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Assessment of Water Quality Parameters using Multivariate Chemometric Analysis for Markanda River, India

Rout Chadetrik and Bhatia Upain Kumar
Department of Civil Engineering, Maharishi Markandeshwar University, Mullana-133207, Ambala, Haryana, INDIA

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Abstract

The present study uses several univariate and multivariate statistical techniques to evaluate and interpret a water quality data set obtained from the Markanda River within the state of Himachal Pradesh and Haryana, India. Data was collected from August-November 2013 and 2014 for eight parameters used to assess the status of the water quality, namely pH, electrical conductivity, total dissolved solids, total hardness, chloride, sulphate, biochemical oxygen demand and chemical oxygen demand. Water quality was monitored at 8 sampling stations along the Markanda river. The data were first analysed using univariate statistical tools, followed by principal component analysis and hierarchical cluster analysis that reduced the data dimensions for better interpretation. This study also presents the usefulness of different statistical methods for evaluation and interpretation of river water quality data for the purpose of monitoring the effectiveness of water resource management. Higher values of EC, BOD and COD indicate that river water is not safe for drinking purposes as prescribed by Bureau of Indian Standards (BIS).

Keywords: Markanda river, principal component analysis, biplot, cluster analysis, chemometry.

Introduction

The demand for water has multiplied manifold with rapid growth in population, agricultural and industrial activities all over the world which is severely affecting the available water resources now-a-days. Increasing demand of water is degrading the water quality of rivers worldwide, resulting in huge loss of the vital goods and ecosystem services[1]. Several rivers of northern India like the Markanda, Dishradwati, Ghaggar, Ravi, Yamuna, Saraswati, Satluj and the Ganga rivers as mentioned in the ancient Sanskrit literature, have generated much interest among the research community. In recent past years several studies related to monitoring of Indian rivers have been made by various researchers[2-13]. Therefore, the research work is an attempt to assess the physico-chemical parameters of river Markanda which is used for drinking, irrigation and industrial activities.

Material and Methods

Description of the study area: The Markanda river located in the foothills of the Siwalik hills and Gangetic plains of Haryana, is the most well-known stream between the Yamuna and the Ghaggar river systems[14]. The river originates from Nahan in Himachal Pradesh. Its basin spreads between 30° 00′ and 30° 40′ North latitudes and 76° 32′ and 77° 24′ East longitudes in the Siwalik foothills, North West India. The basin covers an area of 1547 km^2. The area falls under subtropical and semi-arid region with the annual average rainfall of 1100 mm in the hilly region and 750 mm in normal areas. The geological strata the basin consists of sedimentary rocks of Tertiary to Quaternary alluvium deposits. Rocks and alluvium deposits belongs to Tertiary and Quaternary age, which occupy the northern and south part of the basin respectively[15]. The sampling was carried out at eight designated sampling stations selected on the basis of accessibility where peoples are using the river water for domestic purposes. The coordinates of sampling locations are as follows: (M1) 30º 30′42.2″ N and 77º 22′ 01.2″ E (M2) 30º 30′50.1″ N and 77º 20′57.4″ E (M3) 30º 31′05.7″ N and 77º 20′01.7″ E (M4) 30º 31′47.4″ N and 77º 18′27.9″ E (M5) 30º 31′00.0″ N and 77º 14′47.4″ E (M6) 30º 30′22.5″ N and 77º 13′18.8″ E (M7) 30º 29′47.2″ N and 77º 12′40.0″ E (M8) 30º 16′33.3″ N and 77º 01′27.1″ E.

Statistical analysis: Principal component analysis (PCA) has been done on the original data set using MATLAB software. The analytical results were compiled using Microsoft Excel, and SPSS 19.0 software was used to perform cluster analysis (CA) on the data. The data were normalized to the Z score (with a mean of "0" and a standard deviation of "1") and then classified using Ward's method. The correlation coefficient distance was used in the CA. The water quality parameters that correlated well were identified and grouped for further analysis. Pearson's correlation matrix has been used to identify the relationship among the water quality parameters to support the results obtained by multivariate analysis.

