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Original Research Paper

Monitoring and assessment of a eutrophicated coastal lake using multivariate approaches

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ABSTRACT: Multivariate statistical techniques such as cluster analysis, multidimensional scaling and principal component analysis were applied to evaluate the temporal and spatial variations in water quality data set generated for two years (2008-2010) from six monitoring stations of Veli-Akkulam Lake and compared with a regional reference lake Vellayani of south India. Seasonal variations of 14 different physicochemical parameters analyzed were as follows: pH (6.42-7.48), water temperature (26.0-31.28°C), salinity (0.50-26.81 ppt), electrical conductivity (47-20656.31 µs/cm), dissolved oxygen (0.078-7.65 mg/L), free carbon-dioxide (3.8-51.8 mg/L), total hardness (27.20-2166.6 mg/L), total dissolved solids (84.66-4195 mg/L), biochemical oxygen demand (1.57-25.78 mg/L), chemical oxygen demand (5.35-71.14 mg/L), nitrate (0.012-0.321 µg/ml), nitrite (0.24-0.79 µg/ml), phosphate (0.04-5.88 mg/L), and sulfate (0.27-27.8 mg/L). Cluster analysis showed four clusters based on the similarity of water quality characteristics among sampling stations during three different seasons (pre-monsoon, monsoon and post-monsoon). Multidimensional scaling in conjunction with cluster analysis identified four distinct groups of sites with varied water quality conditions such as upstream, transitional and downstream conditions in Veli-Akkulam Lake and a reference condition at Vellayani Lake. Principal Component Analysis showed that Veli-Akkulam Lake was seriously deteriorated in water quality while acceptable water quality conditions were observed at reference lake Vellayani. Thus the present study could estimate the effectiveness of multivariate statistical approaches for assessing water quality conditions in lakes.

KEYWORDS: *Cluster analysis (CA); Physicochemical parameters; Principal component analysis (PCA); Multidimensional scaling (MDS). Veli-Akkulam Lake; Vellayani Lake; Water quality*

INTRODUCTION

Inland water bodies are vulnerable to pollution due to their extensive accessibility for disposal of pollutants through natural processes, anthropogenic interventions due to industrial and agricultural activities, eutrophication and invasive alien species. Inappropriate management of water resources has resulted in their major shifts in the quantity and quality of water resources. Aquatic ecosystems have been recognized worldwide as extremely important and are sensitive to anthropogenic activities viz. urban, industrial and agricultural activities. Coastal lakes have been drastically influenced by anthropogenic and natural processes and those not only degrade surface water quality but also impair the whole ecosystem stability to a wider extent irreversibly. Inland resources particularly lakes are essential for the survival of life and are being realized everywhere as the most productive ecosystems with rich biological diversity (Hails 1996; Barbier *et al.,* 1997; Tiner 1999). In addition to its varying biodiversity and ecological productivity, they also provide a variety of ecosystem services to humans in many ways including water for food and

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fiber production, drinking and irrigation, recreations and habitat for economically important fisheries (Carpenter *et al.,* 2011; Schallenberg *et al.,* 2013). Human activities impose negative influence directly or indirectly causing deterioration of water quality and ecological stability. As a result of adverse anthropogenic activities condition of freshwater ecosystems all over the world has severely been degraded. This ultimately leads to loss of biodiversity and thereby alters ecosystem functioning and changes the resilience of ecosystems (Chapin *et al.,* 2000; Woodward 2009; Cardinale *et al.,* 2012).

Water quality monitoring and assessment act as the integral components in the management of lake ecosystems and are essential to provide current status of aquatic ecosystems (Kupfer and Gao 2011; Dudley *et al.,* 2013; Li *et al.,* 2014). The changes in the quality and integrity can threat life and its resources in a wider scale. A large number of sources such as industrial effluents, municipal and sewage wastes inputs, tourist developmental activities, agricultural runoff, and land drainage have created enormous stress on these habitats. Another important leading cause of freshwater ecosystem risk is eutrophication and the rate of eutrophication is manifested mainly by the concentration of nutrients, oxygen saturation and biomass of phytoplankton, causes tremendous reduction and potentially poses risks to freshwater biodiversity (Chislock *et al.,* 2013; Dupas *et al.,* 2015; Azevedo *et al.,* 2015). Since lakes constitute one of the major inland ecosystems, there is an urgent need to prevent and control the pollution. Hence regular routine monitoring of core water quality parameters helps to assess the health of these lacustrine ecosystems. Monitoring of lake water quality recognizes spatio-temporal variations which could be useful for ameliorating adverse effects through effective management.

India faces major challenges in managing freshwater ecosystems due to population expansion and increasing industrial activities (Jain *et al.,* 2004; Reddy and Char 2006). The freshwater resources are seriously being degraded due to the indiscriminate disposal of sewages and industrial effluents (Lokhande *et al.,* 2011; Upadhyay *et al.,* 2011). With regard to these pollution problems regular monitoring and assessment are required for estimating ecological conditions in freshwater lakes. The general study on hydrological and morphological features of Veli-Akkulam Lake was being carried out (Sheela *et al.,* 2011 and 2012). Despite such efforts, information regarding the water quality characteristics, its distribution and the extent of pollution has not been examined at an extensive standardized level. The present study was focused to scale out the water quality variations by comparing with a regional reference lake of the same eco-region in order to forecast the degree of pollution and to elucidate principal factors pertaining to the lake condition. Of late multivariate statistical approaches offer a valuable tool for reliable management of water resources by identifying possible sources that influence water systems as well to facilitate complex data sets for characterizing and evaluating the water quality status (Reghunath *et al.,* 2002; Simeonov *et al.,* 2003; Wang *et al.,* 2006; Mahadev *et al.,* 2010; Satheeshkumar and Khan 2011; Wang *et al.,* 2014; Phung *et al.,* 2015). In this study, multivariate statistical techniques such as Cluster analysis (CA), Multidimensional scaling (MDS) and principal component analysis (PCA) were employed to evaluate and compare the trophic status of water quality in Veli-Akkulam with a regional reference lake Vellayani, South west coast of Kerala, India. This paper provides the information on the scenario of water quality parameters of the study lake as well as enumerates the ecological condition so as to implement management strategies for mitigation of pollution problems and restoration of the lake ecosystem. This study was performed in Veli-Akkulam during 2008-2010.

