A Multivariate Approach for Water Quality Assessment of River Mandakini in Chitrakoot, India

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***Abstract*-The River Mandakini is one of the holy rivers of India, which flows across the Chitrakoot area of the eastern part of Bundelkhand region. Its water is shared by the Indian states of Uttar Pradesh and Madhya Pradesh. Water quality assessment of the river Mandakini from Sati Anusuya to Ramghat was carried out at various locations. Various water quality physico-chemical parameters, including temperature, pH, turbidity, electrical conductivity (EC), total dissolved solids (TDS), total hardness, calcium, magnesium, sodium, potassium, alkalinity, chloride, sulphate, fluoride, nitrate, dissolved oxygen (DO), and bio-chemical oxygen demand (BOD), were analyzed. Correlation analysis was done to identify the highly correlated and interrelated water-quality parameters. Concentrations of conductivity, TDS, hardness, alkalinity and fluoride higher than their prescribed standard were observed at some locations, while other parameters were observed within their prescribed limits. Higher values of turbidity, BOD, chloride and nitrate were observed at the downstream end of the river, which could be due to the cumulative pollution load from the sewerage discharge from nearby urban settlement, sacred mass bathing points, and agricultural runoff discharge into the river. A schematic diagram was used to trace point and non-point sources of pollutants responsible for governing the river water quality in a spatial scale.**

Keywords- Mandakini River; Water Quality; Conductivity; TDS; Hardness; Alkalinity; Chloride; Nitrate

I. INTRODUCTION

Rivers play a key role in integrating and organizing landscapes and shaping the ecological setting of basins (Kumar et al., 2011). They are very important factors for controlling the global water cycle and act as dynamic agents for mineral transport (Garrels et al., 1975). River water quality of a region is mainly determined by the cumulative effect of processes like precipitation, weathering, soil erosion, urban settlement around the bank, agricultural activities, disposal of human-waste, and domestic wastes with increasing exploitation/deterioration of water resources (Carpenter et al., 1998). The hydrogeochemistry of river water is also controlled by a series of factors, such as climate, vegetation, topography, and geology of the catchment area (Alaez et al. 1988; Avtar et al., 2013a, 2013b). The seasonal variations in the precipitation levels, surface run-off, ground water flow, interception, and abstraction of river water have a strong effect on the concentration of river water pollutants. The surface run-off during the rainy season also affects the river water quality (Kazi et al., 2009). The river water ecosystem is affected by fluctuations in the physical and chemical characteristics of the river (Guissani et al., 2008). The spatio-temporal variations in the hydrochemical properties of river water due to the natural and anthropogenic activities in Indian river basins have been widely studied by Avtar et al. (2011, Ken-Betwa), Gupta and Chakrapani (2005, Narmada), Kannel et al. (2007, Bagmati), Sundaray et al. (2006) and Chakrapani and Raymahasay (2005, Mahanadi).

The river Mandakini is one of the major rivers of the Chitrakoot region, known as the lifeline for the people of Chitrakoot. It fulfills the demands for water for drinking, domestic, and agriculture use. River Mandakani originates from the hills of Khillora near Pindra village, Majhagawan block (25^o 09'24.8”N, 80^o 52'55.3”E), district Satna, Madhya Pradesh (M.P.) from an elevation of 156 m above the mean sea level (Fig. 1). The catchment area of the river is 1956.3 km^2. The basin of river Mandakani is shared by the states of Madhya Pradesh (M.P.) and Uttar Pradesh (U.P.). The perennial reach of river Mandakini is Sati Anusuiya, from where a large number of springs feed the river. Afterwards, it passes through Sphatikshila, Jankikund, Pramodvan, Ramghat, etc. and finally joins river Yamuna in Rajapur (U.P.). Although the river Mandakini has a very small catchment area in comparison to other holy Indian rivers, it has a great historical and religious importance to Hindu ethos. It is believed that Lord Ram dwelled here for 12 years during his 14 years of exile. For such reason, many people visit here with spiritual emotions on the occasion of *Amawasya* (no moon day), *Purnima* (full moon day), *Ram Navami*, *Deepawali* (festival of lights), etc. and take holy baths in the river. Thus, Mandakini receives large quantity of pollution due to the mass bathing (Kannan, 1995). Besides the above, the discharge of wastewater from nearby urban settlements also deteriorates the water quality of river Mandakini. The objective of this study is to find the point and non-point sources of water pollution in the river Mandakini. In order to trace the point and non-point sources of pollution, water samples were collected in between the point of origin of river Mandakini and its downstream up to a stretch of approximately 15 km. Names of the sampling points were Sati Anusuya (SA), Sphatikshilla (SS), Vaidehi Vatika (VV), Janki Kund (JK), Pramod Van (PV), Ramghat upstream (RG Up), and Ramghat downstream (RG Dw) (Fig. 1). Table 1 shows the locations of the sampling sites.

