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# Environmental monitoring of sediment quality and trace metal status in a tropical perennial river in South India: an exploration using multivariate analysis

## Monitoramento ambiental da qualidade dos sedimentos e do status dos vestígios de metais em um rio tropical perene no sul da Índia: uma exploração usando análise multivariada

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**Abstract: Aim:** The Kallada River is exposed to several kinds of pollution from domestic, civic, recreational, and agricultural activities and human settlements. The objectives of the study were to assess sediment quality, especially the trace metal concentration and to compare with the previous reports on the sources of pollutants in the Kallada River. **Methods:** A total of 12 sediment variables including the following metals: iron (Fe), manganese (Mn), chromium (Cr), and zinc (Zn) were analyzed. Atomic Absorption Spectrophotometer (AAS) was used to detect trace metal concentration in the sediment samples. Statistical tools such as Pearson's correlation, Principal component analysis (PCA), and Cluster analysis (CA) were employed to analyze the data and source of pollutants. **Results:** This investigation indicated that Fe was the most accumulated element in the sediments, and the midstream ($K_6$ and $K_{10}$) and downstream sites ($K_{11}$ to $K_{15}$) showed a much higher concentration level than the upstream sites. The concentrations of trace metals in sediment samples followed the order Fe> Mn> Cu>Zn. **Conclusions:** The present study concluded that major sources of pollutants were sewage and civic effluents and agricultural discharges. These may cause a severe threat to the Kallada River and health risk to the local populations, which rely on the river, primarily for drinking purposes. Hence, appropriate conservation policies to reduce pollution are therefore essential.

**Keywords:** sediment quality; trace metal; Kallada river; anthropogenic activities; Ashtamudi estuary.

**Resumo: Objetivo:** O Rio Kallada está exposto a vários tipos de poluição decorrentes de atividades domésticas, cívicas, recreativas, agrícolas e assentamentos humanos. Os objetivos do estudo foram avaliar a qualidade do sedimento, especialmente a concentração de metais traços, e comparar com relatórios anteriores sobre as fontes de poluentes no Rio Kallada, India. **Métodos:** Um total de 12 descritores de sedimento, incluindo os seguintes metais: ferro (Fe), manganês (Mn), cromo (Cr) e zinco (Zn), foram analisados. Um espectrofotômetro de absorção atômica foi usado para detectar a concentração de metais traços nas amostras de sedimento. Correlação de Pearson, análise de componentes principais (PCA) e análise de agrupamento (CA) foram usadas para analisar os dados e fontes de poluentes. **Resultados:** Esta pesquisa indicou que o Fe foi o elemento mais acumulado nos sedimentos, e os locais de meio do rio ($K_6$ e $K_{10}$) e jusante ($K_{11}$ a $K_{15}$) mostraram um nível de concentração muito mais alto do que os locais a montante. As concentrações de metais traços nas amostras de sedimento seguiram a ordem Fe > Mn > Cu > Zn. **Conclusões:** O presente estudo concluiu que as principais fontes de poluentes foram esgotos, efluentes domésticos e descargas agrícolas. Estes podem representar uma ameaça severa ao Rio Kallada e riscos à saúde das populações locais, que dependem principalmente do rio para fins de consumo de água. Portanto, políticas de conservação apropriadas para reduzir a poluição são essenciais.

**Palavras-chave:** qualidade do sedimento; metais traço; rio Kallada; atividades antropogênicas; estuário Ashtamudi.

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## 1. Introduction

Rivers serve as the essential pathways for the distribution of aquatic and terrestrial constituents such as sediments, nutrients, and effluents to downriver (Zhang et al., 2021; Leibowitz et al., 2018). Sediments are a concern in riverine ecosystems due to their interdependence with a wide range of ecological aspects. Riverine sediments perform a significant role in the hydrological cycle and reveal the pollution status of the river. In many freshwater systems, pollutant load, including heavy metals leads to increased sediment concentrations that have the ability to destruct aquatic life (Ebadi & Hisoriev, 2018; Gaur et al., 2005). Physicochemical analysis of water summarizes the effect of pollutants at the time of sampling though the bottom sediments characterization provides a collective evaluation of pollution. The recent reports disclosed that sediment contamination is also a leading cause of deterioration occurred in rivers (Achi et al., 2021). Deterioration of the aquatic ecosystems by toxic metals is a global threat due to their harmfulness, imperishable nature, resilience, and deposition in several riverine habitats (Custodio et al., 2021; Kafilat Adebola et al., 2018). Sediment quality assessments are valuable to recognize the capability of pollutants within sediment to instigate biotic effects and compare contaminant concentration in sediment with the quality standards.

The integrity of freshwater resources is greatly affected by rapid population growth, urbanization, urban runoff, and various wastewater effluents (Ustaoğlu & Tepe, 2019). The discharge of heavy metals from sediments into the river water under propitious conditions makes the riverine environment extremely susceptible to contamination (Müller et al., 2020; Pandey et al., 2019). Sediments may serve as the sources of discharged contaminants in freshwater systems, which either attach to the layers of sediments or are dissolved in the surrounding water (Singh et al., 2017). The sediment quality is a major aspect of water bodies, as it can impact the quality of both the water column and the benthic life (Chon et al., 2012). River sediment influences the habitat structures of various benthic organisms (Garcia et al., 2012). Variations in the sediment quantity and distribution pattern significantly affect the channel characteristics (Jia et al., 2022). Furthermore, the type of sediment in the water column reveals water transparency (Baxa et al., 2021). In the case of perennial rivers, sediment transportation is manly contributed by water flow and upstream sediment supply. Alteration in sediment quality can have substantial effects on aquatic ecosystems (Bussi et al., 2021).

The sediment pollution is also an alarming environmental condition on riverine ecosystems in India (Mukhopadhyay et al., 2020). Recent reports in India recognized sediment as the most common pollutant in rivers, streams, and estuaries (Khuman et al., 2020; Dhamodharan et al., 2019). Similarly, heavy metals are an important group of contaminants in the riverine habitats that affect the transport and storage of various constituents present in the sediment (Kumar et al., 2022). According to, Iordache et al. (2022), trace metals are toxic and these metals could remain and accumulate in the bottom sediments without deteriorating in riverine environments. The multiple anthropogenic stresses on aquatic systems such as agriculture, sewage discharge and industrialization significantly contribute to the increased levels of metals in sediments (Bashir et al., 2020). Trace metal analysis allows the detection of pollutants and its spatial and temporal distribution reveals the pollution status of an ecosystem (Herath et al., 2022). In the case of Kallada River, the World Bank aided and the second biggest irrigation project in Kerala 'The Kallada Irrigation Project' (KIP) is centered on this river and currently this scheme is benefited 92 villages (Adarsh et al., 2018). Regrettably, recent reports revealed the effects of various anthropogenic activities such as sand mining, sewage and civic effluents, are weakening the ecological health of Kallada River. Moreover, recent reports also revealed the trace metal contamination in Kallada River (Mohan & Krishnakumar, 2022).