MATERIALS AND METHODS

Study area

Veli-Akkulam lake is located in the southwest coast of India (08°30′– 08°31′ N and 76°52′–76°53′ E; area=1 km^2; depth= <1 m) is a smallest inland lake, separated from the Arabian Sea on its western side by a sand bar and remains connected with the sea only during monsoon season (Fig. 1). Veli-Akkulam Lake exists as two portions separated by a bund across its length. The western part of the lake towards the sea with a length of 1.25 km and a width of around 100 m forms the Veli Lake whereas the north-eastern part is the Akkulam Lake, an extension of Veli Lake lies starting from the bund. Mud flats in the shallow regions of the Akkulam part of the lake get exposed during ebb tide and the siltation in Akkulam Lake affects the free flow of water towards the Veli Lake. Six different sampling stations were chosen along the Veli-Akkulam Lake: station 1, Veli Bar mouth receive neritic waters form the Arabian sea at its mouth; Station 2, Veli boat club is the

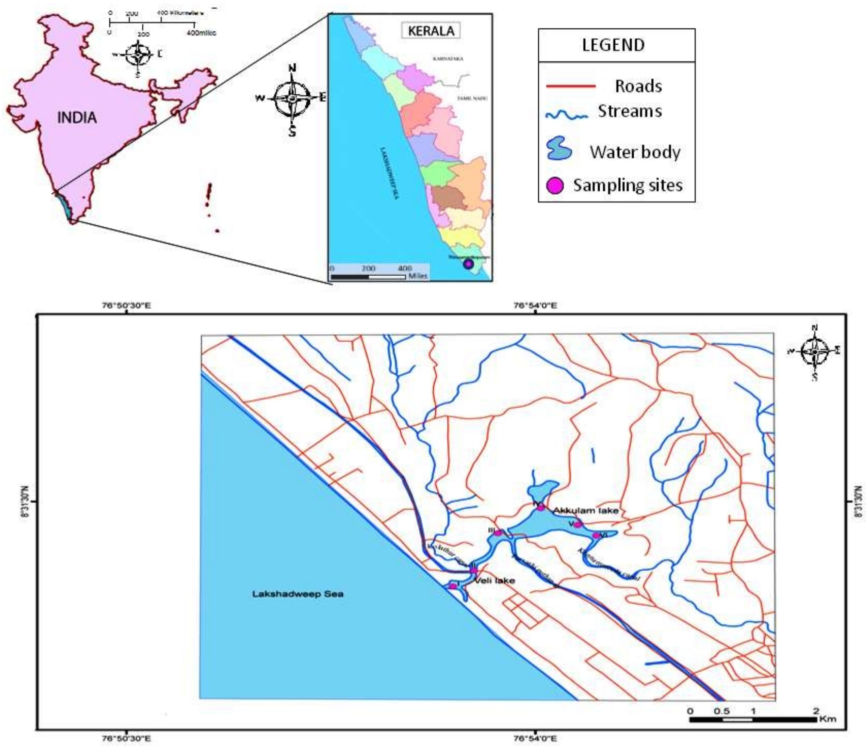

Fig. 1: Location map of Veli-Akkulam lake, India showing monitoring stations

station subjected to maximum human disturbance due to boating activities, oil pollution and dumping of solid wastes; Station 3, Veli Parvathy Puthen Ar is the wider area of the lake receiving two canals, viz. the Chakka canal and Parvathy Puthen Ar (Channankara Canal). Dumping of sewages from Muttathara Sewage Farm makes Parvathy Puthen Ar extremely polluted; Station 4, Akkulam NISH is heavily disturbed due to anthropogenic activities such as washing of vehicles, disposal of wastes, recreation, dredging etc. Severe eutrophication and heavy sediment load was observed during most of the study period; Station 5, Akkulam Boat club is subjected to heavy infestation with water hyacinth, pollution and siltation; Station 6, Akkulam Kannammoola canal region is heavily polluted by sewage and hospital wastes from the Thiruvananthapuram City. Vellayani Lake (8"24’09" - 8"26’30" N; 76°59’08"-76°59’47" E) another inland lake located in the same region was analysed for monitoring and assessment of Veli-Akkulam Lake. Vazhavila (station 7) of Vellayani Lake was selected as the reference site for comparing water quality conditions of Veli-Akkulam Lake.

Sampling and method of analysis

Mean annual and seasonal rainfall data was obtained from Regional Meteorological Department, Thiruvananthapuram. Water samples were collected monthly for a period of two years from surface and bottom during October 2008 – September 2010. For different laboratory analysis water samples were collected using Teflon coated Niskin water sampler having 5L capacity and stored in a 2L acid cleaned polythene bottles and packed appropriately in well-insulated ice boxes filled with ice cubes. Water temperature was measured using a high quality standard mercury-filled Celcius thermometer (± 0.1°C accuracy). Salinity was recorded by using a high quality Salinometer (Model #85/10 FT, YSI Incorporated, Ohio, USA). pH were measured in the laboratory using a digital pH meter (Model No.LI-120 pH meter, Elico, India). Electrical conductivity of water (EC) was measured using conductivity meter. The samples for Dissolved Oxygen (DO) were fixed immediately in BOD bottles (300 ml) *in situ* following Winkler method (Strickland and Parsons, 1972). For analysis of biochemical oxygen demand (BOD) samples were collected in BOD bottles (300 ml) and kept in an ice box for transportation. After reaching the laboratory, the samples for BOD analysis was immediately measured by incubating samples in BOD incubator at 20°C for 5 days following APHA (2005). Parameters such as free carbon-dioxide (CO_2), chemical oxygen demand (COD), total hardness, total dissolved solids (TDS), total hardness, nitrate, nitrite, phosphate and sulfate were estimated following Grasshoff *et al.,* (1983) and APHA, (2005).