Collection and characterization of water samples: River water samples were collected on monthly basis from 8 selected locations in 1-L airtight sampling bottles. All the water samples were analyzed immediately after collection of the samples in the Environmental Engineering Laboratory of Maharishi

Markandeshwar University, Mullana, Ambala, Haryana. All the water quality parameters (pH, EC, TDS, TH, Cl, SO_4^{2-}, BOD and COD) were analyzed according to the standard methods[16]. The monitoring was made over a period of 8 months (August-November, 2013 and 2014), comprising of one session i.e. post-monsoon. All measurements were done in triplicates. Analytical reagent (AR) grade chemicals were used throughout the study without any further purification. Distilled water was used for experimental purpose. A comparison of water quality parameters of the Markanda river as observed with drinking water quality standards (Indian) was given in table-1.

Results and Discussion

pH: The pH values of the river water samples varied from minimum 7.09 at sampling station 1 to maximum 8.32 at sampling station 8 (table 1 and 2). The results shows that pH values of the river water collected from eight different sampling stations were found within the desirable permissible limit (6.5-8.5) of drinking water quality standards of BIS (table 1). Similar results were obtained in studying the effect of dye effluents on pH of river Kshipra, Ujjain City[17]. Statistical summary for pH in river water samples is presented in table-2.

Electrical conductivity (EC): The EC values of the river water samples varied from minimum 0.30 mS/cm at sampling station 1 to maximum 0.6 mS/cm at sampling station 5 (table-1 and 2). The results shows that EC values of the river water collected from 8 different sampling stations were not satisfying the maximum permissible limit (0.3 mS/cm) of drinking water quality standards of BIS (table 2). Statistical summary for EC in river water samples is presented in table-3.

Total dissolved solids (TDS): The TDS content of the analysed river water samples varied from minimum 183 mg/l at sampling station 1 to maximum 330 mg/l at sampling station 5 (table-1 and 2). High content of dissolved solids affects the density of water, influences osmoregulation of freshwater organisms, hence reduces solubility of oxygen, and utility of water for drinking[18]. The results shows that TDS content of river water collected from eight different sampling stations were satisfying the prescribed limit (500 and 2000 mg/l) of drinking water quality standards of BIS (table-2). Statistical summary for TDS in river water samples is presented in table-3.

Total hardness (TH): The total hardness content of river water samples varied from minimum 80 mg/l at sampling station 1 to maximum 410 mg/l at sampling station 6 (table-1 and 2). The results shows that total hardness content of river water collected from eight different sampling stations were within the prescribed maximum permissible limit (600 mg/l) of drinking water quality standards of BIS (table-2). Statistical summary for total hardness in river water samples is presented in table-3.

Chloride (Cl^-): The chloride content of the analysed river water samples varied from minimum 7.9 mg/l at sampling station 1 to maximum 55.8 mg/l at sampling station 8 (table-1 and 2). The results shows that chloride content of river water collected from eight different sampling stations were within the prescribed limit (250 and 1000 mg/l) of drinking water quality standards of BIS (table-2). Statistical summary for Cl^- in river water samples is presented in table-3.

Table-1
Water quality parameters (average) at different sampling stations of river Markanda

Sample No	pH	EC	TDS	TH	Cl^-	SO_4^{2-}	BOD	COD
1	7.09	0.30	183	80	7.9	8	2	9
2	7.94	0.37	221	248	21.7	14.7	10	64
3	8.08	0.39	235	155	13.5	16.5	8	75
4	8.19	0.33	199	392	30.9	10.6	10	50
5	7.45	0.60	330	290	15.8	12	6	45
6	7.55	0.31	192	410	27.5	7.0	13	90
7	8.19	0.35	210	304	32.4	28	5	48
8	8.32	0.46	282	375	55.8	11.5	4	40

Sulphate (SO_4^{2-}): The sulphate content of the analysed river water samples varied from minimum 7 mg/l at sampling station 6 to maximum 28 mg/l at sampling station 7 (table-1 and-2). The results shows that sulphate content of river water collected from eight different sampling stations were within the prescribed permissible limit (200 and 400 mg/l) of drinking water quality standards of BIS (table-2). Similar results were obtained in studying the sulphate content of river Kapila, Nanjangud, Karnataka[19]. Statistical summary for SO_4^{2-} in river water samples is presented in table-3.

Biological oxygen demand (BOD): The biological oxygen demand of the analysed river water samples varied from minimum 2 mg/l at sampling station 1 to maximum 13 mg/l at sampling station 6 (table-1 and 2). The results shows that BOD content of river water collected from eight different sampling stations were exceeding the prescribed limits (<2 mg/l) of drinking water quality standards of BIS (table-2). Similar results were obtained in studying the BOD of river Ghataprabha, Belgaum, Karnataka[20]. Statistical summary for BOD in river water samples is presented in table 3.

