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# Distribution of Heavy Metals in the Surface Waters of Neyyar River, Kerala, India

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## Abstract

Heavy metal discharge from diverse anthropogenic sources and heavy metal pollution of the river environment are significant concerns. In the present study, the concentration of eight heavy metals was analyzed in the surface water samples from Neyyar river (Thiruvananthapuram, Kerala) using inductively coupled plasma mass spectrometry (ICP-MS) from June 2015 to May 2016. According to rainfall pattern, the study period has been portioned into three major seasons, namely monsoon season (from June 2015 to September 2015), post-monsoon season (from October 2016 to January 2016) and pre-monsoon season (from February 2016 to May 2016). The concentration of heavy metals recorded were in the order Fe>Zn>Mn>Cu>Cr>Pb>Ni>Cd. They were found to be accumulated in all the six sampling sites in the order S6>S5>S4>S3>S2>S1 for Cd, Cr, Fe, and Ni. The values of Mn, Zn, Pb and Cu have shown marginal removal from the surface water at high salinity conditions, even though substantial quantities of anthropogenic pollutants exist there. The mean concentration of heavy metals such as Cd, Cr, Cu, Fe and Ni during post-monsoon was comparatively higher than in the other seasons. The concentration of Zn, Pb and Mn were marginally higher during pre-monsoon than that in other seasons. Statistical interpretations of the values were made with the help of Two-way analysis of variance (ANOVA) and Pearson correlation matrices for each heavy metal between stations and seasons. The ANOVA showed a significant difference at a 5% level between stations in all heavy metals. The analytical data of all the metals other than Zn were above the desirable limit of BIS (Bureau of Indian Standards: 1050) specification for drinking water in nearly all seasons except at upstream stations. The spatial distribution maps of heavy metals in the river water were prepared by using GIS software (Arc GIS 10.4) to compare the values between monsoon, post-monsoon and pre-monsoon. The Pearson correlation matrix clearly indicated that the metal Fe has a very significant positive correlation with salinity. The escalated heavy metal contaminations at downstream of the river suggest a polluted environment. The results point out the need for rational planning of pollution control strategies to keep a check on the release of toxic heavy metals in the river.

**Keywords:** Neyyar, Heavy metal, Anova, Correlation

## 1. Introduction

The surface water contaminations increased over the past years due to various types of pollutants emerged by human activities. The contamination of heavy metals is in association with regions where industrial activities are intense. The term heavy metal is a common combined term that applies to a group of metalloids with an atomic density 4g/cm$^3$ greater than water (Duruibe et al., 2007). They are also known as trace elements because they occur in minute concentrations in biological systems. The natural input of metals in the river environment is essentially from the catchments as suspended particulate phase. Heavy metals can reach from industrial and domestic sources because rivers are considered the convenient means of pathways for the disposal of such wastes. Industrial waste and municipal solid waste have emerged as one of the leading causes of surface water pollution. Metals such as Cd, Cr, Cu, Ni, Pb and Zn also have toxicological importance in the river ecosystem (Jose and Takako, 2012). Numerous researchers have worked out heavy metal contamination in the freshwater ecosystems of the world. The heavy metal analysis of Euphrates River water in Iraq was made by Hassan (2010). The heavy metal contamination study in Yeongsan River in China was conducted by Kang et al. (2010). The heavy metal contamination study in Kwekwe river water in Zimbabwe was made by Chinhanga (2010). Heavy metal distributions in waters of Okemeshi River in Nigeria were analyzed by Ekeanyanwu et al. (2011), and Orogodo River in southern Nigeria was assessed by Chukwujindu et al. (2012). The heavy metal concentrations in the water of Dongjiang River in China were analyzed by Jiang et al. (2012). The heavy metal evaluation in Ona River water in Nigeria was made by Aina et al. (2012). Heavy metal assessment in surface water of North Alabama was conducted by Okweye (2013). The monitoring of heavy metals in Nile River water in Egypt was done by Abeer et al. (2014). In Indian rivers, one of the major issues causing damage to the water is heavy metal accumulation (Unni, 2002). Several investigators have worked out heavy metal contamination in the freshwater ecosystems of our country. The heavy metal concentration in river waters of Eastern Ghats was studied by Reza and Singh (2010). Sehgal et al. (2012) and Nupur (2014) conducted a heavy metal contamination study in Yamuna River water. The heavy metal contamination status of Indian rivers was assessed by CWC (2014). The analysis of toxic heavy metals in Narmada river water was made by Hussain et al. (2014). The evaluation of toxic metals in Cauvery river water was carried out by Bhuvaneshwari et al. (2016) and Abida et al. (2009). Heavy metal distribution in the waters of the entire Godavari river basin was studied by Jakir et al. (2017). Heavy metal distribution in Noyyal river water in

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Tamilnadu was analyzed by Babunath and John (2017). Assessment of heavy metal contamination in the River Ghaghara, a major tributary of the River Ganga in Northern India, was made by Singh et al. (2017a). Assessment of river water quality and ecological diversity through multivariate statistical techniques and earth observation dataset of rivers Ghaghara and Gandak was conducted by Singh et al. (2017b). Heavy metals pollution in the soil-water-vegetation continuum irrigated with groundwater and untreated sewage were studied by Bharose et al. (2013), and the development of a fuzzy analytic hierarchy process based water quality model of the Upper Ganga river basin was made by Singh et al. (2021).

In Kerala, heavy metal pollution in freshwater resources is a serious problem because safe drinking water is decreasing at an alarming rate. Numerous scientists and researchers have studied heavy metal contamination in the rivers of Kerala. The heavy metal dynamics of Chithrapuzha river water was studied by Joseph (2002). Maya (2005) studied heavy metal contamination in Periyar and Chalakkudy river waters. The heavy metal pollution in the waters of Aruvikkara and Peppara reservoirs were studied by Arun (2007). The metal composition of two small catchment river waters in the southwest region of Kerala was analyzed by Maya et al. (2007). The heavy metal contamination in Bharathapuzha river water was studied by Nikhil and Azeez (2009). The trace metal contamination in Meenachil river water at Kottayam was monitored by Indu et al. (2011). The seasonal distribution of heavy metals in Periyar and Muvattupuzha river waters were analyzed by Anju et al. (2011). In the present study area (Neyyar river), water pollution is one of the major concerns. The intensity of water pollution is increasing in recent times due to indiscriminate land-use practices and the emergence of industrial and chemical pollution sources around the river. So the chances of heavy metal contamination are so high. These metals are partitioned amongst their various components in the water body, i.e., water, sediment, and biota. The heavy metals in water produce toxic effects when they go beyond safe levels. Identifying and quantifying heavy metals primarily in Neyyar river water is necessary to plan management strategies to keep the river water clean and protect the river from severe degradation. Only a few studies are available on the heavy metal contamination in Neyyar river water. Heavy metal contamination in Neyyar river water above safe levels was analyzed by Krishnakumar (2002). The heavy metal distribution in the surface waters of Neyyar River at Poovar was studied by Arunkumar (2007). The trace metal analysis in Neyyar river water was conducted by Ancy Mol et al. (2016). The heavy metal contamination in the surface waters of Neyyar River was analyzed by Badusha and Santhosh (2019a). Therefore, there is an urgent need for continuous monitoring of heavy metal contamination in river water so as to safeguard public health threats from using this water. This paper analyzes the heavy metal contamination in Neyyar river water, Kerala, India.

## 2. Materials and Methods

Neyyar is the southernmost and small catchment river of Kerala State with a total basin area of 462.26 $Km^2$ between 77º0'0'' to 77º20'0''-E longitude and 08º15'0'' to 8º40'0''-N latitude. This small river originates from Agasthya malai (Agasthyakoodam) in the Western Ghats Mountain ranges. It flows through extremely mottled geologic and physiographic provinces of the area for a length of about 56 Km. Neyyar is a unique system with various geomorphological features and flowing through highly undulating terrain. Six sampling stations such as Neyyar Dam (Station-1), Kallikkadu (Station-2), Mandapathinkadavu (Station-3), Aruvippuram (Station-4), Neyyattinkara (Station-5) and Poovar (Station-6) are depicted in Fig.1. These sites were selected on the basis of physiographic conditions as well as the ecological condition of the zone. The Neyyar Dam (S1) and Kallikadu (S2) are situated at the highland physiographic area with less anthropogenic activities, whereas Mandapathinkadavu (S3), Aruvippuram (S4) and Neyyattinkara (S5) are physiographically mid-land in position and located in a polluted environment. The Poovar (S6), physiographically lowland in position, is with severe pollution activities. The sampling site at Poovar is located in the lowland physiographic area. Poovar is located near the Coast of Lakshadweep Sea, where the river water is stagnant. All the pollutants from the upstream are concentrated in this region. The pollutants that emerged from various sources, including vehicle service stations, hospitals and boat painting areas, were observed during our field visits. Wastewater drainages are very common in this region. The site is located just above the Poovar estuary. Saltwater intrusion is common in this region. The major land use around this area is coconut plantation with mixed tree crops. Built-up areas are mainly concentrated in the lowland, especially at Poovar. The intensity of paddy reclamation was huge in this region. The majority of paddy fields and wetlands are reclaimed in the Neyyar river basin and are reclaimed in lowland physiographic areas, especially at Poovar. The sand mining activities were comparatively more in this region. The reclaimed area near the main course of the river has become waterlogged and marshy.