Statistical analysis

Physicochemical parameters of Veli-Akkulam and Vellayani Lakes for two years sampling period were analyzed for spatio-temporal variations. Temporal variations of water quality parameters were examined by pooling data on monthly basis for two years from all stations of Veli-Akkulam and Vellayani Lakes. Seasonal pooling of hydrographical observations was made based on the effect of southwest monsoon and treated seasonally as pre-monsoon, monsoon and post-monsoon respectively. Analysis of variance (ANOVA) for physicochemical parameters was performed with stations, seasons and water layers (surface-bottom) as factors using statistical package for the social science (SPSS) Version 20.

Multivariate techniques were employed to examine the spatio-temporal patterns and trends in complex water quality data so as to provide reliable information. It can also be used to identify water quality characteristics during different periods or ecoregions. Data of physicochemical parameters were subjected to four multivariate techniques: cluster analysis, MDS and principal component analysis using PRIMER software version 6 (Clarke and Gorley, 2006). Water quality data was first seasonally averaged in each station, variables were normalized to minimize variations between samples and resemblance matrix was also obtained. Comparisons between stations based on the measured environmental variables were performed using group cluster analysis. Cluster diagram was plotted based on Euclidean distance among samples. Similarity profile (SIMPROF) test was applied in conjunction with cluster analysis in order to differentiate significant variation statistically among samples. This method was really meant for clustering all stations in accordance with their similarities in relation to the set of water quality variables. Multidimensional scaling of similarity based on normalized Euclidian distances was also done to visualize the differences among stations. The variations in hydrographical parameters were also analyzed using PCA after the data had been seasonally averaged in each station and were further normalized. Correlation analyses of environmental variables were performed using Draft's man plot to find out the associations among the entire group of variables. The highest degree of correlation variables was selected and points were plotted from this correlation matrix using PCA after log transformation to check whether there was a quality gradient among the samples.

RESULTS AND DISCUSSION

Physicochemical parameters of lakes

Rainfall data showed wide fluctuations during the entire study period. From the year 2008 to 2010 the recorded seasonal precipitation was 287 mm during pre-monsoon, 1786 mm during monsoon and 1218 mm during post-monsoon. Seasonal data showed fluctuations with highest rainfall during monsoon season than the post-monsoon and pre-monsoon periods. In tropical water bodies monsoon represented the season of highest rainfall which brings characteristic changes in hydrological cycles. ANOVA showing significant differences in water quality parameters of Veli-Akkulam and Vellayani lake are given in Table 1. Water quality parameters compared with CPCB (2008) and US EPA (2001) standards of inland surface water quality are presented in Table 2.

Water temperature during the study period ranged between 24°C to 33.5°C. In Veli-Akkulam lake surface water temperatures varied from 26°C to 30.75°C with highest value recorded at station 2 during pre-monsoon season and lowest at station 4 during post-monsoon. Similarly bottom water temperatures varied from 27.15°C to 29.9°C at station 2 with highest value recorded during pre-monsoon and lowest during monsoon season. In reference Vellayani lake, the surface water temperatures varied from 29.5°C to 31.28°C and bottom water temperature ranged between 28.64°C to 31.09°C respectively. The highest warm temperature during pre-monsoon months may be due to the clear sky and more solar radiation (Jagadeesan *et al.,* 2011; Verma *et al.,* 2012). The lowest temperatures recorded during post-monsoon at station 4 could be attributed to the cooling effect created by dense growth of macrophytes vegetation along the banks and heavy precipitation. Significant seasonal and spatial

Table 1: ANOVA of water quality parameters of Veli-Akkulam and Vellayani Lakes at significant level (p-value <0.05)

	Max	Min	Stations		Seasons		Surface-bottom	
			F value	p value	F value	p value	F value	p value
Temperature (C°)	24	33	13.730	0.000	14.253	0.000	9.951	0.002
pH	6.01	8.87	5.437	0.000	14.702	0.000	0.004	0.949
Salinity (‰)	0.5	35	51.304	0.000	35.013	0.000	1.632	0.202
Conductivity (µS/cm)	24	45967	26.557	0.000	13.808	0.000	0.049	0.825
Dissolved Oxygen (mg/L)	0.03	8.16	438.538	0.000	11.490	0.000	5.940	0.015
TDS (mg/L)	65.9	7900	40.76	0.000	8.841	0.000	0.102	0.750
Hardness (mg/L)	24	6425	16.72	0.000	6.420	0.002	0.196	0.658
Free CO_2 (mg/L)	1.28	77	77.39	0.000	25.29	0.000	2.970	0.086
Nitrate (mg/L)	0.6	32	5.92	0.000	3.703	0.026	0.011	0.915
Nitrite (mg/L)	0.01	4.5	3.29	0.004	3.353	0.036	0.472	0.493
Phosphate (mg/L)	0.01	9.61	50.96	0.000	18.53	0.000	0.012	0.914
Sulphate (mg/L)	0.1	77.34	24.94	0.000	8.990	0.000	0.001	0.975
BOD (mg/L)	1.24	36.85	43.85	0.000	0.926	0.399	0.000	0.000
COD (mg/L)	3.82	96.5	106.43	0.000	22.23	0.000	0.000	0.000

variations of temperature were noticed across stations of Veli-Akkulam and Vellayani lakes ($p<0.05$).

In the study lake, salinity distribution is of mixohaline nature, showing a clear stratification with bottom waters showed higher salinity than the surface waters. In Veli-Akkulam lake maximum surface and bottom water salinity was recorded at station 1 (16.7 ppt and 26.8 ppt) that is due to saline water intrusion brought about by opening of bar mouth during monsoon season. The lowest values in surface and bottom waters were observed at station 6 (0.99 ppt and 0.88 ppt) that was due to the freshwater influx from adjacent Kannammoola canal. Clear density stratification in salinity distribution was noticed throughout the study period progressively in the marine zone of Veli lake due to salt water intrusion and the finding agrees with the studies reported in Ashtamudi Lake by Sujatha *et al.,* (2009). Vellayani lake showed very narrow range of salinity throughout the investigation revealing significant seasonal and spatial scale variations ($p<0.05$).

