Seasonal and Environmental Pollution Impact on the Quality of Water of River Poonch near District Kotli , Pakistan

Muhammd Aslam Mirza, Muhammad Aziz Choudhary, Muhammad Yar Khuhawar, Rafee Arain

***Abstract*— The River Poonch enters Distric Kotli near Tata Pani, collects the total sewage of Kotli city and ultimately embraces River Jhelum in Mangla Dam. The present work was carried out for the estimation of trace metals in the samples collected from River Poonch in 3 seasons (summer, winter & autumn) in one hydrological year during 2004-2005. Physicochemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), HCO_3^-, 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), Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, and Co^{2+} were determined. The TDS was found within the range 133-208 µg/ml with average value 164 µg/ml. Pd and Cd crossed the threshold value prescribed by WHO. Chemical analyses of the River water indicates the order of major ions as: $Ca^{2+} > Mg^{2+} > Na^+ > K^+ = HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. Study of elemental composition indicates that Ca^{2+} - Mg^{2+} - Na^+ - HCO_3^- , Ca^{2+} – Na^+ – Cl^- - SO_4^{2-} and Na^+ - Cl^- are the dominant hydro chemical types; likewise SAR values set the criterion for its agricultural utility. Correlation coefficient was also established to identify the common origin of the analytes. Seasonal variations were insignificant with a few exceptions.**

***Index Terms*— River Poonch, Physicochemical parameters, agricultural utility.**

I. INTRODUCTION

River Poonch enters Kotli district from the north at a place called Tata Pani and flows towards south passing west of Kotli town and finally enters Mirpur district before falling in to Mangla Lake**.** Jhelum River makes the western boundary of the district and flows in north-south direction. The Rangpur Nala (main stream) is an important western tributary of the Poonch River while two important streams namely Ban Nala and Mahuli Nala join it from the east. While flowing between Kotli city and Mangla Lake, it embraces numerous small streams.

The whole of Kotli district (run way of River Poonch) is a hilly area with narrow valleys. These hills are the southern limits of the Pir Punjal range. The average height in the eastern and central part of the district is about 1000 meters above sea level. The rest of the area is less than 1000 meters in altitude. Hills are generally covered with coniferous trees.

The climate of the study area is generally hot in summer and cold in winter. The eastern and northern parts are dry and cold whereas the western areas are a little bit hot. June is the hottest month with the mean maximum and minimum temperature of about 38 ºC to 25 ºC respectively. January is the coldest in month with the mean maximum and minimum temperatures of about 18 ºC and 5 ºC respectively. The mean annual rainfall is about 1300 millimeters, more than half of which occurs during July and August [1].

The river is fed by snow melt and rainfall. It is one of the main sources of irrigation, electricity generation, drinking water and food. Most of the flow of the river is contributed during the high run off or flood period. The amount of water contributed during the dry weather periods is only a small part of the total (Hymavathi et al. 1999). The quality of the river water may change due to the ecological and anthropogenic factors.

Hymavathi (1999) described the water quality of stream Mudasarlova, India and Sastre et al. (1998), reported the study of samples from the stream surface. Mirza et al. **(2005-2009)** reported the quality of ponds water in District Bhimber (Aslam et al. 2006); chemistry of torrent water (Aslam Mirza et al. 2007) ; quality of springs water in the catchment areas of Indus River in Kashmir, Pakistan (Aslam Mirza et al. 2006); quality of snow melt in Sudhanoti and Poonch Distrcts (Aslam Mirza et al. 2005), quality of rain water in Ditrict Bhimber (Aslam Mirza et al. 2005). The present work examines the physicochemical characteristics of water of Poonch River within the area of Kotli and Mirpur Districts and seasonal changes in the water quality.

II. SAMPLING STRATEGY

The study involves preliminary survey, monitoring of river and testing of water to ascertain the physicochemical parameters. The objective of the field survey was to locate the sampling stations for study. The rivers can be considered as representative of surface water (Magaritz et al 1980). Three stations namely, RS-1, RS-2 and RS-3 were selected for study of water quality. Samples were collected from the station RS-2 to assess the effect of domestic waste of Kotli city on the quality of river water. One sample was collected from each of the RS-1, RS-2 and RS-3 [Table 1]. The sampling was focused regarding the population density. The samples were collected three times during the months of July, November 2008 and February during 2009 and analyzed in the

Manuscript received November 23, 2014.