Water samples for heavy metal analysis were collected monthly from June 2015 to May 2016 in plastic bottles previously soaked and washed with 10% $HNO_3$ and double-distilled water. The collected samples were immediately acidified with 2 mL ultra-pure nitric acid to adjust the pH to 2. Normally 2 mL of $HNO_3$ is required per litre of sample. The samples thus preserved were stored at 4ºC in sampling kits and brought to the lab for metal analysis. In the lab, heavy metals such as Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in water samples were analyzed using an inductively coupled plasma-mass spectrometry system (ICP-MS; Thermo Scientific ICAPQc). The external calibration solutions were prepared from standard certified multi-element solutions (MERCK). The ion optics was tuned using Thermo scientific Tune-B-ICAPQ solution. Mass and detector calibration was conducted using

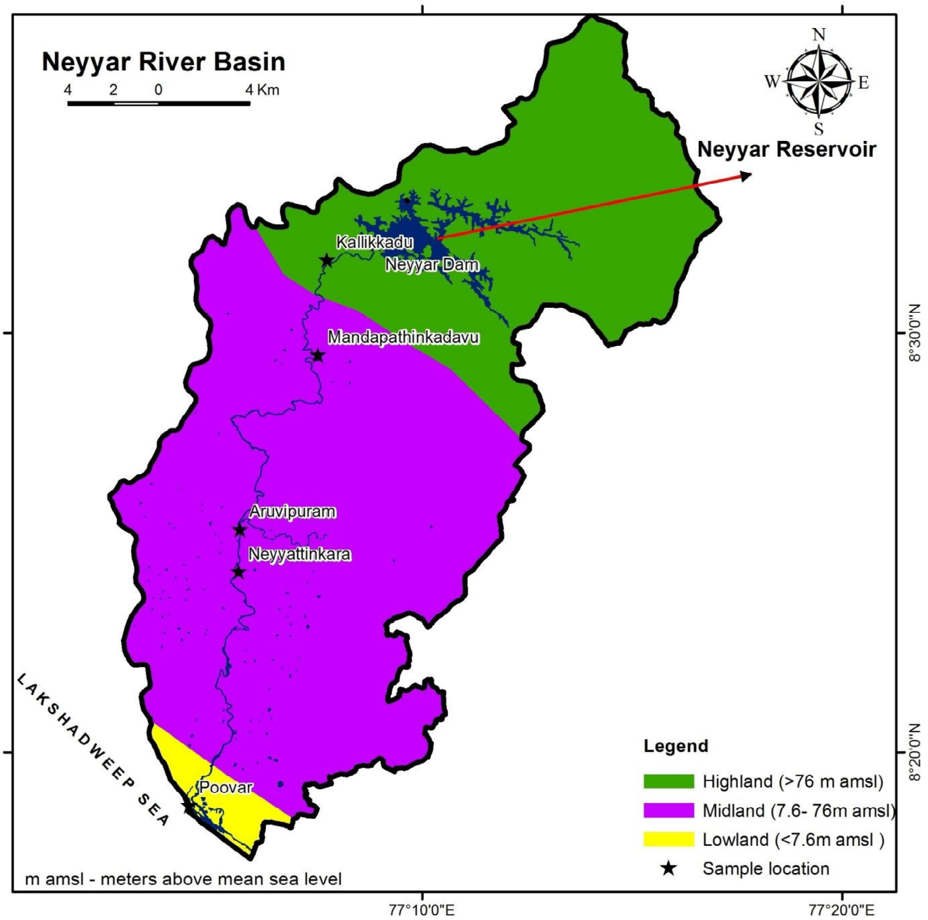


**Fig. 1.** Location map of Neyyar river basin, Kerala, India

Thermo scientific Setup Solution ICAPQ. All the analysis was carried out by using standard methods suggested by ASTM (2010) and APHA (2012).

**Operating Conditions:** Plasma RF forward Power = 1550 W, Sample uptake = 30 s, Cool flow read back = 14.00 L/min, Nebulizer flow = 0.97 L/min, Auxiliary flow read back = 0.80 L/min, Integration time = 10 s, Peristaltic pump speed = 40 rpm, Sampler & Skimmer Cones = Ni, Analysis mode = eQuant.

Two-way analysis of variance (ANOVA) for each heavy metal between stations and seasons was analyzed using SPSS 16 software and Pearson correlation coefficients between various heavy metals of different stations and seasons. The mean and standard deviation of the different heavy metals for the three seasons were also worked out. The spatial distribution maps of heavy metals in water were prepared by using GIS software version Arc GIS 10.4.

## 3. Results and Discussion

Heavy metals are of considerable environmental and health significance because of their increasing mobilization and toxicity to many life forms. The monthly variation of Cd at six different sampling stations of the study area is illustrated in Fig. 2. The ranges of Cd during monsoon, post-monsoon and pre-monsoon seasons are 0.005 ppm at S1 to 0.033 ppm at S6, 0.007 ppm at S1 to 0.040 ppm at S6 and 0.005 ppm at S1 to 0.033 ppm at S6 respectively. The spatial distribution maps of Cd in three seasons were shown in Fig. 3. Two-way ANOVA showed a significant difference in Cd between stations and between seasons (Table 1). The annual averages of all heavy metals in water from the present study area were compared with drinking water quality standards of WHO (2008) and BIS (2012) and USEPA (2000) (Table 2). Cadmium is a highly toxic heavy metal routinely detected in most surface waters, both in the dissolved and particulate phases (Nriagu and Pacyna, 1988).

In the present study, the analytical data of cadmium in all the stations were above the prescribed limits of BIS (2012) and WHO (2008) (0.003 ppm) in three seasons. According to USEPA (2000), maximum contamination (0.005 ppm), the Neyyar dam (S1) was within the limit during monsoon and pre-monsoon. The possible sources of contamination of cadmium might be due to runoff from agricultural soil. The entire study area is covered by agricultural land where rock phosphate is used as phosphorous fertilizers in which cadmium is a common impurity, as supported by Stoeppler (1991). The increase in cadmium concentration in lowland areas of Neyyar river water invariably showed the anthropogenic sources of cadmium emissions to the river. The seasonal influence was considerable in the distribution of Cd in the present study. The higher concentration of Cd in the post-monsoon season might be due to the addition of Cd rich impurities from the diverse pollution sources of the entire river basin to the overlying waters through the heavy rainwater. In the present study, the post-monsoon period is with maximum rainfall (974 mm), followed by monsoon (693 mm) and pre-monsoon (595 mm) (Source: IMG, Thiruvananthapuram). The higher

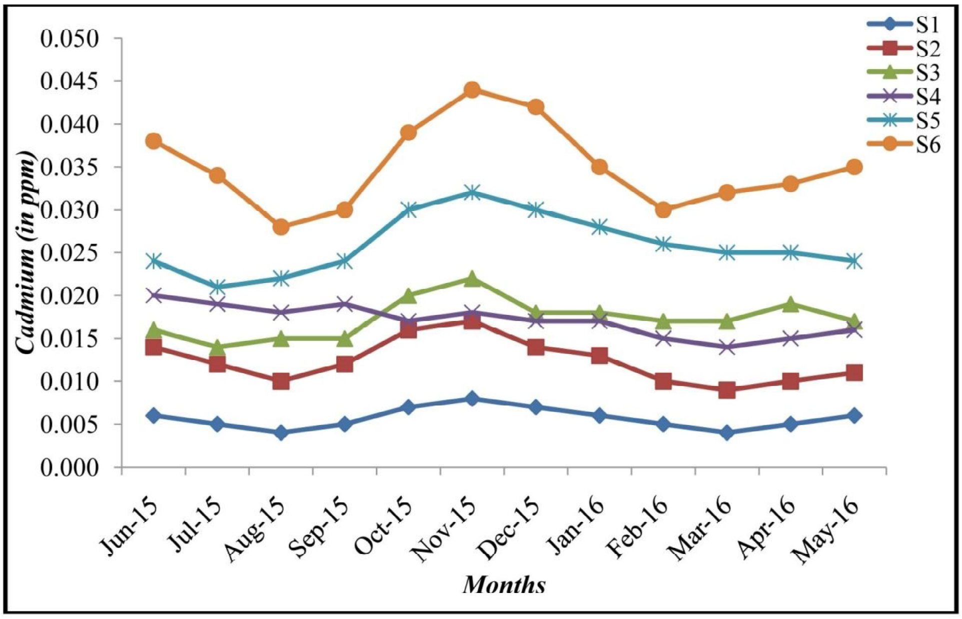


**Fig. 2.** Monthly variation of cadmium (in ppm) in the water from different stations of Neyyar river

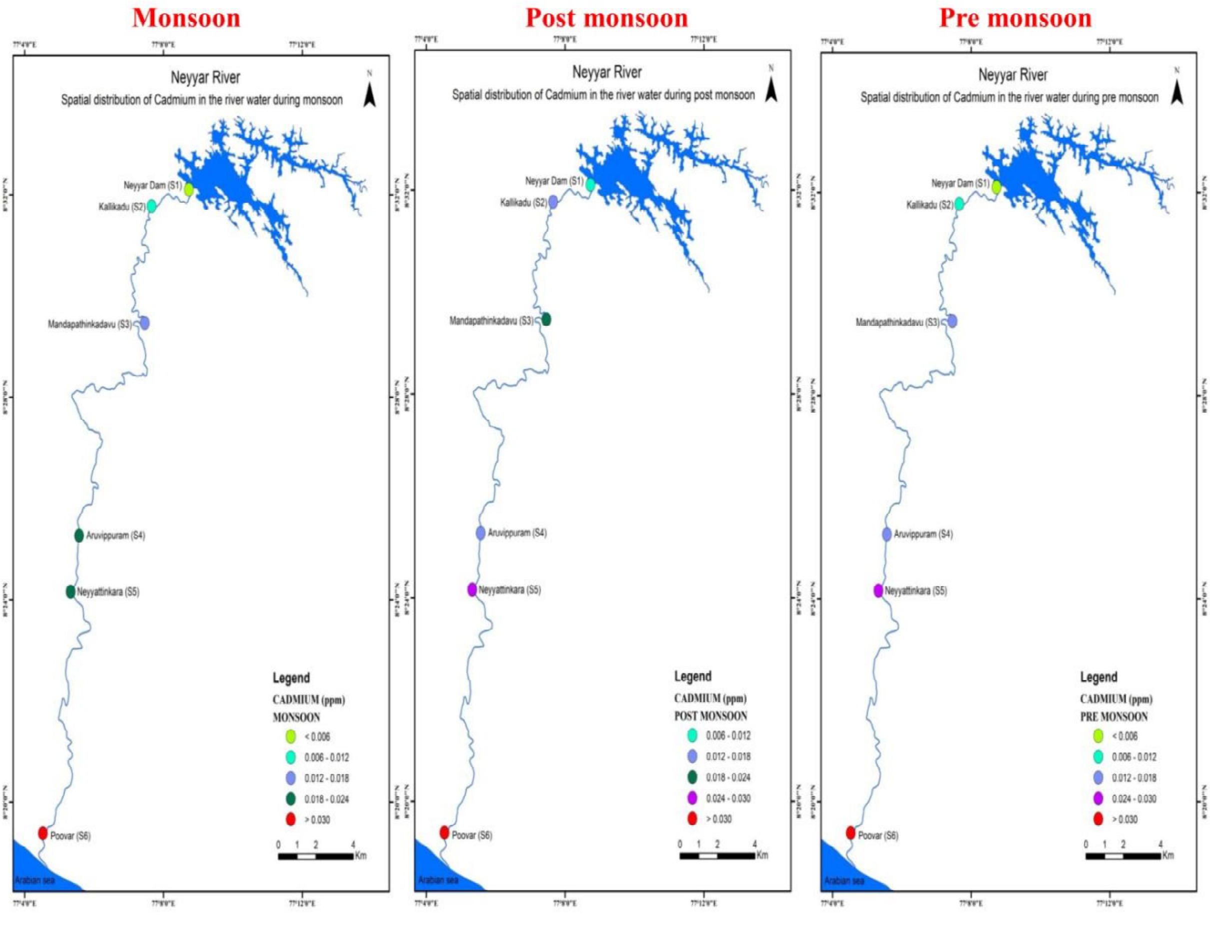


**Fig. 3.** Spatial distribution of Cd in Neyyar river water during three seasons

**Table 1.** Two-way analysis of variance (ANOVA) of heavy metals in water between stations and seasons

| Metals | Comparison | F | P-value | F-crit |
|---|---|---|---|---|
| Cd (ppm) | Between sites | 81.84 | 8.79E-08 | 3.33 |
| | Between seasons | 7.63 | 0.00973 | 4.1 |
| Cr (ppm) | Between sites | 27.07 | 1.70E-05 | 3.33 |
| | Between seasons | 1.51 | 0.26737 | 4.1 |
| Cu (ppm) | Between sites | 28.98 | 1.20E-05 | 3.33 |
| | Between seasons | 0.6 | 0.56896 | 4.1 |
| Fe (ppm) | Between sites | 65.69 | 2.50E-07 | 3.33 |
| | Between seasons | 3.72 | 0.06184 | 4.1 |
| Mn (ppm) | Between sites | 5.81 | 0.00901 | 3.33 |
| | Between seasons | 3.27 | 0.08093 | 4.1 |
| Ni (ppm) | Between sites | 21.99 | 4.20E-05 | 3.33 |
| | Between seasons | 2.04 | 0.18122 | 4.1 |
| Pb (ppm) | Between sites | 5.4 | 0.01154 | 3.33 |
| | Between seasons | 0.08 | 0.92237 | 4.1 |
| Zn (ppm) | Between sites | 7.72 | 0.00326 | 3.33 |
| | Between seasons | 2.55 | 0.12738 | 4.1 |

concentration of Cd in the post-monsoon season agrees with the observations of Stoeppler (1991).

