of climate and is away from the reach of snowmelts and irrigation system of Punjab Pakistan because of mountainous geological formations. In this area, drinking and agricultural resources totally depend on degree of precipitation that raises water table and feeds running streams. The suitability of rain water for drinking and agriculture was assayed by modeling it on hydrochemistry of District Bhimber. Physicochemical parameters such as temperature of air and water, pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH) HCO_3^-,CO_3^{2-}, Cl^-,SO_4^{2-}, NO_2-N, NO_3-N, Kjeldahl nitrogen (KN), orthophosphate (O-PO4), acid hydrolysable phosphate (T-PO4), dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), Na^+,K^+,Ca^{2+},Mg^{2+}, Fe^{2+},Cu^{2+}, Ni^{2+}, Zn^{2+},Pb^{2+},Cd^{2+}, and Co^{2+} were determined. Chemical analyses of the rain water shows that the mean concentration of ions is of the order $Ca^{2+} > Na^+ > Mg^{2+} > K^+ = HCO_3^- > Cl^- \geq SO_4^{2-} > NO_3^- > CO_3^{2-}$. Interpretation of Piper plot on elemental composition indicates that Ca-Mg- HCO_3^- /CO_3^{2}, Ca – Cl and Na- Cl are the dominant hydro chemical types, likewise salinity hazard index sets the criterion for its agricultural utility. Higher concentrations of NO_3^- and SO_4^{2-} and pH < 7 indicate acid rains in the study area. Seasonal variations were found insignificant.

Introduction

Bhimber District lies at a latitude 32.48 to 33.34º and longitude 73.55 to 74.45° and comprises of 1516 square Kilometer area. It is situated at the foot hills of Himalayas at 275 - 975 meters above sea level with a population of above 0.335 million [1]. The average rainfall is 15 cm and average population density is 232 heads per square Km [1]. It is 50 km from Mirpur and is linked with the main Peshawar – Lahore Grand Trunk road at Gujrat.

In District Bhimber, the main water availability comes from hand pumps, wells, springs, streams and ponds, which are also used for drinking and agriculture. Being detached from snowmelt and irrigation system of Pakistan, precipitation affects the abundance of surface and underground water in the study area. The quality of water varies as do ecological and anthropogenic factors [2].

Hymavathi [3] while describing the water quality of stream Mudasarlova, India and Sastre et al [4] have reported the study of surface run off but the quality of water of Bhimber District is under studied. The present work examines the effect of physical and chemical characteristics of rainwater on the quality of water of the area.

Climate of the Area

In the state of Azad Jammu and Kashmir, there are hot plains of the Bhimber and Mirpur districts and cold lands of Rawalakot, Forward Kahuta, Leepa, Trarkhal, Kel and Taobat etc. The

*Corresponding Author

area has different weather conditions at different places because of the lofty mountains like the Pirpanjal that check the moisture-laden winds from entering the valleys. In summers, the outer plains and the outer hills receive rainfall from monsoon winds while in winters, winds from the Mediterranean cause snowfall and rainfall in the Valleys of Kashmir.

The unique climatic conditions found in the zone of the Middle Mountains and its valleys, are determined by the altitude, which in turn determines the degree of coolness and elevation in the form of precipitation and summer temperature. Winters are cold and of long duration and with increasing altitude, it gets colder still, as snow falls. Summers, however, are milder but short. Winters last from November to March. Spring begins after 15th of March. Humidity in the monsoon season stretching over July and August is as high as 70% and with increasing temperature summers can be uncomfortable [1]. Climate of the Bhimber District from the mountainous Districts of Azad Kashmir and is as hot as Jhelum and Gujrat, the adjoining districts of Punjab, Pakistan.

Sampling

Strategy

Prior to sampling a detailed survey of the area was undertaken considering the distance from the industrial areas and degree of seasonal rains. Sampling location and in situ testing of physicochemical parameters was carried out in order to plan proper sampling strategy. The objective of the field survey was to locate and select the sampling station for the study. Samahni town, the subdivision head quarter, was selected as sampling station. In Azad Kashmir, monsoon and winter are most wet seasons compared to others. However, random precipitation is also observed in spring, summer and autumn.

