Chapter 1

INTRODUCTION

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The Vembanad Lake is the largest wetland ecosystem in Kerala and the second largest in India. This backwater system is located on the southwest coast of India and forms part of the Vembanad-Kol wetland system; Ramsar Site No 1214. It extends from Azheekode in the north to Alappuzha in the south, a length of about 96 km and width varying between a few hundred meters to about 8 km. The Vembanad region of the wetland has an area of about 1512 sq. km spread into three districts, viz. Emakulam, Kottayam and Alappuzha. The lake has an approximate area of 233 sq. km. The western side of the lake is bordered by a narrow strip of land separating it from the Arabian Sea. The lake is narrow and sinuous in the north while much broader in the south with two openings to the sea; one at Cochin and the other at Munambam.\(^1\)

The lake consists of a dominant freshwater southern zone and the dominant salt water northern zone. The northern zone is usually referred to as the Cochin backwaters and the southern zone as the Vembanad Lake. The drainage basins can be divided into three zones: the highlands, the middle reaches, and the lowlands. The wetland system is fed by seven rivers, originating from the Western Ghats and joining the Arabian Sea. The major rivers that join the wetland are Chalakkudi, Periyar, Muvattupuzha, Meenachil, Manimala, Pamba and Achenkovil. The lake surrounds the islands of Pathiramanal, Perumbalam and Pallippuram. The Cochin port is located at the lake's outlet to the Sea.

The origin of the lake is closely related to the evolution of the coastal plains of Kerala. The numerous rivers flowing to the Arabian Sea with its large load of sediments created numerous spits and offshore bars in the nearshore regions and the body of the water behind these formed the nuclei of the present day lagoons or estuaries. There are about 34 major lagoons or estuaries in Kerala, out of which the biggest one is the Vembanad estuary.\(^2\)
The lake is ecologically significant due to its mangrove patches and habitat for resident and seasonal migratory birds. The Kumarakom bird sanctuary is a haunt of rare migratory birds from different parts of the world. The lake harbors a rich resource of live clam and sub-fossil deposits. The estuarine system plays an important role in the life cycle of many shrimps and the entire wetland acts as a nursery for important fish varieties. Many species of fish depend on this wetland for food, spawning and nursery.

The Vembanad Lake and the connected backwater system exert considerable influence on the socioeconomics of the surrounding area. A large proportion of the 1.6 million people living on the banks of the lake depend on this wetland ecosystem for their livelihoods. Major livelihood activities include agriculture, fishing, tourism, inland navigation, coconut-husk retting, lime-shell collection, shrimp farming and sediment mining. Apart from all this, the importance of the lake for the local transport of people and goods is considerable.

Kuttanad, popularly known as the “Holland of Kerala”, is the low-lying area surrounding the Vembanad Lake on the eastern and southern sides. The Kayal lands of Kuttanad are extensive areas of the lake reclaimed and protected by dikes for paddy cultivation. This is perhaps the only region in the world where farming is done 1.5m to 2.5m below sea level. Inland waterways that flow above land level is an amazing feature of the region.

The Vembanad wetland is especially noted for its aesthetic value. Alappuzha, Kumarakom and Pathiramanal are important destinations attracting thousands of tourists every year. Punnamada near Alappuzha is famous for its boat race. House boats with all modern and traditional facilities are another major tourist attraction. The picturesque Vembanad Lake, the simmering waterways, sprawling paddy fields, lush green vegetation, and serene atmosphere attracts tourists from all over the world.
1.1.1 Thanneermukkom Barrage

The Thanneermukkom barrage is a regulator-cum-bridge constructed at Thanneermukkom near Cherthala, the narrowest point of Vembanad Lake, to prevent the incursion of seawater into the paddy fields of Kuttanad.\(^3\) It also controls the flow of the four rivers, viz. Pamba, Achankovil, Manimala and Meenachil which debouch into the southern region of the lake. The barrage has 93 vent ways, each 12.2m wide and 5.5m high. The sill is at an elevation of 4.28m below mean sea level. The shutters of the barrier are kept open during monsoon to let out flood water and closed during December when tides bring in seawater from the north.

The commissioning of the barrage in the year 1976 has converted the lake into two entirely different ecosystems, retaining estuarine conditions in the northern sector (the downstream region from Cochin to Thanneermukkom) and transforming the southern sector (the upstream region from Thanneermukkom to Alappuzha) into a predominantly freshwater zone. Restricted flow and prevention of natural flushing of the lake and the adjacent waterways by tides have led to stagnation of water which causes severe pollution.

After the commissioning of the barrier, a total change in the distribution of salinity has taken place in the lake.\(^4\) This has resulted in many negative ecological impacts in the wetland system. They include deterioration of water quality, destruction of fishery and shell life, proliferation of weeds, and increased morbidity due to stomach and skin diseases.\(^5\) The Vembanad area virtually turns into a cesspool due to the absence of tidal flushing during the period when the regulator is kept closed. The prevention of salinity intrusion has resulted in the choking of the lake by water weeds such as Salvinia (Salvinia auriculata) with local name ‘African Payal’ and Water Hyacinth (Eichhornia crassipes) with local name ‘Pola’, which has adversely affected water quality and water transport.
me obstruction caused to me natural now of water Has led to the deposition of soil and other wastes in the lake bed, raising its level and lowering the water-holding capacity. Every year, about 90,000 tones of silt gets deposited in the lake. The average depth of the lake has been reduced from 6.7m to 4.4m between the years 1920 and 1980.6

1.1.2 Lake pollution

The Vembanad Lake is eutrophic; shallow with silky bottom and having sufficient nutrients supporting large population of plants and animals. The lake receives huge quantities of mineral nutrients, industrial wastes, pesticides, organic wastes, land and agricultural runoff and excreta and exudates of animals and humans. These provide plenty of phosphates and nitrates etc which lead to eutrophication. Pollution of the lake has reached alarming levels in recent years.

Population explosion and urbanization are posing serious threats to backwaters. It is estimated that the area of the lake has shrunk from 230sq. km in 1968 to about 179sq. km today. The backwater area is only one third of its size in the beginning of the twentieth century. Shrinkage of water spread is caused by reclamation and utilization of lake area for various developmental activities. Out of 36,500ha of backwaters which existed till the middle of the nineteenth century, only about 23,750ha is remaining now as open waters.7

Backwater tourism is a major source of pollution in the lake. The mushrooming of hotels and resorts all around has adversely affected the scenic beauty of the lake. Waste materials are dumped directly into the lake. Pesticides and chemical fertilizers applied in the sprawling paddy fields of Kuttanad also reach the lake. Other sources of pollution include drainage and solid wastes from Alappuzha, Kumarakom and other towns, released directly into the lake.

Bacterial contamination of the lake is another major problem. Microbial pollution has special significance because of deleterious effects on human health. The bacterial
organisms to be looked for in natural waters are the coliforms, Escherichia coli, faecal streptococci, staphylococcus aureus, sulphite reducing anaerobes, pseudomonas aeruginosa, salmonella and shigella, vibrio cholera and yeast and mould. The presence of coliforms in water is the indication of faecal contamination of animal or human origin. The total number of coliform bacteria indicates the degree of pollution.

1.1.3 Water quality

Water quality is the physical, chemical and biological characteristics of water, characterized through methods of hydrometry. It determines the suitability of water for a particular purpose and also indicates the concentrations of substances in quantities above their natural background levels that could negatively affect plant and animal life. Water quality is a concern because water is a critical resource that is easily abused and polluted.

The fluvial dynamics of Vembanad Lake is influenced by the discharge from the perennial rivers flowing into it. The rapid deforestation taking place in the Western Ghats, where the rivers originate, has enhanced the silting of the lake. The lake has fresh water during Monsoon and Post-monsoon periods, when the Thanneermukkom bund was open and the waters were flowing towards north. During the dry season, though the bund was closed to prevent ingress of sea water into the lake, the waters were rendered brackish progressively over larger and larger areas and by the summer period, the entire spread of lake water became brackish.8

Water quality of the lake is deteriorating day by day. The lake acts as a sink for the rivers and as an effective aquifer for the dug wells in the neighbouring areas which supply drinking water to people. Pollution is the chief source of deterioration of water quality of the lake. Industrial effluents, municipal sewage, runoff from agricultural lands, tourism activity etc are the important factors that contribute to water pollution.
Proliferated growth of aquatic weeds is another major contributor to ecological problems in the lake. The weeds form thick mats over the water surface and cause depletion of dissolved oxygen. It also provides habitat and food for several harmful animals and vectors of water borne diseases.

