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QUALITY ASSESSMENT OF WATER IN RIVERS OF CENTRAL KERALA (INDIA) WITH SPECIAL REFERENCE TO MERCURIC CONTAMINATION DURING MONSOON SEASON

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ABSTRACT

Rivers flowing through the central part of Kerala viz. River Periyar, River Muvattupuzha, River Chitrapuzha and River Kadambrayar were selected for the present study. Twelve sampling stations representing all the four rivers were analyzed during the monsoon seasons for two years (2018-2019)for temperature, pH, dissolved oxygen (DO) concentration, biochemical oxygen demand (BOD), chloride ion concentration (Cl) , total alkalinity (TA), acidity, total solids (TS), Carbon dioxide (CO2), phosphate ([PO4]3−) and total hardness (TH) using standard methods. For assessing the level of mercury contamination sampling was done from ten selected sampling sites; from surface water, river sediment and plant samples of riparian area, and analyzed using Direct Mercury Analyzer. Among the water quality parameters all the physico-chemical parameters were found within permissible limits of water quality standards suggested by different agencies. While the analytical results of the assessment of mercury contamination in water, sediments and plant tissues indicates that there is noticeably high mercury pollution load in rivers from industrial areas of Ernakulum especially Eloor - Edayar industrial area. It can be attributed that the water pollution in these rivers is due to anthropogenic interference especially industrial activities.

Keywords: *River Periyar, River Muvattupuzha, River Chitrapuzha and River Kadambrayar, Water Quality, Mercury pollution, BOD, DO.*

1. INTRODUCTION

Rivers are indispensable to society as they provide fresh water for human needs, agriculture, industry, irrigation and transportation (Singh et al., 2020; Yotova et al., 2021). Besides these rivers play a vital role in livestock production, forestry, hydropower generation, fisheries, tourism development and other creative activities. Urbanization around the world has exerted enormous pressure on river ecosystem and has polluted them with a myriad of pollutants including different types of emerging contaminants, industrial effluents and toxic heavy metals. Besides these pollutants quality of river water has been deteriorated due to factors such as increasing population, anthropogenic activities such as, industrialization, (Shil et al.,2019), geochemical factors, chemical composition of river basin (Giridharan et al., 2010), domestic wastewater and agricultural drainage water to the river, natural processes, agricultural runoff, soil erosion, land degradation etc. These factors drove the degradation of surface river water quality making it unsuitable for drinking, industry, agriculture and other purposes. However, the industrial effluents, domestic sewages and agricultural drainage water are the major sources of the river water pollution (Barakat et al., 2016). It makes the river water become inaccessible for day-to-day life.There are plenty of efforts taken for the assessment of water quality from river system, around the world(Mohamed et al., 2015) and several researchers have studied and reported the water quality and pollution status of various Indian rivers (Bhutiani et al.,2016).

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Besides rapid urbanization, fast growing population growth and industrialization leading to a major threat of heavy metal pollution in Indian rivers (Ahmad et al., 2010). These toxic heavy metals enter river systems from either natural or anthropogenic sources such as disposal of untreated and partially treated industrial effluents and toxic metals containing sewages, as well as metal chelates from different industries and heavy metal-containing fertilizers and pesticides from agricultural fields etc. (Reza and Singh, 2010). These toxic heavy metals are not readily degradable in nature and entering of these pollutants into the environment may lead to bioaccumulation and biomagnifications in the animal as well as human bodies. When accumulation happens beyond a certain limit, it may lead to undesirable results.

Among the heavy metals, Mercury (Hg) is one of the most studied highly toxic trace metal and which is naturally occurring in air, water, and soil (Li et al., 2009) Increased industrialization, associated with fossil fuel combustion, mining activities, industrial products and processes had drove Hg emissions in aquatic systems and also into the atmosphere (Driscoll et al., 2013).Mercury though less soluble in aqueous solution it is easily adsorbed on water-borne suspended particles. Finally, this water borne Hg accumulates and quantify. This may reflect the status of the pollution in the water body (Selvaraj et al., 2004). Like other heavy metals and many environmental contaminants, mercury undergoes bioaccumulation and biomagnifications. (Porcella et al., 2012).