We are privileged enough to get access to this riverine ecosystem for conducting two-year research. The Kallada River is largely influenced by the southwest monsoon (Sreelash et al., 2018); therefore, evaluating the temporal variations should be an imperative to reveal the significant factors controlling the ecological integrity of Kallada River. A seasonal investigation of trace metal concentration over a spatial scale is appropriate to assess the contamination due to various anthropogenic activities. Also, the influence of seasonal trends on trace metal concentration was assessed. As mentioned earlier, sediment quality influences both biotic and abiotic components and they serve as important markers for assessing trace metal pollution. In this perspective, the current effort is significant in a freshwater ecosystem like Kallada River. Hence, we regarded it imperative to assess the sediment quality. The main objectives of the present investigation are to (i) assess the spatio-temporal variations in sediment variables using multivariate statistical tools (ii) discuss the source of various trace metals (iii) recommend appropriate conservation policies.

## 2. Materials and Methods

### *2.1. Details of study area and sampling framework*

The tropical perennial Kallada River originates from Karimalai-Kodakkal at an elevation of 1524 m and debouches into the Ashtamudi estuary. The Kallada River is the most important water resource for agricultural needs in the Quilon district (Jennerjahn et al., 2008). Geographically, the Kallada River has classified into precambrian crystalline, tertiary and laterite quaternary sediments. National Bureau of Soil Survey (NBSS, 2006), reported that the Kallada river basin includes 17 major soil series. The land use pattern along the Kallada River is mainly consist of plantation, barren land, forest, agriculture and urbanized parts (Aju et al., 2019). A total of fifteen sampling stations were selected within a stretch of 121 km (Figure 1). Based on altitude, these stations were categorized into, upstream, midstream and downstream. The upstream consists of the most undisturbed part of Kallada River. However, midstream and downstream stations facing manyfold anthropogenic stresses such as sand mining, urbanization, bridge construction, tourism, water transport, and wastewater discharge. The sampling sites were selected based on diversifying of habitat types and accessibility. The GPS tracker application (GPS - Virtual Maze) was employed to fix the geographic coordinates. Characteristics of the sampling stations are shown in Table 1. Sampling was done bi-monthly from February 2019 to January 2021 for two years. The study periods were categorized, into three different seasons as pre-monsoon (PrM), monsoon (MoN), and post-monsoon (PoM) for sediment analysis.

### *2.2. Analysis of sediment samples*

For the sediment quality analysis, 12 parameters were studied, including pH, organic carbon (OC), phosphate ($PO_4^{3}$-), sulphate ($SO_4^{2}$-), boron (B), potassium ($K^+$), calcium ($Ca^{2+}$), and magnesium ($Mg^{2+}$), and trace metals such as zinc (Zn), iron (Fe), copper (Cu), and manganese (Mn). Sediment samples were collected using a Van Veen grab of 0.04 $m^2$ (van Veen, 1933). This manually controlling grab sampler is a clam shell-type scoop instrument connected with a rope or cable. The hook holds the sampler mouth to an open position and once the sampler collects the sediment at the bottom of the river, it gets pulled back to a closed position.

**Table 1.** Sampling stations names, site codes and GPS coordinates of the sampling stations.

| Sampling station | Site code | GPS Coordinates |
|---|---|---|
| Thenmala | $K_1$ | 8.957740 N, 77.065018 E |
| Urukunnu | $K_2$ | 8.986332 N, 77.022788 E |
| Ottakkal | $K_3$ | 8.971937 N, 77.044585 E |
| Ayiranelloor | $K_4$ | 8.986937 N, 76.99278 E |
| Edamon | $K_5$ | 8.002679 N, 76.981768 E |
| Punalur | $K_6$ | 9.019580 N, 76.922699 E |
| Kamukumcherry | $K_7$ | 9.017823 N, 76.925923 E |
| Pidavoor | $K_8$ | 9.075653 N, 76.856850 E |
| Pattazhy | $K_9$ | 9.080699 N, 76.797195 E |
| Enathu | $K_{10}$ | 9.091344 N, 76.755375 E |
| Kadapuzha | $K_{11}$ | 9.012168 N, 76.632633 E |
| West Kallada | $K_{12}$ | 9.013375 N, 76.596572 E |
| Munroe Island | $K_{13}$ | 8.999644 N, 76.627733 E |
| Arinalloor | $K_{14}$ | 9.023025 N, 76.648671 E |
| Koivila | $K_{15}$ | 8.996483 N, 76.578357 E |

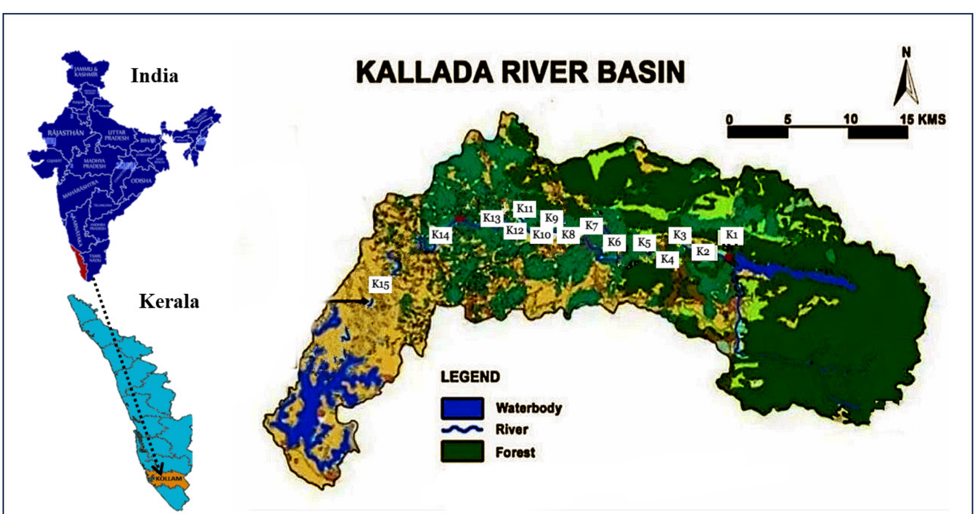


**Figure 1.** Location of sampling sites in Kallada River, India (Direction of river flow is east to west).

The samples were kept in clean plastic bags and brought to Zoology Research Centre, Pathanapuram for further laboratory analysis.

For trace metal analysis, KEL PLUS digestion unit (KES 04L) was employed for the digestion of dry sediment samples. The digested samples were analyzed for trace metals in Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer AA 800). Analysis of sediment variables were done by using the standard protocol (Jackson, 1967).

### *2.3. Data analysis*

Pearson correlation (r) was used to determine the way and amount of association between sediment variables. One-way analysis of variance (ANOVA) was done by using the Microsoft Excel Spreadsheet function and the probability (p) values <0.05 were obtained to elucidate the significant variance. The principal component analysis (PCA) was applied for the analysis of sediment variables with the purpose to expose the sources of pollutants (Jolliffe & Cadima, 2016; Reid & Spencer, 2009). Both PCA and correlation were done by using XLSTAT version 2021.4 (Melki et al., 2018). Additionally, cluster analysis was also employed to decrease the dimensionality of the dataset, and squared Euclidean distance measures the distance between the clusters. Cluster analysis was performed by using the statistical software PAST, version 4.03 (Hammer & Harper, 2001).