Mode

The sampling was carried out in monsoon, autumn and winter seasons in one hydrological year during 2004-2005. Samples were collected in pre-washed high-density polythene containers directly, from deferent locations of the town, during rainfall in predetermined seasons. Sub-samples thus taken were later integrated into a composite sample. Field measurements included pH, EC, TDS, DO, Cl^- , hardness, HCO_3^- and temperature of the water and air as well. For elemental analysis each sample was acidified to pH < 2; for organic matter, fixed with $HgCl_2$. Separate samples were taken for specific analysis.

Experimental

Temperature of air and water was measured with mercury thermometer. Dissolved oxygen (DO) in the samples was determined by Wrinkler method [5]. Chemical oxygen demand (COD) was estimated by micro-dichromate oxidation method. Hardness, chloride and alkalinity were determined by titration with standard E.D.T.A, 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 [5]. 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 orthophosphate. Nitrate was determined after derivatization with brucine sulphate. Nitrite was estimated using N-naphthyl ethylenediamine as derivatizing reagent as reported [5]. 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 at the conditions recommended by the manufacturer.

The analysis was carried out in triplicate with integration and delay time 3 seconds each. Na, K, Ca and Mg were determined after appropriate dilution. Sample (250 ml) containing nitric acid (1 ml) was heated gently at 90- 95 ºC and was concentrated to about 5 -8 ml. The solution was transferred to volumetric flask and final volume was 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.

pH, Electrical Conductivity and Total Dissolved Solids

The pH varied between 5.72 to 6.55 in one hydrological year with average value6.11.The pH < 7 (lower value) may be because of acidic rains due to natural phenomenon (oxidation process during thunder and lightening) and anthropogenic activities [6,7]. The seasonal changes in pH are insignificant and fall within the WHO water quality standards [8] (Table 1). The electrical conductivity (EC) and total dissolved solids (TDS) (Table 1) indicated a significant inter seasonal variation among the samples [Fig.1]. EC and TDS varied within the range 27-60 µS/cm and 17.28-38.4 mg/L. However, throughout the hydrological year, EC &TDS values were observed within prescribed limits of WHO [9, 10].

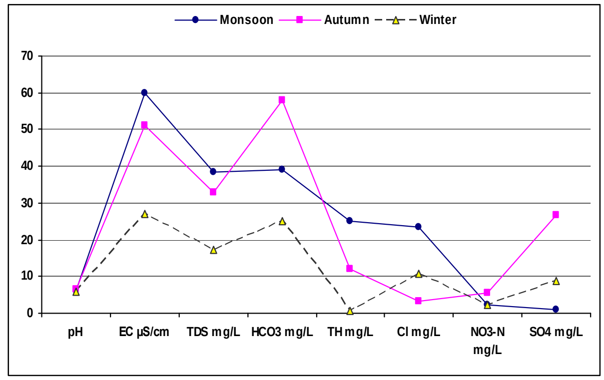

Fig.1. Seasonal variation in pH, EC, TDS, HCO_3, TH, Cl, NO_3-N and SO_4 contents

Table 1. Data showing seasonal physicochemical analysis of rain water in Azad Kashmir

Parameters	Units	Monsoon	Autumn	Winter	Mean
Date	-	06/07/2004	11/10/2004	22-01-2005	-
Time	-	3.00 PM	5:00 PM	7:00 AM	-
Location	-	Smahni town	Smahni town	Smahni town	-
Temp. of air	ºC	30	20.5	6	18.833
Temp. of water	ºC	28	19	7	18.000
pH	-	6.06	6.55	5.72	6.110
EC	µS/cm	60	51.2	27	46.067
TDS	mg/L	38.4	32.77	17.28	29.483
Salinity	g/L	BDL	BDL	BDL	BDL
HCO3	mg/L	39.2	58	25	40.733
TH	mg/L	25	11.9	0.54	12.480
Cl	mg/L	23.55	3.191	10.9	12.547
SO4	mg/L	1.067	26.566	8.788	12.140
N02-N	mg/	BDL	BDL	0 BDL	BDL
NO3-N	mg/L	2.23	5.603	2.283	3.372
O-PO4	mg/L	0.124	0.082	0.678	0.295
T-PO4	mg/L	0.127	0.086	0.701	0.305
DO	mg/L	4.87	6.54	11.28	7.563
BOD	mg/L	1.35	1.01	0.95	1.103
COD	mg/L	1.88	2.11	1.35	1.780
Na	mg/L	9.88	17.261	8.8	11.980
K	mg/L	7.67	0.571	3.256	3.832
Ca	mg/L	24.05	29.114	18.9	24.021
Mg	mg/L	4.22	11.6	3.949	6.590
Fe	mg/L	0.006	0.015	0.015	0.012
Cu	mg/L	0	0	0.011	0.004
Zn	mg/L	0.008	0.012	0.028	0.016
Ni	mg/L	0.011	0.011	0.019	0.014
Pb	mg/L	0.009	0.066	0.008	0.028
Cd	mg/L	0.006	0.002	0.1477	0.052
Co	mg/L	0.011	0.032	0.091	0.045
SAR	-	0.689	0.778	0.565	0.677