1.1.4 Sodium Absorption Ratio

Sodium hazard is typically expressed as the sodium absorption ratio (SAR). Excess sodium in irrigation water, relative to calcium and magnesium or to total salt content, can affect soil structure, soil aeration, flow rate, permeability, infiltration, etc. SAR is a ratio of the sodium to the combination of calcium and magnesium in relation to known effects on soil dispersibility.

It is accepted that SAR and electrical conductivity of irrigation water can be assessed for the potential to cause dispersion in soil. Sandy soils are not affected by sodium but the plants growing on them may be affected. Loss of soil permeability commences as low as SAR 3 when the electrical conductivity is about the same from domestic wastewater. Internationally, SAR 6 is accepted as a level above which soil permeability and structural stability may be affected.

1.1.5 Water Quality Index

Water quality index is defined as a rating reflecting the composite influence of different water quality parameters on the overall quality of water. The main objective of WQI is to turn complex water quality data into information that is understandable by the public. WQI provides a single number that expresses overall water quality at a certain location and time, based on several water quality parameters. WQI has been regarded as one of the most effective ways to assess the quality of water and is communicated on the basis of calculated water quality indices.
Water quality index is a useful tool for the quick assessment of any water system. The estimated quantitative values of water quality parameters and their standards\textsuperscript{10,11} are used for the calculation of water quality indices. These indices differ from country to country but the concept is similar, where a few important parameters are selected and compounded to numerical rating of water quality.

1.1.6 Sediments

Sediments play an important role in aquatic systems. Bottom sediments regulate the fresh water ecosystem.\textsuperscript{12} Lakes perform the work of erosion and deposition just like sea, but on a lesser scale. Most of the lake floor is covered by organic and inorganic particulate deposits that are brought in by rivers and winds mixed with shells and skeletons of aquatic organisms. The rivers that join the lake in this region flow through the Precambrian formations in the upper reaches that supply dissolved and solid material during monsoon, by way of bed load as well as suspended load.

Much of the present knowledge on physicochemical and biogeochemical processes taking place within lakes originates from studies on the sediments. The bulk of the inorganic sediment is formed by the interaction of the atmosphere and the hydrosphere on the crust of the earth. Depending on the origin, sediments are classified as lithogenous, biogenous, hydrogenous and cosmogenous sediments.

Lithogenous sediment is primarily derived from the breakdown of silicate rock and carbonate shelves on the continents during weathering and soil formation. The most common biogenous sediments consist of calcite, which is the insoluble remains of bones, teeth or shells of aquatic organisms, often found in the sediment. Hydrogenous sediment is formed by chemical reactions occurring in water or within the sediment. Cosmogenous sediment is composed of particles and objects that fall into the earth from outer space.
Organic matter in sediments usually originates from atmospheric and revirine introduction of pollutants, industrial and domestic wastes, agricultural and mining runoff, accidental spillages, and decompositional debris from aquatic organisms. The organic molecules remain primarily as the controlling factor in aquatic environments. Organic molecules in aquatic sediments possess reactive functional groups to which inorganic cations such as heavy metals can be coordinated. In this manner aquatic sediments can take up metals. The exchange capacity of sediments depends on the organic component. The metal complexes and chelates thus formed could further coordinate inorganic anions such as sulphate, chloride and phosphate and could be easily attached or detached under redox conditions. In this manner the transport or the migration of nutritionally important anions such as phosphate is regulated in sediment.

The inorganic components in sediment behave as chromatographic substrates. Upon contact, the organic molecules could be preferentially adsorbed, fractionated, precipitated, eluted or desorbed. In this fashion simple inorganic and organic molecules introduced into the lake water could be adsorbed and released. Due to exchange reactions, heavy metal ions can also be liberated from sediments to lake waters. Thus the lake sediments act as a source of heavy metal ions.

Most trace elements and nutrients can exist in several forms that differ in toxicity and availability. Studies on sediments can provide information about their role as a reservoir and a source of nutrients and the sediment water exchange process. Since sediment is an important reservoir of trace contaminants, sediment chemistry gives a measure of water quality and potential pollutants.

1.1.7 Trace metals

The term “trace metal” is used to denote those metals that are distributed in the earth’s crust in very low concentrations. It includes iron, lead, copper, cadmium, nickel,
chromium, manganese, mercury and arsenic. These metals and their compounds are industrially important and find a variety of uses in all fields of human endeavour. Trace metals are a major category of globally distributed pollutants.

Contamination of the environment by toxic metals may arise in a number of ways. Metals are introduced into aquatic system as a result of the weathering of soils and rocks, and from a variety of human activities. Industrial waste disposal is a major route for metal contamination in aquatic ecosystems. Zinc, copper and lead are three of the most common heavy metals released from roadways. Heavy engineering and chemical industry coupled with increased vehicular traffic causes serious environmental pollution associated with metals.

The mechanisms by which trace elements are taken up by the sediments include adsorption to clays, metal oxides/hydroxides and organic matter, biological uptake and physical accumulation of metal enriched particulate material by sedimentation and entrainment. The indiscriminate use of agrochemicals and merciless dumping of heavy metals can cause acute and long-term side effects on living beings. The five major sources of heavy metals in inland waters are geological weathering, industrial processing of ores and minerals, use of metals and metal compounds, heavy metals in animal and human excretion and leaching of metals from garbage and soil waste dumps.

1.1.8 Chemometrics

Chemometrics is a multivariate mathematical and statistical approach to the analysis and interpretation of analytical data. These methods have been extensively used for the classification and comparison of environmental samples. They are useful in identifying factors that are combinations of measurable variables, illustrating groups or cluster associations among samples, assessing spatial distribution of environmental factors or perturbations and predicting a property of interest. They can also be used to discern
structure in a data set as a whole, even when individual measurements show only slight degrees of correlation.

Some of the methods used in chemometrics are basic statistical methods for the determination of mean, median, standard deviation, coefficient of variation, minimal and maximal values of measured parameters, Analysis of Variance (ANOVA), Correlation Coefficients, Linear Regression Analysis, Cluster Analysis (CA), Factor Analysis using Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA).

1.1.8.1 Analysis of Variance

One-way ANOVA gives an overall comparison of means and investigates whether the population means are likely to be same or different. When data is classified into groups according to only one characteristic or factor, it is called one-way classification and the corresponding ANOVA is called the one-way ANOVA or one-factor ANOVA. When data is classified according to two characteristics or factors, it is called two-way classified data and the corresponding ANOVA is called the two-way ANOVA or two-factor ANOVA.  

1.1.8.2 Correlation Analysis

Correlation analysis is conducted to measure the degree of association between two sets of quantitative data. The Pearson’s correlation coefficient $r$ gives the intensity of the linear relationship between the two variables.

1.1.8.3 Simple Linear Regression

Simple linear regression analysis is a statistical technique used to study the cause and effect relationship between one dependent variable (response) and one independent (predictor) variable. It provides a mathematical model relating to the response variable which is often called the effect with different explanatory variables called the factors or causes. In the bivariate regression model, linear regression (LR) equations of the type

$$y = c + mx + s$$
where, $c$ is the slope, $m$ is the intercept and $s$ is the random error component. It is possible to predict or estimate the value of one variable by knowing another variable.

The regression equation is judged for its usefulness based on the overall F-test for the model. Correlation and regression are generally performed together.

### 1.1.8.4 Multiple Linear Regression

The objective in multiple regression analysis is to develop a mathematical model that relates one variable with several other variables. The general form of a multiple regression model with $n$ explanatory variables is given by

$$y = c + m_1x_1 + m_2x_2 + ... + m_nx_n + s$$

where, $c$ is the intercept and $m_1, m_2, \ldots, m_n$ are the coefficients

The $n$ regression coefficients are estimated by the method of least squares. The regression coefficient $m_i$ corresponding to $x_i$ gives the marginal partial contribution of the variable $x_i$ to the response $y$ while the other variables are held at constant level.

The beta coefficients, which are the regression coefficients obtained when all the variables are converted into standardised form, gives an understanding the relative importance of predictor variables. The $R^2$ value is the percentage of the total variance in $y$ explained by all the independent variables in the regression equation. The regression equation is judged for its usefulness based on the overall F-test which should show a $p$-value of less than 0.05 on the ANOVA table in the output.