The monthly variation of Cr at six different sampling stations of the study area is illustrated in Fig.4. The chromium ranges during monsoon, post-monsoon, and pre-monsoon seasons are 0.051 ppm at S1 to 0.150 ppm at S6, 0.063 ppm at S1 to 0.170 ppm at S6 and 0.040 ppm at S1 to 0.152 ppm at S5, respectively. The spatial distribution maps of Cr in three seasons were shown in Fig.5. Two-way ANOVA showed a significant difference in Cr between stations and no significant difference in Cr between seasons (Table 1). In the present study, the analytical data of chromium in all the stations were above the prescribed limits of BIS (2012) and WHO (2008) (0.05 ppm) in three seasons except at the reservoir station (S1) during pre-monsoon. But according to USEPA (2000) maximum contamination (0.1 ppm), the Neyyar dam (S1) and Kallikadu (S2) stations were within the prescribed limit during three seasons. The primary sources of chromium include domestic waste water from both central and non-central sources, manufacturing processes involving metals and the dumping of sewage sludge. Similar observations were made by Abeer et al. (2014). The sources of chromium are mainly observed in the midland and lowland areas. The seasonal influence was less in the distribution of chromium in the Neyyar River. The near estuarine region at Poovar (S6) is noted for the marginal decrease in the concentration of chromium during pre-monsoon, which might be due to the removal from surface waters at elevated salinity conditions.

The monthly variation of Cu at six different sampling stations of the study area is illustrated in Fig. 6. The ranges of copper during monsoon, post-monsoon and pre-monsoon seasons are 0.070 ppm at S1 to 0.140 ppm at S5, 0.070 ppm at S1 to 0.130 ppm at S5 & S6 and 0.060 ppm at S1 to 0.140 ppm at S5, respectively. The spatial distribution maps of Cu in three seasons were shown in Fig.7. Two-way ANOVA showed a significant difference in Cu between stations and no significant difference between seasons (Table 1). The analytical data of Cu content showed that all the stations recorded higher values than the BIS (2012) desirable limit (0.05 ppm). But according to WHO (2008) guideline (2 ppm) and USEPA (2000) maximum contamination (1 ppm), all the samples were within the prescribed limit. The sources of copper include leaching from copper water pipes and tubing, industrial and mining waste, wood preservatives and natural deposits. Copper compounds are used as insecticides and algicides. The seasonal influence was less in the distribution of Cu in the Neyyar River. During the monsoon season, the Cu values were slightly increased in Neyyar river water. The near estuarine zone of Neyyar River (S6) ha as shown a marginal decrease in the content of Cu.

The monthly variation of Fe at six different sampling stations of the study area is illustrated in Fig. 8. The ranges of Fe during monsoon, post-monsoon and pre-monsoon seasons are 0.301 ppm at S1 to 0.681 ppm at S6, 0.240 ppm at S1 to 0.720 ppm at S6 and 0.351 ppm at S1 to 0.654 ppm at S6, respectively. The spatial distribution maps of Fe in three seasons were shown in Fig.9. Two-way ANOVA a showed significant difference in Fe between stations and no significant difference between seasons (Table 1). Iron has little direct toxicological significance; it often controls the concentration of other elements, including toxic heavy metals, in surface waters (Reimann et al., 2003). In the present study, the analytical data of Fe in all the stations were above the prescribed limits of BIS (2012), WHO (2008) and USEPA (2000) (0.3 ppm)

**Table 2.** The comparison of heavy metals in water from the present study area with national and international drinking water quality standards

| Metals | Annual average | | | | | | WHO guideline (in ppm) | BIS desirable limit (IS10500) (in ppm) | USEPA maximum contamination (in ppm) |
|---|---|---|---|---|---|---|---|---|---|
| | S1 | S2 | S3 | S4 | S5 | S6 | | | |
| Cd (ppm) | 0.006 | 0.012 | 0.017 | 0.017 | 0.026 | 0.035 | 0.003 | 0.003 | 0.005 |
| Cr (ppm) | 0.051 | 0.076 | 0.12 | 0.11 | 0.142 | 0.148 | 0.05 | 0.05 | 0.1 |
| Cu (ppm) | 0.067 | 0.087 | 0.111 | 0.103 | 0.137 | 0.12 | 2 | 0.05 | 1 |
| Fe (ppm) | 0.297 | 0.384 | 0.483 | 0.53 | 0.605 | 0.685 | 0.3 | 0.3 | 0.3 |
| Mn (ppm) | 0.102 | 0.117 | 0.127 | 0.113 | 0.131 | 0.1 | 0.1-0.5 | 0.1 | 0.1 |
| Ni (ppm) | 0.023 | 0.04 | 0.06 | 0.053 | 0.09 | 0.104 | 0.02 | 0.02 | 0.1 |
| Pb (ppm) | 0.063 | 0.07 | 0.083 | 0.07 | 0.093 | 0.077 | 0.01 | 0.01 | 0.015 |
| Zn (ppm) | 0.117 | 0.142 | 0.165 | 0.17 | 0.195 | 0.162 | 3 | 5 | 5 |
| Reference | - | - | - | - | - | - | WHO (2008) | BIS (2012) | USEPA (2000) |

**Table 3.** Pearson correlation matrix showing correlation coefficients between the various heavy metals in monsoon season

| MON | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Cl | Sal | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 1 | | | | | | | | | | |
| Cr | .952** | 1 | | | | | | | | | |
| Cu | 0.802 | .934** | 1 | | | | | | | | |
| Fe | .980** | .985** | .890* | 1 | | | | | | | |
| Mn | 0.198 | 0.436 | 0.678 | 0.329 | 1 | | | | | | |
| Ni | .988** | .946** | 0.78 | .956** | 0.182 | 1 | | | | | |
| Pb | 0.564 | 0.751 | 0.787 | 0.674 | 0.431 | 0.593 | 1 | | | | |
| Zn | .813* | .887* | .945** | .888* | 0.636 | 0.749 | 0.578 | 1 | | | |
| Cl | 0.773 | 0.594 | 0.274 | 0.652 | -0.38 | .812* | 0.236 | 0.264 | 1 | | |
| Sal | 0.774 | 0.595 | 0.275 | 0.653 | -0.379 | .812* | 0.237 | 0.265 | 1.000** | 1 | |
| pH | .893* | 0.734 | 0.454 | 0.799 | -0.187 | .899* | 0.286 | 0.494 | .961** | .961** | 1 |

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

**Table 4.** Pearson correlation matrix showing correlation coefficients between the various heavy metals in post monsoon season

| POM | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Cl | Sal | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 1 | | | | | | | | | | |
| Cr | .944** | 1 | | | | | | | | | |
| Cu | .943** | .935** | 1 | | | | | | | | |
| Fe | .969** | .982** | .954** | 1 | | | | | | | |
| Mn | 0.494 | 0.53 | 0.644 | 0.504 | 1 | | | | | | |
| Ni | .997** | .949** | .940** | .978** | 0.446 | 1 | | | | | |
| Pb | 0.726 | 0.79 | .884* | 0.795 | .871* | 0.712 | 1 | | | | |
| Zn | 0.773 | .816* | .889* | .870* | 0.633 | 0.786 | .920** | 1 | | | |
| Cl | 0.776 | 0.714 | 0.565 | 0.723 | -0.116 | 0.797 | 0.165 | 0.331 | 1 | | |
| Sal | 0.778 | 0.716 | 0.567 | 0.725 | -0.113 | 0.798 | 0.168 | 0.334 | 1.000** | 1 | |
| pH | .894* | .884* | 0.738 | .866* | 0.191 | .902* | 0.432 | 0.512 | .944** | .945** | 1 |

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

**Table 5.** Pearson correlation matrix showing correlation coefficients between the various heavy metals in pre monsoon season

| PRM | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Cl | Sal | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 1 | | | | | | | | | | |
| Cr | .817* | 1 | | | | | | | | | |
| Cu | 0.741 | .982** | 1 | | | | | | | | |
| Fe | .935** | .900* | .820* | 1 | | | | | | | |
| Mn | -0.205 | 0.349 | 0.49 | -0.048 | 1 | | | | | | |
| Ni | .900* | .940** | .911* | .910* | 0.2 | 1 | | | | | |
| Pb | 0.366 | 0.68 | 0.796 | 0.348 | 0.758 | 0.644 | 1 | | | | |
| Zn | 0.434 | .859* | .902* | 0.59 | 0.75 | 0.756 | .814* | 1 | | | |
| Cl | 0.742 | 0.233 | 0.115 | 0.537 | -0.778 | 0.4 | -0.198 | -0.27 | 1 | | |
| Sal | 0.743 | 0.235 | 0.117 | 0.539 | -0.777 | 0.402 | -0.197 | -0.268 | 1.000** | 1 | |
| pH | .932** | 0.573 | 0.47 | 0.806 | -0.526 | 0.683 | 0.073 | 0.086 | .925** | .926** | 1 |

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level

in three seasons except at Neyyar dam (S1) during post-monsoon. The sources of Fe include leaching of cast iron pipes in water distribution systems, and iron sulphate is also used as fertilizer and herbicide. The Neyyar reservoir station (S1) was seen with less pollution sources. The seasonal influence was marginal in the distribution of Fe in Neyyar River. The Poovar region (S6) is noted for the increase in the concentration of iron, which clearly indicated the estuarine influence.

