Final Project Report

HYDROCHEMISTRY OF VEMBANAD BACKWATER WITH SPECIAL REFERENCE TO POLLUTION PROBLEMS AND ITS MANAGEMENT MEASURES

Submitted to

KERALA STATE POLLUTION CONTROL BOARD
GOVERNMENT OF KERALA

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FINAL PROJECT REPORT

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EXECUTIVE SUMMARY

Vembanad Kol Wetland is the largest wetland along the south-west coast of India covering around 35, 000 to 50, 000 hectares, lying between 9°00’ and 10°40’ N latitude and 76°00’ and 77°30’ E longitude. It is one of the most impacted zones from multiple issues like pollution from various organic or household waste, industrial activities and from different anthropogenic activities like agricultural disposal, land reclamation etc. It is nourished by over six to ten rivers extending from the Alleppey in the south to Azhikode in the north and it is connected to the network of other backwaters all along the 590 km coastal stretch of the state. Even though there are several studies conducted in the lake, only some scattered information are available on the heavy metal and pesticide contamination especially from Alleppey to Cochin. However no serious information on a seasonal or monthly basis has been evolved from the area. So, it is in this background, the Kerala State Pollution Control Board (KSPCB) entrusted the major task of assessing heavy metal contamination in Vembanad backwater along with pesticide in water, sediment and in the organisms and its relation to the changing environmental conditions.

The study was conducted during premonsoon (February and April) and monsoon (June and August) period in the year 2017 for the collection and analysis of water, sediment and organisms. Nineteen different stations were selected for the field sampling from both northern and southern parts of the Thanneermukkom barrage, having different ecological entities, extending from Aroor in north to Ranikayal in south of Vembanad backwater. The TMB (1975) was constructed across the estuary to prevent salinity intrusion during summer, dividing it into predominantly fresh water zone in southern region and a northern region dominated with brackish water, which has grossly altered the eco-biology of the region. During the present study, it was observed that the earthen portion was almost dismantled; new shutters were being constructed so that the continuity of the rest of the shutters was being provided. So the opening and closing of these shutters have definitely an impact on the environmental conditions of the wetland ecosystem. From this study it is found that, Vembanad estuary showed drastic decrease in depth and transparency in most of the stations. The salinity pattern in the southern part (stations south of TMB) of estuary showed a limnetic to oligohaline condition. The pH was slightly acidic to alkaline. Higher alkalinity values were observed towards the northern high saline stations. Most of the southern stations recorded low DO level whereas BOD level was higher. Houseboat tourism and related activities, sewage discharge and spread of invasive water plants play a crucial role in dissolved oxygen content and BOD level of the southernmost stations of Vembanad estuary. Phosphate, silicate and ammonia were recorded higher in southern part whereas nitrite and nitrate showed higher values towards the northern part of the estuary. Sulphide concentration was observed maximum in Punnamada. The increasing organic load from houseboat and eutrophication might be the reason for lower GPP and NPP values in southern stretch.

In Vembanad backwater, the average concentration of heavy metals in water followed the trend Cd<Ni<Cu<Pb<Zn<Fe. Zn showed higher values in most of the southern stations and the highest value was observed in Nehru trophy finishing point region (442.85 µg L^{-1}). In sediment, the heavy metals concentration followed the trend Cd<Pb<Cu<Ni<Zn. The Ni concentration was observed higher in most of the stations in the southern stretch and the Chithirakayal region was found to be extremely contaminated with the metal. The Marthandam region showed higher values of heavy metals in the study period and the overall concentration was observed to be increasing during PRM. Cd showed a high geo-accumulation index (6.24) and contamination factor (9.36) values throughout the estuary. The pollution load index (PLI) values were very high during the study and it ranged from 0.48 to 5.15, showing the extent of pollution in the backwater. The present study indicates that, the southern part of the Vembanad backwater was facing serious heavy metal pollution. Dumping of wastes, rusted boats festered along the canals of Alappuzha, use of agro-chemicals such as fertilizers and pesticides, metaliferous mining activities, ore dressing and processing, sewage-sludge, municipal runoff and other developmental activities are the main contestant in anthropogenic enrichment of heavy metals in estuarine system. In the case of organisms, high concentrations of Cu, Ni and Zn were observed. The Zn concentration showed high values in *Ambassis* sp. (136.14 mg kg^{-1}), *Channa* sp. (121.18 mg kg^{-1}) and *Villorita* sp. (99.51 mg kg^{-1}). In *Penaeus indicus,* the bio concentration rate of Ni (91.05) was found very high. One of the adverse effects from heavy metal pollution has been the marked decline in the clam fishery (*Villorita* sp.) of this estuary over the years.

Water and soil were analysed for various organochlorine and organophosphorus pesticides. However no pesticide residues were detected in the study. But emerging pollutants (EP) were detected in the backwater and they were identified as benzyl benzoate, cyclic octaatomicsulphur, benzenepropanoic acid, cyclonasiloxane and cycloheptasiloxane were observed in most of the study locations of Vembanad backwater. Sources of most of these compounds are pharmaceutical in origin, that are used in day to day life and are found in almost all the stations which are mainly important tourist spots like Pathiramanal, Punnamada, Thanneermukkom etc. Scientific information about these emerging pollutants i.e., its source and its effects on aquatic organisms is still lacking. In this context, a detailed study about this is more relevant. The implementation of better management solutions must be urgently developed in order to avoid the further destruction of the estuary.

From this study, it is concluded that, the Vembanad backwater and the wetland system are seriously affected by environmental contamination and various emerging pollutants. The fluctuating environmental conditions and productivity pattern also influence the metal and other emerging pollutant distribution in the backwater. So, further detailed studies on a monthly basis and also eco toxicological evaluation are required to establish our deeper understanding on the environmental health of the backwater and its resources.

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1. INTRODUCTION

1.1 Wetlands

Wetlands are areas of land where the water level remains near or above the surface of the ground for most of the year. It covers about 6 % of the earth's land surface. They are critical for the maintenance of biodiversity and perform a great role in the biosphere and are often referred to as the "kidneys" of the earth. As they support a variety of plant and animal life, biologically they are one of the most productive systems in world. Utility wise, wetlands directly and indirectly support millions of people by providing services such as food, fiber and raw materials, storm and flood control, clean water supply, scenic beauty, along with educational and recreational benefits.

The value of the world's wetlands is increasingly receiving due attention as they contribute to a healthy environment in many ways, as they support different food chain, food webs, regulate hydrological cycle, recharge ground water, trapping of energy and shelter to large numbers of flora and fauna having great ecological and economical value. They provide suitable habitats for endangered and rare species of birds and animals, endemic plants, insects besides sustaining migratory birds. Many wetlands are seriously threatened by reclamation through drainage and landfill, pollution (discharge of domestic and industrial effluents, disposal of solid wastes), hydrological alterations (water withdrawal and inflow changes) and over exploitation of their natural resources resulting in loss of biodiversity and destruction in goods and service provided by wetlands. Among these, the effects of human-based threats are more devastating. In most countries these ecosystems were unluckily being destructed by human interferences which resulted in considerable loss of wetlands in all over the world. It is in this context, that the Ramsar convention becomes relevant.

The convention on wetlands, called Ramsar Convention, is an intergovernmental treaty that provides the framework for national action and international cooperation for the conservation and wise use of wetlands and their resources. The Ramsar Convention on Wetlands was developed as a means to conserve the wetlands by way of international attention to prevent the loss of wetland habitats, due to lack of understanding of their important functions, values, goods and services. Ramsar Convention describes wetlands as "Area of Marsh, Fen, Peat land or water whether natural or artificial, permanent or temporary with water, that is static or flowing, fresh, brackish or salt including areas of marine water, the depth of which does not exceed 6 meters" (https://www.bgci.org/resources/article/0373/). Wetlands are categorized into marine (coastal wetlands), estuarine (including deltas, tidal marshes, and mangrove swamps), lacustrine (lakes), riverine (along rivers and streams), and palustrine ('marshy'- marshes, swamps and bogs) based on their hydrological, ecological and geological characteristics (Cowardin *et al*., 1979). Ramsar Convention is the only global environment treaty dealing with a particular ecosystem. The main features of Ramsar Convention include recommendations for monitoring of biodiversity and anthropogenic impact; improvement of the legislation for protection of the wetlands; elaboration of economic mechanisms for the biodiversity protection while in nature management; organization of new protected areas.

1.2 Wetlands in India

World Wide Fund for Nature-India (WWF-India) observed that the wetlands are one of the most vulnerable of all ecosystems in India and are directly or indirectly linked with major river systems. Indian wetlands occupy 9.70 million ha. which is around 6.94 % of the geographic area (inland wetlands - 5.58 m ha. and coastal wetlands - 4.12 m ha) (Anon, 2011). Of the 27,403 wetlands in India, 23,444 are inland wetlands and 3,959 are coastal wetlands **(**http://pib.nic.in/). Coastal wetlands occupy an estimated area of 6,750 sq. km, dominated by mangrove vegetation. Coastal wetlands contain the vast intertidal areas, mangroves and lagoons along the 7500 km long coastline in West Bengal, Orissa, Andhra Pradesh, Tamil Nadu, Kerala, Karnataka, Goa, Maharashtra and Gujarat; Mangrove forests of Sundarbans, West Bengal and Andaman and Nicobar Islands; offshore coral reefs of Gulf of Kutch, Gulf of Mannar, Lakshadweep and Andaman and Nicobar Islands. It is assessed that wetlands support nearly one fifth of the known range of biodiversity in India and possess about 25 estuaries along its 7500 km coastline (Qasim, 2003) of which those heavily influenced by the south west monsoon (June-September) rainfall are referred to as monsoonal estuaries (Vijith *et al*., 2009).

Wetlands are being destroyed at an alarming rate of one percent per year (Gopalan *et al*., 1983). Concerns about changes in the size and quality of many of the world's wetland systems have been growing to a great extent owing to urbanization and pay ways to crucial environmental and ecological changes. Significant studies on various physico-chemical and biological aspects of estuarine coastal wetlands in India was done by various authors (Qasim, 2004; Madhu *et al*., 2007; Jayachandran *et al*., 2012; Bhattacharya *et al*., 2014 and Asha *et al*., 2016).

India is a signatory to the Ramsar Convention for the conservation and wise use of wetland, which includes in its ambit a wide variety of habitats such as rivers and lakes, coastal lagoons, mangroves, peat lands, coral reefs and numerous man made wetlands.

The National Environment Policy (2006) recognize the ecological services provided by wetland and emphasize the need to set up a regulatory mechanism consistent with the Ramsar Convention to maintain the ecological charter of the identified wetlands and develop a national inventory of such wetlands.

Kerala is located on the southernmost tip of India and blessed with a stretch of coastal wetlands. It provides a wide variety of aquatic habitats like rivers, streams, swamps, lakes, ponds, estuaries and backwater, which are considered as sites of exceptional biodiversity in the country. Kerala is blessed with 44 rivers and 217 wetlands, covers one-fifth of the total land mass. Among the 44 rivers, 41 of them flow westward and 3 eastward. Apart from these 44 rivers, their tributaries and distributaries and a countless number of streams and rivulets crisscross the land making it green and fertile and also serves as inland waterways. International Convention on wetlands designated three wetland ecosystems in Kerala (Fig. 1.1) Vembanad, Ashtamudi and Sasthamkotta as Ramsar sites for the conservation of biological diversity for sustaining human life through ecological and hydrological functions they perform (http://www.kerenvis.nic.in/; Bijoy Nandan, 2008). Among these, Vembanad wetland system is the largest wetland ecosystem in Kerala which plays an important role in the ecology and economy of the southwest coast of India. Based on the rich biodiversity and socio-economic importance, Vembanad backwater was declared as a Ramsar site (Ramsar site no.1214), a wetland of international importance in November 2002.

Fig. 1.1 Map showing the three Ramsar sites and Rivers of Kerala (Source: Modified from Wikimedia.org)

1.3 The Vembanad estuary

Vembanad wetland is the largest tropical wetland of south-west coast of India. It is the biggest 'Kayal system' on the south-west coast renowned, globally for its scenic beauty, pristine environmental conditions, diversity in bio-resources and livelihood conditions. Vembanad estuary along with adjacent Kol lands is the largest Ramsar site in India. Vembanad ecosystem is the third largest wintering waterfowl population in the country. The wetland contributes to over 50 % of the total area of backwater (Kayal) in the Kerala state. The estuarine system spreads across Ernakulam, Kottayam and Alappuzha districts of Kerala has occupied a total surface area of 36,500 ha. It is a complex system of backwater, marshes, lagoons, mangrove forests, reclaimed land and an intricate network of natural and manmade canals. It is an indispensable habitat to a variety of biologically and economically important resident, migratory aquatic and avian fauna. So the Vembanad ecosystem is identified as an Important Bird Area (IBA) by Birdlife International. More than 20,000 fishermen are directly dependent on the aquatic resources of this wetland fetching over 7000 t of fish and shellfish annually. The Thanneermukkom barrage constructed in 1975 across the Vembanad estuarine system separates the water body into a freshwater dominant zone on the south and a salt water dominant zone on the north, resulting complete changes in physical, chemical and biological structure of the wetland system. The bund was constructed to regulate salt water intrusion to the Kuttanad agrarian system (Bijoy Nandan *et al.*, 2014).

The ecosystem is unique in terms of physiography, geology, climate, hydrology, land use and flora and fauna. There are two rainy seasons in Kerala, the southwest monsoon and northeast monsoon. On an average 60 % of the annual rainfall occurs during the southwest monsoon period and 30 % occurs during the north east monsoon. The remaining 10 % occurs during December to May as occasional dry spell. Vembanad backwater receives the mean annual rainfall of 2245.55 mm. Vembanad backwater obtains freshwater discharge from six rivers viz. Periyar (5400 km^2, 244 km) and Muvattupuzha (1550 km^2, 121 km) on the north, the Meenachil (1250 km^2, 78 km) Manimala (850 km^2, 90 km), Pamba (2250 km^2, 176 km) and Achankovil (1500 km^2, 128 km) in the southern region (Anon, 2008; www.nio.org) (Fig. 1.2). These rivers which originate from Western Ghats - the biodiversity hotspot drain to the estuary and eventually join the Arabian Sea.

The Vembanad and other backwater systems of Kerala have great potential for fisheries and ecotourism development. Tourist resorts around the backwater and houseboat playing in the backwater are the economic evolution marketing the scenic beauty and natural charm of Vembanad estuary. The Vembanad estuary with its vast extend of water, greenery along the border with paddy fields and very vibrant nature around the estuary attract tourist from India and abroad. There are drastic growths in tourism sector in and around Vembanad estuary for the past two decades. Hike in tourism sector in Alappuzha district improve employment potential in these area and got minimum one or two members from each family of Kuttanad area got employment in tourism industry as houseboat operators or other employment related to houseboat and backwater tourism. Apart from recreational activities, thousands of houseboats and shikkari boats, plying on a luxury basis is creating serious environmental concerns associated with overcrowding of the estuary (Plate 1). Even though the tourism sector in the region has greater economic benefits which are a source of employment and income, there also involve negative socio-environmental impacts (Vijayakumar, 2009). Operation of houseboats is also affecting the environment and ecosystem of Vembanad estuary. Waste generates from houseboats such as sewage from toilets, oil from engines, plastic wastes and food wastes which leads to the degradation of the estuarine ecosystem.

Plate 1 Various source of pollution attributes in Vembanad backwater system
(a) & (b) Undisposed wastes in backwater **(c) Unused rusted boats in backwater**
(d) Toilet directly in contact with backwater **(e) Water discharges from agricultural fields**

1.4 Kuttanad wetland system

Kuttanad is a deltaic trough like formation shaped by the confluence of four major rivers of the state, the Meenachil, the Manimala, the Pamba and the Achankovil and is the part of the Vembanad - Kol wetland system. Geologically Kuttanad is considered as a recent sedimentary formation. In the geological past, the entire area was a part of the Arabian Sea. Though the boundary of Kuttanad is rather loosely defined and the extent of its area has been variously computed at different times, now it encompasses 79 revenue villages, 10 taluks and 3 districts. Cherthala, Ambalappuzha, Chengannur, Kuttanad, Karthikappally and Mavelikkara taluks in Alappuzha districts, Thiruvalla taluk in Pathanamthitta district and Changanassery, Vaikkom and Kottayam taluks in Kottayam districts covering an area of 870 sq. km (http://www.kuttanadpackage.in/). In ancient days, the term, '*Kuttanad'* referred to a much larger area than what it denotes at present. During those times, the region extended from Karunagappally to Alwaye that comprised the "Kuttanad". There was no historical record on the origin of Kuttanad, there are certain folklore connected with Kuttanad. In the geological past, the Kuttanad region was a part of the shallow coastal area of the Arabian Sea. As a result of a geological uplift, a shallow bay was formed into which several rivers discharged. The silt deposited at river mouths gave rise to the present delta and the shallow bay formed into a lake-lagoon backwater system opening on to the Arabian Sea through the Kochi barmouth.

1.4.1 Agriculture in Kuttanad

Kuttanad is a land reclaimed from Vembanad backwater. The rivers and the topography categorize it into three major ecological zones - Upper Kuttanad, Lower Kuttanad and Kayal land

Upper Kuttanad - This area located in the south eastern side of Kuttanad and is comparatively high lands. The elevation ranges from 0.5 to 6 m above MSL (Anon, 2007). Upper Kuttanad area is comparatively low risk from saline intrusion and flood. Three major rivers include Achankovil, Pampa and Manimala enter Kuttanad in this zone.

Lower Kuttanad- It is located north of upper Kuttanad. The area lies in 1 to 2 m below MSL in some parts and experiences flood and saline water intrusion. The flood season is slightly of more duration compared to other zones. The presence of a number of small islands with human habitation is a special feature of this zone.

Kayal lands -This zone lies north of lower Kuttanad. The area includes Kayal rice fields, which were reclaimed by earthen bunding of the shallow portions of south eastern part of the Vembanad backwater. These fields lie 1 to 2 m below MSL. The flood risk and saline water intrusion is high.

Kuttanad - the 'rice bowl of Kerala' (1.5 to 2 m below sea level) spread over 1100 km^2 and has been declared as a Globally Important Agricultural Heritage Systems by United Nation's Food and Agriculture Organisation for its below sea-level farming system (Anon, 2013a). The Kuttanad region is dominated by the groups of paddy lands known as *padasekharams* (polders) protected by bunds for *punja* (dry season) rice cultivation (Plate 2). Agriculture is the main economic activity about 40 % of the population in Kuttanad. Paddy is the main crop and coconut is grown in the outer bunds of polders. Major constrain to agricultural production is flooding which leads to crop loss. Flooding is worst where the rivers from the upper catchments enter the area in upper Kuttanad, and the least near the backwater. The flood storage capacity of the wetland in turn is closely related to the land use pattern, mainly the extent of rice cultivation in polders. Thottappally spillway and Thanneermukkom barrage protect the 'Punja Padams' of Kuttanad from tidal intrusion of saline water and to regulate flood water-Thottappally spillway (1955) and Thanneermukkom barrage (1976) was constructed as a comprehensive scheme for development of Kuttanad was drawn up by Government of Kerala. Kuttanad area and the community associated with the region were facing extreme agrarian distress over the last five decades mainly due to various factors. Based on the request of Government of Kerala to address the perennial problems faced in Kuttanad, the Union Government entrusted Dr. M. S. Swaminathan Research Foundation (MSSRF), Chennai to conduct a detailed scientific study of the region and to suggest suitable measures to mitigate agrarian distress in Kuttanad. The MSSRF recommended a number of schemes to be executed as a Kuttanad package with a total outlay of Rs. 1,840 crore which was accepted by Govt. of India.

Plate 2 Showing major highlights of Vembanad backwater

(a) & (b) Agricultural fields **(c) & (d) Houseboat tourism activities**

(e) Fishing activities and **(f) A view of Pathiramanal Island**

1.4.2 Kuttanad package

Considering the prevailing severe agrarian distress-Kuttanad Agriculture, Government of India for special consideration to go into the economic and ecological problems of the Alappuzha district as well as the Kuttanad wetland ecosystem as a whole. The objective of the package was to propose measures for strengthening ecological security of Kuttanad and for expanding sustainable livelihood opportunities for the local people through work and income security (http://www.kuttanadpackage.in/). The package recommended a variety of interventions to be implemented with a total cost outlay of Rs. 1,840 crore. The report contains a malady-remedy analysis of the problems and potential solutions and the suggestions include - creation of Special Agricultural Zone (SAZ), restoration of natural drainage systems, minimizing ecological damage caused by TMB, functional restoration of Thottappally spillway, reducing pollution of Kuttanad waters, improving logistics of padasekharams, revitalization of fisheries, promoting environmentally sustainable water tourism, promoting group farming, enhancing income from coconut farming system, improving productivity and profitability of rice farming. The main tasks recommended in the package are: (1) protection and ecological restoration of the water spread area; (2) measures for salinity and flood management in Kuttanad; (3) measures for pollution control; (4) total elimination of aquatic weeds; (5) measures for augmenting biodiversity in the backwater; (6) improving health and sanitation; (7) declaring Kuttanad a Special Agricultural Zone; (8) provide infrastructure support to paddy cultivation; (9) enforce crop calendar; (10) strengthening of research and extension; (11) strengthening economic viability of farming; (12) coconut-based enterprises and integrated farming; (13) actions to promote fishery wealth of Vembanad backwater; (14) promoting fish infrastructure and (15) infrastructure support to facilitate responsible tourism (under water tourism and local ecology) (Anon, 2007).

When the Kuttanad package was launched at 2008, it had only one aim - the overall development of the region and its people. But after the tenure of the package in 2013 the progress of work being done in the name of the package was a big failure. In the name of development, Kuttanad has been subjected to indiscriminate human interventions. Criss-cross roads have come up in the State's granary by reclaiming paddy fields and canals. Added to these are multi-storied buildings for business and residential purposes. Thus, the carrying capacity of Kuttanad has already reached its peak. Therefore, the attempt to dump several lakh tonnes of granite boulders and concrete pile and slabs in this fragile area would have serious ecological and environmental impact. Expressing his dissatisfaction over the implementation of the Kuttanad package M. S. Swaminathan admitted the fault in the implementation of the Kuttanad package in a time bound-manner. He said that lack of time bound implementation and some kind of criteria/standards affect the productive nature of the project accomplishment. He added that the failure to set a time schedule and the lack of coordination among various government departments were the major factors that adversely affected the implementation of the package (Anon, 2013c). Poor research and development support for package lead to its failure of implementation and the lack of right resources with the right skills also increases the impact. Lack of establishment of professional implication triggered the complete failure of the package.

The State Government had requested the Govt. of India to extend the time frame for completion of various schemes proposed under the Kuttanad Package up to December 2016. So the Govt. of Kerala can go ahead with work in 231 paddy polders of Kuttanad having a total outlay of Rs. 379.05 crore and 12 works with a total outlay of Rs. 248.39 crore for the Onattukara region. In the meantime the Union government has also issued orders extending the time frame for completion of work in 14 paddy polders in Kuttanad falling under Group 1 and work in four polders in the backwater.

Union Govt. has sanctioned the renovation of the Thanneermukkom bund converted into barrage at an estimated cost of Rs. 255.34 crore under the Flood Management Scheme (FMS) (Anon 2014b). The third phase of construction of the Thanneermukkom barrage was started on September 16, 2014 and works worth Rs. 240 crore is envisaged to be undertaken in the project as part of the Kuttanad package. The earthen bund is being replaced with 31 steel shutters, which had been originally envisaged in the project. The construction of the shutters is being carried out at a cost of Rs. 181 crore. In addition, the existing shutters, many of that are damaged, will be replaced with stainless steel at a cost of Rs. 45 crore. An amount of Rs. 13.4 crore will also be utilized for enhancing the capacity of the leading channel of the Thottappally spillway. The works will be undertaken by the Irrigation Department and the project is targeted to be completed within three years (Anon, 2014).

1.5 Major rivers draining into Vembanad backwater

Pamba River is the third largest river in Kerala and is popularly called as Dakshina Ganga. It has a length of about 176 km and a catchment area of about 2235 km^2. The river originates from Pulachimala in the Western Ghats at an altitude of about 1650 m above msl and flows through highly varied geologic and geomorphic provinces of the state like Ranni, Ayroor, Pathanamthitta, Kuttanad etc. and then finally ends up in the Vembanad backwater. The river drains through Pathanamthitta (Major portion) and Alappuzha (minor portion) district and enters into the Vembanad backwater near Kainakary. The river displays dendritic to suddendritic drainage pattern. Pamba basin is surrounded by Western Ghats on the east, Manimala river basin in the north and Achankovil River in the south.

Achankovil River originates from the hills of Achankovil in Pathanamthitta district and flows through Mavelikkara, Thiruvalla and Karthikapally taluk and it join with river Pamba at Veeyapuram, in Alappuzha district, near the Vembanad backwater (http://kerala-rivers.blogspot.in/). The total length of the river is 128 km and its average annual stream flow is 2600 mm^3. Achankovil River shares its northern boundary with Manimala river basin.

Manimala River is one of the perennial rivers of Kerala with a length of about 90 km and a catchment area of about 847 km^2. The river originates from the Thattamalai hills at an elevation of 1156 m above msl and drains through the highland, midland and the lowland physiographic provinces of Kerala. The river spreads over Idukki, Kottayam and Pathanamthitta districts and empties into the Vembanad backwater, after merging with the Pamba at Valanjavattom near Thiruvalla. Manimala River displays a dendritic drainage pattern. The extensively developed sandy plains and point bars, used for holding annual religious congregations are vanishing at rapid rate due to indiscriminate sand mining.

Meenachil River flows through the heart of Kottayam district of Kerala and have a length of 78 km and water spread area of 1208.11 km^2 and flows through Poonjar, Teekoy, Erattupetta, Palai, Ettumanoor and Kottayam before emptying itself into the Vembanad backwater at Kumarakom, the famous tourist place of Kerala. The Meenachil River is formed by several streams originating from the Western Ghats. The general elevation ranges from 77 m to 1156 m in the high lands and less than 2 m in the lowlands and 8 to 68 m in the midlands. The river has a total annual yield of 2,349 million cubic meters and an annual utilizable yield of 1110 million cubic meters. The river has 38 tributaries including major and minor ones. The river has 47 sub watersheds and 114 micro watersheds.

Muvattupuzha River has a length of 121 km and has an average annual stream flow of 3560 mm^3. The word "Muvattupuzha" is composed of three words 'Moonu' meaning three, 'Aaru' meaning small river and 'Puzha' which also means river. As the word indicates, Muvattupuzha River is also composed of three rivers namely Kothamangalam River, Kaliyar River and the Thodupuzha River, all of which together forms the Muvattupuzha River draining into Vembanad backwater near Vaikkom region. The industrial activities mainly by the Hindustan Newsprint Limited situated near the banks of Muvattupuzha River and the effluent from the industry affect the water quality of the river.

Periyar River is the longest river in Kerala state having a length of about 244 km. It originates from Sivagiri hills of Western Ghats. The average annual stream flow of Periyar was 4867 mm^3. The river flows along almost virgin forests in places such as Kokaripara, Neriamangalam, Edamalayar and Malayattoor. At Alwaye the river bifurcates into two, Marthandavarma and Mangalapuzha branches. The Mangalapuzha branch joins Chalakudy River and empties into the Arabian Sea at Munambam while the Marthandavarma branch flows southwards, through the Udyogmandal area and joins the Cochin backwater system at Varapuzha (Periyar Valley Irrigation Project (PVIP), 1972). Periyar River plays a major role in the economy of Kerala. Major portion of Kerala's electrical power get through the hydroelectric projects in Periyar River. Kochi city depend up on Periyar River for the drinking water source. Twenty five percent of Kerala's industries are situated along the banks of Periyar River.

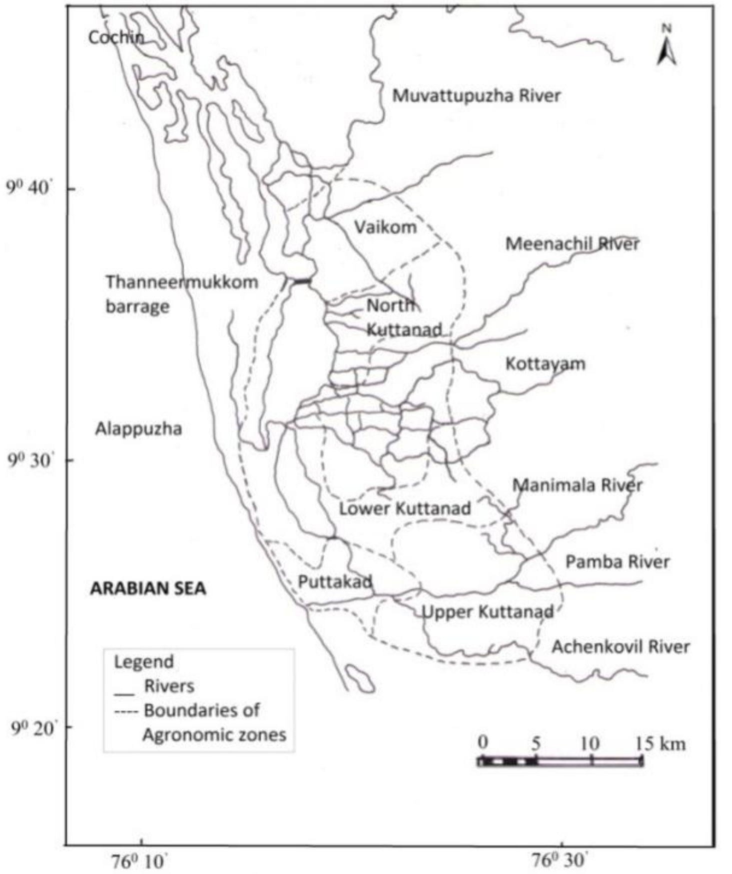


Fig. 1.2 Map showing the rivers joining the Vembanad backwater

1.6 Significance of the study

The Vembanad backwater have acquired a new status on account of their unique physical, biological and aesthetic values and are recognized as Ramsar site of international importance being a significant value not only for the country, but also for humanity as a whole. As a transitional ecotone between sea and land, Vembanad estuarine system is a highly productive environment, providing feeding, spawning and rearing areas for fishes, supporting rich fishery resources (eg. variety of finfish, shellfish, several species of marine fishes and shrimps). It also acts as a sink and transformer for the agricultural and municipal wastes discharged into it. The hydrological significance of tropical water bodies has often been overlooked by acute needs of human requirements such as population growth, progressive industrialization, enhanced food production and recreation. The coastal region around Vembanad backwater is one of the most thickly populated areas of Kerala and it is a single ecosystem next to the Arabian Sea in terms of supporting maximum livelihood activities and large numbers of people are directly dependent on the backwater.

Over the last three decades the ecological status of the Vembanad estuary is under severe environmental stress mainly due to the anthropogenic intervention notably from land reclamation, pollution due to discharge from various sources, reduction and shrinkage of water body, due to natural and human intervention, habitat changes, depletion and extinction of bio resources thereby affecting the livelihood condition. Alterations in natural hydrologic regime of Vembanad wetland started with the commissioning of Thanneermukkom barrage (TMB) across the backwater system in 1975, to prevent saline water intrusion, which adversely affected the eco-biology of the water body (Asha *et al*., 2016) and transformed the estuary into two distinct ecosystems, a fresh water zone on the south and a brackish water zone on the northern side of the barrage. However, faulty designing and partial construction of the barrage had brought up with unanticipated misfortunes to agriculture and biotic components in the system including fishery sectors of the region. The most discernible among them was a virtual stagnation of water body in the southern sector and its adjoining canals and water ways during summer months, resulting in serious changes in the eco-hydrobiology of the area.

Pollution from various sources affects the water and soil quality condition, unfriendly fishing practices leading to depletion and extinction of resources. The drastic growth in tourism sector in and around Vembanad backwater for the past two decades mainly, the houseboat tourism leads to the degradation in water quality of the estuarine system eventually resulting in health and sanitation problems. Vembanad backwater has been continuously subjected to the land reclamation for various purposes such as agriculture expansion, agriculture practices, harbor development, urban development and other public and private uses. Wastes from aquaculture fields, coconut husk retting yards, fish processing, plants and animals bone processing units have increased the organic pollution in the Vembanad backwater.

Because of the persistent nature, inherent toxicity, vast sources and non-degradability, heavy metals in effluents are considered as one of the most burning problem. Heavy metals from various sources such as mining, smelting, agriculture, petrochemical industry, printing, aquaculture, electronic industry and municipal waste discharged to the aquatic environment can be bioaccumulated by the organism and biomagnified through food chain. Metal contamination in aquatic systems is a serious problem that affects human health and many of the organisms particularly fish forms, an integral part of human diet. Therefore a better understanding of the status of heavy metal pollution is inevitable for the sustainable development of the coastal marine ecosystem (Anu *et al.*, 2014). The chemical industries near the Vembanad backwater release nearly 260 million L of effluents/day to the wetland system. Sixteen major industries around Cochin discharge nearly 0.104 mm^3/d of waste containing organic load into the nearby Cochin estuary (Balachandran *et al*., 2006).

Pesticides are chemicals or mixtures of chemicals, which are used for controlling, preventing, destroying, repelling, mitigating or reducing any pests. Many of the pesticides are available today for the control of unwanted organisms. Pesticides have made a great impact on human health, production and preservation of foods, fiber and other cash crops by controlling disease vectors and by keeping in check many species of unwanted insects and plants. More than 55 % of the land used for the agricultural production in developing countries uses about 26 % of the total pesticides produced in the world.

However, the rate of increase in the use of pesticides in developing countries is considerably higher than that of developed countries. Like many other nations of Asia, India is predominantly an agricultural country. In Kerala, rice is the predominant cereal crop, of which Kuttanad area accounts for more than 20 % of rice production. The use of pesticides in rice is more compared with other crops. Several persistent pesticides, including DDT were banned for use in agriculture, but are still used for the eradication of vector transmitted diseases. Environmental contamination of water and sediment by pesticide residues is of great concern. The Vembanad backwater receives considerable amounts of agricultural run-off from the "padasekharams" and run-off from four major rivers. Preliminary investigations revealed that the most prominent organic pollutants discharged to these estuarine waters were mainly pesticide residues and their metabolites (Babu, 2001).

According to the survey conducted by South Asian Network for Development and Environmental Economics (SANDEE, 2007) in Kuttanad, 19 different insecticides, 3 different weedicides and 4 different fungicides, including both organochlorine and organophosphate pesticides were used to protect crops in Kuttanad. These were considered to be the main source of metal and pesticide pollution in the Vembanad backwater system. Though isolated studies are available on the distribution of trace metals and pesticides in water, sediment and biota of the entire region of the Vembanad backwater system, no major in - depth and long term ecological monitoring studies based on vital/broad parameters are available on the entire region of the Vembanad wetland ecosystem.

The Vembanad backwater has immense conservational importance as it supports a large aquatic biodiversity and is the most important migratory bird habitat. The deterioration of quality leads to the degradation of wetland, therefore, a great threat for sustainable economic growth of the entire region. In this context, the objectives of the study are;

Since, Vembanad backwater is facing multiple threats from various anthropogenic issues like, pollution, encroachment for various developmental activities and related matters it is relevant to update and have a reliable data and information on the current environmental quality of the wetland area. The reported information also suggests that, there is deep lacunae in our knowledge on the heavy metal and pesticide contamination in the water body and associated area.

1.7 Objectives of the study

- To study the critical water and sediment quality of Vembanad backwater.
- To assess nutrient loading in the backwater from various sources.
- To study selected trace metal and other contaminants.
- To propose an ecosystem model for management based on the data generated.

2. MATERIALS AND METHODS

2.1 Study area

The Vembanad estuarine system (09˚00’ - 10˚40’ N and 76˚00’ - 77˚30’ E) forming a major part of Vembanad Kol wetland, a Ramsar site on the south west coast of India is the largest estuarine system well known internationally for its unique, endemic biodiversity and livelihood opportunities. It is bordered by Alappuzha, Kottayam and Ernakulam districts of Kerala covering an area of about 200 sq. km and extending 80 km in a NW-SE direction from Munambam in the north to Alappuzha in the south, with an average depth of <1 m to 9 m. The estuary has two permanent openings into the Arabian Sea - at Cochin and Azhikode. The Cochin gut is 450 m wide, at the same time Azhikode gut is 100 m wide and fairly deep. Manimala, Meenachil, Pamba and Achankovil rivers flows into the estuary through the south of Thanneermukkom and Periyar, Muvattupuzha River flows into the north of Thanneermukkom barrage.

