INTERNATIONAL JOURNAL OF ENVIRONMENT

Volume-5, Issue-1, Dec-Feb 2015/16 **ISSN 2091-2854**

Received:11 December 2015 *Revised:26 December 2015* *Accepted:05 February 2016*

ASSESSMENT OF SURFACE WATER QUALITY USING HIERARCHICAL CLUSTER ANALYSIS

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Abstract

This study was carried out to assess the physicochemical quality river Varuna in Varanasi, India. Water samples were collected from 10 sites during January-June 2015. Pearson correlation analysis was used to assess the direction and strength of relationship between physicochemical parameters. Hierarchical Cluster analysis was also performed to determine the sources of pollution in the river Varuna. The result showed quite high value of DO, Nitrate, BOD, COD and Total Alkalinity, above the BIS permissible limit. The results of correlation analysis identified key water parameters as pH, electrical conductivity, total alkalinity and nitrate, which influence the concentration of other water parameters. Cluster analysis identified three major clusters of sampling sites out of total 10 sites, according to the similarity in water quality. This study illustrated the usefulness of correlation and cluster analysis for getting better information about the river water quality.

Key words: Correlation analysis, Cluster analysis, BOD, COD, River Varuna, Sampling sites.

Introduction

Water is a most abundant natural resource and is a prime necessity for all living beings. Its quality plays an important role in promoting agricultural production and standard of human health. The rapid population growth, accelerated pace of industrialization, lack of ecological education and over exploitation of natural resources has severely affected the water resources by increasing the pressure on urban hydrology (Misra, 2011; Barai and Kumar, 2013; Ramakrishnaiah et al., 2009; Sinha, 2003).These factors have deteriorated the quality of surface water for drinking purposes and cause great damage to riverine biota (Singh et al., 2015; Varol, 2013). Therefore, constant monitoring of a river system is required to evaluate the effects of environmental factors on water quality for proper utilization and sustainable development of the resource (Cosmas and Samuel, 2011).

In present study the physico-chemical characteristics of River Varuna a minor tributary of river Ganga was monitored at Varanasi, India. Varuna River originates from Manahan (a place near Phulpur, Allahabad) and flows from west to east for about 100 Km and join River Ganga in down stream of Varanasi at Rajghat (Kumar et al., 2015). The river water consumption in urban areas for municipal, agricultural and industrial purposes is estimated between 100-1500 lit/person/day. The 80% of the municipal water supply is discharged into river Varuna as waste water through 22 municipal drains located on both sides of river (Singh et al., 2015; Singh et al., 2010; Singh et al., 2007; Kumar et al., 2012). Therefore, the objective of the present study was to assess the physico-chemical characteristics of River Varuna at Varanasi and to establish correlation between various water parameters and sampling sites on the basis of Pearson correlation analysis and cluster analysis.

Materials and Methods

River Varuna flowing through Varanasi was selected as a study area. It is tributary of river Ganga and originates from Jhignatal (Phulpur) near Allahabad (Barai and Kumar 2013; Singh et al., 2015; Kumar et al., 2015). River flows east-to-southeast for some 100 km and joins the Ganges at Rajghat, just downstream of Varanasi. Water samples were collected from ten predetermined sites every month during the period of January to June 2015. The details of these sampling sites are listed in Figure 1 and Table 1.

Figure 1: Sampling locations at Varuna River Stretch

The selected water quality parameter were Temperature, pH, Electrical Conductivity (EC), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total dissolved Solids (TDS), Total Hardness (TH), Dissolved Oxygen (DO), Total Alkalinity (TA), Total Acidity (TA), Chloride, Nitrate following the standard protocols of APHA (2005) (Rana and Chhetri 2015).