The monthly variation of Mn at six different sampling stations of the study area is illustrated in Fig.10. The ranges of manganese during monsoon, post-monsoon and pre-monsoon seasons are 0.092 ppm at S1 to 0.121 ppm at S5, 0.110 ppm at S1 to 0.132 ppm at S5 and 0.080 ppm at S6 to 0.140 ppm at S5, respectively. The spatial distribution maps of Mn in three seasons were shown in Fig.11. Two-way ANOVA showed a significant difference in Mn between stations and no significant difference between seasons (Table 1). In natural waters, manganese is rarely present in excess of 1 ppm and in surface waters occur in its quadrivalent state and trivalent state in a relatively stable and soluble complex (APHA, 1998). In the present study, the analytical data of manganese content showed that all the stations recorded higher values than the prescribed limits of BIS (2012) and USEPA (2000) (0.1 ppm) except at Poovar (S6) during pre-monsoon and at Neyyar dam (S1) during monsoon. According to WHO (2008) guideline (0.1-0.5 ppm), all the samples were within the limit. The sources of Mn include landfills, deposits in rocks and soil. The seasonal influence was less in the distribution of manganese in the Neyyar River. The estuarine region is noted for the decrease in the concentration of manganese. This is in agreement with Krishnakumar (2002).

The monthly variation of Ni at six different sampling stations of the study area is illustrated in Fig.12. The ranges of nickel during monsoon, post-monsoon and pre-monsoon seasons are 0.020 ppm at S1 to 0.102 ppm at S6, 0.030 ppm at S1 to 0.120 ppm at S6 and 0.020 ppm at S1 to 0.110 ppm at S5, respectively. The spatial distribution maps of Ni in three seasons were shown in Fig.13. Two-way ANOVA showed a significant difference in Ni between stations and no significant difference between seasons (Table 1). In the present study, the analytical data of Ni in all the stations were above the prescribed limits of BIS (2012) and WHO (2008) (0.02 ppm) in three seasons except at Neyyar dam (S1) during pre-monsoon and monsoon. According to USEPA (2000), maximum contamination (0.1 ppm), the Poovar station (S6) was above the limit during monsoon and post-monsoon and the Neyyattinkara station (S5) was above the limit in pre-monsoon. The sources of Ni include fertilizers, steel works, metal plating and coinage, fuel combustion and detergents, as supported by Reimann and de Caritat (1998). In the present study, an increase in the concentration of Ni was observed in downstream stretches of Neyyar. The Poovar region (S6) is noted for the marginal decrease in the concentration of Ni during pre-monsoon. The seasonal influence was less in the distribution of Ni in Neyyar River.

The monthly variation of Pb at six different sampling stations of the study area is illustrated in Fig.14. The ranges of lead during monsoon, post-monsoon and pre-monsoon seasons are 0.060 ppm at S2 to 0.090 ppm at S5, 0.060 ppm at S1 to 0.090 ppm at S5 and 0.060 ppm at S1 & S4 to 0.100 ppm at S5, respectively. The spatial distribution maps of Pb in three seasons were shown in Fig.15. Two-way ANOVA showed a significant difference in Pb between stations and no significant difference between seasons (Table 1). A major source of lead pollution in the environment is due to exhausts from vehicles (Veerabhadraswamy and Lokesh, 1993). In the present study, the analytical data of lead in all the stations were above the prescribed limits of BIS (2012) & WHO (2008) (0.01 ppm) and USEPA (2000) (0.015 ppm) in three seasons. The pollutants from vehicles and vehicle service stations were present at all stations with varying degrees during the study. The estuarine region has shown lower lead values than the upper and middle reaches of the Neyyar River. Lead exhibits only a marginal variation spatially and temporally in Neyyar River.

The monthly variation of Zn at six different sampling stations of the study area is illustrated in Fig.16. The ranges of Zn during monsoon, post-monsoon and pre-monsoon seasons are 0.100 ppm at S1 to 0.180 ppm at S5, 0.136 ppm at S1 to 0.195 ppm at S5 and 0.115 ppm at S1 to 0.210 ppm at S5, respectively. The spatial distribution maps of Zn in three seasons were shown in Fig.17. Two-way ANOVA showed a significant difference in Zn between stations and no significant difference between seasons (Table 1). Zinc is an essential micronutrient required in trace amounts for body growth (APHA, 2012). There are several major sources including the discharge of domestic waste water, manufacturing processes involving metals and atmospheric fallouts. Zinc most commonly enters the domestic water supply from deterioration of galvanized iron and zincification of brass (APHA, 1998). In the present study, the analytical data of zinc content showed that all the stations recorded lower values than the prescribed limits of BIS (2012), USEPA (2000) (5 ppm) and WHO (2008) (3 ppm) in three seasons. The near estuarine region at Poovar (S6) is noted for a marginal decrease in zinc concentration. The seasonal influence was less in the distribution of Zn in Neyyar River. Pearson correlation matrix was computed between the different heavy metals in the river water during three seasons. The correlation coefficients between the various heavy metals in water during monsoon, post-monsoon and pre-monsoon are shown in Table 3, Table 4 and Table 5, respectively. Correlation coefficient analysis of the heavy metals demonstrates the type and degree of relationship among them. The heavy metals showed fluctuations spatially and temporally. So, the correlation clearly between parameters within the six sampling stations and three seasons. The spatial correlation analysis shows that anomalous behaviour is present in the correlation pattern of all heavy metals at S1, S2 and S4. But S3 and S5 have shown a similar correlation pattern. The direct discharge of pollutants from the waste canal was noticeable from S3 and S5 throughout the study period. The constant positive correlation of heavy metals at S6 was indicative of the intensity of various pollutants that emerged from multiple sources. The negative correlation of all heavy metals with chloride, salinity and pH might be due to the peculiar estuarine property of the sampling station at Poovar (S6). The constant seasonal positive correlation of heavy metals in the study area indicated that the metals were dissolved in the river water irrespective of the seasons. Though the negative correlation between Mn-Cl, Mn-Sal, Mn-pH, Pb-Cl, Pb-Sal, Zn-Cl and Zn-Sal were less significant during the pre-monsoon season, the marginal decrease in the concentration of these metals might be due to their inability to dissolve at elevated salinity conditions. This phenomenon is more prevalent spatially at Poovar (S6).

## 4. Conclusion

In the Neyyar river, although heavy metals like Mn, Zn, Pb and Cu exhibits minor removal from overlying waters at high salinity conditions (at S6), the metal Fe exhibits an increase towards high saline zone (at S6). This might be due to the addition of iron-rich finer particulates from the mining centres to the overlying waters and the geochemical peculiarities of this element under natural waters. The higher concentration of metals in the lower stretches of Neyyar River clearly indicates the substantial quantities of anthropogenic pollutants exist there. In addition, this region also receives toxic contaminants from various sources.

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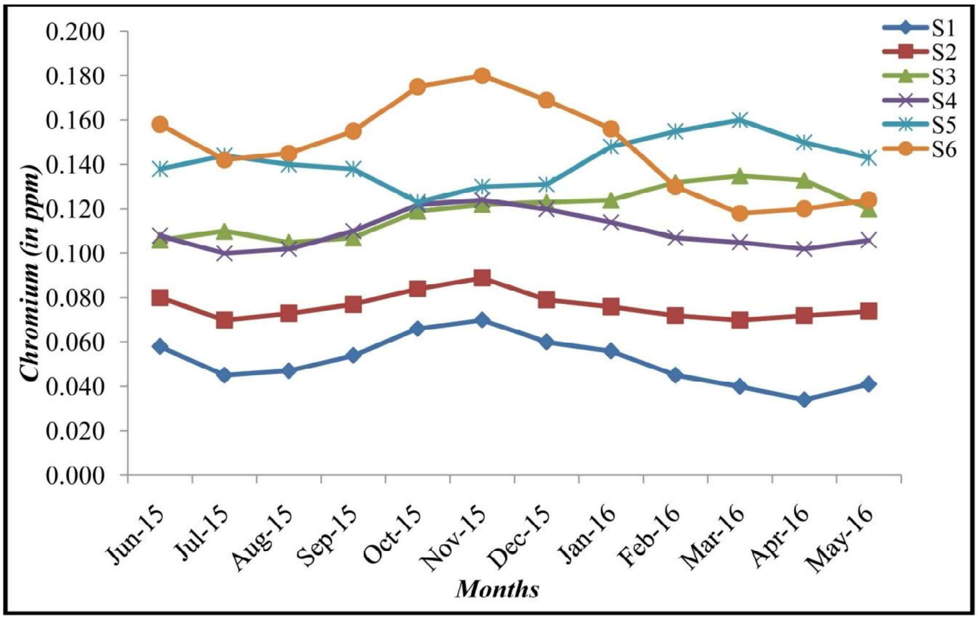