Table 2. Statistical description of physicochemical parameters of rain water

Parameters	Min.	Max.	Mean	Range	Count	Skewness	Median	SD	SE	CL95%
PH	5.72	6.55	6.11	0.83	3	0.532	6.06	0.417	0.241	1.037
EC μS/cm	27	60	46.067	33	3	-1.231	51.2	17.088	9.866	42.45
TDS mg/L	17.28	38.4	29.483	21.12	3	-1.230	32.77	10.937	6.314	27.169
HCO_3 mg/L	25	58	40.733	33	3	0.413	39.2	16.553	9.557	41.121
TH mg/L	0.504	25.000	12.480	24.460	3	0.213	11.900	12.240	7.067	30.407
Cl mg/L	3.191	23.550	12.547	20.36	3	0.703	10.900	10.279	5.935	4.800
SO_4 mg/L	1.067	26.566	12.140	25.50	3	1.078	8.788	13.076	7.549	32.483
NO_3 mg/L	2.23	5.603	3.372	3.373	3	1.731	2.283	1.932	1.116	4.800
o-PO_4 mg/L	0.082	0.678	0.295	0.596	3	1.701	0.124	0.333	0.192	o.854
t-PO_4 mg/L	0.086	0.701	0.305	0.615	3	1.704	0.127	0.344	0.198	0.826
DO mg/L	4.87	11.28	7.563	6.41	3	1.254	6.54	3.326	1.920	8.260
BOD mg/L	0.95	1.35	1.103	0.40	3	1.582	1.01	0.216	0.124	0.536
COD mg/L	1.35	2.11	1.78	0.76	3	-1.079	1.88	0.390	0.225	0.968
Na mg/L	8.8	17.261	11.980	8.461	3	1.626	9.88	4.605	2.659	11.43
K mg/L	0.571	7.67	3.832	7.099	3	0.705	3.256	3.584	2.069	8.904
Ca mg/L	18.9	29.114	24.021	10.21	3	-0.025	24.05	5.107	2.949	12.687
Mg mg/L	3.949	11.6	6.590	7.651	3	1.724	4.22	4.341	2.506	10.784
Fe mg/L	0.006	0.015	0.012	0.009	3	-1.732	0.015	0.006	0.003	0.013
Cu mg/L	0	0.011	0.004	0.011	3	1.732	0	0.006	0.004	0.016
Zn mg/L	0.008	0.028	0.016	0.02	3	1.458	0.012	0.011	0.006	0.026
Ni mg/L	0.011	0.019	0.014	0.008	3	1.732	0.011	0.005	0.003	0.012
Pb mg/L	0.008	0.066	0.028	0.058	3	1.730	0.009	0.033	0.019	0.082
Cd mg/L	0.002	0.148	0.052	0.146	3	1.728	0.006	0.083	0.048	0.206
Co mg/L	0.011	0.091	0.045	0.08	3	1.246	0.032	0.042	0.024	0.103

Min. = minimum, Max. =maximum, SD = standard deviation, SE = standard error, CL = confidence level

Nitrite, Nitrate & Kjeldahl nitrogen (K N)

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 in waste water [11]. 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 wastewater. Nitrate nitrogen is highest oxidized form of nitrogen in water and WHO standards prescribe 10 mg/L as maximum permissible nitrate concentration of potable water [8]. 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 [12]. The consequences of high concentration of nitrogen in drinking water are toxic and cause blue baby disease, methaemoglobinaemia in children and gastric carcinomas [13, 14].

Nitrite and Kjeldahl nitrogen are highly toxic forms of nitrogen. Maximum permissible limit of WHO for both is 1.0 mg / L. Nitrite and Kjeldahl nitrogen were found absent in all the selected seasons [Table 1,2]. Nitrate nitrogen indicated values within 2.23-5.60mg/L and average value of 3.372 mg/L and was well within the prescribed limits for drinking water [Fig.1].