Of the four rivers flowing through the central part of Kerala considered for the study, River Periyar is the largest perennial river which is known as the lifeline of Kerala. It is one of the main drinking water sources in several major towns in Idukky and Ernakulum district. It receives different leachates and different forms of municipal waste water from sewage system and many of these are directly discharged into the river and is experiencing deterioration by these pollutants. Twenty five percent of industries of Kerala are along the banks of River Periyar and the upstream of the river is relatively free of seawater intrusion and pollutants. (Sreelakshmi & Chinnamma 2018).

River Muvattupuzha a very calm river which is composed of three rivers - River Kothamangalam, River Thodupuzha and River Kaliyar. These three rivers are joined to form a single river and flow as River Muvattupuzha. This river receives large quantity of agricultural wastes and effluents from paper and pulp industries.

River Chitrapuzha one of the tributaries of River Periyar flows through Amabalamedu, Kochi. The river receives different types of effluents ranging from fertilizer, refinery and other industries. Fertilizers And Chemicals Travancore (FACT), Hindustan Organics Chemicals Limited (HOCL) and Kochi Refinery Limited (KRL) are the major industries housed at Ambalamedu Kochi area. The effluents from these industrial units along with agricultural and other anthropogenic wastes find their way into River Chitrapuzha which finally confluence into Cochin backwaters. (Deepa & Magudeswaran 2014)

River Kadambrayar is a tributary of the River Periyar is an eco-tourism destination, and prime hang out place, very close to Kochi city. News papers reported that about 90 percent of the open wells on the shores of River Kadambrayar and River Chitrapuzha, are contaminated with fecal matter.

In the present study, an attempt has been made to find out the water quality and pollution status in rivers of Central Kerala with special emphasis to Mercuric contamination during Monsoon Season for two years (2018-2019).

2. MATERIALS AND METHODS.

The four rivers; the River Periyar, River Muvattupuzha, River Chitrapuzha and River Kadambrayar located on the central part of the state Kerala with the details of the sampling sites are presented in figure 1.

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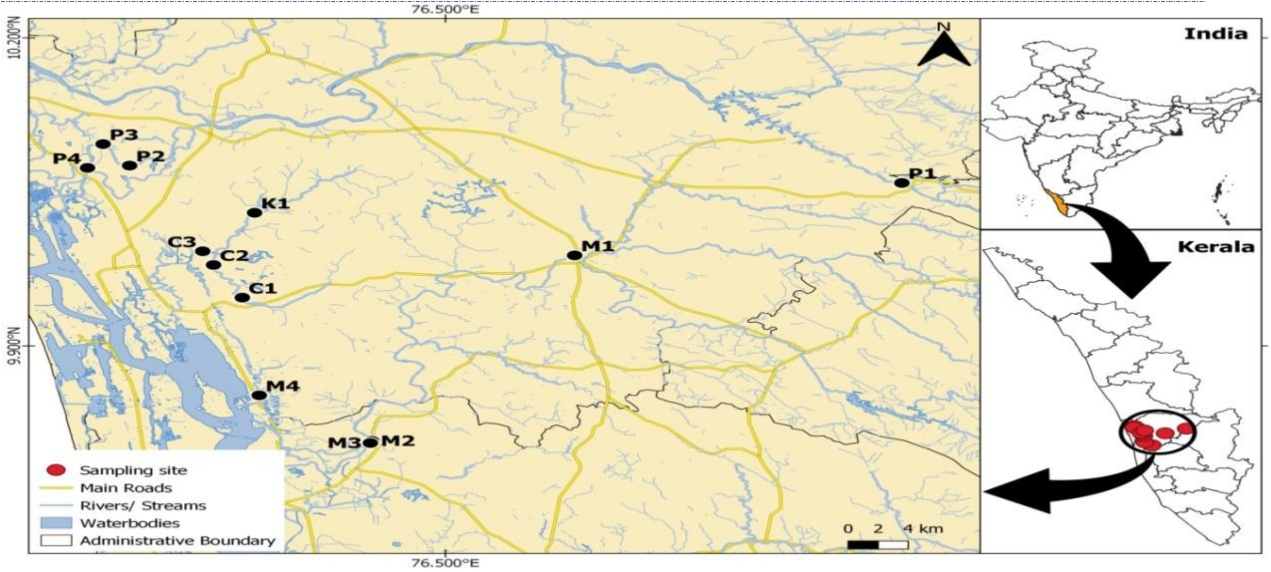

Fig. 1 Sampling site from the rivers studied River Periyar, River Muvattupuzha, River Chitrapuzha and River Kadambrayar in Kerala

Of the twelve sampling sites selected, four sites (P1 – P4) were in River Periyar. P1 was the upstream sampling site near Neryamangalam Bridge (latitude 10.058708°, 76.777255° longitude). Site P2 was at Eloor – Edayar industrial area which coordinates at latitude 10.075612° and longitude 76.308124°. P3 lies at latitude 10.096597° and longitude 76.292007°near Methanam ferry. Site P4was a downstream sampling site at Eloor ferry which lies between 10.073385°latitude and 76.282530° longitude.