Muhammd Aslam Mirza, Mirpur University of Science and Technology (MUST), Mirpur, Pakistan

Muhammad Aziz Choudhary, Mirpur University of Science and Technology (MUST), Mirpur, Pakistan

Muhammad Yar Khuhawar, Institute of Advance Research Studies in Chemical Sciences /Dr. M.A Kazi Institute of Chemistry University of Sindh, Jamshoro, Pakistan

Rafee Arain, Institute of Advance Research Studies in Chemical Sciences /Dr. M.A Kazi Institute of Chemistry University of Sindh, Jamshoro, Pakistan

laboratories of Chemistry department university of Sindh Jamshoro. Measurements of 30 parameters were obtained through field and laboratory analysis of grab samples. The homogenized sample was transferred to a clean 1.5 L plastic bottle after rinsing three times with the sample

III. Experimental

The temperature of water and air 1m above the surface of water was noted with mercury thermometer. The pH was recorded with Orion 420A pH meter. Conductivity, salinity, and total dissolved solids (TDS) were measured with Orion 115 conductivity meter. Hardness, chloride and alkalinity were determined by titration with standard EDTA, silver nitrate and hydrochloric acid. Total nitrogen was determined using Kjeldahl method (APHA, 1989). Spectrophotometry techniques were used to determine orthophosphate, nitrite and nitrate. Orthophosphate was determined by reducing phosphomolybdic acid formed with ascorbic acid to molybdenum blue. Total phosphate was estimated by persulphate acid digestion method, followed by determination as of orthophosphate. Nitrate was determined after derivatization with brucine sulphate. Nitrite was estimated using N-naphthyl ethylenediamine as derivatizing reagent as reported (Magaritz et al 1980) [12]. Sulphate was determined by turbidimetry as $BaSO_4$ using double beam Hitachi 220 Spectrophotometer. The dissolved oxygen (DO) in the samples was determined by Wrinkler method (APHA, 1989). Chemical oxygen demand (COD) was estimated by micro-dichromate oxidation method (Symons et al. 1960).

The metal ions were determined with Varian Spectr AA-20 atomic absorption spectrometer with standard burner head and air acetylene flame. The analysis was carried out in triplicate with integration time 3 second and delay time 3 sec. Na, K, Ca and Mg were determined after appropriate dilution. Sample (250ml) containing nitric acid (1ml) was heated gently at 90-95 $^{\circ}$C and was concentrated to about 5 – 8 ml. The final volume was then 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 at the conditions recommended by the manufacturer.

IV. Results and Discussion

The average results of physicochemical characteristics of river water are summarized in table 1 and reveal varying nature of the river water. The difference in the quality of river water may be due to some difference in the bed rock, human activity and different recharge zones (Aslam et al. 2006). Flow of river varies considerably throughout the year, depending upon the rate of precipitation. Maximum flow rate is observed in moon soon season (July-August) due to heavy rainfall and minimum in the months of May – June because of dry and hot climate.

A. pH of the River Water

The pH of all the river water was found 7.21 – 7.64. The sample RS-2 which was collected after addition of city sewage in the river surrounded by high population density, indicated pH towards basic side may be because of human activity. However, the river samples indicated pH values within the threshold limits of WHO for drinking water. A significant change was not observed in the water pH during different seasons.

B. Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

EC and TDS varied within the range 209-330 µS/cm and 134-211 mg/L respectively [Table1]. The sample RS-2 indicated higher values of EC and TDS may be because of thick population around the river. The river samples RS1, RS2 and RS3 indicated values of EC and TDS well within the permissible limits of WHO standards for drinking water. The higher values of EC and TDS for sample RS2 may be suggested because of mixing of the domestic waste of Kotli city with the river water.

C. Bicarbonates and Hardness

The bicarbonates of the river water showed concentration within 127.4- 165.0 mg/L calculated as $CaCO_3$. The hardness indicated the parallel behavior with bicarbonates in all the three samples and showed concentration in the range 99.2-187.0 mg/L as $CaCO_3$ [Table1]. The values of both the parameters were found within permissible limits of WHO for drinking water**.**

D. Total Chlorides

The total chlorides of river water indicated the variation within 32.0-44.0 mg/L. A little variation in chloride concentration was observed with seasons and higher values were indicated in autumn, may be because of anthropogenic activity [Table1] [Fig 1-4].

