



## Hydrochemistry of Snowmelt in Sudhanoti and Poonch Districts of Azad Jammu and Kashmir, Pakistan

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(Received 1<sup>st</sup> June 2006 Revised 22<sup>nd</sup> November 2006)

### Abstract

A study was conducted to assay the quality of snowmelt in Sudhanoti and Poonch Districts of Kashmir, Pakistan. In this area, primary source of water for drinking and agricultural use is rain, snowfall and snowmelts. Physicochemical parameters; pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH)  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$ , Kjeldahl nitrogen (KN), orthophosphate (o- $\text{PO}_4$ ), acid hydrolysable phosphate (t- $\text{PO}_4$ ), dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD),  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Co}^{2+}$  were determined. Chemical analyses of the snowmelts indicate the presence of major ions as:  $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ = \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$ . Ternary plot on elemental composition indicates Ca - Na - Mg -  $\text{HCO}_3^-/\text{CO}_3$ , Ca - Na -  $\text{SO}_4$  and Na - Cl as the dominant hydro chemical types; while salinity hazard index sets the criterion for its agricultural utility. Higher concentration of  $\text{SO}_4^{2-}$  and  $\text{pH} < 7$  manifests the effect of industrial pollution as acid rains on hydrological cycle.

**Keywords:** Snowmelt hydrochemistry, Kashmir, Pakistan

### 1. Introduction

Pallandri, the sub-division of Sudhanuti District is situated at 1372 m above sea level and is located 97 Km off Rawalpindi, Pakistan. Trarkhal is a small town situated 129 Km from Kohala and 1982 m above sea level. Rawalakot, the district headquarter, is situated in the heart of District Poonch at 1615 m above the sea level. The area of Poonch District is 855  $\text{Km}^2$ , population 0.449 million and population density 525 persons  $/\text{Km}^2$ . The area of Sudhanoti District is 569  $\text{Km}^2$ , population 0.242 million and population density 425 persons  $/\text{Km}^2$ . The average rainfall is 15cm. The quality of water has linear correlation with ecological and anthropogenic factors (Hem, 1985; Hymavathi *et al.*, 1999) while describing the water quality of the stream Mudasarlova, India and Sastre *et al.*, (Sastre *et al.*, 1988) have reported the study of surface run off. Mirza *et al.*, (Mirza *et al.*, 2006) reported physicochemical study of pond and rainwater in Distict Bhimber but the quality of water of Sudhanoti and Poonch Districts is under studied. The present work examines the effect of physicochemical characteristics of snowmelts on the quality of water.

### 2. Climate of the Area

The state of Azad Jammu and Kashmir stretches between longitude  $73^\circ - 75^\circ$  and latitude  $33^\circ - 36^\circ$  and the altitude rises steeply from 360 meters to 6325 meters above sea level. There are the hot plains of the Bhimber and Mirpur districts and coldest lands of Kel, Taubat, Sharda, Leepa, Forward Kahuta, Rawalakot, Pallandri, Trarkhal, Fatehpur etc. The 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 hills receive rainfall from monsoon winds while in winters, winds from the Mediterranean cause snowfall and rainfall in the Valleys of Kashmir causing sub zero temperatures [Mirza *et al.*, 2006].

### 3. Geology of the Area

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. The rocks

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consist of granite and crystalline groups. The rocks of the area and mainly composed of chlorite, muscovite schists, mica granite, sand stone, quartzite, calcite, pyrite, etc (Chaudhry and Ashraf, 1984).

#### 4. Sampling

Before sampling a detailed survey of the area was undertaken. 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 stations for the study. Pallandri, the district head quarter of Sudhanoti, Trarkhal town and Rawalakot, district head quarter of Poonch were selected as sampling stations.

The sampling was carried out in February-March 2005. Samples were collected in pre-washed high-density polythene containers directly, from selected locations. Field measurements included pH, EC, TDS, and DO, Cl<sup>-</sup>, hardness and bicarbonates. For elemental analysis each sample was acidified to pH<2; for organic matter, fixed with HgCl<sub>2</sub>. Separate samples were taken for specific analysis.