Dissolved Oxygen (DO), Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

The DO, BOD and COD seasonal values range from4.87-11.28 mg/L,0.95-1.35 mg/L and1.35-2.11mg/L respectively**.** DO exceed the limit of WHO for the sample collected in February

2005 may possibly because of high solubility at lower temperature. The BOD and COD indicated ingnificant inter seasonal variation among the samples [Fig. 2] [Table 1,2].

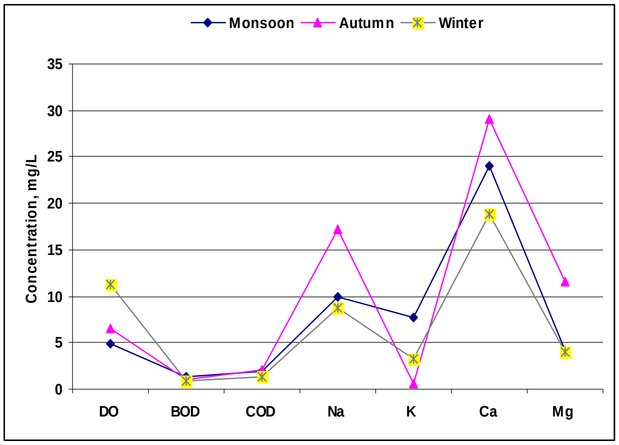

Fig. 2. Seasonal variation in the DO, BOD, COD, Na, K, Ca and Mg contents`

Total Chlorides, Sulphates and Phosphorous

The chloride concentration of rain water varied between 3.19-23.55mg/L and average value was observed 12.55 mg/L**.** The variations in the chloride content among different seasons suggest a difference in the input level of impurities that contaminate the rainwater. However, seasonal variation was little [Fig. 1]. Sulfate concentration in the hydrological year 2004-2005 ranges from 1.07 mg/L to 26.57mg/L with average value of 12.14 mg/L. No significant seasonal changes were observed in sulfate content [Fig. 1]. All the values of chlorides and sulfates were in the range of WHO [9, 10] drinking water standards.

The results of analysis for the rainwater were orthophosphate 0.08-0.68 mg/L and total phosphate0.086-0.701 mg/L with average values0.295 mg/L and 0.305g/L respectively [Table 1]. Seasonal variation was not significant.

Chemistry of Metal Elements

The concentration of Na^+, K^+, Ca^{2+}, and Mg^{2+} varied moderately within the seasonal rainwater samples and Ca^{2+} was dominant throughout [Table1,2] [Fig. 2,3] in the following order: $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. The concentration range for the samples investigated varied within Ca^{2+} 18.9-29 mg/L; Na^+ 8.8-17.26 mg/L; Mg^{2+} 3.95-11.6 mg/L, and, K^+ .57-7.67 mg/L [Fig. 4]. No specific trend of Na^+, K^+, Ca^{2+}, and Mg^{2+} with seasons was observed.

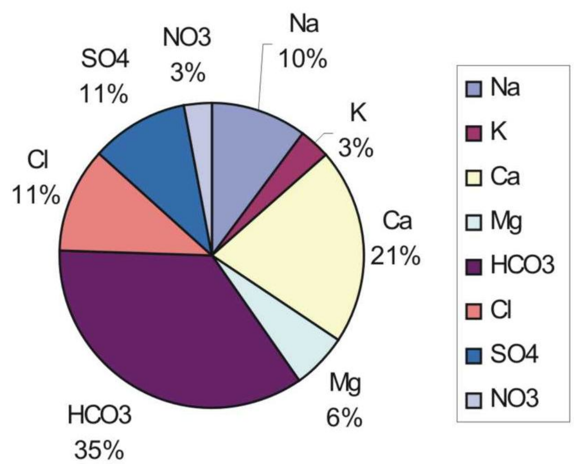

Fig . 3. Pie graph showing relative abundance of major ions.