E. Sulphates

All the river samples indicated presence of SO_4^{2-} in the water. The concentration varied within 13.8-27.8 mg/L [Table1]. Seasonal variation indicated parallel results as for chloride with higher values observed in autumn. The highest concentration of sulphate was observed in sample RS-2 may possibly be due to mixing of the waste water of the Kotli city. A significant change was not observed in the sulphate content during different seasons [Fig 1-4].

F. Phosphorus

The phosphorus in the form of orthophosphate and acid hydrolysable phosphate in water may be due to anthropogenic activity and geological reasons and indicated concentrations within the range 0.053-0.147 mg/L and 0.071-0.190 mg/L respectively [Table1]. The highest concentration of orthophosphate and acid hydrolysable phosphate was found in sampling point RS-2 located at low lying side of Kotli city may be because of dissolution of the rock phosphate in water and human activity.

G. Nitrites, Nitrates and Total Nitrogen

Nitrites, nitrates, and organic nitrogen are commonly known forms of nitrogen. Their presence in the water body is caused by the decomposition of proteinous compounds in waste water (Voznaya, 1981). In natural waters, the presence of nitrogen of mineral origin is rare and presence of nitrogen compounds like nitrites, nitrates and organic nitrogen in water indicate pollution with domestic waste water. Nitrate nitrogen is the highest oxidized form of nitrogen in water and maximum permissible limit of nitrate concentration in potable

water prescribed by WHO is 10mg/L. Water of all the samples indicated nitrate concentration within the permissible limits of WHO.

Nitrite is more toxic and permissible limit of WHO for nitrite is 1.0 mg/L All the samples indicated nitrite values within the permissible limits. Total nitrogen (Kjeldahl method) in the samples RS-2 and RS-3 crossed the limit of WHO which may be due to the decomposition material of biological origin and human activity [Table 1]. Seasonal changes were not significant in nitrogen contents [Fig 1-4].

H. Dissolved Oxygen (DO)

The dissolved oxygen indicated the variation within 6.38-7.80 mg/L [Table1]. The lowest oxygen content was observed in sample RS-2 may be because of less solubility due to pollution content of Kotli city. Dissolved oxygen (DO) in the water body is required to prevent odor and is suitable for use by aquatic plants and other life in water. Summer season indicated slightly lower value of DO content in stream water due to less solubility at higher temperature; however, the change was insignificant [Fig 1-4].

I. Biological Oxygen Demand (BOD)

BOD is considered important parameter to estimate concentration of waste water and to decide about the quality of the drinking water. The water of river surrounded by high population indicated relatively higher values within the range 8.48-13.50 mg/L for BOD [Table1]. A slight change in BOD value may be due to human activity and dilution factor during dry and rainy seasons [Fig 1-4].

J. The Cation Chemistry

The concentration of major metal contents (Na, K, Ca, and Mg) varied within the samples and Ca was dominant throughout, followed by Mg > Na > K with the ranges Na 6.89-11.20 mg/L, K 6.76-8.21 mg/L, Ca 51.23-61.20 mg/L, and Mg 18.25- 51.20 mg/L [Table1]. It was observed that the concentration of major metal contents was higher in autumn [Fig. 5]. It may be due to less dilution of the salt contents within the catchments area of the river during the dry season of autumn in Kotli District.

The minor metal contents were observed within the limits; Fe 0.060-0.158 mg/L, Zn 0.009- 0.035 mg/L, Ni 0.021-0.032 mg/L, Cu 0.001- 0.005 mg/L, Pb 0.021-0.075 mg/L, Cd 0.035- 0.045 mg/L and Co 0.084-0.260 mg/L. The waters indicate the following decreasing order:

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

All the samples indicated results within the permissible limits of WHO for metal ions except Pb and Cd. However, Pb and Cd crossed the limits of 0.01 mg/L and 0.003 mg/L respectively in all the samples [Table1] [Fig 6]. It may be due to geological nature of catchments area. Seasonal variation did not affect the concentration of metal contents significantly except Fe, Pb, Cd and Co that may be due to dissolution of metal contents during land sliding or anthropogenic activity.

K. Sodium Adsorption Ratio (SAR)

Sodium adsorption ratio was calculated and the results obtained were within 0.5-1.8 and it is suggested that the water is suitable for agricultural purposes **(**Aslam et al, 1980**)**.