**Fig. 4.** Monthly variation of chromium (in ppm) in the water from different stations of Neyyar river

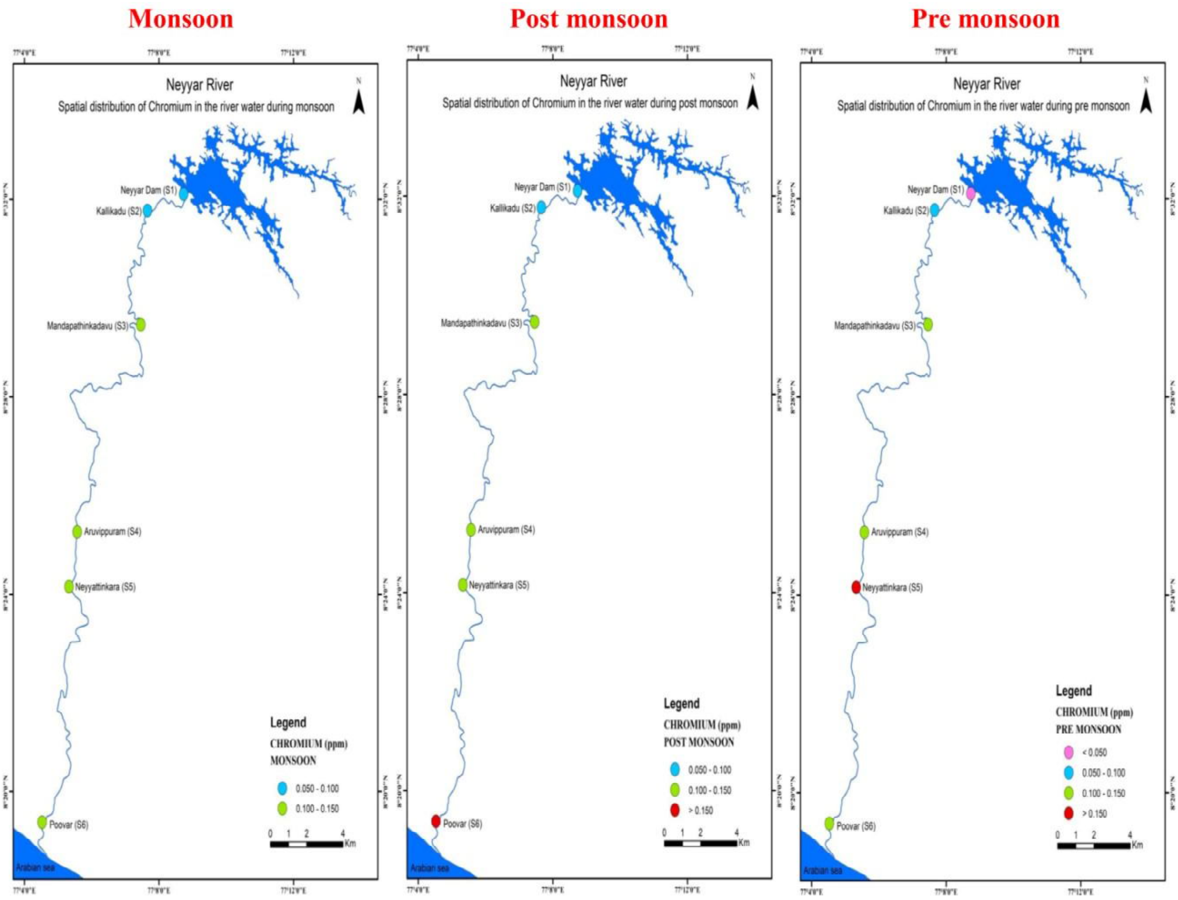


**Fig. 5.** Spatial distribution of Cr in Neyyar river water during three seasons

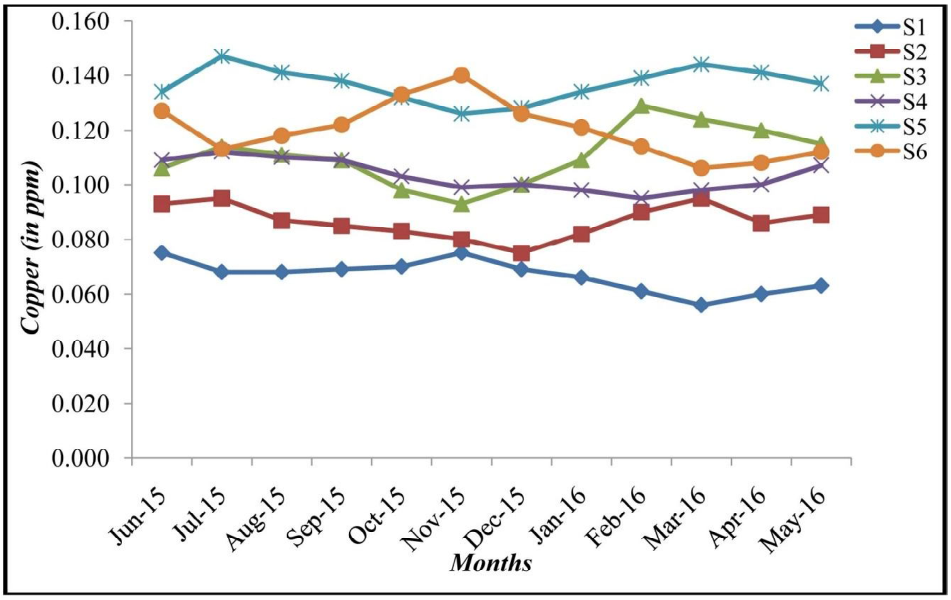


**Fig. 6.** Monthly variation of copper (in ppm) in the water from different stations of Neyyar river

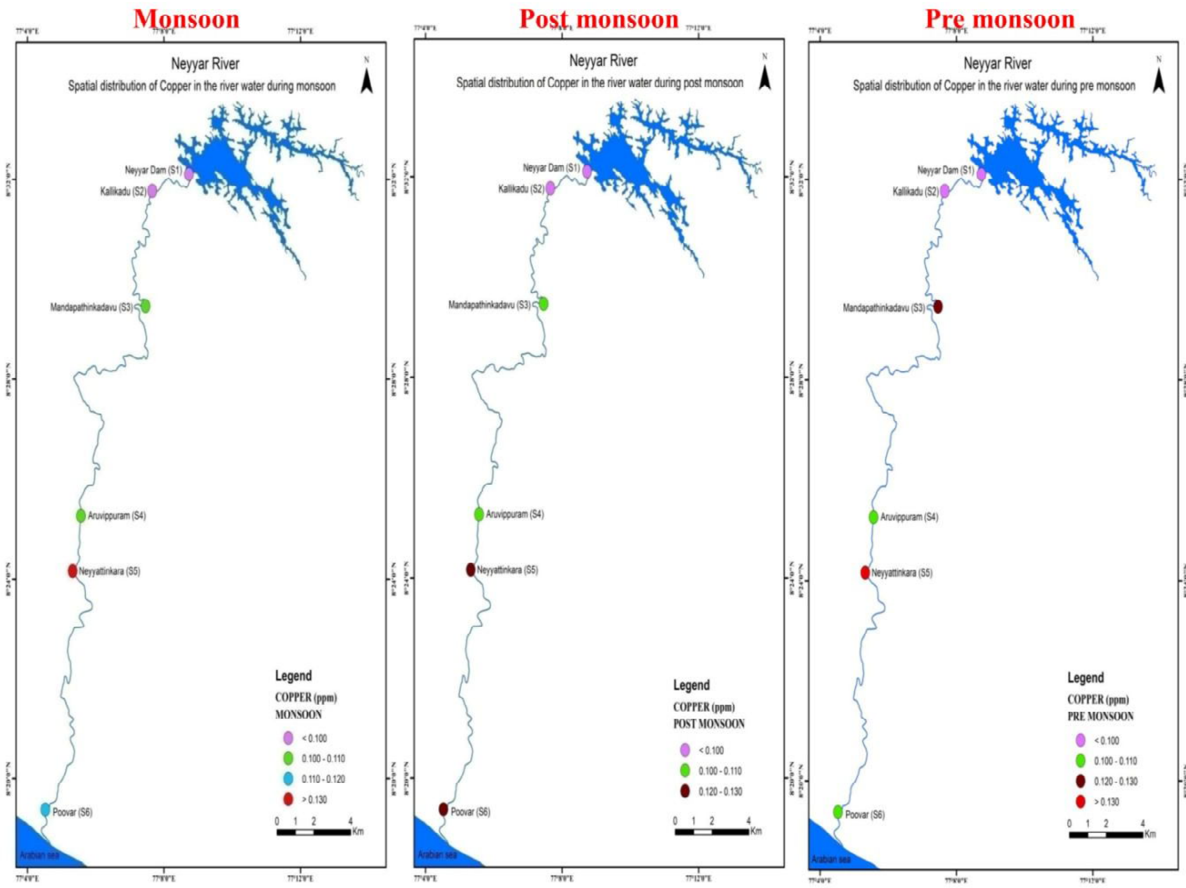


**Fig. 7.** Spatial distribution of Cu in Neyyar river water during three seasons

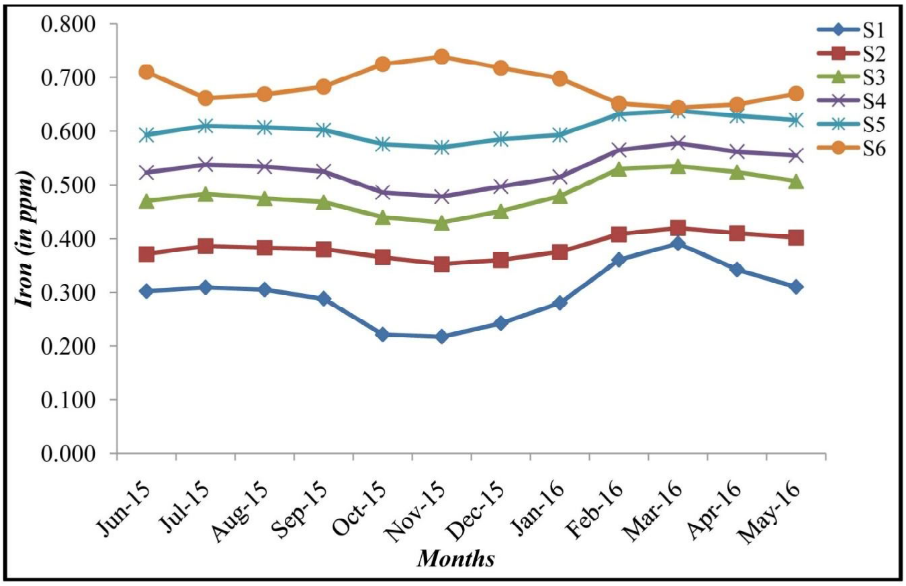


**Fig. 8.** Monthly variation of Iron (in ppm) in the water from different stations of Neyyar river

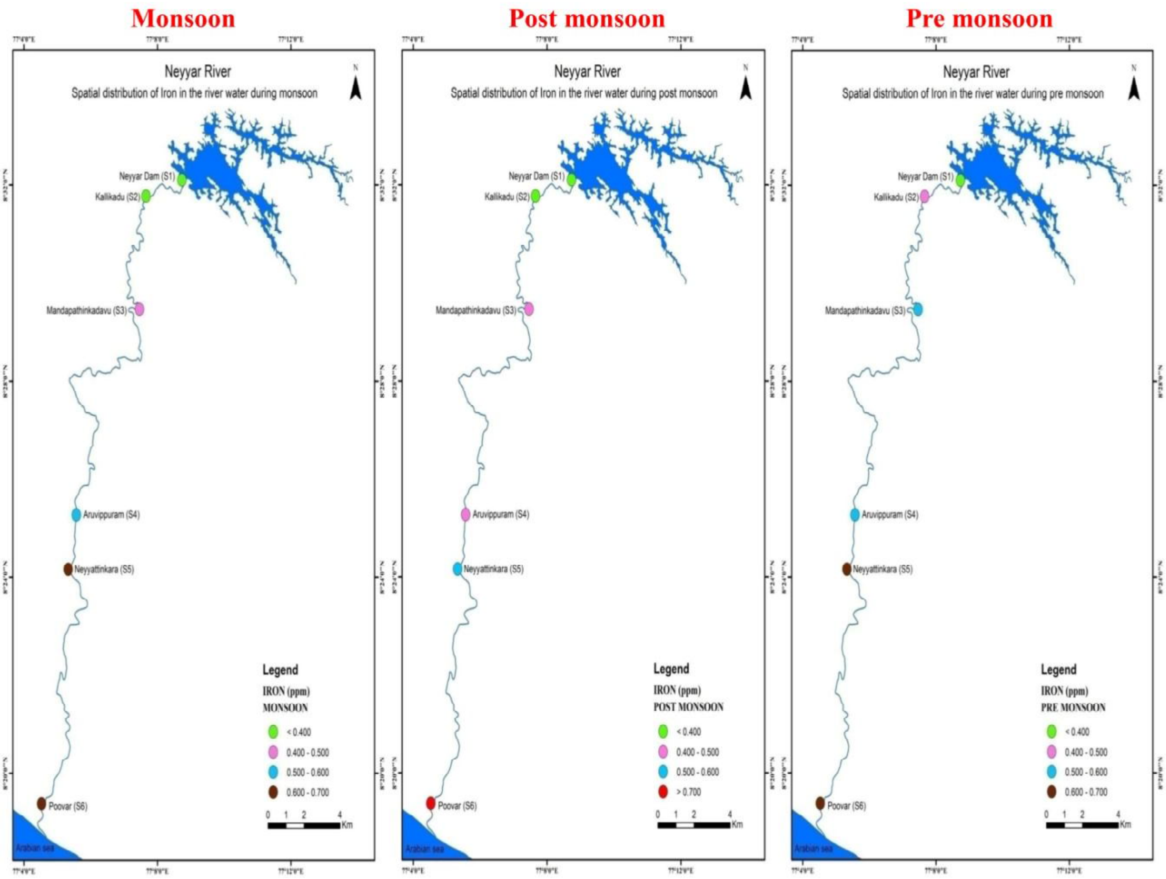


**Fig. 9.** Spatial distribution of Fe in Neyyar river water during three seasons

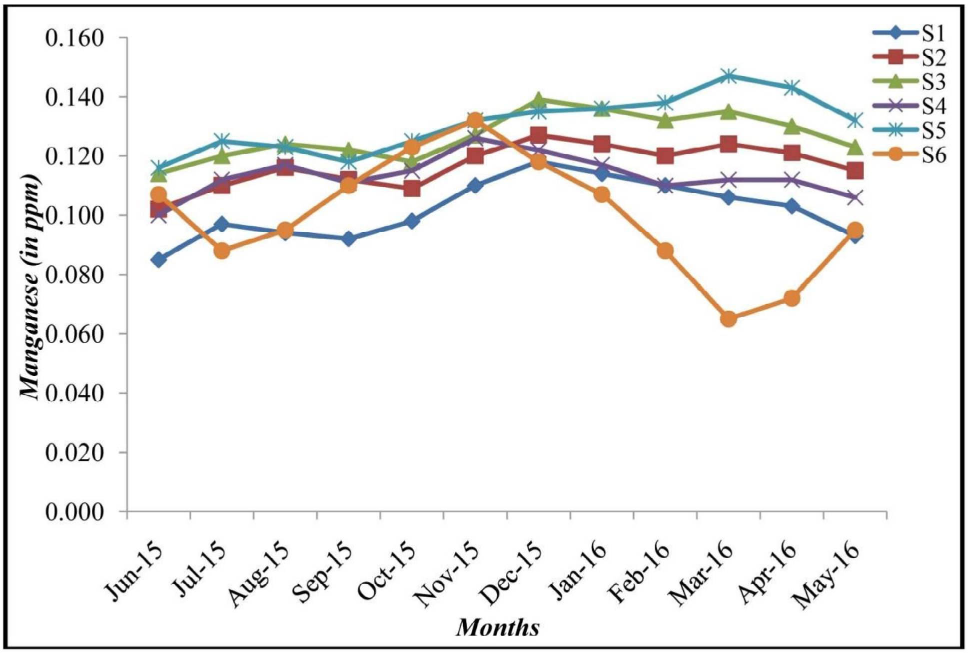


**Fig. 10.** Monthly variation of manganese (in ppm) in the water from different stations of Neyyar river

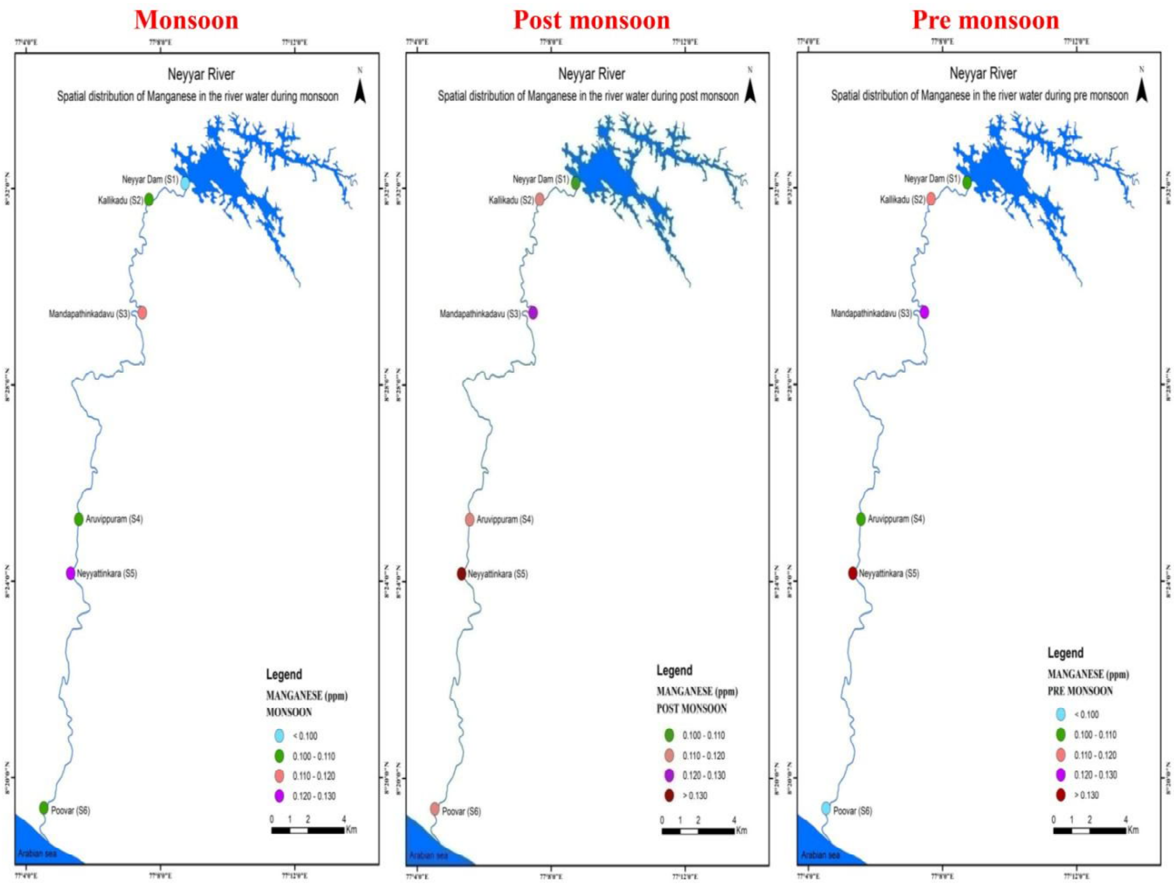


**Fig. 11.** Spatial distribution of Mn in Neyyar river water during three seasons

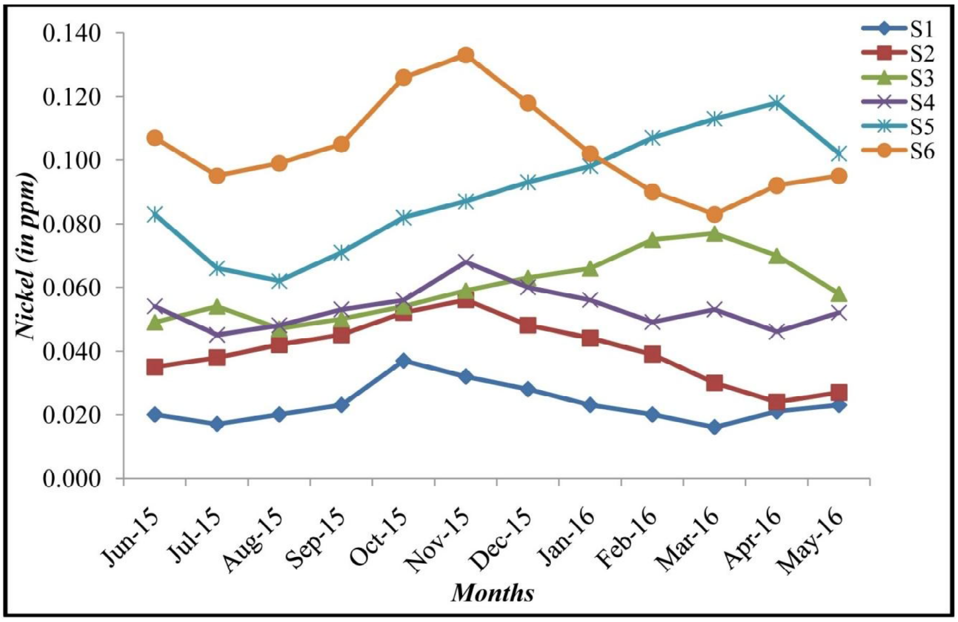


**Fig. 12.** Monthly variation of nickel (in ppm) in the water from different stations of Neyyar river

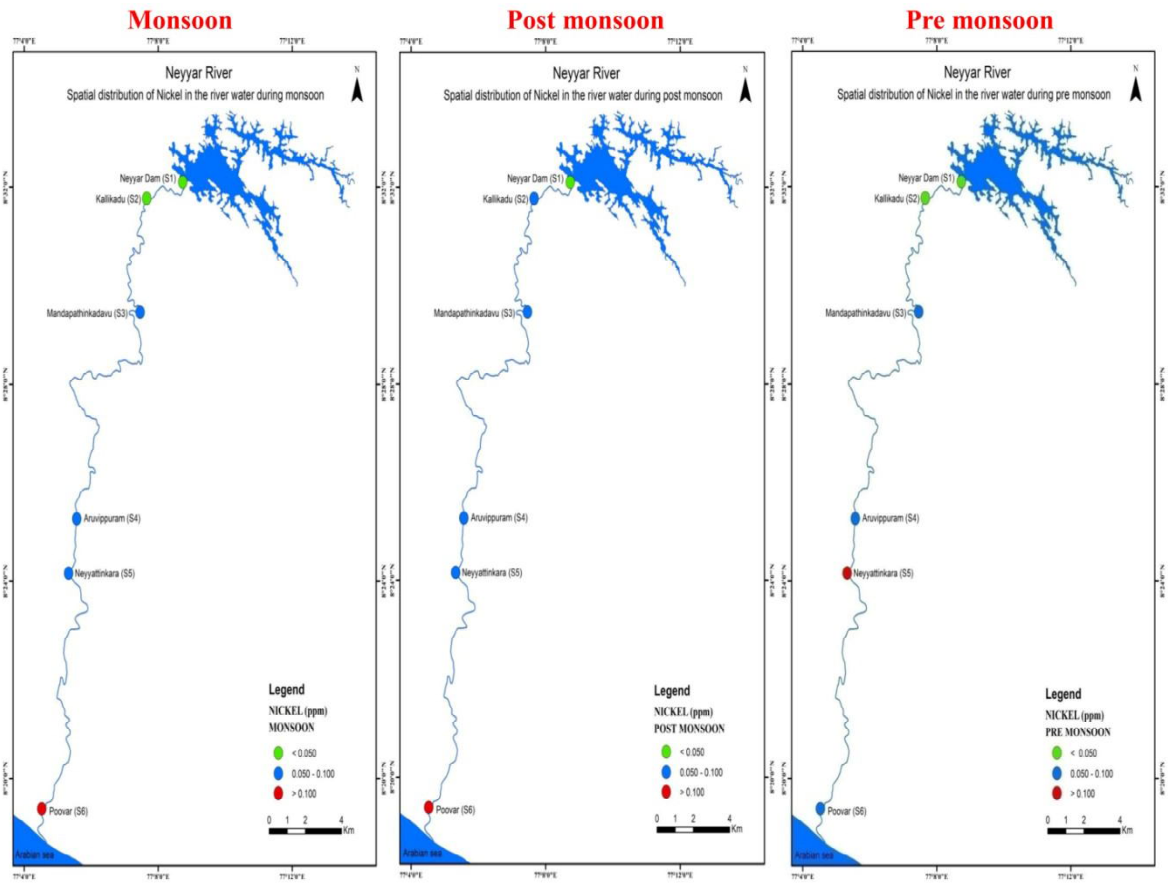


**Fig. 13.** Spatial distribution of Ni in Neyyar river water during three seasons

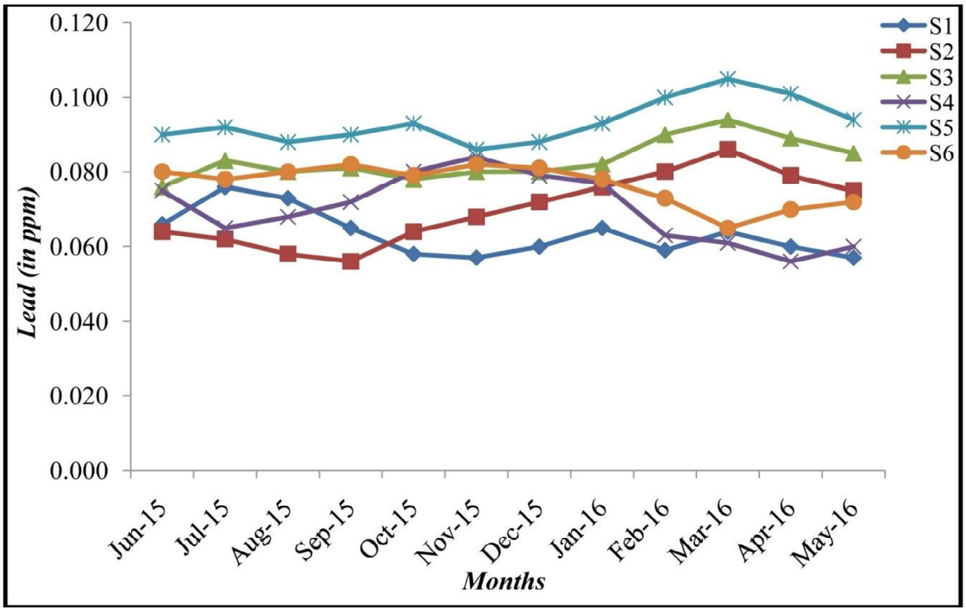


**Fig. 14.** Monthly variation of lead (in ppm) in the water from different stations of Neyyar river

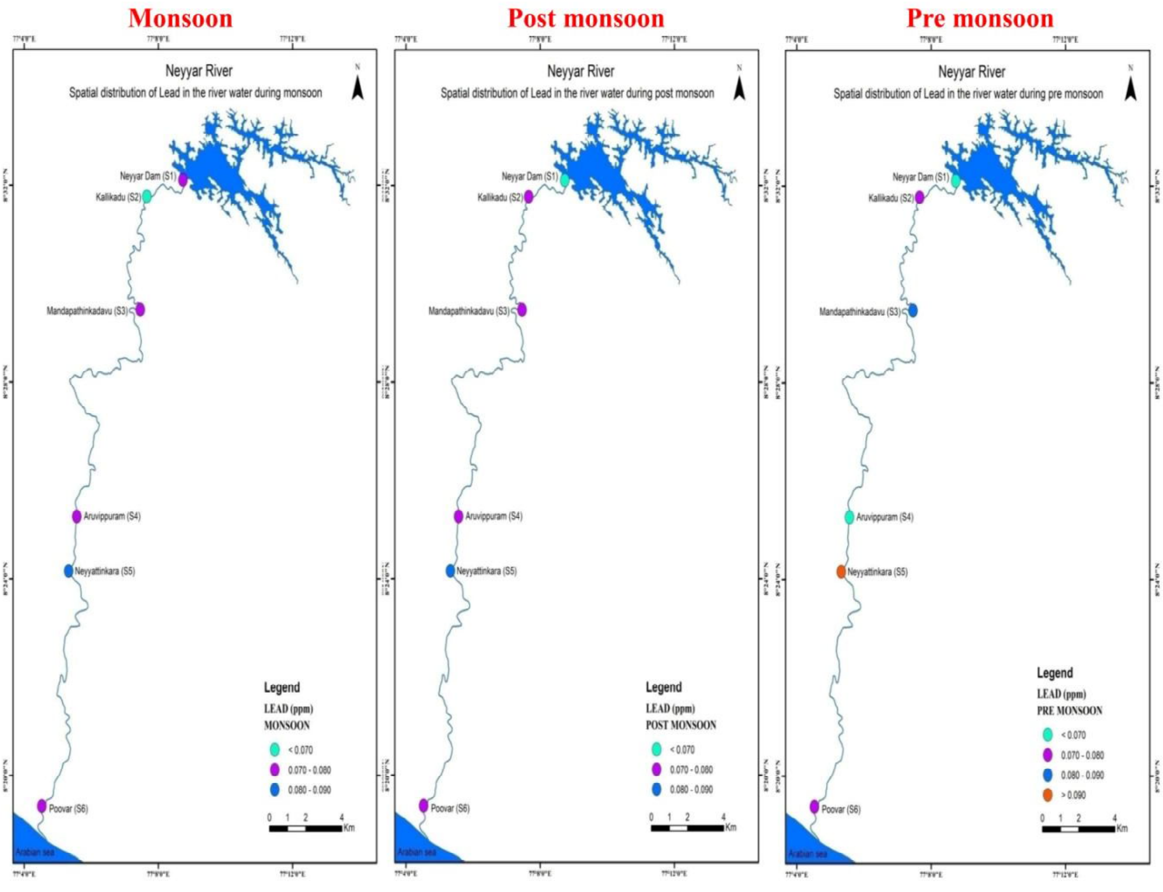


**Fig. 15.** Spatial distribution of Pb in Neyyar river water during three seasons

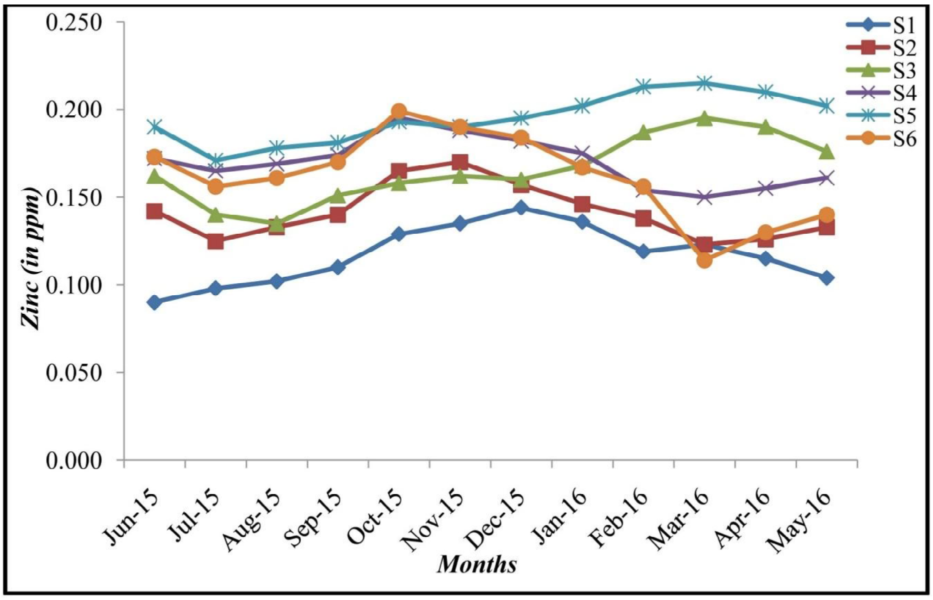


**Fig. 16.** Monthly variation of zinc (in ppm) in the water from different stations of Neyyar river

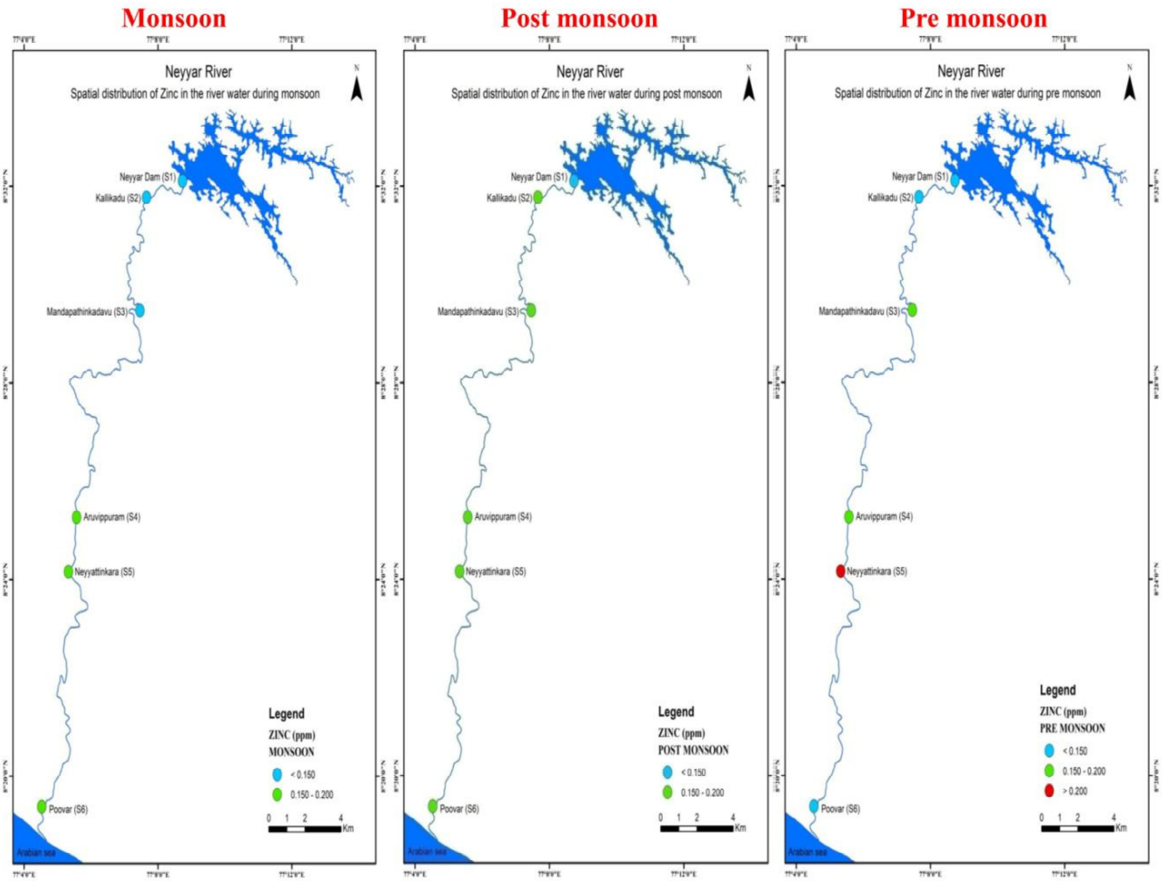


**Fig. 17.** Spatial distribution of Zn in Neyyar river water during three seasons

## 5. References

Abeer, M.B., Noha, A.M., and Alaa, E. (2014). Assesment of Heavy metal levels in water and their toxicity in river Nile basin at Greater Cairo, Egypt. *Global Veterinaria*, 13(4): 432-443.

Abida, B., Ramaiah, M., Harikrishna, M., Irfanulla, K., and Veena, K. (2009). Heavy Metal Pollution and Chemical Profile of Cauvery River Water. *Journal of Chemistry*, 6(1): 47-52.

Aina, O.A., Taofeek, A.B., and Azubuike, V.C. (2012). Spatial and Temporal Variations in Water and Sediment Quality of Ona River, Ibadan, Southwest Nigeria. *European Journal of Scientific Research*, 74(2): 186-204.