#### 5. Experimental

Dissolved oxygen (DO) in the samples was determined by Wrinkler method (APHA, 1989). 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 (APHA, 1989). Orthophosphate, nitrate and nitrite were determined by spectrophotometry. 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 (APHA, 1989). Sulphate was determined by turbidimetry as BaSO<sub>4</sub> 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 (250ml) containing nitric acid (1ml) was heated gently at 90- 95°C and was concentrated to about 5-8ml. 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.

#### 6. Results and Discussion

The pH varied between 6.28- 6.5 in one hydrological year with average value 6.36. The pH < 7 may be because of acidic rains due to natural phenomenon (oxidation process during thunder and lightning) and anthropogenic activities but fall within the WHO water quality standards (Table-1). The electrical conductivity (EC) and total dissolved solids (TDS) (Table-1) indicate insignificant inter sample variation. EC and TDS varied within the range 13 - 20µS/cm and 8.32-12.8mg/L. However, EC & TDS values were observed within prescribed limits of WHO [WHO, 1971, 1983].

Table 1. Analysis of physicochemical parameters of snowmelt from three sampling stations of Azad Jammu and Kashmir, Pakistan.

Parameters	Pallandri S <sub>1</sub>	Trarkhal S <sub>2</sub>	Rawalakot S <sub>3</sub>	Mean
PH (25°C)	6.500	6.300	6.280	6.360
EC µS/cm	55.000	50.000	45.000	50.000
TDS mg/L	35.200	32.000	28.800	32.000
HCO <sub>3</sub> mg/L	BDL	BDL	BDL	BDL
TH mg/L	23.000	21.000	20.000	21.333
Cl mg/L	3.200	2.900	2.800	2.967
SO <sub>4</sub> mg/L	12.430	9.110	8.001	9.847
NO <sub>3</sub> mg/L	BDL	BDL	BDL	BDL
o-PO <sub>4</sub> mg/L	BDL	BDL	BDL	BDL
t-PO <sub>4</sub> mg/L	BDL	BDL	BDL	BDL
DO mg/L	8.230	7.880	8.448	8.186
BOD mg/L	BDL	BDL	BDL	BDL
COD mg/L	BDL	BDL	BDL	BDL
Na mg/L	0.19	0.21	0.217	0.206
K mg/L	0.111	0.06	0.037	0.069
Ca mg/L	1.99	1.89	1.671	1.850
Mg mg/L	0.14	0.13	0.105	0.125
Fe mg/L	0.095	0.082	0.072	0.083
Cu mg/L	0.011	0.013	0.017	0.014
Zn mg/L	0.016	0.020	0.010	0.015
Ni mg/L	0.020	0.021	0.019	0.020
Pb mg/L	0.092	0.082	0.093	0.089
Cd mg/L	0.080	0.090	0.107	0.092
Co mg/L	0.070	0.060	0.052	0.061

S<sub>1</sub> = station 1. S<sub>2</sub> = station 2; S<sub>3</sub> = station 3; BDL = below detection limit

Table 2. Statistical description of physicochemical parameters of snowmelt in Azad Kashmir.