2.2 Study stations

Nineteen different stations were identified for field sampling based on ecological importance. The geographic positions of study stations were fixed using GPS (Global Positioning System). The study stations, selected were St.1 - Aroor, St.2 - Perumbalam, St.3 - Thanneermukkom north, St.4 - Thanneermukkom south, St.5 - Pathiramanal, St.6 - Punnamada, St.7 - Nehru trophy finishing point, St. 8 - Pangankuzhipadam, St.9 - Pallathuruthy, St.10 - Meenappally, St.11 - Kainakary, St.12 - C Block Cherukayal, St.13 - Kuttamangalam, St.14 - Ranikayal, St.15 - Marthandam, St.16 - Chithirakayal, St.17 - Varanadu, St.18 - Kuppapuram, St.19 - Meenappally Vattakayal. The map showing the study stations are given in Fig. 2.1

Table 2.1 Study stations in Vembanad estuary

Sl. No.	Station	Geographic Position
1.	Aroor	9^{0} 52’ 22’’N and 76^{0} 19’ 47’’E
2.	Perumbalam	9^{0} 49’ 48.59’’N and 76^{0} 21’ 56.22’’E
3.	Thanneermukkom-north	9^{0} 40’ 41.47’’N and 76^{0} 23’ 36.25’’E
4.	Thanneermukkom-south	9^{0} 40’ 32.72’’N and 76^{0} 23’ 36.45’’E
5.	Pathiramanal	9^{0} 37’ 18.76’’N and 76^{0} 22’ 30.55’’E
6.	Punnamada	9^{0} 30’ 18.41’’N and 76^{0} 21’ 19.39’’E
7.	Nehru trophy finishing point	9^{0} 29’ 59.71’’N and 76^{0} 21’ 22.66’’E
8.	Pangankuzhipadam	9^{0} 30’ 23.30’’N and 76^{0} 21’ 55.74’’E
9.	Pallathuruthy	9^{0} 48’ 695’’N and 76^{0} 36’ 491’’E
10.	Meenappally	9^{0} 29’ 50’’N and 76^{0} 23’ 02’’E
11.	Kainakary	9^{0} 31’ 32’’N and 76^{0} 22’ 35’’E
12.	C Block Cherukayal	9^{0} 31’ 17.47”N and 76^{0} 23’ 34.60”E
13.	Kuttamangalam	9^{0} 29’ 37.25’’N and 76^{0} 23’ 04.83’’E
14.	Ranikayal	9^{0} 32’ 10.91’’N and 76^{0} 22’ 54.45’’E
15.	Marthandam	9^{0} 53’ 560’’N and 76^{0} 40’ 500’’E
16.	Chithirakayal	9^{0} 32’ 35’’N and 76^{0} 24’ 19’’E
17.	Varanadu	9^{0} 41’ 586’’N and 76^{0} 22’ 185’’E
18.	Kuppapuram	9^{0} 41’ 586’’N and 76^{0} 22’ 185’’E
19.	Meenappally Vattakayal	9^{0} 29’ 23.12’’N and 76^{0} 22’ 46.87’’E

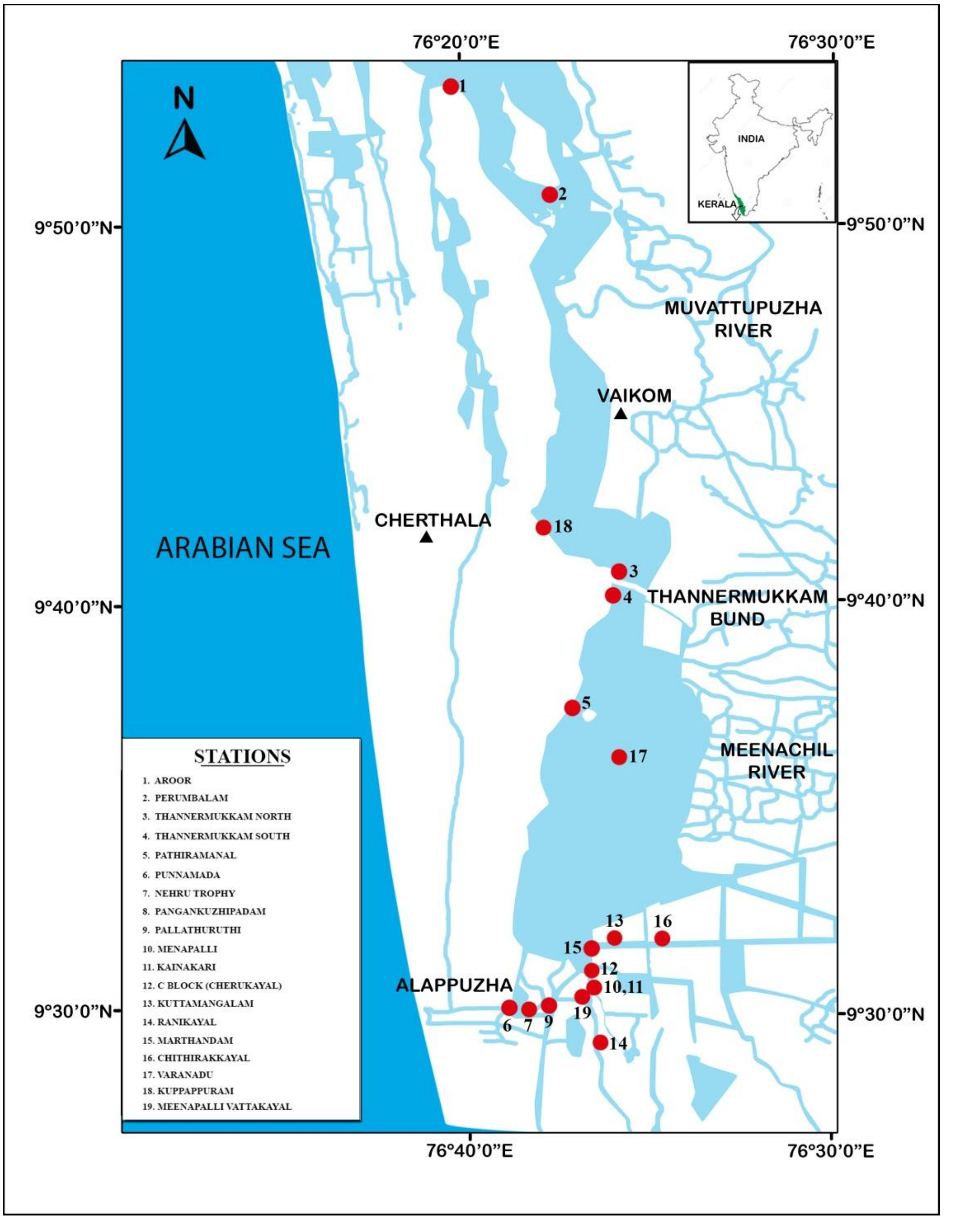


Fig. 2.1 Map of Vembanad estuarine system showing the study stations

Station 1: Aroor (lat. 9^0 52’ 22’’N and long. 76^0 19’ 47’’E)

The station is situated near to barmouth (about 9 km) of the estuary and is highly influenced by the tidal action, currents and saline water intrusion from the nearby Lakshadweep Sea. It is seafood related industrial area located at the south of Kochi. The abundance of marine wealth and logistical advantages has helped the seafood export grow especially around Aroor. Thus the station is also affected by the discharges from seafood industries situated in the banks of the estuary. Sewage wastes from the Kochi city is also a major threat to the station. The Cochin Shipyard and the Cochin Port are releasing sizable quantities of waste oil, metal and paint scrapings into the station. Fishing activities with stake nets and cast nets by traditional fishermen could be observed here. The heavy movement of motor boats was observed across the station.

Station 2: Perumbalam (lat. 9^0 49’ 48.59’’N and long. 76^0 21’ 56.22’’E)

Perumbalam is an island, located in the central part of the Vembanad backwater, which is wedge shaped, pointing towards the barmouth. It is bordered by Ernakulam district on the north and Kottayam district on the south. Most beautiful attraction in this island is backwater and traditional fishing. Perumbalam is also famous for its coir products and a land of lush paddy fields. The station is about 14 km away from Cochin barmouth and is highly influenced by anthropogenic interventions like encroachment, land filling and construction activities in the small islands of the water body. Mining by local fishermen for clam fishery was widely observed in the area and fishing by cast nets, stake nets could also be seen here. There was a number of illegal construction activities in the lake especially in small private Island Nediyanthuruthu situated near to the Perumbalam Island.

Station 3: Thanneermukkom north (lat. 9^0 40’ 41.47’’N and long. 76^0 23’ 36.25’’E)

This station is located on the northern side of the Thanneermukkom barrage, at a distance of about 150 m north of the barrage and 40 km from the Cochin barmouth. The station acts as a transition zone between north and south of the backwater. This station experiences the action of tides and currents arising from the barmouth at Cochin. Intense fishing activity, sand mining and inland water transport activities were seen actively in this zone. The station is a major source of clam, *V. cyprinoides,* which provides livelihood for thousands of fisher-folk.

Station 4: Thanneermukkom south (lat. 9^0 40’ 32.72’’N and long. 76^0 23’ 36.45’’E)

This station is located on the south of Thanneermukkom barrage, about 400 m away from barrage and on the narrowest part of Vembanad estuary. This station is influenced by tides and currents arising from the Cochin barmouth on the northern side of the water body. It is also part of the main basin of the estuary and is almost the central part of the water body extending from Alappuzha to Cochin. Intense fishing activity, sand mining and inland water transport activities were observed in this zone. The unscientific operations of the Thanneermukkom barrage have blocked the connectivity of the water body to the sea for a good part of the year. Thanneermukkom barrage severely affects the ecological characteristics of this zone and restrained the seasonal intermixing of fresh and saline water and thereby interfering with natural cleansing mechanisms of wetland and threatening accelerated loss of habitats and biodiversity.

Station 5: Pathiramanal (lat. 9^0 37’ 18.76’’N and long. 76^0 22’ 30.55’’E)

The study station is a small island (28.505 ha.), in Muhamma panchayat of Alappuzha district, harboring rich biological diversity which is the fresh water zone of Vembanad backwater. The island is fringed by mangroves and associates and is around 7.5 km away from the barrage. It emerged as an important roosting site for water birds due to availability of food and negligible human habitation was observed in the surrounding areas. Oriental darter, a near-threatened bird species and the vulnerable spot billed pelican *Pelicanus philippensis*, is known to visit here. It is the home for 91 local species of birds and 50 migratory birds from different parts of the world. The island stands out in terms of species diversity, 24 species of dragonflies and damselflies, 23 spiders, 34 butterflies, 88 birds, 58 fishes and 7 reptiles have been recorded from here. Land drainage from the island could be observed particularly during the monsoon period. The island has been beautified by State Tourism Department by laying road ways and planting trees that has probably altered the topography of the area. Fishing activity, clam fishery mining and tourism related activities are seen in the area. Operation of Thanneermukkom barrage, have altered the natural ecological characteristics of the station.

Station 6: Punnamada (lat. 9^0 30' 18.41''N and long. 76^0 21' 19.39''E)

Punnamada is the southern region of the Vembanad backwater. This portion of the Vembanad backwater is located in Kuttanad region in Alappuzha district. Punnamada is one of the leading tourist destinations in the world. The well-known Nehru trophy boat race is annually being conducted in Punnamada Lake. This station is severely influenced by houseboat tourism activities and sewage disposal from Alappuzha city. Schools, churches, temples, big and small resorts, home stay etc. are seen around on either side of the Punnamada station. The Water Sport Centre under the Sports Authority of India is also located in this station. The unrestricted operation of houseboats in Punnamada Lake has caused serious environmental pollution. Fishing activities are also active in Punnamada region. The riverine inflow from Pamba, Achankovil and Manimala plunge into Vembanad backwater is through Punnamada. Organic and inorganic fertilizers from the Kuttanad paddy fields directly get drained into this station.

Station 7: Nehru trophy finishing point (lat. $9^0$29'59.71''N and long. $76^0$21'22.66''E)

The station is situated on the southern region of the estuary which is the finishing point of the famous Punnamada boat race. The station is influenced by the river discharge from Pamba, Manimala and Achankovil. Temples, resorts, boat jetties are seen around the station. Sewage discharge from houseboats, resorts and Alappuzha town seriously affects the station. Fishing activities by local fishermen can also be observed.

Station 8: Pangankuzhipadam (lat. 9^0 30' 23.30''N and long. 76^0 21' 55.74''E)

Most of the land in this area is used for paddy cultivation and people living in this area are engaged mainly in agricultural practices and fishing. Agricultural runoff including pesticide residues and fertilizers from these paddy fields and domestic sewage are major factors which affects the hydrology of this zone.

Station 9: Pallathuruthy (lat. 9^0 48' 695''N and long. 76^0 36' 491''E)

This station is situated on the south eastern side of the estuary with low lying paddy fields bordering it. It is about 45 km away from the Thanneermukkom barrage. It is a water bound region surrounded by the Vembanad backwater and the Pallathuruthy canal passes through the region. Pallathuruthy has become an inevitable tourist spot, vital vein for houseboats as well as artisanal fishing activity. Like the rest of Kuttanad, most of the land in Pallathuruthy is used for paddy cultivation. Riverine inflow from Pamba, Achankovil and Manimala influence the station. Human disturbances, mainly by large scale tourism developments in Pallathuruthy are increasing; and have a negative impact on its natural beauty. Agricultural runoff from the polders (padasekharams), sewage disposal from houseboats, human settlements and floating weeds around seems to be affecting the station. Agrochemicals including fertilizers, insecticides, domestic sewage and urban wastes from Alappuzha town severely affect the water quality of Pallathuruthy. Usage of these polluted waters for domestic purposes has led to several waterborne epidemics.

Station 10: Meenappally (lat. $9^0$29' 50''N and long. $76^0$23' 02''E)

This is a small village on the southernmost part of the estuary. The station is influenced by the discharges from Pamba River. Increased houseboat tourism and boat jetties around the station have negative impacts. Church, temple and other human settlements are also seen on either side of the station. The major income is agriculture and fishing.

Station 11: Kainakary (lat. $9^0$31' 32''N and long. $76^0$22' 35''E)

The station is famous for its pristine scenic beauty. It is situated on the eastern side of the estuary. The lush green coconut trees and paddy fields surrounded by blue water make this area an attractive tourist spot. The station is influenced by the river discharge from Pamba and Manimalayar. Kainakary is synonymous with 'Kettuvallam' or houseboats. It is famous for its snake boat race rowers. The major income is from agriculture and fishing. Human settlements and large scale tourism activities have negative impacts. Sewage discharge from houseboats and domestic wastes also affects the station.

Station 12: C Block Cherukayal (lat. 9^0 31' 17.47"N and long. $76^0$23'34.60"E)

The station is situated on the eastern side of the estuary. It is influenced by the field discharge from nearby padasekharams and riverine inflow from Pamba and Manimala. R block is the nearest padasekharams situated on the eastern side of the station.

Station 13: Kuttamangalam (lat. 9^0 29' 37.25''N and long. 76^0 23' 04.83''E)

The station is situated on the eastern side of the estuary, which is a small village; the green paddy fields were boarded by coconut trees. This station is influenced by the riverine inflow from Manimala and Pamba River.

The solid waste from houseboats and runoff from agricultural fields probably influences the station. Churches and temples are also seen around the station.

Station 14: Ranikayal (lat. 9^0 32’ 10.91’’N and long. 76^0 22’ 54.45’’E)

The station is influenced by the riverine inflow from Pamba and Manimala. Field discharge from nearby R and C block padasekharams affects the station. Increased houseboat tourism and related activities have negative impact on the hydrology of the zone. This station is situated on the eastern side of the estuary.

Station 15: Marthandam (lat. 9^0 53’ 560’’N and long. 76^0 40’ 500’’E)

This station is situated on the eastern side of the estuary and is influenced by the discharges from Pamba and Manimala River. The station is about 32 km away from Thanneermukkom barrage. The R Block and C Block are the nearest padasekharams situated on the eastern side of this station. Agricultural runoff including pesticide residues and fertilizers from these padasekharams is a major factor which affects the hydrology of this zone. It is also a major area of clam (*V. cyprinoides*) fishery. The station is a major site for night halting of majority of the houseboats apart from Punnamada and Kainakary. The station gives way for the inland water way for transport boats. All these boating activities trigger fuel emissions from boat motors, suspension of bottom sediments, decreased water transparency, shoreline erosion, destruction of fish spawning areas and loss of valuable fish. Uncontrolled houseboat tourism in the peak of tourism season subjects this station to indiscriminate exploitation beyond its carrying capacity. The solid waste from boats and runoff from agricultural fields probably influences the station**.**

Station 16: Chithirakayal (lat. $9^0$32’ 35’’N and long. $76^0$24’ 19’’E)

The station is situated on the eastern side of the estuary which is influenced by the field discharge from R and H block padasekharams. Agricultural runoff including pesticide residues and fertilizers from these padasekharams and riverine inflow from Pamba and Manimala are the major factors affecting the hydrology of this zone. Houseboat tourism and related activities also affects the station.

Station 17: Varanadu (lat. 9^0 41’ 586’’N and long. 76^0 22’ 185’’E)

This station is influenced by discharge from Mc Dowell and Company’s distillery unit situated on the western side of the water body. Both raw and treated effluents from the distillery are being directly discharged into this station with high organic load causing severe fouling of the atmosphere. It is about 34 km away from Cochin barmouth and 5 km from the barrage. Fishing activity by local fishermen using cast nets and traps could be seen around. Continuous dredging for clam shell beds by the Travancore Cements Ltd. (TCL) for the production of white cement was evident in the area, which adversely affects the water quality and benthic biodiversity.

Station 18: Kuppapuram (lat. $9^0$30’ 06’’N and long. $76^0$22’ 56’’E)

This is a small village situated on the southern part of the estuary. Most of the land in Kuppapuram is used for paddy cultivation and people living in this area are engaged mainly in agricultural practices and fishing. Field discharge, including pesticide residues and fertilizers and domestic sewage are major factors which affects the hydrology of this zone. This area is influenced by the discharges from Pamba River. Church, temple, boat jetties are seen around the station.

Station 19: Meenappally Vattakayal (lat. $9^0$29’23.12’’N and long. 76^0 22’ 46.87’’E)

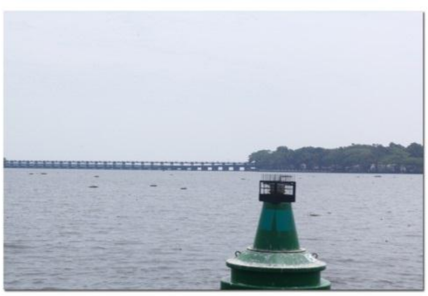
Paddy and coconut are the main agricultural crops in this area. The station is situated on the southern region of the estuary. The discharges from nearest paddy fields have negative impacts along with the sewage discharge from houseboats, home stays and resorts. Riverine inflow from Pamba and Manimala also influence the station.

Station 1. Aroor

Station 4. Thanneermukkom South

Station 2. Perumbalam

Station 5. Pathiramanal



Station 3. Thanneermukkom North

Station 6. Punnamada

Station 7. Nehru Trophy

Station 10. Meenapalli

Station 8. Pangankuzhipadam

Station 11. Kainakary

Station 9. Pallathuruthi

Station 12. C Block (Cherukayal)


Station 13. Kuttamangalam


Station 14. Ranikayal


Station 15. Marthandam


Station 16. Chithirakayal


Station 17. Varanad


Station 18. Kuppappuram


Station 19. Meenapalli Vattakkayal

Plate 3 Showing different study stations in Vembanad backwater during 2017

2.3 Field sampling

The study is based on field collections and analysis for which the sampling was conducted in Vembanad backwater during pre-monsoon (PRM) and monsoon (MN) period in the year 2017. Field samples were collected from both northern and southern parts of the Thanneermukkom bund on February, April, June and August. Sixteen sampling sites were selected for the PRM period, thirteen from the southern side and three from the northern side of the bund based on its ecological importance, sewage and land/agricultural runoff. During MN, three more sites were added to the existing sampling sites (One in the northern side and 2 in the southern side of the bund) for better understanding of anthropogenic disturbances based on the observations during PRM. The geographic positions were fixed using Global Positioning System (GPS - Magellan ® Triton 200/300). These sites are located in the inland channels of the backwater and are influenced by discharge from company distillery units, padasekharams, agricultural runoff etc.

2.4 Methodology

2.4.1 Water quality - physico-chemical characteristics

Water quality parameters are important for the survival of aquatic flora and fauna. Some important physical and chemical factors which are influencing the aquatic environment such as depth, temperature, transparency, pH, salinity, dissolved oxygen and major inorganic nutrients like phosphate-phosphorus, ammonia-nitrogen, nitrite-nitrogen, nitrate-nitrogen and silicate-silicon were analysed.

The surface water samples were collected using a plastic bucket and bottom water samples were collected using a standard Niskin sampler (General Oceanics, 5 L capacity). Preservation and transportation of the water samples to the laboratory for analysis were based on standard methods (Grasshoff *et al*., 1999). The water temperature, water depth and transparency were measured at each site. Depth was measured in the field by lowering a graduated weighted rope until it touches the bottom of the estuary. Water transparency was measured with the Secchi disc (20 cm in diameter) and expressed in meters (Strickland and Parsons, 1972). Water temperature was measured onboard using a standard 0-50 ^{0}C degree centigrade mercury thermometer with an accuracy of ± 0.01 ^{0}C. pH measurements were made using a digital pH meter (MODEL alpha 01). Salinity was measured from the field using a calibrated analogue handheld refractometer (Model- EW-81150-20, accuracy ±1.00 ppt, and range 0-100 ppt) and counter checked by Mohr-Knudsen titrimetric method (Grasshoff *et al*., 1999) and expressed in parts per thousand (ppt). The water samples for dissolved oxygen (DO) and biological oxygen demand were collected in DO glass bottles. The samples for dissolved oxygen were fixed on-board and estimated using the modified Winkler's method (APHA, 2005; Strickland and Parsons, 1972) and expressed in milligram/liter (mg L^{-1}). Biological oxygen demand (BOD) was measured by APHA (2005) and it was expressed in milligrams per litre (mg L^{-1}). The remaining water samples for the analysis of other parameters were collected in thoroughly washed 1 litre polythene bottles and stored in containers with ice. The preserved samples were brought to the laboratory at the earliest and analysis was completed soon.

Dissolved inorganic phosphate-phosphorus was measured by ascorbic acid method (Strickland and Parsons, 1972; Grasshoff *et al*., 1999). In an acid solution containing molybdic acid, ascorbic acid and trivalent antimony, inorganic phosphate forms a reduced phosphomolybdenum complex and the absorbance was measured at 880 nm; that of silicate-silicon in the water was estimated by molybdosilicate method (Grasshoff *et al*., 1999). When an acid sample is treated with a molybdate solution, a yellow silicomolybdic acid is formed. This is further reduced by ascorbic acid in presence of oxalic acid (to prevent interference from phosphate) to form a blue coloured complex (molybdenum blue). The absorbance was measured at 810 nm. Ammonia-nitrogen was measured by the phenate method (Grasshoff *et al*., 1999). In a moderately alkaline medium, ammonia reacts with hypochlorite to form monochloramine, which forms indophenol blue in the presence of phenol, a catalytic amount of nitroprusside ions and excess hypochlorite. The blue colour was measured at 640 nm. Nitrite-nitrogen was measured using the diazotised method (Strickland and Parsons, 1968; Grasshoff *et al*., 1999). In this method, the nitrite in the water samples was allowed to react with sulphanilamide and later with N-(1-Naphthyl) ethylenediamine dihydrochloride. The absorbance was measured at 543 nm. Nitrate-nitrogen was measured by cadmium reduction method (Strickland and Parsons, 1968; Grasshoff *et al*., 1999). Nitrate-nitrogen in the water sample was quantitatively reduced to nitrite by passing through a reduction column filled with copper coated cadmium granules and measured as nitrite using diazotized method and the absorbance was measured at 543 nm. The inorganic nutrients were analysed using a spectrophotometer (Systronics UV-VIS spectrophotometer, Model No.117), after proper calibration. The values were expressed in the unit of micromole per litre ($\mu mol\ L^{-1}$).

2.4.2 Sediment quality

The sediment samples were collected using a standard van Veen grab of size 0.04 m^2. Sediment temperature was determined using standard degree centigrade thermometer in the field. pH was measured using Systronics water analyser model 371. Separate samples of sediment were taken for the analysis of heavy metals and pesticide residues.

2.4.3 Heavy metal analysis

2.4.3.1 Analysis of heavy metals in water samples

The heavy metals copper (Cu), cadmium (Cd), nickel (Ni), lead (Pb), zinc (Zn) and iron (Fe) were analysed from the study. Copper (Cu), zinc (Zn), nickel (Ni) and iron (Fe) are required in trace amounts but their higher dose causes toxic effects. Metals that are not suitable for biological function such as lead (Pb) and cadmium (Cd) are analysed to study its impact. For heavy metal analysis, the samples were filtered using 0.45 µm millipore filter paper and stored in pre-cleaned, acid washed polyethylene bottle. The sample was acidified with supra-pure nitric acid to a pH between 2-3. Samples were stored at low temperatures (-10 to -40 ºC) to avoid evaporation. Four hundred milliliters of the sample was taken in a separating funnel and ammonium acetate buffer was added to adjust the pH of the sample to 4.5. Ten milliliters of 2 % Ammonium Pyrolidine Dithio Carbamate (APDC) solution was added to the sample followed by 15 ml of Methyl Isobutyl Ketone (MIBK). The funnel was shaken well using reciprocating shaker (Model: RS M1) and the 2 phases were allowed to separate, the lower aqueous layer was drained to another separating funnel. The extraction process was repeated by adding 5 ml of APDC and 10 ml of MIBK 2 or 3 times. The MIBK layer was shaken well after adding 0.1ml of conc. HNO_3 and 9.9 ml of distilled water. The layers were separated and the aqueous layer collected in 25 ml standard flask and made up to mark with Milli-Q (Brooks *et al*., 1967).

During the study period (February-August, 2017) water samples were pre-concentrated by APDC-MIBK method in laboratory facility at CUSAT and the metal analysis was done at NIOT (National Institute of Ocean Technology, Chennai)**,** using Atomic Absorption Spectrophotometer (AAS) Model: Spectra AA 220 FS at National Centre for Coastal Research (NCCR), National Institute of Ocean Technology (NIOT) campus, Chennai (formerly ICMAM). The water samples collected during June and August were analysed at KSPCB (Kerala State Pollution Control Board), Kochi using Atomic Absorption Spectrophotometer Model Perkin Elmer AAnalyst 700.

2.4.3.2 Analysis of heavy metals in sediment samples

Heavy metals such as copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb) and zinc (Zn) were analysed in sediment samples. The sediment samples were oven dried to a constant weight at 80 ˚C and then crushed using mortar and pestle and sieved through 2 mm sieve. Nitric-Perchloric acid digestion was performed, following the procedure recommended by the AOAC, (1990).

Approximately 0.5 g of homogenized dry sediment samples were accurately weighed and digested using nitric acid and Perchloric acid in 5:1 ratio in KEL PLUS macro four sample (250 ml) digestion unit (model KES 04L) at an initial temperature of 80 ˚C for 1 hour, 100 ˚C for 2 hrs. and 150 ˚C for 2 hrs. The supernatant solution was filtered using 42 mm filter paper and made up the volume to 50 ml using doubled distilled water (Grasshoff *et al*., 1999).

During the study period (February-August, 2017) acid digested sediment samples were filtered at CUSAT lab and analysis was done at the National Centre for Coastal Research (NCCR), National Institute of Ocean Technology (NIOT) campus, Chennai (formerly ICMAM)**,** using Atomic Absorption Spectrophotometer (AAS) Model: Spectra AA 220 FS at NCCR, NIOT campus (formerly ICMAM).

2.4.3.3 Analysis of heavy metals in organisms

Organisms from 7 selected study stations were analysed for heavy metals such as copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb) and zinc (Zn). The organisms collected were *Penaeus indicus* (St.3-Thanneermukkom north), *Channa* sp. (St.4-Thanneermukkom south), *Etroplus maculatus* (St.5-Pathiramanal), *Villorita* sp. (St.6-Punnamada), *Puntius* sp. (St.11-Kainakary), *Ambassis* (St.12- C block Cherukayal) and *Macrognathus* sp. (St.14-Ranikayal). The collected organisms for heavy metal analysis were rinsed with Milli-Q water, weighed and dried in oven at 60 °C and was ground to fine powder using mortar and pestle. The processed samples were transferred to boiling tubes which were then placed into a Kjeldhal digestion block (KEL PLUS digester (Model: KES 04 L) and samples were digested by diacid 1:5 ($HClO_4$: HNO_3) treatment at 180 ºC for 4.5 hr and the supernatant solution was filtered in Whatmann filter paper (1µm) and made up to 25 ml for measurement (Grasshoff *et al*., 1999). Following preparation; samples of organisms were analysed in Atomic Absorption Spectrophotometer (Model: Spectra AA 220

FS) at National Centre for Coastal Research (NCCR), National Institute of Ocean Technology (NIOT) campus, Chennai (formerly ICMAM).

2.4.4 Analysis of pesticide and other residues

2.4.4.1 Water samples

As a part of the study, a survey was conducted among the farmers of Kuttanad to get an idea about the organochlorine and organophosphorus pesticides that are widely used in the agricultural fields. The samples were analysed for these pesticides and also for commonly used ones. Liquid - Liquid extraction gas chromatographic method was used for the extraction and analysis of pesticide compounds (APHA, 1995; AOAC, 1995). The pesticides were extracted with a mixed solvent, diethyl ether/hexane. The extract was cleaned up by adsorption-chromatography. The individual pesticides were then determined by gas chromatography using electron capture detector (ECD).

The sample was shaken well and transferred 450 ml sample to the separating funnel having 500 ml capacity. Then 15 ml 15 % diethyl ether in hexane was added, shaken vigorously for 2 minutes and allowed to settle for 10 minutes. The extract was taken out using 5 ml auto pipette to a 50 ml stoppered measuring cylinder through funnel containing sodium sulphate plugged with little glass wool. After complete transfer of upper layer little solvent was added and draw out as above. Repeated the extraction twice using 10 ml and 5 ml of 15 % diethyl ether in hexane and transferred the extract using auto pipette and filtered through the funnel. Sodium sulphate in the funnel was washed with 10 ml solvent. The measuring cylinder was kept on a hot water bath at 85-90 ˚C by putting a small piece of porcelain chip. Then evaporated and concentrated to less than 5 ml and made up to 10 ml. 2 µl of the sample was injected on a split less injector and recorded the chromatogram.

2.4.4.2 Sediment samples

Pesticides in sediments were extracted using hexane-acetone mixture and analysed by gas chromatography (AOAC, 1995). 10 g dried and crushed sediment sample was weighed, put into 100 ml conical flask and then 25 ml acetone (HPLC grade) was added and shaken overnight. The supernatant was collected with filter paper and transferred to a 500 ml capacity separating funnel. 25 ml of acetone was added followed by 300 ml Milli-Q water, 15 g Nacl and 15 ml hexane. Shaken well for 10 minutes and allowed to settle, then filtered the extract through a funnel containing sodium sulphate plugged with little glass wool. The extraction was repeated using 10 ml and 5 ml of hexane. The extract then evaporated and concentrated to less than 5 ml and made up to 10 ml with hexane.

Extractions of water and sediment samples were performed in the CUSAT lab. The analysis was done at Centre for Water Resources Development and Management (CWRDM), Kozhikode by Gas Chromatography-Mass spectrometry (GC-MS) using the instrument Thermo scientific IT 900. Full scan analysis (mass range: 45-550) was the method used in the analysis and the column used in GC-MS was Phase-TG5MS.

The analysis was done initially on the GC-MS for the qualitative aspects of the pesticide and other residues in the samples. Based on this, quantitative analysis can be conducted on the specific contaminants.

2.4.5 Primary productivity

The primary productivity (gross and net production) was estimated by in situ incubation method employing the Light and Dark bottle method (Strickland and Parsons, 1972). Water samples were collected and transferred to 125 ml capacity DO bottles (light and dark bottles). The light and dark bottles were incubated for 3 hours. After the incubation period the oxygen content was determined by the modified Winkler's method and calculated hourly rate of primary production multiplied by the number of day light hours (~12 hours) and it was expressed in gram Carbon/meter cube/day (g C m^{-3} day^{-1}).

2.5 Statistical analysis

2.5.1 Principal Component Analysis (PCA)

It is a powerful tool that tries to elucidate the variance of a large dataset of inter-correlated variables with a smaller set of independent variables (Simeonov *et al*., 2003). PCA was conducted on environmental data to detect trends of variation of ecological characteristics across the study area. The assessment of the index was done using a Pearson correlation between the scores in PCA axis and the environmental variables. This analysis uses an ordination plot to project the points of higher similarities closer together while samples more dissimilar are further apart. In this study, significant environmental variables measured have been included for the PCA.

2.5.2 Bio concentration Factor (BCF)

Bio concentration Factor (BCF) was calculated to estimate the amount of heavy metal input from the surrounding environment. Bio concentration is defined as the net result of the adsorption, distribution and elimination of a substance in an organism, after an exposure through water (USEPA, 2000).

BCF = M tissue / M water

Where, M tissue is metal concentration in soft tissue;

M water is metal concentration in water.

2.6 Pollution Indices

2.6.1 Sediment Quality Guidelines (SQG)

Ecological risk and toxicity of the metals were analysed by comparing metal concentration with reference values that were developed by the U.S National Oceanic and Atmospheric Administration (NOAA). The reference table uses three standards, non-polluted, moderately polluted and heavily polluted that considers all adverse biological effects associated with elevated metal concentrations (Long *et al*., 1995; MacDonald *et al*., 1996). The concentrations that comes in non-polluted range represent a minimal effects range, concentration that comes in moderately polluted range represent a possible effect range within which adverse biological effects would occasionally occur and concentrations that comes in heavily polluted range represent adverse biological effects would frequently occur (Buchman, 2008).

Table 2.2 Concentration of heavy metals and its pollution status based on the sediment quality guidelines (SQG)

Element (mg/Kg)	SQG non-polluted	SQG moderately polluted	SQG heavily polluted
Cu	<25	25-50	>50
Zn	<90	90-200	>200
Cd	<1	1-6	>6
Pb	<40	40-60	>60
Ni	<20	20-50	>50

2.6.2 Geo accumulation Index (Igeo)

Igeo index derived by Muller (1979) is one of the reliable index to calculate the degree of pollution in sediment. It can be calculated using the equation;

$$I_{geo} = \log_2 (C_n)/1.5B_n$$

Where: C_n - concentration of metal in sediment, B_n - geochemical background value in average shale (Turekian and Wedpohl, 1961).

Muller has determined seven classes of I_{geo}: unpolluted (<0; class 0), uncontaminated to moderately contaminated (0-1; class 1), moderately contaminated (1-2; class 2); moderately to strongly contaminated (2-3;

class 3), strongly contaminated (3-4; class 4), strongly to extremely strongly contaminated (4-5; class 5), extremely contaminated (>5; class 6).

2.6.3 Contamination Factor (CF)

Contamination Factor gives a quantitative value of contamination by pollutants in an ecological system. It is represented as;

$$CF = \frac{\text{Metal content in sediment}}{\text{Back ground value of metal}}$$

According to Hakanson, 1980; CF values were interpreted as CF < 1 indicates low contamination factor, 1 ≤ CF ≤ 3 refers to moderate contamination factor; 3 ≤ CF ≤ 6 means considerable contamination factor and CF > 6 indicates very high contamination factor.

2.6.4 Pollution Load Index (PLI)

PLI is a widely used index to access overall pollution loadings of heavy metals and its contamination level, which is the geometric mean of the contamination factor of each metal present in the study area (Tomlinson *et al*., 1980; Sarala and Uma, 2013). It is represented as;

$$PLI = (CF_1 x CF_2 x CF_3 x \ldots\ldots\ldots\ldots\ CF_n)^{1/n}$$

Where, n represents the number of metals and CF represents the contamination factor for the respective metals. According to Tomlinson *et al*. (1980), PLI = 0 indicates unpolluted state, PLI = 1 lower pollution due to the presence of contaminants, PLI > 1 polluted sediment.

3. WATER QUALITY - PHYSICO-CHEMICAL CHARACTERISTICS

3.1 Introduction

Water quality is an aspect vital to the survival and well-being of organisms in the coastal and estuarine areas. To identify and quantify the trends in water quality in a geographical area, monitoring of water quality is necessary. Such monitoring is done to understand the condition of the water, and from there, the various types of problems caused by inferior quality of water. It is also necessary to identify if the source of the problem is natural or man-made. Such an understanding of relationships between human activities and water chemistry is required to identify and manage sources of anthropogenic stress in Great Lakes and coastal wetlands (Morrice *et al*., 2008). Water quality in aquatic systems is facing deterioration due to the high levels of urbanization, coastal development and industrial expansion taking place today. Such activities have resulted in high levels of nutrient enrichment, depletion of dissolved oxygen, rise in dissolved and particulate organic matter and increased release of carbon dioxide. At the same time, demand for water for varied purposes such as residential usage, agriculture and industrial usage has increased. The environmental effects of these changes are directly reflected in the parameters of water quality.

Estuarine environment is a complex, continuously changing habitats, that has wide range of physical and chemical variations that occur with several events. It represents one of the most sensitive and ecologically important habitats on earth. Physical condition and functioning of majority of the estuaries in the world are threatened due to various levels of interactions mainly from anthropogenic pressure, which stands top; industrial and agriculture pollution, over exploitation of natural resources and various developmental activities within the estuarine environment (Morant and Quinn, 1999). Most of the coastal estuaries are experiencing degradation mainly due to urban growth and development. Consequently input of nutrients especially nitrogen and phosphorus is increasing tremendously causing several environmental problems including water quality deterioration and probable biodiversity loss (Glibert *et al*., 2010).

Throughout the world, estuaries and coastal waters have experienced degradation. The successful management of estuaries and coastal waters requires an eco-hydrology based approach. Without effective thinking and management concepts, estuaries and coastal waters will continue to degrade, whatever integrated coastal management plans are implemented. To help in this process of change there is a need to develop a profound understanding on the effects of biota and biotic processes on mediating estuary response to change hydrology, sediment and nutrient flux on the biota and hydrology. About 60 % of the world's population lives along the estuaries and the coast (Lindeboom, 2002). The increase of human populations in the river basins, from natural growth and internal migration within the hinterland, has resulted in a doubling of the population along many coasts over the last 20 years. This is degrading estuarine and coastal waters through pollution, increasing turbidity from eutrophication, overfishing and habitat destruction. Estuaries are often regarded as sites for future development and expansion, and have been increasingly canalized and dyked for flood protection, and their wetlands were modified for residential areas (Wolanski *et al*., 2004).

Deleterious changes in estuarine areas affect the economy of the area as well, primarily on the fishing industry. Optimal primary and secondary production is required for profitable and sustainable fishing practices. The pre-requisite for such optimal production is the prevalence of favourable hydrological conditions. This includes physical factors such as temperature (atmospheric and surface water), salinity, depth, transparency, and chemical factors such as dissolved oxygen, pH, total alkalinity, biological oxygen demand, nutrients (ammonia, nitrite, nitrate, phosphate and silicate) and hydrogen sulphide.

Over the years the availability of domestic and industrial wastes, urban discharges and agricultural effluents increase the nutrient concentration by many times to the levels that occur naturally causing several environmental modifications in estuarine and coastal waters. Sustaining good water quality condition was important not only for ecosystem health, but also for providing service and health to people. The Vembanad estuary is passing through a phase of rapid ecological modifications. Several changes have been taken place on the hydrology and environmental quality in the estuary. There has been lot of alterations in the upland areas of Vembanad, on account of the various projects as well as the increased use of water for a wide array of activities. There are also in-situ changes in the Vembanad area on account of various interventions. Scientific information on the ecosystem based analysis of the ecological processes on a comprehensive basis is severely lacking from the Vembanad estuarine system after the commissioning of the barrage. These unrestricted human interferences have caused irrevocable adverse effects on the environmental characteristics of the estuary. As such changing estuarine environments are affecting its productivity characteristics; it is a prerequisite to assess the changes in water quality of the area for implementing sustainable management measures for its restoration.

3.2 Results

3.2.1 Physical characteristics

The physical characteristics of surface and bottom water like depth, temperature, transparency and salinity were determined in the study area and its spatial and temporal variations were explained.

3.2.1.1 Depth

The average depth of the Vembanad estuary in February was 2.14 ± 1.10 m and 2.52 ± 0.65 m in April. In February, the lowest depth recorded was 0.5m at station 6 (Punnamada) and highest depth of 5 m at station 1 (Aroor). In April station 1 (Aroor) showed the highest depth of 4 m and station 6 recorded the lowest depth of 1.15 m (Fig. 3.1).

In June, the highest depth of 7 m was recorded in station 4 (Thanneermukkom south) and station 9 (Pallathuruthy), whereas station 5 (Pathiramanal) recorded the lowest depth of 0.9 m. The average station wise value observed was 3.24 ± 1.89 m. During August, station 1 (Aroor) recorded the highest value of 8m while station 15 (Marthandam) showed the lowest value of 1 m (av. 3.21 ± 2.04 m). Most of the stations south of TMB showed lower depth compared to the northernmost stations, whereas station 9 (Pallathuruthy) showed 7 m for both the months (June and August).