Table 1: Description of the Sampling Stations

Sampling stations	Geographical Coordinates	Description
S-1	25°20'14.2"N 82°57'34.4"E	**Phulwariya:** It is situated in cantonment area of Varanasi.
S-2	25°20'26.3"N 82°58'52.8"E	**Shastri bridge**: It is 1st road bridge over Varuna in Varanasi. The bridge connects Kachehari (trans Varuna region) to old Varanasi (cis- Varuna region).
S-3	25°20'04.7"N 82°59'47.8"E	**Chaukaghat Bridge**: It is the 2nd bridge over Varuna in Varanasi. It also connect Pahadia (trans Varuna region) to old Varanasi (cisVaruna region)
S-4	25°20'28.7"N 83°00'33.0"E	**Nakkhighat**: It is the 3rd bridge over Varuna in Varanasi. It is situated near Varanasi city railway station and connect Pandeypur (trans Varuna region) to Old Varanasi. The site was used earlies for solid waste disposal by municipality.
S-5	25°20'28.9"N 83°01'21.7"E	**Before Old Bridge**: It is the 4th bridge over Varuna in Varanasi. It connect Sarnath, Ashapur (trans Varuna region) to Golgadda bus stand, Kashi railway station.
S-6	25°20'31.0"N 83°01'23.2"E	**After Old Bridge:** It is located near municipal solid waste dumping site.

S-7	25°20'26.3"N 83°01'42.6"E	**Konia:** It is located near Jalalipura village on GT road**.**
S-8	25°20'07.6"N 83°02'12.2"E	**Khalispur Rail Bridge**: It is located near Aadikeshavmandir, khalispur, Aadikeshavghat.
S-9	25°19'52.3"N 83°02'15.0"E	**Raj Ghat :**It is located near VasantKanya P.G. College, Varanasi.
S-10	25°19'46.0"N 83°02'39.0"E	**Varuna-Ganga Confluence:** It is the site, where River Varuna joins river Ganga in downstream of Varanasi.

The results were subjected to statistical analysis to assess the spatio-temporal variations in river water quality using Microsoft $Excel_{2007}$ and $SPSS_{16}$. Pearson correlation coefficient was used to determine the interrelationships between physico-chemical parameters. Cluster analysis (CA) was done for identifying the relatively homogeneous groups of variables based on their similarities (Shrestha and Kazama, 2007). A dendrogram is constructed, where cohesiveness and correlations among the variables can be clearly observed (Yongming et al., 2006). It presents a visual summary of intra-relationship amongst variations in water parameters, which can lead to a better understanding of governing factors of river water quality (Pejman et al., 2009).

In this study for the assessment of the quality of water, identification of key water parameters, which influence the other parameters and to determine the sources of pollution in the river Varuna in Varanasi region, Pearson correlation analysis and cluster analysis was used.

Results and Discussion

Physical and Chemical Characteristics

Physico-chemical parameters results of all ten sampling sites and Indian standard limits are given in table-1. In the present study Temperature of surface water in study region varied from 18.25^0C to 23.4^0C. The site wise results showed an increasing trend from S1 to S10 of the river may be due to the common effect of intensity of solar radiations, ambient temperature and urban discharge (Gyananath et al., 2000). In the present study, pH ranges from a minimum value of 6.30 in S3 and maximum value of 7.32 in S10, which is a safe range 6.5-8.5 for Class-A (As drinking water source without conventional treatment but after disinfection) purpose suggested by the Bureau of Indian Standards (IS: 2296-1982). Though the pH value has no direct effect on health, it can alter the taste of water.

Results of Electrical conductivity in present study showed a gradual increasing trend of minimum 0.43 µS in S1 and maximum 0.82 µS in S3. This is a safe range (1000 to 2250 µS) for class-D (For fish culture and wild life propagation) and Class-E (For irrigation, industrial cooling or controlled waste disposal) purpose suggested by the Bureau of Indian Standards (IS: 2296-1982). Chloride value in present study varied from minimum 44.38 mg/l in S1 to maximum 88.75 mg/l in S3. This is a safe range against the guideline value of 250 mg/l for class-A purpose suggested by the Bureau of Indian Standards (IS: 2296-1982). In the present study, the minimum total dissolved solid of 300 mg/l is recorded in S10 and the maximum value of 600 mg/l is recorded in S3. This is much higher than the guideline value of maximum 500 mg/l for Class-A purpose suggested by the Bureau of Indian Standards (IS: 2296-1982). The high value of TDS produces aesthetically displeasing color, odor and taste to water and causes gastro intestinal irritation on consumption (Sharma and Kansal, 2011; Bhat et al., 2009; Soni and Thomas, 2013). In present study total acidity of water samples were observed minimum 43 mg/l in S8 and maximum 89 mg/l in S3. The decreasing acidity in down stream indicates the release of organic matter by hydrophytes through photosynthesis process. Total acidity shows the inverse relationship with pH in present study. In the present study, the minimum total alkalinity of 196 mg/l is recorded in S1 and the maximum value of 770 mg/l is recorded in S3. This is higher than the guideline value of 200–600 mg/l suggested for drinking water by the Bureau of Indian Standards (IS: 105000-1991). This may be due to higher concentration of salts of carbonates and bicarbonates with hydroxyl ions in a free state from limestone nature of rock, which constitute alkalinity (Singh et al., 2005a; Singh et al., 2005b). In the present study the minimum total hardness value of 166 mg/l is observed in S3 and the maximum value of 275.50 mg/l is observed in S5. This is lower than the guideline value of maximum 300 mg/l suggested by the Bureau of Indian Standards (IS: 2296-1982).