Parameters	Min.	Max.	Mean	Range	Count	Median	SD	SV
PH	6.28	6.50	6.36	0.22	3	6.3	0.122	0.015
EC $\mu$ S/cm	45	55	50	10	3	50	5	25
TDS mg/L	28.8	35.2	32	6.4	3	32	3.2	10.24
HCO <sub>3</sub> mg/L	0.00	0.00	0.00	0.00	3	0.00	0.00	0.00
TH mg/L	20	23	21.33	3	3	21	1.53	2.33
Cl mg/L	2.8	3.2	2.97	0.4	3	2.9	0.21	0.04
SO <sub>4</sub> mg/L	8.001	12.43	9.87	4.429	3	9.11	2.305	5.311
NO <sub>3</sub> mg/L	0.00	0.00	0.00	0.00	3	0.00	0.00	0.00
o-PO <sub>4</sub> mg/L	0.00	0.00	0.00	0.00	3	0.00	0.00	0.00
t-PO <sub>4</sub> mg/L	0.00	0.00	0.00	0.00	3	0.00	0.00	0.00
DO mg/L	7.88	12.24	8.186	0.568	3	8.23	0.286	0.082
BOD mg/L	0.00	0.00	0.00	0.00	3	0.00	0.00	0.00
COD mg/L	0.00	0.00	0.00	0.00	3	0.00	0.00	0.00
Na mg/L	0.19	0.217	0.206	0.027	3	0.21	0.014	0.0002
K mg/L	0.037	0.111	0.069	0.074	3	0.06	0.038	0.001
Ca mg/L	1.671	1.99	1.850	0.319	3	1.89	0.163	0.027
Mg mg/L	0.105	0.14	0.125	0.035	3	0.13	0.018	0.0003
Fe mg/L	0.072	0.095	0.083	0.023	3	0.082	0.012	0.0001
Cu mg/L	0.011	0.017	0.014	0.006	3	0.013	0.003	9.33
Zn mg/L	0.01	0.02	0.015	0.01	3	0.016	0.005	2.53
Ni mg/L	0.019	0.021	0.02	0.002	3	0.02	0.001	1.00
Pb mg/L	0.082	0.093	0.089	0.011	3	0.092	0.006	3.7
Cd mg/L	0.08	0.107	0.092	0.027	3	0.09	0.014	0.0002
Co mg/L	0.052	0.07	0.061	0.018	3	0.06	0.009	3.13

Min = minimum, Max = maximum, SD = standard deviation, SV = sample variance

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 wastewater (Voznaya, 1981). 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 (Fresenius, *et al.*, 1988). 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 (Tindall *et al.*, 1995). The consequences of high concentration of nitrogen in drinking water are toxic and cause

blue baby disease, methaemoglobinaemia in children and gastric carcinomas (Comly, 1945; Gilly *et al.*, 1984).

Nitrite and Kjeldahl nitrogen are highly toxic forms of nitrogen. Maximum permissible limit of WHO for both is 1.0 mg/L. Nitrate and Kjeldahl nitrogen were found absent in all the selected samples [Table 1,2]. Nitrite nitrogen indicated values within 0.00 – 0.021mg/L and average value of 0.007 mg/L and was well within the prescribed limits for drinking water.

The DO values range from 7.88 – 8.45 mg/L with an average value of 8.19 mg/L. The BOD and COD were found absent in the samples [Table 1, 2].

The chloride concentration of snowmelt varied between 2.8-3.2mg/L and average value was observed 2.97mg/L. Sulfate concentration range from 8.001 – 12.43mg/L with average value of 9.847 mg/L. No significant inter sample changes were observed in sulfate content [Fig. 1].

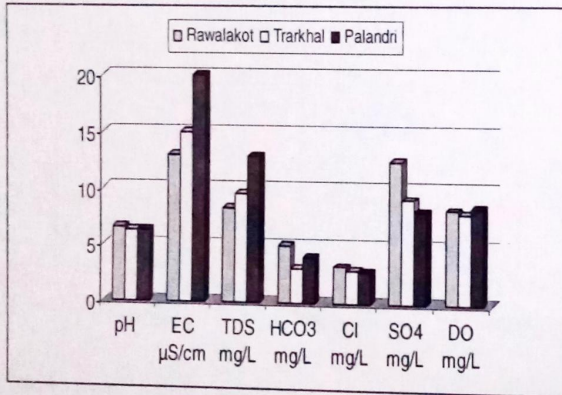


Fig 1: Inter-sample variation in pH, EC, TDS, HCO<sub>3</sub>, Cl, and SO<sub>4</sub> DO contents.

All the values of chlorides and sulfates were within WHO (WHO, 1971, 1983) drinking water standards. Orthophosphate and total phosphate were not detected [Table 1].