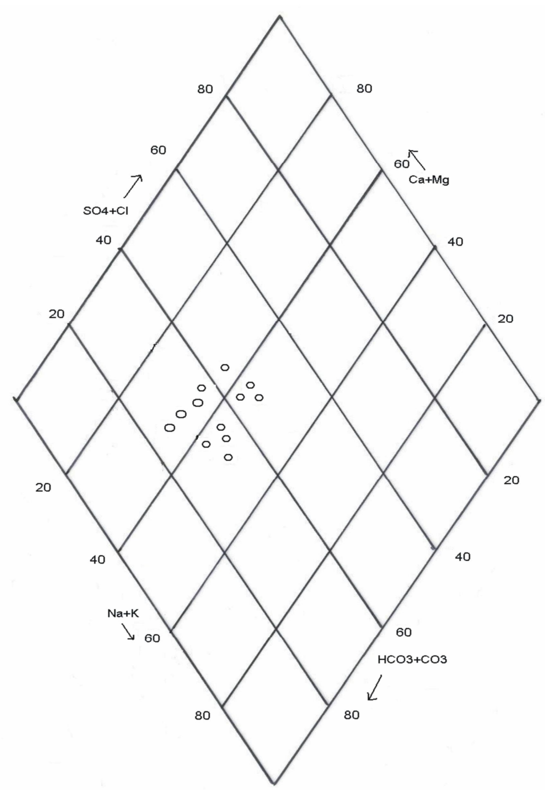

Fig 4. Piper diagram showing the distribution of major ions.

Minor elements like Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, and Co^{2+} were determined lying within the permissible limits of WHO for metal ions. Lead in autumn 2004 (0.066mg/L) and cadmium in winter 2005 (0.148mg/L) exceed the permissible limits (0.01 mg/L) and (0.005 mg/L respectively [Fig. 5]. The metal ions were measured as Fe^{2+} 0.006-0.015 mg/L; Cu^{2+} 0.00-0.011mg/L; Zn^{2+} 0.008-0.028g/L; Ni^{2+} 0.011-0.09mg/L; Co^{2+} 0.011-0.091 mg/L; Pb^{2+} 0.008-0.066 mg/L and, Cd^{2+} 0.002-.147mg/ml in the following order:

$Cd^{2+} > Co^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Fe^{2+} > Cu^{2+}$ [Fig. 6].

Elemental ion composition was almost independent of seasonal change [Fig.2, 5].

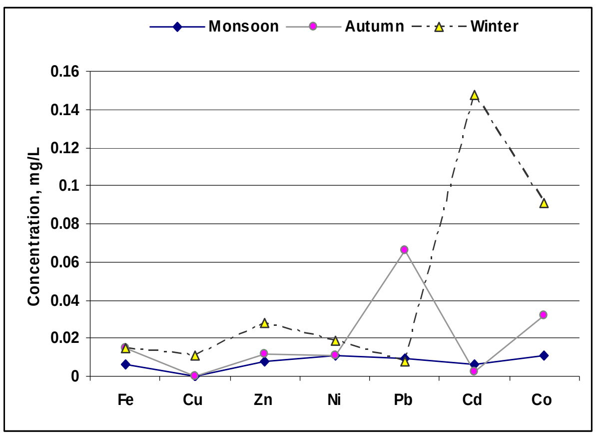

Fig 5. Seasonal variation in Fe, Cu, Zn, Ni, Pb, Cd and Co contents

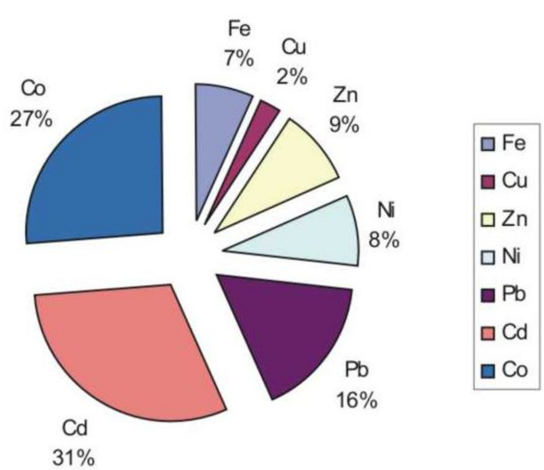

Fig 6. Pie graph showing relative abundance of minor cations.

Mass Charge Balance of Major Ions

Mass charge balance of major cations and anions was calculated considering concentrations in meq/L. The sequence of the abundance of major ions was in the following order:

$Ca^{2+} > Na^{+} > Mg^{2+} > K^{+} = HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$ [Fig. 3].

Major cations and anions indicated concentrations 1.49meq/L and 1.33 meq/L respectively. Hence it is suggested that a good mass charge balance between major cations and anions is maintained throughout the hydrological year of the rainwater.