The pH varied from 6.01 to 8.87, pH in surface waters was maximum at station 3 (7.53) during pre-monsoon and minimum at station 1 (6.80) during monsoon. pH at station 3 remained alkaline throughout the study period may be due to the continuous discharges of sewages which brought in through the Parvathy Puthen Ar river. High pH due to the discharges of silt, clay and agricultural waste towards the mouth of Khordak River into Loktak Lake was reported by Sharma *et al.,* (2013). pH has direct and indirect effects on water chemistry and the biota of aquatic ecosystems and even short term reduction in pH can create lethal condition to biota (Wetzel 2001; Dodds and Whites 2010). Bottom waters showed maximum mean pH at station 2 (7.48) during pre-monsoon and minimum at station 1 (6.42) during monsoon season. In lake ecosystems anthropogenic activities can cause considerable short-term fluctuations in pH level. Very low values observed at station 1, Veli Bar mouth during monsoon season may be due to heavy precipitation, saline water intrusion and industrial effluent runoff. In reference lake pH varied from 6.79 to 7.06, the higher values were observed in surface waters than the bottom. pH showed significant spatial and seasonal variations throughout the study period ($p<0.05$).

Dissolved oxygen content plays an important role in maintaining ecological stability and integrity. Wetzel and Likens (2000) opined that oxygen is an important parameter of lakes and reservoirs, which is essential for metabolic activities of all aquatic organisms and is utilized by inorganic chemical reactions in water. Dissolved oxygen concentrations ranged from 0.03 mg/L to 8.16 mg/L during the study period. In Veli-Akkulam lake maximum mean surface and bottom water DO were observed at station 1 (3.97 mg/L and 3.65 mg/L) during monsoon that was due to increased precipitation as well as the breaching of sand bar due to increased flooding of freshwaters from canals and rivers. There showed a drastic decline of DO at station 5 and station 6 (0.25 mg/L and 0.078 mg/L) that was due to heavy eutrophication, sedimentation and pollution due to the discharges of hospital wastes, sewages, domestic wastes etc. Degraded water quality leads to severe

Table 2: Comparison of water quality parameters of Veli-Akkulam and Vellayani lakes with standards of CPCB and US EPA inland surface water quality classification

Parameters	CPCB, (2008)					CPCB standards of effluent discharge	US EPA, (2001)	Veli-Akkulam Lake (study lake)	Vellayani Lake (reference lake)
	Class A	Class B	Class C	Class D	Class E				
pH	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	5.5-9.0	5.5-9.0	6.01-8.87	6.79-7.06
Dissolved Oxygen (mg/L), min.	6	5	4	4	--	--	5	0.08-3.97	7.648-7.15
BOD (5-days at 20° C, mg/L, min.	2	3	3	--	--	30	3	5.01-25.78	1.57-2.91
COD mg/L, max.	--	--	--	--	--	250	40	23.01-71.14	5.35-5.58
Total Dissolved Solids, mg/L, max.	500	--	1500	--	2100	--	--	304-4195	84.66-100.28
Total Hardness (as $CaCo_3$), mg/L, max.	300	--	--	--	--	--	200	78.40-2166	27.20-40.13
Nitrate-Nitrogen, mg/L	20	--	50	--	--	10	50	16-32	1.2-0.72
Nitrite-Nitrogen, mg/L	--	--	--	--	--	0.03	0.03	0.12-0.79	0.024-0.082
Dissolved Phosphates (as P), mg/L, max	--	--	--	--	--	5	0.5-0.7	0.5-5.9	0.04-0.2
Sulphates (as SO_4), mg/L, max.	400	--	400	--	1000	--	200	2.06-27.8	0.27-1.53
Electrical Conductance at 25° C, µS/cm	--	--	--	1000	2250	--	1000	47-20656	116-146
Free Carbon dioxide (as CO), mg/L, max.	--	--	--	6	--	--	--	6.64-51.80	3.80-4.4

oxygen depletion, indicates heavy eutrophication (Rabalais *et al.,* 2009). In comparative station 7 surface and bottom water DO varied from 7.648 mg/L and 7.147 mg/L respectively. DO showed significant seasonal and spatial scale variations ($p<0.05$) among stations of Veli-Akkulam and Vellayani Lakes. The required standard DO for inland surface water is >5 mg/L (USEPA, 2001) and for propagation of wild life and fisheries is 4 mg/L (CPCB, 2008). DO level in Veli-Akkulam lake was below these standard limits, indicated severe oxygen depletion and bad water quality conditions of the lake.

Total Dissolved Solids (TDS) varied from 65.90 mg/L to 7900 mg/L, showed significant spatial and seasonal variations ($p<0.05$) among the stations of Veli-Akkulam and Vellayani Lakes. The highest mean surface and bottom water TDS were reached in downstream station 1 (3363.4 mg/L and 4195 mg/L) during monsoon and lowest surface and bottom water TDS were observed in upstream station 5 (335.4 mg/L) and station 6 (304.60 mg/L). Highest TDS at downstream stations of Veli lake was due to the opening of bar mouth due to heavy precipitation, bringing solid wastes and effluents from industries (Titanium factory and English Indian Clays Ltd), land runoff, organic decomposition and pollution. In the present investigation TDS value of the study lake was beyond the permissible limits (500-2100 mg/L) of CPCB (2008) indicating degraded water quality conditions while in comparative station at Vellayani Lake, TDS ranged between 84.66 mg/L to 100.28 mg/L were within the standard limits, indicating good surface water quality.

Electrical conductivity during the study period ranged between 24 µs/cm and 45967 µs/cm. The highest surface and bottom EC values were recorded at station 1 (15509.5 µs/cm and 20656.31 µs/cm) during the monsoon season and lowest values were observed at station 6 (48 µs/cm and 47 µs/cm) during the same season. An important aspect of having high conductivity at station 1 was due to the intrusion of salinity in marine zones that was brought about by the monsoon rains. Very lowest seasonal conductivity values at station 6 during monsoon revealed heavy precipitations, flooding due to freshwater ingress and land drainage. In Vellayani Lake EC values ranged between 116.48 µs/cm to 146.87 µs/cm respectively. Spatial and seasonal trend in EC showed marked significant variations among stations of Veli-Akkulam and Vellayani Lakes ($p<0.05$). Inland surface water criteria for EC are 1000 µS/cm (USEPA 2001) and 1000-

2250 µS/cm (CPCB 2008). Here, the maximum values observed at Veli Lake stations 1, 2 and 3 were beyond the safe standard limits of USEPA whereas in Vellayani lake EC values were within the desired specified limit of CPCB and USEPA standards indicated its good condition.