3.2.1.2 Temperature

The water temperature in Vembanad estuary ranged between 27 - 38.5 °C in February (av. 31.38 ± 3.21 °C) and 30-33 °C in April (av. 31.21 ± 0.92 °C). In February the lowest temperature of 27 °C was observed at station 9 (Pallathuruthy) and in April, station 7 (Nehru trophy finishing point), 8 (Pangankuzhipadam), 10 (Meenappally) and 11 (Kainakary) showed lowest value of 30 °C. The highest value of 38.5 °C was recorded at station 3 (Thanneermukkom north) in February. During April, 33 ˚C was observed at station 2 (Perumbalam) and 6 (Punnamada) (Fig. 3.2).

In June, the surface water temperature ranged between 28 – 30 °C with an average value of 28.97 ± 0.68 °C. The lowest value of 28 °C was observed in southernmost stations such as station 10 (Meenappally), 11 (Kainakary), 14 (Ranikayal) and 15 (Marthandam). The highest value of 30 °C was observed in station 3 (Thanneermukkom north), station 4 (Thanneermukkom south), station 5 (Pathiramanal) and station 19 (Meenappally Vattakayal). The bottom water temperature ranged between 27 – 30 °C with an average value of 28.74 ± 0.75 °C. Station 1 (Aroor) recorded the lowest value of 27 °C. The highest value of 30 °C was observed in station 5 (Pathiramanal) and 19 (Meenappally Vattakayal). In August, the highest value of surface water temperature was observed in station 17 (Varanadu) with 33 °C. The lowest value of 29.5 °C was observed at station 13 (Kuttamangalam). The average value observed was 31.37 ± 0.91 °C. The bottom water ranged between 30-33 °C with an average value of 31.11 ± 0.83 °C. Similar to the surface water temperature, station 17 recorded the highest value of bottom water temperature (33 °C). Stations 1, 9, 10 and 13 were recorded the lowest value of 30 °C.

3.2.1.3 Transparency

During the study period the highest transparency of 1.15 m was observed in station 16 (Chithirakayal) in February and lowest of 0.2 m in stations 7 (Nehru trophy finishing point) and 10 (Meenappally). In April, stations 1 (Aroor) and 2 (Perumbalam) showed the highest transparency of 1 m and lowest transparency of 0.4 m was recorded in stations 8 - Pangankuzhipadam and 14 - Ranikayal) (Fig. 3.3). The average transparency of the water column during February and April was 0.53 ± 0.30m and 0.59 ± 0.18m respectively.

In June, the transparency was ranged between 0.4 – 4 m with an average value of 0.89 ± 0.78 m. Station 5 (Pathiramanal) recorded the highest value of 4 m, whereas the lowest value of 0.4 m was observed in station 7 (Nehru trophy finishing point). In August, station 4 (Thanneermukkom south) recorded the highest value of 1.5 m. The lowest value of 0.2 m was observed in stations 10 (Meenappally), 11 (Kainakary) and 15 (Marthandam) (av. 0.63 ± 0.34m).

3.2.1.4 Salinity

The salinity values ranged from 2 to 29.5 ppt for surface water in February and 0 to 11 ppt in April. In the present study station 1 (Aroor) recorded the highest salinity of 29.5 ppt in February and 28.5 ppt in April. Salinity in surface water showed lowest value of 2 ppt in station 10 and for bottom water lowest salinity of 1 ppt was observed in stations 9 and 10 in February.

The surface water salinity for the month of June was ranged between 0-3 ppt with an average value of 0.16 ± 0.69 ppt. Station 1 (Aroor) recorded the highest value of 3 ppt. All other stations exhibited limnetic to oligohaline condition. The bottom water salinity showed the highest value at station 1 (Aroor) with 25 ppt. All other stations except station 2 recorded nil values. In August, the surface water salinity ranged between 0-19 ppt (av. 4.21 ± 5.81). Station 1 recorded the highest value of 19 ppt. The southernmost stations such as 11, 12, 13, 14, 15, 16 and 19 recorded nil values. The highest value of bottom water salinity was recorded in station 1 with 27 ppt; however, stations 10, 11, 12, 13, 14, 15, 16 and 19 recorded nil values (Fig. 3.4). The average value observed was 5.42 ± 7.58 ppt. During the study period the stations north of the TMB showed higher salinity as compared to the stations south of the TMB.

3.2.2 Chemical characteristics

The chemical characteristics of surface and bottom water in the study area and its spatial and seasonal variations were determined. pH, alkalinity, dissolved oxygen, biological oxygen demand, hydrogen sulphide were determined.

3.2.2.1 pH

In February, the pH value of surface water ranged between 6.45 - 7.5 (av. 6.93 ± 0.39) and 6.52 - 7.52 (av. 7.05 ± 0.33) for bottom water. The highest pH for surface water was 7.5, which was observed at stations 1 and 6. For bottom water, stations 6 and 8 showed the highest pH of 7.52. In April, station 6 (Punnamada) showed the highest value for both surface (7.56) and bottom water (7.61). The value ranged from 6.45 - 7.56 (av. 6.99 ± 0.37) for surface water and 6.5 - 7.61 (av. 7.11 ± 0.33) for bottom water. During both the months, the average pH of bottom water was high when compared to surface water. It varied from 6.93 ± 0.39 (surface) to 7.05 ± 0.33 (bottom) in February and 6.99 ± 0.37 (surface) to 7.11 ± 0.33 (bottom) in April (Fig. 3.5).

The pH of the surface water ranged between 4.92-8.2 with an average of 7.11 ± 0.68 in June and 5.38 - 7.82 (av. 7.01 ± 0.55) in August. In June, station 10 (Meenappally) recorded the highest value of 8.2 and station 1 (Aroor) recorded the lowest value of 4.92. In August, the highest surface water pH (7.82) was recorded in station 11 (Kainakary), while station 13 (Kuttamangalam) recorded the lowest value of 5.38. In June, station 15 (Marthandam) recorded the highest bottom water pH (7.98) and the lowest value of 6.42 was observed in station 9 (Pallathuruthy) (av. 7.21 ± 0.38). In August, the value ranged from 6.43-8.05 (av. 6.91 ± 0.37). Station 1 (Aroor) recorded with the highest value of 8.05, whereas, the lowest value of 6.43 was observed in station 9 (Pallathuruthy).

3.2.2.2 Alkalinity

The alkalinity value for surface water ranged between 20-100 mg L^{-1} in February (av. 35.31 ± 19.01 mg L^{-1}) and 15 to 90 mg L^{-1} in April (av. 32.11 ± 16.01 mg L^{-1}). The highest value was observed in station 1 (Aroor) for surface and bottom water. The highest value for surface water was 100 mg L^{-1} in February and 90 mg L^{-1} in April. Lowest value of 20 mg L^{-1} was observed in station 4, station 5 and station 6 in February and 15 mg L^{-1} at station 5 in April (Fig. 3.6). Bottom water (35.31 ± 19.01 mg L^{-1}) showed comparatively higher alkalinity than surface water in February (44.38 ± 20.32 mg L^{-1}) and similar trend was observed during April and it was 32.11 ± 16.01 mg L^{-1} and 37.89 ± 17.27 mg L^{-1} for surface and bottom water respectively. Alkalinity of bottom water showed the highest value in station 1 (Aroor) for both the months, the values were 110 mg L^{-1} in February and 100 mg L^{-1} in April.

In June, the alkalinity of surface water ranged between 10-80 mg L^{-1} with an average value of 30.79 ± 15.48 mg L^{-1}. The highest value of 80 mg L^{-1} was recorded in station 1 (Aroor) and the lowest value of 10 mg L^{-1} was observed in station 14 (Ranikayal). The bottom water showed the highest value of 100 mg L^{-1} in station 1 and lowest value of 20 mg L^{-1} was recorded in stations 5, 12, 14 and 18. The bottom water showed an average value of 33.16 ± 17.65 mg L^{-1}. In August, the surface water alkalinity ranged between 25-100 mg L^{-1} (av. 38.16 ± 16.60 mg L^{-1}). Similar to June, station 1 recorded the highest value. The lowest value of 25 mg L^{-1} was observed in stations 14, 18 and 19. The bottom water showed highest value of 50 mg L^{-1} at station 1 and lowest value of 15 mg L^{-1} at station 5 (Pathiramanal) with an average value of 33.16 ± 10.03 mg L^{-1}.

3.2.2.3 Dissolved oxygen

The DO values in the Vembanad estuary for surface water ranged between 3.94 to 9.45 mg L^{-1} (av. 5.46 ± 1.30 mg L^{-1}) in February and 1.57 to 11.81 mg L^{-1} (av. 4.80 ± 2.6 mg L^{-1}) in April. During February, lowest value of 3.94 mg L^{-1} was recorded for surface water at station 14 and highest of 9.45 mg L^{-1} in station 4. For bottom water the lowest value of 3.94 mg L^{-1} was recorded at stations 3, 7 and 13 and highest value of 5.51 mg L^{-1} was recorded at stations 4, 8, 9, 10, 11, 15 and 16. In April the lowest value of 1.57 mg L^{-1} was observed at station 11 for surface water and 2.36 mg L^{-1} was observed for bottom water (stations 9, 11, 12 and 18). Station 13 (Kuttamangalam) showed the highest value of 11.81 mg L^{-1} and 9.45 mg L^{-1} in April for surface and bottom water respectively (Fig. 3.7). Station 6 (Punnamada) showed a DO value of 4.72 mg L^{-1} for both surface and bottom water in February; and in April it varied from 8.66mg L^{-1} in surface water and 3.94 mg L^{-1} in bottom water. The average DO for bottom water in February was 4.92 ± 0.61 mg L^{-1} and in April was 4.14 ± 1.76 mg L^{-1}.

The DO value, in the month of June ranged between 3.94-7.87 mg L^{-1} with an average value of 6.01 ± 1.06 mg L^{-1}. Station 5 (Pathiramanal) recorded the highest value of 7.87 mg L^{-1}. The lowest value of 3.94 mg L^{-1} was observed in station 1 (Aroor). Southernmost stations such as stations 7 (Nehru trophy finishing point), 9 (Pallathuruthy) and 13 (Kuttamangalam) also showed a lower value of 4.72 mg L^{-1}. The DO value of bottom water ranged between 4.72-8.66 mg L^{-1}. The highest value of 8.66 mg L^{-1} was recorded at station 3 (Thanneermukkom north) and the lowest value of 4.72 mg L^{-1} was observed at station 7 (Nehru trophy finishing point) (av. 6.67 ± 1.09 mg L^{-1}). In August, the DO value of surface water ranged between 5.51-9.45 mg L^{-1} (av. 7.83 ± 1.03 mg L^{-1}). The highest value of 9.45 mg L^{-1} was observed in station 4 (Thanneermukkom south) and station 11 (Kainakary). The lowest value of 5.51 mg L^{-1} was observed in station 16 (Chithirakayal).

3.2.2.4 Biological Oxygen Demand (BOD)

During February, the biological oxygen demand (BOD) value ranged from 0.79 mgL^{-1} to 7.87 mg L^{-1} with an average value of 3.69 ± 1.67 mg L^{-1}. Station 4 (Thanneermukkom south) showed the highest value of 7.87 mg L^{-1} in February. In April, station 13 (Kuttamangalam) showed the highest value of 10.23 mg L^{-1} and 7.87 mg L^{-1} for surface and bottom water respectively. Station 6 (Punnamada) also showed an increased BOD level (6.3 mg L^{-1}) for surface water in April (Fig. 3.8).

In June, the BOD value of surface water ranged between 1.57-5.51 mg L^{-1} (av. 4.10 ± 1.07 mg L^{-1}). Southern most stations such as stations 6 (Punnamada), 14 (Ranikayal), 16 (Chithirakayal) and 19 (Meenappally Vattakayal) recorded the highest value of 5.51 mg L^{-1}. The lowest value of 1.57 mg L^{-1} was observed in station 10 (Meenappally). Similar to the surface water, the bottom water showed the highest value of 5.51 mgL^{-1} at stations 4 (Thanneermukkom south), 6 (Punnamada), 11 (Kainakary), 14 (Ranikayal), 15 (Marthandam) and 19 (Meenappally Vattakayal). In August, the BOD value of surface water ranged between 2.36 - 7.87 mg L^{-1} (av. 4.31 ± 1.47 mg L^{-1}). Station 12 (C Block Cherukayal) recorded the highest value of 7.87 mg L^{-1}. The lowest value of 2.36 mg L^{-1} was observed in station 16 (Chithirakayal). The bottom water showed highest value of 5.51 mg L^{-1} in station 13 (Kuttamangalam) and lowest value of 2.36 mg L^{-1} at station 17 (Varanadu) with an average value of 3.69 ± 0.74 mg L^{-1}.

3.2.2.5 Hydrogen sulphide

During the study period, high concentration of hydrogen sulphide was observed in the upstream. In February, the hydrogen sulphide ranged between 0.05 to 27.92 µmol L^{-1} (av. 2.60 ± 6.79 µmol L^{-1}) for surface water and 0.05 to 2.58 µmol L^{-1} (av. 0.50 ± 0.66 µmol L^{-1}) for bottom water (Fig. 3.9). In February, station 6 (Punnamada) was recorded the highest value for surface water whereas station 13 (Kuttamangalam) showed the highest value of 2.58 µmol L^{-1} for bottom water. In April, most of the stations showed higher concentrations of H_2S. The value ranged between 0.33 to 9.90 µmol L^{-1} (av. 6.15 ± 2.79 µmol L^{-1}) for SW and 1.17 to 3.14 µmol L^{-1} (av. 2.31 ± 0.54 µmol L^{-1}) for BW.

The sulphide concentration of surface water for the month of June ranged between 0.05 - 13.84 µmol L^{-1} with an average value of 1.28 ± 3.10 µmol L^{-1}. Station 6 (Punnamada) recorded the highest value of 13.84 µmol L^{-1} whereas, the lowest value of 0.05 µmol L^{-1} was observed in stations 3, 10, 15, 16 & 19. The bottom water concentration ranged between 0.05 - 1.45 µmol L^{-1} (av. 0.52 ± 0.41 µmol L^{-1}). Similar to the SW, station 6 recorded the highest value of 1.45 µmol L^{-1} however, the lowest value of 0.05 µmol L^{-1} was observed in stations 1, 5, 9, 13 & 16. In August, the surface water concentration ranged between 0.05 - 8.49 µmol L^{-1} with an average value of 2.74 ± 2.72 µmol L^{-1}. The highest value of 8.49 µmol L^{-1} was recorded in station 14 (Ranikayal) while, station 2 (Perumbalam) and st.7 (Nehru trophy finishing point) recorded the lowest value of 0.05 µmol L^{-1}. The bottom water showed higher concentration (2.86 µmol L^{-1}) of sulphide in station 17 (Varanadu) whereas, station 12 and 14 recorded the lowest value of 0.33 µmol L^{-1}. The average bottom water concentration observed was 1.50 ± 0.79 µmol L^{-1}.

3.2.3 Inorganic Nutrients

3.2.3.1 Phosphate-Phosphorus

The phosphate-phosphorus concentration in the present study ranged from 9.08 to 39 µmol L^{-1} with an average of 24.29 ± 8.86 µmol L^{-1} in February and 9.86 to 22.46 µmol L^{-1} with an average value of 12.85 ± 3.35 µmol L^{-1} (SW) in April. In February, station 11 and station 15 showed the lowest value of 9.08 µmol L^{-1} and station 10 showed the highest value of 39.8 µmol L^{-1}. For bottom water, station 12 (C Block Cherukayal) showed the highest value of 95.73 µmol L^{-1}. In April, the highest value was observed at station 1 (Aroor) for both surface and bottom water (Fig. 3.10). During February, an average value of 24.29 ± 8.86 µmol L^{-1} was observed in surface water and 38.08 ± 30.09 µmol L^{-1} in bottom water. During April, an average value of 12.85 ± 3.35 µmol L^{-1} was observed in surface water and 14.01 ± 4.18 µmol L^{-1} in bottom water.

In the present study, the phosphate concentration in surface water ranged between 3.22 - 5.85 µmol L^{-1} (4.51 ± 0.62 µmol L^{-1}) in June. The highest value of 5.85 µmol L^{-1} was observed in station 10 (Meenappally) and the lowest value of 3.22 µmol L^{-1} was recorded in station 18 (Kuppapuram). The phosphate concentration in bottom water ranged between 3.28 - 12.79 µmol L^{-1} (av. 4.72 ± 2.57 µmol L^{-1}). Station 12 (C Block-Cherukayal) was recorded the highest value of 12.79 µmol L^{-1}. The lowest concentration of 3.28 µmol L^{-1} was recorded in stations 4 (Thanneermukkom south) and 17 (Varanadu). In August, the value ranged between 3.22 - 4.44 µmol L^{-1} for surface water with an average value of 3.48 ± 0.32 µmol L^{-1}. Station 1 (Aroor) recorded the highest value of 4.44 µmol L^{-1} and the lowest value of 3.22 µmol L^{-1} was recorded in stations 12 (C Block Cherukayal) and 16 (Chithirakayal). The bottom water showed highest value of 4.83 µmol L^{-1} at station 1 and the lowest value of 3.22 µmol L^{-1} was observed in station 4 (Thanneermukkom south) (av. 3.73 ± 0.48 µmol L^{-1}). Station 6 recorded higher concentration during the entire study period when compared to the other stations.

3.2.3.2 Silicate-Silicon

The silicate-silicon values in Vembanad estuary ranged from 13.64 to 129.72 µmol L^{-1} and 1.72 to 19.42 µmol L^{-1} in February and April respectively. The highest value of 129.72 µmol L^{-1} was observed in February at station 10 and lowest value of 13.64 µmol L^{-1} in station 12. In February, the average values for surface and bottom water were 53.16 ± 30.03 µmol L^{-1} and 55.92 ± 37.1 µmol L^{-1} respectively. Bottom water exhibited a highest value of 161.44 µmol L^{-1} at station 10 in February (Fig. 3.11).

In June, the surface water silicate concentration ranged between 13.27 to 91.85 µmol L^{-1} with an average value of 48.15 ± 20.69 µmol L^{-1}. The highest value of 91.85 µmol L^{-1} was recorded at station 10 (Meenappally). Station 1 was recorded with the lowest value of 13.27 µmol L^{-1}. The bottom water showed silicate concentration of 25.58 to 155.29 µmol L^{-1} (av. 56.32 ± 29.22 µmol L^{-1}). Station 10 recorded the highest value of 155.29 µmol L^{-1} while, the lowest value of 25.58 µmol L^{-1} was observed at station 13 (Kuttamangalam). In August, the surface water showed silicate concentration that ranged from 16.11 to 48.30 µmol L^{-1} (av. 31.99 ± 10.22 µmol L^{-1}). Station 8 (Pangankuzhipadam) recorded the highest silicate concentration of 48.30 µmol L^{-1} whereas the lowest value of 16.11 µmol L^{-1} was observed at station 12. The bottom water silicate concentration ranged between 10.43 to 48.30 µmol L^{-1}. The lowest value of 10.43 µmol L^{-1} was observed at station 6 (Punnamada). Station 16 (Chithirakayal) was recorded the highest value of 48.30µmol L^{-1}. The average value observed was 24.41 ± 8.68 µmol L^{-1}.

3.2.3.3 Ammonia-Nitrogen

In February, the ammonia values ranged between 0 (Stations 2, 8, 9 & 11) to 14.38 µmol L^{-1} (station 7-Nehru trophy finishing point). Average values of ammonia in surface and bottom water were 4.24 ± 4.76 µmol L^{-1} and 2.07 ± 2.51 µmol L^{-1} respectively. During April, the highest value of 14.27 µmol L^{-1} was recorded at station 8 and lowest value of 3.06 µmol L^{-1} at station 17. The bottom water showed the highest value of 34.95 µmol L^{-1} at station 10 and lowest value of 0.89 µmol L^{-1} at station 1 (Fig. 3.12). The average value of surface and bottom water ammonia in April was 5.62 ± 2.41 µmol L^{-1} and 7.50 ± 7.49 µmol L^{-1} respectively.

In June, the surface water concentration ranged between 0.78-10.53 µmol L^{-1} (av. 3.15 ± 3.46 µmol L^{-1}). Stations 1 (Aroor) and 7 (Nehru trophy finishing point) recorded the highest value of 10.53 µmol L^{-1} while, the lowest value of 0.78 µmol L^{-1} was observed in stations 4, 8, 9, 13, 15, 16 and 18. The bottom water showed highest concentration of 7.28 µmol L^{-1} at station 8 (Pangankuzhipadam), the lowest value of 0.13 µmol L^{-1} was observed in station 9 (Pallathuruthy) (av. 1.80 ± 2.24 µmol L^{-1}). In August, the concentration of ammonia in the surface water ranged between 0.24-5.66 µmol L^{-1} with an average value of 3.77 ± 1.80 µmol L^{-1}. The highest value of 5.66 µmol L^{-1} was recorded in stations 9 (Pallathuruthy), 13 (Kuttamangalam) and 15 (Marthandam). Stations 2 (Perumbalam), 3 (Thanneermukkom north) and 10 (Meenappally) recorded the lowest value of 0.24 µmol L^{-1}. The ammonia concentration in bottom water ranged between 0.78-15.40 µmol L^{-1} (av. 6.10 ± 4.10 µmol L^{-1}). Station 17 (Varanadu) recorded the lowest value of 0.78 µmol L^{-1} however, the highest value of 15.40 µmol L^{-1} was recorded in station 12 (C Block Cherukayal).

3.2.3.4 Nitrite-Nitrogen

Nitrite-nitrogen concentration for surface water in February ranged between 0.62 to 1.76 µmol L^{-1} with an average of 0.87 ± 0.37 µmol L^{-1}. Lowest value of 0.62µmol L^{-1} was recorded in stations 5, 11, 12, 14 and 15 while, highest value of 1.31 µmol L^{-1} was observed in station 3 (Thanneermukkom north). In April, the nitrite concentration of surface water ranged between 0.65 to 2.01 µmol L^{-1}. Station 2 showed the highest value of 2.01 µmol L^{-1} whereas the lowest value of 0.65 µmol L^{-1} was observed in station 3 (Fig. 3.13). In April, average bottom water concentration of nitrite was higher as compared to surface water; for surface water it was 0.83 ± 0.31 µmol L^{-1} and 1.27 ± 0.98 µmol L^{-1} for bottom water. In February, the average value of surface water (0.87 ± 0.37 µmol L^{-1}) was slightly higher compared to the bottom water (0.85 ± 0.42 µmol L^{-1}).

In June, the nitrite concentration for surface water ranged between 0.69-1.99 µmol L^{-1} with an average of 1.04 ± 0.30 µmol L^{-1}, whereas in August, it ranged between 0.65-2.44 µmol L^{-1} (av. 0.95 ± 0.50 µmol L^{-1}). In June, the highest value of 1.99 µmol L^{-1} was recorded in station 6 (Punnamada) however, station 4 (Thanneermukkom south) recorded the lowest value of 0.69 µmol L^{-1}. In August, the highest concentration (2.44

µmol L^{-1}) was observed in station 7 (Nehru trophy finishing point) while, the lowest concentration (0.65 µmol L^{-1}) was recorded in stations 2 (Perumbalam) and 18 (Kuppapuram). For bottom water, the concentration ranged between 0.65-1.76 µmol L^{-1} (av. 0.95 ± 0.35 µmol L^{-1}) in June. The highest value of 1.76 µmol L^{-1} was recorded in station 6 (Punnamada) whereas, stations 2 (Perumbalam) and 4 (Thanneermukkom south) recorded the lowest value of 0.65 µmol L^{-1}. In August, the bottom water showed higher concentration (2.44 µmol L^{-1}) in station 1 (Aroor) and lower concentration (0.65 µmol L^{-1}) in stations 5 (Pathiramanal) and 12 (C Block Cherukayal). The average value observed was 1.01 ± 0.48 µmol L^{-1}.

3.2.3.5 Nitrate-Nitrogen

In February, the nitrate concentration ranged between 1.29 to 8.20 µmol L^{-1} with an average of 2.66 ± 1.84 µmol L^{-1}. Stations 2 and 6 showed the lowest value of 1.29 µmol L^{-1}, whereas station 1 showed the highest value of 8.20 µmol L^{-1} for surface water. The average bottom water concentration during February was 5.33 ± 4.43 µmol L^{-1}, which was higher than the surface water (2.66 ± 1.84 µmol L^{-1}). Similar trend was observed during April with an average value of 2.25 ± 1.52 µmol L^{-1} (BW) and 2.14 ± 1.22 µmol L^{-1} (SW). In April, the surface value ranged between 1.29 to 6.38 µmol L^{-1}. The lowest value of 1.29 µmol L^{-1} was recorded at stations 2, 9, 10 and 19. Station 1 showed the highest value of 6.38 µmol L^{-1} for surface water and 7 µmol L^{-1} for bottom water (Fig. 3.14). In general, during the study period, station 1 showed higher concentration of nitrate when compared to the other stations.

In June, the nitrate concentration in surface water ranged between 1.24-7.22 µmol L^{-1} with an average value of 1.90 ± 1.36 µmol L^{-1}. The highest value of 7.22 µmol L^{-1} was recorded in station 1 (Aroor), the lowest value of 1.24 µmol L^{-1} was recorded in stations 17, 18 and 19. In bottom water, nitrate concentration ranged between 1.42-6.56 µmol L^{-1} (av. 2.88 ± 1.50 µmol L^{-1}). Station 1 recorded the highest value of 6.56 µmol L^{-1} whereas, the lowest value of 1.42 µmol L^{-1} was recorded in station 17 (Varanadu). In August, the surface water value ranged between 1.33-5.67 µmol L^{-1} (av. 2.00 ± 1.01 µmol L^{-1}). Station 1 recorded the highest value of 5.67 µmol L^{-1} and the lowest value of 1.33 µmol L^{-1} was observed in stations 2 and 17. The bottom water showed highest value of 5.67 µmol L^{-1} in stations 1 and 3 (Thanneermukkom north). The lowest value of 1.29 µmol L^{-1} was recorded in stations 9 (Pallathuruthy) and 10 (Meenappally) (av. 2.16 ± 1.33 µmol L^{-1}).

3.2.4 Primary productivity

The average gross primary productivity (GPP) value in Vembanad estuary during February was 1.94 ± 1.14 gC m^{-3} day^{-1}. Station 4 showed the highest value of 4.43 gC m^{-3} day^{-1} and lowest value of 0 in station 12. During April, the GPP value ranged between 0 to 9.59 gC m^{-3} day^{-1} with an average value of 2.29 ± 2.66 gC $m^{-3}day^{-1}$. Highest GPP value of 9.59 gC m^{-3} $^{d}day^{-1}$ was recorded at station 13 and 0 was recorded at stations 9, 10 and 11. The net primary production (NPP) varied from 0 to 1.48 gC m^{-3} day^{-1} with an average of 0.60 ± 0.56 gC m^{-3} day^{-1} during February. Stations 11, 13 and 14 showed highest NPP value of 1.48 gC m^{-3} day^{-1}. During April, values ranged from 0 to 3.69 gC m^{-3} day^{-1} with highest value at station 5 (Pathiramanal).

In June, the GPP value ranged between 0.74 to 2.21 gC m^{-3} day^{-1} with an average value of 1.44 ± 0.52 gC m^{-3} day^{-1}. Station 3, 5, 11 and 14 recorded the highest value of 2.21 gC m^{-3} day^{-1} whereas the lowest value of 0.74 gC m^{-3} day^{-1} was recorded in station 7, 10, 12, 17 and 18. In August, the average GPP value was 1.83 ± 0.51 gC m^{-3} day^{-1}. Station 3 and 8 recorded the highest value of 2.95 gC m^{-3} day^{-1}. The lowest value of 1.48 gC m^{-3} day^{-1} was recorded in stations such as station 1, 2, 5, 6, 7, 10, 11, 13, 14, 16, 17 and 18. During June, station 14 showed the highest NPP value of 2.21 gC m^{-3} day^{-1}. The average value observed was 0.93 ± 0.41 gC m^{-3} day^{-1}. In August, the value ranged between

0.74 to 4.43 gC m^{-3} day^{-1} (av. 1.17 ± 0.96 gC m^{-3} day^{-1}). Station 13 showed the highest value of 4.43 gC m^{-3} day^{-1}.

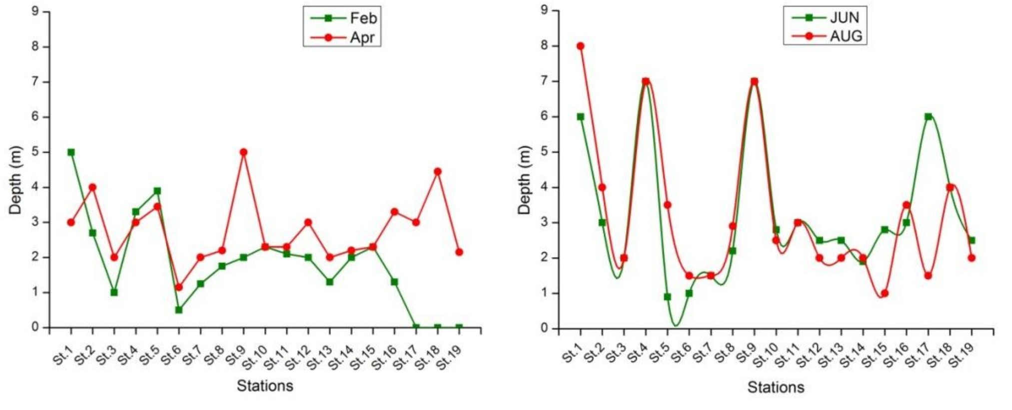


Fig. 3.1 Spatial variation of water depth (m) in Vembanad backwater during PRM & MN

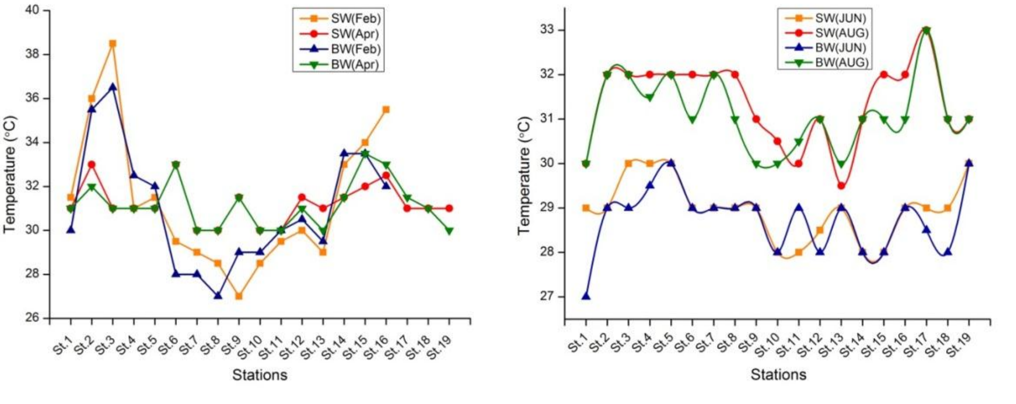


Fig. 3.2 Spatial variation of surface and bottom water temperature (°C) in Vembanad backwater during PRM & MN

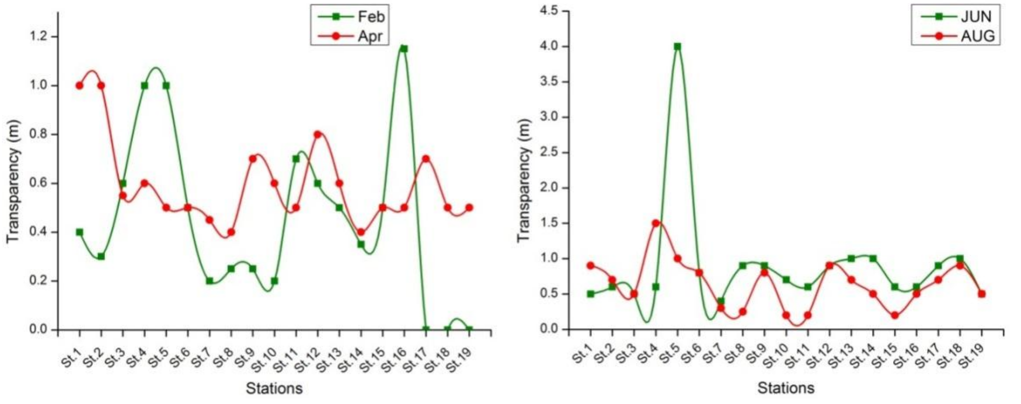


Fig. 3.3 Spatial variation of transparency (m) in Vembanad backwater during PRM & MN

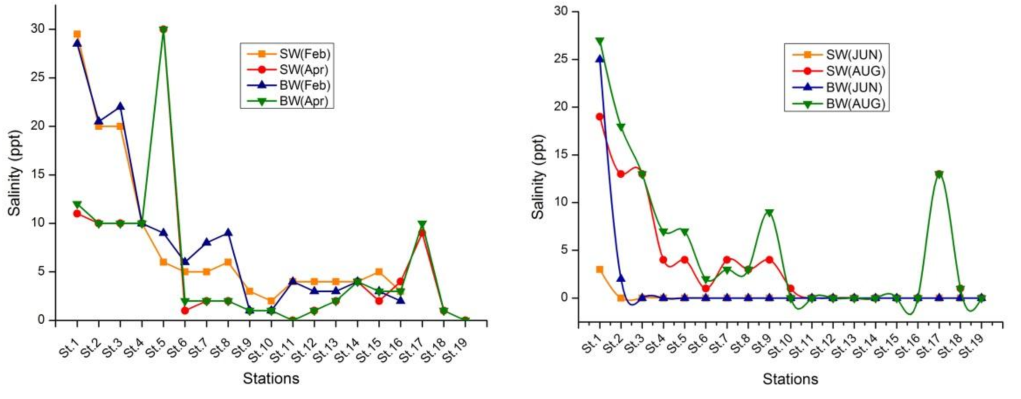


Fig. 3.4 Spatial variation of surface and bottom water salinity (ppt) in Vembanad backwater during PRM & MN

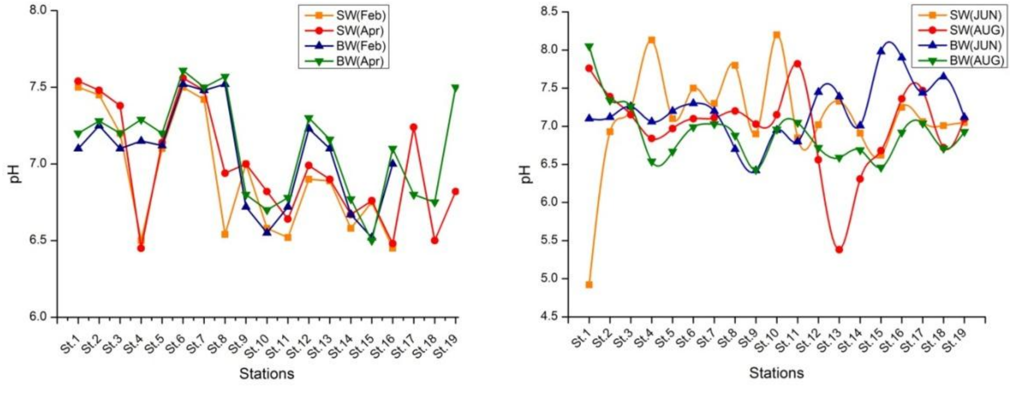


Fig. 3.5 Spatial variation of surface and bottom water pH in Vembanad backwater during PRM & MN

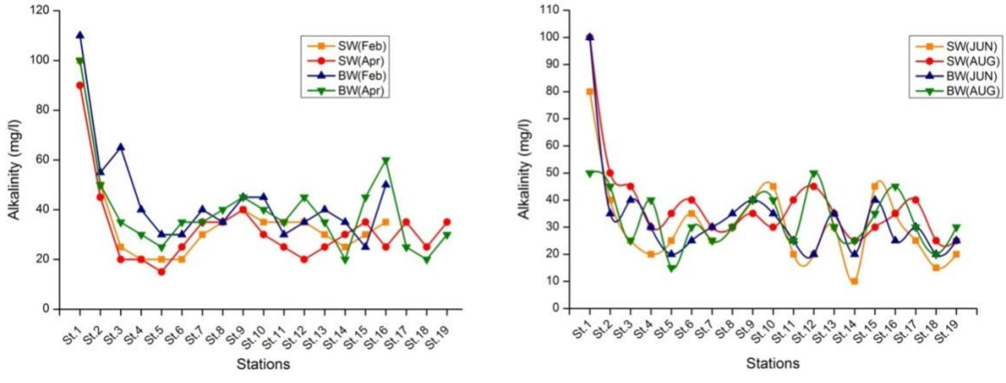


Fig. 3.6 Spatial variation of surface and bottom water alkalinity (mg L^{-1}) in Vembanad backwater during PRM & MN

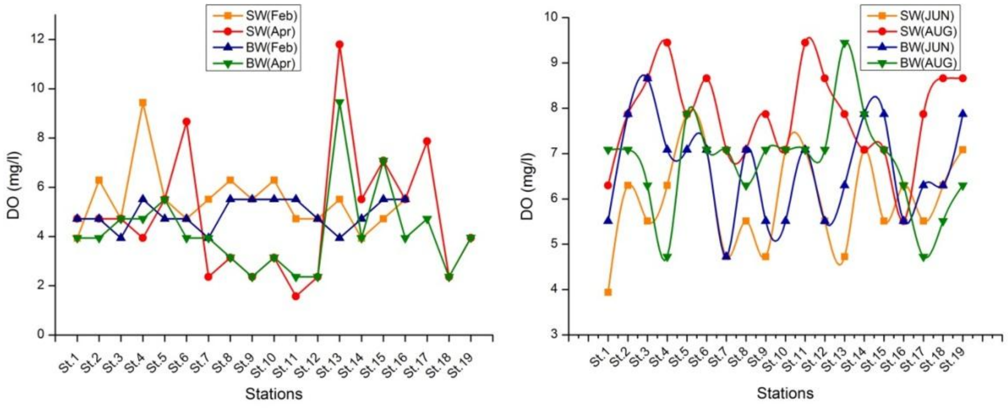


Fig. 3.7 Spatial variation of surface and bottom water DO (mg L^{-1}) in Vembanad backwater during PRM & MN

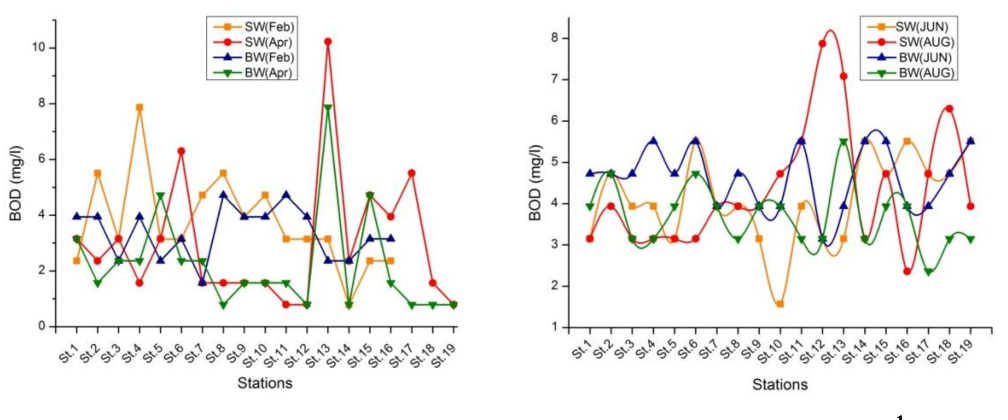


Fig. 3.8 Spatial variation of surface and bottom water BOD (mg L^{-1}) in Vembanad backwater during PRM & MN