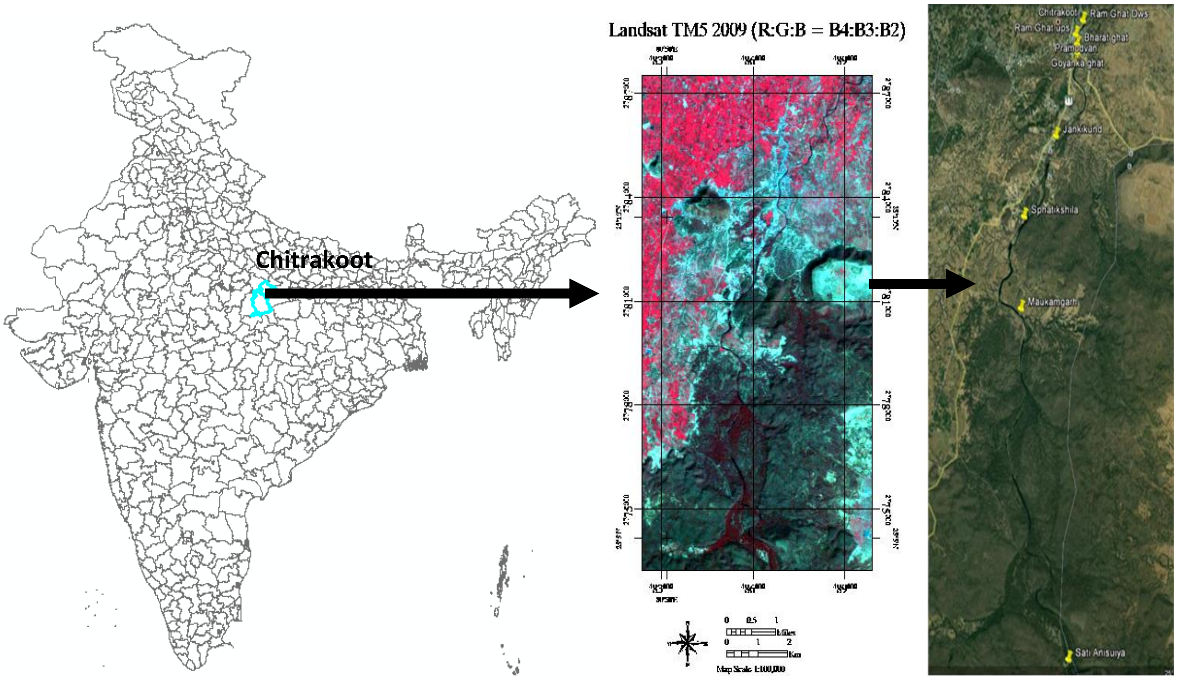

Fig. 1 Location of the study area, Landsat TM5 2009 data in R: G:B color composite, Google earth image shows the location of the sampling point

TABLE 1 LOCATION OF THE SAMPLING SITES

S. No.	Sampling station	Location	Latitude and Longitude
1	Sati Anusuiya (SA)	A upstream station, 15.0 Km in the south of Chitrakoot	25^0 4' 26.5" N and 80^0 52' 2.6" E
2	Sphatikshilla (SS)	A upstream station, 3.0 Km in the south of Chitrakoot	25^0 8'46.5" N and 80^0 51' 25.1" E
3	Vaidehi Vatika (VV)	A midstream station, 2.0 Km in the south of Chitrakoot	25^0 9' 25.9" N and 80^0 51' 46.7" E
4	Jankikund (JK)	A midstream station, 1.5 Km in the south of Chitrakoot	25^0 9'31.6" N and 80^0 51' 51.4" E
5	Pramod Van (PV)	A midstream station, 1.0 Km in the south of Chitrakoot	$25^0$10'15.2" N and 80^0 52' 1.1" E
6	Ramghat (Ups)	A downstream station, 0.0 Km from Chitrakoot	$25^0$10'32.8" N and 80^0 52' 9.1" E
7	Ramghat (Dws)	A downstream station, 0.1 Km in the north of Chitrakoot	$25^0$10'40.8" N and 80^0 52' 15.9" E