Total hardness varied from 24 mg/L to 6425 mg/L, with highest mean values recorded at station 1 during monsoon (2166 mg/L and 2152.7 mg/L). Maximum effect of hardness at station 1 in both surface and bottom waters may be due to ingress of salinity as well as heavy loading of industrial effluents containing toxic elements particularly heavy metals. Lowest mean surface and bottom hardness was recorded at station 6 during post-monsoon (78.81 mg/L and 78.40 mg/L) ensured its freshwater influence and low saline condition. Jain *et al.* (2002) opined that the main reason of increased level of hardness in freshwater is mainly due to anthropogenic influence. In reference lake, total hardness values ranged from 27.20 mg/L to 40.13 mg/L, showing significant spatial variations across all stations of Veli-Akkulam Lake ($p<0.05$). The highest hardness recorded at Veli downstream stations were beyond the proclaimed inland surface water quality standards of 200 mg/L (USEPA 2001) and 300 mg/L (CPCB 2008), indicating influence of saline water intrusion and inorganic chemical inputs from adjacent industries.

Free CO_2 in water ranged from 1.28 mg/L to 77 mg/L respectively. Maximum mean surface and bottom free CO_2 in Veli-Akkulam was recorded at station 6 during pre-monsoon period (50.50 mg/L and 51.80 mg/L) that was due to severe pollution load, oxygen depletion, eutrophication, decomposition, evaporation and sedimentation in Akkulam Lake. Minimum mean surface (6.64 mg/L) and bottom (7.46 mg/L) values in Veli-Akkulam were recorded during monsoon period at downstream station 1. In Vellayani Lake (reference station), free CO_2 varied from 3.80 mg/L to 4.4 mg/L and these were within the standard limits of inland surface water quality of 6 mg/L (CPCB 2008). But in Veli-Akkulam free CO_2 values recorded were beyond the standard limits indicating severe organic pollution.

BOD during the study period ranged from 1.24 mg/L (station 7) to 36.85 mg/L (station 5) respectively, with highest mean surface value was recorded at station 6 (25.78 mg/L) and the lowest value at station 1 (5.01 mg/L) during pre-monsoon periods. In Veli-Akkulam Lake BOD values were beyond the permissible standard limits (3 mg/L) of USEPA (2001). But at the reference lake, the values were found to be very low and it ranged from 1.57 mg/L to 2.91 mg/L. Generally BOD values above 5 mg/L in a water body are considered polluted and these could be used as a direct measurement of the state of pollution (Tijani *et al.,* 2005). A general rise in BOD was critically observed during Veli-Akkulam Lake, which had severely been hampered by pollution due to the dumping of sewages, hospital wastes, agricultural wastes and eutrophication. Very high BOD as a result of absorption of pollutants by aquatic flora was reported at Bellandur Lake (Chandrasekhar *et al.,* 2003).

COD ranged from 3.82 mg/L to 96.50 mg/L, showing highest mean values at station 6 (71.139 mg/L) during monsoon and lowest values at station 1 (23.01 mg/L) during post-monsoon season. High COD in Veli-Akkulam Lake indicates siltation, sedimentation, organic matter fortification as well as anthropogenic sources of pollution. In reference lake COD values varied from 5.35 mg/L to 5.58 mg/L, revealed significant spatial and seasonal variations with Veli-Akkulam Lake ($p<0.05$). In Veli-Akkulam Lake COD values recorded were beyond the standard permissible limits of USEPA (40 mg/L), indicated highly polluted condition of the lake.

The nutrient nitrate ranged from 0.65 mg/L and 32.7 mg/L respectively, showing maximum mean surface nitrate concentration recorded at station 6 (32.15 mg/L) during monsoon season. The presence of high nitrate content during monsoon was due to influx of nitrogen rich flood water discharged from Kannamoola canal containing sewage wastes, agricultural fertilizers and surrounding leachates that variably resulted in the formation of algal blooms (Verma *et al.,* 2012). But highest bottom concentration observed at station 2 (32.13 mg/L) was due to nitrate enrichment as a result of the regeneration from sediment or through organic matter decomposition. Nitrate content of Vellayani Lake varied from 1.2 mg/L and 0.72 mg/L and showed well-marked significant spatial and seasonal variations with Veli-Akkulam Lake ($p<0.05$).

Nitrite concentrations ranged from 0.01 mg/L to 4.50 mg/L, the higher mean values at surface and bottom waters were reached at station 4 (0.446 µg/ml) and station 2 (0.793 µg/ml) during monsoon and lowest values were recorded at station 3 (0.119 µg/ml and 0.142 µg/ml) during pre-monsoon. Excess nitrogen in aquatic habitats can lead to eutrophication and levels of ammonia, nitrite and nitrate are toxic to all biotic components (Carpenter *et al.,* 1998; Marco *et al.,* 1999). In comparative station (Vellayani Lake) nitrite concentrations at both surface and bottom waters varied from 0.024 µg/ml to 0.082 µg/ml respectively, represented significant seasonal and spatial variations ($p<0.05$) among all other stations of Veli-Akkulam Lake. Inland surface water quality standard concentration for nitrite is 0.03 mg/L according to USEPA, (2001) and CPCB, (2008). The excessive nutrient load of phosphate is considered as one of the key factors causing eutrophication, which nourishes algal growth causing major threats to aquatic life (Andersen *et al.,* 2004; Fang *et al.,* 2004; Smith 2006, Rabalais *et al.,* 2009). Phosphate content during the present investigation varied from 0.01 mg/L to 9.61 mg/L, showed wide fluctuations throughout, with highest mean phosphate in station 5 (5.88 mg/L and 5.45 mg/L) during monsoon in both surface and bottom waters that attributed to heavy sewage loads, discharges of agricultural wastes, hospital wastes and eutrophication in Veli-Akkulam lake. Maximum concentration of phosphate during rainy seasons may be due to surface runoff carrying large amounts of domestic sewage, cattle dung and detergents from the surrounding catchment area (Verma *et al.,* 2012). Phosphate showed significant seasonal and spatial variations among stations of Veli-Akkulam and Vellayani Lakes ($p<0.05$). The highest phosphate values recorded at Veli-Akkulam Lake were beyond the safe limits of inland surface water standards of USEPA (0.5-0.7 mg/L) and CPCB (5 mg/L), indicated severe eutrophication whereas in Vellayani Lake, surface and bottom phosphate varied from 0.04 mg/L to 0.2 mg/L, revealed accepted water quality standards. Sulphate ranged from 0.10 mg/L to 77.34 mg/L, with highest mean surface and bottom water sulphate content were observed at station 1 (26.6 mg/L and 27.8 mg/L) and lowest at station 6 (2.06 mg/L and 2.42 mg/L). Sulphate concentration was maximum towards the lower reaches of the Veli Lake that could be due to the influx of sea water discharging industrial water supplies containing sulphur compounds. Sulphate content varied from 0.27 mg/L to 1.53 mg/L at Vellayani Lake, and the values indicated significant seasonal and spatial variations among stations of Veli-Akkulam Lake ($p<0.05$).