Chemical oxygen demand (COD): The chemical oxygen demand of the analysed river water samples varied from minimum 9 mg/l at sampling station 1 to maximum 90 mg/l at sampling station 6 (table-1 and 2). This indicates that pollution load in the river is due to untreated industrial effluents, agricultural runoff and sewage water entering into it from the surrounding areas. Increase in COD could be attributed to an increase in the addition of both organic and inorganic contaminant[21]. The results shows that COD content of river water collected from eight different sampling stations were exceeding the maximum limit (20 mg/l) of drinking water quality standards of WHO. Statistical summary for COD in river water samples is presented in table-3.

Principal component analysis: PCA was performed on covariance correlation matrix data, such that the considered data set can be explained. Analyzing the results (table-5), the cumulative percent variance of PC1 and PC2 is more than 96% and from the third component the cumulative percentage variance is more than 99% therefore, PC1 and PC2 has taken for consideration. The loading values >0.75 signifies "strong", the loading with values in between 0.5-0.75 indicate "moderate" while loading values between 0.3-0.50 denote as "weak"[22]. Using the above classification, two variables in each component (1 and 2) have strong positive loading. Considering the first two components, higher coefficient is observed for pH and total hardness (TH) with 0.7592 and 0.865 in PC1 and electrical conductivity (EC) and total dissolved solids (TDS) with 0.861 and 0.886 in PC2. The coefficients for chloride (Cl^-) with 0.717, BOD with 0.622, COD with 0.686 in PC1 and BOD with 0.598 in PC2 (negative sign is omitted) have moderate loading. The coefficients for other parameters are very less. Biplots of all the physico-chemical parameters are shown in figure-1. The six biplots of pH, EC, TDS, TH, Cl^- and SO_4^{2-} are falling in the first i.e. positive coordinate (figure-1) which indicates similar trend will follow between them and the other two biplots i.e. BOD and COD are falling in the second coordinate (figure 1), which indicates similar trend will also follow between them. The group of water quality parameters (pH, EC, TDS, TH, Cl^- and SO_4^{2-}) which are falling in the first coordinate will not affected by the parameters of second coordinate (BOD and COD) and *vice-versa*. Hence the quality of river water can be well differentiated by taking the six parameters having higher coefficients. Variables, with higher PC1 and PC2 values indicating that concerned parameters are responsible for development of poor water quality along all the sampling locations of river Markanda. The reason for poor water quality is probably due to disposal sewage and industrial effluents into the river without any treatment.

Table-2
Comparison of average water quality parameters of river Markanda with drinking water quality standard (Bureau of Indian Standards)

Parameters	Observed Range of Samples		Indian Standards (BIS)	
	Minimum	Maximum	Desirable limit	Maximum limit
pH	7.09	8.32	6.5-8.5	No Relaxation
EC (mS/cm)	0.03	0.60	-	0.3
TDS (mg/l)	183	330	500	2000
TH (mg/l)	80	375	300	600
Cl^- (mg/l)	7.9	55.8	250	1000
SO_4^{2-} (mg/l)	7.0	16.5	200	400
BOD (mg/l)	2	13	<2	<2
COD (mg/l)	9	90	-	-

Table-3
Statistical analysis of physico-chemical parameters of Markanda river water

	pH	EC	TDS	TH	Cl^-	SO_4^{2-}	BOD	COD
N	8	8	8	8	8	8	8	8
Min	7.09	0.3	183	80	7.9	7	2	9
Max	8.32	0.6	330	410	55.8	28	13	90
Mean	7.85	0.388	231.5	281.75	25.68	13.53	7.25	52.62
Std. error	0.154	0.035	17.83	41.35	5.27	2.34	1.29	8.63
Variance	0.191	0.0098	2543.71	13681.36	222.98	43.97	13.35	596.55
Stand. dev	0.437	0.099	50.43	116.96	14.93	6.63	3.65	24.42
25 prcntil	7.475	0.315	193.75	178.25	14.075	8.65	4.25	41.25
75 prcntil	8.19	0.442	270.25	387.75	32.02	16.05	10	72.25
Skewness	-0.771	1.619	1.281	-0.715	1.103	1.675	0.155	-0.27
Kurtosis	-0.718	2.604	0.925	-0.485	1.698	3.377	-0.85	0.755
Coeff. var	5.57	25.55	21.78	41.51	58.13	48.98	50.41	46.41