The concentration of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> varied moderately within the samples and Ca<sup>2+</sup> was dominant throughout [Table 1, 2] [Fig. 2,4]

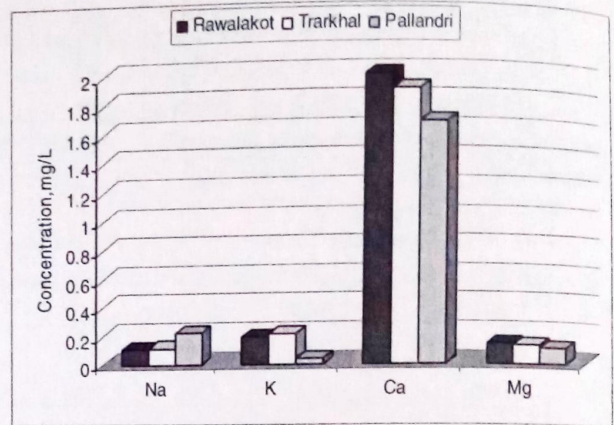


Fig 2: Inter-sample variation in the DO, BOD, COD, Na, K, Ca and Mg contents.

in the following order: Ca<sup>2+</sup> > Na<sup>+</sup> > Mg<sup>2+</sup> > K<sup>+</sup>. The concentration range for the samples investigated varied within Ca<sup>2+</sup> 1.67 – 1.99 mg/L; Na<sup>+</sup> 0.19 – 0.217 mg/L; Mg<sup>2+</sup> 0.105 – 0.140 mg/L, and, K<sup>+</sup> 0.0370 – 0.111 mg/L [Table 1].

Minor elements like Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, and Co<sup>2+</sup> lye within the permissible limits of WHO for metal ions. Lead (0.082-0.093mg/L) and cadmium (0.08-0.107mg/L) exceed the

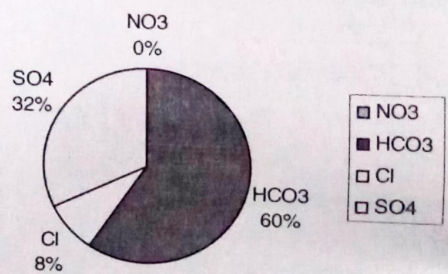


Fig 3: Pie graph showing relative abundance of major anions.

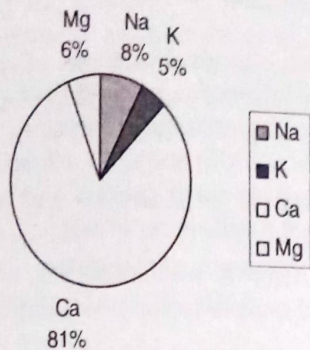


Fig 4: Pie graph showing relative abundance of major cations.

permissible limits (0.01mg/L) and (0.005) mg/L respectively. The metal ions were measured as  $Fe^{2+}$  0.072-0.095mg/L;  $Cu^{2+}$  0.011-0.017mg/L;  $Zn^{2+}$  0.010-0.02mg/L;  $Ni^{2+}$  0.019-0.021mg/L;  $Co^{2+}$  0.052-0.07mg/L;  $Pb^{2+}$  0.082-0.093mg/L and,  $Cd^{2+}$  0.08-0.107 mg/ml in the following order:

$Fe > Pb > Cd > Co > Ni > Zn > Cu$  [Fig. 5 & 6].

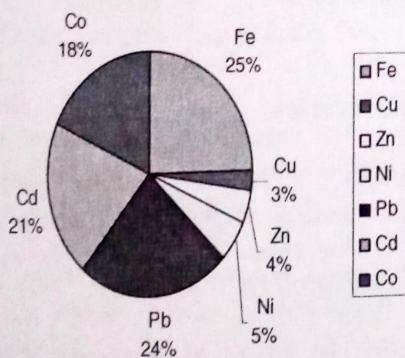


Fig 5: Pie graph showing relative abundance of minor cations.