## 3. Results and Discussion

### *3.1. Sediment variables and heavy metal status*

Sediments of riverine systems are regarded as the destination for pollutants discharged from various sources in freshwater and offer a repository for detecting pollution status (Hasaballah et al., 2019; El-Amier et al., 2015). The mean values of sediment variables were shown in Table 2. During the sediment quality analysis, the pH was in the range of 6.29-8.77. Sediment pH values at upstream were significantly different from those of downstream of the Kallada River. The $K_{15}$ showed the maximum mean value (7.81 ± 0.43) while $K_6$ showed minimum (6.78 ± 0.49) during PrM. Higher pH at $K_{15}$ might be due to the influence of Ashtamudi estuary. The low pH might be due to the increased rate of decomposition of organic matter at $K_6$ during PrM. The pH of the sediment is a significant variable that reveals the decomposition status of the benthic region (Catianis et al., 2018; Reeves & Liebig, 2016). Sediment pH values at upstream were significantly different from those downstream of the Kallada River (Table 3).

This specifies the fact that the effluent has significantly impacted the sediment pH. This suggests that the metal concentrations would probably be more noticeable in downstream than upstream. Similar findings were reported by Venkatramanan et al. (2015) from Tirumalairajan River, Tamil Nadu. In this investigation, organic carbon % ranged between 0.02 in $K_8$ (MoN) and 1.68 in $K_6$ (PoM). The higher percentage of organic carbon at $K_6$ was due to the entry of organic waste either from the nearby town area or through some wastewater drains of the locality. Similar findings were reported by Sreelakshmi & Chinnamma (2018) from Bharathapuzha, Kerala. The water-holding ability, ion transfer, and microbial activities are controlled by the amount of organic carbon present in the sediments.

**Table 2.** Statistical summaries of sediment variables analyzed in Kallada River during the study period.

| Variables | PrM | | | MoN | | | PoM | | |
|---|---|---|---|---|---|---|---|---|---|
| | Minimum | Maximum | Mean ± SD | Minimum | Maximum | Mean ± SD | Minimum | Maximum | Mean ± SD |
| pH | 5.92 | 8.77 | 7.12 ± 0.89 | 6.29 | 7.96 | 7.32 ± 0.37 | 6.35 | 7.98 | 7.20 ± 0.57 |
| OC (%) | 0.05 | 0.55 | 0.21 ± 0.11 | 0.02 | 0.84 | 0.29 ± 0.27 | 0.24 | 1.68 | 0.61 ± 0.35 |
| $PO_4^{3-}$ (ppm) | 4.73 | 17.04 | 9.15 ± 3.90 | 1.79 | 8.11 | 4.39 ± 1.64 | 3.12 | 12.52 | 6.73 ± 2.72 |
| $K^+$ (ppm) | 31.95 | 198.16 | 99.67 ± 57.26 | 21.15 | 89.07 | 42.22 ± 19.51 | 30.99 | 175.52 | 71.53 ± 44.31 |
| $Ca^{2+}$ (ppm) | 106.81 | 680.21 | 297.18 ± 220.76 | 27.32 | 394.75 | 91.66 ± 83.51 | 66.25 | 659.26 | 253.78 ± 219.96 |
| $Mg^{2+}$ (ppm) | 4.45 | 109.92 | 27.84 ± 14.25 | 2.45 | 67.11 | 16.45 ± 14.51 | 3.45 | 89.18 | 22.66 ± 20.41 |
| B (ppm) | 0.34 | 0.92 | 0.56 ± 0.14 | 0.16 | 0.49 | 0.29 ± 0.09 | 0.25 | 0.49 | 0.37 ± 0.08 |
| S (ppm) | 2.18 | 10.36 | 5.41 ± 2.61 | 0.52 | 5.17 | 2.43 ± 1.43 | 1.44 | 8.93 | 3.86 ± 2.23 |
| Fe (ppm) | 4.83 | 183.73 | 68.07 ± 44.15 | 0.43 | 89.55 | 26.01 ± 17.41 | 6.21 | 154.88 | 54.74 ± 53.86 |
| Mn (ppm) | 5.21 | 98.12 | 39.34 ± 31.12 | 0.51 | 51.69 | 20.87 ± 15.63 | 6.25 | 64.03 | 29.53 ± 20.82 |
| Cu (ppm) | 4.05 | 69.45 | 31.87 ± 23.22 | 0.21 | 32.49 | 14.67 ± 10.81 | 5.36 | 45.75 | 22.84 ± 15.32 |
| Zn (ppm) | 3.33 | 56.95 | 25.56 ± 16.74 | 0.21 | 17.32 | 10.28 ± 6.41 | 5.11 | 43.12 | 21.17 ± 11.81 |

PrM: Pre-monsoon; MoN: Monsoon; PoM: Post-monsoon; %: Percentage; ppm: Parts Per Million; B: Boron; Cu: Copper; Fe: Iron; Zn: Zinc; $PO_4^{3-}$: Phosphate; $K^+$: Potassium; $Ca^{2+}$: Calcium; $Mg^{2+}$: Magnesium; Mn: Manganese; S: Sulphate; OC: Organic carbon.

**Table 3.** Stream-wise ANOVA results of sediment variables analyzed in Kallada River during the study period.

| Variables | Upstream | | | Midstream | | | Downstream | | |
|---|---|---|---|---|---|---|---|---|---|
| | *dF* | *F* | *p* | *dF* | *F* | *p* | *dF* | *F* | *p* |
| pH | 3 | 27.26 | 0.001 | 3 | 25.75 | 0.029 | 3 | 11.07 | 0.025 |
| OC (%) | 3 | 52.74 | 0.001 | 3 | 80.57 | 0.007 | 3 | 13.80 | 0.001 |
| $PO_4^{3-}$ (ppm) | 3 | 35.59 | 0.001 | 3 | 32.90 | 0.036 | 3 | 14.15 | 0.008 |
| $K^+$ (ppm) | 3 | 22.49 | 0.001 | 3 | 16.75 | 0.016 | 3 | 13.38 | 0.001 |
| $Ca^{2+}$ (ppm) | 3 | 17.04 | 0.001 | 3 | 13.74 | 0.002 | 3 | 17.46 | 0.001 |
| $Mg^{2+}$ (ppm) | 3 | 63.58 | 0.001 | 3 | 36.94 | 0.001 | 3 | 12.60 | 0.033 |
| B (ppm) | 3 | 72.53 | 0.001 | 3 | 29.10 | 0.006 | 3 | 18.29 | 0.003 |
| S (ppm) | 3 | 81.43 | 0.001 | 3 | 12.73 | 0.016 | 3 | 10.24 | 0.008 |
| Fe (ppm) | 3 | 16.80 | 0.001 | 3 | 12.81 | 0.048 | 3 | 12.73 | 0.001 |
| Mn (ppm) | 3 | 56.19 | 0.001 | 3 | 10.00 | 0.003 | 3 | 45.59 | 0.001 |
| Cu (ppm) | 3 | 23.98 | 0.035 | 3 | 10.51 | 0.002 | 3 | 52.53 | 0.001 |
| Zn (ppm) | 3 | 74.72 | 0.002 | 3 | 16.42 | 0.001 | 3 | 20.98 | 0.066 |

%: Percentage; ppm: Parts Per Million; *dF*: Degree of freedom; *F: -* Significance test; *p: –* Significance.