### 1.1.8.5 Factor Analysis

Factor analysis is a statistical treatment applied to data to group those parameters that have identical attributes. It is a method for reducing data complexity by reducing the number of variables being studied. Factor analysis can be used for identifying latent or underlying factors from an array of seemingly important variables.
The first step is the determination of the parameter correlation matrix to find the degree of mutually shared variability between individual pairs of water quality variables. Then, eigenvalues and factor loadings for the correlation matrix are determined. Only the first few factors are needed to account for much of the parameter variability. Once the correlation matrix and eigenvalues are obtained, factor loadings are used to measure the correlation between the variables and factors. Factor rotation is used to facilitate interpretation by providing a simpler factor structure.\(^1\)

1.1.8.6 **Cluster** Analysis

Hierarchical cluster analysis is a multivariate procedure for combining similar objects/samples together. The agglomeration schedule displays the cases or clusters combined at each stage, the distances between the cases or clusters being combined, and the last cluster level at which a case joined the cluster. The proximity matrix gives the distances or similarities between items. Cluster membership displays the cluster to which each case is assigned at one or more stages in the combination of clusters.

Dendrograms are used to assess the cohesiveness of the clusters formed and provide information about the appropriate number of clusters to keep. Once the clusters are identified, a AT-means clustering algorithm (non-hierarchical method) specifying the number of clusters gives the initial and final cluster centres. The final cluster centres contain the mean values of for each variable in the cluster. By combining the information on all variables for each cluster, the cluster is interpreted and given a name.

1.1.8.7 **Discriminant Analysis**

Linear discriminant analysis is used to classify samples or parameters into groups based on some of their characteristics. Discriminant analysis is similar to multiple regression technique. This model can be used for predicting where a new sample should be
classified, if the values of the independent variables are known. The form of the equation in an \( n \) variable discriminant analysis is
\[
y = a + k_1x_1 + k_2x_2 + \ldots + k_nx_n.
\]

\( Y \) is the dependent variable (grouping variable) and \( x_1, x_2, \ldots, x_n \) are the independent variables, \( k_1, k_2, \ldots, k_n \) are coefficients (Unstandardised discriminant function coefficients) of the independent variables and ‘\( a \)’ is a constant. \( Y \) in this case is a categorical variable.\(^{17}\)

The use of discriminant analysis requires data on all independent variables and the categories to which each belongs. Then, a discriminant model (linear equation) is built, and tested for its usefulness based on its significance. This model can be used for predicting where a new sample should be classified, if the values of the independent variables are known.

Application of chemometrics to environmental analysis can help in the detection of pollution. It is useful in evaluating biological response to natural or toxic factors, and in identifying the source of the contamination. Pattern recognition methods have been used to reveal and evaluate complex relationships in a variety of environmental applications. Chemometric analysis in sediment studies can effectively attribute a source to an environmental contaminant. It can be used to speed methods development and make routine the use of statistical models for data analysis. Patterns in the physical and chemical data are modeled, and the models can be routinely applied to future data in order to predict comparative consequences.

1.2 Review of Literature

Lakes all over the world are heavily overexploited with consequent alteration and degradation of local ecosystems. The important threats to coastal and lake ecosystems are pollution, habitat destruction and over exploitation. The Vembanad Lake has been the
subject for a lot of scientific studies dealing with varied aspects such as hydrography, nutrients, sediments, trace metals, planktons, fishes and other biotic resources. A lot of literature on environmental studies of the Cochin estuary is available but only a few are related to the region south of the Thanneermukkom Barrage.

1.2.1 Previous Studies on Water Quality

Xie et al.\textsuperscript{19} investigated the status of nitrogen and phosphorus pollution of twelve rivers and three lakes in Changshu region. The water bodies in the region were severely polluted by nitrogen and phosphorus. Thomas\textsuperscript{20} reported that phosphorus plays a key role, especially in the early stages of eutrophication, partly through stimulating bacterial production of growth factors used by algae. Zhao et al.\textsuperscript{21} studied concentrations of nitrogen and phosphorus in samples of surface water and their spatial variations. The results showed that industrial wastewater and domestic sewage were the main contributors of nitrogen and phosphorus pollution in the surface water, rather than agriculture fields. Van Der Vlugt and Klapwijk\textsuperscript{22} analysed water quality of the Reeuwijk lakes and reported that eutrophication is a major problem in the lake.

Pauer and Auer\textsuperscript{23} performed a study on Onondaga Lake and the adjoining Seneca River, a hypereutrophic system with high ammonia concentrations (2–10 mg N L\textsuperscript{-1}). No apparent nitrification was observed in the water column of the lake or river, despite high ammonia concentrations. Veldre et al.\textsuperscript{24} determined the concentrations of NO\textsubscript{3}−, NO\textsubscript{2}−, and NH\textsubscript{4}+ in water samples from Lakes Peipsi, Pihkva, and Lammijarv, Estonia. Lake Peipsi had the lowest concentrations of NO\textsubscript{3}−. The highest concentrations of NO\textsubscript{3}− were in the waters of the Emajogi and Velikaya rivers, which are polluted with sewage and fertilizers. The concentrations of NH\textsubscript{4}+ and NO\textsubscript{2}− in the lake water were much lower than that of NO\textsubscript{3}−.
Yin Chengqing\textsuperscript{25} reported that Yuxi River-Chaohu Lake water suffers from eutrophication, high turbidity, organic pollution, disappearance of littoral macrophytes, bank erosion and reduction of fish products. The problems are caused by high nutrient load, high spring water level and improper management. The point sources of pollution from cities and industries contribute about 50 percent of nutrient load. Tatsumoto \textit{et al.}\textsuperscript{26} examined the variation in water quality and components of the dissolved organic matters for Lake Tega-numa the most polluted lake in Japan which has a high pollutant load in its catchment area. The annual mean value of soluble organic matter was 20.2, 9.9, and 7.7 mg/L in the upper, medium, and lower reaches, respectively.

Avoine \textit{et al.}\textsuperscript{27} found that, in the Seine estuary, the majority of pollutants carried into coastal waters come from the river basin. Dissolved pollutants are evacuated downstream the estuary within 2-30 days. The majority of nutrients are consumed in the Bay of the Seine. Mean concentration of dissolved trace metals are close to background values, except for Zn and Cd. Tankere \textit{et al.}\textsuperscript{28} attributed the large inputs of Mn to reductive solubilisation and diffusion from the sediment water interface. Excess particulate manganese concentrations were due to the oxidation of dissolved manganese.

Penn and Auer\textsuperscript{29} monitored the concentrations of copper and iron in surface water of the eutrophic Lake Kasumigaura, the second largest lake in Japan. The concentrations of copper in the water were in the range $10^{-9}$ to $5 \times 10^{-8}$ M and showed clear seasonal changes, being higher in summer and lower in winter. The values of dissolved chemical oxygen demand showed a similar behavior. The concentrations of iron showed wide variation, but no obvious seasonal change. The concentrations of iron decreased markedly during flow of water through the lake. Davison\textsuperscript{30} reported that iron cycle is capable of markedly influencing the concentration of humic substances, which sometimes increase in the anoxic waters of a seasonally stratified lake/ reservoir due to release from dissolving iron oxides.
Fytianos et al.\textsuperscript{31} reported that rivers and lakes in northern Greece are highly polluted by anthropogenic activity, based on heavy metal content of their waters. Nojiri et al.\textsuperscript{32} monitored background levels of trace metals in Lake Mashu, a deep oligotrophic lake in Hokkaido, Japan famous for the highest transparency in the world. The trace metal concentrations were extremely low: Fe 2.6; Al 1.2; Mn 0.76; Zn 0.63; V 0.15; Cu 0.069; Ti 0.06; Pb 0.05; Ni 0.027; Cd < 0.006; and Co < 0.004 µg L\textsuperscript{-1}. The suitability of Lake Mashu for a background level monitoring station for global environmental pollution was assessed by the comparison to reference data for other lakes in the world.

Das et al.\textsuperscript{33} investigated lotic wetlands of Guwahati city to assess water quality changes affecting dependent organisms. Results showed extremely polluted water in Bharalu river, indicated by very low DO and ES, and high BOD, COD, phosphate, and ammonia concentrations, unsuitable for aquatic life. The four major city drains had low DO, high BOD, COD, chloride, sulphate, and NH\textsubscript{3}-N. However, water quality in the Bahini and Brahmaputra rivers did not exhibit gross deterioration.