Multivariate statistical analysis

Cluster analysis was performed to find out similar groups between sampling sites during three different seasons based on water quality features. Cluster analysis estimated the water quality characteristics for all the six stations of Veli-Akkulam Lake and reference Vellayani Lake (Fig. 2). Cluster analysis

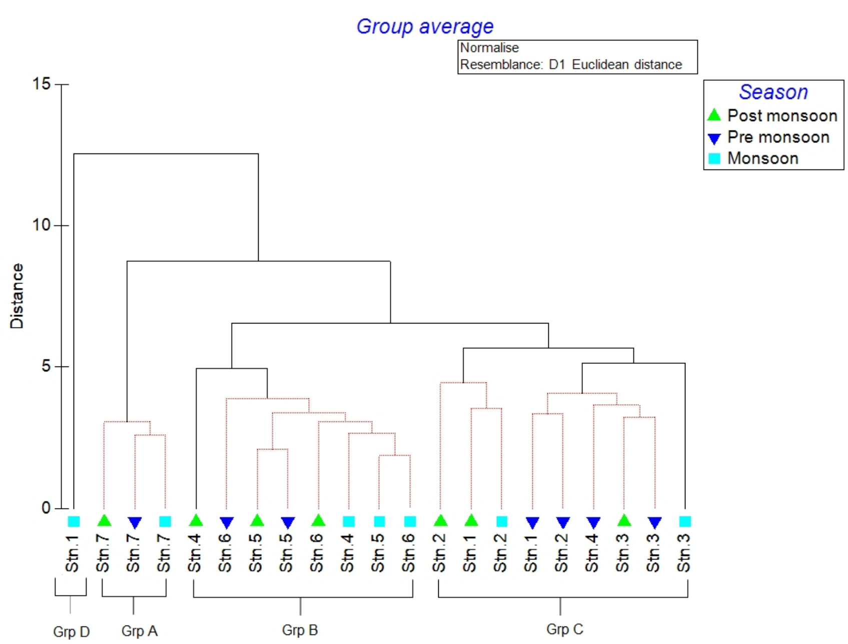

Fig. 2: Cluster dendrogram shows resemblance matrix based on normalized Euclidean distance among stations of Veli-Akkulam and Vellayani Lakes

generated dendrograms of sampling sites into five distinct groups based on the Euclidean distance. In cluster plot red dashed lines indicate no significant difference between sampling sites (SIMPROF, p=>0.05) and solid black lines indicate significant differences (SIMPROF, p=<0.05) after SIMPROF permutation test. Group A included station 7, the comparative study lake forming three branches with seasons; pre-monsoon, monsoon and post-monsoon, showing no significant differences statistically (SIMPROF, p>0.05). Group B with eight significant substructures considered as two groups, group B1 and group B2. Group B1 included station 4 during post-monsoon which shows significant difference with other stations formed by group B2. Group B2 included station 4 (monsoon), station 5 (pre-monsoon, monsoon and post-monsoon), station 6 (pre-monsoon, monsoon and post-monsoon), showing no significant differences during these seasons (SIMPROF, p<0.05). Group C included sub-groups such as group C1, group C2 and group C3 with nine branches. Group C1 included station 1 and station 2, showed no significant differences among them (SIMPROF, p>0.05). Group C2 included stations 1, 2, 3 and 4, showing no significant differences among them (SIMPROF, p>0.05). Group C3 comprised of station 3 which was statistically differed from other groups during monsoon season (SIMPROF, p<0.05). Group D included station 1 which showed no significant difference from all other stations during monsoon season (SIMPROF, p<0.05).

Cluster analysis offers reliable classification of the whole lake surface water quality based on the similarity relationships within sample groups and between sample groups in order to deliver overall sampling strategies (Singh *et al.,* 2004; Wang *et al.,* 2006; Salah *et al.,* 2012). Cluster grouping of Veli-Akkulam and Vellayani Lakes indicated that Vellayani Lake formed a separate cluster during all the three seasons. Group A, reference site was influenced by seasonal variations in water quality being associated with high concentration of nutrients through freshwater runoff from streams. Veli-Akkulam Lake showed three distinct groups namely Group B, C and D. In this cluster analysis it was clear that Veli-Akkulam Lake exhibited two distinct zones such as an upstream and downstream, revealed seasonal variations in water quality characteristics. However, station 4 acted as a transition zone flanked by them. Stations included in cluster B were exhibited mostly in all the three seasons, where station 4 is relatively free of tides and the pollutants incoming from both the tidal inlets of Veli bar mouth and the Akkulam Kannammoola canal reach the station making a domain of transitional environment with fluctuating water quality. Moreover upstream stations 4, 5, 6 are seriously affected by pollution due to sewage from Municipal Corporation, heavy industrial waste discharges, agricultural runoff, hospital wastes from nearby hospitals and clay washings from the clay factory, severe eutrophication and sedimentation.