II. MATERIALS AND METHODS

A. *Geology of Chitrakoot Area*

The entire area of the Chitrakoot mainly lies on the Vindhyan plateau, which extends from the Kaimur hill range in the South to the edge of the Ganga valley in the North. The study area falls in the Bundelkhand granitic region of Archaens age, and is divided by small isolated hills and hillocks of limestone and sandstone, specifically small hillocks of Inselberg, Butte, Mesa, ridges and curvilinear ridges. On the topmost portion, the area is covered with recent deposits. It is an alluvial plain gullied area but dominated by silt & clay, which is a typical type of badland topography (karst topography) well known in the river basement of Mandakini River. In the study area, sedimentary structures like bedding current bedding, cross bedding, graded bedding show marine environmental conditions. Topographically, the U.P. portion especially the Ramghat area of Chitrakoot comes under the basement portion of Bundelkhand granitic area and some of the portion is well known as tirohan dolometic-limestone. The geology of this area is mainly characterized by Bundelkhand granite**,** Vindhyan system and alluvial deposits, which are from the Archean, late Proterozoic and Quaternary, respectively (Gupta, 2010).

B. Sample collection and analysis

A total of eighteen water samples from the selected sites and in-between the sites of river Mandakini were collected during summer (May - June 2011). The samples were collected from central part of the river conduit at about 30% below the water surface at each selected sampling point of the river. For the determination of bio-chemical oxygen demand (BOD) (five days at 20 ^{o}C), separated water samples were taken with BOD glassware bottles from above said sites. The collected BOD samples were kept in icebox and subsequently transferred to the refrigerator in laboratory. Except for BOD samples, water samples were taken with pre-cleaned polypropylene bottles with necessary precautions. The temperature and dissolved oxygen (DO) were analyzed at each selected sampling site with prescribed graduated mercury thermometer and Winker azide modification method, respectively. The physico-chemical parameters investigated for the river water quality were temperature, pH, turbidity, electrical conductivity (EC), total dissolved solids (TDS), total hardness, calcium, magnesium, sodium, potassium, alkalinity, bicarbonate, chloride, sulphate, fluoride, nitrate, dissolved oxygen (DO) and BOD. The samples collected for major-ion analysis were acidified using 1% HNO_3 to stabilize the trace metals, while the samples collected for nitrate analysis were acidified with HBO_3 acid. The concentration of bicarbonate was analyzed by acid titration (using Metrohm Multi-Dosimat) while other anions viz. chloride, sulphate, fluoride and nitrate were analyzed by DIONEX ICS-90 ion chromatograph. Major cations were determined with inductively coupled plasma-mass spectrometry (ICP-MS). AR grade chemicals, obtained from Qualigen, Hi-Media, E-Merck, etc. and borosilicate grade glassware obtained from Shott Duran were used in field and laboratory analyses of samples. The analyses of water samples were done using the Standard Methods for Examination of Water and Wastewater (APHA-AWWA, 1992).

III. RESULTS AND DISCUSSION

A. Physico-chemical parameters

Statistical analysis of the physico-chemical parameters observed at various sampling locations of river Mandakini, along with their comparison with the recommended standards prescribed by WHO (1993) are illustrated in Table 2. Temperature is one of the most significant parameters for a riverine system. Photosynthesis reaction by aquatic plants in a riverine system occurs due to temperature change. The variation in the temperature of surface water affects the solubility of salts, content of DO, organic biodegradation rate of materials and other physico-chemical parameters (Rao and Rao, 2010). The temperatures were found in the range of 27.6^{o} to 31^{o}C. The lowest and highest temperatures were recorded at SA and RG Dw, respectively. The values were mostly noticed in increasing order due to increasing solar radiation, since the monitoring was carried out from morning at SA (starting monitoring point) to noon at RG Dws (final monitoring point).