Table-2 Use based classification of surface waters in India (IS: 2296-1982)

CLASS OF WATER	DESIGNATED BEST USE	CRITERIA
Class A	Drinking water source without conventional treatment but after disinfection	1. pH between 6.5 and 8.5 2. Dissolved Oxygen 6 mg/l or more 3. Biochemical Oxygen Demand 5 days 20^{o}C 2 mg/l, Max 4. Total Dissolved Solids, 500 mg/l, Max 5. Total Hardness (as $CaCO_3$), 300 mg/l, Max 6. Chlorides (as Cl), 250 mg/l, Max 7. Total Alkalinity (as $CaCO_3$), 600 mg/l, Max
Class B	Outdoor bathing	1. pH between 6.5 and 8.5 2. Dissolved Oxygen 5 mg/l or more

		3. Biochemical Oxygen Demand 5 days 20^{o}C 3 mg/l, Max
Class C	Drinking water source with conventional treatment followed by disinfection.	1. pH between 6.5 and 8.5 2. Dissolved Oxygen 4 mg/l or more 3. Biochemical Oxygen Demand 5 days 20^{o}C 3 mg/l, Max 4. Total Dissolved Solids, 1500 mg/l, Max 5. Chlorides (as Cl), 600 mg/l, Max 6. Nitrate (as NO_3), 50 mg/l, Max
Class D	Fish culture and wild life propagation	1. pH between 6.5 and 8.5 2. Dissolved Oxygen 4 mg/l or more 3. Electrical Conductance at 25°C, 1000 µS, Max
Class E	Irrigation, industrial cooling or controlled waste disposal	1. pH between 6.0 and 8.5 2. Electrical Conductance at 25°C, 2250 µS, Max 3. Total Dissolved Solids, 2100 mg/l, Max 4. Chlorides (as Cl), 600 mg/l, Max

Table 3: Physico-Chemical Characteristics of river Varuna at different sampling site