In the River Muvattupuzha, also four sites (M1 – M4) were selected.M1was the upstream sampling site in River Muvattupuzha which is near Muvattupuzha town, immediately after the triveny sangamam (latitude 9.988134°, longitude76.578470°), Site M2 near the Hindusthan News Print factory, Velloor which coordinates at latitude 9.807451°and longitude 76.455283°and M3 lies at latitude 9.805363°and longitude 9.805363°at Vettikkattumuk Bridge while Site M4 was the downstream sampling site near Puthenkavu which lies between 9.851802°latitude and 76.386876°longitude.

Three sites were selected in River Chitrapuzha (C1 – C3) and one site in River Kadambrayar for water quality analysis. C1 was the upstream sampling site of River Chitrapuzha which is near Thiruvankulum (latitude 9.946992°, 76.376596° longitude) and Site C2 was near the Vettikkavu Bhagavathy temple which coordinates at latitude 9.978820°and longitude 76.359121° while C3 lies at latitude 9.992167°and longitude 76.352545°from Kakkanadu Boat Jetty.

Site K1 from River Kadambrayar was the only sampling site in the river which is near the Manakkakkadavu Bridge which lied between 10.029638° latitude and 76.384039° longitude.

The South West monsoon and the North East monsoon are the two rainy seasons experienced in Kerala. South west monsoon is obtained during June – August and North East monsoon from October to November. First sampling was carried out during the period of June – November 2018. Second sampling was done during June – November 2019.Water samples were collected in polypropylene bottles and kept refrigerated and were stored at 4°C. Sediment and plant samples for analyzing Hg were collected in polythene bags and were dried at 45^{0}c. The basic water quality parameters such as biological oxygen demand (BOD), dissolved oxygen (DO), CO2, acidity, alkalinity, total solids, hardness and various inorganic ions such as chloride, sulphate, and phosphate were analyzed in the laboratory while onsite measurement of pH and temperature was carried using standard methods. (APHA 1976 & Trivedi and Goel 1984). Mercury content in water, sediment and plant samples were determined by DMA (Direct Mercury Analyzer- DMA 80 model)

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3. RESULT AND DISCUSSION

Water quality assessment

The physicochemical characteristics studies are depicted in the table 1. pH (Potential of Hydrogen) is usually used for indicating the measure of the acidity or alkalinity of water. In the present study, the average pH values in River Periyar water was ranging from 6.8 to 8.3. PH was 8.3 in the upstream sampling site (P1), which was more alkaline in nature. The rest of the sampling sites showed slightly alkaline pH except for the site P3 (6.8) at the downstream. The pH levels in River Periyar showed similarity with values obtained in River Bounamoussa which varied between 6.94 and 8.02 as reported in the studies of Ramdani & Laifa 2017). Similar pH range are also reported in the studies of Magadumn et.al., 2017. In River Muvattupuzha, the PH was alkaline and it varied between 7.83 (M1) and 7.36 (M4), whereas River Chitrapuzha showed slightly acidic pH. The observed values showed that the pH in the River Kadambrayar is slightly alkaline (7.53).pH levels in River Muvattupuzha was almost similar to the values obtained in surface water of Mokeshbeel which varied between 7.3 and 7.77. (Jannat et. al 2019). Average value of pH in River Kadambrayar was 7.53.These values were within permissible limits prescribed by BIS standard. According to the World Health Organization (WHO, 1984) water samples with values of pH in between 7.0–8.5 can be used for industrial, agricultural and domestic purposes.