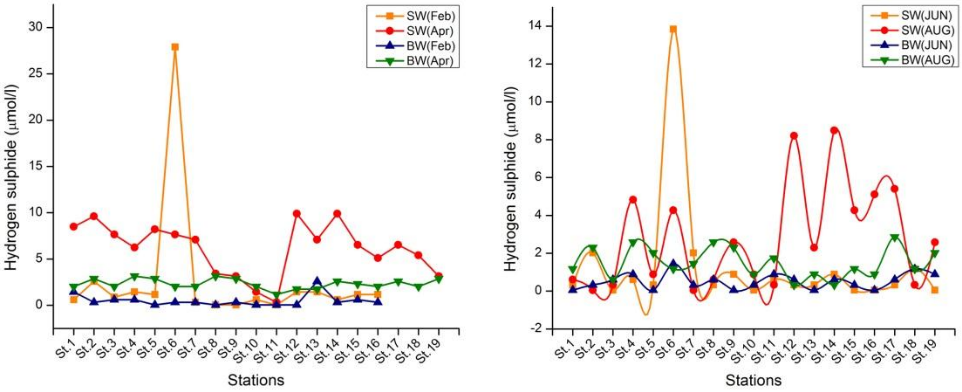


Fig. 3.9 Spatial variation of surface and bottom water hydrogen sulphide (µmol L^{-1}) in Vembanad backwater during PRM & MN

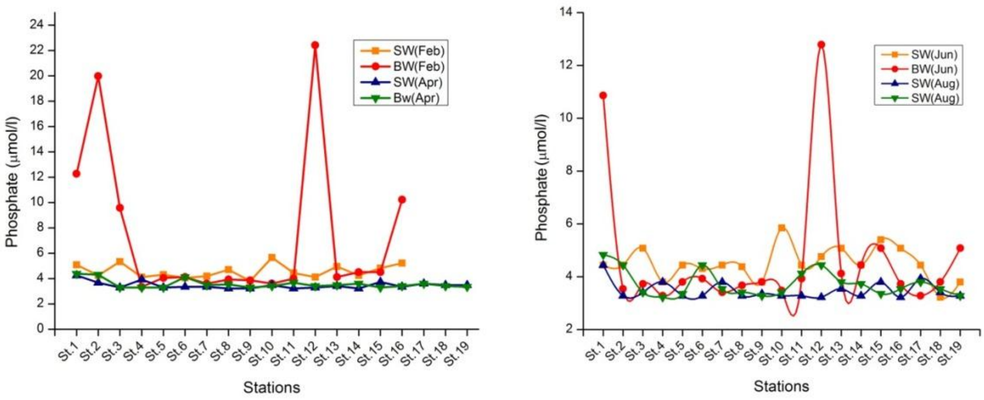


Fig. 3.10 Spatial variation of surface and bottom water phosphate (µmol L^{-1}) in Vembanad backwater during PRM & MN

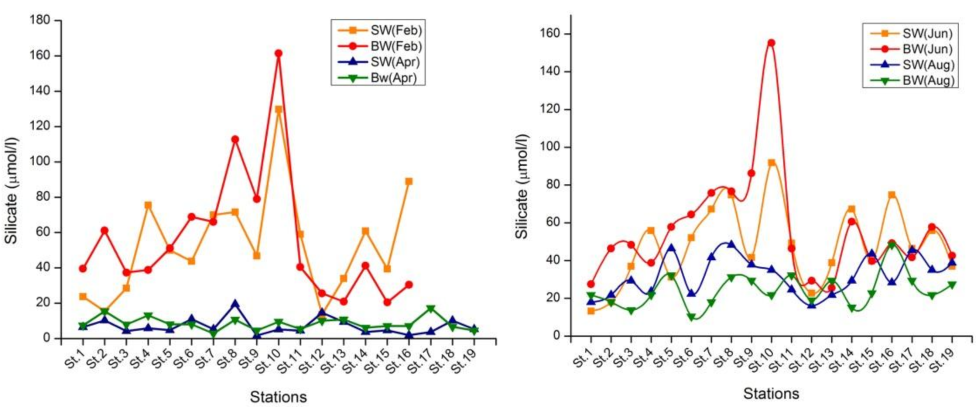


Fig. 3.11 Spatial variation of surface and bottom water silicate (µmol L^{-1}) in Vembanad backwater during PRM & MN

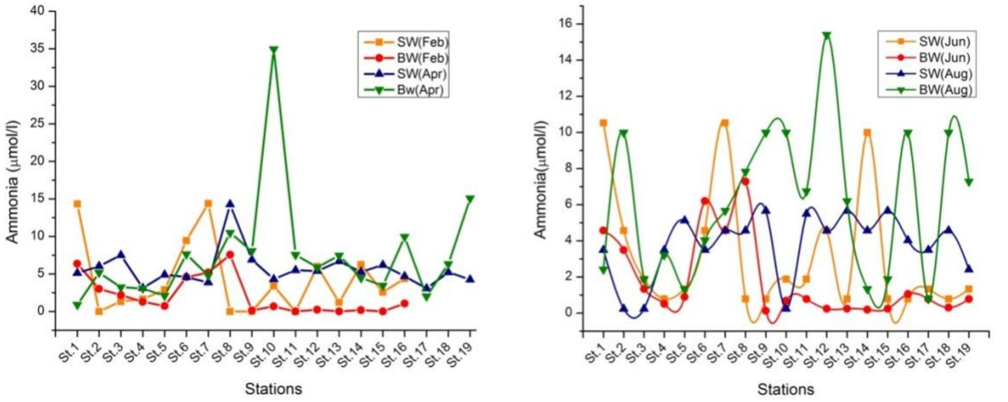


Fig. 3.12 Spatial variation of surface and bottom water ammonia (µmol L^{-1}) in Vembanad backwater during PRM & MN

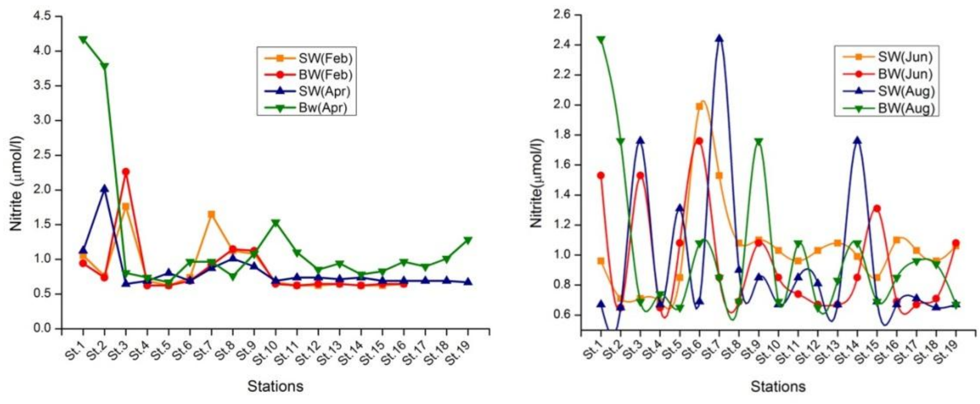


Fig. 3.13 Spatial variation of surface and bottom water nitrite (µmol L^{-1}) in Vembanad backwater during PRM & MN

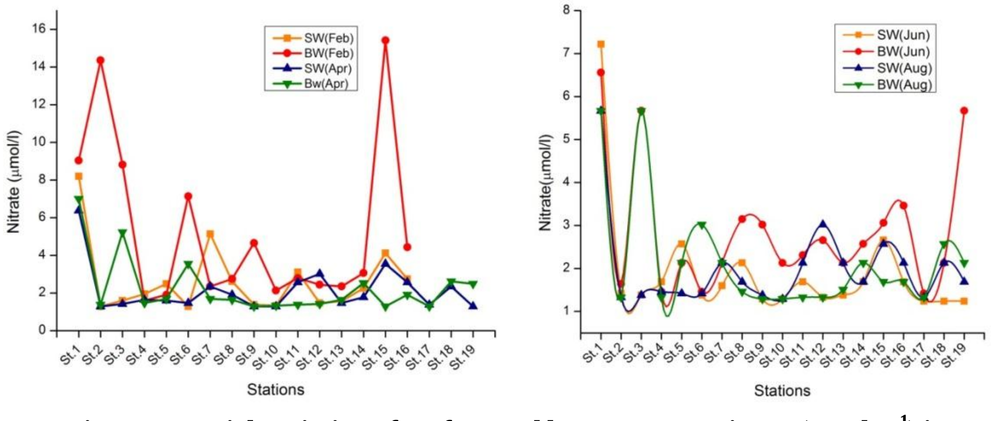


Fig. 3.14 Spatial variation of surface and bottom water nitrate (µmol L^{-1}) in Vembanad backwater during PRM & MN

3.3 Discussion

Estuaries are highly dynamic environments that display strong temporal and spatial variation in their physical, chemical and biological characteristics. So, this dynamism leads to a large variability in estuarine characteristics. The ecological health of estuaries depends on the 'successful' interaction and the limits to the possible interaction that are imposed by the temporal and physical variability between organisms and variations in salinity, currents, waves, suspended particulate matter (SPM), temperature, air exposure, wetland contaminants and biodiversity (Wolanski *et al*., 2004).

Depth of a water body has an important bearing on the physical properties of water. The depth of Vembanad estuary reveals that, it is alarmingly decreasing at 1 % per year and its rate increased after the construction of Thanneermukkom barrage particularly the cofferdam situated in the middle of the estuary. Gopalan *et al*., (1983) gave a brief account on the variation in depth and water holding capacity of the estuary. In the present study, station 1 (Aroor) was deeper compared to the other stations in the northern part of the estuary, which could be attributed to periodic dredging, carried out at the mouth to maintain the port. The depth ranged between 3 - 8 m at station 1 during the study period. Similarly, southern stations were comparatively shallower compared to northern parts of the estuary (Cochin estuary), the shallowness in the southern region of the estuary was due to siltation from the riverine inflow, which was very much reflected in station 6 (Punnamada). The absence of periodic traditional 'kattakuthu' (the clay digging is called kattakuthu, which involves diving 20-25 m deep in to the Kayal-bed. It needs enormous amount of physical strength, skill, experience and ingenuity for the persons engaged) process in the outer boundaries of the padasekharams attributed to the increased silting in the southernmost stations. During June and August station 9 (Pallathuruthy) was recorded with highest depth of 7 m which might be due to the indiscriminate mining of lime shells and river sands in the southern zone, which causes severe damage to the lake system (Maya, 2006). Dredging along with waste disposal and accumulation is altering the depth of the most of the stations. Land reclamation and other illegal construction activities have also caused serious alterations in the depth of the estuary. The estuary has an area of 216.53 km^2 at 1m amsl (average mean sea level) and a volume of 611.47 MCM. Reclamation of estuarine areas for agriculture has led to drastic decline in water holding capacity from 2.4 km^3 to 0.6 km^3 during the last 50 years changes in depth of estuary at various locations (MSSRF, 2007).

Water **temperature** depends upon water depth, solar radiation, climate and topography. It may be mentioned that no other single factor has so much profound direct or indirect influence on physico-chemical, biological, metabolic and physiological behavior of aquatic ecosystem than temperature (Welch, 1952). During the present study, the northern region showed comparatively higher temperature than the southern region. In February, the water temperature ranged between 31.5-38.5 °C in the northernmost stations whereas in stations south of TMB the value ranged between 27-35.5 °C. Similar trend was observed in April, June and August. Sankaranarayanan and Qasim (1969) stated that the influx of fresh water and influx of cold water from the sea in to the estuarine system may be a significant factor which brings down the water temperature in the estuary. According to Haridas *et al*. (1973), the temperature usually decreased with depth. Riverine inflow from Pamba, Manimala and Achankovil influenced the water temperature of these southernmost stations. In February, station 3 (Thanneermukkom north) recorded the highest temperature (38.5 °C) however, in April, stations 2 (Perumbalam) and 6 (Punnamada) showed the highest temperature (33 °C). This increasing trend of temperature in summer months was attributed to the high intensity of solar radiation (Govindasamy *et al.*, 2000). In June, stations 5

(Pathiramanal) and 19 (Meenappally Vattakayal) showed the highest temperature (30 °C). Station 17 (Varanadu) recorded the highest value of 33 °C in August. Over the years, while comparing the previous studies, the temperature regime of Vembanad estuary was slightly higher (Gopalan *et al*., 1987). This might be the reflection of global warming associated with the impacts of climate change.

Transparency is an indicator of relative primary production and pollution levels in the marine environment. During the present study, in February, stations 7 (Nehru trophy finishing point) and 10 (Meenappally) recorded the lowest transparency (0.2 m) and the highest transparency of 1.15 m was recorded in station 16 (Chithirakayal). Stations north of TMB were also recorded with lowest transparency. Station 1 (Aroor) recorded with 0.4 m transparency while station 2 (Perumbalam) with 0.3 m. Many shell fish industries are located in the vicinity of stations 1 and 2. The effluents from these industries along with the urban sewage discharges from Kochi city would have reduced the transparency of these stations. Similarly the increased clay fraction in the sediments of the area may be re-suspended by strong tidal currents that reduce the transparency and increase turbidity. In February, the average transparency was 0.53 ± 0.30 m. In April, stations 1 (Aroor) and 2 (Perumbalam) recorded the highest transparency of 1m. The lowest transparency of 0.4 m was recorded in stations 8 (Pangankuzhipadam) and 14 (Ranikayal). The main basin of the estuary gets clogged with the water plants, *Eichhornia* sp., *Salvinia* sp. and other aquatic weeds during the pre-monsoon season that reduced the visibility of the water body. Bijoy Nandan (2008), observed that during pre-monsoon season, a lower transparency in the retting zones of backwater systems of Kerala, mainly due to the accumulation of coir pith and ret liquor containing organic acids like pectin, pentosan, phenol, tannin, etc. in the water body. In June, stations north of TMB showed lower transparency compared to the southernmost stations. Station 7 recorded the lowest transparency while station 5 recorded the highest transparency in June. In August, lowest transparency was observed in stations 10, 11 and 15 whereas station 4 recorded the highest transparency. Renjith (2006) observed that lower transparency during monsoon was not mainly from the suspended matter, and might be due to the cloudiness associated with rain fall. Increased river discharge, intense rain fall and the cloud cover during monsoon reduces the solar radiation and large input of suspended materials makes the estuarine water turbid.

Salinity is the amount of salt dissolved in water. It controls the types of species that can live in an estuary. Salinity is one of the major hydrological parameter that influences the physical and chemical processes such as flocculation and amount of dissolved oxygen in the water. The gradual increase in salinity from the head towards the mouth of the system is a typical estuarine character (Manikoth and Salih, 1974; Stickney, 1984; Dauvin and Desroy, 2005; Martin *et al*., 2011). Mixing of sea water with fresh water in estuaries created brackish water to be more saline than fresh water but less saline than sea water. Salinity of estuaries usually increases away from a freshwater source such as a river, although evaporation sometimes causes the salinity at the head of an estuary to exceed seawater (Manna *et al*., 2012). Salinity regime of the Vembanad estuary is governed by inflow from sea through Cochin barmouth. According to Sujatha *et al*. (2009), the salinity of Vembanad backwater ranged from 4.5 to 33.1 ppt. In the present study, during February, station 1 (Aroor) recorded highest value of 29.5 ppt and station 10 (Meenappally) showed the lowest value (2 ppt). In station 10, fresh water influx from Pamba, Manimala and Achankovil rivers was the main factor for the low salinity level. According to Martin *et al*. (2013), in Cochin estuary during pre-monsoon season, due to increasing sea water intrusion, the lower reaches of the backwater behaved as an extension of Arabian Sea with fairly high salinity ranges to 31-33 ppt. Compared to other stations, Aroor- station

10 was closest to Arabian Sea. In February, the southern stations showed a salinity value ranged between 2-10 ppt. In northern stations it was ranged between 20-29.5 ppt. Similarly in April, most of the southern stations showed lower salinity compared to the north. In June, station 1 recorded the highest salinity (3 ppt) and all other stations recorded with 0 ppt. Similarly, in August, most of the southern stations recorded lower salinity values. Stations 11, 12, 13, 14, 15, 16 and 19 showed a limnetic to oligohaline nature. Agricultural runoff from the nearby paddy fields and the southwest monsoon bring enormous amounts of freshwater into these southern stations, creating a pure limnetic condition. As the salinity intrusion from Arabian Sea is blocked during the bund closure period, stations in the southern part of TMB remains oligohaline throughout all the seasons. Qasim (2004) has given the details of salinity pattern of most of the estuaries in India and also noted that in most of the estuaries annual variation in salinity was large from mouth to upstream. Menon *et al*. (2000) stated that the major hydrological variable in the Cochin backwater is salinity, and noted a salinity of 30 ppt at the entrance of the estuary to 0.2 ppt at the point of entry of the rivers and found that salinity gradient in the Cochin backwater supports diverse species of flora and fauna depending on their capacity to tolerate oligohaline, mesohaline or marine conditions. Joseph (1974) pointed out that salinity varied from time to time depending on the fresh water influence and penetration of sea water into the Cochin estuary. High value of salinity was observed during pre-monsoon where fresh water discharge was minimum. A homogeneous condition was established until the outbreak of south west monsoon. He also observed that during monsoon period the estuary become completely fresh due to the enormous volume of fresh water discharges by rivers. In the present study, during southwest monsoon season the salinity declined nearly zero mainly due to the heavy rainfall and river discharge. The salinity in the Kol wetland and a part of Vembanad estuary, north of Thanneermukkom barrage, was observed to be

in the range of 10-15 ppt during 1990s. Inter basin transfer of water from Periyar to Muvattupuzha and discharge of water from tail races of hydropower projects have changed salinity gradient in the central part of estuary which presently tends towards freshwater condition. The Thanneermukkom barrage plays a critical role in influencing salinity.

pH is considered as an important ecological factor whose variation in any aquatic system affects the inhabitants as they are adapted to an optimum pH and cannot withstand abrupt changes. The processes of primary production, respiration and mineralization of organic matter may alter the pH of the system because they can cause significant changes in the oxygen and carbon dioxide concentrations of aquatic environments. In the present study period, a slight acidic to alkaline condition was observed in the Vembanad estuary, indicating the sea water influence through Cochin bar mouth (Jayachandran *et al*., 2013; Asha *et al*., 2015) and higher biological activity (Das *et al*., 1997). During February, station 1 (Aroor) recorded the highest value, which is located close to the Cochin barmouth; seawater plays a significant role in controlling the pH. The pH value of stations south of TMB ranged between 6.45-7.5. This observed variations in pH in the southernmost stations could be ascribed to the relatively higher freshwater discharge from rivers like Manimala, Meenachil, Pamba and Achankovil which drain into the Vembanad estuary in the southern region. These rivers and streams transport large quantities of humic material in colloidal suspension which are frequently slightly acidic which upon meeting sea water, the colloidal particles get coagulated and the pH shifts towards the alkaline side (Ried, 1961). Hence, the values were higher towards downstream, in the northern zone and a similar trend was observed in April. Southernmost station like station 13 (Kuttamangalam) had a minimum range of pH in August (5.38). It was noted that the soil of Kuttanad area was highly acidic (Thampatti and Jose, 2000) and this will impart low pH in the southern stations. The ‘kari’ soils in

Kuttanad region are acidic in nature (due to rich organic carbon) especially in the dry months. The runoff from these agricultural fields with the onset of the southwest monsoon may also attribute to the acidic pH in station 13. Removal of CO_2 by photosynthesis through bicarbonate degradation, dilution of seawater by freshwater influx, reduction of salinity and temperature and decomposition of organic matter can be related with the fluctuations in pH values (Upadhyay, 1988; Rajasegar, 2003; Paramasivam and Kannan, 2005). The low variation of pH observed in the estuary, suggests that the water mass remained well buffered throughout the study period and indicates the presence of biodegradable organic matter in the water column (Sarkar *et al*., 2007). During June and August, the pH of the southern stations were little higher, this may be due to the lack of tidal flushing so that all the pollutants including house hold wastes, houseboat discharges get accumulated in the southern zone which in turn make the area alkaline.

Alkalinity of water is another important factor which can be correlated with productivity. It is generally caused by the carbonates and bicarbonates of calcium and magnesium, which along with dissolved carbon dioxide in the water, form an equilibrium system $CO_2+CO_3+H_2O \leftrightharpoons (HCO_3)_2$ which play a very important role in the ecology of the environment. This equilibrium also acts as a buffer system for limiting the fluctuation of pH (Pathak *et al*., 2004). Moyle (1949) based on the study of a large number of lakes and ponds, showed that alkalinity ranging from 40 to 90 mg L^{-1} gives medium productivity whereas highly productive waters have alkalinity values more than 90 mg L^{-1}. Additionally, alkalinity measurements help to understand the estuary’s ability to neutralize acid pollution from rainfall and waste water discharge. According to the Bureau of Indian Standards (BIS), the desirable limit of alkalinity of drinking water specification is 200 mg L^{-1}; beyond this limit, taste becomes unpleasant. Range of alkalinity in the present study area was within this limit. Compared to other stations, station 1 (Aroor) signified with higher alkaline condition (50-100 mg L^{-1}) during the entire study period. Station 1, which is located close to the Cochin barmouth region where, seawater plays a significant role in controlling the alkalinity of the station. The usage of dissolved carbon dioxide for photosynthesis by phytoplankton leads to decrease in CO_2 in the aquatic medium which in turn creates an alkaline condition. Mogalekar *et al*, (2015) noted a relatively higher alkalinity (139 mg L^{-1}) in the Vembanad estuary at Panangad-Kumbalam mangrove patches. At the same time, in stations 4, 5, 6 and 14, fresh water from rivers such as Pamba, Manimala and Achankovil uphold a reduced condition of alkalinity. During the present study, the southern zone of Vembanad was having less alkalinity compared to northern zone. The decreased alkalinity level may be due to the increased lime shell and live clams collection from the region over the years. Similar condition of low alkalinity related to the low lime content of rock was noted in the Ibiekuma stream, southern Nigeria (Edokpayi and Osimen, 2002). The saline water containing high amount of carbonate, bicarbonate and hydroxide compounds from the Arabian Sea increases the alkalinity in north. According to Bijoy Nandan (2008), retting zones in the coastal wetlands of Kerala had higher alkalinity value (103 mg L^{-1}) compared to non-retting area (91 mg L^{-1}).

The concentration of **dissolved oxygen (DO)** is an important indicator of the environment water quality. Sufficient dissolved oxygen (DO) in estuarine waters is a basic requirement for the health of aquatic organisms. The diversity of organism is directly dependent upon the DO concentrations. Fish kills, benthic defaunation (Global, local or functional extinction of animal populations or species from ecological communities), and decreased diversity of fish and benthic invertebrates have often been attributed to hypoxia (insufficient DO to support biological processes) or anoxia (absence of DO) (Engle *et al*., 1999). It varies due to a number of factors like season, temperature, salinity and time of the day. The lowest level of DO in station 1 (Aroor) during February was mainly augmented by the resuspended silt particles from the dredging activities in the Cochin navigational channel. According to Brown and Clark (1968), due to dredging the resuspension of oxidizable bottom sediments in a tidal waterway caused significant reduction in the dissolved oxygen concentration of water in Raritan Bay in U.S, where during dredging, DO was reduced between 16-83 % below normal. Similarly the decreased DO level in southern stations like station 6 (Punnamada), 11 (Kainakary), 12 (C Block, Cherukayal), 14 (Ranikayal) and 15 (Marthandam) was mainly responsible for the proliferation of aquatic weeds in the surface layer during the period of sampling, the estuary gets clogged with, *Eichhornia*, *Salvinia* and other aquatic weeds, which reduces the oxygen dissolution in water, light penetration and ultimately the photosynthesis. Similarly the decomposition of sewage effluent and organic discharges from the houseboats, along with nutrient rich runoff from agricultural lands situated close proximity to the stations. This will reduce the rate of dissolution of oxygen in the water column; along with the decaying weeds also probably affect the DO level. In April, station 13 (Kuttamangalam) recorded the highest DO value. Station 7 (Nehru trophy finishing point), 9 (Pallathuruthy), 12 (C Block, Cherukayal) and 18 (Kuppapuram) were recorded the lowest DO value (2.36 mg L^{-1}). The thick layer of water hyacinth and the oil film from the houseboat and other boats in the southern zone may prevent the diffusion of atmospheric oxygen into the water column. Similarly during the closure period of TMB, the organic wastes from animals and humans, and also the crop debris, food wastes, rubber, plastic wastes are increasingly accumulated in the southern zone. Such wastes require more oxygen to decompose and which reduces the oxygen level in the southern zone. Houseboat tourism and related activities, sewage discharge and spread of invasive water plants play a crucial role in dissolved oxygen content of the southernmost stations of

Vembanad estuary. Alterations of the natural hydrological regime have led to serious clogging of the channels of the Kuttanad area, which obviously alters the dissolved oxygen level of the area (Asha *et al*., 2016). In June and August, the DO values of most of the stations were higher compared to the previous months. This could be due to the fresh water runoff from the rivers of Pamba, Manimala, Achankovil, Meenachil and Muvattupuzha as oxygen solubility is higher for fresh water. Along with this, the increased precipitation and river discharge during the monsoon season may also increase the DO level in the Vembanad estuary.

Biological Oxygen Demand (BOD) is a measurement of the amount of dissolved oxygen (DO) that is utilized by aerobic microorganisms when decomposing organic matter in water. According to WHO (1984), permissible limit of BOD is 5 mg L^{-1}. Increased BOD level is attributed to the biodegradation of organic materials which exerts oxygen stress in the water (Gupta, 2009) and also gives an idea about the extent of pollution in the water body. During February and April, the maximum level of BOD observed in southern stations such as station 4 (Thanneermukkom south), 6 (Punnamada) and 13 (Kuttamangalam). Spreading of water hyacinth in the southern region of TMB during the closure period of bund and its decaying affects station 4, the thick layer of water hyacinth prevent the diffusion of atmospheric oxygen into the water column, leads to low DO level and hence affects the decomposition process, resulting in low BOD level. Increased BOD level in station 6, Punnamada was mainly due to the enhanced organic load from houseboat tourism activities which resulting the microbial oxidation of organic matter. The polluted and flow restricted Alappuzha canal carrying waste water from the town directly entering the Punnamada region of Vembanad estuary and these events enhances the BOD level in Punnamada station. Faecal contaminants from houseboats, municipal garbage from Alappuzha town and organic pollutants from nearby agriculture fields leads to the proliferation of coliform in southern region (Asha *et al*., 2016) and the southern zone were more prone to waterborne diseases (Chandran *et al*., 2013). Similar situation was noted in station 13 (Kuttamangalam) also, where the houseboat tourism plays an important role. The increased BOD level in the northern station such as station 17 (Varanadu) was attributed to the effluent discharges from the distillery. Lakshmi and Jaya (2007) noted that after the treatment of effluent discharges from the distillery situated near Varanadu, there was 99 % drop in BOD load and 98 % drop in the nutrient level of effluent. In June, southern stations such as station 6 (Punnamada), 14 (Ranikayal), 16 (Chithirakayal), 19 (Meenappally Vattakayal) and in August, station 12 (C Block, Cherukayal) and 18 (Kuppapuram) were recorded the highest BOD value. The desire for short term profit from houseboat tourism caused environmental degradation of the system; even though the operators understood that sustainability of the industry is connected to the environmental quality of the system (Karlaganis and Narayanan, 2014). As a result of increased industrialization and urbanization in the Cochin area, a daily discharge of about 104 million liters of untreated effluents and 260 m^3 of raw sewage enter into the estuarine system (Qasim, 2003; Balachandran *et al*., 2005). Numerous open toilets on the banks of the Vembanad estuary especially on the northern zone have increased the sewage load of whole Vembanad estuarine system which in turn increased the oxygen demand in northern stations such as station 1 (Aroor) and 2 (Perumbalam). In the Tapi estuary Borade *et al*. (2014), clearly noted a strong relationship between BOD and microbial populations and found that BOD level in the estuarine system was mainly controlled by the fecal indicator bacteria.

Hydrogen sulphide is a very toxic compound that can cause acute mortalities in aquatic animals at relatively low concentrations by affecting the nervous systems (Augspurger *et al*., 2003). During the study period high concentrations of hydrogen sulphide were observed in the upstream. During

February, station 1 (Punnamada) showed the maximum concentration. Bijoy Nandan (2008) observed an alarming concentration level of dissolved sulphides in the south west coast of India, during the pre-monsoon season. The mean value of total sulfides in the retting zone was 8.8 μg L^{-1} and in the non-retting zone was 3.01 μg L^{-1}. High concentrations of dissolved hydrogen sulphide were the characteristic feature of the water quality in retting zone. Hydrogen sulphide concentration in the retting zone ranged from 8.8 to 12.8 μg L^{-1} and in the non-retting zone 0.8 - 1.12 μg L^{-1} in the backwater of Kodungallur in Kerala (Manoj *et al*., 2014). Depletion of dissolved oxygen and production of hydrogen sulphide accompanied with the retting of coconut husk has been reported earlier from the Edava-Nadayara estuary by Abdul Azis and Nair (1986). The decomposition of the organic matter in the retting zones by bacteria results in the utilization of dissolved oxygen and production of hydrogen sulphide. The organic load at the retting zones was always high resulting in generation microbial decomposition leading to depletion of oxygen which eventually led to a state of anoxia. In Periyar River, the hydrogen sulphide in surface water ranged from 37.10 μmol L^{-1} to 173.96 ± 12.62 μmol L^{-1} during 2014 period. According to the Environmental Protection Agency, a maximum acceptable level of H_2S for fish and aquatic life is 0.062 μmol L^{-1} (KSPCB, 2014). In the present study, the sulphide concentration exceeds this level. Most of the southern stations were recorded higher sulphide concentration; which may be due to the various pollution problems in this region

Phosphorus is an important plant nutrient that may limit algal biomass production in tidal fresh to brackish zones of estuaries and some sub temperate to tropical marine coastal systems. There are no common stable gaseous forms of phosphorus, so the phosphorus cycle is endogenic, without an atmospheric component (Manahan, 1997). The main natural reservoirs of phosphorus are poorly soluble minerals (eg. hydroxyapatite) in the geosphere. Erosion of these materials from terrestrial sources and their transport to the sea was found to be important sources of new phosphorus in seawater. The phosphorus entering the sea is mostly orthophosphate, PO_4^{-3} (Kennish, 1989). Orthophosphates are typically preferred by autotrophic phytoplankton, although some assimilation of organic phosphorus may occur, especially during subsequent periods shows P deficiencies. When plants die, or are eaten, the organic phosphorus is rapidly converted to orthophosphates through the action of phosphorylases within faecal material, phosphatases in the plant cells, and finally by bacteria (Riley and Chester, 1971). In the case of phosphorus, increasing anthropogenic events especially, agricultural activities including use of superphosphate fertilizers and urban expansion and the diffuse nature of its associated nonpoint source pollution from surface runoff and ground water contamination have become a major water quality problem. Phosphorus undergoes sedimentary cycle with no significant role in the gaseous phase so it tends to accumulate in wetland systems (Renjith, 2006). During the present study, maximum phosphate concentration was observed in station 1 (Aroor). Saline incursion, discharge from sea food industries, urban and municipal discharge from Cochin City makes this station rich in inorganic materials. Agricultural runoff with phosphate containing fertilizers from Q, S, T, R and C blocks contribute the major share of phosphate-phosphorus in the southern stations, such as station 12 (C Block, Cherukayal) and station 16 (Chithirakayal). During the present study, higher value was always observed in bottom water (7.38 ± 6.06 µmol L^{-1}) compared to the surface water (4.58 ± 0.54 µmol L^{-1}). Higher concentrations of phosphate and nitrite in Cochin estuary were restricted to the near bottom salt wedge (Shivaprasad *et al*., 2013). Concentrations of all the nutrients changed with tides (Qasim and Gopinathan, 1969). The phosphorus value increased at flood and decreased at ebb tide time, representing that the phosphorus accompanied with the incursion of sea water. The nitrate-N showed high value with the inflow of freshwater in the Cochin estuary. Nair *et al*. (1975) reported a high value of phosphate-phosphorus in Vembanad backwater during monsoon and pre-monsoon period of about 15 $\mu g\ L^{-1}$. In estuaries, distribution of nutrients was mainly depending up on the marine influence and fresh water discharge. Qasim (2004), pointed out that during monsoon the increased rainfall and land runoff is associated with increased phosphorus runoff gets settled to the bottom, from where it is released to the surface. According to Liu *et al*. (2009), in coastal and estuarine waters, sea water act as a major source of phosphate except those get freshwater containing domestic wastes including detergents as well as discharges of phosphate-phosphorus fertilizers and pesticides from agriculture field. In the present investigation, both sea water and fresh water discharges act as a major phosphate contributor because higher values were observed in the extreme south and northern stations. Sujatha *et al*. (2009) reported higher levels of inorganic phosphate in Vembanad estuary compared to Ashtamudi estuary. According to Jyothibabu *et al*. (2006), Cochin estuary receives large amount of nutrients from rivers, apart from this, increased supply of nutrients are mainly received from various domestic and industrial activities. The excessive input of inorganic phosphate fertilizers, detergents, and fungicide in the Vembanad estuary has been reported from several studies (Remani *et al*., 1983; James, 2011). In Kuttanad agrarian zone the annual consumption of fertilizer was 8409 tonnes of nitrogen, 5044 tonnes of phosphorus and 6786 tonnes of potassium and the pesticides/fungicides/weedicides were about 500 tonnes/annum (James, 2011).

Silicate is as an important algal nutrient. Dissolved silicate is a product of weathering and erosion of rocks on land with subsequent transport to the sea (Conley and Malone, 1992). Silicate has no human sources, except possibly from erodible soils under human influence; it is not a strong candidate for regulation. Silica (Si) may limit diatom production at relatively high levels of N and P. During the study period, the increased silicate concentration in st.10

(129.72 µmol L^{-1}) could be due to the influence of discharges from Pamba and Achankovil rivers and terrestrial runoff from padasekharams. The municipal discharges from the Alappuzha town may be enhancing the silicate input in station 6 (68.85µmol L^{-1}). Tripathy *et al*. (2005) noted the high concentration of SiO_4-Si (142.0 µmol L^{-1}) concentration in the Gautami-Godavari estuarine system of Andhra Pradesh indicates the impact of terrestrial runoff. During the present study, maximum silicate concentration was observed in February and June. The increased river fall and land runoff in the monsoon season may become a major contributor of silicon (Sankaranarayanan and Qasim, 1969; Anirudhan and Nambisan, 1990; Bhattacharya *et al*., 2002; Renjith, 2006). The concentration of SiO_4-Si in the estuary is influenced by mixing of fresh water with seawater (Anirudhan *et al*., 1987) and the irregular summer showers during the month of April and May that affects the distribution pattern of silicate. The effect of local rains and its uneven intensity rain fall and associated runoffs altogether affects the spatio-temporal variation of nutrients in Vembanad estuary. Sankaranarayanan *et al*. (1984) reported maximum SiO_4-Si concentration in Cochin backwater during south west monsoon. According to Shivaprasad *et al*. (2013a), elevated levels of silicate (120.66 µmol L^{-1}) concentration in the Cochin estuary were found at the surface water indicating that freshwater runoff is the principal source of silicate inputs. This is substantiated by the fact that higher silicate concentrations in wet season were due to heavy runoff from the river input. In the present study, most of the southern stations were recorded with higher silicate concentration, it was mainly attributed to the large amount of silicate input from rivers such as Pamba, Manimala, Achankovil and Meenachil, which may retained over the year into the Vembanad estuarine system. Increased amount of waste water inputs from agricultural runoff and industrial activities might also contributed to the higher silicate concentration.

Ammonia-nitrogen is a primary product of microbial degradation of organic materials, and if not used directly by autotrophic algae and vascular macrophytes and microbial heterotrophs for growth, it may be oxidized through nitrification to nitrite and nitrate. In estuaries, nitrogen compounds exert a significant oxygen demand through microbially mediated nitrogen conversion (Grabemann *et al*., 1990). Organic nitrogen is hydrolyzed to ammonia and the excess ammonia enters the estuaries via the tributary of rivers and also as wastewater discharges. Ammonia is present in terrestrial and aquatic environments. Plants and animals excrete ammonia; it is produced by the decomposition of organisms and by the activity of microorganisms (Prosser and Embley, 2002). The higher values observed in the northernmost stations (st.1 and st.2), indicates its direct relation with salinity as stated by Miranda *et al*. (2008) who studied the relationship between salinity and ammonia. In the present study, the increased concentration of ammonia in southernmost stations such as station 6 (Punnamada), 7 (Nehru trophy finishing point), 8 (Pangankuzhipadam) and 19 (Meenappally Vattakayal) have considerably been impacted by houseboat tourism activities. These areas were the hub of houseboat tourism activities, in which more than thousands of houseboats are plying in this region. The untreated wastes from the houseboats are directly dumped into the water body. Similarly the polluted Alappuzha canals with restricted flow, carrying waste water from the town directly enter the Punnamada region of Vembanad estuary which also enhances the ammonia-nitrogen in the estuary. Occurrence of ammonia indicates the presence of sewage in the water body. Apart from this, sewage load from Sabarimala through Pamba and Manimala also contribute a major share of ammonia in the water body. The usage of NPK fertilizers and Factamphos (20N:20P) from the padasekharams (Q, S, T, R and C blocks may get leached out during monsoonal rains to these southern stations can also contribute high ammonia concentration. There were several reports indicating the sewage pollution with increasing fecal coli forms, along with unobstructed tourism in conjunction with operation of thousands of houseboats in the estuary and also by the waste disposal and oil pollution causing severe ecological implications in the southern zone of Vembanad estuary (Hatha *et al*., 2008; Anon, 2012a; Safoora Beevi and Devadas, 2014). According to Asha *et al*. (2016), the shoddy operation of sewage treatment plants by District Tourism Promotion Council, Govt. of Kerala for processing the sewage and other effluents from the houseboats and other domestic sources has consistently affected the water quality of the southern zone. According to Joseph and Ouseph (2010), the ammonia content in Cochin estuary was contributed by the Periyar River and its associated tributaries including Chitrapuzha, which flow through the industrial zones. The higher values during the summer months (February and April) could be due to the death and subsequent decomposition of phytoplankton and also due to the excretion of ammonia by planktonic organisms (Segar and Hariharan, 1989; Rajasegar, 1998). In estuaries, the main sources of nutrients are river discharges containing load of urban wastewater, agriculture fertilizers and organic manure (Bricker *et al*., 2008).