L. Correlation Coefficient Matrix

Correlation matrix of 11 selected metals was prepared (Table 2). A strong linear correlation was observed between Fe and Na, Zn and Cu, Ni and Na, Ni and Fe, Pb and Na, Pb and Fe, Pb and Ni, Cd and Zn, Co and , Co and Mg. This positive correlation indicates the common origin of these metals on the behalf of geological and anthropogenic activities. Similarly, a correlation was established among the parameters such as EC,TDS,HCO_3,TH,Cl^-,SO_4,NO_2-N,NO_3-N,K-N and O-PO_4 (Table 3). A strong linear correlation was observed between the pairs: TDS and EC; TH and HCO_3; NO_2-N and SO_4; O-PO_4 and Cl^-, T-PO_4 and Cl^- and T-PO_4 and O-PO_4. Most of the variables are negatively correlated showing their random origin. The base value of every cell content represents the Pearson coefficient which shows the significance of correlation. If the value of P coefficient is less than 0.05 then correlation is considered significant and if value of P coefficient is greater than 0.05 then correlation is considered non-significant**.**

V. Conclusion

As an outcome of this study it is concluded that seasonal variation in different physicochemical parameter values for each river sample is not significant. Population density which varies considerably around the river has some effect on water quality of river water. Higher concentrations of Pb, Cd, and organic nitrogen than permissible limits need some attention for the use of river water for drinking purposes. The higher concentration of lead and cadmium in river water may be due to geological nature of the catchments area and anthropogenic activity. SAR values suggest the suitability of river water for agricultural purposes.

References

[1] www.ajk.gov.pk.com
[2] Hymavathi, V., Aruna, P., Rao, L. M. (1999). Pollut. Res; 18(1), 83.
[3] Sastre, A. V., Santinelli, N. H., Otano, S. H., Ivanissevich, M. E. (1998). Verch. Int. Ver. Theor. Angew. Limnol; 26(3), 951.
[4]. Aslam, M., Arain, G.M., & Khuhawar M.Y. (2006). J. Chem. Soc. Pak., 28, 430.
[5]. Aslam Mirza, M., Khuhawar, M.Y., Kandhro, A.J. (2005). Pak. J. Anal. Chem., 16, 72.
[6]. Aslam Mirza, M., Khuhawar, M. Y., Arain, R. (2008). Asian Journal of Chemistry, 20, 5915.
[7]. Aslam Mirza, M., Khuhawar M. Y., Arain, R. (2009). Asian J. Chem., 21, 3651.
[8]. Aslam Mirza, M. Khuhawar, M.Y., Arain, R. (2007). The Nucl. 44(1-2).
[9]. Aslam Mirza, M., Khuhawar, M.Y., Asian, R.. J. (2007). Chem. 19(6), 5279.
[10]. Aslam Mirza, M., Khuhawar, M. Y. (2006). SURJ, Pak., 38(2), 25.
[11]. Aslam Mirza, M., Khuhawar, M. Y., Kandhro, A. J. (2005). J. Anal. Chem. Pak. 16(6), 72.
[12]. Magaritz, M., Brenner, I. B., Ronen, D. (1980). .Appl. Geochem. 5, 555.
[13]. APHA, (1989). Standard Methods for Examination of Water and Waste water, 17th Ed. American Public Health Association, Washington, DC, 1467.
[14]. Symons, J. M., McKing R. E., Hassis. H. H. (1960). J. Water Pollut. Control Fed. 32, 841.
[15]. Aslam, S. M., Ahmed, S., Azmi, A. R., Naqvi, S. S. M., Sultan, R. Pak. (1980). J. Sci. Ind. Res. 31, 830.
[16]. Voznaya, N. F. (1981). Chemistry of Water and Microbiology. Moscow: Mir Publishers, 347.
[17]. Aslam, S. M., Ahmed, S., Azmi, A. R., Naqvi S. S. M., Sultan, R. (1980). Pak. J. Sci. Ind. Res. 31, 830.