Values of pH of the samples ranged from 7.8 to 8.4, showing slightly alkaline nature of the river water. Alkaline nature could be due to the presence of high extent of limestone rocks in the area and the use of soaps/detergents during baths of the pilgrims in the river. Alkalinity of water occurs in the form of carbonate, bicarbonate, and hydroxide. It was found to be in the range of 300 to 398 mg/L (Table 2). The minimum and maximum values were noticed at PV and SA sampling locations. All values were found higher than their prescribed limits (Table 2). High concentration of alkalinity was recorded in the form of HCO_3^- and CO_3^{2-} in the water samples and can be attributed to the occurrence of carbonate rocks in the area. Turbidity values were recorded between 2.0 to 18.0 NTU. Most values were found within their permissible limit (10 NTU) except for samples from RG Ups and RG Dws. The minimum values of the turbidity were found in samples from SA and SS. Sharp increases in the values for samples from JK and PV respectively were found, and it may be attributed to the mass sacred bathing, while the maximum values for samples from RG Ups and RG Dws were found because of the great depth and low velocity of water flow and upstream pollution load. Electrical conductivity (EC) was observed in the range of 385 to 910 μs/cm. EC values of most of the locations were recorded higher than the permissible limit of 500 μs/cm, indicating the high concentrations of dissolved solids contributed by anthropogenic activities and runoff of various soil types.

The trend in the average values of anions was $HCO_3^-> Cl^-> SO_4^{2-}> NO_3^->F^-$, whereas for cations the trend was $Ca^{2+}>Mg^{2+}>Na^+>K^+$. The scatter plot between total cations (Tz+) and ($Ca^{2+}>Mg^{2+}$) and ($Na^+>K^+$) is shown in Fig. 2. A Linear trend was found for the relation between Tz+ and ($Ca^{2+}>Mg^{2+}$), however the trend was poor between Tz+ and ($Na^+>K^+$), indicating that the contributions of (Ca2+>Mg2+) among the cations are major and carbonate weathering may be the dominating process responsible for the water type.

Total hardness of the water samples is a measure of carbonate, bicarbonate, sulphate and chloride salt of Calcium and magnesium. Total hardness values were found in the range of 240 to 552 mg/L. Most of the values of total hardness of all samples were observed to be higher than their permissible limit of 300 mg/L due to the dissolution of limestone and other minerals, as this region is rich in these minerals. Gupta (2010) also reported a similar finding. Values of calcium and magnesium were recorded in the range of 23.2 to 122 mg/L and 8.9 to 74 mg/L, respectively. Higher levels of both ions in water may cause health issues and scaling in water heater, domestic water supply pipelines and boilers.

Values of sodium and potassium were recorded in the range of 10 to 28.1 mg/L and 2.4 to 30 mg/L, respectively. All values of sodium and potassium were found within their permissible limit of 200 mg/L, indicating the absence of minerals like feldspar, a common natural source of sodium and potassium. However, the gradual increase of potassium at very downstream points strongly indicates the effect of agricultural runoff from nearby regions on the water quality.

Chloride was found to be in the range of 9.1 to 102 mg/L. Chloride is the second most inorganic anion after the bicarbonate. Chloride plays a major role in causing permanent hardness of water (Manjappa and Naik, 2007). Since the water samples of all locations of river Mandakini get temporary hardness in calcium carbonate and carbonate forms because higher alkalinity in all the samples, the values of chloride were lower than the permissible limit. The upstream region has relatively less human settlements and as a result the water sample shows relatively lower concentrations of chloride as compared to water samples from the downstream.

Sulphate generally enters water either by the use of soap and detergent for washing clothes or due to the presence of sulphur containing minerals and ores in the area. Sulphate was found to be in the range of 10 to 91 mg/L. All the values of samples were recorded within their permissible limit (200 mg/L) as prescribed by WHO. Fluoride was found in the range of 0.3-1.8 mg/L. The values of fluoride for the upstream samples were found to be more than their permissible limit (1.5 mg/L) prescribed by WHO. Since this area is rich in calcium containing minerals, fluoride might appear as fluorspar (CaF_2), appetite ($(CaF_2.Ca_3PO_4)_3$), or floropatite ($3Ca_3PO_4.CaF_2$).