Table-4
Correlation matrixes among the physico-chemical characteristics of river water

	pH	EC	TDS	TH	Cl^-	SO_4^{2-}	BOD	COD
pH	1							
EC	0.018	1						
TDS	0.094	0.991	1					
TH	0.469	0.114	0.147	1				
Cl	0.698	0.094	0.194	0.732	1			
SO_4^{2-}	0.518	0.028	0.023	-0.062	0.117	1		
BOD	0.163	-0.239	-0.253	0.517	-0.0067	-0.207	1	
COD	0.304	-0.084	-0.07	0.437	0.069	0.048	0.873	1

Table-5
Factor loading for Markanda river water quality

	Components							
Variables	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
pH	0.7592	0.214	-0.494	0.119	-0.308	-0.149	-0.029	0
EC	0.048	0.861	0.460	0.2	0.020	-0.044	0.006	0
TDS	0.105	0.886	0.420	0.151	-0.054	0.020	0.008	0
TH	0.865	0.066	0.16	-0.340	0.309	-0.080	-0.051	0
Cl^-	0.717	0.354	-0.305	-0.482	-0.037	0.167	0.057	0
SO_4^{2-}	0.189	0.232	-0.673	0.623	0.259	0.016	0.022	0
BOD	0.622	-0.598	0.443	0.179	0.004	-0.137	0.074	0
COD	0.686	-0.410	0.351	0.428	-0.078	0.213	-0.038	0
Eigenvalue	13987.9	2495.95	491.62	89.6	36.27	0.821	0.026	0
% Variance	81.79	14.594	2.8746	0.52388	0.212	0.0048	0	0
Cumulative % Var.	81.79	96.384	99.286	99.995	99.999	100	100	100