Ancy Mol, P., Paul Raj, K., and Shaji, E. (2016). Assessment of trace elements concentration in various aquatic ecosystems of Nedumangadu and Neyyattinkara taluk of Thiruvananthapuram district in Kerala, India. *International Journal of Emerging Trends in Science and Technology*, 3(1): 3422-3430.

Anju, A.K., Dipu, S., and Sobha, V. (2011). Seasonal Variation of Heavy Metals in Cochin Estuary and Adjoining Periyar and Muvattupuzha Rivers, Kerala, India. *Global Journal of Environmental Research*, 5(1): 15-20.

APHA. (1998). Standard methods for examination of water and waste water (20th edition). American public health association, Washington D.C, pp. 1-1268.

APHA. (2012). Standard Methods for examination of water and wastewater (22nd edition). American Public Health Association, Washington D.C, pp. 1-1175.

Arun, P.R. (2007). Sedimentology and hydro geochemistry of Aruvikkara and Peppara reservoir basins, Kerala, India. Ph.D thesis, Cochin University of Science and Technology, Kochi

Arunkumar, K.S. (2007). Integrated geoenvironmental assessment and management of the coastal zone of Thiruvananthapuram district, south west coast of India. Ph.D thesis, University of Kerala.

ASTM (American Standard Test Method). (2010). Standard Test Method for Elements in Water by Inductively Coupled Plasma-Mass Spectrometry. ASTM International (D5673-10), Pennsylvania, United states, pp. 1-9.

Babunath, R., and John, G. (2017). A Study on Physico Chemical and Heavy Metals Characteristics of River Noyyal, Tamilnadu, India. *Environ. Sci. Ind. J.*, 13(1).

Badusha. M., and Santhosh. S. (2019a). Determination of Heavy Metals in Surface Waters of Neyyar River, Kerala. In the Proceedings of the National Seminar on Ecology and Conservation, Organized by Department of Zoology, University of Kerala, Kariavattom. Paper id: ECOR 25.

Bharose, R., Lal, S. B., Singh, S. K., and Srivastava, P. K. (2013). Heavy metals pollution in soil-water-vegetation continuum irrigated with ground water and untreated sewage. *Bulletin of Environmental and Scientific Research*, *2*(1), 1-8.

Bhuvaneshwari, R., Paneer Selvam, A., Srimurali, S., Padmanaban, K., and Babu Rajendran, R. (2016). Human and Ecological Risk evaluation of Toxic Metals in the Water and Sediment of River Cauvery. *International Journal of Scientific and Research Publications*, 6(3): 415-421.

BIS (Bureau of Indian Standards). (2012). Drinking Water Specification (Second Revision), IS 10500.

Chinhanga, J.R. (2010). Impact of industrial effluent from an iron and steel company on the physicochemical quality of Kwekwe river water in Zimbabwe. *International Journal of Engineering, Science and Technology*, 2(7): 29-40.