Irrigation Water Suitability
Alkalinity and Salinity Hazards

The rainwater samples were also tested to suggest their suitability as irrigation water. Two parameters EC and TDS were specifically monitored as these are lineally correlated and are a measure of salinity hazard to crops. Since it reduces osmotic activity of plants and interferes with the absorption of nutrients [15], sodium adsorption ratio (SAR) was specifically calculated to determine the suitability of rainwater for irrigation [16] as follows.

$$SAR = \frac{Na^{+}}{(Ca^{2+} + Mg^{2+})^{1/2} /2}$$

where the concentrations are in meq/L.

The SAR values range from 0.565-0.778with an average value of 0.677 during the one hydrological year (2004-2005). Rainwater samples fall in the low sodium class. This implies that no alkali hazard is anticipated to the crops [Fig. 7]. If the SAR value is greater than 6-9, the irrigation will cause permeability problems on shrinking and swelling types of clays [15].

Sodium %

The sodium percentage (Na %) is defined by

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

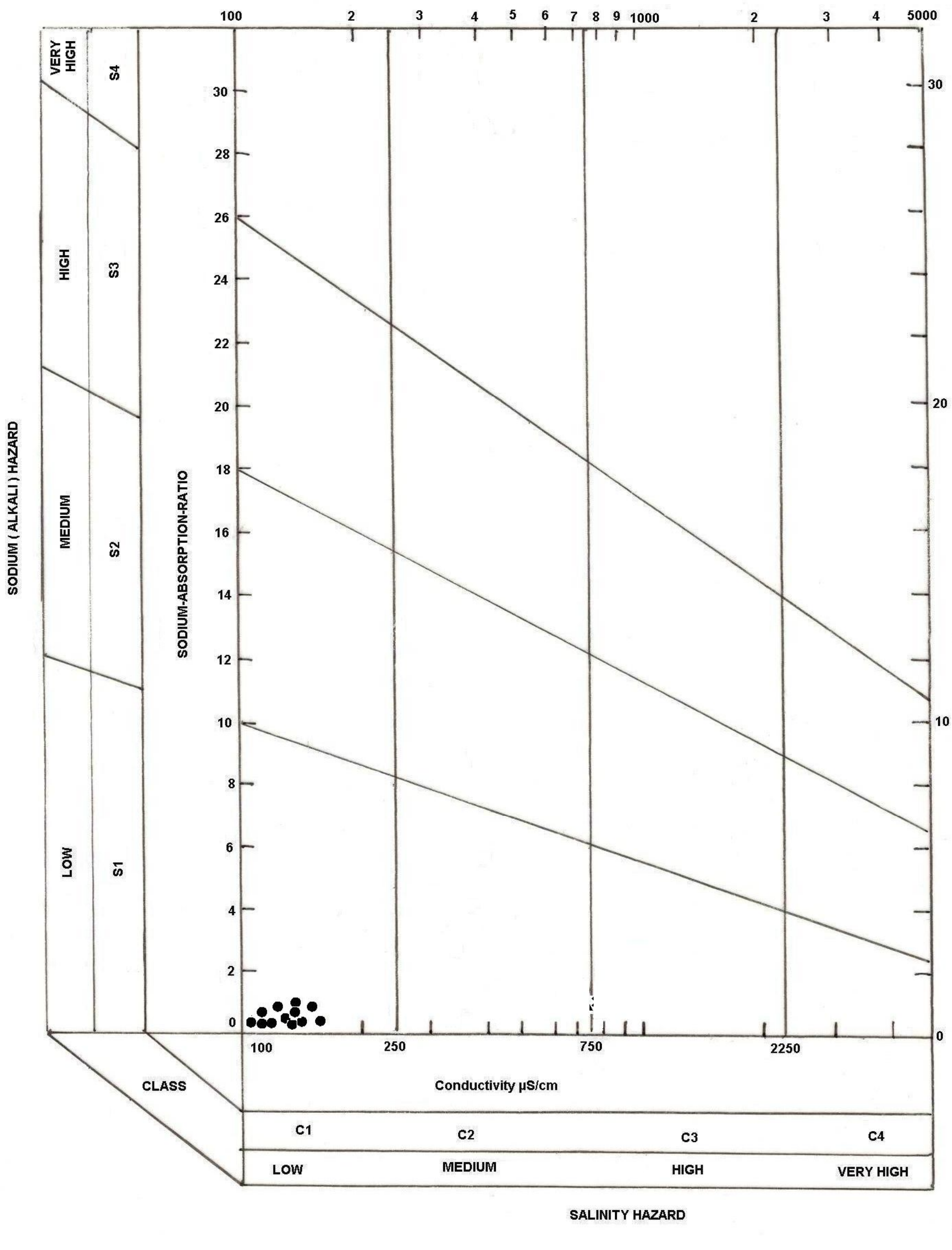

Fig 7. Salinity and alkalinity hazard of irrigation water in US salinity diagram.

where all the concentration are expressed in meq/L.