Non-metric MDS was done to illustrate spatial pattern of similarity or differences between samples as well as to identify the parameters which were more influenced at stations during the study period (Fig. 3). MDS plot clearly distinguished four groups as in the cluster diagram approximately at 60% similarity between stations during different seasons. Station 7 (Group A) of MDS is formed by Vellayani Lake which is separated as a distinct unit in the MDS plot, showing 60% similarity among seasons; pre-monsoon, monsoon and post-monsoon. In Veli-Akkulam Lake the upstream stations 4, 5 and 6 formed by Group B shows 60% similarity during all the three seasons. Here, station 4 shows more similarity with upstream stations 5 and 6 during monsoon as well as with downstream stations 2 and 3 during pre-monsoon periods. Thus it acts as a transitional zone sharing water quality characteristics of both zones of the Veli-Akkulam Lake. Even though station 1 (Group D) stood separately from other stations during monsoon; it shares greater level of similarity (60%) with downstream stations 1, 2, 3 of Veli-Akkulam Lake. From this it is obvious that Veli-Akkulam Lake is drastically affected by recurring pollution caused by agricultural inputs, industrial waste run off, sewages, activities due to dredging, eutrophication and sedimentation.

Principal component analysis was performed on the normalized data sets (14 variables) separately for the four different regions as delineated by cluster diagram so as to compare the compositional pattern between analyzed water samples as well as to identify the factors influencing each one. The results of PCA are shown in Fig. 4. PCA rendered a total of five principal components (PCs), in which first two PCs were extracted (with Eigen value >1 is considered significant) thus, contributed cumulatively 75% of variability in overall distribution of water quality characteristics during the study period. The other components eliminated have less important role in the qualitative changes of water among stations.

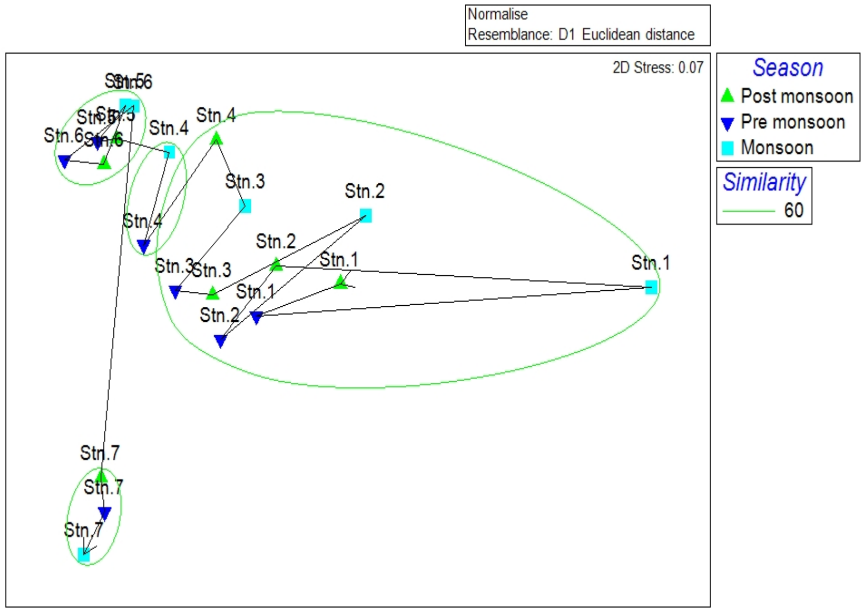

Fig. 3: MDS plot illustrates seasonal percentage similarity of sampling stations based on Euclidean cluster plot

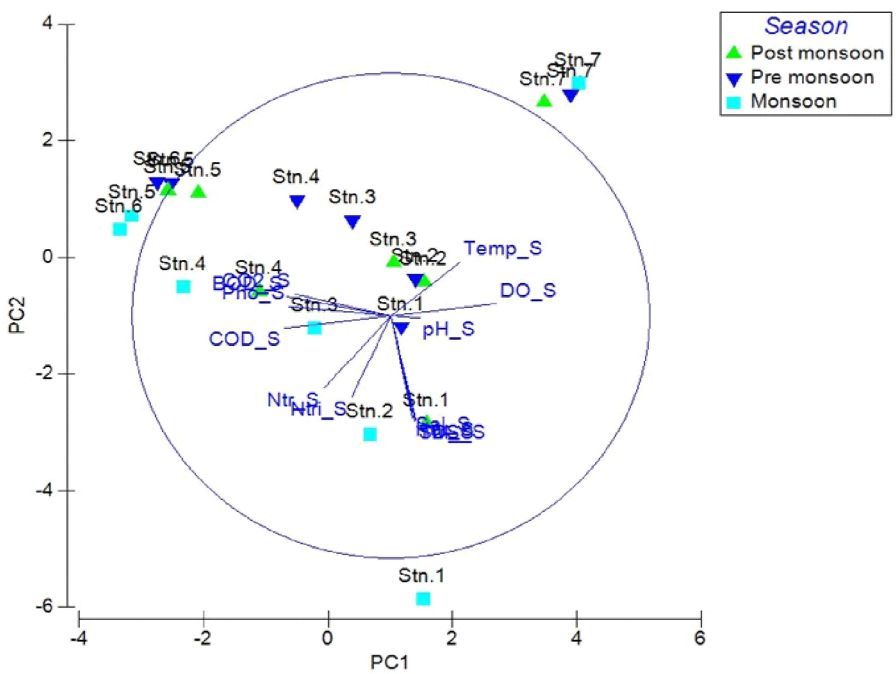

Fig. 4: PCA plot of water quality parameters of Veli-Akkulam and Vellayani Lake

Stations close together in the plot represent their similarities and Eigen vectors of hydrographical parameters indicate their contribution to the station assemblage pattern.

PC1 (principal component axis 1), accounts for 41.8% of total variances, has strong positive loadings of DO and temperature along with negative loadings of free CO_2, BOD, COD and phosphate. Additionally PC1 has strong principal component score at station 7, as it stands separate in the plot, its loading with PC1, is very high during all the three seasons. Here, the results reveal that seasonal variation in DO and temperature may be responsible for determining water quality characteristics at station 7. It's correlation with other parameters is very negligible as it is seen from the loadings plot. PC1 also showed negative principal scores at station 4 (monsoon), station 5 and 6 (pre-monsoon, monsoon and post-monsoon). PC2 explains 33.6% of total variance, has positive loadings of variables such as temperature and negative loading of variables like salinity, TDS, total hardness, sulphate, nitrate, and nitrite. PC2 has strong positive principal component scores at station 7 (pre-monsoon, monsoon and post-monsoon) and has negative principal component scores at stations 1 (monsoon and post-monsoon) and station 2 (monsoon).