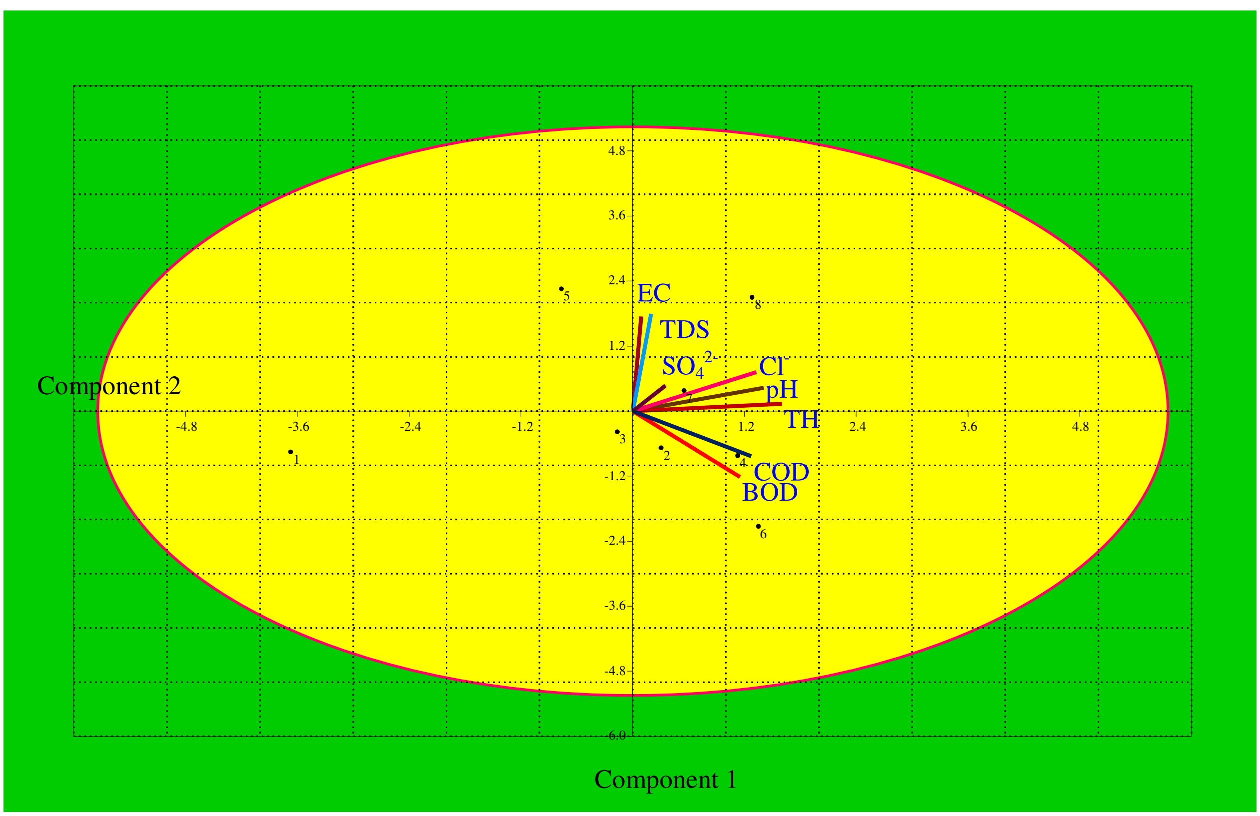

Figure-1
Scatter plots of the principal component analysis of river water

Cluster analysis results: The cluster analysis results are illustrated in the hierarchical clustering dendrograms shown in figure-2. The cluster analysis results for the river water indicate that the physico-chemical parameters could be split into three main groups. The first group (cluster I) included EC and TDS; the second group (cluster II) included BOD and COD; and the third group (cluster III) included pH, TH, Cl and SO_4^{2-} (figure 2). The cluster results indicate that three different factors were responsible for the development of the water quality in the Markanda river. EC and TDS (cluster I) have one source; BOD and COD (cluster II) are derived from another source; and pH, TH, Cl and SO_4^{2-} (cluster III) are associated with other sources.

Correlation matrix analysis: Water collected from River Yamuna and correlation matrix was used to know the correlationship between physico-chemical properties of river water[23]. Correlation matrix was prepared[24] between eight different water quality parameters and is presented in table 4. The highest positive correlation is observed between electrical conductivity (EC) and total dissolved solids (TDS) with 0.991. There is also strong positive correlation exists between BOD and COD (0.873), total hardness and chloride (0.732), pH and chloride (0.698), pH and sulphate (0.518) and total hardness and BOD (0.517). Other physico-chemical parameters having insignificant positive as well as negative correlation (table 4).

Conclusion

This study assessed some physico-chemical properties of Markanda River from eight different locations, during the months of August to November 2013 and 2014. Based on the eight environmental parameters such as pH, electrical conductivity, total dissolved solids, total hardness, chloride, sulphate, biological oxygen demand and chemical oxygen demand for water quality, it was able to identify three main sources which are responsible for deteriorating the water quality of Markanda River at all the sampling stations. Water quality parameters like BOD and COD were exceeding the level of pollution. Therefore it is concluded that River Markanda is polluted and unsafe for human consumption. Overall, this study recommends identifying the pollution sources and monitoring the water quality parameters from time to time so that will help researcher to interpret data and implementation of remediation actions to protect the quality of the river water from deterioration.