Nitrate values were found to be in the range of 5.3 to 61 mg/L. Values for most of the samples were found within their permissible limit (45 mg/L) as prescribed by WHO, except for samples from a few sampling stations in the extreme downstream regions like RG Ups and RG Dws. These high concentrations from recommended values are due to the pollution load from agricultural runoff discharge as these points showed extensive fertilizer usage. In order to confirm the origin of nitrate, scatter plot was drawn between NO_3^- and K^+ (shown in Fig.3), and the plot indicates high association, and hence reveals that fertilizer was the main source of nitrate.

TABLE 2 STATISTICAL SUMMARY OF PHYSIOCHEMICAL PARAMETERS OF MANDAKINI RIVER WATER QUALITY ALONG WITH THE STANDARD WATER QUALITY RECOMMENDED BY WHO, 1993

Parameters	Average	Minimum	Maximum	St. Dev	WHO, 1993 (Recommended)
Temperature(^{0}C)	28.7	27.6	31.0	1.6	25
pH	8.1	7.8	8.4	0.2	7.0-8.5
Turbidity(NTU)	6.6	2.0	18.0	4.5	5
EC(μscm^{-1})	687.0	385.0	910.0	180.3	500
TDS (mg/l)	473.7	278.4	592.0	108.0	500
TH as $CaCO_3$ (mg/l)	438.1	240.0	552.0	112.6	300
Alkalinity (mg/l)	339.7	300.0	398.0	31.9	200
Ca^{2+} (mg/l)	87.1	23.2	122.0	40.8	30
Mg^{2+} (mg/l)	49.9	8.9	74.0	28.1	200
Na^+ (mg/l)	19.4	10.0	28.1	4.6	200
K^+ (mg/l)	11.4	2.4	30.0	8.1	200
HCO_3^- (mg/l)	183.4	71.6	262.0	66.5	75
Cl^- (mg/l)	44.9	9.1	102.0	28.4	250
SO_4^{2-} (mg/l)	28.9	10.0	91.0	20.4	200
F^- (mg/l)	1.1	0.3	1.8	0.6	1.5
NO_3^- (mg/l)	27.0	5.3	61.0	17.9	45
DO (mg/l)	6.3	4.8	7.8	1.0	4
BOD (mg/l)	6.6	2.0	17.5	4.0	6

Dissolved oxygen (DO) is one of the most important parameters for measuring the health of the aquatic life in river water. Oxygen in water occurs through the diffusion from air and the photosynthesis activities by aquatic plants. The DO values for the river water samples range from 4.8 to 7.8 mg/L. The minimum and maximum values were recorded at PV and SA, respectively. Low value was found in the origin point at Sati Anusuiya due to the springs coming from ground water, which resulted in in the low DO.

Biochemical oxygen demand (BOD) values were recorded in the range of 2.0 to 17.5 mg/L. The extent of BOD for all samples were found under the limit prescribed by WHO, except for samples from RG Ups and RG Dws. BOD values at those two spots (RG Ups and RG Dws) were higher due to drains entering the river. The organic pollution load is being carried from the upstream region. The high value of BOD can also be evidenced by the easily visible algal bloom because of eutrophication.