Description of diagrams:

Fig. 1 : Seasonal variation in the chloride, sulphate, DO, BOD, nitrate and organic nitrogen contents in the station RS-1.
Fig. 2 : Seasonal variation in the chloride, sulphate, DO, BOD, nitrate and organic nitrogen contents in the stream RS-2
Fig. 3 : Seasonal variation in the chloride, sulphate, DO, BOD, COD, nitrate and organic nitrogen contents in the stream RS-3
Fig. 4 : Impact of domestic pollution on the quality of river water.
Fig. 5 : Seasonal variation in Na, K, Ca and Mg contents in sample RS-1.
Fig. 6 : Seasonal variation in minor metal contents in sample RS-1.
Note : Two samples (RS-1 & RS-2) from the river were collected to assess the effect of waste water of Kotli city.

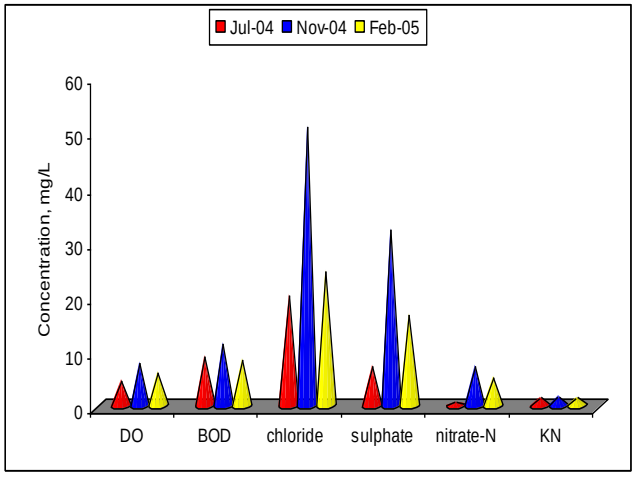

Fig.1: Seasonal variation in the chloride, sulphate, DO, BOD, nitrate and organic nitrogen contents the river water (RS-1).

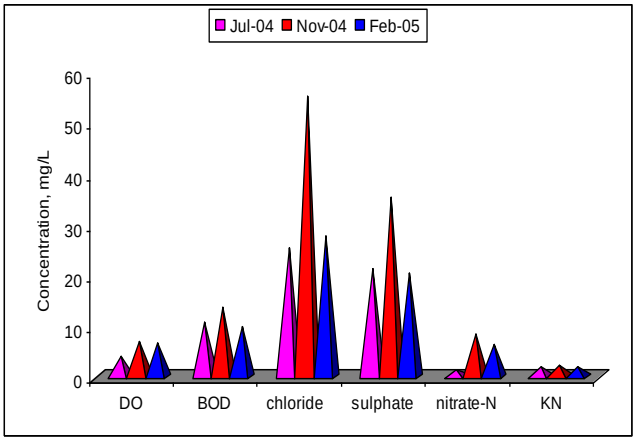

Fig. 2: Seasonal variation in the chloride, sulphate, DO, BOD, nitrate and organic nitrogen contents in the river water (RS-2).

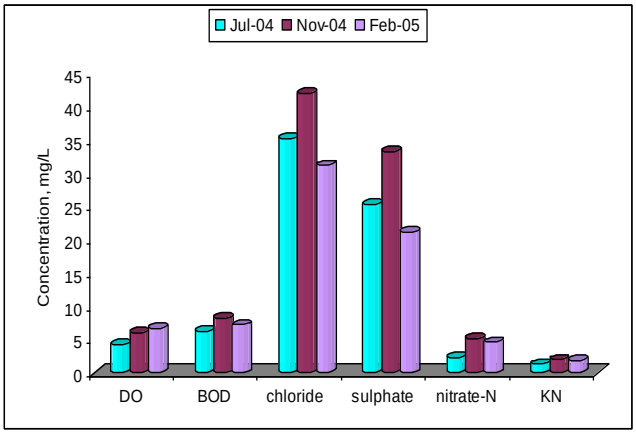

Fig. 3: Seasonal variation in the chloride, sulphate, DO, BOD, COD, nitrate and organic nitrogen contents in the river water (RS-3).