However, the river sediments had relatively low organic carbon content, probably because of high precipitation of $CaCO_3$ in downstream sites, land runoff, and effective mineralization of organic content due to the effective mixing of the overlying water (Hou et al., 2013).

The $PO_4^{3-}$ and $K^+$ were in the range of 1.79-16.50 ppm and 21.95-198.16 ppm respectively. The maximum value of $PO_4^{3-}$ at $K_{10}$ were due to the dead organic matter settling from surface and are associated to the permeability of the sediment during the PoM and tends to increase towards the downstream parts. Similar outcome was documented by Lola Catherine & Mary Helen (2018) from the Manakudy estuary. Similarly, the maximum values of $K^+$ were noticed during the PoM season. Concentration of $K^+$ along the upstream stations might be due to the weathering processes. Contrarily, increasing tendency of $K^+$ towards downstream may attributed to the contribution from agricultural lands. The trend of potassium distribution in this study corroborates to George & Joseph (2017) from Meenachil River. The distribution of $Ca^{2+}$ oscillates around a minimum of 27.32 ppm in $K_4$ (MoN) and a maximum of 680.21 ppm in $K_{15}$ (PrM). The higher calcium content at $K_{15}$ was probably due to the large number of remains of shelled organisms. Similar findings were also documented by Sobha et al. (2009) from the aquatic systems of Thiruvananthapuram. The $Mg^{2+}$ shows a similar trend as $Ca^{2+}$ towards the downstream. The $Mg^{2+}$ ranged between 3.45 and 109.92 ppm. The highest $Mg^{2+}$ value was recorded at $K_{15}$ during PrM and the lowest at $K_1$ during MoN. The influence of Ashtamudi estuary was also mirrored in the downstream in the case of $Mg^{2+}$ during all the seasons. Similar trends were observed by Nair & Kumar (2019) at Vamanapuram River. In the case of boron, $K_6$ (PrM) have comparatively high levels and lowest values were found at $K_1$ (MoN). Boron is a vital micronutrient for the survival of aquatic flora.

The major source of boron includes weathering of rocks, fertilizers, and pesticides, the burning of wood and coal (Copaja & Muñoz, 2018). However, boron may enter into rivers due to various anthropogenic inputs as suggested by Kadam et al. (2020). Sulphate shows maximum concentration at $K_{13}$ and minimum at $K_1$ during PrM and MoN seasons respectively. Sulphate concentrations ranged from 0.52 to 10.36 ppm. The accumulation of sulphate in river water may be due to precipitation, groundwater, and weathering of minerals and anthropogenic sources including effluents, mining, petroleum refineries, and industries (Chakrapani & Veizer, 2006). In the present context, the higher sulphate could be due to the dissolution of minerals and the decaying of organic matter during the PoM season.

The highest concentrations of trace metals were observed during PrM followed by PoM and MoN seasons. The trace metal status (Fe and Mn) showed a maximum value at the $K_{13}$ station, except for Cu and Zn for which maximum values were recorded at $K_6$ station. The values of Cu ranged between 0.21 to 68.15 ppm. The low values of Cu at the upstream sites revealed that there was no significant source of pollution. The maximum Cu concentration was found at $K_{10}$ during PrM and the minimum at $K_1$ during MoN. It may be attributed to sewage effluents and agricultural runoff (Hussain et al., 2017). The major sources of Cu include plant and animal wastes, and a small portion may come from human excreta as documented by Dharan & William (2015) from Pamba River, Kerala.

Zn is a crucial element for all organisms as well as for mankind. Zn concentration varies from 0.21 to 56.95 ppm. Maximum zinc concentration was recorded during PrM at $K_6$. Similar seasonal fluctuations were noticed by Asha & Joseph (2017) from the Periyar River. Results also indicate that high concentrations of Zn and Cu were also observed in downstream sites. Deposition of trace metals such as Cu and Zn may attributed to the diverse anthropic sources such as dredging, municipal effluents, and reclamation (Kumar et al., 2020). The Fe is a dynamic constituent for life and it plays a crucial role in an array of metabolic processes including oxygen transport and DNA synthesis. Among the trace metals, the presence of iron in river sediments received great importance due to its substantial effects on the governance of other trace metal concentrations in freshwater ecosystems. In an aquatic environment, Fe plays a critical role in the geochemical cycling of several ions (Dhanakumar & Mohanraj, 2013). In the present investigation, Fe concentrations ranged from 0.43 to 183.73 ppm. The maximum value at $K_{13}$ during PrM season might be due to the mixing of the sewage effluents. Similar to other trace metals, the Fe content also tends to increase towards the downstream stations. The concentration of Mn value was found between 0.50 and 98.12 ppm. Maximum concentration of Mn was recorded during PrM over MoN and PoM seasons. The elevated Mn towards downstream ($K_6$ to $K_{15}$) was ascribed to the deposition of animal wastes, municipal wastes, and sewage discharges as revealed by Kashid et al. (2009) from Tarkarli River. The present results suggest that Fe, Cu, Mn, and Zn in the bottom sediment are associated with organic matter and transported into the river while attached to organic matter comes normally from natural sources.

### *3.2. Principal component analysis*

The sources of the trace metals found in the bottom sediments in the Kallada River were investigated using PCA. The concentrations and sources of trace metals in the sediments of Kallada River was determined in order to propose develop measures to protect the river. The PCA results for the trace metal concentrations and other variables are shown in Figure 2. Results of the PCA specify that the variables can be batched into two principal components. Component 1 (F1) is positively associated with the Fe, and Zn concentrations. Component 2 (F2) is associated with the Cu concentration. F1 and F2 explain 57.94% (eigenvalue: 6.95) and 17.89% (eigenvalue: 2.14) respectively, of the total variance and (Figure 2a). Mn has a high loading for both F1 and F2. It is seen that pH and organic carbon are significantly positively correlated with $K^+$, $Ca^{2+}$, $Mg^{2+}$, S, and Fe and negatively correlated with boron. Similar results were reported from Yenshui River by Tsai et al. (2003). Similarly, phosphate is significantly correlated with, S, Fe, Mn, and Cu and negatively correlated with B, $K^+$, $Ca^{2+}$ and $Mg^{2+}$. The results of the PCA indicate that organic carbon, $PO_4^{3-}$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, S, Fe, and Zn predominantly came from the sources like sewage effluents. Cu and Mn came mainly from the agricultural and municipal effluents. Fe is significantly correlated with Zn and negatively with boron. Mn significantly correlated with Cu and Zn.