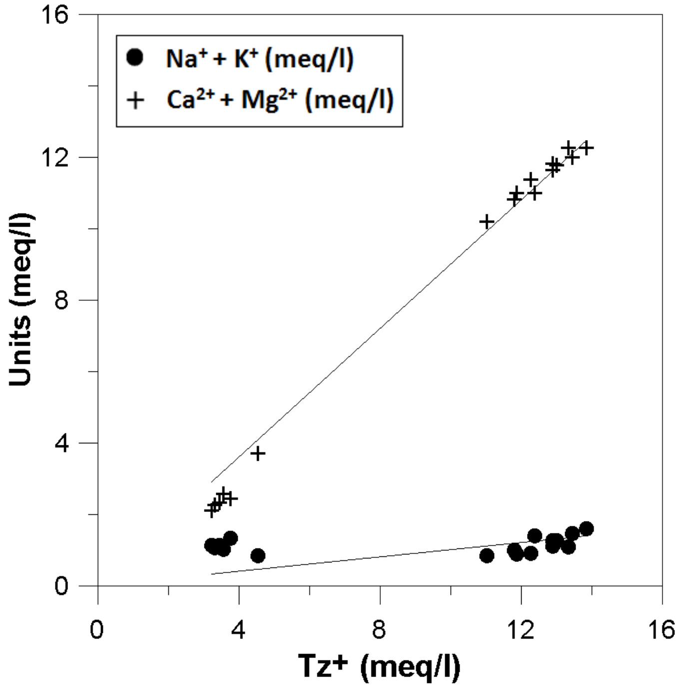

Fig. 2 Scatter plot between total cation (Tz+) and $Ca^{2+} + Mg^{2+}$, $Na^{+} + K^{+}$

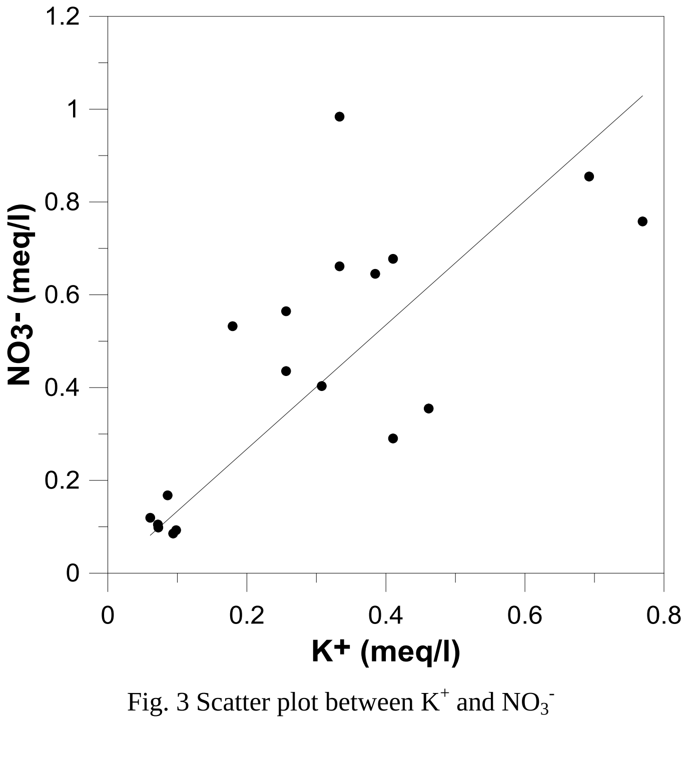

Fig. 3 Scatter plot between K^{+} and NO_3^{-}

B. Water types

The distinction between water types and the classification of samples into groups are necessary to discern regional trends and identify chemical processes (Stuyfzand, 1999). The presentation of geochemical data in the form of graphical chart such as Piper diagram is helpful to recognize and differentiate between various water facies (Piper, 1994). The major ions analyzed for the river water samples are depicted in the Piper Trilinear equivalence diagram (Fig. 4). Based on the geochemical facies diagram, two types of water samples were defined: (i) $Ca\text{-}HCO_3$ and (ii) $Mg\text{-}HCO_3$.