The sample temperature of all the study sites was determined on the site. Temperature is considered one of the most important abiotic factors in the riverine ecosystem. Measuring of temperature is inevitable for the understanding the biological, chemical and mineralogical processes that occur in a river. Temparature in River Periyar water was found ranging from 23.25 to 28^{0}C, while in River Muvattupuzha it was from 27 to 28.5. Average value of temperature in River Kadambrayar was 26^{0}C.While River Chirapuzha it was 29^{0}C in all sampling sites.

All the water samples showed zero phenolphthalein alkalinity and showed methyl orange alkalinity only. It can be inferred that the alkalinity of the samples is due to bicarbonate and not by carbonate and hydroxide ions.(Arasu2007).The values were within permissible limits prescribed by BIS standard (200 mg/).Afrin et al.,(2015) and Rahman et al.,(2021) reported that the TA values of the River Turag water and an urban river water ranged from 104.54 to 367.33 mg/L and 165 to 302 mg/L. In the present study value of TA from all four rivers were relatively low than in River Turag.

Acidity in water is caused by the presence of strong mineral acids, weak acids and hydrolyzing salts of strong acids. However, in natural unpolluted freshwaters, the acidity is mostly due to the presence of free CO_2 in the form of carbonic acid. An average value of acidity in River Periyar water ranged from 13.75 to 22.5mg/l, while in River Muvattupuzha it was from 11.66 to 34.58. Average value of acidity in Rriver Kadambrayar was 9. 37. This was the lowest value of acidity in all the sites studied. In River Chirapuzha the values were 11.25 to 18 mg/l. The highest value (34.58) observed was at M2 in the site of River Muvattupuzha.

In the present study the concentrations of free CO_2 in River Periyar water was found ranging from 5.68 to 7.7, while in River Muvattupuzha it ranged from 7.51 to 10.8. In River Chitrapuzha highest value observed was from the site C2 and least in C1. Among the water samples studied from various sites highest value was observed from the site C2 (14.96) and least in P1 (5.68).

TS (Total Solids) are determined as the residue left after evaporation of the unfiltered sample. The minimum and maximum amount of TS for the monsoon period was observed at Site P1 (152.08) and P4 (966.66).

The concentrations of chloride ion showed variation between11.36 and 37.21 mg/l in River Periyar, 14.80 to 62.243 in River Muvattupuzha and 18.10 to 41.45 in River Chitrapuzha. River Kadambrayar showed 27.92mg/l chloride ion concentration in its sampling sites. The prescribed minimum tolerance limit for chloride in drinking water is 200 mg/l (WHO, 1984) and it is 250 mg/l in BIS and ICMR standards. It produces salty taste at 250 mg/l to 500 mg/l (Trivedy 1988). These values were within permissible limits prescribed by WHO and within safe limits in BIS and ICMR standards. In all the sampling sites in the four rivers, the presence of chloride ions was found within the limit. It is an indication of degree of pollution where the river water can be found suitable for domestic and industrial purposes. Gangwar and coworkers reported similar result in river Ramganga.(Gangwar etal., 2013).

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In the present study the total hardness value ranged between 20.33 and 44.09 mg/l in River Periyar, 22.66 and 128.16 mg/l in River Muvattupuzha. While in River Chitrapuzha it ranged from 16.58 and 38.8 mg/l. River Kadambrayar showed 26.12 mg/l in its sampling site. The maximum limit of permissible total hardness for drinking water is 300mg/l (WHO, 1984).

Table 1: Value of different physico – chemical parameters in the monsoon period of 2018 – 19 in the selected sites of the for rivers studied

	River Periyar sites				River Muvattupuzha sites				River Chitrapuzha & River Kadambrayar sites			
	P1	**P2**	**P3**	**P4**	**M1**	**M2**	**M3**	**M4**	**C1**	**C2**	**C3**	**K1**
PH	8.3	7.45	6.8	7.43	7.83	7.22	7.58	7.36	6.82	6.81	6.53	7.53
Temperature	23.25	27.5	27.25	28	27	27.5	27	28.5	29.5	29.5	29.5	26
Alkalinity	30	47.5	73.33	46.66	40.83	131.25	40.83	41.66	42.5	55.33	51.33	60
Acidity	22.5	13.75	22.5	13.75	11.66	34.58	20	20.62	11.25	18	15.16	9.37
CO2	5.68	6.26	7.7	6.41	10.86	10.08	7.51	7.51	8.84	14.96	12.46	7.15
Ts	152.08	500	733.33	966.66	185.41	504	275	300	195.83	246.66	263.33	329.16
Chloride	11.36	36.14	37.21	29.64	14.08	62.24	22.12	51.17	18.10	41.41	38.52	27.92
Hardness	20.33	44.09	25.66	40.45	22.66	128.16	24.5	47.75	16.58	35.53	38.8	26.12
DO	9.65	8.46	8.59	8.21	8.38	5.54	6.43	5.25	4.78	4.41	4.28	3.73
BOD	2.11	4.502	4.775	4.56	3.22	4.19	2.09	2.83	2.84	2.11	1.89	1.85
phosphate	0.28	0.04	0.29	0.04	0.03	0.05	0.10	0.09	0.35	0.78	0.51	0.2