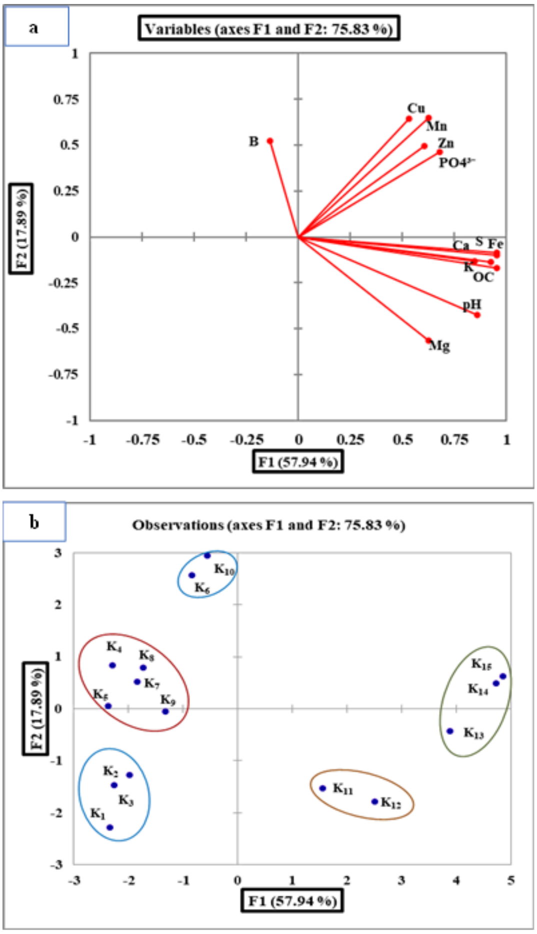


**Figure 2.** (a) Contribution plot using PCA based on sediment quality variables. %: Percentage, F1: Component 1, F2: Component 2, B: Boron, Cu: Copper, Fe: Iron, Zn: Zinc, $PO_4^{3-}$: Phosphate, K: Potassium, Ca: Calcium, Mg: Magnesium, Mn: Manganese, S: Sulphate, and OC: Organic carbon; (b) Grouping of stations in PCA analysis. $K_1$ to $K_{15}$ are the sampling sites.

Cu negatively correlated with boron. The positive association among sediment variables markedly reveals their interrelationship, specific trait, and common source of pollution. According to the PCA results, pH, OC, $K^+$, $Ca^{2+}$, S, Fe, Cu, Mn, and Zn were determined to have strong relationships with only F1. The multivariate investigation reveals that Fe, Cu, Mn, and Zn in the river sediment are associated with various anthropogenic inputs and shifted into the bottom sediments as documented by Pandey & Singh (2017) from Ganga River. Moreover, different strong positive correlations were found between the concentrations of Fe, Cu, and Zn. Pearson's correlation results (Figure 3) also support the contention that these trace metals have common sources.

### *3.3. Cluster analysis*

During the cluster analysis, various sampling sites in the study area were classified into six major clusters based on the similarity in trace metal concentration (Figure 4). Application of hierarchical clustering in the sediment analysis of Indian rivers were previously documented by Khan et al. (2020) and Kumar et al. (2019) in various aquatic systems. In this scenario, one group included the three upstream stations ($K_1$, $K_2$ and $K_3$) and the second cluster consisted of the remaining upstream stations $K_4$ and $K_5$. The third cluster consisted of two midstream stations ($K_7$, $K_8$ and $K_9$). The aforementioned stations were found to be the most undisturbed part of the Kallada River during the study period. The midstream stations $K_6$ and $K_{10}$ were recognized as the fourth cluster. The downstream stations $K_{11}$ and $K_{12}$ formed the fifth cluster while the remaining downstream stations $K_{13}$, $K_{14}$ and $K_{15}$ comprised the last cluster. Trace metal concentrations were comparatively higher in fourth and last clusters during the study period. Sewage and civic effluents were the serious issues in these stations. The PCA grouping of sampling stations (Figure 2b) also confirmed the findings of cluster analysis.

The outcome of this investigation shows that concentration of trace metals in river sediment is rising. Spatial and temporal distribution revealed different levels of pollution. A constantly mounting trend at the mid and downstream stations indicating perilous impacts of various sources including civic and sewage effluents. A number of wastewater channels at different points along the cities largely contributed to the trace metal concentration in river sediments. These drains should be monitored and wastewater to be properly treated. The upstream of Kallada River was found to be the most undisturbed part while the stations such as $K_6$, $K_{10}$, and $K_{13}$ showed higher values. The multivariate statistical analysis also revealed the influence of sewage and agricultural inputs in controlling trace metal concentration. The study provides significant database for future research on Kallada River and for developing conservation and restoration measures for river basin management.

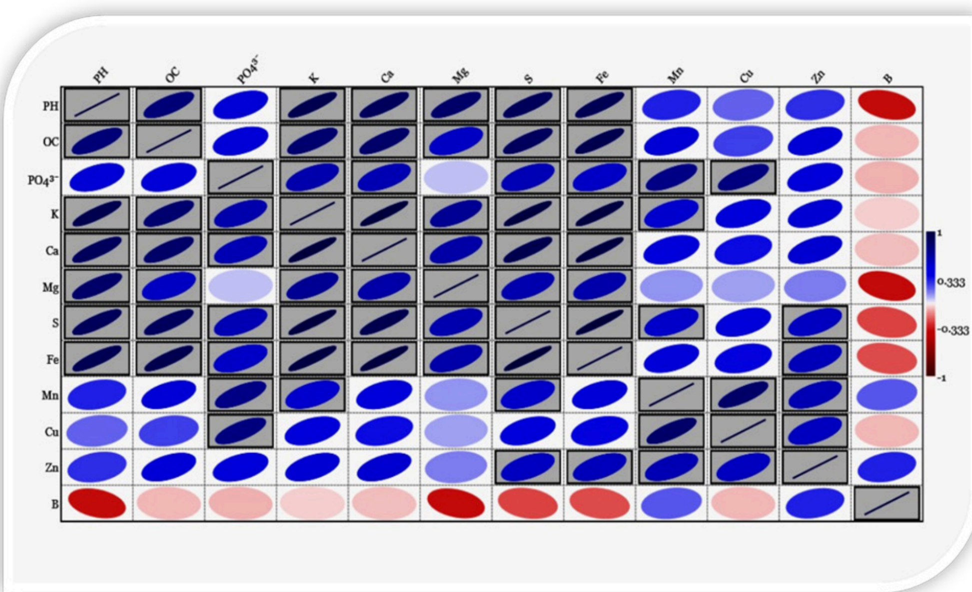


**Figure 3.** Plot depicting Pearson correlation coefficients between sediment variables ($p$<0.05 boxed values). *p:* Significance, B: Boron, Cu: Copper, Fe: Iron, Zn: Zinc, $PO_4^{3-}$: Phosphate, K: Potassium, Ca: Calcium, Mg: Magnesium, Mn: Manganese, S: Sulphate, and OC: Organic carbon.