Nitrite is one of the most unstable forms of dissolved inorganic nitrogen species in water (Mohanty *et al*., 2014, SreedharanManikoth and Salih, 1974 and Laksmanan *et al*., 1987) followed by ammonia and nitrate in the process of nitrification. The decomposition of dead and decaying plants and organisms, nitrogenous wastes create ammonia. The ammonia is then converted into nitrite and which is then converted to nitrates (NO_3) by bacteria. The reactivity of nitrite is very high, leading to a lower concentration of nitrite in the aquatic system compared to ammonia and nitrate. To support algal growth inorganic nitrogen above 0.03 μmol L^{-1} is required, and high level of nitrite in water may not be suitable for growth of aquatic organisms (Wang *et al*., 2006). In the present study, the increased level of nitrite in station 1 (Aroor) is highly influenced by the discharges from Kochi metro city along with the effluent from shell fish industry situated along the estuarine bank at Aroor and are often associated with the unsatisfactory microbial quality of water. There were a number of reclamation activities on the banks of Vembanad estuary mainly in the Aroor, Thevara region under the guise of industrial, tourism and urban development has threatened the bathymetry of the region. The reclamation and economic activities in the Cochin estuary initiated with the development of the Cochin Port Trust in 1938, later with Vallarpadam International Container Transshipment Terminal, Kochi (2011), the Liquefied Natural Gas (LNG) regasification terminal in Puthuvype, Kochi (2013) and other establishments. Apart from this, the population of the area is expected to increase by 5×10^6 by 2025 (Balachandran *et al*., 2005) that also, signifies the need for environmental conservation plans to minimize the excessive pollution in the estuarine area. Station 2 (Perumbalam) and station 3 (Thanneermukkom north) were also recorded the increased nitrite concentration. This may be supported by some nitrogenous compounds being added to the estuary from external sources around these stations. Nitrogen loading to the Vembanad estuary increased mainly due to extended aquaculture, agricultural practices and aqua-tourism (Martin *et al*., 2010). During the study period maximum value of nitrite was observed in the northern zone compared to the southern zone which clearly indicates that the source of nitrogen is from the coastal waters of Arabian Sea. The possible cause of lower values observed in the southern most stations might be the highly unstable nature of nitrite, as it remains as a transient species by the oxidation of ammonia or by the reduction of nitrate and are often released into water as an extracellular product of planktonic organisms (Santschi, 1990; Chandran and Ramamurthy, 1984). Increased uptake of nitrite by the planktonic communities could also attribute to the low levels of nitrite in these stations. Southern stations such as stations 7 and 10 showed a slightly higher nitrite concentration. This may be due to the discharge from houseboats and input of nitrogen containing fertilizers from the agricultural fields of Kuttanad that end up in the Vembanad estuary.

Nitrate-nitrogen forms one of the most thermodynamically stable forms of inorganic nitrogen in well oxygenated waters and its variation in aquatic bodies are predominantly the results of biologically activated reactions (Satpathy *et al*., 2010). Natural waters in their unpolluted state contain only minute quantities of nitrates (Manikannan *et al*., 2011). The excessive sources of nitrates can usually be traced from agricultural activities, human wastes and industrial pollution. Excess levels of nitrates in water can create adverse conditions that make it difficult for aquatic organisms to survive. In hypertrophic conditions, the water body experienced the nitrate levels of >10 mg L^{-1}. During the study period, stations 1 (Aroor) and 2 (Perumbalam) showed increased nitrate concentration, indicating a nitrate input from either sea water or its origin from industrial effluent, sewage discharges from the shell fish industries, residential and urban areas situated close proximity to the stations. Nitrate values could also be influenced by the organic materials received from the catchment area during ebb tide (Das *et al*., 1997). Another possible way of nitrates entry is through oxidation of ammonia form of nitrogen to nitrite formation (Rajasegar, 2003). In the present study, compared to the southernmost region, the northernmost region of Vembanad estuarine system represented higher nitrate concentration. Increased concentration of nitrate in the northernmost stations was influenced by the sea water intrusion from Arabian Sea and also from urban discharges. According to DoECC report (2013) the average nitrate-nitrogen in the Cochin estuary was 13.12 µmol L^{-1}. In the Kodungallur-Azhikode estuary the average nitrate value was 10.2 ± 12.8 µmol L^{-1} (Jayachandran *et al*., 2012). Pillai (1991) reported the nitrate concentration in Cochin estuary as 20.21 µg L^{-1}. Similarly Martin *et al*. (2013) reported a high nutrient concentration in Cochin estuarine area and these observation agrees with the previous studies of Vijayan *et al*. (1976); Saraladevi *et al*. (1991); Qasim (2003). The lower levels of nitrate observed in southernmost stations may be due to the variation in freshwater input, salinity and also their utilization by phytoplankton. Increased level of nitrate in station 15 (Marthandam) may be due to the runoff from agriculture areas and sewage discharge from houseboats and nearby resorts. Station 6 (Punnamada), station 7 (Nehru Trophy finishing point) and station 9 (Pallathuruthy) were also recorded higher nitrate level. These stations were highly influenced by the houseboat tourism activities and station 6 (Punnamada) was found to be the hub of house boats which eventually leads to an increase in the nitrate concentration in the southernmost stations.

Primary production is defined as the amount of organic materials by which the activity of organisms in unit time is synthesized in unit volume of water or in unit area. The floating micro-algae remove dissolved carbon-dioxide and micro-nutrients from the water and using solar energy convert them into complex organic compounds of high potential energy with the help of chlorophyll. In aquatic ecosystems, the major limiting factors to primary production are light (solar energy) and nutrients (Simmons *et al*., 2004); though temperature and seasonal variations in light intensity also exert influences on the distribution of phytoplankton (Vaillancourt *et al*., 2003). Gross primary productivity (GPP) represents the total autotrophic conversion of inorganic carbon to organic forms. In the present study, the higher GPP values observed in station 3, 4, 5, 8, 11, 13 and 14 could be attributed to the increasing phytoplankton density and nutrient enrichment in these stations. Light penetration also plays a key role in primary production. The lower values of GPP observed in the southern stations such as station 7, 9, 10, 11, 12 and 18 could be due to the presence of decaying weeds, enhancing the organic load in the area, adversely impacting the transparency of the aquatic body. In addition, increased organic load from houseboat (Safoora Beevi and Devadas, 2014) during the peak tourism period also negatively affects the transparency of the estuary, leading to decreasing phytoplankton production. Moreover, phytoplankton production is strictly linked to variability in water quality, bio-geochemical processes including aquatic-atmospheric CO_2 exchange and production at higher trophic levels (Cloern, 2014). Gowda *et al*. (2002) reported that the phytoplankton pigments and primary production is largely determined by the species composition of phytoplankton as they are the major producers in the aquatic ecosystems. In Valanthakad backwater Meera and Bijoy Nandan (2010) observed a variation of GPP value from 0.24 to 3 gC m^{-3} day^{-1}. Qasim (1969) studied the organic production of the Cochin backwater using various techniques and stated that the gross production ranged from 272 to 293 gC m^{-2} yr^{-1} with an average of 280 gC m^{-2} yr^{-1}. During the present study, the highest value of NPP in station 5, 11, 13 and 14 could be due to greater photosynthetic activities in this region. The higher NPP value in station 5 during summer month (April) could be due to increased phytoplankton population and low respiration rates. Meera and Bijoy Nandan (2010) observed a variation of NPP value from 0.12 to 1.8 gC m^{-3} day^{-1} in Valanthakad backwater. According to Nair *et al*. (1984c) the gross productivity in Ashtamudi estuary varied from 88.68 to 1596.3 mgC m^{-3} day^{-1} and the net productivity was 22.41 to 1330.25 mgC m^{-3} day^{-1}. The highest production recorded in the Cochin estuary was 245 mgC m^{-3} day^{-1} (Pillai *et al*., 1975). Increased organic load and eutrophication in most of the southern stations accounts for the greater respiration in southern part of the TMB, which corroborates with the lowest NPP values in the present study.

4. HEAVY METALS AND OTHER CONTAMINANTS

4.1 Introduction

Many studies are going on various topics of heavy metal impacts on aquatic systems since the last decade. As many of these elements are stable they are bio accumulative, and assessment of their safe limits is very difficult in the ecosystem. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (International Occupational Safety and Health Centre, 1999). Trace metals are mainly natural elements present in aquatic ecosystems, but deposits of anthropogenic origin have caused a progressive increase in their concentration, creating environmental problems in coastal zones, lakes, and rivers. Untreated industrial and sewage deposits are the main sources responsible for such problems in most cases. The concentration of these elements above tolerable levels is a disturbance factor for species survival and ecosystem stability. Among the various toxic pollutants, heavy metals are particularly severe in their action due to tendency of bio magnification in the food chain. Metal ions can be incorporated into food chains and concentrated in aquatic organisms to a level that affects their physiological state (Fig. 4.1). Heavy metals are high priority pollutants because of their relatively high toxic and persistent nature in the environment. The heavy metal pollution of aquatic ecosystems is often most obvious in sediments, macrophytes and aquatic animals, than in elevated concentrations in water. According to Tappin *et al*. (1995) the distribution of trace metals in the marine environment is influenced by many factors such as boundary inputs, particle water exchanges and advection and mixing within the basin. The abundance, geochemical and mineralogical composition and distribution pattern of trace metals in the Arabian Sea and Bay of Bengal depend on the biogeography, hydrography and topography of the brackish waters that transport these inputs to the seas. Few metals, such as Fe, Zn, Cu, Co, Cr, Mn and Ni, are required for biological metabolism in trace amounts; however, their higher dose may cause toxic effects. Others, such as Pb, Hg, Cd and As, are not suitable for biological functions and are positively toxic. In the present study, water, sediment and organism samples were analysed for heavy metals viz. copper (Cu), zinc (Zn), nickel (Ni), cadmium (Cd), lead (Pb) and iron (Fe).

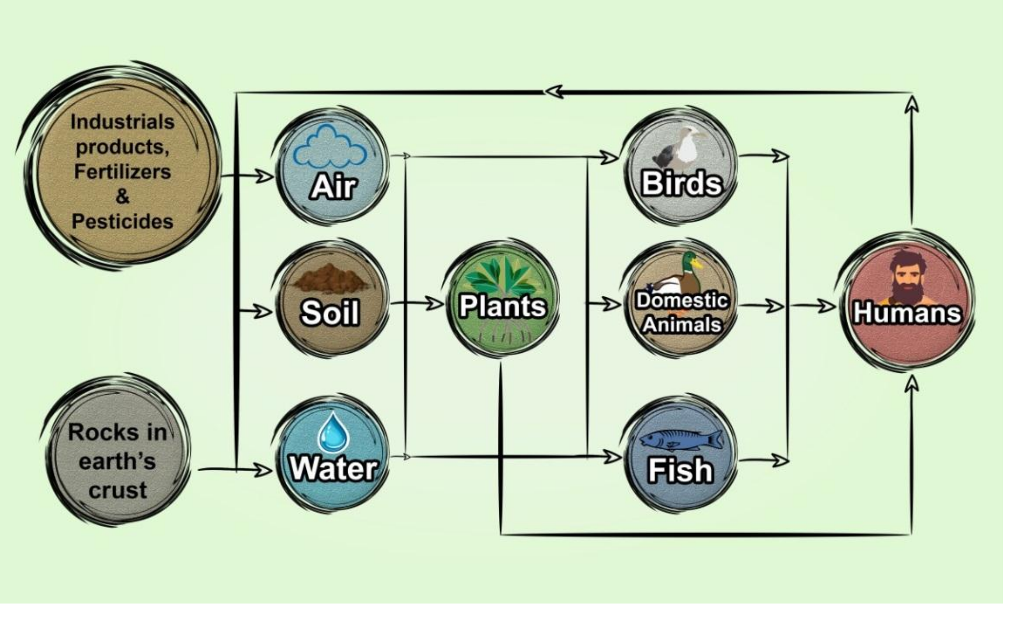


Fig. 4.1 Sources of heavy metals and their cycling in the soil-air-water and organisms

4.2 Results

4.2.1 Distribution of heavy metals in water

The distribution of **copper** in water samples of Vembanad backwater ranged from 0.75 to 8.56 µg L^{-1} in the pre-monsoon season and 20 to 130 µg

L^{-1} in the monsoon season (Fig 4.2). The highest value of copper was noted in February at station 7 (8.56 µg L^{-1}) and a lowest value of 1.13 µg L^{-1} was noted at station 2 (Table 4.1). In April, the highest value of 3.75 µg L^{-1} was noted at station 2 and lowest value of 0.75 µg L^{-1} was noted at station 19 (Table 4.2 and Fig 4.3). In the monsoon season (June) the concentration of Cu in all the stations were found to be below detectable level (Table 4.3 and Fig 4.4). In August, the highest value was noted in station 5 (130 µg L^{-1}) and lowest value of 20 µg L^{-1} in stations 4, 7, 13 and 16 (Table 4.4 and Fig 4.5). In the present study copper showed a positive correlation with salinity (r = 0.183), sulphide (r = 0.208), sediment bound lead (r = 0.163) [$p<0.05$], DO (r = 0.269) and water bound metals like lead (r = 0.636), zinc (r = 0.622) and iron (r = 0.727) [$p<0.01$]. Copper also showed a negative correlation with sediment bound Zn (r = -0.168) [$p<0.05$].

The **nickel** concentration ranged from 0.06 to 9.56 µg L^{-1} during pre-monsoon. During February, minimum concentration of 0.06 µg L^{-1} was noted in station 14 and maximum concentration of 2.31 µg L^{-1} in station 1 (Table 4.1 and Fig 4.2). In April, maximum concentration (9.56 µg L^{-1}) was found in station 18 and minimum concentration (0.13 µg L^{-1}) in station 8 (Table 4.2 and Fig 4.3). The concentration of Ni was below detectable level in all the 19 stations during the monsoon season (Table 4.3 and Fig 4.4). In the present study, nickel was found to be positively correlated with nitrate (r = 0.186) [$p<0.05$], nitrite (r = 0.318) and water bound cadmium (r = 0.523) [$p<0.01$], but was negatively correlated with phosphate (r = -0.201), water bound zinc (r = -0.198) [$p<0.05$], silicate (r = -0.316) and water bound iron (r = -0.218) [$p<0.01$].

The **cadmium** concentration was below detectable level in most of the stations during February (Table 4.1 and Fig 4.2) and in April and it ranged from 0 to 1.44 µg L^{-1} (Table 4.2 and Fig 4.3). The minimum concentration was found in station 9 and maximum in station 2. In the monsoon season, the cadmium concentration was below detectable level in every station (Table 4.3 and Fig 4.4). Cadmium is one of the most toxic elements in the biological systems. In this study, the cadmium concentration in water samples recorded in April was two times higher than the concentration in February. Cadmium showed a positive correlation with nitrite (r = 0.560), nitrate (r = 0.335), water nickel (r = 0.523), and sediment bound metals like cadmium (r = 0.433) and zinc (r = 0.234) but it was negatively correlated with DO (r = -0.279), phosphate (r = -0.312), silicate (r = -0.440) and water bound metals like zinc (r = -0.280) and iron (r = -0.321) [$p<0.01$].

The concentration of **lead** ranged from 0.38 to 48.06 µg L^{-1} during pre-monsoon. In February, the maximum concentration (11.88 µg L^{-1}) was found in station 15 and minimum concentration (0.38 µg L^{-1}) in station 2 (Table 4.1 and Fig 4.2). The maximum concentration was found in April (48.06 µg L^{-1}) at station 18 and minimum concentration (7.13 µg L^{-1}) at station 19 (Table 4.2 and Fig 4.3). In monsoon season the concentration ranged from 50 to 370 µg L^{-1} (Table 4.3 and Fig 4.4). In August, the maximum concentration (370 µg L^{-1}) was found at station 5 and minimum concentration (70 µg L^{-1}) at station 14 (Table 4.4 and Fig 4.5). Lead showed a positive correlation with DO (r = 0.348) and water bound metals like copper (r = -0.636), zinc (r = 0.851) and iron (r = 0.661) [$p<0.01$]. Lead was negatively correlated with silicate (r = -0.187) [$p<0.05$] and sediment bound metals like nickel (r = -0.225) and zinc (r = -0.214) [$p<0.01$].

The concentration of **zinc** was maximum (101.8 µg L^{-1}) in station 15 and minimum (11.62 µg L^{-1}) in station 19 during February (Table 4.1 and Fig 4.2). In April, the maximum concentration (58.38 µg L^{-1}) was recorded in station 1 and minimum (9.26 µg L^{-1}) in station 19 (Table 4.2 and Fig 4.3). During monsoon season, the concentration ranged from 20 to 1400 µg L^{-1}. In June, the minimum concentration (20 µg L^{-1}) was found at station 9 and the maximum concentration (240 µg L^{-1}) at station 1 (Table 4.3 and Fig 4.4). The maximum concentration of 1400 µg L^{-1} was noted in station 5 and minimum of 130 µg L^{-1} was noted in station 15 in the month of August (Table 4.4 and Fig 4.5). Zinc showed a positive correlation with DO (r = 0.414), water bound copper (r = 0.622), water bound lead (r = 0.851) and water bound iron (r = 0.649) [$p<0.01$]. Zinc showed negative correlation with nitrite (r = -0.179), water bound nickel (r = -0.198), sediment bound nickel (r = -0.209) [$p< 0.05$], water bound cadmium (r = -0.280) and sediment bound zinc (r = -0.279) [$p<0.01$].

During February, a maximum **iron** concentration of 1445.4 µg L^{-1} was found in station 4 and a minimum concentration of 284.69 µg L^{-1} in station 15 (Table 4.1 and Fig 4.2). In April, the concentration was maximum (1127.36 µg L^{-1}) at station 18 and minimum (326.56 µg L^{-1}) at station 14 (Table 4.2 and Fig 4.3). A range of 284.69 to 1445.40 µg L^{-1} during pre-monsoon and that in monsoon season, from 2320 to 45900 µg L^{-1} was noted for iron. The maximum concentration (12100 µg L^{-1}) was found in station 16 and minimum concentration (2320 µg L^{-1}) in station 3 in the month of June (Table 4.3 and Fig 4.4) whereas the concentration was maximum (45900 µg L^{-1}) in station 2 and minimum (3820 µg L^{-1}) in station 5 during August (Table 4.4 and Fig 4.5). Iron concentration in water samples of each station showed that there is a gradual increase in the value during the study period. Iron showed a positive correlation with DO (r = 0.392), water bound copper (r = 0.727), water bound lead (r = 0.661) and water bound zinc (r = 0.649) [$p<0.01$]. Iron was negatively correlated with nitrite (r = -0.218), water bound nickel (r = -0.218), water bound cadmium (r = -0.321) and with sediment bound metals like copper (r = -0.425), nickel (r = -0.217) and zinc (r = -0.365) [$p<0.01$]. During February, in stations 3-14 and 16 the concentrations of iron were very high compared to the standard limits. In April, concentration of iron in all stations increased beyond the standard limits.

Table 4.1 Metal concentration in water samples (Feb, 2017)

Sl.No.	Month	Station	Concentration in sample (µg L^{-1})					
			Cu	Ni	Cd	Pb	Zn	Fe
1	February, 2017	St.1	2.13	2.31	BDL	3.19	31.65	182.63
2		St.2	1.13	BDL	BDL	0.38	24.16	161.44
3		St.3	3.06	0.19	BDL	8.56	25.77	431.81
4		St.4	4.81	BDL	BDL	2.44	26.37	1445.40
5		St.5	2.13	BDL	BDL	BDL	11.62	799.01
6		St.6	4.38	BDL	BDL	BDL	18.26	310.94
7		St.7	8.56	BDL	0.38	BDL	22.17	435.25
8		St.8	2.81	BDL	BDL	BDL	12.73	474.88
9		St.9	7.31	BDL	BDL	0.75	23.43	356.50
10		St.10	5.06	BDL	BDL	BDL	25.88	508.13
11		St.11	3.00	0.75	BDL	BDL	39.41	458.13
12		St.12	3.00	BDL	BDL	BDL	31.83	424.00
13		St.13	1.38	BDL	BDL	BDL	36.29	419.56
14		St.14	1.38	0.06	BDL	BDL	47.98	506.55
15		St.15	2.75	BDL	BDL	11.88	101.81	284.69
16		St.16	1.75	BDL	BDL	BDL	61.86	326.38

Table 4.2 Metal concentration in water samples (Apr, 2017)

Sl.No.	Month	Station	Concentration in sample (µg L^{-1})					
			Cu	Ni	Cd	Pb	Zn	Fe
1	April, 2017	St.1	1.69	2.50	0.44	40.63	58.38	480.81
2		St.2	3.75	BDL	1.44	47.06	56.90	605.14
3		St.3	2.31	BDL	0.69	42.06	28.88	495.13
4		St.4	2.88	BDL	0.75	43.38	53.17	501.25
5		St.5	2.25	BDL	0.56	46.81	26.76	436.63
6		St.6	2.06	BDL	0.81	39.56	29.84	416.63
7		St.7	1.19	BDL	1.06	52.25	39.22	394.13
8		St.8	3.31	0.13	0.31	27.63	18.33	507.69
9		St.9	3.25	BDL	0.00	24.06	15.95	420.88
10		St.10	3.13	BDL	0.06	28.25	13.58	332.13
11		St.11	2.69	BDL	0.31	33.63	13.26	828.71
12		St.12	3.50	BDL	0.56	36.44	35.73	534.31
13		St.13	2.19	8.19	0.81	34.88	30.15	416.81
14		St.14	2.81	7.38	0.56	26.63	20.61	326.56
15		St.15	2.00	8.94	0.63	40.75	19.56	897.60
16		St.16	1.06	6.75	0.69	28.88	26.45	447.06
17		St.17	1.94	8.69	0.69	22.88	17.71	384.88
18		St.18	5.06	9.56	0.94	48.06	48.03	1127.36
19		St.19	0.75	2.31	BDL	7.13	9.26	378.31

Table 4.3 Metal concentration in water samples (Jun, 2017)

Sl No.	Month	Station	Concentration in sample (μg L^{-1})					
			Cu	Ni	Cd	Pb	Zn	Fe
1	June, 2017	St.1	BDL	BDL	BDL	BDL	240	10550
2		St.2	BDL	BDL	BDL	60	240	4890
3		St.3	BDL	BDL	BDL	BDL	240	2320
4		St.4	BDL	BDL	BDL	BDL	BDL	2790
5		St.5	BDL	BDL	BDL	50	90	4200
6		St.6	BDL	BDL	BDL	BDL	180	1950
7		St.7	BDL	BDL	BDL	BDL	520	10410
8		St.8	BDL	BDL	BDL	BDL	170	10550
9		St.9	BDL	BDL	BDL	BDL	20	7110
10		St.10	BDL	BDL	BDL	BDL	30	4160
11		St.11	BDL	BDL	BDL	BDL	BDL	4750
12		St.12	BDL	BDL	BDL	BDL	30	8150
13		St.13	BDL	BDL	BDL	BDL	BDL	8240
14		St.14	BDL	BDL	BDL	BDL	50	5910
15		St.15	BDL	BDL	BDL	BDL	BDL	7910
16		St.16	BDL	BDL	BDL	BDL	120	12100
17		St.17	BDL	BDL	BDL	BDL	60	9820
18		St.18	BDL	BDL	BDL	BDL	40	9600
19		St.19	BDL	BDL	BDL	BDL	70	8600

Table 4.4 Metal concentration in water samples (Aug, 2017)

Sl No.	Month	Station	Concentration in sample (μg L^{-1})					
			Cu	Ni	Cd	Pb	Zn	Fe
1	August, 2017	St.1	40	BDL	BDL	110	440	12900
2		St.2	120	BDL	BDL	170	790	45900
3		St.3	50	BDL	BDL	300	780	40600
4		St.4	20	BDL	BDL	BDL	150	8820
5		St.5	130	BDL	BDL	370	1400	3820
6		St.6	80	BDL	BDL	290	1100	7800
7		St.7	20	BDL	BDL	180	1190	2450
8		St.8	30	BDL	BDL	220	680	27080
9		St.9	30	BDL	BDL	190	490	7400
10		St.10	BDL	BDL	BDL	280	1370	10750
11		St.11	BDL	BDL	BDL	130	950	10120
12		St.12	BDL	BDL	BDL	80	390	11980
13		St.13	20	BDL	BDL	290	780	10890
14		St.14	BDL	BDL	BDL	70	340	10150
15		St.15	BDL	BDL	BDL	BDL	130	4550
16		St.16	20	BDL	BDL	360	890	14120
17		St.17	BDL	BDL	BDL	260	320	18410
18		St.18	BDL	BDL	BDL	160	510	18990
19		St.19	20	BDL	BDL	150	830	16700

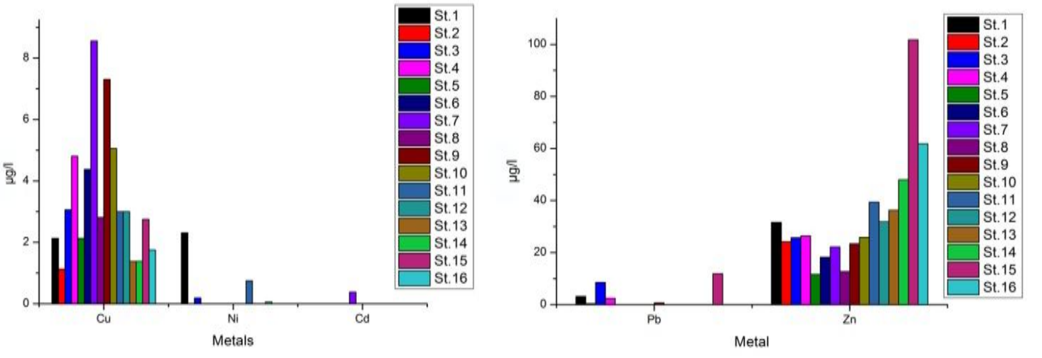


Fig. 4.2 Spatial variation of heavy metals in water samples (Feb, 2017)

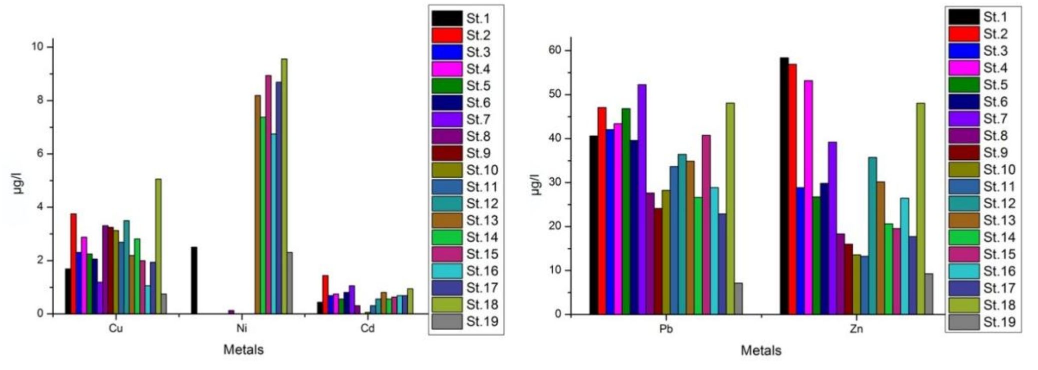


Fig. 4.3 Spatial variation of heavy metals in water samples (Apr, 2017)

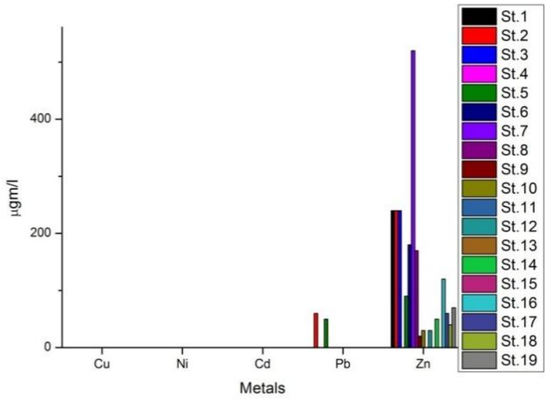


Fig. 4.4 Spatial variation of heavy metals in water samples (Jun, 2017)

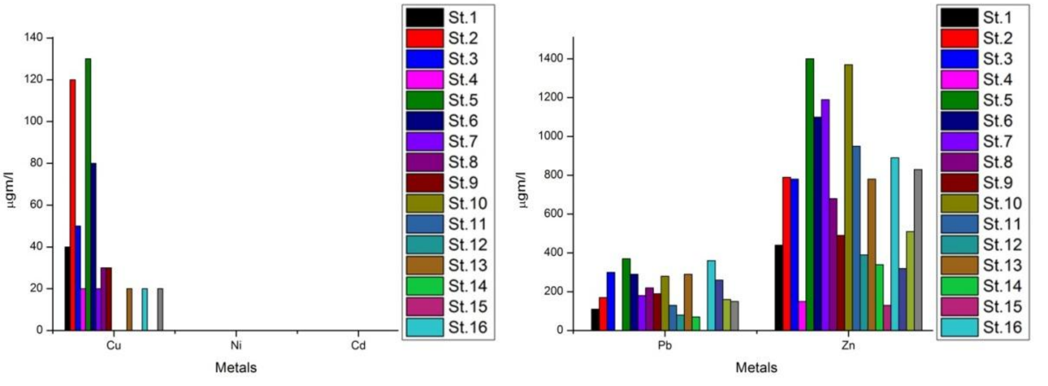


Fig. 4.5 Spatial variation of heavy metals in water samples (Aug, 2017)

4.2.2 Distribution of heavy metals in sediment

In February, the **copper** showed maximum concentration (177.6 mg kg^{-1}) in station 10 and minimum concentration (8.10 mg kg^{-1}) in station 1 (Table 4.5 and Fig 4.6). During April, the minimum concentration of 9.70 mg kg^{-1} was found in station 17 and maximum concentration of 66.70 mg kg^{-1} in station 7 (Table 4.6 and Fig 4.7). The highest concentration was found in June having 47.56 mg kg^{-1} at station 9 and minimum (8.53 mg kg^{-1}) at station 19 (Table 4.7 and Fig 4.8). The highest value of 87.50 mg kg^{-1} was found in station 2 and the lowest value (9.23 mg kg^{-1}) was in station 17 during August (Table 4.8 and Fig 4.9). In the present study, copper was positively correlated with silicate (0.317) and sediment bound metals like nickel ($r = 0.400$), cadmium ($r = 352$), lead ($r = 0.584$) and zinc ($r = 0.674$) [$p < 0.01$]. Cu was negatively correlated with nitrate ($r = -0.425$) [$p < 0.05$]. In February, it was found that stations 4 (Thanneermukkom south), 6 (Punnamada), 11 (Kainakary), 13 (Kuttamangalam), 14 (Ranikayal) and 16 (Chithirakayal) were moderately polluted with copper and stations 2 (Perumbalam), 5 (Pathiramanal), 7 (Nehru Trophy finishing point), 8 (Pangankuzhipadam), 9 (Pallathuruthy), 10 (Meenappally), 12 (Cherukayal) and 15 (Marthandam) were heavily polluted with copper. By April, stations 6 (Punnamada) and 7

(Nehru Trophy finishing point) get heavily polluted and all other stations except stations 3 (Thanneermukkom north), 4 (Thanneermukkom south), 11 (Kainakary), 17 (Varanadu) and 19 (Meenappally Vattakayal) get moderately polluted with copper.

Nickel concentration was maximum (194 mg kg^{-1}) in station 16 and minimum (16.8mg kg^{-1}) in station 1 during the month of February (Table 4.5 and Fig 4.6). During April, the concentration was maximum (102.30 mg kg^{-1}) in station 1 and minimum (37.20 mg kg^{-1}) in station 19 (Table 4.6 and Fig 4.7). In the monsoon season, concentration ranged from 25.67 mg kg^{-1} to 78.80 mg kg^{-1}. During June, concentration was maximum (90.63 mg kg^{-1}) in station 2 and minimum (20.13 mg kg^{-1}) in station 19 (Table 4.7 and Fig 4.8). The maximum and minimum concentration in August was 78.80 mg kg^{-1} and 25.67 mg kg^{-1} in station 3 and 2 respectively (Table 4.8 and Fig 4.9). A positive correlation was observed between nickel with phosphate ($r = 0.190$) [$p < 0.05$] and sediment bound metals like copper ($r = 0.400$), cadmium ($r = 0.235$), lead ($r = 0.509$) and zinc ($r = 0.467$) [$p < 0.01$]. Nickel was negatively correlated with water bound metals like zinc ($r = -0.209$) [$p < 0.05$], lead ($r = -0.225$) and iron ($r = -0.217$) [$p < 0.01$]. During February, station 1 (Aroor) was the only station that was not polluted with nickel. Station 3 (Thanneermukkom north) and station 13 (Kuttamangalam) was moderately polluted and all other stations were heavily polluted. In April, stations 4 (Thanneermukkom south), 17 (Varanadu) and 19 (Meenappally Vattakayal) were moderately polluted and all other stations were heavily polluted.

The **cadmium** concentration in the sediment depicted a moderately higher concentration when compared to standard Sediment Quality Guidelines (SQG) (Perin *et al.*, 1997). The Cd concentration ranged from 0.5 to 7.1 mg kg^{-1} during pre-monsoon. Highest concentration (4.90 mg kg^{-1}) was found in station 5 and lowest (0.50 mg kg^{-1}) in station 1 during February (Table 4.5 and Fig 4.6). In April, the Cd concentration was higher (7.10 mg kg^{-1}) in station 2 and lower (0.6 mg kg^{-1}) in station 19 (Table 4.6 and Fig 4.7). In monsoon, Cd concentration ranged from 0.25 to 4.78 mg kg^{-1}. Highest concentration of 3.89 mg kg^{-1} was found in station 11 in August (Table 4.7 and Fig 4.8) and lowest of 0.25 mg kg^{-1} was found in station19 during June (Table 4.8 and Fig 4.9). In the month of August, Cd values ranged from 0.56 to 4.78 mg kg^{-1}. The maximum was found in station 11 and minimum in station 7. Cadmium was positively correlated with nitrite (r = 0.212) [$p < 0.05$], water bound cadmium (r = 0.433) and sediment bound metals like copper (r = 0.352), nickel (r = 0.235), lead (r = 0.541) and zinc (r = 0.454) [$p < 0.01$]. In February, station 1 (Aroor) was the only station which is non-polluted, whereas all the other stations were moderately polluted with cadmium metal. But in April, station 19 (Meenappally Vattakayal) was the only non-polluted station. Station 2 (Perumbalam) get heavily polluted and all other stations get moderately polluted with the heavy metal.

Lead showed the maximum concentration of 122.1 mg kg^{-1} in station 11 and minimum of 7.22 mg kg^{-1} in station 1 during the month of February (Table 4.5 and Fig 4.6). In April, the concentration was maximum (99.9 mg kg^{-1}) in station 1 and minimum (14.50 mg kg^{-1}) in station 4 (Table 4.6 and Fig 4.7). In June; the concentration was maximum (76.20 mg kg^{-1}) in station 1 and minimum (8.70 mg kg^{-1}) in station 4 (Table 4.7 and Fig 4.78). The highest value of 90.25 mg kg^{-1} was found in station 15 and lowest value of 9 mg kg^{-1} was found in station 1 during August (Table 4.8 and Fig 4.9). Pb showed positive correlation with sulphide (r = 0.197) water bound copper (r = 0.163) [$p < 0.05$] and sediment bound metals like copper (r = 0.584), nickel (r = 0.504), cadmium (r = 0.541) and zinc (r = 0.640) ($p < 0.01$). During February, all the stations except stations 1 (Aroor), 13 (Kuttamangalam) and 16 (Chithirakayal) were heavily polluted with lead. In April, stations 3 (Thanneermukkom north), 4 (Thanneermukkom south), 12 (Cherukayal), 17 (Varanadu), 18 (Kuppapuram) and 19 (Meenappally Vattakayal) were non-polluted stations and stations 1 (Aroor), 2 (Perumbalam), 5 (Pathiramanal), 6 (Punnamada), 7 (Nehru Trophy finishing point), 14 (Ranikayal) and 16 was however heavily polluted with the lead.

The concentration of **zinc** ranged from 27.4 to 210 mg kg^{-1} during pre-monsoon season. The maximum concentration was found in station 10 and minimum concentration in station 1 in the month of February (Table 4.5 and Fig 4.6). In April, maximum and minimum concentration was 50.09 mg kg^{-1} and 170.90 mg kg^{-1} in stations 17 and 7 respectively (Table 4.6 and Fig 4.7). In the monsoon season, the concentration ranged from 35.88 to 121.78 mg kg^{-1}. The highest value (120.29 mg kg^{-1}) of June was found in station 16 and lowest value (35.88 mg kg^{-1}) in station 3 (Table 4.7 and Fig 4.8). During August, maximum concentration of 121.78 mg kg^{-1} was found in station 18 and minimum concentration of 45.67 mg kg^{-1} was found in station 3 (Table 4.8 and Fig 4.9). Zn showed positive correlation with water bound cadmium ($r = 0.234$) and sediment bound metals like copper ($r = 0.674$), nickel ($r = 0.467$), cadmium ($r = 0.454$) and lead ($r = 0.640$). But zinc showed negative correlation with water bound copper ($r = -0.168$) [$p < 0.05$], DO ($r = -0.229$) and water bound metals like lead ($r = -0.214$), zinc ($r = -0.274$) and iron ($r = -0.365$) [$p < 0.01$]. During February, stations 1 (Aroor), 13 (Kuttamangalam) and 16 (Chithirakayal) remained non-polluted, station 10 (Meenappally) get heavily polluted and all other stations get moderately polluted with zinc. But in April, station 3 (Thanneermukkom north), 4 (Thanneermukkom south), 10 (Meenappally), 17 (Varanadu) and 19 (Meenappally Vattakayal) were appeared to be non-polluted and all other stations were moderately polluted.