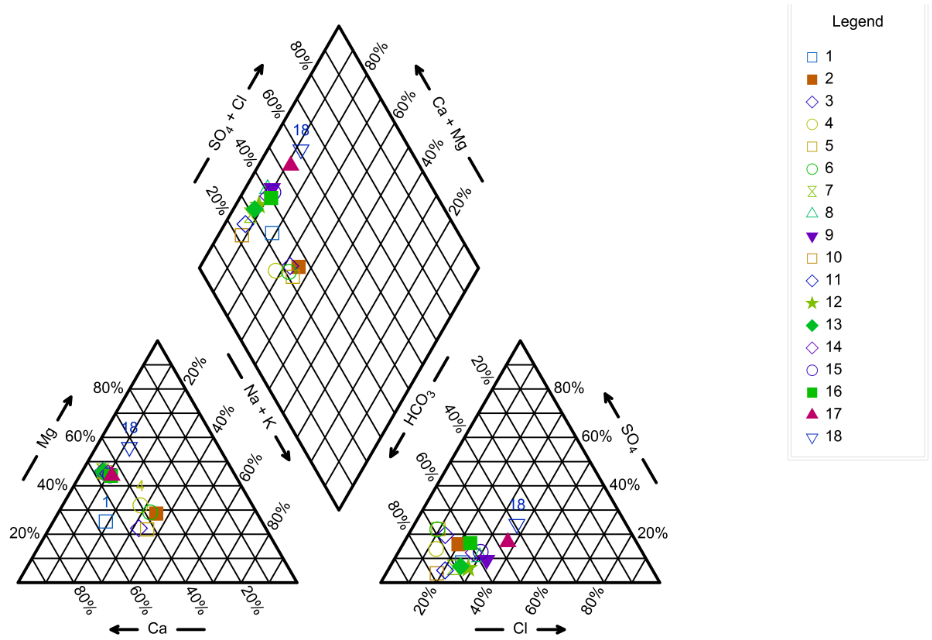

Fig. 4 Piper diagram for water quality

A correlation matrix of the physiochemical parameters of the water samples is shown in Table 3. The correlation matrix shows good to moderate positive correlations of pH with EC, TDS, Ca^{2+}, HCO_3^- and Cl^-. Similarly, EC and TDS shows good correlations with Ca^{2+}, Mg^{2+}, HCO_3^-, NO_3^- and Cl^-. Good to moderate correlations were observed between the following pairs: Ca^{2+}-Mg^{2+}, Ca^{2+}-HCO_3^-, Ca^{2+}- SO_4^{--}, Ca^{2+}-F^-, Mg^{2+}-HCO_3^-, Na^+- K^+, Na^+- NO_3^-, K^+- NO_3^-, HCO_3^- -Cl^-, Cl^-- SO_4^{2-}, Cl^-- NO_3^- and SO_4^{2-}- NO_3^-. The pair-wise relationships between the physiochemical parameters show that the water quality is mainly controlled by carbonate weathering. There are also chances of presence of dolomite, a common source of Ca and Mg. The presences of minerals like fluorspar, apatite and floropatite are also indicated by the good correlation between calcium and fluoride. Anthropogenic sources, especially excess use of fertilizers and mass bathing, may control the geochemistry at point scales and can be shown by the high correlations between chloride, sulphate and nitrate (Avtar et al., 2013). Thus, it is observed that hydrogeochemistry of river Mandakini water is mainly controlled by natural or geogenic processes.

TABLE 3 CORRELATION MATRIX FOR THE MANDAKINI RIVER WATER SAMPLES

	pH	**EC**	**TDS**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**	**F^-**
EC	0.66										
TDS	0.61	0.98									
Ca^{2+}	0.74	0.77	0.80								
Mg^{2+}	0.36	0.75	0.79	0.99							
Na^+	0.20	0.37	0.92	0.37	0.87						
K^+	0.28	0.15	0.26	0.25	0.74	0.89					
HCO_3^-	0.79	0.84	0.62	0.80	0.47	-0.44	-0.16				
Cl^-	0.60	0.52	0.56	0.29	0.29	0.56	0.68	0.52			
SO_4^{2-}	0.30	0.48	0.54	0.51	0.52	0.68	0.64	-0.53	0.88		
F^-	0.09	0.27	0.18	0.57	0.16	0.06	0.35	0.20	0.44	0.34	
NO_3^-	0.03	0.67	0.74	0.58	0.56	0.81	0.77	-0.31	0.55	0.59	-0.14

Keeping above results in sight, the possible mechanisms responsible for hydro chemical evolution of the Mandakini River are represented by a conceptual diagram shown in Fig. 5. In the upstream region, water is of good quality as Ca-HCO_3 type of water. At Janki kund, the mid-stream of the river, because of many famous sacred places, there is huge urban setup and sacred mass bathing, resulting in change in the ionic characteristic of the water samples. At the receiving end of the downstream sampling location, the water quality gets further deteriorated due to nitrate and chloride enrichment, and water type changes to Mg-HCO_3.