Water Parameter	Statistical Parameter	SAMPLING SITE									
		1	2	3	4	5	6	7	8	9	10
Temp. (Deg C)	Mean	18.25	19.75	23.40	21.15	21.65	20.35	21.75	21.15	20.25	21.65
	Std.dev.	0.35	0.35	0.56	0.21	0.21	0.49	0.35	0.21	0.35	0.21
pH	Mean	7.10^{A}	7.01^{A}	6.30^{E}	7.10^{A}	6.80^{A}	6.90^{A}	7.00^{A}	7.06^{A}	7.03^{A}	7.32^{A}
	Std.dev.	0.01	0.01	0.44	0.01	0.33	0.02	0.06	0.09	0.03	0.14
EC (in µS)	Mean	0.43^{A}	0.57^{A}	0.82^{A}	0.55^{A}	0.68^{A}	0.62^{A}	0.55^{A}	0.61^{A}	0.45^{A}	0.46^{A}
	Std.dev.	0.01	0.01	0.05	0.13	0.01	0.01	0.01	0.05	0.01	0.01
Chloride (in mg/l)	Mean	44.38^{A}	62.10^{A}	88.75^{A}	84.14^{A}	68.52^{A}	69.23^{A}	66.61^{A}	74.20^{A}	57.51^{A}	65.68^{A}
	Std.dev.	6.50	0.54	16.00	0.50	0.50	1.50	2.82	2.51	1.00	5.52
DO (in mg/l)	Mean	3.56^{*}	2.24^{*}	2.40^{*}	2.48^{*}	2.00^{*}	1.68^{*}	2.02^{*}	3.28^{*}	3.52^{*}	3.78^{*}
	Std.dev.	0.16	0.45	0.22	0.56	0.11	0.11	0.53	0.79	0.45	0.13
Acidity (in mg/l)	Mean	49.00	61.00	89.00	45.00	77.00	71.50	45.00	43.00	49.00	45.00
	Std.dev.	7.07	1.41	1.41	1.41	7.07	9.19	9.89	1.41	1.41	1.14
Total Alkalinity (in mg/l)	Mean	196.00^{A}	221.00^{A}	770.00^{*}	254.00^{A}	242.50^{A}	235.00^{A}	238.00^{A}	226.00^{A}	204.00^{A}	204.00^{A}
	Std.dev.	14.14	12.72	169.70	2.82	10.60	9.89	2.82	2.82	2.82	2.82
TDS (in mg/l)	Mean	510.00^{A}	405.00^{A}	600.00^{A}	387.50^{A}	510.00^{A}	392.50^{A}	525.00^{A}	337.50^{A}	340.00^{A}	300.00^{A}
	Std.dev.	127.27	77.78	141.42	88.38	127.27	12.53	106.06	88.38	84.85	141.42
Total Hardness (in mg/l)	Mean	218.00^{A}	223.00^{A}	166.00^{A}	273.00^{A}	275.50^{A}	265.00^{A}	204.00^{A}	254.00^{A}	200.00^{A}	197.00^{A}
	Std.dev.	45.25	9.89	5.65	24.04	57.27	52.32	45.25	42.42	8.48	7.07
BOD (in mg/l)	Mean	67.50^{*}	75.00^{*}	65.50^{*}	77.50^{*}	92.50^{*}	87.50^{*}	32.50^{*}	70.00^{*}	65.00^{*}	66.00^{*}
	Std.dev.	3.53	4.24	2.12	3.53	3.53	3.53	3.53	8.48	4.24	2.82
COD (in mg/l)	Mean	137.50^{*}	145.00^{*}	166.00^{*}	170.50^{*}	183.00^{*}	177.00^{*}	131.00^{*}	122.50^{*}	135.00^{*}	130.00^{*}
	Std.dev.	10.60	4.24	5.65	7.77	4.24	7.07	5.65	10.60	9.89	7.07

Nitrate (in mg/l)	Mean	55.00*	59.00*	65.50*	58.50*	72.00*	67.50*	43.00C	57.00*	51.00*	53.00*
	Std.dev.	4.24	4.24	2.12	4.94	5.65	3.53	4.24	7.07	4.24	4.24

A Satisfy class A category, B Satisfy class B category, C Satisfy class C category,
D Satisfy class D category, * Higher than the tolerance limit

In the present study the minimum Nitrate value of 43 mg/l is observed in S7 and the maximum value of 72 mg/l is observed in S5. This is much higher that the tolerance limit of maximum 20 mg/l for class-A purpose suggested by the Bureau of Indian Standards (IS: 2296-1982). The high value of nitrate is linked to run-off of the organic matter from the agricultural land located at the bank of river and impeded microbial and bacterial activities (Soni and Thomas, 2013; Sreenivasulu et al., 2014). The presence of excess nitrate causes health hazards to humans. This will cause methaemoglobinemia (Blue baby disease) and it influences the growth of algae (House, 1999; Sharma and Kansal, 2011; Bhat, 2009).

Correlation analysis:

Among the various physiochemical parameters of surface water, only few parameters exhibited significant correlations (Table 3). In present study the values of electrical conductivity (EC) shown a statistically significant positive correlation with Temperature ($r=0.702$, $p<0.05$), Chloride ($r=0.749$, $p<0.05$), Nitrate ($r=0.657$, $p<0.05$), Total Acidity ($r=0.787$, $p<0.01$), Total Alkalinity ($r=0.784$, $p<0.01$) and negative correlation with pH ($r=-0.880$, $p<0.01$).