Table 4.5 Metal concentration in sediment samples (Feb, 2017)

Sl No.	Month	Station	Concentration in sample (mg kg^{-1})				
			Cu	Ni	Cd	Pb	Zn
1	February, 2017	St.1	8.10	16.80	0.50	7.20	27.43
2		St.2	97.60	89.80	4.00	99.40	191.69
3		St.3	18.50	44.50	2.50	60.70	152.60
4		St.4	47.10	76.90	4.00	103.20	136.91
5		St.5	115.80	81.50	4.90	106.50	172.85
6		St.6	48.80	69.90	2.10	64.20	127.00
7		St.7	81.50	62.70	4.50	71.80	153.06
8		St.8	156.80	56.50	2.00	62.00	138.51
9		St.9	110.00	89.00	3.80	109.70	182.06
10		St.10	177.60	93.90	5.30	99.80	**210.52**
11		St.11	49.20	112.10	5.80	122.10	185.89
12		St.12	69.20	95.00	2.60	98.60	141.81
13		St.13	26.10	39.70	1.60	30.50	46.39
14		St.14	26.10	64.00	4.10	69.00	91.48
15		St.15	137.00	112.30	4.10	99.50	191.50
16		St.16	27.30	194.50	0.60	10.00	40.09

Table 4.6 Metal concentration in sediment samples (Apr, 2017)

Sl No.	Month	Station	Concentration in sample (mg kg^{-1})				
			Cu	Ni	Cd	Pb	Zn
1	April, 2017	St.1	38.30	102.30	4.20	99.90	152.77
2		St.2	37.50	84.70	7.1	73.30	135.43
3		St.3	11.80	25.10	4.60	25.00	59.88
4		St.4	16.10	36.20	4.90	14.50	57.19
5		St.5	45.30	78.90	4.10	83.90	128.72
6		St.6	62.30	80.50	3.20	82.50	137.71
7		St.7	66.70	86.90	4.90	96.50	**170.90**
8		St.8	47.10	68.40	3.40	57.90	97.70
9		St.9	43.90	58.50	2.00	52.10	111.40
10		St.10	49.10	69.30	3.10	46.80	87.50
11		St.11	19.70	58.70	4.20	54.90	133.80
12		St.12	34.30	52.50	2.20	27.20	110.10
13		St.13	36.80	73.70	3.40	51.60	129.05
14		St.14	42.70	72.00	2.60	65.10	155.32
15		St.15	35.70	65.10	2.70	46.60	132.10
16		St.16	34.10	57.20	1.90	61.20	126.29
17		St.17	9.70	22.00	1.60	BDL	50.09
18		St.18	38.00	63.30	2.30	24.60	125.02
19		St.19	20.00	37.20	0.60	BDL	66.68

Table 4.7 Metal concentration in sediment samples (Jun, 2017)

Sl No.	Month	Station	Concentration in sample (mg kg^{-1})				
			Cu	Ni	Cd	Pb	Zn
1	June, 2017	St.1	12.30	89.25	1.20	76.20	62.56
2		St.2	18.56	90.63	0.78	56.74	80.75
3		St.3	10.23	15.23	2.78	31.26	35.88
4		St.4	15.46	30.25	3.05	8.70	68.94
5		St.5	20.45	80.56	2.89	60.78	104.57
6		St.6	20.19	74.20	3.14	71.23	106.58
7		St.7	20.01	57.41	3.89	45.65	98.65
8		St.8	10.23	49.63	2.78	37.67	63.98
9		St.9	47.56	35.67	1.89	46.76	91.40
10		St.10	10.23	33.21	2.45	28.12	77.50
11		St.11	17.56	30.25	3.45	32.87	63.71
12		St.12	24.30	60.23	1.25	18.16	90.60
13		St.13	17.80	78.55	2.45	54.21	94.30
14		St.14	22.75	68.89	1.45	38.40	65.42
15		St.15	26.53	56.78	0.56	51.75	97.50
16		St.16	45.68	50.12	0.78	11.45	**120.29**
17		St.17	12.53	32.15	0.98	10.23	67.89
18		St.18	21.45	47.54	1.15	11.60	115.07
19		St.19	8.53	20.13	0.25	8.65	70.56

Table 4.8 Metal concentration in sediment samples (Aug, 2017)

Sl No.	Month	Station	Concentration in sample (mg kg^{-1})				
			Cu	Ni	Cd	Pb	Zn
1	August, 2017	St.1	10.56	78.80	1.23	9.00	57.89
2		St.2	87.50	71.45	3.56	80.12	58.37
3		St.3	27.47	25.67	1.98	56.34	45.67
4		St.4	37.45	35.67	3.98	99.76	70.89
5		St.5	56.32	78.46	4.05	91.25	98.56
6		St.6	28.78	57.89	1.98	67.85	90.75
7		St.7	24.56	41.56	0.56	74.20	81.45
8		St.8	27.89	40.57	1.27	57.41	50.27
9		St.9	54.78	28.97	2.56	49.63	85.67
10		St.10	46.86	33.54	4.02	35.67	79.86
11		St.11	56.53	50.23	4.78	33.21	66.75
12		St.12	45.67	57.86	3.85	88.02	87.64
13		St.13	24.56	27.86	2.01	20.34	85.67
14		St.14	21.03	55.78	3.78	37.89	89.64
15		St.15	27.89	45.67	4.19	90.25	99.87
16		St.16	47.28	47.56	0.56	14.57	110.27
17		St.17	9.23	35.64	1.45	10.27	78.95
18		St18	11.47	27.89	2.75	10.45	121.78
19		St.19	19.87	25.67	2.40	11.27	89.45

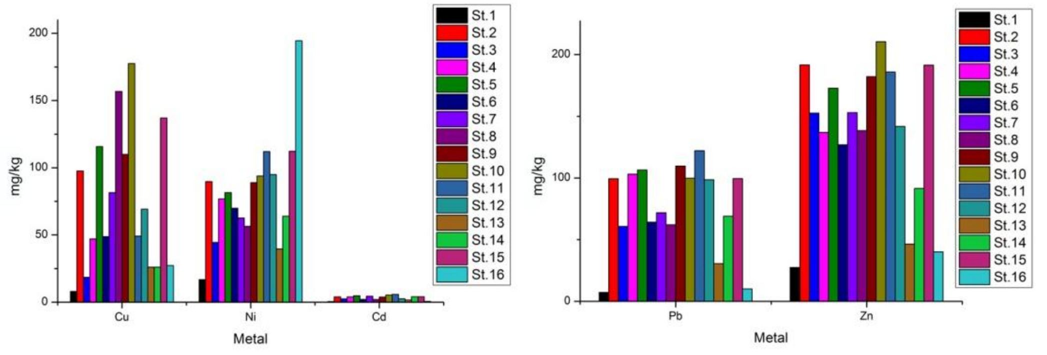


Fig. 4.6 Spatial variation of heavy metals in sediment samples (Feb, 2017)

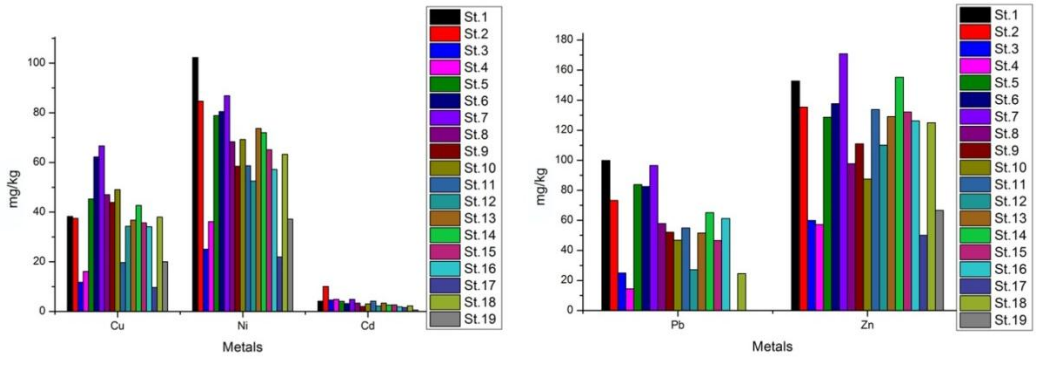


Fig. 4.7 Spatial variation of heavy metals in sediment samples of Vembanad backwater during April, 2017

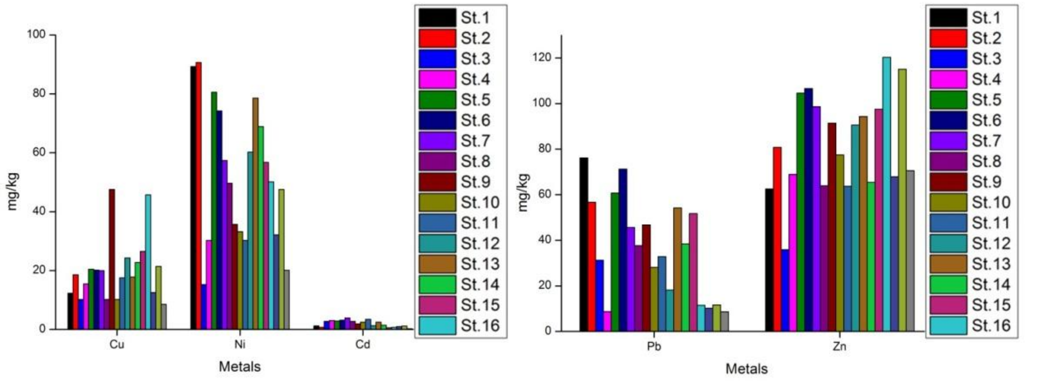


Fig. 4.8 Spatial variation of heavy metals in sediment samples of Vembanad backwater during June, 2017

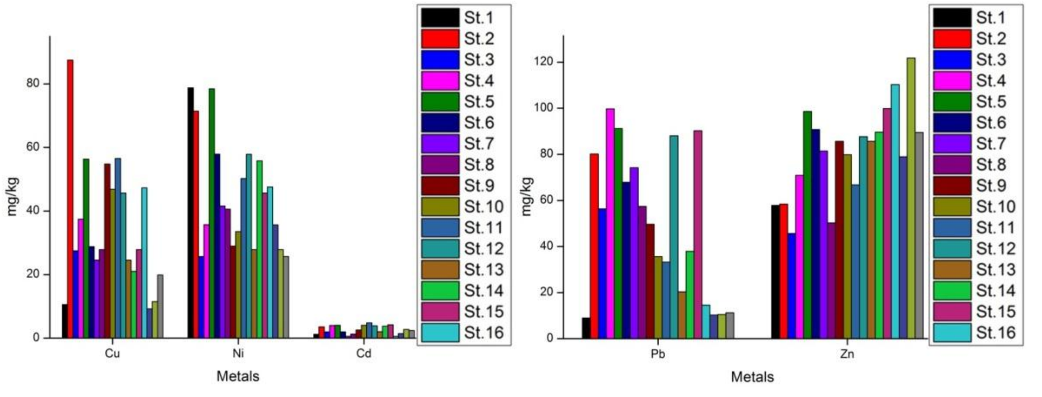


Fig. 4.9 Spatial variation of heavy metals in sediment samples (Aug, 2017)

4.2.3 Principal Component Analysis (PCA)

A multivariate correlation analysis was carried out to determine the influence of various physicochemical parameters over selected stations in Vembanad backwater (Fig. 4.10). Principal component analysis helps to determine the correlation of variables in relation to each other and also their pattern of variability in Vembanad backwaters. The first five principal components accounted for 65.6 % of variability between stations. The first PC accounted for 23.9 % variability with an eigen value of 5.5 and second PC accounted for 14.2 % variability with Eigen value of 3.28 (Table 4.9). In PC 1, nitrite, nitrate, phosphate, silicate, water bound Cd and Fe were the important determinants. In PC 2, sediment bound Cu, Pb and Zn were the important determinants.

Table 4.9 Two-dimensional Principal Component Analysis (PCA) of environmental conditions at each sampling stations in Vembanad backwater

PC	PC1	PC2	PC3	PC4	PC5
Eigen values	5.5	3.28	3.2	1.71	1.41
% Variation	23.9	14.2	13.9	7.4	6.1
Cum% Variation	23.9	38.1	52	59.5	65.6
Variables					
Temperature	-0.136	0.039	0.275	0.125	0.270
pH	0.021	-0.040	0.003	-0.034	0.407
Salinity	-0.153	0.126	0.233	0.202	0.478
Alkalinity	0.001	0.003	0.227	0.315	0.142
DO	0.211	-0.013	0.237	-0.477	0.223
BOD	0.178	0.039	0.093	-0.559	0.197
Ammonia	-0.183	-0.107	0.074	0.056	-0.354
Nitrate	-0.281	-0.136	0.030	-0.206	-0.031
Nitrite	-0.372	-0.114	-0.046	-0.072	-0.031
Phosphate	0.380	0.128	-0.013	0.131	0.098
Silicate	0.355	0.146	-0.051	0.018	0.053
Sulphide	0.000	0.051	0.415	0.107	-0.058
Cu (Water)	-0.044	0.100	0.406	0.160	0.007
Ni (Water)	-0.244	-0.148	0.004	-0.168	0.230
Cd (Water)	-0.363	-0.043	-0.014	-0.210	0.047
Pb (Water)	-0.136	-0.117	0.423	-0.107	-0.179
Zn (Water)	0.119	-0.059	0.426	-0.059	-0.264
Fe (Water)	0.282	-0.169	0.174	-0.176	-0.271
Cu (Sediment)	-0.076	0.454	0.051	-0.056	-0.012
Ni (Sediment)	-0.112	0.385	-0.027	0.057	-0.126
Cd (Sediment)	-0.128	0.320	0.018	-0.189	-0.043
Pb (Sediment)	-0.033	0.446	0.066	-0.067	-0.176
Zn (Sediment)	-0.136	0.402	-0.078	-0.183	-0.059

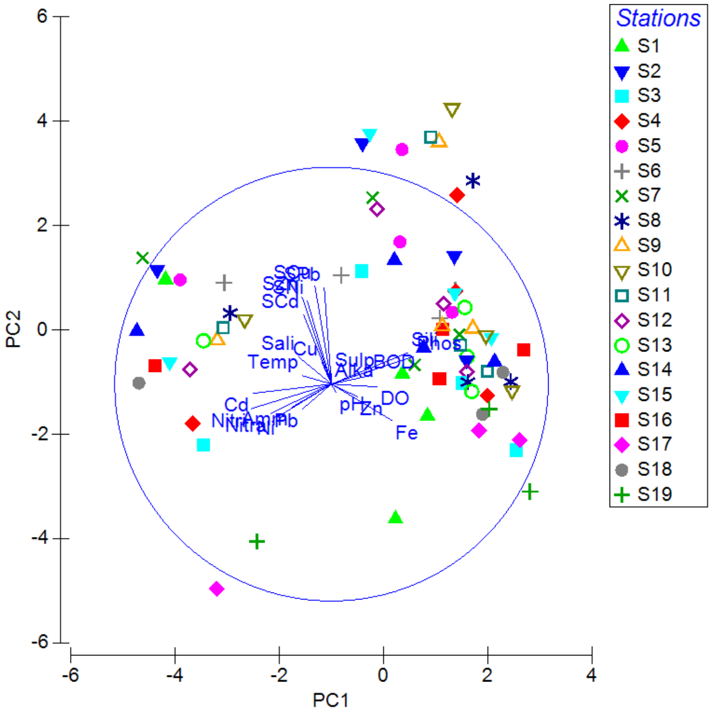


Fig. 4.10 Two-dimensional Principal Component Analysis (PCA) of environmental conditions at each sampling stations in Vembanad backwater

4.2.4 Pollution Indices

a. Geo accumulation Index (Igeo)

Copper

During the study period, Igeo value of Cu ranged from a minimum value of 0.12 at station 1 to a maximum value of 2.63 at station 10 in February (Table 4.10 and Fig 4.11). During April, the value was maximum (0.99) in station 7 and minimum (0.14) in station 17 (Table 4.11 and Fig 4.12). But in June, the highest value of 0.70 was found at station 9 and lowest value of 0.13 at station 19 (Table 4.112and Fig 4.13). In August, the value ranged from 1.30 at station 2 to 0.14 at station 17 (Table 4.13 and Fig 4.14). The analysis revealed that, stations 1, 3, 4, 6, 11, 13, 14 and 16 were found in class 1 (uncontaminated to moderately contaminated), stations 2, 5, 7, 9 & 12 in class 2 (moderately contaminated) and stations 8, 10 & 15 in class 3 (moderately to strongly contaminated) during February. In April and June, all the stations were found in class 1, while in August station 2 was found in class 2 and all other stations in class 1.

Nickel

The Igeo value of Ni ranged from a minimum value of 0.56 at station 1 to a maximum value of 6.48 at station 16 in February (Table 4.10 and Fig 4.11). During April, the value was maximum (3.41) in station 1 and minimum (0.73) in station 17 (Table 4.11 and Fig 4.12). In the case of June, the highest value of 3.02 was found at station 2 and lowest value of 0.53 at station 3 (Table 4.12 and Fig 4.13). In August, the value ranged from 0.86 at station 3 to 2.63 at station 1 (Table 4.13 and Fig 4.14). The study showed that station1was found in class 1 (uncontaminated to moderately contaminated), stations 3, 8 & 13 was found in class 2 (moderately contaminated) and stations 2, 4, 5, 6, 7, 9 & 14 was found in class 3 (moderately to strongly contaminated), stations 10, 11, 12 & 15 were found in class 4 (strongly contaminated) and station 16 was found in class 6 (extremely contaminated) during February. In April and June, all the stations were found in class 1. However in August, station 2was found in class 2 and all other stations were found in class 1.

Cadmium

The Igeo value of Cd ranged from a minimum value of 1.11 at station 1 to a maximum value of 12.89 at station 11 in February (Table 4.10 and Fig 4.11). During April, the value was maximum (15.78) in station 2 and minimum (1.33) in station 19 (Table 4.11 and Fig 4.12). In June, the highest value of 8.64 was found at station 7 and lowest value of 0.56 at station 19 (Table 4.12 and Fig 4.13), whereas in August, the value ranged from 1.24 at station 16 to 10.62 at station 11 (Table 4.13 and Fig 4.14).The study showed that stations 1 & 16 were found in class 2 (moderately contaminated), station 13 in class 3 (moderately to strongly contaminated), station 6 in class 5 (strongly to extremely strongly contaminated) and all other stations were found in class 6 (extremely contaminated) during February. In April, station 19 was found in class 2 (moderately contaminated), station 17 was found in class 4 (strongly contaminated), stations - 9, 12 and 16 were found in class 5 (strongly to extremely contaminated) and all other stations in class 6 (extremely contaminated). During June, stations 2, 15 & 16 were found in class 2 (moderately contaminated), stations 1, 17 & 18 in class 3 (moderately to strongly contaminated), station 9 was found in class 4 (strongly contaminated) and all other stations were found in class 6 (extremely contaminated). While in August, station 7 & 16 were found in class 2 (moderately contaminated), station 1 & 8 in class 3 (moderately to strongly contaminated) stations 3, 6 and 13 were classified in class 5 (extremely strongly contaminated).

Lead

The Igeo value of Pb ranged from a minimum value of 0.24 at station 1 to a maximum value of 4.07 at station 11 in February (Table 4.10 and Fig 4.11). During April, the value was maximum (3.22) in station 7 and minimum (0.48) in station 4 (Table 4.11 and Fig 4.12). In June, the highest value of 2.37 was found at station 6 and lowest value of 0.29 at station 4 (Table 4.12 and Fig 4.13) While in August, the value ranged from 0.30 at station 1 to 3.33 at station 4 (Table 4.13 and Fig 4.14). The study showed that stations 1 & 16 were found in class 1 (uncontaminated to moderately contaminated), station 13 was found in class 2 (moderately contaminated), stations 3, 6, 7, 8 & 14 were found in class 3 (moderately to strongly contaminated), station 11 was found in class 6 (extremely contaminated) and all other stations were found in class 5 (strongly to extremely strongly contaminated) during February. In April, stations 3, 4, 12, 17, 18 & 19 were found in class 1 (uncontaminated to moderately contaminated), stations - 8, 9, 10, 11, 13 & 15 were found in class 2 (moderately contaminated), stations 2, 5, 6, 14 & 16 were found in class 3 (moderately to strongly contaminated) and stations 1 & 7 were found in class 4 (strongly contaminated). During June, stations - 4, 10, 12, 16, 17, 18 & 19 were found in class 1 (uncontaminated to moderately contaminated), stations 1, 5 & 6 were found in class 3 (moderately to strongly contaminated) and all others were found in class 2 (moderately contaminated). In August, stations 1, 13, 16, 17, 18 & 19 were found in class 1 (uncontaminated to moderately contaminated), stations 3, 8, 9, 10, 11 & 14 were found in class 2 (moderately contaminated), stations 2, 6, 7 & 12 in class 3 (moderately to strongly contaminated) and stations 4, 5 and 14 were found in class 4 (strongly contaminated).

Zinc

During the study period, Igeo value of Zn ranged from a minimum value of 0.19 at station 1 to a maximum value of 1.48 at station 10 in February (Table 4.10 and Fig 4.11). During April, the value was maximum (1.20) in station 7 and minimum (0.37) in station 17 (Table 4.11 and Fig 4.12). In June, the highest value of 3.37 was found at station 6 and lowest value of 0.29 at station 4 (Table 4.12 and Fig 4.13). However, in August, the value ranged from 0.32 at station 3 to 0.77 at station 16 (Table 4.13 and Fig 4.14). The present study revealed that, stations 1, 4, 6, 8, 13, 14 and 16 were found in class 1 (uncontaminated to moderately contaminated) and all other stations were found in class 2 (moderately contaminated) during February. In April, stations 1, 7 & 14 were found in class 2 (moderately contaminated) and all other stations were found in class 1 (uncontaminated to moderately contaminated). While in June and August, all the stations were found in class 1 (uncontaminated to moderately contaminated).

Table 4.10 Geo accumulation Index during February, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.12	0.56	1.11	0.24	0.19
st2	1.45	2.99	8.89	3.31	1.35
st3	0.27	1.48	5.56	2.02	1.07
st4	0.70	2.56	8.89	3.44	0.96
st5	1.72	2.72	10.89	3.55	1.21
st6	0.72	2.33	4.67	2.14	0.89
st7	1.21	2.09	10.00	2.39	1.07
st8	2.32	1.88	4.44	2.07	0.97
st9	1.63	2.97	8.44	3.66	1.28
st10	2.63	3.13	11.78	3.33	1.48
st11	0.73	3.74	12.89	4.07	1.30
st12	1.03	3.17	5.78	3.29	1.00
st13	0.39	1.32	3.56	1.02	0.33
st14	0.39	2.13	9.11	2.30	0.64
st15	2.03	3.74	9.11	3.32	1.34
st16	0.40	6.48	1.33	0.33	0.28
Status	**Moderately contaminated**	**Moderately to strongly contaminated**	**Extremely contaminated**	**Moderately to strongly contaminated**	**Uncontaminated to moderately contaminated**

Table 4.11 Geo accumulation Index during April, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.85	5.12	14.00	5.00	1.61
st2	0.83	4.24	33.67	3.67	1.43
st3	0.26	1.26	15.33	1.25	0.63
st4	0.36	1.81	16.33	0.73	0.60
st5	1.01	3.95	13.67	4.20	1.35
st6	1.38	4.03	10.67	4.13	1.45
st7	1.48	4.35	16.33	4.83	1.80
st8	1.05	3.42	11.33	2.90	1.03
st9	0.98	2.93	6.67	2.61	1.17
st10	1.09	3.47	10.33	2.34	0.92
st11	0.44	2.94	14.00	2.75	1.41
st12	0.76	2.63	7.33	1.36	1.16
st13	0.82	3.69	11.33	2.58	1.36
st14	0.95	3.60	8.67	3.26	1.63
st15	0.79	3.26	9.00	2.33	1.39
st16	0.76	2.86	6.33	3.06	1.33
st17	0.22	1.10	5.33	0.00	0.53
st18	0.84	3.17	7.67	1.23	1.32
st19	0.44	1.86	2.00	0.00	0.70
Status	**Uncontaminated to moderately contaminated**	**Moderately to strongly contaminated**	**Extremely contaminated**	**Moderately contaminated**	**Uncontaminated to moderately contaminated**

Table 4.12 Geo accumulation Index during June, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.18	2.98	2.67	2.54	0.44
st2	0.27	3.02	1.73	1.89	0.57
st3	0.15	0.51	6.18	1.04	0.25
st4	0.23	1.01	6.78	0.29	0.48
st5	0.30	2.69	6.42	2.03	0.73
st6	0.30	2.47	6.98	2.37	0.75
st7	0.30	1.91	8.64	1.52	0.69
st8	0.15	1.65	6.18	1.26	0.45
st9	0.70	1.19	4.20	1.56	0.64
st10	0.15	1.11	5.44	0.94	0.54
st11	0.26	1.01	7.67	1.10	0.45
st12	0.36	2.01	2.78	0.61	0.64
st13	0.26	2.62	5.44	1.81	0.66
st14	0.34	2.30	3.22	1.28	0.46
st15	0.39	1.89	1.24	1.73	0.68
st16	0.68	1.67	1.73	0.38	0.84
st17	0.19	1.07	2.18	0.34	0.48
st18	0.32	1.58	2.56	0.39	0.81
st19	0.13	0.67	0.56	0.29	0.50
Status	**Uncontaminated to moderately contaminated**	**Moderately contaminated**	**Strongly to extremely contaminated**	**Moderately contaminated**	**Uncontaminated to moderately contaminated**

Table 4.13 Geo accumulation Index during August, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.16	2.63	2.73	0.30	0.41
st2	1.30	2.38	7.91	2.67	0.41
st3	0.41	0.86	4.40	1.88	0.32
st4	0.55	1.19	8.84	3.33	0.50
st5	0.83	2.62	9.00	3.04	0.69
st6	0.43	1.93	4.40	2.26	0.64
st7	0.36	1.39	1.24	2.47	0.57
st8	0.41	1.35	2.82	1.91	0.35
st9	0.81	0.97	5.69	1.65	0.60
st10	0.69	1.12	8.93	1.19	0.56
st11	0.84	1.67	10.62	1.11	0.47
st12	0.68	1.93	8.56	2.93	0.62
st13	0.36	0.93	4.47	0.68	0.60
st14	0.31	1.86	8.40	1.26	0.63
st15	0.41	1.52	9.31	3.01	0.70
st16	0.70	1.59	1.24	0.49	0.77
st17	0.14	1.19	3.22	0.34	0.55
st18	0.17	0.93	6.11	0.35	0.85
st19	0.29	0.86	5.33	0.38	0.63
Status	**Uncontaminated to moderately contaminated**	**Moderately contaminated**	**Extremely contaminated**	**Moderately contaminated**	**Uncontaminated to moderately contaminated**

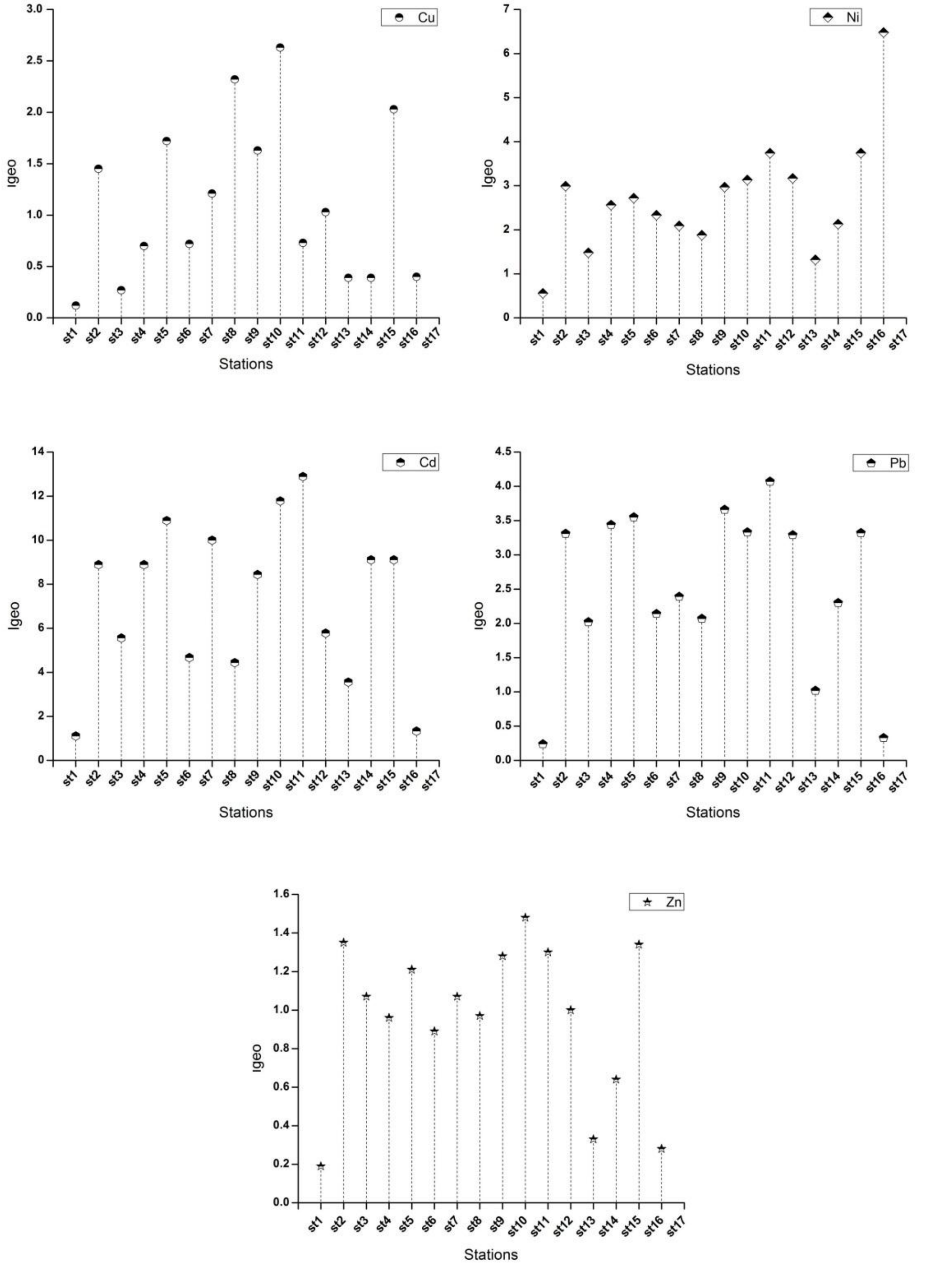


Fig. 4.11 Spatial variation in Geo accumulation Index (Feb, 2017)

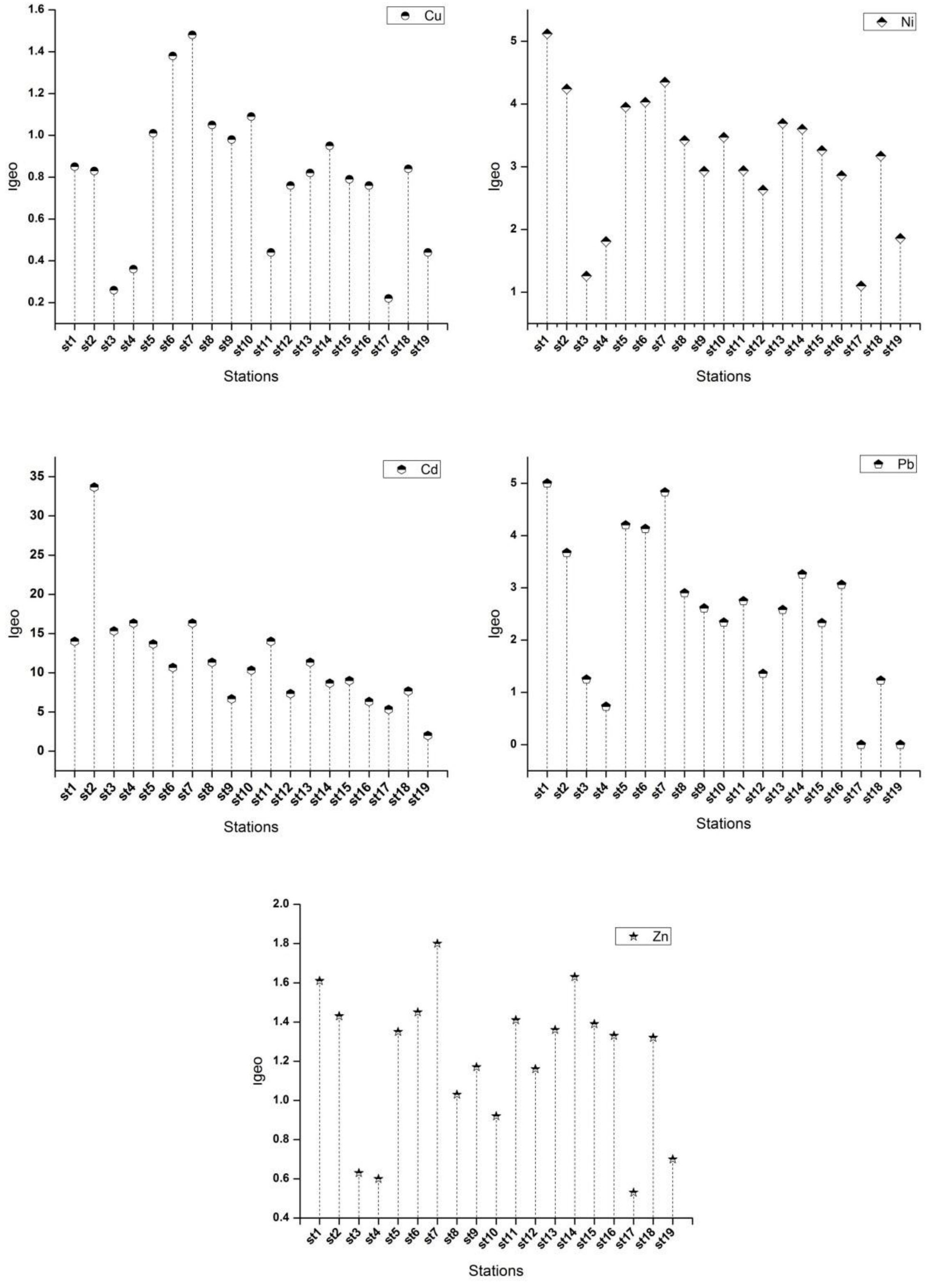


Fig. 4.12 Spatial variation in Geo accumulation Index (Apr, 2017)

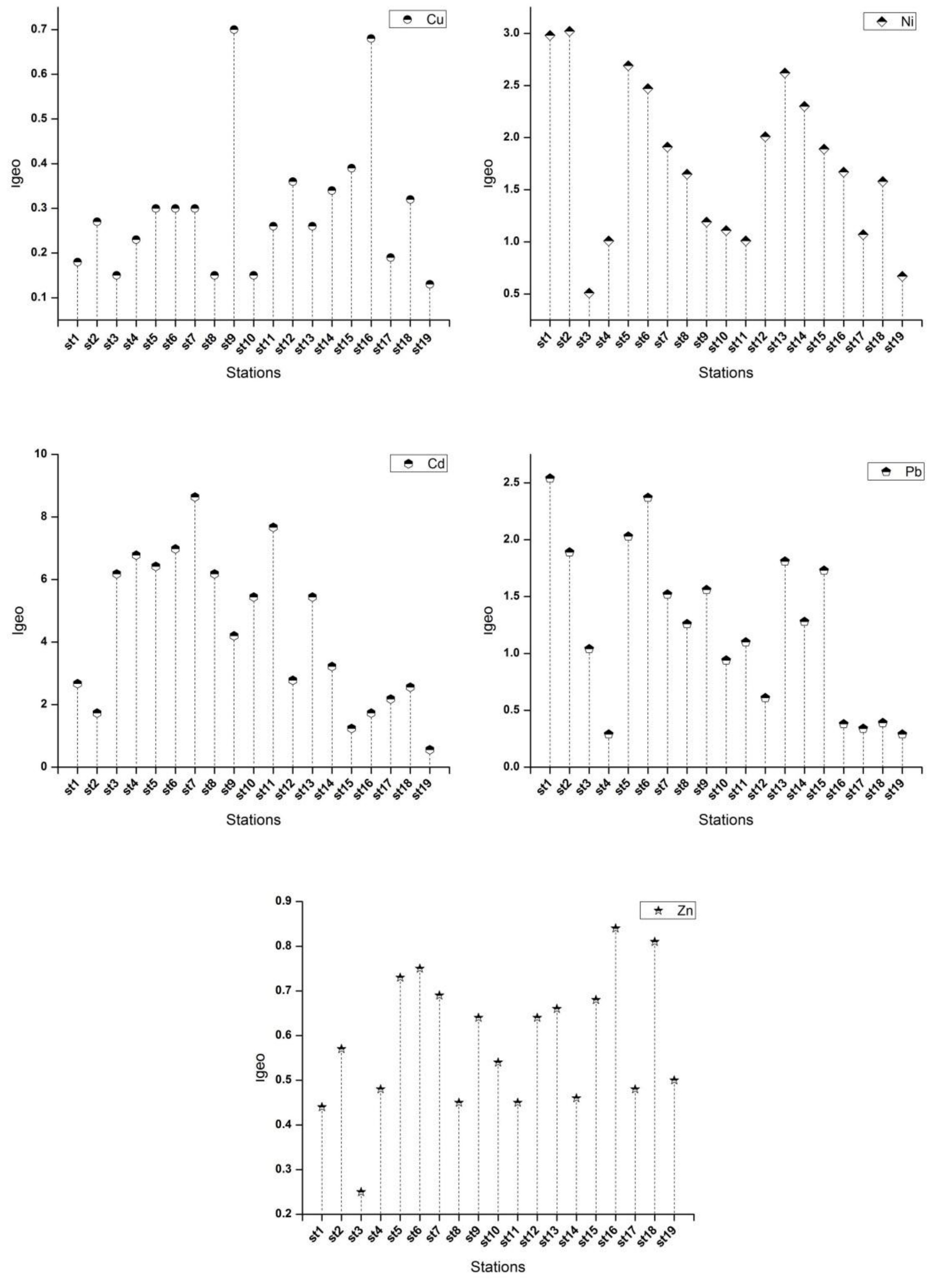


Fig. 4.13 Spatial variation in Geo accumulation Index (Jun, 2017)

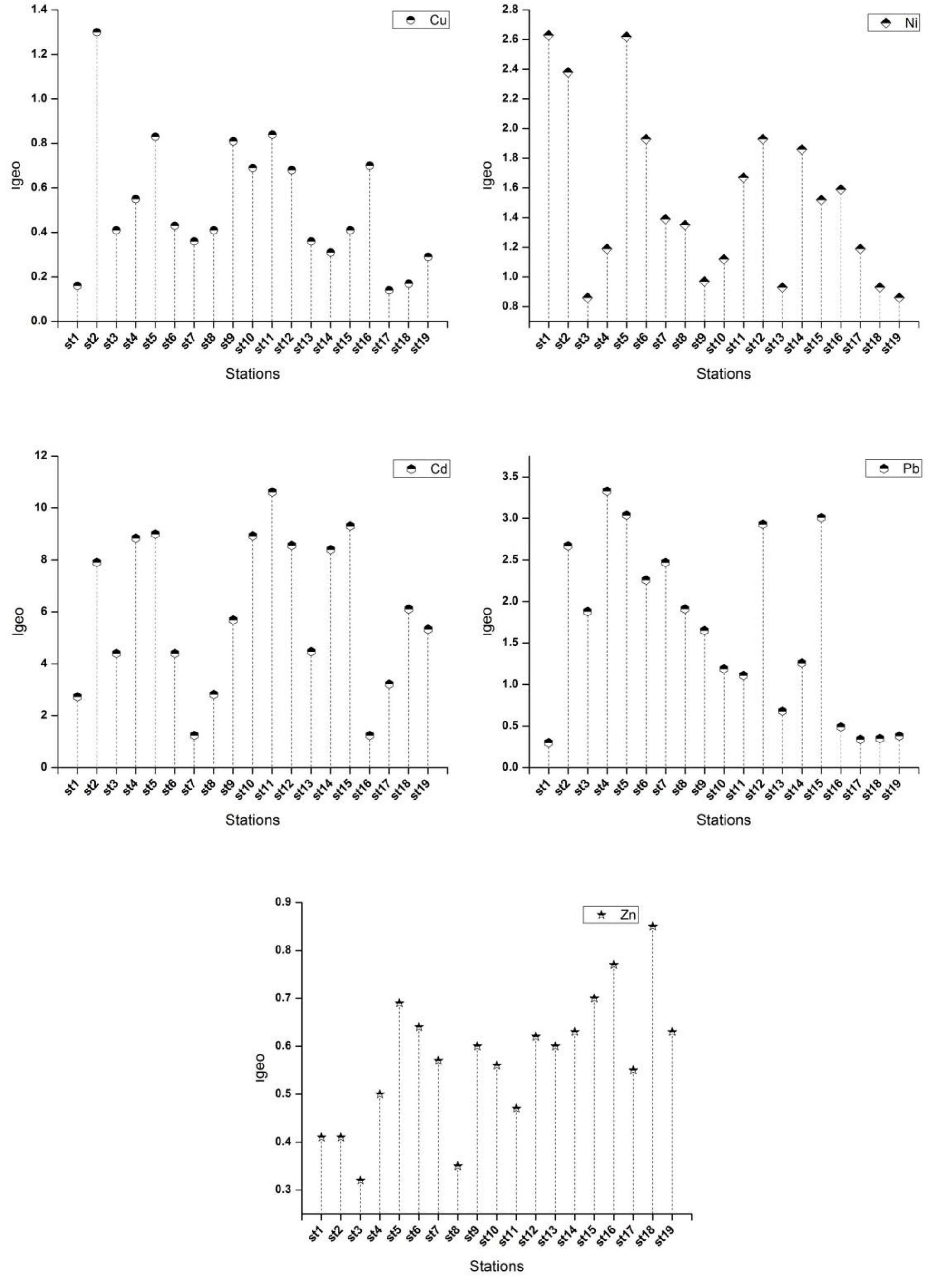


Fig. 4.14 Spatial variation in Geo accumulation Index (Aug, 2017)

b. Contamination Factor (CF)

Copper

During the study period, contamination factor (CF) value of Cu ranged from a minimum value of 0.41 at station 3 to a maximum value of 3.95 at station 10 in February (Table 4.14 and Fig 4.15). During April, the CF was maximum (1.48) in station 7 and minimum (0.22) in station 17 (Table 4.15 and Fig 4.16). In June, the highest value of 1.06 was found at station 9 and lowest value of 0.9 at station 19 (Table 4.16 and Fig 4.17). In August, the value ranged from 0.21 at station 17 to 1.94 at station 2 (Table 4.17 and Fig 4.18). As per the present study, stations 1, 3, 13, 14 and 16showed low contamination factor, stations 2, 4, 5, 6, 7, 9, 11 & 12 showed moderate contamination factor and stations 8, 10 & 15 showed considerable contamination factor during February. In April, stations 5, 6, 7, 8 and 10 showed moderate contamination factor and all other stations showed low contamination factor. During June, stations 9 and 16 showed moderate contamination factor and all other stations showed low contamination factor. Stations 2, 5, 9, 10, 11, 12 and 16 showed moderate contamination factor and all other stations showed low contamination factor in case of August.