Fokmare and Mohammed\textsuperscript{34} studied the quality of Kapshi Lake and Purna River waters to evaluate their suitability for drinking purpose. The parameters studied included pH, alkalinity, EC, TDS, TH, chlorides, salinity, sulfates, phosphates, nitrates, DO, BOD and COD. Higher values of phosphates in Puma River water can be attributed to pollution from detergent and domestic waste while high BOD of the same suggests organic enrichment. Kapshi Lake water is suitable for drinking purpose when compared to Puma River water.

Jeelani et al.\textsuperscript{35} studied temperature, pH, conductivity, DO, Ca, Mg, total alkalinity, chloride nitrate-N and total phosphorus and reported maximum DO during colder months for the Dal Lake in Kashmir. Ca concentrations varied between 17.6-55.3mg/L and that of Mg between 2.4-20.4mg/L. Total alkalinity ranged from 42mg/L to 100mg/L. The lake
was rich in chloride and the concentrations of NO₃-N content ranged between 113-910µg/L and total phosphorus fluctuated between 120-580µg/L. The water was alkaline, moderately hard and rich in nutrients.

Brijraj Das[^36] studied environmental pollution impact on water and sediments of Kumaun Lakes. The study of water and sediment chemistry of the Lakes have shown that the water of these lakes are alkaline and that electrical conductivity, total dissolved solid and bicarbonate levels are much higher in Nainital than in the other three lakes. Johny Joseph[^37] reported alkalinity fluctuations depending upon the locations, seasons, plankton population and nature of bottom deposits in the natural waters.

Chitra and Ramanibai[^38] reported that in an estuarine ecosystem, nitrogen and phosphorous are the most limiting nutrients for phytoplankton production. Both nitrate and phosphate are highly influenced by agricultural and sewage inputs and is responsible for nutrient loading which in turn plays a unique and important role in eutrophication. Tripathy et al.[^39] made an assessment of water quality of Gautami–Godavari mangrove estuarine ecosystem of Andhra Pradesh. High concentrations of nutrients in the mangrove ecosystem compared to the bay and estuarine ecosystems reveal the importance of this zone as a source of nutrients to the adjacent coastal ecosystems.

Assessment of water quality of Orathupalayam reservoir in Tamil Nadu was carried out by Kavitha et al.[^40]. The study has shown heavy contamination of water of the reservoir, making it unsuitable for irrigation purpose. Rokade and Ganeshwade[^41] studied the impact of pollution on water quality of Salim Ali Lake at Aurangabad, Uttar Pradesh. Results showed high fluctuations in the physico-chemical parameters indicating the intensity of pollution. Ganapathi[^42] opined that the increasing volume of waste materials and introduction of new persistent chemicals in industries have created severe threat to estuarine ecosystems in many parts of the world.
Mahapatro and Padhy\textsuperscript{43} studied the Rushikulya, a typical tidal and well mixed estuary on the east coast of India and reported that the highly productive features of estuaries alter the concentration levels of some biogeochemically important elements like fluorine. The report studies the behaviour of fluoride in different seasons with respect to chlorinity in Rushikulya estuary. Sabitha Sebastian \textit{et al.}\textsuperscript{44} studied the distribution and behavior of fluoride in Azhikode Estuary and reported that fluoride concentration was considerable during Post-monsoon season when there is fresh water influx.

Pollution of Ninital Lake was studied by Rai and Rathore\textsuperscript{45}. The physicochemical characteristics of water exhibited remarkably lower values for water transparency, which could be attributed to rich phytoplankton density and higher budgets of suspended and particulate matter due to heavy pollution of organic matter. Studies on water quality characteristics of Shenala Lake, Maharashtra was done by Salaskar and Yeragi\textsuperscript{46}. The highly degraded water body represents a typical urban wet-land, polluted by directly entering domestic sewage from the intensively urbanized catchments. Kerry Blak and Baba have stated that the increase in the number of houseboats lead to direct sewage discharge into the water body, which cause microbial contamination of the Ashtamudi estuary.\textsuperscript{47} Industrial effluents, sewage and fecal disposal, pesticide and chemical fertilizers and retting of coconut husk are the major source of lake-water pollution in Kerala\textsuperscript{48}. Shaw \textit{et al.}\textsuperscript{49} studied the water quality of the Rushikulya river estuary in relation to waste-water discharge from a chloralkali plant. It was concluded that the effluent was not fit for being discharged as such. The estuarine water was completely unfit for supporting aquatic life.

Bejoy Nandan \textit{et al.}\textsuperscript{50} studied water quality in the retting zones of the backwaters of Kerala and reported that the Kadinamkulam backwater is exposed to severe pollution from retting of coconut husk. Kadeeja Beevi \textit{et al.}\textsuperscript{51} reported that the major livelihood activities like coir retting plays a key role in contributing large amount of organic
pollutants into the Kayamkulam backwaters in south Kerala. Shibu Vardhanan et al.\textsuperscript{52} have reported a green technology for control of pollution of backwaters due to coir retting which plays a key role in contributing large amounts of organic pollutants.

Muralidharan Nair et al.\textsuperscript{53} studied the Akkulum - Veli lakes and found that lack of nutrient flushing and elevated values of nutrient content helps the prolific growth of aquatic weeds. The uncontrolled tourism activity may damage the rare fauna and flora of the ecosystem. Rema Devi and Abdul Aziz\textsuperscript{54} assessed the water quality of Ashtamudi estuary and found that the estuary is heavily polluted from various anthropogenic sources. Mukundan and Thomas\textsuperscript{55} reported that the wide fluctuation in the water characteristics of the backwaters of Kerala was greatly influenced by the pattern of monsoon.

Mahapatro\textsuperscript{56} studied the behaviour of major elements viz. calcium and magnesium has been studied in the well mixed Rushikulya estuary. These elements indicated an increasing trend in their concentrations from river to estuarine end. They exhibited higher concentrations in May-June and lower concentrations in July-September and were predominant in seawater. The ratios of Ca/Cl and Mg/Cl at varying chlorine concentrations were always within the normal oceanic ranges. Singh et al.\textsuperscript{57} conducted hydrochemical assessment of reservoirs of Damodar river basin in India and reported that seasonal data showed a minimum concentration for most of the ions in Post-monsoon and a maximum concentration in Pre-monsoon seasons, reflecting the concentrating effects due to elevated temperature and increased evaporation during the low water level period of the Pre-monsoon season.

1.2.2 Previous Studies on Water Quality of Vembanad Lake

Thampatti and Padmakumar\textsuperscript{58} reported that seasonal variations of pH were only marginal in almost all the locations except in the lowland locations in North Kuttanad (Kaipuzhayaar), where pH values were comparatively lower (5.43 to 6.45), apparently
due to surfacing of sub-soil acidity in these acid-sulphate soil tracts consequent to the curtailing of salinity. Higher pH values in the range of 5.7 to 7.75 were characteristic at locations close to the barrage where saline influences were more pronounced.

Harikumar et al.\textsuperscript{59} studied variations in water quality parameters such as pH, DO, BOD and nutrient concentrations of Vembanad Lake and reported severe pollution. The southern region has become less oxygenated and Punnamada near Alappuzha has reached hypereutrophic stage. The salinity, conductivity and chloride were found to decrease progressively from the north to the south of the lake.

Anvar Batcha\textsuperscript{60} studied the distribution of surface and bottom water dissolved oxygen content of Vembanad Lake in different seasonal periods and reported very large variation. Higher dissolved oxygen concentrations were observed during monsoon which ranged from 4.08ml/L to 11.22ml/L in the surface waters and from 0.9ml/L and 7.37ml/L in the bottom waters. During Post-monsoon the DO varied between 2.49 and 10.49 and during Pre-monsoon the values were 3.83ml/L to 7.49ml/L respectively.

Harilal et al.\textsuperscript{61} reported low DO (1.0-4.7mg/L), high biological oxygen demand(10.4-35.7mg/L) and nutrient rich water having high count of coliform bacteria (10-325 count/mL) in the Vembanad Lake. The pH values (6.58 -7.87), EC (870-2650\textmu mhos), TDS (573.4-2172.6mg/L) total hardness (100- 344mg/L), nitrite (2.96-4.45\textmu mol/L), nitrate (0.64 - 12.98\textmu mol/L), phosphate (1.46- 5.12\textmu mol/L) and chloride content (239.93- 819.75mg/L) exhibited spatial variation.