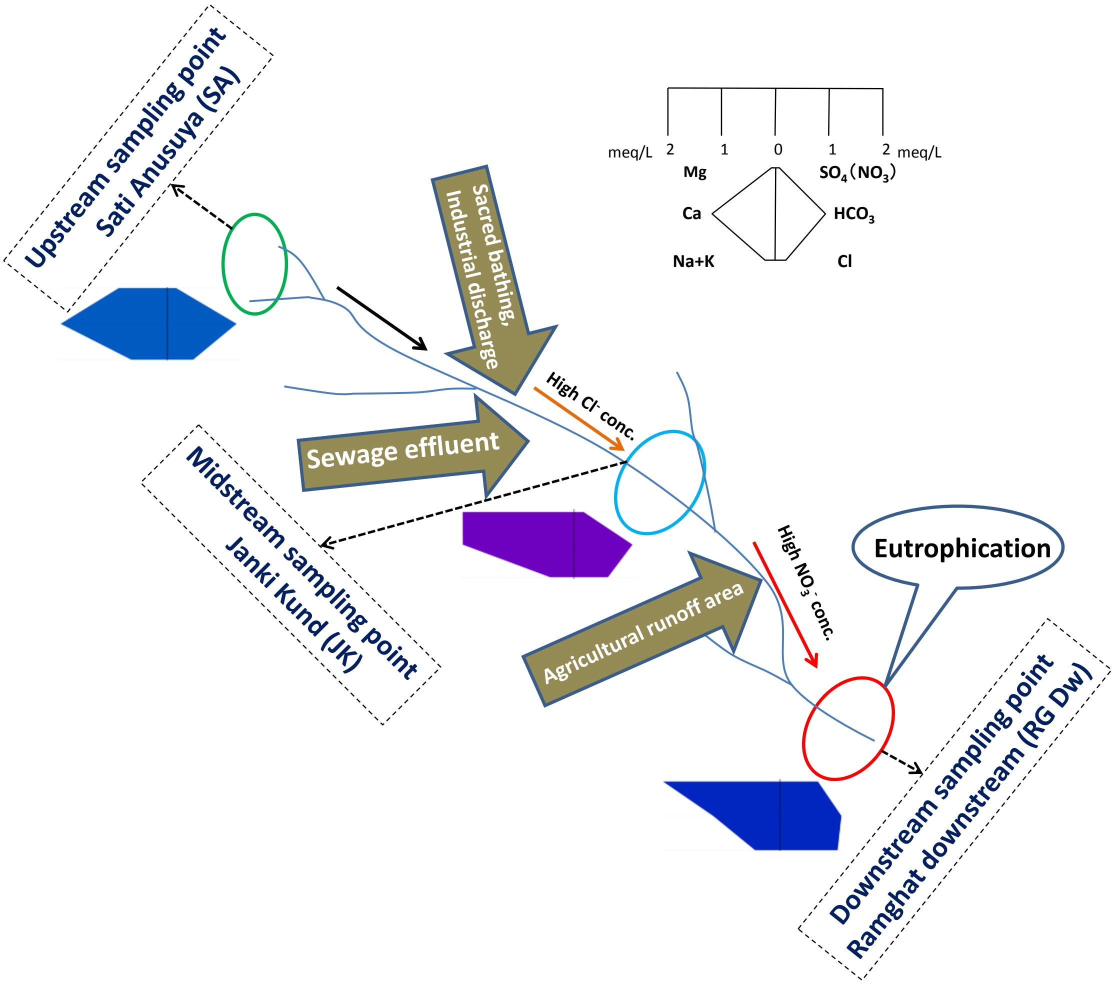

Fig. 5 Schematic diagram showing hydro-chemical evolution of the surface water in Mandakini River

IV. CONCLUSIONS

This study depicts the overall ongoing geochemistry and water quality of river Mandakini. The trend in the average contents of anions is HCO3-> Cl-> SO42-> NO3->F- whereas, for cations the trend is Ca2+>Mg2+>Na+>K+. Most of the analyzed physico-chemical parameters are within permissible limits prescribed by WHO, except turbidity and nitrate, chloride and fluoride at some places. Although the water quality of river Mandakini is mainly controlled by carbonate weathering consistent with its geological signature, the anthropogenic activities like mass bathing and the disposal of domestic drainage into the river, which deteriorate the water quality, are a matter of concern, and need attention from municipal or local level policy makers for mass awareness on the importance of river water quality and for tapping the sources of pollution.

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