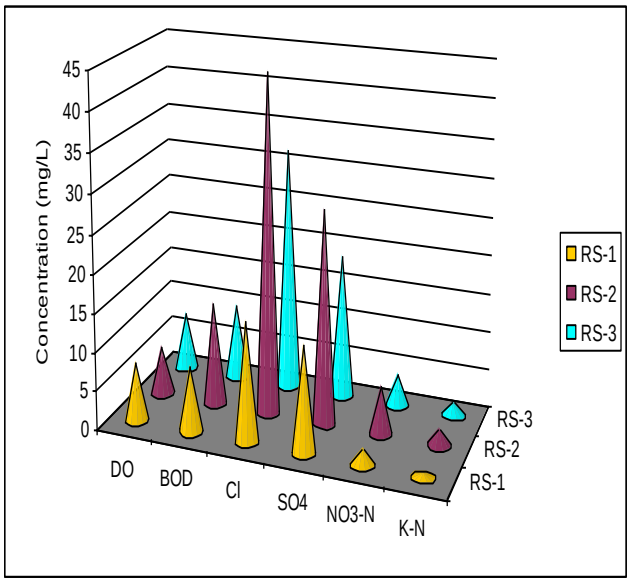

Fig. 4: Impact of domestic pollution on the quality of river water.

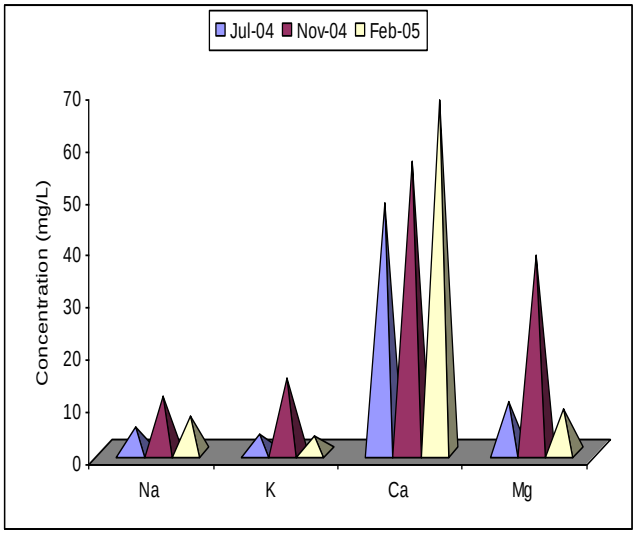

Fig. 5: Seasonal variation in Na, K, Ca and Mg contents in sample RS-1.

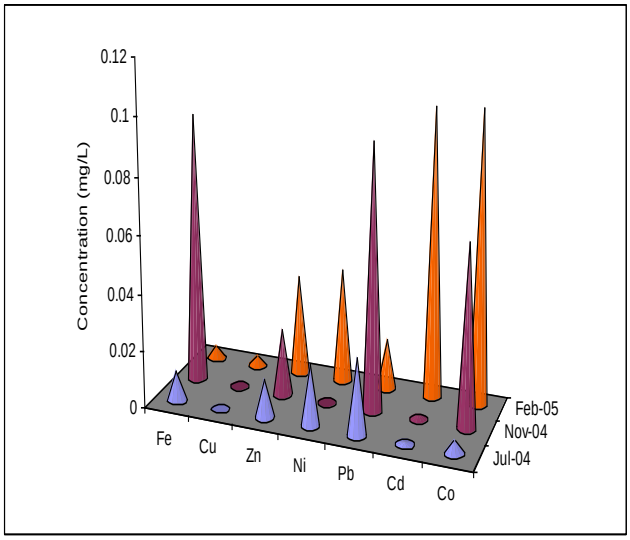

Fig. 6: Seasonal variation in minor metal contents in sample RS-1.

Parameters	Poonch Kotli (RS-1)	Poonch Kotli (RS-2)	Poonch Siakh (RS-3)
Color	Turbid	Turbid	Turbid
Odor	odorless	odorless	odorless
Temperature of air (ºC)	16	16.5	17
Temperature of water (ºC)	15	15.5	16
pH (25 ºC)	7.51	7.64	7.21
EC µS/cm	209	330	256.3
TDS mg/L	133.7	211	164.0
Salinity g/L	0.1	0.1	0.1
HCO_3 mg/L	145	165	127.4
TH mg/L	180	187	99.17
Cl mg/L	15.5	44	32.02
SO_4 mg/L	13.8	27.8	18.85
NO_2-N mg/L	0.001	0.01	0.008
NO_3-N mg/L	2.13	6.25	4.406
K-N mg/l	0.496	2.13	1.627
O-PO_4 mg/L	0.058	0.053	0.147
T-PO_4 mg/L	0.076	0.071	0.190
DO mg/L	7.86	7.65	6.380
BOD mg/L	8.48	13.5	9.98
Na mg/L	6.89	11.2	7.573
K mg/L	6.76	8.21	7.013
Ca mg/L	51.23	61.2	57.04
Mg mg/L	18.25	51.20	45.40
Fe mg/L	0.060	0.158	0.123
Cu mg/L	BDL	0.005	0.001
Zn mg/L	0.009	0.035	0.025
Ni mg/L	BDL	0.032	0.021
Pb mg/L	0.021	0.075	0.046
Cd mg/L	BDL	0.045	0.035
Co mg/L	0.084	0.260	0.190