Table 4: List of significant positive and negative correlated water quality parameters

Level of Significance	Positively Correlated Parameters	Negatively correlated Parameters
α= 0.05	EC-Temperature (r=0.702) EC-Chloride (r=0.749) EC-Nitrate (r=0.657) Chloride-Total Alkalinity (r=0.643)	pH-TDS (r=-0.736)
α= 0.01	Temperature-Chloride (r=0.826) Temperature-Total Alkalinity (r=0.670) EC-Acidity (r=0.787) EC-Total Alkalinity (r=0.784) Acidity-Total Alkalinity (r= 0.769) Acidity-TDS (r=0.680) Total Hardness-BOD (r=0.813) BOD-COD (r=0.792) BOD-Nitrate (r=0.803) COD-Nitrate (r=0.824)	pH-EC (r=-0.880) pH-Acidity (r= -0.787) pH-Total Alkalinity (r=-0.886) DO-Nitrate (r=-0.821)

The positive correlation of chloride, nitrate and total alkalinity with EC indicates that an increase in impurities in surface water enhances the number of free ions in the water leading to increased EC (Singh et al., 2015).The inverse relationship between EC and pH indicates that the increased ionic load to water bodies enhance the oxidation of organic matter resulting in nutrient release and decrease in pH (Watkar and Barbate, 2015). The inverse relationship of pH with TDS ($r=-0.736$, $p<0.05$), Acidity ($r=-0.787$, $p<0.01$) and Total Alkalinity ($r=-0.886$, $p<0.01$) indicates that an increased load of dissolved solid influence the pH of water.

Statistically significant positive correlation shown by total alkalinity with Chloride ($r=0.643$, $p<0.05$), Temperature ($r=0.670$, $p<0.01$) and Acidity ($r=0.769$, $p<0.01$). This indicates that carbonate, bicarbonate and hydroxide alkalinity of water influence acidity and chloride content of water (Vishwakarma and Tripathi, 2015).

Nitrate was found to have significant positive correlation with BOD ($r=0.803$, $p<0.01$), COD ($r=0.824$, $p<0.01$) and negative correlation with dissolved oxygen ($r=-0.821$, $p<0.01$). The positive correlation of nitrate with BOD and COD indicates that the higher concentration of nitrate in run off from agricultural land near the bank of river contribute to BOD and COD both. The oxidation of nitrate consumes dissolved oxygen of water and show inverse relationship between nitrate and dissolved oxygen. BOD shown significant positive correlation with total hardness ($r=0.813$, $p<0.01$) and COD ($r=0.792$, $p<0.01$) indicates that concentration of total hardness and COD influence BOD value of water. Significant positive correlation between temperature and chloride ($r=0.826$, $p<0.01$) indicates that the solubility of inorganic salts increases with the increasing temperature of water (Soni and Thomas, 2013).Significant positive correlation between acidity and TDS ($r=0.680$, $p<0.01$) indicates that the oxidation of organic matter in water release nutrients and enhance acidity.

Cluster Analysis:

Hierarchical Cluster analysis (CA) was applied to detect spatial similarity among sites under the monitoring network. It rendered a dendrogram as shown in (Fig. 2), grouping all the ten sampling sites on the river into three statistically significant clusters. The clustering procedure generated three groups of sites in a very convincing way, as the sites in these groups have similar characteristic features and same source of contamination. Cluster-1 (Chaukaghat, Before Old Bridge, Konia, Khalispur Road Bridge, Raj Ghat, Varuna-Ganga Confluence), Cluster 2 (Phulwariya, Nakkhighat, After Old Bridge) and cluster 3 (Shastri bridge) are the clusters that correspond to contamination of water. It is evident that this technique is useful in offering reliable classification of river water in the whole region. So instead of monitoring ten sites, only three sites could be selected in future spatial sampling strategy without affecting the result. The reduction in sampling sites in the monitoring network will be more economical without losing any significance of the outcome (Bajpai et al., 2013; Vishnu et al., 2014; Sreenivasulu et al., 2014).