Josanto\textsuperscript{62} observed that the maximum salinity value in locations north of the barrage was significantly lower than that recorded (23ppt) in this part of the estuary during pre-barrage period. The maximum salinity of 32.75% was recorded at Cochin gut region and the minimum value of 4.32% in the canal region between the paddy fields of the lake. According to Babu\textsuperscript{63} the operation of the salinity barrier at Thanneermukkom plays a
major role in the distribution of salinity in the backwaters of Kuttanad. Salinity in
Vembanad Lake exhibited extreme variations in different seasons of the year. Varying
degrees of salinity from fresh water to seawater exist in the lake and the back water system
depends on the amount of fresh water discharged by the various river systems. Thomas et
al.\(^4\) reported that water quality status of Kuttanad region varies in different ecological
regions. Salinity in Vembanad Lake exhibited variations during the different seasons of
the year. Variation in salinity of the back water system depends on the amount of fresh
water discharged by the rivers.

Unnithan et al.\(^7\) presented an overview of the water and sediment quality of
Vembanad Lake, south of Thanneermukkom barrage and reported a definite pattern of
variation influenced by a combination of saline water intrusion through the barrage, and
extent of discharge by the four rivers into the lake. Most of the water quality parameters
including salinity exhibited marked variation during Pre-monsoon, monsoon and Post-
monsoon seasons. The sediment characteristics also showed wide fluctuations.

Jacob et al.\(^8\) reported that chloride content was below 50mg/L in the southern and
between 60mg/L and 114mg/L in the northern regions of the Vembanad Lake. The
shallow ground waters in the region contained chloride in the range 17 to 238mg/L during
Pre-monsoon and 14-176mg/L during Post-monsoon periods. The ground waters of
Kuttanad have iron content in the range of 0.8 to 14.0mg/L. The iron is leached out
largely from the clay layers.

Harikumar and Madhavan\(^5\) reported health problems due to excessive intake of
fluoride in Alappuzha and Cherthala regions. Nair and Resy George\(^6\) reported that the
Kanjikuzhi and Aryad regions of Alappuzha district were seriously affected with drinking
water shortage, which was due to salinity intrusion, pollution and the presence of fluoride
and iron. Traditionally the floodwaters infiltrating into the soil used to wash out the
excessive salinity and some of the pollutants. Land reclamation and floodwater diversion
have adversely affected the cycle. The acidic water from coir factories aggravates the
water contamination at many locations in the lake.

Anirudhan\textsuperscript{67} reported that the inter basin transfer of water from Periyar river to
Muvattupuzha river, construction of Thannermukkom bund and extensive dredging and
harbor operations resulted in an extensive change in the hydrographic conditions of the
estuary. An inverse relationship was observed between inorganic and organic nitrogen
fractions. Ramachandran Nair et al.\textsuperscript{2} studied fish mortality and ammonia pollution in
Cochin back waters. They observed the presence of excess amount of ammonia in water,
where massive killing of fishes occurred.

Sankaran Unni et al.\textsuperscript{68} reported that fertilizer and pesticide inflow from the
agricultural fields and plantations situated in the upland catchments of Achencovil, Pamba,
Manimala, and Meenachil Rivers are significant. Hospital wastes and sewage from all
towns and villages located along the river course flows into Kuttanad. Apart from this,
20,000 tons of fertilizer per year added to the rice fields and 50 tons of pesticides
contribute to the pollution load. The canals in Kuttanad region are heavily contaminated
with different types of pathogenic bacteria.

Kunjukrishnapillai\textsuperscript{69} reported that the physicochemical characteristics of a dynamic
estuarine system shows significant changes in time and space in the annual cycle since it is
influenced to a large extent by the tidal flows from the sea as well as from the fresh water
discharges by the rivers into the lake. The various anthropogenic activities are the major
reasons for the change in hydrography and increased silt load in Vembanad Lake.

The hydrographic conditions of an estuary depends on the intrusion of sea water
associated with tides, influx of water from rivers, bottom topography, geographical
conditions, precipitation, evaporation and weather.\textsuperscript{70} Qasim and Madhuprathap\textsuperscript{71} reported
that the wide fluctuation in the water characteristics of the backwaters of Kerala was greatly influenced by the pattern of monsoon. Sankaranarayanan and Quasim\textsuperscript{72} showed that nutrient concentrations in the Cochin backwaters were higher during south-west monsoon period.

Madhusoodhana Kurup \textit{et al.}\textsuperscript{73} pointed out that the construction of Thanneermukkom barrier and large-scale reclamation activities have resulted in the reduction of lake area along with reduction in prawn wealth of the lake. Marykutty \textit{et al.}\textsuperscript{74} conducted a study on the potential effects of fertilizer residue on algae of Kuttanad and concluded that there are chances for the increase in nitrate level leading to algal blooms, due to the prevention of natural mixing of water by the Thanneermukkom barrier. They also found that draining of water from the paddy fields could be the contributing factor to increased nutrient levels in Kuttanad region.

Babu Jose\textsuperscript{75} observed that the Cochin estuary is subjected to increasing human interference and receives considerable amount of pollutants from industrial units, domestic sewage, fishery industry, coconut husk retting yards and the Cochin sea port that handles large quantities of petroleum products and industrial chemicals. Somanathan Pillai\textsuperscript{76} observed that Kuttanad wetland is under large-scale reclamation for construction of buildings, hotels, houses, industries and roads to a very large extent. This will affect the microclimate of the region. Retting of coconut husk leads to deterioration in environmental quality of wetlands due to the formation of anoxic sulphide rich habitats. Unnikrishnan\textsuperscript{77} reported that retting of coconut husk results in the production of hydrogen sulphide, methane and phenolic compounds into the lake ecosystem, which kill flora and fauna. Sabarimala, one of the largest pilgrim centres in south India, situated on the banks of the Pamba River, a major source of water to Vembanad Lake, has a major role in polluting the river and consequently the wetland.
Bindu and Harikumar\textsuperscript{78} assessed the level of eutrophication in the Vembanad wetland and concluded that the lake is infested with phytoplankton during pre-monsoon and the beginning of monsoon. They also stated that the southern, eastern and western parts of the lake were polluted by diffused pollutants such as agricultural and municipal effluents in addition to the nutrient load received by the lake due to point sources.

John Mathew \textit{et al.}\textsuperscript{79} observed that exotic species showed very aggressive growth and high abundance in terms of spatial and temporal frequency and percentage of cover. Maya \textit{et al.}\textsuperscript{80} reported that the growth of certain algae in fresh water could lead to the loss of recreational value of fresh waters. They were also found to impart bad odour to water and increase sludge deposits in water treatment.

\textbf{1.2.3 Previous Studies on SAR and WQI}

Singh \textit{et al.}\textsuperscript{57} conducted SAR assessment of reservoirs of Damodar river basin in India. The SAR in the study area ranged from 0.40 to 0.85 in the pre-monsoon and 0.35-0.90 in the post-monsoon season. Chandrasekhar and Mohammed Hakeel\textsuperscript{81} reported SAR values ranging from 0.2 to 2.2 with a mean of 0.79 for Pocharam Lake in Andhra Pradesh for waters used for irrigation. Chandrasekhar\textsuperscript{82} studied the suitability of water of Kondakaria Lake in Andhra Pradesh for irrigation.

Tiwari and Mishra\textsuperscript{83} reported that Water Quality Index is regarded as the most effective way to communicate water quality. WQI is calculated by weighted index method to determine suitability of ground water for drinking purposes. Many countries use water quality indexing method to assess the overall status of their rivers. These indices differ from country to country but the concept is similar, where a few important parameters are selected and compounded to numerical rating for evaluation of the river water quality.\textsuperscript{84,85}

Mamun \textit{et al.}\textsuperscript{86} proposed a revised water quality index (NWQI) for assessing water quality in Malaysia which was found to be more stringent than the existing index. The
case studies revealed that on average, during the dry days the NWQI produced 8 to 10 points less than the existing WQI equations. During the rainy days the difference was higher which varied between 13 and 20 points.