The average sodium % of the rain water was observed 26.14 i. e. < 40 that indicates that the rain water is good for irrigation [17].

Residual Sodium Carbonate (RSC)

The quality of irrigation water based on Residual Sodium Carbonate test [17] with value 0.21 i.e. <1.25 puts rain water samples into good category of irrigation water.

Conclusion

Interpretation of hydro chemical analysis reveals that the abundance of major ions in the rainwater in one hydrological cycle is in the following order:

$Ca^{2+} > Na^{+} > Mg^{2+} > K^{+} = HCO^{3-} > Cl^{-} \geq SO_4^{2-} > NO_3^{-}$

Alkali earth (Ca^{2+} + Mg^{2+}) = 0.875 meq/L) exceed alkalis (Na^{+} + K^{+}) = 0.619 meq/L) and weak acids (HCO_3^{-} + CO_3^{2-}) = 0.668 meq/L) exceed strong acids (Cl^{-} + SO_4^{2-}) = 0.605 meq/L) This leads to Ca – Mg – HCO_3^{-} / CO_3^{2-} type of rain water.

The concentrations of major ions are within the permissible limits for drinking. Major elemental ion composition is almost independent of seasonal changes. Among minor metal ions lead in autumn 2004 and cadmium in winter 2005 shows higher concentrations compared to other seasons. Kjeldahl nitrogen and nitrite nitrogen concentrations were found below detection limits. Sodium adsorption ratio (SAR), sodium percent (Na %) and residual sodium carbonate (RSC) indicate that the quality of the rainwater is suitable for agricultural use.

References

1. www.ajk.gov.pk.com
2. J. D. Hem Study and Interpretation of the chemical chactersitics of natural water. *USGS Water Supply pap* (1985) 2254.
3. M. A Khan; D. P. Zutshi, Primary productivity and Trophic status of a Kashmir Himalayan Lake. *Hydrobiologia* 68(1) (1978) 3.
4. D. P. Zutshi and K. K. Vass. Limnological studies on Dal lake Sirinagar III Biological features Proc. *Indian natn. Sci. Acad B* 48(2) (1982) 234.
5. K. D. Kumar, S. Rawat, R. Joshi, *Envirn. Geology* 31 (1997) 150.
6. APHA, Standard methods for examination of water and waste water, 17th Ed. American Public Health Association, *Washington DC* (1989) 1497.
7. S. E. Alen, Chemical Analysis of ecological materials Blach well scientific publ., 2nd Ed., *Oxford* (1989).
8. W. Fresenius, K. E. Quentin, W. Schneider; Water analysis, Berlin; Springer, (1988) 725.
9. WHO International standards for drinking water. World Health Organization, *Geneva* (1971).
10. WHO Guidelines to drinking water quality. World Health Organization, *Geneva* (1983) 186.
11. N. F. Voznaya, Chemistry of water and microbiology, Moscow: *Mir Publishers*, (1981) 347.
12. J. A. Tindall, R. L. Petrusak, P. B. McMohan, Nitrate transport and transformation process in unsaturated porous media. *J. Hydrol* 169, (1995) 51.
13. H. H. Comly, Cyanosis in infants caused by nitrates in well water. *J. Am Mwd Assoc*., 129 (1945) 12.
14. G. Gilly, G. Corrao, S. Favilli, Concentr-ations of nitrates in drinking water and incidence of gastric carcinomas. First descriptive study of the Piemonate Region, *Italy. Sci. Total Environ*. 34 (1984) 35.
15. A. Saleh, F. Al-Ruwaih, M. Shehata, Hydr-ogeochemical processes operating within the main aquifers of Kowait. *J. Arid Environ*., 42 (1999) 195.
16. K. R. Karanth, Groundwater asswssment, development and management. Tata McGraw Hill New Delhi (1987) 720.
17. H. M. Ragunath, Groundwater. Wiley *Eastern Ltd, New Delhi* (1987) 563.