Table 1Mean values (n=3) of physico-chemical parameters of water of r Poonch.

Table 2
Correlation Coefficient Matrix of selected metals.

	Na	K	Ca	Mg	Fe	Cu	Zn	Ni	Pb	Cd	Co
K	-0.020										
	0.956										
Ca	-0.214	0.427									
	0.553	0.218									
Mg	-0.217	0.523	0.797								
	0.547	0.121	0.006								
Fe	**0.792**	0.345	-0.025	0.244							
	0.006	0.328	0.946	0.497							
Cu	0.424	-0.203	-0.073	-0.187	0.145						
	0.222	0.573	0.840	0.605	0.689						
Zn	0.206	-0.445	-0.357	-0.544	-0.238	**0.787**					
	0.569	0.198	0.311	0.104	0.509	0.007					
Ni	0.818	0.137	0.053	0.175	0.717	0.238	0.013				
	0.004	0.705	0.885	0.629	0.020	0.508	0.972				
Pb	0.922	0.013	-0.016	-0.070	0.703	0.286	0.171	0.884			
	0.000	0.972	0.965	0.848	0.023	0.423	0.638	0.001			
Cd	0.458	0.100	-0.071	-0.068	0.274	0.854	0.736	0.410	0.397		
	0.183	0.783	0.846	0.853	0.443	0.002	0.015	0.239	0.257		
Co	-0.001	0.830	0.280	0.671	0.483	-0.067	-0.375	0.265	0.005	0.229	
	0.998	0.003	0.433	0.034	0.158	0.854	0.285	0.459	0.989	0.524	

Cell Contents: Pearson correlation P-Value

Table 3

Correlation Coefficient Matrix of selected physicochemical parameters..

	EC	TDS	HCO3	TH	Cl-	SO4	NO2-N	NO3-N	K-N	O-PO4	T-PO4	DO	BOD
TDS	0.999 0.000												
HCO3	0.352 0.318	0.357 0.311											
TH	0.360 0.306	0.358 0.309	0.952 0.000										
Cl-	0.384 0.274	0.382 0.276	0.112 0.759	0.168 0.643									
SO4	0.463 0.178	0.465 0.175	-0.351 0.319	-0.306 0.390	0.557 0.094								
NO2-N	0.018 0.961	0.008 0.983	-0.385 0.272	-0.320 0.368	0.529 0.116	0.575 0.082							
NO3-N	0.420 0.227	0.411 0.238	0.477 0.164	0.674 0.033	0.226 0.530	-0.068 0.852	-0.008 0.983						
K-N	0.376 0.284	0.374 0.287	-0.235 0.513	-0.169 0.641	0.173 0.633	0.225 0.532	0.499 0.142	0.412 0.237					
O-PO4	0.058 0.874	0.066 0.856	-0.120 0.741	-0.131 0.719	0.877 0.001	0.479 0.161	0.535 0.111	-0.055 0.880	0.161 0.656				
T-PO4	0.043 0.906	0.051 0.889	-0.066 0.856	-0.077 0.833	0.887 0.001	0.454 0.188	0.510 0.132	-0.041 0.909	0.102 0.779	0.997 0.000			
DO	0.025 0.946	0.018 0.960	-0.059 0.871	-0.094 0.797	-0.069 0.849	0.326 0.358	0.024 0.947	-0.528 0.117	-0.560 0.092	-0.181 0.616	-0.165 0.648		
BOD	0.319 0.369	0.316 0.374	-0.140 0.700	-0.023 0.950	-0.028 0.938	-0.076 0.834	0.054 0.882	0.568 0.087	0.854 0.002	-0.067 0.853	-0.117 0.747	-0.684 0.029	

Cell Contents: Pearson correlation P-Value