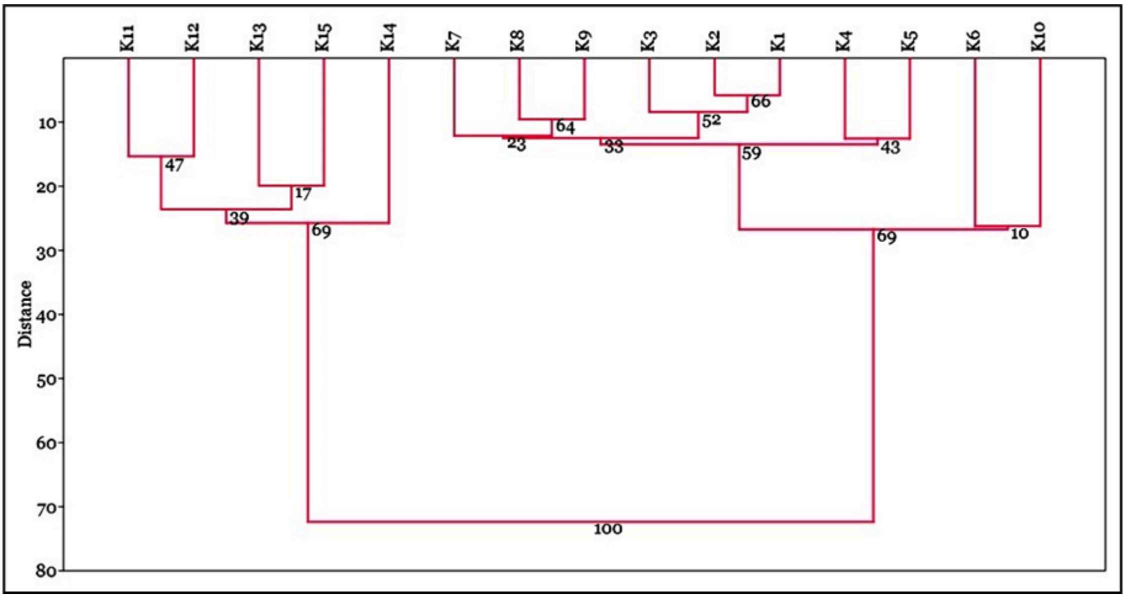


**Figure 4.** Euclidean distance-based cluster analysis (using Ward's method) of sampling stations. $K_1$ to $K_{15}$ are the sampling sites. The numbers in the nodes represent the standard bootstrap P-value.


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## Data availability

Data can be accessed using this link: https://doi.org/10.7910/DVN/9T1ELF

## References


Achi, C.G., Omoniyi, A.M., Coker, A.O., & Sridhar, M.K.C., 2021. Multivariate analysis of sediment quality in River Ogbere, Ibadan, South-West Nigeria. H2Open J 4(1), 1-11. http://dx.doi.org/10.2166/h2oj.2021.057.

Adarsh, S., Dharan, S.D., & Anuja, P.K., 2018. Analyzing the hydrologic variability of Kallada River, India using continuous wavelet transform and fractal theory. Water Conserv. Sci. Eng 3(4), 305-319. http://dx.doi.org/10.1007/s41101-018-0060-8.

Aju, C.D., Reghunath, R., Prasannakumar, V., & Chandran, S., 2019. Terrain characteristics and their influence on the temporal behaviour of hydraulic heads in Kallada River Basin, Kerala. J. Geol. Soc. India 93(1), 61-67. http://dx.doi.org/10.1007/s12594-019-1123-y.

Asha, R., & Joseph, M.L., 2017. Seasonal variation of heavy metals in selected stations of Periyar River at Ernakulam district, Kerala, India. J Pharm Biol Sci. (Online) 12(4), 14-24. Retrieved in 2023, October 3, from https://www.iosrjournals.org/iosr-jpbs/papers/Vol12-issue4/Version-7/C1204071424.pdf

Bashir, I., Lone, F. A., Bhat, R. A., Mir, S. A., Dar, Z. A., & Dar, S. A., 2020. Concerns and threats of contamination on aquatic ecosystems. In: Hakeem, K., Bhat, R., & Qadri, H., eds. Bioremediation and biotechnology: sustainable approaches to pollution degradation. Cham: Springer, 1-26. http://dx.doi.org/10.1007/978-3-030-35691-0_1.

Baxa, M., Musil, M., Kummel, M., Hanzlík, P., Tesařová, B., & Pechar, L., 2021. Dissolved oxygen deficits in a shallow eutrophic aquatic ecosystem (fishpond)–Sediment oxygen demand and water column respiration alternately drive the oxygen regime. Sci. Total Environ. 766, 142647. PMid:33082047. http://dx.doi.org/10.1016/j.scitotenv.2020.142647.

Bussi, G., Darby, S.E., Whitehead, P.G., Jin, L., Dadson, S.J., Voepel, H.E., Vasilopoulos, G., Hackney, C.R., Hutton, C., Berchoux, T., Parsons, D.R., & Nicholas, A., 2021. Impact of dams and climate change on suspended sediment flux to the Mekong delta. Sci. Total Environ. 755(Pt 1), 142468. PMid:33032131. http://dx.doi.org/10.1016/j.scitotenv.2020.142468.

Catianis, I., Secrieru, D., Pojar, I., Grosu, D., Scrieciu, A., Pavel, A.B., & Vasiliu, D., 2018. Water quality, sediment characteristics and benthic status of the Razim-Sinoie lagoon system, Romania. Open Geosci. 10(1), 12-33. http://dx.doi.org/10.1515/geo-2018-0002.

Chakrapani, G.J., & Veizer, J., 2006. Source of dissolved sulphate in the Alakananda-Bhagirathi rivers in the Himalayas. Curr. Sci. 90(4), 500-503.

Chon, H.S., Ohandja, D.G., & Voulvoulis, N., 2012. The role of sediments as a source of metals in river catchments. Chemosphere 88(10), 1250-1256. PMid:22546630. http://dx.doi.org/10.1016/j.chemosphere.2012.03.104.

Copaja, S.V., & Muñoz, F.J., 2018. Heavy metals concentration in sediment of Lluta river basin. J. Chil. Chem. Soc. 63(1), 3878-3883. http://dx.doi.org/10.4067/s0717-97072018000103878.

Custodio, M., Fow, A., Chanamé, F., Orellana-Mendoza, E., Peñaloza, R., Alvarado, J.C., Cano, D., & Pizarro, S., 2021. Ecological risk due to heavy metal contamination in sediment and water of natural wetlands with tourist influence in the central region of Peru. Water 13(16), 2256. http://dx.doi.org/10.3390/w13162256.