Nickel

The CF value of Ni ranged from a minimum value of 0.84 at station 1 to a maximum value of 9.73 at station 16 in February (Table 4.14 and Fig 4.15). During April, the CF was maximum (5.12) in station 1 and minimum (1.10) in station 17 (Table 4.15 and Fig 4.16). In June, the highest value of 4.53 was found at station 2 and lowest value of 0.76 at station 3 (Table 4.16 and Fig 4.17). In August, the value ranged from 1.28 at station 3 to 3.94 at station 1 (Table 4.17 and Fig 4.18). In the study, station1 showed low concentration factor, stations 3, 8 and 13 showed moderate contamination factor, station 16 showed very high contamination factor and all other stations showed considerable contamination factor during February. In April, stations 3, 4, 9, 11, 12, 16, 17 and 19 showed moderate contamination factor and all other stations showed considerable concentration factor. During June, station 1 showed low concentration factor stations 1, 2, 5, 6, 12, 13 and 14 showed considerable contamination factor and all other stations showed moderate concentration factor. Stations 1, 2 and 5 showed considerable contamination factor and all other stations showed moderate concentration factor in August.

Cadmium

The CF value of Cd ranged from a minimum value of 1.67 at station 1 to a maximum value of 19.33 at station 11 in February (Table 4.14 and Fig 4.15). During April, the CF value was maximum (23.67) in station 2 and minimum (2.00) in station 19 (Table 4.15 and Fig 4.16). In June, the highest value of 12.97 was found at station 7 and lowest value of 0.83 at station 19 (Table 4.16 and Fig 4.17). In August, the value ranged from 1.87 at stations 7 & 16 to 15.93 at station 11 (Table 4.17 and Fig 4.18). Stations 1 & 16 had moderate contamination factor, whereas station 13 had considerable contamination factor and all other stations showed very high contamination factor during February. In April, station 19 showed moderate contamination factor and all other stations showed very high contamination factor. During June, station 19 showed low concentration factor, stations 1, 12, 14, 17 and 18 showed considerable contamination factor and all other stations were having very high contamination factor. Stations 7 and 16 showed moderate contamination factor, stations 1, 8 and 17 showed considerable contamination factor and all other stations showed very high contamination factor in August.

Lead

The CF value of Pb ranged from a minimum value of 0.36 at station 1 to a maximum value of 5.49 at station 9 in February (Table 4.14 and Fig 4.15). During April, the CF was maximum (5.00) in station 1 and minimum

(0.73) in station 4 (Table 4.15 and Fig 4.16). In June, the highest value of 3.81 was found at station 1 and lowest of 0.43 at station 19 (Table 4.16 and Fig 4.17). In August, the value ranged from 0.45 at station 1 to 4.99 at station 4 (Table 4.17 and Fig 4.18). In the case of Pb, station 1 and 19 showed low contamination factor, station 13 had moderate contamination factor, station 11 showed very high contamination factor and all other stations were having considerable contamination factor during February. In April, station 4 showed low contamination factor, stations 3, 8, 9, 10, 11, 12, 13, 15 & 17 showed considerable contamination factor and all other stations showed moderate contamination factor. During June, stations 4, 12, 16, 17, 18 and 19 showed low concentration factor, stations 1, 5 and 6 showed considerable contamination factor and all other stations showed moderate contamination factor. Stations 1, 16, 17, 18, and 19 showed low contamination factor, stations 3, 8, 9, 10, 11 and 13 showed moderate contamination factor and all other stations showed considerable contamination factor in August.

Zinc

The CF value of Zn ranged from a minimum value of 0.29 at station 1 to a maximum value of 2.22 at station 10 in February (Table 4.14 and Fig 4.15). During April, the CF was maximum (1.80) in station 7 and minimum (0.53) in station 17 (Table 4.15 and Fig 4.16). In June, the highest value of 1.27 was found at station16 and lowest value of 0.66 at station 1 (Table 4.16 and Fig 4.17). In August, the value ranged from 0.53 at station 8 to 1.28 at station 18 (Table 4.17 and Fig 4.18). In the case Zn, stations 1, 14 and 16 showed low contamination factor and all other stations showed moderate contamination factor during February. In April, stations 3, 4, 10, 17 & 19 showed low contamination factor and all other stations showed moderate contamination factor. During June, stations 6, 7, 15, 16 and 18 showed moderate contamination factor and all other stations showed low contamination factor.

Table 4.14 Contamination Factor during February, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.18	0.84	1.67	0.36	0.29
st2	2.17	4.49	13.33	4.97	2.02
st3	0.41	2.23	8.33	3.04	1.61
st4	1.05	3.85	13.33	5.16	1.44
st5	2.57	4.08	16.33	5.33	1.82
st6	1.08	3.50	7.00	3.21	1.34
st7	1.81	3.14	15.00	3.59	1.61
st8	3.48	2.83	6.67	3.10	1.46
st9	2.44	4.45	12.67	5.49	1.92
st10	3.95	4.70	17.67	4.99	2.22
st11	1.09	5.61	19.33	6.11	1.96
st12	1.54	4.75	8.67	4.93	1.49
st13	0.58	1.99	5.33	1.53	0.49
st14	0.58	3.20	13.67	3.45	0.96
st15	3.04	5.62	13.67	4.98	2.02
st16	0.61	9.73	2.00	0.50	0.42
Status	**Moderate contamination**	**Considerable contamination**	**Very high contamination**	**Considerable contamination**	**Moderate contamination**

Table 4.15 Contamination Factor during April, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.85	5.12	14.00	5.00	1.61
st2	0.83	4.24	33.67	3.67	1.43
st3	0.26	1.26	15.33	1.25	0.63
st4	0.36	1.81	16.33	0.73	0.60
st5	1.01	3.95	13.67	4.20	1.35
st6	1.38	4.03	10.67	4.13	1.45
st7	1.48	4.35	16.33	4.83	1.80
st8	1.05	3.42	11.33	2.90	1.03
st9	0.98	2.93	6.67	2.61	1.17
st10	1.09	3.47	10.33	2.34	0.92
st11	0.44	2.94	14.00	2.75	1.41
st12	0.76	2.63	7.33	1.36	1.16
st13	0.82	3.69	11.33	2.58	1.36
st14	0.95	3.60	8.67	3.26	1.63
st15	0.79	3.26	9.00	2.33	1.39
st16	0.76	2.86	6.33	3.06	1.33
st17	0.22	1.10	5.33	0.00	0.53
st18	0.84	3.17	7.67	1.23	1.32
st19	0.44	1.86	2.00	0.00	0.70
Status	**Low contamination**	**Considerable contamination**	**Very high contamination**	**Moderate contamination**	**Moderate contamination**

Table 4.16 Contamination Factor during June, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.27	4.46	4.00	3.81	0.66
st2	0.41	4.53	2.60	2.84	0.85
st3	0.23	0.76	9.27	1.56	0.38
st4	0.34	1.51	10.17	0.44	0.73
st5	0.45	4.03	9.63	3.04	1.10
st6	0.45	3.71	10.47	3.56	1.12
st7	0.44	2.87	12.97	2.28	1.04
st8	0.23	2.48	9.27	1.88	0.67
st9	1.06	1.78	6.30	2.34	0.96
st10	0.23	1.66	8.17	1.41	0.82
st11	0.39	1.51	11.50	1.64	0.67
st12	0.54	3.01	4.17	0.91	0.95
st13	0.40	3.93	8.17	2.71	0.99
st14	0.51	3.44	4.83	1.92	0.69
st15	0.59	2.84	1.87	2.59	1.03
st16	1.02	2.51	2.60	0.57	1.27
st17	0.28	1.61	3.27	0.51	0.71
st18	0.48	2.38	3.83	0.58	1.21
st19	0.19	1.01	0.83	0.43	0.74
Status	**Low contamination**	**Considerable contamination**	**Very high contamination**	**Moderate contamination**	**Low contamination**

Table 4.17 Contamination Factor during August, 2017

	Cu	Ni	Cd	Pb	Zn
st1	0.23	3.94	4.10	0.45	0.61
st2	1.94	3.57	11.87	4.01	0.61
st3	0.61	1.28	6.60	2.82	0.48
st4	0.83	1.78	13.27	4.99	0.75
st5	1.25	3.92	13.50	4.56	1.04
st6	0.64	2.89	6.60	3.39	0.96
st7	0.55	2.08	1.87	3.71	0.86
st8	0.62	2.03	4.23	2.87	0.53
st9	1.22	1.45	8.53	2.48	0.90
st10	1.04	1.68	13.40	1.78	0.84
st11	1.26	2.51	15.93	1.66	0.70
st12	1.01	2.89	12.83	4.40	0.92
st13	0.55	1.39	6.70	1.02	0.90
st14	0.47	2.79	12.60	1.89	0.94
st15	0.62	2.28	13.97	4.51	1.05
st16	1.05	2.38	1.87	0.73	1.16
st17	0.21	1.78	4.83	0.51	0.83
st18	0.25	1.39	9.17	0.52	1.28
st19	0.44	1.28	8.00	0.56	0.94
Status	**Low contamination**	**Moderate contamination**	**Very high contamination**	**Moderate contamination**	**Low contamination**

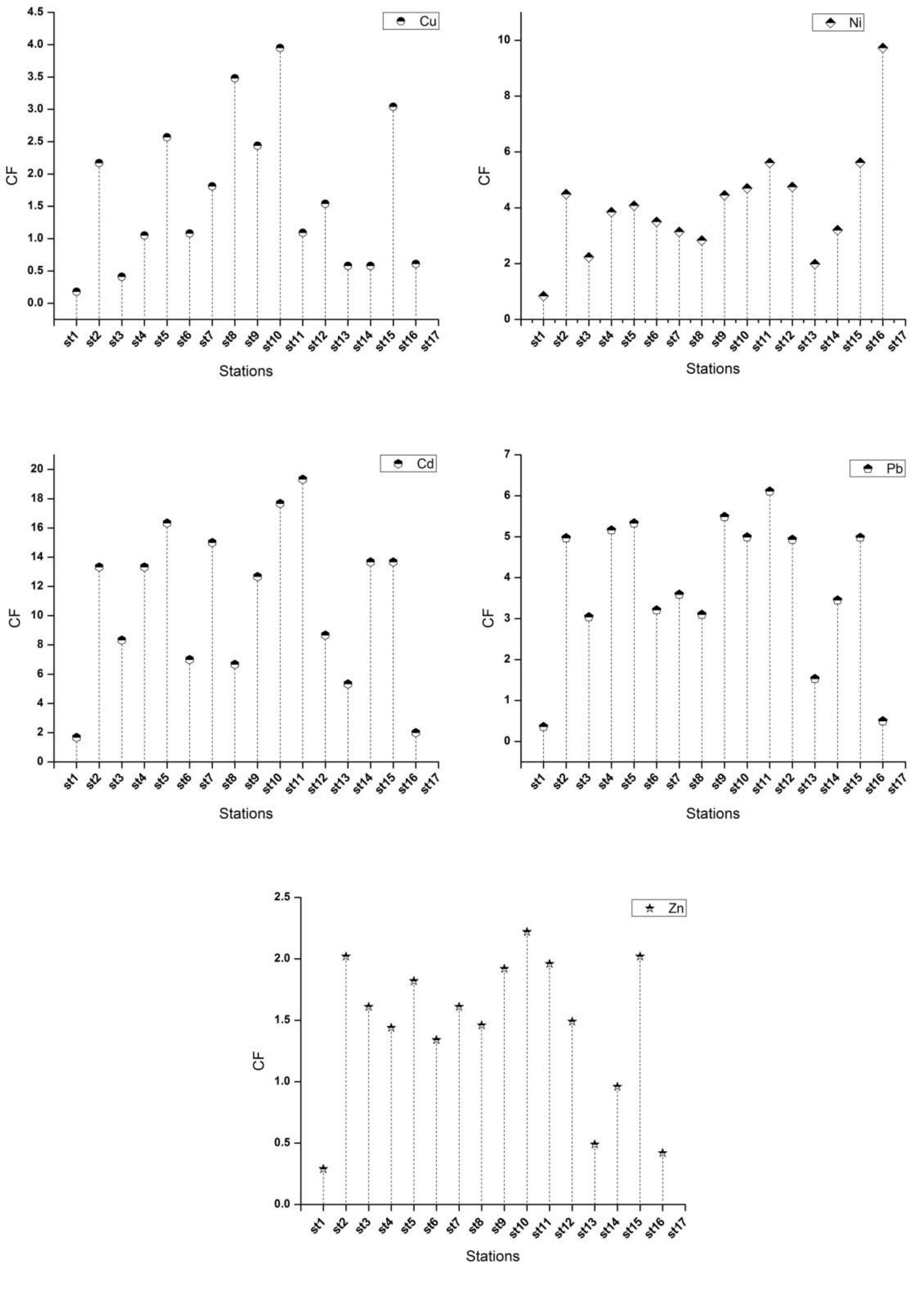


Fig. 4.15 Spatial variation in Contamination Factor index (Feb, 2017)

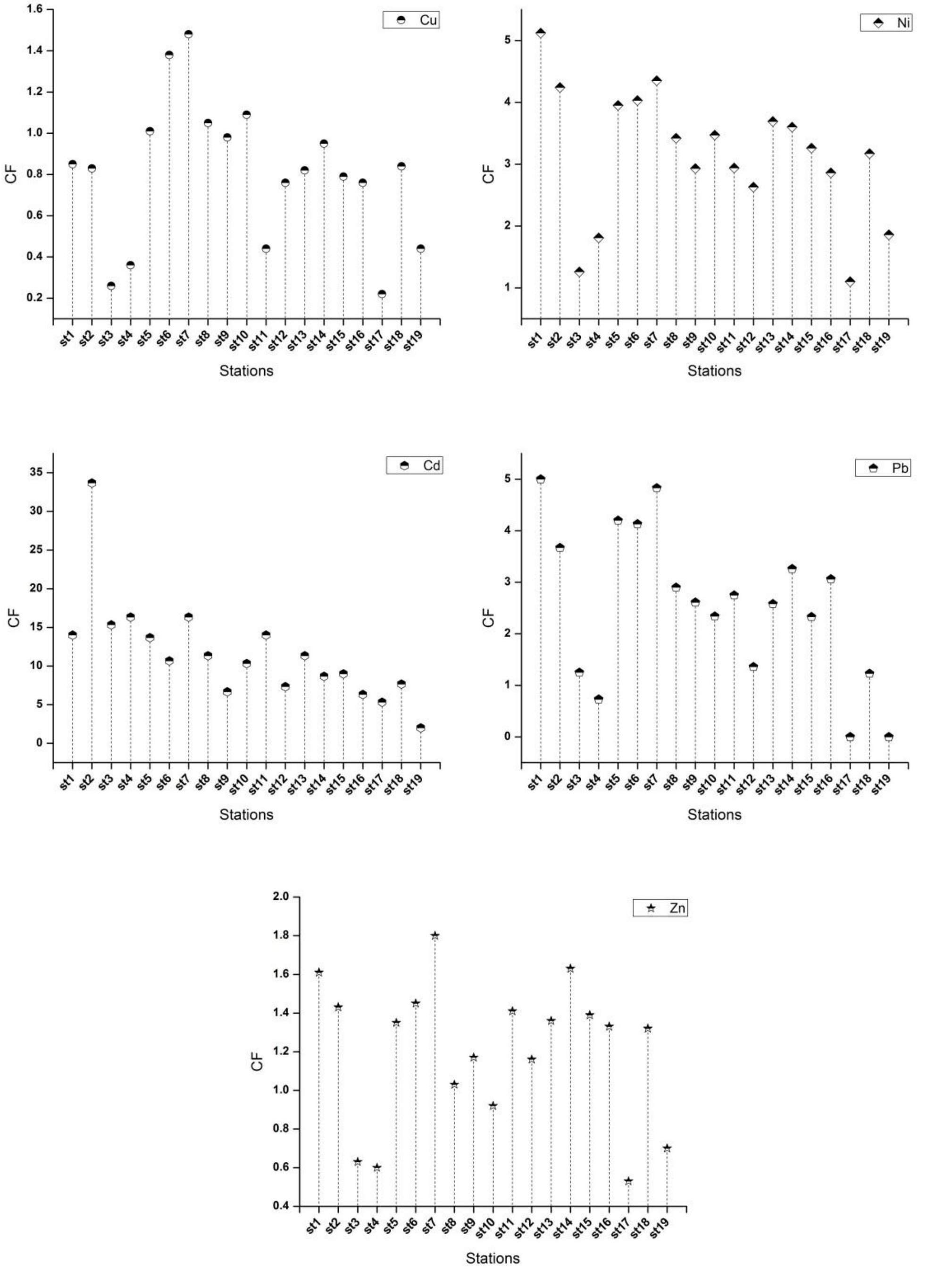


Fig. 4.16 Spatial variation in Contamination Factor index (Apr, 2017)

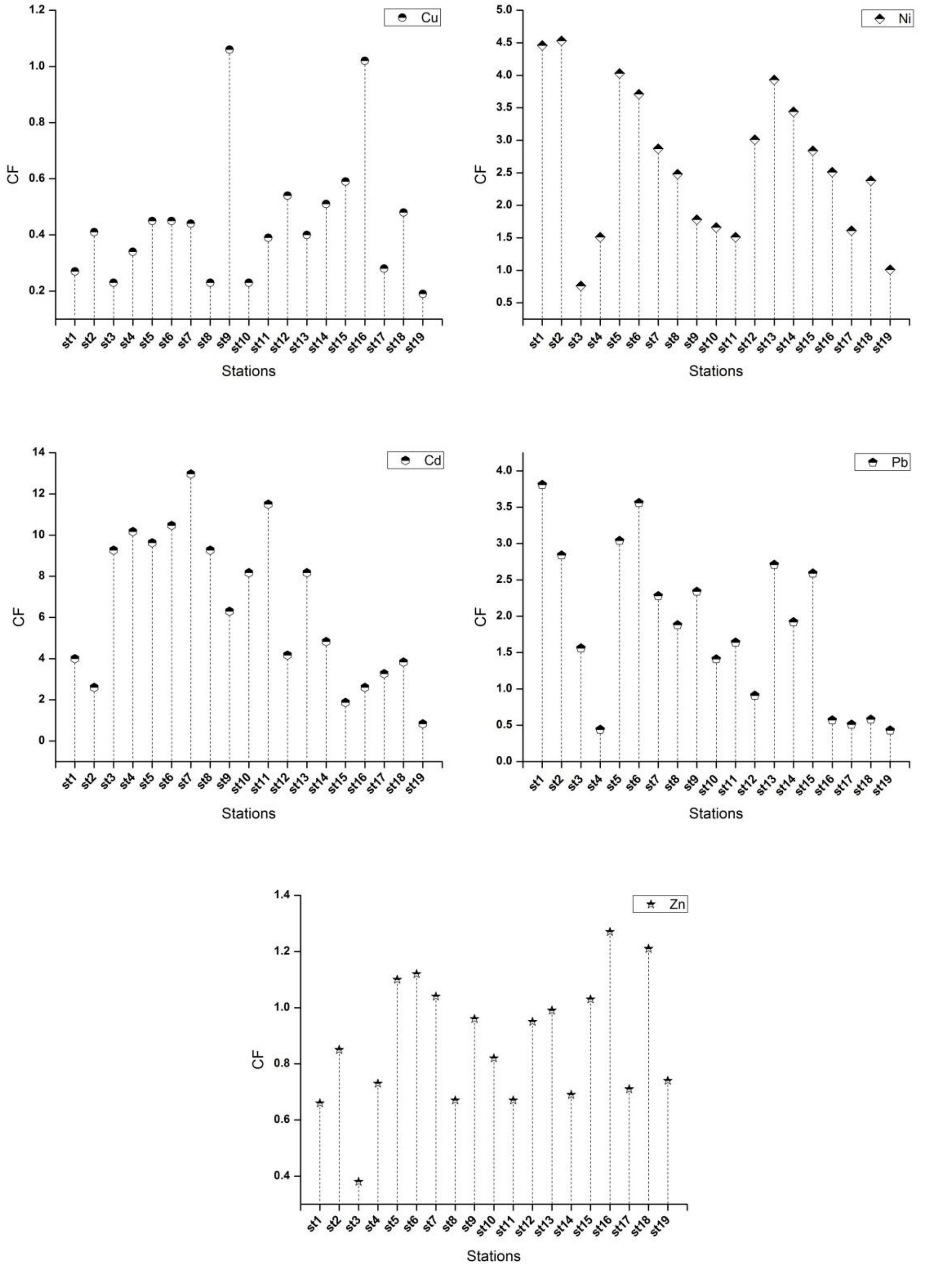


Fig 4.17 Spatial variation in Contamination Factor index (Jun, 2017)

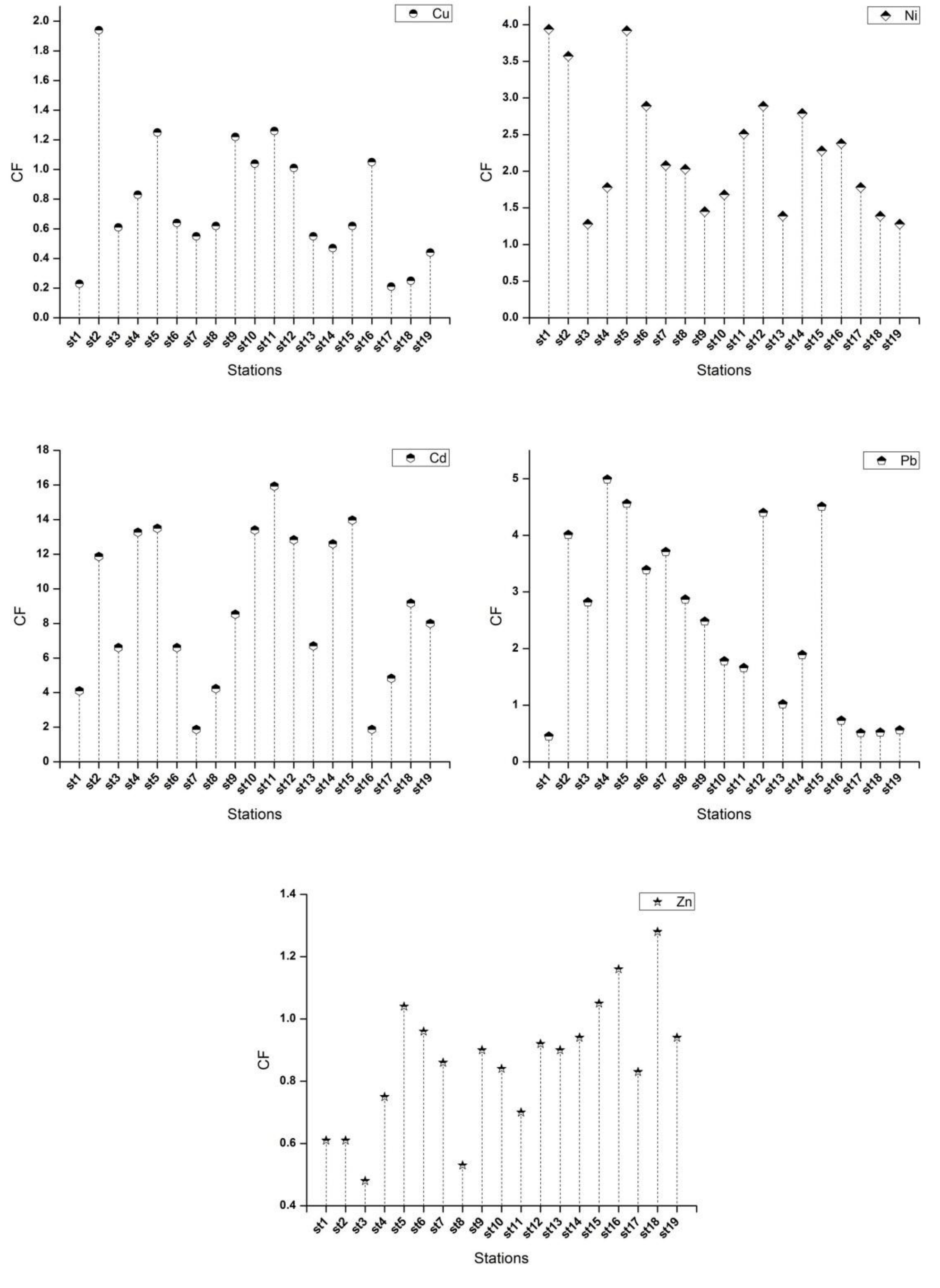


Fig. 4.18 Spatial variation in Contamination Factor index (Aug, 2017)

c. Pollution Load Index (PLI)

In the present study, Pollution Load Index ranged between 0.48 (station 1) to 5.15 (station 10) during February and all the stations were found polluted except station 1 (Table 4.18). However in April, the higher value of 3.91 was found in station 7 and lower value of 1.32 was found in station 3 and all the stations were found to be polluted during the period (Fig. 4.19). During June, the value was high (2.34) in station 6 and low (0.55) in station 19. Except station 3, 17 & 19, all stations were found polluted in this month. While in August the maximum value of 3.16 was found in station 5 and minimum value of 0.95 was found in station 17. All the sediment samples were found to be polluted during the study period since the values were found to be very high. All samples were found polluted except station 17 during this period.

Table 4.18 Pollution Load Index, 2017

Stations	Pollution Load Index			
	Feb	Apr	Jun	Aug
St1	0.48	3.45	1.65	1.01
St2	4.20	3.37	1.64	2.89
St3	2.06	1.32	0.99	1.48
St4	3.31	1.36	1.11	2.36
St5	4.41	3.15	2.26	3.16
St6	2.58	3.24	2.34	2.09
St7	3.46	3.91	2.08	1.46
St8	3.12	2.61	1.46	1.52
St9	4.29	2.25	1.93	2.02
St10	5.15	2.43	1.29	2.04
St11	4.27	2.34	1.50	2.26
St12	3.42	1.87	1.42	2.73
St13	1.36	2.60	2.03	1.36
St14	2.43	2.75	1.62	1.97
St15	4.72	2.37	1.53	2.48
St16	1.20	2.24	1.37	1.32
St17		0.00	0.88	0.95
St18		2.01	1.25	1.17
St19		0.00	0.55	1.19

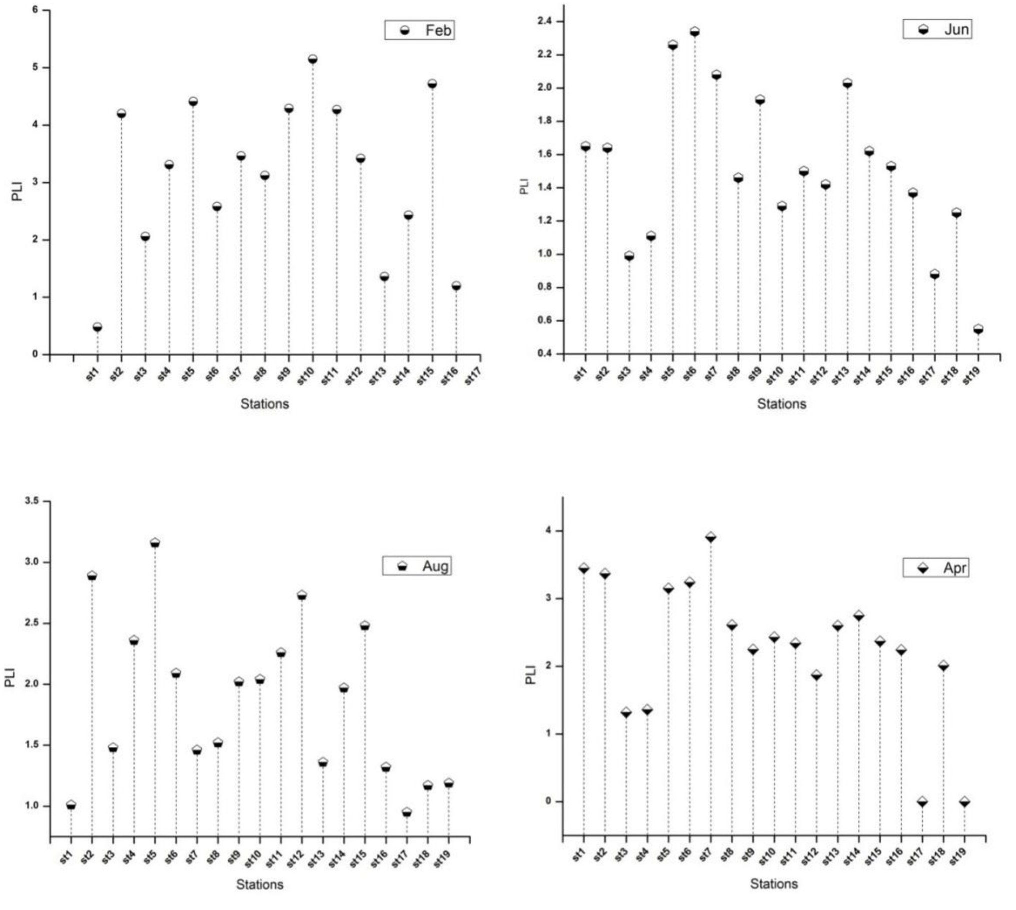


Fig. 4.19 Spatial variation in Pollution Load Index, 2017

4.2.5 Heavy Metals in organisms

In this study, organisms from 7 selected main stations were analysed for heavy metals- copper, nickel, cadmium, lead and zinc in both pre-monsoon and monsoon seasons. The organisms selected were *Penaeus indicus* (St.3-Thnneermukkom north), *Channa* sp. (St.4-Thanneermukkom south), *Etroplus maculatus* (St.5-Pathiramanal), *Villorita* sp. (St.6-Punnamada), *Puntius* sp. (St.11-Kainakary), *Ambassis* sp. (St.12- C block Cherukayal), *Macrognathus* sp. (St.14-Ranikayal). The heavy metal concentrations in these organisms are given in the Tables 4.20 and 4.21.

In *Penaeus indicus*, the concentration of Cu (20.16 mg kg^{-1}) was found high during monsoon period and other heavy metals - Ni (8.65 mg kg^{-1}), Cd (0.25 mg kg^{-1}) and Zn (121.18 mg kg^{-1}) concentrations were found high during the pre-monsoon (Table 4.20 and Table 2.21). The concentration of Pb was below dectable level. In case of *Channa* sp., concentration of Cu (26 mg kg^{-1}) was high during pre-monsoon and concentration of Zn (85.65 mg kg^{-1}) was high during monsoon season (Table 4.20 and Table 2.21). Other heavy metal concentration was below detectable level. The concentration of Cu (9.95 mg kg^{-1}) and Ni (44.50 mg kg^{-1}) were high during the pre-monsoon period in *Etroplus maculatus* (Table 4.20 and Table 2.21). Zn concentration (120.05 mg kg^{-1}) showed high value during monsoon but the Cd and Pb concentration were below detectable level. In *Villorita* sp., the concentrations of Cu (31.28 mg kg^{-1}) and Ni (10.38 mg kg^{-1}) were higher during the monsoon season while Zn concentration (99.51 mg kg^{-1}) was high during pre-monsoon. The concentrations of other heavy metals were below detectable limit (Table 4.20 and Table 2.21). Cu concentration was found higher than the standard limit described by FAO/WHO, 1983 (Table 4.19). *Villorita* sp. is a bivalve filter feeder, so the chances of bioaccumulation of toxic metals will be higher in these organisms. In case of *Puntius* sp., the concentration of Cu (19.85 mg kg^{-1}) and Ni (2.15 mg kg^{-1}) were high during monsoon season and the concentration of Zn (63.64 mg kg^{-1}) was higher during pre-monsoon season. The concentration of lead and cadmium were below detectable limit (Table 4.20 and Table 2.21). The concentration of Cu (9.02 mg kg^{-1}) and Ni (7.55 mg kg^{-1}) were high during monsoon period in *Ambassis* sp. Zn (136.14 mg kg^{-1}) concentration was high during the pre-monsoon period and other heavy metals were below detectable limit (Table 4.20 and Table 2.21). In pre-monsoon and monsoon period, the concentration of Zn was found higher than the standard limits. During pre-monsoon period, the concentration of Cu (19.15 mg kg^{-1}) was higher in *Macrognathus* sp. and in monsoon period, concentration of Ni (5.63 mg kg^{-1}) and Zn (85.27 mg kg^{-1}) were higher (Table 4.20 and Table 2.21). Other heavy metals concentrations were below detectable limit. These observations conclude that the heavy metal pollution is becoming a major threat to the aquatic organisms in the Vembanad backwater.

Bioaccumulation of metals can cause change in community composition, species structure and even biodiversity loss and ecosystem imbalance. It was also evident that the tolerant species will dominate and occupy the niche replacing the less tolerant species which are sensitive to pollution (Pearson and Rosenberg, 1978). Bio concentration Factor (BCF) was calculated to analyse the transfer rate of metals from the surrounding environment (Table 4.22 and Table 2.23). In the present study, all the metals showed high BCF rate during the PRM. Ni showed the high BCF value of 91.05 in *Penaeus indicus* from Thanneermukkom region. The BCF value of Cu ranged from 0.08 to 9.14 and was found high in the *Macrognathus* sp. from Ranikayal region. Cu was followed by Zn and its rate ranged from 0.12 to 4.43 in the study. The high value of Zn was found in *Penaeus indicus* from Thanneermukkom region. Metals Pb and Cd values were Below Dectatable Limit (BDL).

Table 4.19 Standard guidelines of heavy metal concentration in organisms

Heavy Metals	Standard Limit (mg/kg)
Cu	30 (FAO/WHO,1983)
Zn	100 (FAO/WHO,1989)
Ni	70-80 (USFDA, 1993b)

Table 4.20 Metal concentration in organism samples (Apr, 2017)

Sl No.	Month	Stations	Concentration in sample (mg/kg)				
			Cu	**Ni**	**Cd**	**Pb**	**Zn**
1	**April, 2017**	**Sta.3**	18.50	8.65	0.25	BDL	121.18
2		**Sta.4**	26.00	BDL	BDL	BDL	51.57
3		**Sta.5**	9.95	44.50	BDL	BDL	118.66
4		**Sta.6**	26.15	9.15	BDL	BDL	99.51
5		**Sta.11**	17.45	BDL	BDL	BDL	63.64
6		**Sta.12**	6.75	7.55	BDL	BDL	131.14
7		**Sta.14**	19.15	2.50	BDL	BDL	70.96

Table 4.21 Metal concentration in organism samples (Aug, 2017)

Sl No.	Month	Station	Concentration in sample (mg/kg)				
			Cu	**Ni**	**Cd**	**Pb**	**Zn**
1	**April, 2017**	**Sta.3**	20.16	1.27	0.01	BDL	98.23
2		**Sta.4**	15.21	BDL	BDL	0.14	85.65
3		**Sta.5**	5.45	25.76	BDL	BDL	120.05
4		**Sta.6**	31.28	10.38	BDL	BDL	98.23
5		**Sta.11**	19.85	2.15	BDL	BDL	58.32
6		**Sta.12**	9.02	3.24	BDL	BDL	136.14
7		**Sta.14**	6.57	5.63	BDL	BDL	85.27

Table 4.22 Bio concentration Factors in organism samples (PRM, 2017)

Stations	Cu	Ni	Cd	Pb	Zn
Sta.3	6.89	91.05	0.72	BDL	4.43
Sta.4	6.76	BDL	BDL	BDL	1.30
Sta.5	4.54	BDL	BDL	BDL	6.18
Sta.6	8.12	BDL	BDL	BDL	4.14
Sta.11	6.13	BDL	BDL	BDL	2.42
Sta.12	2.08	BDL	BDL	BDL	3.88
Sta.14	9.14	0.67	BDL	BDL	2.07

Table 4.23 Bio concentration Factors in organism samples (MN, 2017)

Stations	Cu	Ni	Cd	Pb	Zn
Sta.3	0.81	BDL	BDL	0	0.19
Sta.4	1.52	BDL	BDL	0	1.14
Sta.5	0.08	BDL	BDL	0	0.16
Sta.6	0.78	BDL	BDL	0	0.15
Sta.11	BDL	BDL	BDL	0	0.12
Sta.12	BDL	BDL	BDL	0	0.65
Sta.14	BDL	BDL	BDL	0	0.44

4.3 Other contaminants

In the present study, detectable pesticide residues were not observed from the samples taken from the study area. But the study shows habitation of emerging pollutants in most of the study locations of Vembanad backwater. According to Lynn Roberts of Johns Hopkins University, compounds that qualify as “emerging pollutants” are those that are “entering into or being generated in the environment in appreciable amounts”, that have “amodicum of persistence,” and “exhibit deleterious effects on organisms”. Now a days in case of environmental pollution, the occurrence of pharmaceuticals and antibiotics in the aquatic environment has been considered as one of the major emerging issue around the world.