Chukwujindu, M.A.I., Arimoro, F.O., Nwajei, G.E., and Osayonmo, I.E. (2012). Concentrations and distribution of trace metals in water and streambed sediments of Orogodo River, Southern Nigeria. *Soil Sediment Contam*., 21(3): 382-406.

CWC (Central Water Commission). (2014). Status of trace and toxic metals in Indian rivers. Ministry of Water Resources, New Delhi, pp. 1-185.

Duruibe, J.O., Ogwuegbu, M.C., and Egwurugwu, J.N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2: 112-118.

Ekeanyanwu, R., Ogbuniyi, C.A., and Elienajirhevwe, O.F. (2011). Trace metals distribution in fish tissue, bottom sediments and water from Okemeshi River in Delta State, *Nigeria. Environ. Res. J.*, 5: 6-10.

Hassan, F.M. (2010). A Study of Physicochemical Parameters and Nine Heavy Metals in the Euphrates River, Iraq. *E-J. Chem*., 7: 685-692.

Hussain, J., Husain, I., and Arif, M. (2014). Occurrence of trace and toxic metals in river Narmada. *Environ. Qual*., 14: 31-34.

Indu, V.N., Kailash, S., Arumugam, M., and Clarson, V. (2011). Monitoring of Trace Metal Pollution in Meenachil River at Kottayam, Kerala (India). *E-Journal of Chemistry*, 8(1): 257-263.

Jakir, H., Ikbal, H., Mohammed, A., and Nidhi, G. (2017). Studies on heavy metal contamination in Godavari river basin. *Appl. Water. Sci*., pp.1-10.

Jiang, Y., Ding, Z., Peng, Q., Liao, J., and Lv, L. (2012). Spatial Distribution and Corresponding Factors of Heavy Metals Concentrations in the Dongjiang River Basin, Southeast China. *Res. J. Env. Earth Sci*., 4: 448-459.

Jose, G.T., and Takako, M.T. (2012). Limnology. CRC press, Taylor and Francis Group, Boca Raton, New York, London, pp. 1-440.

Joseph, P.V. (2002). Dynamics and speciation of heavy metals in the lower reaches of Chithrapuzha- a tropical tidal river. Ph.D thesis, Cochin University of Science and Technology.

Kang, J., Lee, S.W., Cho, K.H., Ki, S.J., Cha, S.M., and Kim, J.H. (2010). Linking land-use type and stream water quality using spatial data of fecal indicator bacteria and heavy metals in the Yeongsan river basin. *Water Res*., 44: 4143-4157.

Krishnakumar, A. (2002). Environmental degradation of two river basins of southern Kerala. Ph.D Thesis, University of Kerala, Thiruvananthapuram.

Maya, K. (2005). Studies on the nature and chemistry of sediments and water of Periyar and Chalakudy rivers, Kerala, India. Ph.D thesis, Cochin University of science and technology.

Maya, K. (2005). Studies on the nature and chemistry of sediments and water of Periyar and Chalakudy rivers, Kerala, India. Ph.D thesis, Cochin University of science and technology.