Dhamodharan, A., Abinandan, S., Aravind, U., Ganapathy, G.P., & Shanthakumar, S., 2019. Distribution of metal contamination and risk indices assessment of surface sediments from Cooum River, Chennai, India. Int. J. Environ. Res. 13(5), 853-860. http://dx.doi.org/10.1007/s41742-019-00222-8.

Dhanakumar, S., & Mohanraj, R., 2013. Fractionation of iron in river-bed sediments: Implications for the assessment of environmental integrity of the Cauvery delta region, India. In: Ramkumar, M., ed. On a sustainable future of the earth's natural resources. Berlin: Springer, 123-137. http://dx.doi.org/10.1007/978-3-642-32917-3_6.

Dharan, R.S., & William, D.S., 2015. Seasonal variation in heavy metal pollution at Pallathuruthy: a converging point of Pamba and Vembanad Lake, Kerala, South India. Int. J. Sci. Res. 6(4), 1520-1525.

Ebadi, A.G., & Hisoriev, H., 2018. Physicochemical characterization of sediments from Tajan river basin in the northern Iran. Toxicol. Environ. Chem. 100(5-7), 540-549. http://dx.doi.org/10.1080/02772248.2018.1460929.

El-Amier, Y.A., Zahran, M.A., & Al-Mamoori, S.O., 2015. Environmental changes along Damietta branch of the River Nile, Egypt. J. Environ. Sci. 44, 235-255.

Garcia, X.F., Schnauder, I., & Pusch, M.T., 2012. Complex hydromorphology of meanders can support benthic invertebrate diversity in rivers. Hydrobiologia 685(1), 49-68. http://dx.doi.org/10.1007/s10750-011-0905-z.

Gaur, V.K., Gupta, S.K., Pandey, S.D., Gopal, K., & Misra, V., 2005. Distribution of heavy metals in sediment and water of river Gomti. Environ. Monit. Assess. 102(1-3), 419-433. PMid:15869200. http://dx.doi.org/10.1007/s10661-005-6395-6.

George, P., & Joseph, S., 2017. Appraisal of nutrient distribution in the surface water and bed sediments of a small mountainous river. Environ. Monit. Assess. 189(4), 183. PMid:28342051. http://dx.doi.org/10.1007/s10661-017-5874-x.

Hammer, Ø., & Harper, D.A., 2001. Past: paleontological statistics software package for educaton and data anlysis r. Palaeont. Electr. (Online) 4(1), 1. Retrieved in 2023, October 3, from http://palaeo-electronica.org/2001_1/past/issue1_01.htm

Hasaballah, A., Hegazy, T., Ibrahim, M., & El-Emam, D., 2019. Assessment of water and sediment quality of the river Nile, Damietta Branch, Egypt. Egypt. J. Aquat. Biol. Fish. 23(5), 55-65. http://dx.doi.org/10.21608/ejabf.2019.64835.

Herath, I.K., Wu, S., Ma, M., & Ping, H., 2022. Heavy metal toxicity, ecological risk assessment, and pollution sources in a hydropower reservoir. Environ. Sci. Pollut. Res. Int. 29(22), 32929-32946. PMid:35020150. http://dx.doi.org/10.1007/s11356-022-18525-3.

Hou, D., He, J., Lü, C., Sun, Y., Zhang, F., & Otgonbayar, K., 2013. Effects of environmental factors on nutrients release at sediment-water interface and assessment of trophic status for a typical shallow lake. ScientificWorldJournal 2013, 716342. PMid:24023535. http://dx.doi.org/10.1155/2013/716342.

Hussain, J., Husain, I., Arif, M., & Gupta, N., 2017. Studies on heavy metal contamination in Godavari river basin. Appl. Water Sci. 7(8), 4539-4548. http://dx.doi.org/10.1007/s13201-017-0607-4.

Iordache, A.M., Nechita, C., Zgavarogea, R., Voica, C., Varlam, M., & Ionete, R.E., 2022. Accumulation and ecotoxicological risk assessment of heavy metals in surface sediments of the Olt River, Romania. Sci. Rep. 12(1), 880. PMid:35042928. http://dx.doi.org/10.1038/s41598-022-04865-0.

Jackson, M., 1967. Soil chemical analysis (Online). New Delhi: Prentice Hall of India. Retrieved in 2023, October 3, from https://www.scirp.org/reference/ReferencesPapers?ReferenceID=105097

Jennerjahn, T.C., Soman, K., Ittekkot, V., Nordhaus, I., Sooraj, S., Priya, R.S., & Lahajnar, N., 2008. Effect of land use on the biogeochemistry of dissolved nutrients and suspended and sedimentary organic matter in the tropical Kallada River and Ashtamudi estuary, Kerala, India. Biogeochemistry 90(1), 29-47. http://dx.doi.org/10.1007/s10533-008-9228-1.

Jia, L., Yu, K.X., Li, Z.B., Li, P., Zhang, J.Z., Wang, A.N., Ma, L., Xu, G., & Zhang, X., 2022. Temporal and spatial variation of rainfall erosivity in the Loess Plateau of China and its impact on sediment load. Catena 210, 105931. http://dx.doi.org/10.1016/j.catena.2021.105931.

Jolliffe, I.T., & Cadima, J., 2016. Principal component analysis: a review and recent developments. Philos. Trans.- Royal Soc., Math. Phys. Eng. Sci. 374(2065), 20150202. PMid:26953178. http://dx.doi.org/10.1098/rsta.2015.0202.

Kadam, A., Wagh, V., Umrikar, B., & Sankhua, R., 2020. An implication of boron and fluoride contamination and its exposure risk in groundwater resources in semi-arid region, Western India. Environ. Dev. Sustain. 22(7), 7033-7056. http://dx.doi.org/10.1007/s10668-019-00527-w.

Kafilat Adebola, B.A., Joseph Kayode, S., & Adebayo Akeem, O., 2018. Integrated assessment of the heavy metal pollution status and potential ecological risk in the Lagos Lagoon, South West, Nigeria. Hum. Ecol. Risk Assess. 24(2), 377-397. http://dx.doi.org/10.1080/10807039.2017.1384694.

Kashid, J.P., Patil, A.K., Samant, J.S., & Raut, P.D., 2009. Seasonal variation in some metals of inshore waters of Malvan, Maharashtra. Nat. Environ. Pollut. Technol. 8(2), 261-266.

Khan, R., Saxena, A., & Shukla, S., 2020. Evaluation of heavy metal pollution for River Gomti, in parts of Ganga Alluvial Plain, India. SN Appl. Sci. 2(8), 1451. http://dx.doi.org/10.1007/s42452-020-03233-9.

Khuman, S.N., Bharat, G., & Chakraborty, P., 2020. Spatial distribution and sources of pesticidal persistent organic pollutants in the Hooghly riverine sediment. Environ. Sci. Pollut. Res. Int. 27(4), 4137-4147. PMid:31828711. http://dx.doi.org/10.1007/s11356-019-06973-3.