1.2.4 Previous Studies on Sediment Quality

Goldberg\textsuperscript{87} estimated that \(1.8 \times 10^{16}\) g yr\(^{-1}\) of suspended solids from rain discharge are transported through estuaries to the ocean, while the contribution of solids by atmospheric transport directly into the ocean is between \(1-5 \times 10^{14}\) g yr\(^{-1}\). Since rivers are responsible for transporting solids to the oceans, estuaries assume an important role in the global sedimentary cycle.

Robertson\textsuperscript{88} studied daily loads of suspended sediment and total phosphorus flow to Lake Michigan and Lake Superior using constituent-transport models. Total phosphorus loads were greatest in rivers entering the middle to southern part of Lake Michigan, especially those draining clayey surficial deposits in agricultural areas. During high flow, loads of phosphorus and suspended sediment from tributaries entering the southwestern part of Lake Superior dominate the total input of these constituents.

Pauer and Auer\textsuperscript{23} performed a study on Onondaga Lake, a hypereutrophic system with high ammonia concentrations (2–10 mg N L\(^{-1}\)). The results clearly demonstrate that there is rapid nitrification in the sediments of both Onondaga Lake (0.37 gN m\(^{-2}\) d\(^{-1}\)) and the Seneca River (0.32 gN m\(^{-2}\) d\(^{-1}\)).

Bouillon \textit{et al.}\textsuperscript{89} reported that nitrogenous components of biological origin are more effectively recycled than other forms of organic matter, when it undergoes degradation. This results in retaining a greater proportion of carbon content in it thereby enhancing the C/N ratio. C/N ratio of organic matter contained in sediment has been effectively utilized in evaluating the source of organic carbon in sedimentary environments.\textsuperscript{90}
Allen and Rae\textsuperscript{93} studied preindustrial sediments of Severn Estuary, Wales-England, for the content of Zn, Cu, and Pb. Comparison of preindustrial and later sediments with respect to metal abundances suggests that the Pb and Zn entered the estuary largely from natural sources within the adjoining river basins but at anthropogenically enhanced rates during the industrial and post industrial periods.

Avila Perez et al.\textsuperscript{92} conducted a study on heavy metal distribution in bottom sediments of Mexican reservoir. The study showed that Ti, Fe, Cu, Zn and Pb in the sediments show a trend of increasing metal concentration with reduction in particle size. But the concentration of Mn increase with increase in particle size. Copper is present in large amounts in clay. Zinc and lead are found in low velocity zones.

Baskaran et al.\textsuperscript{93} studied the Sabine-Neches estuary, a shallow, turbid estuary in southeast Texas with high dissolved organic carbon concentrations. A sediment inventory of Pb(210), Pu(239) and Pu(240) indicated that only a fraction of the particle-associated nuclides reaching the estuary were retained in the sediment. Ratios of dissolved to particulate concentrations of Be(7) and Pb(210) were generally higher than in most other coastal waters.

Broman et al.\textsuperscript{94} studied the spatial and the seasonal variation of flux and concentration of 11 metals (Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn), organic matter, and C and N in settling particulate matter collected with sediment traps. The concentration of Cu, Hg, Pb, and Cd in the interior of the area under investigation were the most elevated of the elements and decreased markedly further out in the archipelago, indicating local anthropogenic input. Zn, Cr, and Fe also showed signs of supply from the urbanized environment.

Cave et al.\textsuperscript{95} compared the trace metal concentrations of sediments with background values in the Humber estuary on the east coast of the UK, with particular
reference to the trace elements; arsenic, copper, lead and zinc. The depositional fluxes of trace metals to the estuary intertidal sediments, and comparison with the inputs, revealed that the estuary sediments were capable of storing 55-97% of the input load of As, 15-27% of Cu, 17-50% of Pb and 11-12% of Zn annually. Sediment quality in the estuary was far from its 'background' state with respect to trace metals.

Cheevporn et al.\textsuperscript{96} analyzed the sediments from the Bang Pakong River estuary for trace metal concentrations (Cu, Pb, Zn, Cd, Cr, and Ni). High concentrations of Cu, Pb, and Zn were found in the sediments. Slight variations with depth in the sedimentary column were found for Cd, Cr, and Ni. Christensen and Juracek\textsuperscript{97} studied trace metal levels of Swanson Lake, Harlan County Lake, Kirwin reservoir, Webster reservoir and Walconda Lake in the Republican River Basin in USA and reported that reservoir sediment cores can be used to reconstruct historical water-quality records. Of the eight metals studied, several had concentrations above threshold effect levels. Cd, Cu, Ni, Pb and Zn had detections greater than their respective TEL's in more than one sample. Median concentrations of Cu and Ni were larger than their TELs. Concentrations were below established PEL's. Increasing trends were indicated for As, Sr and Se. The trends may be related to both natural conditions and increased icheigation activities in the basins.

Dittrich et al.\textsuperscript{98} estimated the dissolved and particulate trace elements in the of the storage lake Bitterfelder Muldestausee to study the sedimentation of 22 elements transported by the highly polluted Mulde river, an affluent of the river Elbe. Despite the wide variation in the concentrations of the suspended matter samples the concentrations of the heavy metals in sediment samples and in the suspended matter were comparable. Results show that the storage lake acts as a sedimentation trap for Zn, Cu, Pb, Ni, Cr, Cd, U, and Co. Fairey et al.\textsuperscript{99} studied sediment quality within San Diego Bay, Mission Bay, and the Tijuana river estuary of California. Cu, Zn and Hg exceeded ERM (effects range
median) or PEL (probable effects level) sediment quality guidelines. Christensen and Chien\textsuperscript{100} studied arsenic, lead, zinc and cadmium in Green Bay and Lake Michigan sediments. Gong \textit{et al.}\textsuperscript{101} analysed the heavy metal content and the degree of pollution of the sediment of Poyang Lake. The results indicated that Poyang Lake was polluted by heavy metals in various degrees. According to the index of geo-accumulation, the decreasing order of heavy metals in the lake was Cu, Pb, Zn and Cd and the ecological risk to Poyang Lake was Cd, Pb, Zn and Cu.

Gomez Ariza \textit{et al.}\textsuperscript{102} studied re-adsorption and redistribution processes that occur in the sediment of the Odiel Marshes Natural Park, southwest Spain. Metals studied were As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. It was concluded that re-adsorption and redistribution occur, the extent of which depended on sediment characteristics. Holdren \textit{et al.}\textsuperscript{103} reported that the concentration of Fe and Mn in estuarine interstitial waters are often reported to be very high and this is due to the dissolution of sediments, Fe and Mn and reducing conditions.

Jones \textit{et al.}\textsuperscript{104} studied Huon and Derwent estuaries in Tasmania and reported trace metal levels in the surface sediments ranging from 40 to 565 times baseline levels. Trace-metal levels in the more recent surficial aquatic sediments are slightly lower than those recorded in a previous study from the area, possibly reflecting the stricter environmental controls now operating.

Loring \textit{et al.}\textsuperscript{105} determined major (Al and Fe), minor (Mn), and trace (As, Cd, Co, Cr, Cu, Hg, Li, Mo, Ni, Pb, Sb, V and Zn) metals, TOC and TN in sediment from the Kara Sea, and the Ob and Yenisey estuaries, Russia. Metal levels in the Kara Sea and the Ob and Yenisey estuaries were close to natural baseline levels. Lu and Chen\textsuperscript{106} reported that the concentration of Fe and Mn in estuarine interstitial waters are often found to be very high and this is due to the dissolution of sediment Fe and Mn and reducing conditions.
Makundi\textsuperscript{107} studied heavy metal pollution in Lake Victoria sediments and reported significant concentrations of toxic elements like As, Cr, Cu, Co, Mn, Zn and Pb in certain areas. The samples taken from the lake shore showed significantly higher concentrations of Fe, Cr and Pb than the sediments from the rivers and streams flowing into the lake. Ramessur and Khurun\textsuperscript{108} quantified Cr, Zn, and Pb in estuarine sediment along the western coast of Mauritius. Mean concentrations in sediment along the estuaries were below the limits of 600, 2500, and 700 mg kg\textsuperscript{-1} quoted for polluted sediment adopted from draft Netherland standards. The significant presence of Zn and Pb downstream in the St Louis River estuary was attributed to road runoff and industrial and urban activity in the area. Basaltic rock can be a source of Cr in the three estuaries.