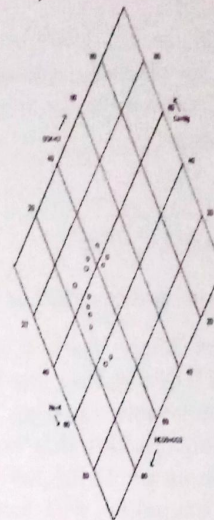


Fig 6: Ternary diagram showing the distribution of major ions.

#### 7. 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:

$Ca^{2+} > Na^+ > Mg^{2+} > K^+ = HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$  [Fig. 3, 4].

Major cations and anions indicated concentrations 0.154meq/L and 0.183meq/L respectively. Hence it is suggested that a mass charge balance between major cations and anions is maintained in the snowmelt.

#### 8. Irrigation Water Suitability Alkalinity and Salinity Hazards

The snowmelt samples were also tested to ascertain their suitability for irrigation. 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 [Saleh *et al.*, 1999] sodium adsorption ratio (SAR) was specifically calculated to determine the suitability of snowmelt for irrigation as per the following expression:

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

(The concentrations are in meq/L.)

The SAR values range from 0.054-0.56 with an average value of 0.055 during one hydrological year (2004-2005). Snowmelt samples fall in the low sodium class. This 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 of clay types (Saleh *et al.*, 1999).

**Sodium %**

The sodium percentage (Na %) is defined by

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

where all the concentration are expressed in meq/L.

The average sodium % of the snowmelt was 4 i. e. < 20 indicating that the snowmelt is really suitable for irrigation (Ragunath, 1987) [fig. 7].

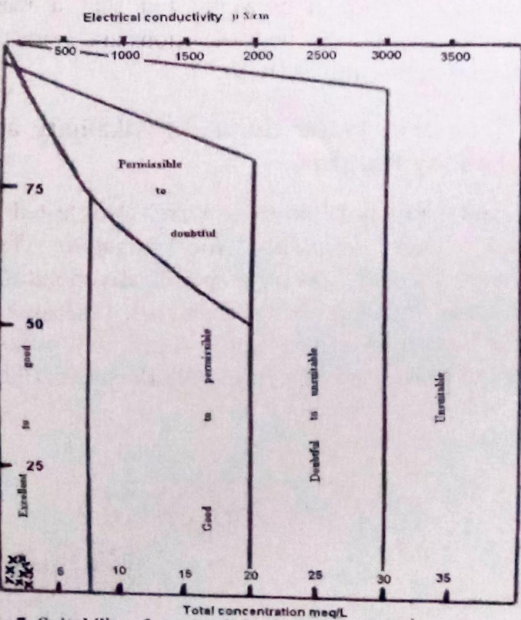


Fig 7: Suitability of snowmelt for irrigation in Wilcox diagram.

**10. Conclusion**

Hydro chemical analysis of snowmelt during a hydrological year compared to the general quality of drinking and irrigation water as reported earlier (Mirza *et al.*, 2006) indicate a mixed abundance of alkali and alkali earth cations and anions as HCO<sub>3</sub> and SO<sub>4</sub> in the following order:

Ca > Na > Mg > K = HCO<sub>3</sub> > SO<sub>4</sub> > Cl > NO<sub>3</sub>. This is attributed mainly to the geochemical interaction of the snow.

Alkali earth (Ca<sup>2+</sup> + Mg<sup>2+</sup>) = 0.103 meq/L) exceed alkalis (Na<sup>+</sup> + K<sup>+</sup>) = 0.011 meq/L) and weak acids (HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup>) = 0.170 meq/L) exceed strong acids (Cl<sup>-</sup> + SO<sub>4</sub><sup>2-</sup>) = 0.066 meq/L). Thus the type of snowmelt is Ca – Mg – HCO<sub>3</sub><sup>-</sup> / CO<sub>3</sub><sup>2-</sup>.

The concentrations of major ions are within the permissible limits of drinking water quality standards, while minor metal ions lead and cadmium exceed threshold values. Kjeldahl nitrogen and nitrite nitrogen concentrations were found below detection limits. Sodium adsorption ratio (SAR) and sodium percent (Na %) make snowmelt suitable for agricultural use.

**11. References**

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