Kumar, M., Goswami, R., Awasthi, N., & Das, R., 2019. Provenance and fate of trace and rare earth elements in the sediment-aquifers systems of Majuli River Island, India. Chemosphere 237, 124477. PMid:31394438. http://dx.doi.org/10.1016/j.chemosphere.2019.124477.

Kumar, M.R., Krishnan, K.A., Vimexen, V., Faisal, A.K., Mohind, M., & Arun, V., 2022. Heavy metal impression in surface sediments and factors governing the fate of macrobenthic communities in tropical estuarine ecosystem, India. Environ. Sci. Pollut. Res. Int. 29(25), 38567-38590. PMid:35080727. http://dx.doi.org/10.1007/s11356-021-18394-2.

Kumar, V., Sharma, A., Pandita, S., Bhardwaj, R., Thukral, A.K., & Cerda, A., 2020. A review of ecological risk assessment and associated health risks with heavy metals in sediment from India. Int. J. Sediment Res. 35(5), 516-526. http://dx.doi.org/10.1016/j.ijsrc.2020.03.012.

Leibowitz, S.G., Wigington Junior, P.J., Schofield, K.A., Alexander, L.C., Vanderhoof, M.K., & Golden, H.E., 2018. Connectivity of streams and wetlands to downstream waters: an integrated systems framework. J. Am. Water Resour. Assoc. 54(2), 298-322. PMid:30078985. http://dx.doi.org/10.1111/1752-1688.12631.

Lola Catherine, V., & Mary Helen, H., 2018. Studies on the monthly variation of sediment parameters of Manakudy estuary with adjoining rivers, South West coast of India. Int J Creat Res Thought 6(1), 1-5.

Melki, M., Isnansetyo, A., Widada, J., & Murwantoko, M., 2018. Distribution of ammonium-oxidizing bacteria in sediment with relation to water quality at the Musi River, Indonesia. Hayati J. Biosci. 25(4), 198-205. http://dx.doi.org/10.4308/hjb.25.4.198.

Mohan, U., & Krishnakumar, A., 2022. Geochemical aspects and contamination evaluation of major and trace elements in the sediments of Kallada river, southern Western Ghats, India. J. Environ. Sci. Health Part A Tox. Hazard. Subst. Environ. Eng. 57(4), 258-267. PMid:35354364. http://dx.doi.org/10.1080/10934529.2022.2053450.

Mukhopadhyay, M., Sampath, S., Muñoz-Arnanz, J., Jiménez, B., & Chakraborty, P., 2020. Plasticizers and bisphenol A in Adyar and Cooum riverine sediments, India: occurrences, sources and risk assessment. Environ. Geochem. Health 42(9), 2789-2802. PMid:31974692. http://dx.doi.org/10.1007/s10653-020-00516-3.

Müller, A., Österlund, H., Marsalek, J., & Viklander, M., 2020. The pollution conveyed by urban runoff: a review of sources. Sci. Total Environ. 709, 136125. PMid:31905584. http://dx.doi.org/10.1016/j.scitotenv.2019.136125.

Nair, V.M., & Kumar, R.B., 2019. Assessment of heavy metal concentration in river sediments along Vamanapuram River Basin, South Kerala, India. Nat. Environ. Pollut. Technol. 18(2), 593-597.

National Bureau of Soil Survey – NBSS, 2006. Soil series of Kerala. Nagpur: NBSS, NBSS Publications, vol. 136.

Pandey, J., & Singh, R., 2017. Heavy metals in sediments of Ganga River: up-and downstream urban influences. Appl. Water Sci. 7(4), 1669-1678. http://dx.doi.org/10.1007/s13201-015-0334-7.

Pandey, L.K., Park, J., Son, D.H., Kim, W., Islam, M.S., Choi, S., Lee, H., & Han, T., 2019. Assessment of metal contamination in water and sediments from major rivers in South Korea from 2008 to 2015. Sci. Total Environ. 651(Pt 1), 323-333. PMid:30240916. http://dx.doi.org/10.1016/j.scitotenv.2018.09.057.

Reeves, J.L., & Liebig, M.A., 2016. Depth matters: soil pH and dilution effects in the northern Great Plains. Soil Sci. Soc. Am. J. 80(5), 1424-1427. http://dx.doi.org/10.2136/sssaj2016.02.0036n.

Reid, M.K., & Spencer, K.L., 2009. Use of principal components analysis (PCA) on estuarine sediment datasets: the effect of data pre-treatment. Environ. Pollut. 157(8-9), 2275-2281. PMid:19410344. http://dx.doi.org/10.1016/j.envpol.2009.03.033.

Singh, A., Singh, D.R., & Yadav, H.K., 2017. Impact and assessment of heavy metal toxicity on water quality, edible fishes and sediments in lakes: a review. Trends Biosci. 10(8), 1551-1560.

Sobha, V., Abhilash, P.R., Santhosh, S., Hashim, K.A., & Valsalakumar, E., 2009. Geochemistry of different aquatic systems in Thiruvananthapuram, Southern Kerala. Ecoscan 2(2), 223-228.

Sreelakshmi, C.D., & Chinnamma, M.A., 2018. Quality assessment of sediments in bharathapuzha with special reference to phosphate fractionation and metallic contamination. Int. J. Eng. Adv. Technol. 5(4), 20-29.

Sreelash, K., Sharma, R.K., Gayathri, J.A., Upendra, B., Maya, K., & Padmalal, D., 2018. Impact of rainfall variability on river hydrology: a case study of Southern Western Ghats, India. J. Geol. Soc. India 92(5), 548-554. http://dx.doi.org/10.1007/s12594-018-1065-9.

Tsai, L.J., Ho, S.T., & Yu, K.C., 2003. Correlations of extractable heavy metals with organic matters in contaminated river sediments. Water Sci. Technol. 47(9), 101-107. PMid:12830947. http://dx.doi.org/10.2166/wst.2003.0502.

Ustaoğlu, F., & Tepe, Y., 2019. Water quality and sediment contamination assessment of Pazarsuyu Stream, Turkey using multivariate statistical methods and pollution indicators. Int. Soil Water Conserv. Res. 7(1), 47-56. http://dx.doi.org/10.1016/j.iswcr.2018.09.001.

van Veen, J., 1933. Onderzoek naar het zandtransport von rivieren. De Ing. B 48, 151-159.

Venkatramanan, S., Chung, S.Y., Ramkumar, T., Gnanachandrasamy, G., & Kim, T.H., 2015. Evaluation of geochemical behavior and heavy metal distribution of sediments: the case study of the Tirumalairajan river estuary, southeast coast of India. Int. J. Sediment Res. 30(1), 28-38. http://dx.doi.org/10.1016/S1001-6279(15)60003-8.

Zhang, F., Zeng, C., Wang, G., Wang, L., & Shi, X., 2021. Runoff and sediment yield in relation to precipitation, temperature and glaciers on the Tibetan Plateau. Int. Soil Water Conserv. Res. 10(2), 197-207. http://dx.doi.org/10.1016/j.iswcr.2021.09.004.

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