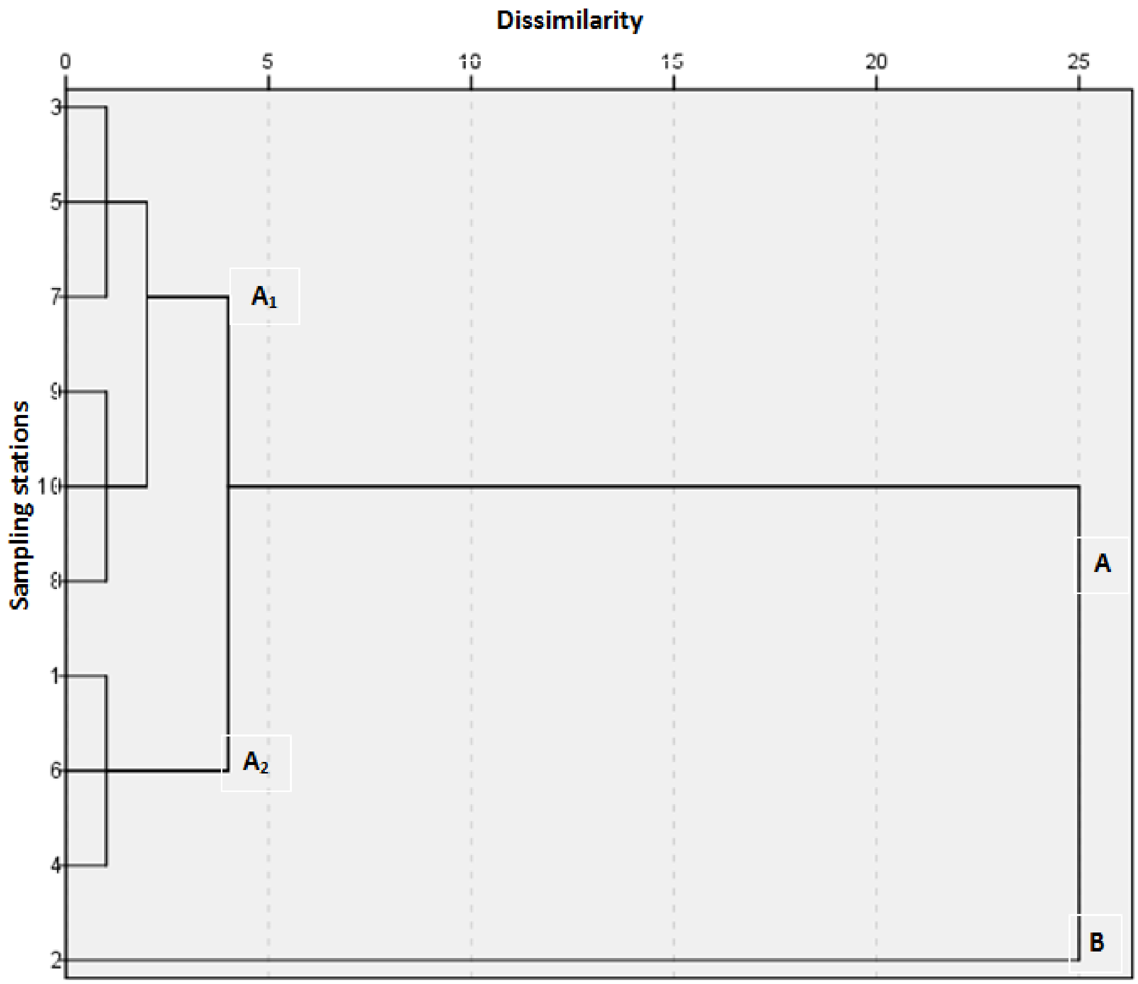

Fig. 2: Dendrogram from Hierarchical Cluster Analysis of Sampling Sites

Conclusion

In this study for the assessment of the quality of water, identification of key water parameters, which influence the other parameters and to determine the sources of pollution in the river Varuna in Varanasi region, Pearson correlation analysis and cluster analysis was used. The result has shown the effect of different pollutant on water quality. Correlation analysis showed that the main parameters responsible for the changes in the quality of water were identified as pH, electrical conductivity, total alkalinity and nitrate. All the 10 sampling stations were divided into three clusters using cluster analysis. Cluster I corresponds to relatively less polluted sites, Cluster II were corresponded to moderately polluted sites and Cluster III corresponds to highly polluted sites.

The present study revealed that the water quality of river Varuna is declining due to disposal of city drains carrying polluted water. It is therefore needful to develop a comprehensive river water quality monitoring program to identify the major polluted spots of a river. The statistical techniques used in the present study will help in future to water resource managers to outline the parameters contributing to pollution for every site. This will make the future monitoring cost more economical and easier without missing much information.

Acknowledgements

The authors are thankful to Head, Department of Science, Sampurnanand Sanskrit University, Varanasi, India and Head, Environmental Science, Department of Botany, Allahabad University, Allahabad, India for providing necessary laboratory facilities to perform the research work.

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