Nikhil Raj., and Azeez, P.A. (2009). Spatial and temporal variation in surface water chemistry of a tropical river, the river Bharathapuzha, India. *Current Science*, 96(2): 245-251.

Nupur, R. (2014). Bioremediation of Yamuna river water at Agra with special reference to heavy metals and pesticides using EM technology. Ph.D thesis, Dayalbagh Educational Institute (Deemed University), Dayalbagh, Agra.

Okweye, P.S. (2013). Seasonal variation in physico chemical parameters and heavy metals assessment in surface water of North Alabama. *Research Journal of Chemistry and Environment*, 17(7): 68-115.

Reimann, C., and de Caritat, P. (1998). Chemical elements in the Environment. Factsheets for the Geochemist and Environmental Scientist, *Springer-Verlag*, Berlin, Germany, pp. 1-398.

Reza, R., and Singh, G. (2010). Heavy metal contamination and its indexing approach for river water. *Int. J. Environ. Sci. Tech*., 7(4): 785-792.

Sehgal, M., Garg, A., Suresh, R., and Dagar, P. (2012). Heavy metal contamination in the Delhi segment of Yamuna basin. *Environ. Monit. Assess.*, 184: 1181-1196.

Singh, V. K., Kumar, D., Singh, S. K., Pham, Q. B., Linh, N. T. T., Mohammed, S., and Anh, D. T. (2021). Development of fuzzy analytic hierarchy process based water quality model of Upper Ganga river basin, India. *Journal of Environmental Management*, *284*, 111985.

Singh, H., Pandey, R., Singh, S. K., and Shukla, D. N. (2017a). Assessment of heavy metal contamination in the sediment of the River Ghaghara, a major tributary of the River Ganga in Northern India. *Applied Water Science*, 7(7), 4133-4149.

Singh, H., Singh, D., Singh, S. K., and Shukla, D. N. (2017b). Assessment of river water quality and ecological diversity through multivariate statistical techniques, and earth observation dataset of rivers Ghaghara and Gandak, India. *International Journal of River Basin Management*, 15(3), 347-360.

Stoeppler, M. (1991). Cadmium. In: Merian E (ed.) - Metals and their compounds in the Environment: Occurrence, Analyses and Biological Relevance, VCH Publishers, New York, pp. 803-851.

Unni, K.S. (2002). Conservation and management of aquatic ecosystems. Daya publishers, New Delhi.

USEPA. (2000). Is your drinking water safe? United State Environmental Protection Agency. Office of water (WH-550) 570/9-80-005.

Veerabhadraswamy, K.T., and Lokesh, K.S. (1993). Lead dispersion studies along highways. *Indian J. Environ. Hlth*., 135: 205-242.

WHO (World Health Organization). (2008). Guidelines for Drinking Water Quality, 3rd edition incorporating the first and second addenda, Volume 1, Recommendations, Geneva.