Based on the above observations it was obvious that the reference lake Vellayani was very distinct in water quality conditions from Veli-Akkulam Lake that was attributed to large extent of variable environmental conditions. Here, station 7 is determined by the parameters DO and temperature. The influence of parameters such as free CO_2, BOD, COD and phosphate at stations 5 and 6 indicate heavy pollution coupled with eutrophication and oxygen depletion. These stations 5 and 6 were affected by anthropogenic wastes from agricultural drainages, wastes from urban and industrial units, hospital wastes discharges, tourism activities such as boating etc. The quality of water in lakes can be affected by the wastes from agricultural drainage, urban and industrial units and sewage treatment plants (Fataei 2011; Zali *et al.,* 2011). Despite the fact that these stations are located near to the hospital zone and affected by pollutants from the hospitals, results indicate that these sections of the lake are also polluted due to other sources such as municipal solid wastes from the entire Thiruvananthapuram city and activities of dredging. Likewise the influence of variables like salinity, TDS, total hardness, sulphate, nitrate and nitrite at stations 1 and 2 clearly indicated the brackishwater characteristics of Veli-Akkulam Lake, with high replenishment of nutrients and salinity intrusion when saline water mixed with freshwater by the opening of sand bar during monsoon.

Multivariate approaches such as cluster, MDS and PCA provided valuable information regarding the spatio-temporal trends in water quality. The physicochemical parameters between Veli-Akkulam and Vellayani Lakes varied significantly both spatially and temporally. In the present investigation cluster analysis and MDS revealed three distinct hydrographical features in Veli-Akkulam Lake as an upstream, downstream and a transitional zone with reference to Vellayani Lake. In these analyses it was clear that station 4 (Akkulam) differed significantly from other upstream stations during post-monsoon as it is seriously affected by pollution due to industrial, municipal, hospital wastes and eutrophication. Station 3 differed significantly from other downstream stations of Veli Lake due to the ingress of freshwater from Parvathy Puthen Ar and Channankara canal, which drains into this area, creating an overall change in water quality characteristics during monsoon period. Station 1 (Veli Bar mouth) was distinctly separated from other stations of Veli-Akkulam Lake that was due to sea water intrusion as a result of the opening of bar mouth during monsoon season and acted as an ecotone. PCA technique was useful to figure out the principal factors influenced on all the stations. In this analysis it was obvious that hydrographical variables such as DO concentration and moderate range of temperature determined the pristine water quality conditions at Vellayani Lake whereas parameters like BOD, COD, free CO_2 and phosphate established the deteriorated water quality conditions at Veli-Akkulam Lake.

Besides, majority of core physicochemical parameters of Veli-Akkulam Lake were beyond the permissible standard limits of inland surface water quality criteria of USEPA and CPCB. Parameters such as pH, EC, free carbon-dioxide, total hardness, TDS, nitrite and phosphate were beyond the safe limits prescribed by USEPA and CPCB standards at Veli-Akkulam Lake. Dissolved oxygen levels at stations 4, 5, 6 were highly depleted indicating anoxic condition at these stations. In Veli-Akkulam Lake BOD and COD were beyond the acceptable standard limits of CPCB and USEPA particularly at stations 4, 5 and 6, indicating severe organic pollution. However, in the reference Vellayani Lake water quality parameters recorded were within the proclaimed standard limits of inland surface water quality revealing its pristine water quality conditions.

CONCLUSION

In this present investigation different reliable multivariate statistical techniques could successfully evaluate the health status of Veli-Akkulam Lake by comparing with a regional reference lake Vellayani. Cluster analysis, MDS and PCA exhibited similar trends regarding the spatial and temporal aspects of water quality. Parameters measured over the entire period of study since 2008 to 2010, rendered a clear distinction in the quality of water as a downstream Veli zone (stations 1, 2, 3), an upstream Akkulam zone (stations 5 and 6), an intermediate transitional zone (station 4). In comparative Vellayani Lake the water quality parameters recorded were within the international standard limits indicating lesser polluted and pristine nature. Veli north western part is being exposed to industrial wastes from Titanium industry, urban waste water, agricultural runoff, tourism activities and Akkulam eastern part is being influenced by sewage wastes, hospital wastes from KIMS hospital as well as dredging and eutrophication. The main characteristic feature of the transitional zone (station 4) at Akkulam was that of their relatively free tidal actions and sedimentation brought about by the pollutants entering from both the tidal inlets of Veli bar mouth and the Akkulam Kannammoola canal reach this station making a domain of transitional environment with fluctuating water quality. PCA rendered the factors which influenced the variation in water quality conditions. From PCA results, it can be concluded that the parameters such as BOD, COD, free CO_2 and phosphate at Veli-Akkulam Lake stations 3, 4, 5, 6 indicated drastic deterioration of the quality of water. But stations 1 and 2 (Veli segment) were greatly affected by saline water intrusion, accumulation of industrial wastes, land drainages and tourism wastes; here water quality is being mostly influenced by changes in salinity, TDS, total hardness, EC and sulphate. In PCA Vellayani Lake exists as a freshwater lake where parameters DO and temperature were greatly determined its quality. Moreover this lucustrine freshwater reservoir with its many small converging tributaries and canals which contribute the major source of oxygen in this water body, carrying free flow of freshwater with negligible eutrophication and pollution. This evaluation provided an authentic picture of the quality of Veli-Akkulam Lake and helped to draw a benchmark picture regarding the degree of pollution and its effects by comparing with a standard reference condition at Vellayani Lake. This work could establish the effectiveness of multivariate statistical techniques for the analysis and interpretation of compound data sets and enabled effective monitoring and assessment of water quality in order to mitigate pollution and its effects through proper management of lake ecosystems.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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