Ravichandran et al.\textsuperscript{109} studied the concentration of trace metals (Co, Cr, Cu, Ni, Pb, and Zn), Al, Fe, Mn, and organic carbon in sediment cores. While the concentrations of Pb and Zn at various depths in the sediment column are slightly enriched, Co, Cr, Cu, and Ni are depleted. The sedimentary and biogenic particles that are presently being deposited are also depleted in trace metals. Lack of strong enrichment for trace metals like Cu can be attributed to the short residence time of water, low salinity conditions, and possibly strong complexation of these metals with organic matter.

Ronco et al.\textsuperscript{110} reported concentrations of Cr, Ni, Cu, Zn, Cd, Hg, Pb, Fe and Mn, grain size, mineralogy and organic matter content in the four streams, considering both geomorphological units at different depositional time. Untreated and iron-normalized trace metal concentrations in the most polluted streams show higher levels in the upper layers of most contaminated sectors and accumulation areas associated. The coastal plain sector behaves as a regional sink between the upstream area and the estuary.

Rubio et al.\textsuperscript{111} analyzed the major and trace elements (Al, Fe, Ti, Mn, Cu, Pb, Cr, Zn, Co, As, Ni, Cd and Sr) from coastal embayment in Galicia, NW Spain. Variations of
metal concentrations reflected differences in textural and carbonate and organic matter content. Geo-accumulation indices and enrichment factors were calculated to assess whether the concentrations observed represent background or contaminated levels. Principal component analysis was used to define background values for metals in the RIA de Vigo area. It was concluded that the RIA was slightly to moderately polluted in terms of some of the studied metals.

Standing et al. investigated time-dependent interactions between trace metals and freshwater sediments and their potential remobilization upon contact with seawater. Trace metals can be remobilized from sediments on contact with seawater in estuaries. Soto Jimenez and Paez Osuna explained that the input of metals into sediment that are located seawards to be low in the total concentration of most of the elements and this could be due to the mixing of enriched particulate material with relatively clean marine sediments.

Spencer et al. found that surface sediment from Medway and Swale estuaries in UK were moderately polluted. Cu, Hg, Pb and Zn concentrations were high in the two estuaries when compared with the local geochemical background concentrations. More than 69% of sample sites in the Medway and Swale estuaries exceeded the effects range low (ERL) for Hg and 51% for Ni.

Taymaz et al. studied the heavy metal concentrations in water, sediments and fish from Izmit Bay, Turkey. Study showed an indication of correlation between the heavy metal concentration of the fish specimens and shoreline sediments. Van Metre and Callender studied spatial and temporal trends of metal concentrations in White Rock Creek Basin using sediment cores from White Rock Lake reservoir, Dallas, Texas.

Zhao et al. studied a lake in Fukuoka Prefecture, Japan and found that the main source of total nitrogen was farm, especially tea garden, and main source of total P was
forest. Concentrations of nitrogen, phosphorus copper, zinc, lead, chromium and cadmium in sediment and their spatial variations were also studied. The results showed that heavy metal pollution was induced mainly by industrial activities and urban surface runoff. N/P ratio in the lake decreased when algal bloom happened; the N/P ratio was 7-58.

Balachandran et al.\textsuperscript{118} studied the seasonal changes in regional distribution of sediments along the central southwest coast reported that the main factors controlling the distribution of trace elements among the various phases in the aquatic system are the textural characteristics and organic carbon content. Ghosh and Chaudhary\textsuperscript{119} studied the nutrient status of sediments of Hoogly estuary in West Bengal. Sivakumar\textsuperscript{120} conducted a study on the seasonal variation of carbon, nitrogen and phosphorus in sediments of Vellar Estuary. The distribution and seasonal variations of organic carbon of the north western continental shelf of India have been studied by Paropakari.\textsuperscript{121}

Padma and Periakali\textsuperscript{122} studied the physico-chemical and geochemical characteristics of Pulicat lake in India. The study showed that heavy rainfall, high run-off and the fresh water input increase the trace metal concentrations in the sediments during Post-monsoon, whereas the decrease during Pre-monsoon is in response to decrease in clay content, Fe-Mn oxides and organic carbon.

Saxena\textsuperscript{123} studied the heavy metal distribution in the suspended sediments, bed sediments and ground water of Krishna Delta and indicated that suspended sediments are comparatively more enriched in metallic trace elements than bed elements and ground water. The considerable variations in the concentration of metallic trace elements may be due to the variations in the sub basin geology and various degrees of human impacts. Zhou et al.\textsuperscript{124} stated that besides anthropogenic enrichment, heavy metals occur naturally in silt and clay-bearing minerals of terrestrial and marine geological deposits. The natural occurrence of heavy metals complicates the assessment of potentially contaminated
estuarine sediments. The measureable concentrations of metals do not automatically infer anthropogenic enrichment in the estuary.

Leena Grace\textsuperscript{125-127} analyzed copper, lead, manganese, nickel and zinc in the sediments of Kadinamkulam estuary and reported that low level of copper was observed in all the stations while comparing other metals. The seasonal variations were also noted for all the five metals. Estuarine sediments form the final trap for most of the heavy metals.

Singh and Jha\textsuperscript{128} reported that the level of total calcium varied between 480.7 and 719.4 mg/100g, total Mg between 70.3 and 126.6 mg/100g in surface sediment of Kawar wetland in Bihar. In 6 inch deep sediment the values of total calcium varied between 590.3 and 640.3 mg/100g, total Mg between 96.4 and 126.4 mg/100g in surface sediment.

Nair \textit{et al.}\textsuperscript{66} analysed trace element (Mn, Cr, Zn, Ni, Cu, Pb, Co) concentrations in surficial sediment samples collected from the Chaliyar River, Beypore estuary. Textural characteristics, major elements, and total organic carbon (TOC) content of sediment substantially affect elemental distribution. Significant variations in Mn, Cr, Zn, Ni, Cu, Pb, and Co concentrations were observed in riverine and estuarine sediment.

\textbf{1.2.5 Previous Studies on Sediment Quality of Vembanad Lake}

Abdulla Bava\textsuperscript{1} reported high organic carbon, nitrogen phosphorus levels in Vembanad estuary sediment. Study revealed that the sediments are rich in organic matter and contain trace metals such as Fe, Mn and Ni. Harikumar \textit{et al.}\textsuperscript{59} conducted physicochemical analyses of Vembanad Lake and found highly nutrient-rich, acidic sediments which are polluted by heavy metals like Fe, Cr, Mn and Co. Severe pollution due to metal accumulation was noticed. Organic matter deposition was found to be high. Low pH which reduces mineralisation of organic matter was evident. Textural analysis has shown that the sediments are sand dominated.
Jayasree and Nair\textsuperscript{129} reported concentrations of Fe, Mn, Cu, Cr, Pb, Sr, Zn, Co, Cd, and Ni in sediments of Cochin estuary. The significance of bottom water salinity and pH and sediment grain size and P content in the distribution of these metals is discussed. Generally, most of metals were enriched in middle estuarine sediments. Significant correlations were observed among Cu, Zn, Cd, Co, Ni, Fe and Mn.

Lizen Mathews\textsuperscript{70} stated that the sedimentary characteristics of an estuary is mainly governed by the hydrography of the over laying water. Large inputs of dissolved Mn were attributed to reductive solubilisation and diffusion from sediment water interface. Excess particulate manganese concentrations were due to the oxidation of dissolved manganese.

Muralidharan Nair \textit{et al.}\textsuperscript{53} found that certain metals exceeded the tolerance level and have deleterious effect on biota. Some aquatic organisms concentrate these toxic metals in their body, which ultimately passes to human beings through food web causing far reaching adverse effects. Nagender Nath \textit{et al.}\textsuperscript{130} studied the influence of provenance, weathering and sedimentary processes on the elemental ratios of the fine grained fraction of the bed load sediments from the Vembanad Lake and adjoining continental shelf. The study revealed that the concentration normalized to the average upper continental crust show that the sediments studied are depleted in Rb, K, Ba, Hf, Na and Ca and enriched in Cs, U, Th, Sc, Fe, Co and Cr.

Ouseph\textsuperscript{131} studied the heavy metal pollution in the sediment of Cochin estuarine system. The level of chromium is comparable to the background values observed from other marine environment. But high concentration of Hg, Pb, Zn and Cd occurs in fine grained sediments. Sandy sediments showed low concentration of metals.