The hardness of the river water was found within the prescribed standard. Hence the river water can be used for drinking (in the absence of biological suitability test, suitable precautions needed) as well as irrigation purposes. Aktar et al., 2017) and Tahmina et al., 2018 have showed entirely different values from our studies at different points in the River Turag, indicating that the river water was not suitable for different household activities and drinking. Sawyer and McCarty (1967) classified the river water as soft (<75 mg/L), moderately hard (75 - 150 mg/L), hard (150 - 300 mg/L), and very hard (>300 mg/L). According to this classification criteria, the water in these studing rivers may be graded as soft water in rainy season except one site M2 (128.16).

Dissolved Oxygen (DO) has significance in sustainable life, metabolic and reproductive activities of the aquatic organism. Very low DO may have a negative impact on the sustainability of the riverine environment and habitat. In the present study, the DO was found ranging from 8.216 to 9.656mg/l in River Periyar, and in River Muvattupuzha lied between 5.255to 8.38 mg/l, while in River Chitrapuzha it was 4.285 to 4.785 mg/l. At all places, except River Chitrapuzha and sites M2 and M4, of River Muvattupuzha the water showed higher DO values and River Kadambrayar showed less DO value than the limit (4-6mg/l) prescribed by United States

Public Health Drinking Water Standard. The highest dissolved oxygen content 9.655 mg/l was recorded at site P1. For the requirements of drinking, the DO concentration ranges classified are 6 mg/L for drinking water, 4 - 5 mg/L for entertainment, 4 - 6 mg/L for fish and domesticated animals, and5 mg/L for industrial applications (WHO, 2017).In that perspective water from these rivers can be assumed to be of portable nature.

The biochemical oxygen demand (BOD) is a test for measuring the amount of biodegradable organic material present in a sample of water. The values of BOD recorded in River Periyar in the present study ranged from 2.11 mg/l for site P1to 4.77 mg/l for station P3 and it ranged from 2.09 to 4.19 mg/l in River Muvattupuzha and it ranged from1.89 to 2.84mg/l in River Chitrapuzha. In River Kadambrayar it was 1.88 mg/l. The higher values of BOD are indicative of the presence of organic pollutants in water. Ahmed et al., 2016) reported the highest BOD concentration of 31 mg/L at the Tongi Station in the River Turag, which is far higher value from our observation.

The presence of phosphates in natural water sources with concentrations above 0.2 mg/l indicated pollution by synthetic detergents, and also by runoff water. (Kumar et al., 2018)The monthly variation of phosphates recorded in the present study is marked by a maximum of 0.78925mg/l in site C3 and a minimum of 0.04 mg/l at site P4.The minimum phosphate value obtained in the present study is higher and maximum value is lower compared to those in the River Guebli which are between 0.01 and 1.10 mg/l.(Boudeffa et al., 2020). Phosphate is non-poisonous and safe to ingest at reasonable levels of concentration and thus poses no threat to aquatic lives and health of human beings (Arasu, 2007). While excess phosphates are considered as a nutrient that, along with nitrogen/nitrates, can cause excess algal growth and eutrofication of water bodies.
According to the WHO (World Health Organization), ISI (Indian Standard Institution) and ICMR (Indian Council of Medical Research) the permissible limits of Mercury in drinking water is 0.001mg/l. While, in USEPA (United States Environmental Protection Agency) standards it is 0.002mg/l. The CPCB (Central Pollution Control Board) standards, also has similar values as base line.

Mercury assessment
The assessment of mercury from water, sediment and plant samples were carried out and results obtained are given in the tale 2.