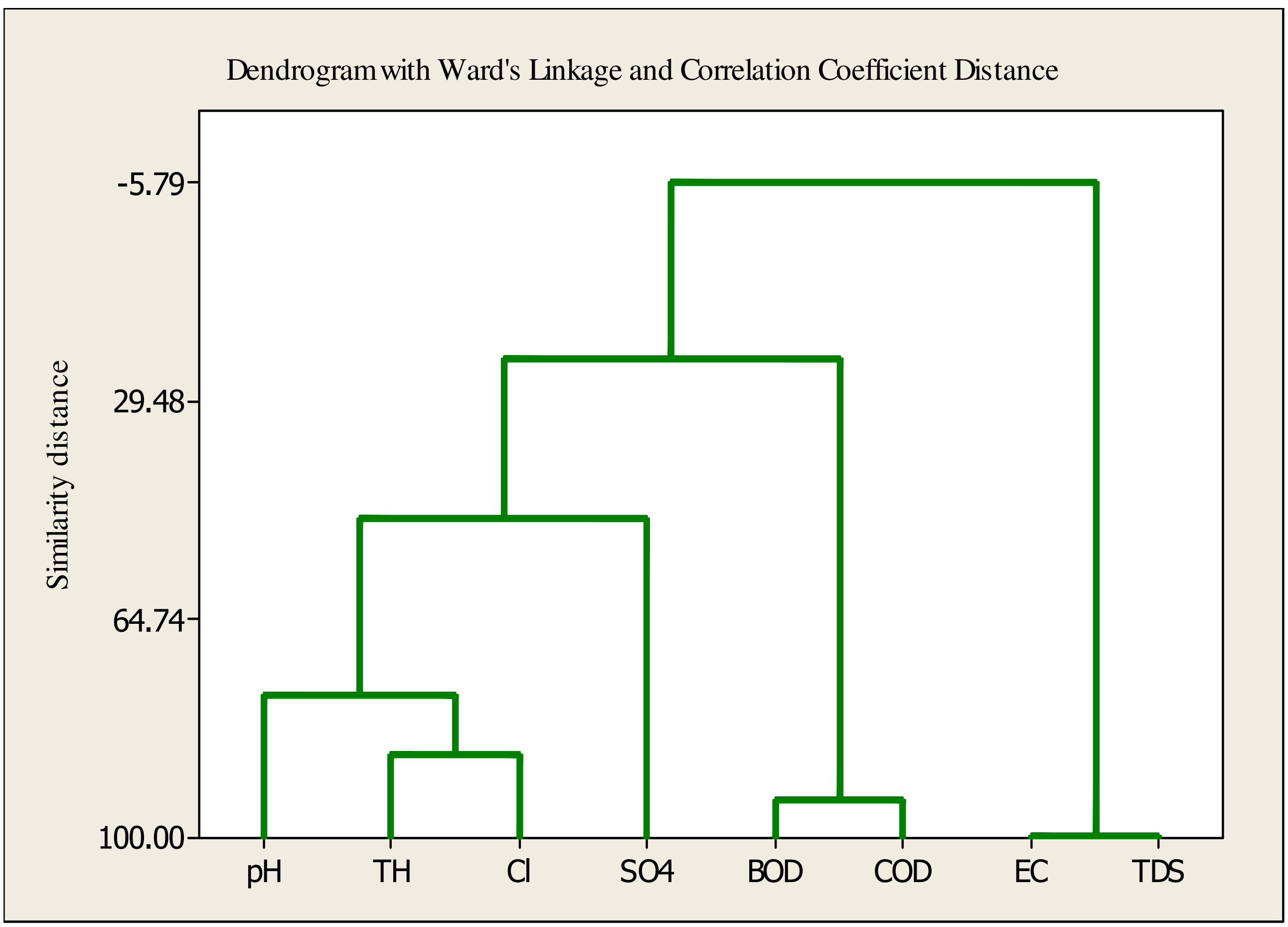

Figure-2
Cluster analysis based on physico-chemical characteristics of river water