Padmalal \textit{et al.}\textsuperscript{132} carried out a study on the Geochemistry of Cu, Co, Ni, Zn, Cd and Cr in the surficial sediments of Vembanad estuary. The study showed that in bulk sediment, the trace metal concentration is controlled mainly by the textural composition of
the sample. Mud, sandy mud and sandy silt register higher concentration of trace metals, than that in sand dominant sediments. The granulometric partitioning studies also reaffirmed the role of particle size in enriching the trace metals.

Padmalal and Srelathan\textsuperscript{133} reported a clear relationship between organic carbon, P and Fe in sediments of Vembanad Lake. Fe and P of sediments showed a clear relationship with organic carbon. The southern sector with low interstitial water salinity is characterized by low sediment P (av. 33.08\(\mu g\cdot g^{-1}\)) and Fe (av. 32.43mg.g\(^{-1}\)), while the northern high interstitial water salinity zone showed showed elevated levels of sediment P (av. 86\(\mu g\cdot g^{-1}\)) and Fe (av. 74.14mg.g\(^{-1}\)). Priju and Narayana\textsuperscript{134} reported that sediments act as sinks and sources of contaminants in aquatic systems because of their variable physical and chemical properties. Metal contents viz., Cu, Ni, Co, Zn and Cd in sediment cores recovered from the Vembanad Lake were analyzed to find out the pollution levels and the impact on the coastal environment. Sanal George \textit{et al.}\textsuperscript{135} reported the presence of heavy metals including Cd, Cr, Fe, Mn, Ni and Pb in different trophic levels of Kuttanad back waters. They also stated that the water and sediments of Kuttanad wetland system are subjected to high level heavy metal contamination.

Seralathan\textsuperscript{136} studied the heavy metal pollution in the sediment of Cochin estuarine system and reported high levels of metal contamination. Sathyanathan\textsuperscript{137} pointed out that heavy metals are ubiquitous, readily dissolved in and transported by water, bioavailable and strongly bounded by sulphydril groups of proteins. Sujatha \textit{et al.}\textsuperscript{138} studied estuarine behavior of some hydride-forming toxic metals such as Hg, As, Sb and Se in the surficial sediments of a tropical estuary, viz. Cochin estuarine system. The order of abundance of these elements is Hg > Sb > Se > As. Unnikrishnan\textsuperscript{77} pointed out that the concentration of dissolved Cu is higher during monsoon, which indicates that the land and river drainage are the major sources of dissolved Cu in estuarine water. The heavy metal contamination in estuaries and lake water has increased considerably in recent years.
Vasudevan Nair\textsuperscript{139} studied the sedimentary characteristics of Cochin estuary and reported large variation in salinity. High organic carbon, nitrogen and phosphorus contents were noticed at the estuarine stations. The sedimentary characteristics are more or less governed by the hydrography of the overlying water. Zeena Ravi\textsuperscript{140} studied pH, salinity, DO, alkalinity, grain-size character, OM, organic nitrogen, carbohydrates, proteins and amino acids of sediments of Cochin estuary. The sediments were low in organic carbon which reflects allochthonous sources. C/N ratios of such sediments are usually much lower than sediments rich in mangrove litter. The preservation of OM is almost exclusively restricted to sediments. SOC and SON are significantly correlated.

1.2.6 Previous Studies – Chemometrics

Christensen \textit{et al.}\textsuperscript{141} conducted real-time measurement of specific conductance, pH, temperature, DO, turbidity, and total chlorophyll and periodic analyses for nutrients, bacteria, and other constituents of concern. Regression equations were developed from the results. The regression equations were used to estimate nutrient, bacteria and other constituents.

Zwolsman \textit{et al.}\textsuperscript{142} studied trace metal spatial and temporal distribution in Scheldt Estuary sediments (Netherlands) to identify trends. Trace metal data were merged into a comprehensive database for analysis using an ANOVA procedure. Sediment trace metal content decreased in the downstream direction due to mixing of metal-rich fluvial sediments and metal-poor marine sediments. Seasonal, spatial and polluting effects on the quality of water of Muggia Bay in Northern Adriatic Sea were examined by exploratory data analysis by Barbieri\textsuperscript{143}. Factor analysis and cluster analysis are often used together to check the results and provide grouping of each variable\textsuperscript{144}.

Seasonal, spatial and polluting effects on the quality of water of San Francisco Bay estuary were examined by exploratory data analysis by Jarman \textit{et al.}\textsuperscript{145} Factor analysis
attempts to explain the correlations between the observations in terms of the underlying factors, which are not directly observable by Jonathan et al.\textsuperscript{146} Karbassi and Amirnezhad\textsuperscript{147} studied the geochemistry of heavy metals in a bay adjacent to Caspian Sea and reported that factor analysis and cluster analysis were explanatory tools in multivariate statistical analysis to discover and interpret relationships between variables. Marengo et al.\textsuperscript{148} have used chemometric methods for evaluating environmental data of lagoon water by exploratory data analysis.

Gupta et al.\textsuperscript{149} conducted statistical analyses on water parameters of coastal regions. There are three stages in factor analysis: for all the variables a correlation matrix is generated; factors are extracted from the correlation matrix based on the correlation coefficients of the variables; and maximise the relationship between some of the factors and variables, the factors are rotated. Voncina et al.\textsuperscript{150} applied chemometrics methods for the classification and comparison of ground water quality of different well samples. Basic statistical methods for the determination of mean, median, standard deviation minimal and maximal values, correlation coefficients, cluster analysis, principal component analysis and linear discriminant analysis were employed.

Yongming et al.\textsuperscript{151} stated that Factor Analysis is widely used to reduce data and to extract a small number of factors depending on the correlation matrix, whereas Cluster Analysis is performed to further classify elements of different sources on the basis of their similarities chemical properties. Hierarchical cluster analysis using dendrograms identifies relatively homogeneous groups of variables in similar properties and combines clusters until only one is left.

Karbassi and Shankar\textsuperscript{152} applied factor analysis to explain the correlations between the observations in terms of the underlying factors, which are not directly observable. Singh et al.\textsuperscript{153} reported that spatial Cluster analysis clustered the monitoring sites into
three groups of relatively non-polluted, moderately polluted and highly polluted sites. Principal component analysis reduced data in terms of eight parameters explaining about 71% of the total variance and evolved six principal components. Temporal and spatial discriminant analysis rendered 97 and 92% correct assignments of the water samples. Multivariate statistical approaches allow deriving hidden information from the data set about the possible influences of the environment on water quality.\textsuperscript{154}

Singh et al.\textsuperscript{57} conducted Factor analysis on seasonal data on hydrochemical assessment of reservoirs of Damodar river basin in India reported that three factors taken together explained about 76% of the total variance in the data matrix indicating that the determined variables, which control the water chemistry are rock weathering with minor contribution from anthropogenic and atmospheric sources. Multivariate statistical approaches allow deriving hidden information from the data set about the possible influences of the environment on water quality.\textsuperscript{155}

1.3 Aim and objectives of the study

The present status of Vembanad Lake is the result of a series of massive human interventions and their consequences. The lake is a source of water for domestic and industrial consumption, transportation, recreation, agriculture and fishing. It exerts considerable influence on the socioeconomy of the surrounding area, as the living resources available in the system plays an important role for the people living around the lake. Despite its economic and domestic importance, there are several activities going on around the lake, which threaten the life of the lake.

The pollution aspects of the lake are of interest due to environmental, economic, domestic and aesthetic implications. Knowledge on the biogeochemical processes is important in understanding an ecosystem. Understanding the sources and fates of environmental contaminants, regulating their discharge or remediating polluted sites
requires detection of the presence of materials of interest and measurement of their concentrations. The combination of low concentrations and complex matrices make environmental measurements a challenging task. Identification and quantisation of pollutants is necessary before decisions can be made and action taken. So the importance of scientific investigations of lakes cannot be overemphasized.

The present study has been carried out with the following aims and objectives:

> To comprehensively understand the water quality situation of Vembanad Lake by determining the seasonal changes in water and sediment quality parameters in different regions of the lake.

> To assess the heavy and trace metal concentrations with respect to available water and sediment-quality guidelines and to identify spatial and temporal trends in metal concentrations.

> To apply Chemometrics methods for the interpretation of data, classification and comparison of environmental samples and pollution source evaluation.