It can be assumed that the rivers carry fresh water during the monsoon time. During the rainy seasons, the values of Hg varied from 0.19 to 0.37 in various samples of River Periyar. Hg level varied from 0.0001 to 0.19 in River Muvattupuzha and 0.68 to 2.29 in River Chitrapuzha. The average values were below the permissible limit recommended by WHO (World Health Organization), ISI (Indian Standard Institution) and ICMR (Indian Council of Medical Research) except in site C1.

The maximum concentration of Hg during the monsoon period was observed at Site P2 (1407.33µg/Kg), and minimum at P1 (36.39µg/Kg). Mercury levels in Eloor - Edayar industrial area of River Periyar was very high (1407.33µg/Kg) compared to other sampling sites. Heavy metal contamination of soil and water causes abiotic stress in plant productivity, growth, yield and quality. (Jewell et al., 2010).At elevated concentrations; heavy metals produce severe toxicity/stress symptoms in plants. (DalCorso et al., 2013)Plants growing in heavy metal-contaminated area generally accumulate higher amounts of heavy metals, and which leads to contaminated food chain. (Singh et al., 2016).

Mercury is a persistent environmental pollutant and a cumulative toxin with bioaccumulation ability in fish, animals, and human beings (Chang etal., 2009). Generally, the terrestrial plants are insensitive to the mercury compounds. However, studies revealed that, mercury affects the photosynthesis and oxidative metabolism by interfering with electron transport in chloroplasts and mitochondria. Also known that it inhibits the activity of aquaporins and reduces plant water uptake (Sas-Nowosielskaetal., 2008). Hence the detection of accumulation and Hg concentration in plant samples from the riparian area of selected sampling sites are also relevant in this context.

Table 2: The amount of mercury recorded from water, sediment and plant samples analyzed during the study period

	River Periyar Sites			River Muvattupuzha Sites			River Chitrapuzha & River Kadambrayar Sites			
	P1	P2	P3	M1	M2	M4	C1	C2	C3	K1
Water (µg/L)	0.37	0.29	0.19	0.0001	0.19	0.0001	2.29	0.85	0.68	0.49
Sediment (µg/Kg)	36.38	1407.33	69.27	87.31	46.56	160	106.76	160	89.21	42.00
Plant (µg/Kg)	9.81	71.56	21.62	15.39	11.87	9.08	36.64	31.17	12.80	11.96

The results showed that the Hg concentration was observed to be the maximum during the monsoon season 71.56 µg/Kg at P2 and the minimum value 9.08µg/Kg at the site M4. Levels of mercury in plant tissue in River Periyar were varied from 9.81 to71.56 µg/Kg. While concentrations in the samples in River Muvattupuzha varied from 9.09 to 15.39 µg/Kg. Concentrations in the River Chitrapuzha varied from12.80 to36.6401 µg/Kg and River Kadambrayar shows 11.96 µg/Kg. In 2017 Li and coworkers reported Mercury pollution in Amarathaceae leaves from areas surrounding coal-fired power plants in China. Its maximum mercury concentration was less compared to our observation 46.40µg/Kg. (Li etal., 2017).

4. CONCLUSION

In this study, water quality status and mercury contamination were studied to evaluate the extent of water pollution in the River Periyar, River Muvattupuzha, River Chitrapuzha and River Kadambrayar during monsoon season. It was found that the water pollution was mainly caused by anthropogenic sources especially industrial activities. Among the water quality parameters and mercury contamination investigated, all the physico -chemical water quality parameters are within permissible limits of water quality standards. While assessment of mercury toxicity in water, sediments and plant tissues indicates that there is a evident mercury pollution in river water from industrial area of Ernakulum especially Eloor – Edayar industrial area. The results revealed that the overall pollution level in the all four rivers were beyond the safe limits in terms of the physic chemical properties of water. However, the physicochemical value in the rainy season of River kadambrayar water had undesirable values of DO (3.73mg/L), and River Periyar had TS (733.33 mg/L), (966.66 mg/L) for intended uses. Pollution levels were likely to change due to the seasonal variations. The study showed that the studied river water at industrial area was suffered from water pollution. This study concluded that proper management of domestic and industrial wastes is required to lower the accumulation of pollutants in the River Periyar, River Muvattupuzha, River Chitrapuzha and River Kadambrayar and to minimize environmental degradation.

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Conflict of interest

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

Life science reporting

No life science threat was practiced in this research

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