References

1. Sahoo N.K., Rout C., Khuman Y.S.C. and Prasad J., Sustainability Links of River Linking, Proceedings National Speciality Conference on River Hydraulics, **145-154,** 29-30 **(2009)**
2. Patra H.S., Rout C., Bhatia U.K. and Garg M.P., Impact of Mining and Industrial Activities on Brahmani River in Angul-Talcher Region of Orissa, India, Proceedings National Speciality Conference on River Hydraulics, **97-205,** 29-30 **(2009)**
3. Rani M., Rout C., Garg V. and Goel G., Evaluation of Water Quality of Yamuna River with Reference to Physico-Chemical Parameters at Yamuna Nagar City, Haryana, India, Proceedings AICTE Sponsored National Conference on River Hydraulics, **67-76,** 22-23 **(2012)**
4. Banerjee S. P., Chavan R.P. and Lokhande R.S. Quality Assessment of River Water with Special Reference to Pearson Correlation Study, *Int. Res. J. Environ. Sci.,* **3(12)**, 39-43 **(2014)**
5. Kumar A., Studies on Qualitative and Quantitative Abundance of Aquatic Entomofauna in Glacial Fed Mountainous Goriganga River of Kumaun Himalaya Uttarakhand, India, *Int. Res. J. Environ. Sci.,* **3(4)**, 51-63 **(2014)**
6. Shahi R. P. and Hamidi M. K., Phytoplankton Primary Production in the River Jharahi at Mairwa, India. *Int. Res. J. Environ. Sci.,* **3(10)**, 62-67 **(2014)**
7. Nighojkar A. and Dohare D., Physico-Chemical Parameters for Testing of Present Water Quality of Khan River at Indore, India. *Int. Res. J. Environ. Sci.,* **3(4)**, 74-81 **(2014)**
8. Chaurasia S. and Raj K., Assessment of Water Quality of River Mandakini during Amawashya in Chitrakoot, India, *Int. Res. J. Environ. Sci.,* **4(2)**, 54-57 **(2015)**
9. Barde V. S., Piplode S., Thakur V. and Agrawal R., Physico-chemical Evaluation of Water Quality of Narmada River at Barwani and Khalghat, MP, India. *Int. Res. J. Environ. Sci.,* **4(3)**, 12-16 **(2015)**
10. Kumar A., Studies on Diversity and Abundance of Fresh Water Diatoms as Indicators of Water Quality in Glacial Fed Goriganga River, India, *Int. Res. J. Environ. Sci.,* **4(4)**, 80-85 **(2015)**
11. Valentina T., Singh H.T., Tamuli A.K. and Teron R., Assessment of Physico-Chemical Characteristics and Fish Diversity of Hill streams in Karbi Anglong district, Assam, India, *Int. Res. J. Environ. Sci.,* **4(5)**, 6-11 **(2015)**
12. Arun L., Chadetrik R. and Ravi P. D., Assessment of Heavy Metals Contamination in Yamuna River in Rural and Semi-urban Settings of Agra, India, *Int. J. Earth Sci. and Engg.,* **8(4)**, 1627-1631 **(2015)**
13. Arun L., Ravi P.D. and Chadetrik R., Assessment of Water Quality of the Yamuna River in Rural and Semi-urban Settings of Agra, India, *Int. J. Earth Sci. and Engg.,* **8(4)**, 1661-1666 **(2015)**
14. Kshetrimayum K. S. and Bajpai V. N., Establishment of Missing Stream Link between the Markanda River and the Vedic Saraswati River in Haryana, India Geoelectrical Resistivity Approach, *Curr. Sci.*, **100(11)**, 1719-1724 **(2011)**
15. Kshetrimayum K.S,. Morphometric Analysis and Vertical Electrical Sounding in Groundwater Prospecting: A Case Study from a Himalayan Foothill River Basin, NW India, *Int. J. Geom. and Geosci.*, **4(1)**, 103-115 **(2013)**
16. APHA, American Public Health Association, Standard Methods for Estimation of Water and Wastewater, AWWA, Water Pollution Control Federation, New York, **19 (1995)**
17. Thoker F.A., Manderia S. and Manderia K., Impact of Dye Industrial Effluent on Physicochemical Characteristics of Kshipra River, Ujjain City, India*, Int. Res. J. Environ. Sci.,* **1(2)**, 41-45 **(2012)**
18. Lokhande R.S., Singare P.U. and Pimple D.S., Study of Physico-chemical Parameters of Waste Water Effluents from Taloja Industrial Area of Mumbai, India, *Int. J. Ecos.*, **1(1)**, 1-9 **(2001)**
19. Hashemzadeh F. and Venkataramana G. V., Impact of Physico-Chemical Parameters of Water on Zooplankton Diversity in Nanjangud Industrial Area, India. *Int. Res. J. Environ. Sci.,* **1(4)**, 37-42 **(2012)**
20. Shivayogimath C.B., Kalburgi P.B., Deshannavar U.B. and Virupakshaiah D.B.M., Water Quality Evaluation of River Ghataprabha, India, *Int. Res. J. Environ. Sci.,* **1(1)**, 12-18 **(2012)**
21. Ogunfowokan A.O., Okoh E.K., Adenuga A.A. and Asubiojo O.I., Assessment of the Impact of Point Source Pollution from a University Sewage Treatment Oxidation Pond on the Receiving Stream-A Preliminary Study, *J. App. Sci*., **6(1)**, 36-43 **(2005)**
22. Liu C.W., Lin K.H. and Kuo Y.M., Application of factor analysis in the assessment of ground water quality in a Blackfoot disease area in Taiwan, *Sci. Tot. Environ.*, **313(1-3)**, 77-89 **(2003)**
23. Rout C., Lavaniya A. and Divakar R. P., Assessment of Physico-chemical Characteristics of River Yamuna at Agra Region of Uttar Pradesh, India, *Int. Res. J. Environ. Sci.,* **4(9)**, 25-32 **(2015)**
24. Rout C. and Sharma A., Assessment of Drinking Water Quality: A Case Study of Ambala Cantonment Area, Haryana, India, *Int. J. Env. Sci.*, **2(2),** 933-945 **(2011)**