The chromatograms of GC analysis of the Vembanad samples from the present study revealed that there is high probability for the occurrence of the following compounds in the sample (Table 4.24).

Benzyl benzoate: A synthetic chemical used as a fragrance ingredient, artificial flavor, preservative, and solvent. It is also considered an over the counter drug and can be used as a scabies or lice treatment. It is an ester of benzyl alcohol and benzoic acid. Benzyl benzoate is relatively nontoxic but may irritate the skin and eyes. Increased pruritus and irritation are common and may be severe in hot humid climates. In the present study, benzyl benzoate presence was noted in almost all the stations during the PRM season.

Cyclic Octaatomic sulphur: Elemental sulfur used in black gunpowder, matches, and fireworks; in the vulcanization of rubber; as a fungicide, insecticide, and fumigant; in the manufacture of phosphate fertilizers; and in the treatment of certain skin diseases. The principal use of sulfur, however, is in the preparation of its compounds. Sulfur has been known and used as a pesticide since very early times in history. Elemental sulfur is granulated to a fine powder (325 mesh) for use as a pesticide (control for mites, insects, fungi and rodents) in livestock production. The particle size for this powder is 44 microns (0.0017 inches) or less. Pesticides are regulated by the US Environmental Protection Agency (EPA). Element sulfur is a ubiquitous, natural component of the environment, but is still required to be registered by the EPA for use as a pesticide. EPA has registered sulfur for use as an insecticide, fungicide and rodenticide on several hundred food and feed crops, ornamental, turf and residential sites. Sulfur is applied in dust, granular or liquid form, and is an active ingredient in nearly 300 EPA registered pesticide products. Octatomicsulphur was present only in some of the stations during PRM, but during the MN season it was present in almost all the stations.

Benzenepropanoic acid: It is an organic compound belonging to the class of phenylpopanoids. This compound is used frequently in cosmetic products such as perfumes, bath gels, detergent powders, liquid detergents, fabric softeners, and soaps as it gives off a floral scent. The acid is commonly used as flavoring for toothpastes and mouthwashes in addition to providing floral scents and possible fruity and herbal flavorings. It acts as a fixative agent. The presence of benzenepropanoic acid was found during the PRM.

Cyclonasiloxane and Cycloheptasiloxane: They are cyclic dimethyl polysiloxanes and are mainly used as ingredients in pharmaceuticals and cosmetics like skin conditioners. The anti-caking property of these compounds makes them suitable for cosmetic production. They also have the quality of softening or soothing the skin and are one of the main components in skin care products.

Table 4.24 Compounds found in GC analysis

Compounds	Stations
Benzyl benzoate	Aroor, Thanneermukkom North, Thanneermukkom South, Pathiramanal, Punnamada, Nehru trophy, Pangankuzhipadam, Pallathuruthy, Meenappally, C Block Cherukayal, Kuttamangalam, Ranikayal, Chithirakayal, Varanadu, Kuppapuram
Benzene propanoic acid	Thanneermukkom North, Thanneermukkom South, Pathiramanal, Punnamada Pallathuruthy, C Block Cherukayal, Kuttamangalam, Ranikayal, Varanadu
Cyclic octaatomicsulphur	Pathiramanal, Nehru trophy, Pallathuruthy, Meenappally, Kainakary, C Block Cherukayal, Ranikayal, Marthandam, Kuppapuram
Cyclonasiloxane	Pangankuzhipadam, Pallathuruthy, Meenappally, Kuppapuram
Cycloheptasiloxane	Thanneermukkom North, Punnamada, Meenappally, Chithirakayal, Varanadu

4.4 Discussion

4.4.1 Heavy metals in water and sediment

Heavy metals are toxic and carcinogenic to living organisms (Clement *et al*., 1995). Because of its toxicity and non-biodegradability, the presence of heavy metals in aquatic system cause great anxiety. Detection of elevated levels of heavy metals in the aquatic system is increasing nowadays, which leads to bioaccumulation and bio magnification of various metals. Vembanad backwater is a source rather than sink of different metals derived both from anthropogenic and natural origins. Distribution, sequestration and concentration of heavy metals in aquatic environment is determined by varying physico-chemical parameters such as temperature, salinity, dissolved oxygen, pH, sediment grain size, supply of nutrients, sulphide concentrations (Li *et al*., 2013). Sediments can incorporate and accumulate many metals added to a body of natural water. The favourable physico-chemical conditions of the sediment can remobilize and release the metals to the water column (Harikumar *et al.,* 2009). Enrichment of heavy metals due to industrialization and urbanization was recorded in sediments and water of Vembanad backwater by many scientists (Remani, *et al*., 1983, Ouseph, 1992, Mahesh Mohan and Omana, 2007) (Table 4.25). In the present study, increased accumulation of heavy metals in water column was observed in the estuary during MN in comparison with the PRM season. The average concentration of heavy metals in Vembanad backwater followed the trend Cd< Ni< Cu< Pb< Zn< Fe. Concentrations of Cd ranged from 0 to 1.44 µg L^{-1}, Ni from 0.06 to 9.56 µg L^{-1}, Cu from 0.75 to 130 µg L^{-1}, Pb from 0.38 to 370 µg L^{-1}, Zn from 9.26 to 101.8 µg L^{-1} and Fe from 284.69 to 12100 µg L^{-1}. The southern stretch of the estuary was found to be more contaminated in the study especially at Punnamada and the Nehru trophy finishing point regions. Concentration of Zn in Nehru trophy finishing point during MN was found 53 fold higher than that in the PRM. Fe and Pb also showed high rate of increase in their concentration. Sewage-sludge and the use of agro-chemicals fertilizers and pesticides are the main sources of zinc in the southern parts of the estuary.

In the case of sediment, the average concentration of heavy metals showed the trend Cd< Cu< Pb< Ni< Zn. The Marthandam region of the backwater showed higher values of heavy metals and the overall concentration was observed to be increasing during PRM. Average concentration was observed high for Cu (70.95 mg kg^{-1}) in Meenappally, Ni (87.35 mg kg^{-1}) in Chithirakayal Cd (4.56 mg kg^{-1}) in Kainakary, Pb (85.61 mg kg^{-1}) in Pathiramanal and Zn (130.24 mg kg^{-1}) in Marthandam regions. The increasing discharges from mining, electroplating works, painting and printing works, automobile battery, and petrochemical industries contain high levels of copper, zinc, cadmium and lead (Dali-youcef *et al*., 2006; Mohan *et al*., 2007). Also from increasing industrialization and urbanization, heavy metal pollution can cause serious threats in the coastal waters of tropical and subtropical countries (Ratheesh Kumar *et al*., 2010). In the present study, the higher ranges of heavy metals denoted a higher chance of anthropogenic impact on the distribution of these metals in the estuary over the years (Table 4.23). The qualitative analysis of the sediment based on Sediment Quality Guidelines (SQG) showed possible risk to aquatic life due to high Ni concentration while moderate pollution for Cu, Cd, Pb and Zn was also noted. The higher concentration of Ni was found in Chithirakayal region of the backwater in the study. Agricultural runoff may be one major source since the station is influenced by discharges from R and H block "padasekharams" as well as riverine inflow from Pamba and Manimala rivers. A study conducted by Harikumar *et al.* **(**2009) reported that at the center of the lake and at the stations Ranimangalam and Kuppapuram, nickel values exceeded the effective range median level based on SQG. The Igeo values showed extreme contamination from Cd, strong contamination from Ni, moderate to strong pollution from Pb and moderate pollution for Cu and Zn. Sudhanandh *et al*.

(2011) also reported that coastal sediments of Kochi have high heavy metal accumulation. High geo accumulation index values were observed for Cd (6.24) and Ni (2.02) which shows that the backwater is facing strong contamination from these two heavy metals. In case of contamination factor (CF), Cd (9.36) showed higher contamination, that for Ni (3.03) showed considerable contamination, Pb and Zn having moderate contamination and Cu depict low contamination. The average pollution load index (PLI) was also higher that ranged from 0.55 to 5.15 which clearly reveal that the study area is having polluted sediments. Shyleshchandran *et al.* (2017) observed PLI values ranging from 0.88 to 6.23 with an average of 2.98 ± 1.91 in Vembanad backwater. So the rise in numerical PLI values suggests the progressive deterioration in sediment quality due to heavy metals from the backwater. Stations in the southern stretch are found more polluted in the study when compared to the heavy metal concentrations in northern stretches. But the concentration of heavy metals Cd and Ni were observed to be higher in both the stretches of the backwater. Enrichment of Cu, Ni, Co, Zn and Cd in sediment cores recovered from the Vembanad backwater and their concentrations, when compared with other Indian rivers suggested that the Periyar River and Cochin estuary are showing heavy anthropogenic contamination (Priju *et al.*, 2007). This study also justifies the increasing contamination of the backwater from heavy metals.

Table 4.25 Comparison of heavy metals in surface sediments of Vembanad estuary especially in the Cochin estuary over the years

Location	Cu	Ni	Cd	Pb	Zn
Purandara, 1990	51 to 271	15 to 94	NM	NM	34.5 to 70.83
Rajamani Amma, 1994	31.87 to 333.78	NM	ND to 10	20 to 120	29.29 to 290.5
Martin *et al.*, 2012	3.6 to 123.5	8.5to 103.7	0.2 to 40.7	6.8 to 99.6	10.0 to 2233
Balachandran *et al.*, 2005	5.4 to 53.2	5.1 to 72.1	0.59 to 14.9	19.3 to 71.3	92 to1266.0
Dipu and Kumar, 2012	6.36 to 655.125	NM	1.375 to 24.75	12 to 79.625	72.75 to 1306.5
Ratheesh Kumar *et al.*, 2010	0.28 to 41.8	3.12 to 74.26	ND to 11	ND to 34.5	51.93 to 741.93
Nasir and Harikumar, 2011	38.87 to 1723.75	49.59 to 75.70	0.27 to 26.35	21.70 to 162.59	70.07 to 1963.67
Harikumar *et al.*, 2009	16.73 to 56.13	36.53 to 74.47	0.07 to 2	0.61 to 80.03	103.39 to 305.29
Asha *et al.*, 2016	3 to 232.7	NM	ND to 3.1	12 to 81.7	9 to 8950
Present Study	8.10 to 177.6	16.8 to 194	0.25 to 4.78	7.22 to 122.1	27.4 to 210

The PCA analysis showed that nitrate, nitrite, phosphate and silicate were the main determinants of variability in the system. The concentration of these nutrients was higher in MN during the study period. Increasing anthropogenic events especially, agricultural activities including use of superphosphate fertilizers, urban expansion and the diffused nature of its associated nonpoint source pollution from surface runoff and ground water contamination have become a major water quality problem. The Cd concentration showed a positive correlation with the nitrite in the study period. Nitrites reach the water body mainly from fertilizers through run off water, sewage and mineral deposits. The annual fertilizer consumption in Kuttanad alone is estimated as 20000 tons. Agriculture and aquaculture practices prevalent in the drainage basins are also partly responsible for eutrophication through deposition of eroded top soil and agrochemicals and pesticides. The modern aquaculture also demands the use of many nutrients, inducing changes in the ecosystem. All these diversified**,** agriculture and aquaculture practices have contaminated the water and sediment of Vembanad backwater.

4.4.3 Heavy metals accumulation in organisms

In organisms, the heavy metal pollution is becoming a major threat in Vembanad backwater and their consumption is becoming a danger to the humans. In the present study the metal concentration followed the trend Zn > Cu> Ni> Cd> Pb. The concentration of Zn was observed to be very high in all the organisms. The Zn concentration showed high values in C-block Cherukayal and Thanneermukkom regions in *Ambassis* sp. (136.14 mg kg^{-1}) and *Channa* sp. (121.18 mg kg^{-1}). The bivalves are well known for their ability to concentrate heavy metals in their tissues. In *Villorita* sp., from Punnamada region, the concentration of Zn (99.51 mg kg^{-1}) was also observed to be comparatively higher. Similar trend was observed in the study conducted in *Villorita cyprinoides* Var. *cochinensis* in the Cochin estuary by Ranjitha Raveenderan and Sujatha, (2011). Ramani (1979) reported that accumulation of zinc in mussels and oysters were higher than the standard limit. Zn is essential trace element in living systems for the normal cell differentiation and growth. It forms an essential part of a number of metalloenzymes and a co-factor for regulating the activity of zinc specific enzymes. It also acts as a structural component in many enzymes taking part in the energy metabolism. Earlier studies by Kiekens, 1990 shows deficiency of Zn can result in severe growth depression, skin scratch and sexual immaturity. But prolonged exposure to sub lethal concentration of Zn could cause extensive edema and necrosis of liver tissues (Leland and Kuwabara, 1985). *Penaeus indicus* showed high BCF values of Ni (91.05) and Zn (4.43). Several investigations by various authors on the accumulation of metals by marine organisms support our results. Heavy metals were reported from marine fishes from the Cochin area by Martin *et al*. (2008). They reported increased levels of Cu, Zn, Fe and Mn in gills and alimentary canal compared to the muscle. Concentration of Cu in organisms like *Villorita* sp. and *Penaeus* sp. in the Punnamada and Thanneermukkom regions was also found to be increasing during the study period. *Macrognathus* sp. showed a high BCF value of 9.14 in the current study. Sublethal effects including decrease in erythrocyte count, haemoglobin, haematocrit and mean corpuscular haemoglobin in *Puntius* sp. on Cu and Zn exposure was reported by Ciji and Bijoy Nandan (2014) in Cochin estuary. One of the adverse effects due to heavy metal pollution has been the marked decline in the clam fishery (*Villorita* sp.) of this estuary over the years. Here, pollution tolerant benthic organisms (opportunistic species) like polychaetes are found to take over the vacated niche (Gopalan *et al.*, 1983; Saraladevi *et al.*, 1992). The reduced biodiversity and high biomass of such tolerant species observed in this region are also indicative of pollution stress. Jiya *et al.* (2011) reported that high concentrations of Zn (2758 mg kg^{-1}) and Nickel (259 mg kg^{-1}) at geographical location close to industrial belt and metal accumulation at this level in the sediment ultimately resulted in adaptation/reduction in bacterial distribution, diversity and enzyme expression profile, thereby emergence of resistant strains. Sediment linked metals cause serious threat to detritus and deposit feeding benthic fishes and act as sources of contamination when the metals are released into water and impose serious impacts on living organisms and act as good indicators of environmental pollution (Asa and Rath, 2014). Trophic transfer of heavy metals in food chains may contribute to long-distance transport of these elements in the environment. Primary producers are very important in trophic transfer of heavy metals because they bridge metal fluxes between abiotic and biotic components of ecosystems. Higher concentrations of heavy metals in fish may lead to toxic effects on humans. Consumption of wild fish on regular basis from water bodies with industrial contamination may pose a greater risk to human health. Long-term intake of unsafe levels of heavy metals through foods may result in disruption of many biological and biochemical processes in humans.

The unplanned development and economic activities for supporting the needs of increasing population continues to exert ever growing pressure on the ecosystem. The Vembanad estuary receives effluents from chemical and engineering industries, food and drug manufacturing industries and also from paper, rayon, rubber, textiles and plywood industries. It is estimated that nearly 260 mld of such industrial effluents reach the estuary from the industrial belt of Greater Kochi. In addition, the Cochin shipyard and port are releasing sizable quantities of waste oil, paints, metal and paint scrapings. The traditional retting practice in coir sector of this area also exerts pressure on the system. There are over 1,500 houseboats cruising the backwater of Kerala according to the records of the Port office (Alappuzha) there are only 638 houseboats that have proper licenses to operate. It is estimated that every day, a total of 4.25 tonnes of wastes are drained to the Vembanad backwater by the houseboat tourism industry in Kerala. Among the total wastes dumped daily, 1.2 tonnes belong to inorganic waste category, which can be a source of heavy metals in the backwater (Michael *et al.*, 2017).

4.4.4 Other contaminants

Even though detectable pesticide residues were not been observed from the samples, some compounds which may be classified in to the group of “emerging pollutants” were observed and recorded which have not been reported from the study area. Among them, the most commonly found compound is Benzyl benzoate and it is recorded in all most all the stations of the backwater. Benzyl benzoate is relatively nontoxic but may irritate the skin and eyes. In case of hot humid climates, increased pruritus and irritation are common and may be severe. Benzenepropanoic acid, Cyclonasiloxane and Cycloheptasiloxane are the other compounds which were recorded from the study area that are major ingredients in pharmaceuticals and cosmetics like skin conditioners. Sources of most of these compounds are pharmaceuticals that are used in day to day life and are found in almost all the stations which are mainly important tourist spots like Pathiramanal, Punnamada, Thanneermukkom etc. It was also detected from the locations like Kainakary, Pallathuruthy, Kuppapuram regions which are populated areas. The chromatograms showed high peaks of these compounds in the analysis from the samples taken from the sites that are more and more associated with human habitat showing impudent behavior of humans on water bodies.

Pharmaceuticals is a milestone in human scientific development as it have lengthened life spans, cured millions from deadly diseases, and improved the quality of life, but this very success has now led to their emergence as rapidly growing environmental contaminants. Pollution from pharmaceuticals in surface and ground waters is becoming recognized as an environmental concern in many countries leading to the area of study labeled “PIE” for “Pharmaceuticals in the Environment”. Pharmaceuticals are ubiquitous in the natural environment with concentrations expected to rise as human population increases. Pharmaceuticals are inherently biologically active and often exquisitely potent. They are also designed to be resistant to biodegradation because metabolic stability usually improves pharmacological action. This contributes to their environmental persistence. Environmental risk assessments are available for a small portion of pharmaceuticals in use, raising concerns over the potential risks posed by other drugs that have little or no data. With >1900 active pharmaceutical ingredients in use, it would be a major task to test all of the compounds with little or no data (Burns *et al*., 2018). Desk-based prioritization studies provide a potential solution by identifying those substances that are likely to pose the greatest risk to the environment and which, therefore, need to be considered a priority for further study.

Rivers worldwide are polluted with antibiotics that exceed environmental safety thresholds by upto 300 times (Alistair *et al*., 2018). These antibiotics in water lead to evolution of bacteria that are resistant to antibiotics, which then grow in numbers and spread in the environment. In some parts of the study area, it is observed that toilets are constructed in the backwater and the waste is directly driven in to the water bodies. This type of practices is one of the prime reasons for occurrence of antibiotics in water bodies that affects the health of aquatic organisms. Small scale industries and other livelihood earning activities like fish processing units, boat building yards, food processing units, slaughter houses, etc., are also noticed. The effluents released from such units include fish spoilage and residues, slaughter house wastes, waste oil, paints, metal and paint scrapings etc. Overuse and misuse of the drugs are thought to be the main causes of antimicrobial resistance. A new study done by researchers from the Banaras Hindu University (BHU) has found a large number of bacteria which are resistant to commonly used antibiotics in stretches of river Ganga (Aditi, 2019). An antibiotic residue leads to adverse effects in the environment, such as the development of resistant bacteria/resistance genes and may eventually become a threat to human health. In another study in India, antibiotic pollution and resistance and resistance genes were found in water of the Kshipra River during various seasons of a year (Diwan *et al*., 2018). River sediments are important antibiotic resistance reservoirs where various antibiotic resistant bacteria or resistance genes are concentrated. The occurrence and resistance to antibiotics in water and sediment in different seasons is mainly influenced by the physicochemical and environmental factors (pH, temperature, sorption, degradation etc.)

In Asia and Africa, the safety limits were most frequently exceeded and studies shows that the problem is global in scope. The situation could pose a danger to human health as infection with such kind of resistant bacteria could become untreatable. The World Health Organisation (WHO) has warned that the world is running out of antibiotics that still work, and has called on industries and governments to urgently develop a new generation of drugs. Studies are needed to examine the fate of antibiotic residues and to assess the risk of their effect on resistance in all environmental compartments, to set up regulatory standards by the authorities and to control the dissemination of these "pollutants" in the environment.

Vembanad-Kol wetlands are situated amongst an intensive development landscape. The wetland is located in one of the most populous coastal segments of the Malabar coastline, in the vicinity of one of the largest industrial belts of Kerala, includes the rice bowl of the state and is a center of backwater tourism. Degradation of Vembanad-Kol will reflect badly on ecological and economic security of the entire coastal zone of Kerala state. Even after numerous studies and report on the status of the backwater, there is still no development in the management policies. The present system for monitoring the wetland complex is highly fragmented and disjointed. A few agencies (for example, Department of Water Resources, Central Water Commission, Central Ground Water Board, State Pollution Control Board, Zoological Survey of India, NGOs as Kottayam Nature Society) collect information on specific parameters of interest. There is no system at present systematic collection of data on various wetland features and collating the same to support management. This severely limits the possibility of objectively defining the status and trends of various wetland features, and identification of related drivers and pressures.

5. SUMMARY AND CONCLUSION

Vembanad wetland ecosystem, the largest Ramsar site on the south west coast of India, is a massive and vibrant coastal wetland ecosystem of international importance with unique priceless ecosystem values. Vembanad estuary (backwater) is bordered by Kuttanad on south - the ‘rice bowl of Kerala’, situated 1.5 to 2 m below mean sea level, and Kol lands on north, which are interlinked by rivers, estuaries and mangrove marshes, well interconnected by a complex network of natural and manmade channels spreading over 1512.5 km^2. Regardless of their ecosystem services, it has been subjected to endless threats like eutrophication; land reclamation, and urbanization; distressing its ecosystem processes. Unrestricted human interventions like construction of Thanneermukkom barrage (TMB) and Thottappally spillway along with other anthropogenic impacts have created irrevocable consequences on the environmental entity of this Ramsar site, altering its production potential.

However over the past several years, the Vembanad estuary is passing through a phase of rapid ecological modifications mainly due to the unrestricted human interference for heterogeneous purpose. Alterations in natural hydrologic regime of Vembanad wetland started with the commissioning of TMB (regulator), across the backwater system in 1975, to prevent saline water intrusion, which structurally and functionally separated the Vembanad estuary into two different entities creating a permanently limnetic zone on south and a brackish to marine zone in north of TMB resulting in gross changes in physical, chemical and biological entity of the wetland system (Anon, 2001). Scientific information on the ecosystem based analysis of the environment on a comprehensive basis is severely lacking from the estuarine system after the commissioning of the barrage. Apart from this, intense tourism related activities and waste dumping, oil and other contaminants have seriously afflicted the estuary. So, the present study tried to understand the critical water and sediment quality of Vembanad backwater along with the nutrient loading and its various sources, heavy metal pollution and other contaminants.

According to the present study, Vembanad estuary showed drastic decrease in depth in most of the stations, this is supported by the study of Gopalan *et al*., 1983. Reclamation of estuarine areas for agriculture has led to drastic decline in water holding capacity from 2.4 km^3 to 0.6 km^3 during the last 50 years changes in depth of estuary at various locations (MSSRF, 2007). Apart from this, the rate has been increasing after the construction of TMB particularly its cofferdam situated in the middle of the estuary. The water temperature was generally lower during monsoon period (June & August) compared to pre-monsoon period (February & April) and showed an increasing trend, compared to previous years probably indicating the effects of higher intensities of solar radiation and climate change. Transparency values were found to be lower in the southern zone when compared to the northern zone of TMB. The main basin of the estuary get clogged with the water plants, *Eichhornia* sp., *Salvinia* sp. and other aquatic weeds during the pre-monsoon season that reduced the visibility of the water body. Salinity was noticed with a wide variation from 2 to 29.5 ppt progressively increasing towards station 1 (Aroor). The salinity pattern in the southern part of estuary showed a limnetic to oligohaline condition. The northern stations exhibited a limnetic to oligohaline during monsoon and mesohaline to polyhaline condition during the pre-monsoon season. The pH was slightly acidic to alkaline with maximum value in station 1. Alkalinity values showed a progressively increasing trend towards the northern high saline stations. Station 1 (Aroor) showed the highest alkalinity which is one of the closest region to Arabian Sea. The dissolved oxygen values were higher in the surface waters of the estuary. Houseboat tourism and related activities, sewage discharge and spread of invasive water plants play a crucial role in dissolved oxygen content of the southernmost stations of Vembanad estuary resulting low DO level in most of the southern stations. The BOD level showed increasing trend towards the southern zone, st. 13 (Kuttamangalam) recorded the highest value. Station 4 (Thanneermukkom south) and 6 (Punnamada) also showed higher BOD level during the study period. Houseboat tourism activities and waste water discharge from Alappuzha town leads to the increased BOD level in these southern stations. The phosphate concentration was higher in southern zone compared to the northern zone. Station 12 (C Block, Cherukayal) showed the highest concentration (95.73 µmol L^{-1}) for bottom water. The increased human induced sources such as partially treated and untreated sewage runoff mainly the fertilizers and other discharges from agriculture sites of Kuttanad trigger the phosphate load in Vembanad estuary. The silicate concentration showed a maximum value of 129.72 µmol L^{-1} at station 10 (Meenappally). Most of the southern stations were recorded higher silicate concentration, might be attributed to the large amount of silicate input from rivers such as Pamba, Manimala, Achankovil and Meenachil, which may retained over the years in the Vembanad estuarine system. Increased amount of waste water inputs from agricultural runoff and industrial activities might contribute a major share. In the present study, the increased concentration of ammonia in southernmost stations such as station 6 (Punnamada), 7 (Nehru trophy finishing point), 8 (Pangankuzhipadam) and 19 (Meenappally Vattakayal) have considerably been impacted by houseboat tourism activities. The untreated wastes from the houseboats are directly dumped into the water body. Similarly, the polluted Alappuzha canals with restricted flow, carrying waste water from the town directly enter the Punnamada region of Vembanad estuary which also enhances the ammonia-nitrogen in the estuary. The nitrite-nitrogen exhibit an increasing trend towards the northern zone of the estuary, especially in station 1 (Aroor), which is highly influenced by the discharges from Kochi metro city along with the effluent from shell fish industry, situated along the estuarine bank at Aroor and are often associated with the unsatisfactory microbial quality of water. During the present study, the nitrate concentration in northernmost region of Vembanad estuarine system was higher when compared to the southernmost region. Increased concentration of nitrate in the northernmost stations may be influenced by the seawater intrusion from Arabian Sea and also from urban discharges. The maximum concentration of sulphide was observed in station 6 (Punnamada). High concentrations of dissolved hydrogen sulphide were the characteristic feature of the water quality in retting zone. The lower values of GPP observed in the southern stations such as station 7, 9, 10, 11, 12 and 18 could be due to the increased organic load from houseboat (SafooraBeevi and Devadas, 2014) during the peak tourism period, which is negatively affecting the transparency of the estuary, leading to decreased phytoplankton production. Increased organic load and eutrophication in southern stations accounts for the greater respiration and which corroborates with the lowest NPP values in stations south of TMB.

In water, the average concentration of heavy metals in Vembanad backwater followed the trend Cd<Ni<Cu<Pb<Zn<Fe. Compared to other metals, iron showed high concentration in the water samples. Among the heavy metals, iron is an important transition element and is required for both plants and animals and act as a modulator of the impact of other substance. It plays an important role in aquatic systems. Iron usually enters from the dumped waste into the aquatic ecosystem. During the study period, zinc concentration in water samples in most of the southern stations showed higher values and maximum concentration was observed in station 5 (1400 µg L^{-1}). Similarly, lead concentration was also observed higher in station 5 (370 µg L^{-1}). Ni showed higher concentration in station 18 (9.56 µg L^{-1}) whereas copper was recorded highest in station 5 (130 µg L^{-1}). In sediment, the heavy metals concentration followed the trend Cd<Pb<Cu<Ni<Zn. During

the study period, Cd showed a high geo accumulation index (6.24) and contamination factor (9.36) values throughout the estuary. Similar to water, the sediment showed higher concentration of Zn when compared to other heavy metals. Station 15 recorded the highest Zn concentration (130.24 mg kg^{-1}). The pollution load index (PLI) values were very high during the present study, showing the extent of pollution in the backwater. The higher concentration of cadmium is the main reason for the increase in PLI. The main sources of cadmium pollution are usually the industrial and municipal wastes. Apart from this, Vembanad backwater has been continuously subjected to the land reclamation for various purposes such as agriculture expansion, agriculture practices, harbour development, urban development and other public and private uses and fertilizers are assumed to be one of the major sources of Cd. Fertilizers produced from phosphate ores constitute a major source of diffused cadmium pollution. In the case of lead, geo accumulation index and contamination factor were in a moderate range. Lead showed an increasing trend during the study period, which might have been contributed by anthropogenic effects such as improper handling of battery discharges, and waste incinerators. Most of the southern stations were highly polluted with copper during the study period. Increased mining activities, agriculture, metal and electrical manufacturing, sludge from publicly-owned treatment works (POTWs) were the major sources of copper. During the present study, station 15 (Marthandam) was heavily polluted with zinc and other southern stations were moderately polluted. Use of agro-chemicals such as fertilizers and pesticides, metaliferous mining activities, ore dressing and processing, sewage-sludge were the main sources of zinc. The nickel concentration was higher in most of the southern stations during the present study, while station 16 (Chithirakayal) was found to be extremely contaminated. Dumping of wastes, rusted boats festered along the canals of Alappuzha, municipal runoff and other developmental activities are the main contestant in anthropogenic enrichment of heavy metals in estuarine system. The present study indicates that, the southern part of the Vembanad backwater was facing serious heavy metal pollution. This observation is supported by the study of Harikumar *et al*., 2009.

From the study, it is observed that the concentration of metals Zn, Cu and non-essential metal Ni is very high. The Zn concentration showed high values in *Ambassis* sp. (136.14 mg kg^{-1}) and *Channa* sp. (121.18 mg kg^{-1}). In *Villorita* sp., also the concentration of Zn (99.51 mg kg^{-1}) was observed comparatively high and the *Macrognathus* sp. showed a high BCF value of 9.14. Concentration of Cu in organisms like *Villorita* sp. and *Penaeus* sp. was also found to be increasing during the study period. The nickel concentration was observed high in the *Etroplus maculatus* (44.5 mg kg^{-1}) and in *Penaeus indicus,* the bio concentration rate of Ni (91.05) was found very high. One of the adverse effects due to heavy metal pollution has been the marked decline in the clam fishery (*Villorita* sp.) of this estuary over the years. So, from this study, it is clear that, copper, zinc and nickel are getting accumulated and its concentration is high in most of the organisms taken into consideration. Compared to these metals, the concentration of cadmium and lead were below detectable limit. So, from these observations it can be concluded that the heavy metal pollution is becoming a major threat to the aquatic organisms in the Vembanad backwater.

In the present study, detectable pesticide residues were not been observed from the samples taken from the study area. But the presence of emerging pollutants such as benzyl benzoate, cyclic octaatomicsulphur, benzenepropanoic acid, cyclonasiloxane and cycloheptasiloxane were observed in most of the study locations of Vembanad backwater. These compounds are mainly used in pharmaceuticals, as preservative, fungicide, insecticide in the treatment of certain skin diseases, in cosmetic products such as perfumes, bath gels, detergent powders, liquid detergents, fabric softeners, soaps and also in skin care and cosmetic products. Compounds which are active pharmacologically, persistent in aqueous systems, resistant to degradation, exhibit harmful effects in organisms, and also having negative impact on human health were categorized into "Active Pharmaceutical Ingredients (API)". Scientific information about these emerging pollutants i.e., its sources and its effects on aquatic organisms is still lacking. In this context, a detailed study about this is more relevant.

The present study indicates that the estuary is being imposed with major geomorphic changes at several segments, resulting in reduction in the extent. According to the studies conducted by Dinesh Kumar *et al*. (2014) and Dipson (2012), the alterations in the geomorphic characteristic in the estuary occurred over the decades modifying estuarine flows, which ultimately affect the dynamic processes within the estuary. The overall study points out the human impact on the ecological health of the system which in turn depends on factors like estuarine flushing. The seasonal intermixing of fresh and saline water has seriously affected by the construction of TMB (1975) to prevent saline intrusion into to the paddy polders of Kuttanad and thereby interfering with the natural cleansing mechanisms of the estuary. Based on various studies and also on the present investigation it has been revealed that unscientific construction of TMB and its faulty operation especially during the tidal regimes as the main problem leading to various environmental and social issues in the wetland system. Drastic fluctuations in salinity decrease in depth and carrying capacity, and increased eutrophication reveals an over view of a degrading system. The increasing human influences in and around the aquatic systems and their catchment areas also contributed in decline of water quality and to their accelerated habitat loss to a large extent. Constant discharge of industrial discharges and sewage into backwater has led to water quality deterioration and blowout of freshwater invasive as water hyacinth. In spite of all hydrological interventions, rice production in Kuttanad has declined over the years, converting it from the ‘Rice bowl of Kerala’ to a land of distress. Due to its importance as being a Ramsar site, proper management and conservation of Vembanad estuarine system is become more relevant. Hence the implementation of better management solutions must be urgently developed in order to avoid the further destruction of the estuary. Therefore based on the study the following recommendations are put forth for proper management of Vembanad estuary:

1. The Vembanad wetland system, mainly represented by the backwater ecosystem is structurally and functionally two different entities, due to the Thanneermukkom barrage (TMB, 1975), that has permanently created a limnetic zone on the south and a brackish to marine zone on the northern side resulting in major eco biological alterations leading to major social issues in the wetland system.

2. The Vembanad estuarine system is one of the world largest aquatic ecosystems, undergoing severe threat due to various anthropogenic activities mainly from encroachment, land filling, dredging, construction activities, houseboat tourism, urbanization, sand mining, several polluting sources such as coir factory, and waste disposal from industries. So immediate attention is needed for restoration of the ecosystem and its biotic resources.

3. High geo accumulation index (Igeo) and contamination factor (CF) values were observed for Cd and Ni that shows the backwater is facing strong contamination from these two heavy metals. The Igeo values showed moderate to strong pollution from Pb and moderate pollution from Cu and Zn. The Pollution Load Index **(**PLI) was also

found high which clearly reveal that the study area is having polluted sediments. The rise in numerical PLI values suggests the progressive deterioration in sediment quality due to heavy metals. The qualitative analysis of the sediment based on Sediment Quality Guidelines (SQG) showed possible risk to aquatic life due to high Ni concentration. Hence, in the present study, an alarmingly high concentration of Zn, Cu, Pb, Ni and Cd has been observed in the sediments of Vembanad backwater, which could have serious health issues related to bio magnification. Therefore it is high time to implement bioremediation solutions to reduce the environment load, preferably at the site of generation.

4. It is evident from the study that the concentration of metals like Zn, Cu and Ni are showing an increasing trend in organisms. The high BCF values also prove that it is becoming a big problem as it may lead to toxic effects on humans through trophic transfer. Long-term intake of unsafe levels of heavy metals through foods may result in disruption of many biological and biochemical processes in humans. To avoid this severe conditions a water quality guideline should be established based on field data and eco toxicological experimental data on organisms of different trophic level.

5. In the present study, some compounds including benzyl benzoate (compounds which may be classified in to the group of “emerging pollutants”) were observed in almost all the stations which are important tourist spots that get exposed to more anthropogenic activities than other sites. Most of these compounds are persistent in environment and cause adverse impacts on human health and the environment. Hence, the environmental risk assessments are available for a small portion of pharmaceuticals in use, raising

concerns over the potential risks posed by other drugs that have little or no data. So, desk-based prioritization studies are necessary to provide a potential solution by identifying those substances that are likely to pose the greatest risk to the environment and which, therefore, need to be considered a priority for further study.

6. Damaged TMB and its erratic functioning have had a strong influence on the physico-chemical and biological entities in the ecosystem. Both the sectors of the water body were experiencing increasing agricultural operations (use of pesticides, weedicides) tourism (houseboat and pollution problems) interventions and waste disposal from fishing and allied activities (landing centre: Thanneermukkom) that created isolated stressed environments referred to as microhabitats.

7. The hydrology and regular flows from the rivers into the estuary has been seriously affected by the faulty operation of TMB, waste disposal, unplanned construction of roads, polders and other structures especially under the Kuttanad package that has led to seasonal flooding and biodiversity loss. So detailed studies on the hydrology of the backwater, salinity, inorganic nutrient regime in different sectors, river flows and patterns are to be undertaken before any future agrarian and fishery based reforms are further implemented. Online monitoring of the above factors at different strategic locations is to be strictly put forth.

8. The study has strongly established that ecological decay of the wetland is on the rise due to intense pollution problems and unauthorized construction activities from southern to northern regions of the backwater. Violation and relaxation of the Coastal regulation zone norms has been recorded in many regions. The

luxury resort-Mini Muthoot at Nediyanthuruthu Island, Perumbalam and many others are some of the cases in this regard. So strict enforcement of the CRZ norms for the backwaters have to be implemented. National Green Tribunal has to take cognisance of the violations in CRZ norms in the region.

9. Based on various studies and also the present investigation it has been detailed that unscientific construction of TMB and its faulty operation especially during the tidal regimes has been the main problem leading to various environmental and social issues in the wetland system. As part of the Kuttanad package, construction of new shutters has been initiated in the central region (filled with red laterite soil having road-coffer dam) of the TMB in September, 2014. With the opening of the coffer dam portion, the environmental and biotic changes are in the offing which is going to modify the ecological character of the wetland system. Future studies are to be conducted to understand its implications on the system.

10. Vembanad wetland was declared a Ramsar site on August 2002, but no serious actions have been implemented by both, Central and State Government to date to improve the overall ecology and wise use of the wetland. But, it has further degraded to a state of total destruction even with the additional support from the Kuttanad package for agrarian reforms. The reforms under the Ramsar and Kuttanad package needs to be strengthened. Having the unique backwaters and resources, the Vembanad and associated backwater system needs to be considered as UNESCO world Heritage site for conservation and sustainable utilization.

11. Since tourism activity is increasing in Vembanad wetland due to its international attraction, there is an urgent need to restrict various

pressures associated with this on the wetland and its resources especially the rampant increase in houseboats. A carrying capacity based model needs to be developed on the impact of tourism and related pressures in the wetland. Action for protecting Pathiramanal Island should be implemented. Special attention should be taken by Tourism Department for restricting nature tourism without involving any ecological modification of the islands and promote mangrove afforestation. Strengthening water bird habitat assessment and monitoring network through training, awareness and participation programmes is to be enforced.

12. Kuttanad region encompassing the Vembanad wetland lying about av. 2 m below mean sea level, supports indigenous farming technologies and species (fishery and agriculture) being propagated by local population that has been developed through indigenous knowledge. Such practices have been followed for decades and are being protected on a sustainable basis. In the present changing climatic regime, with impending gradual sea level rise and associated issues the farming techniques being implemented here would be useful for the overall benefit to the population. So more research and development oriented works should be evolved in Vembanad and used as a model in other parts of the country for coping (adaptive) with possible climate change issues in future.

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