

Analysis and Evaluation of Heavy Metal Pollution in Kosasthalaiyar River near Ennore Creek Using Geo Statistical Approach

Sanghita Sen

Department of Civil Engineering, SRM Institute of Science and Technology, Kattankulathur-603203, Tamilnadu

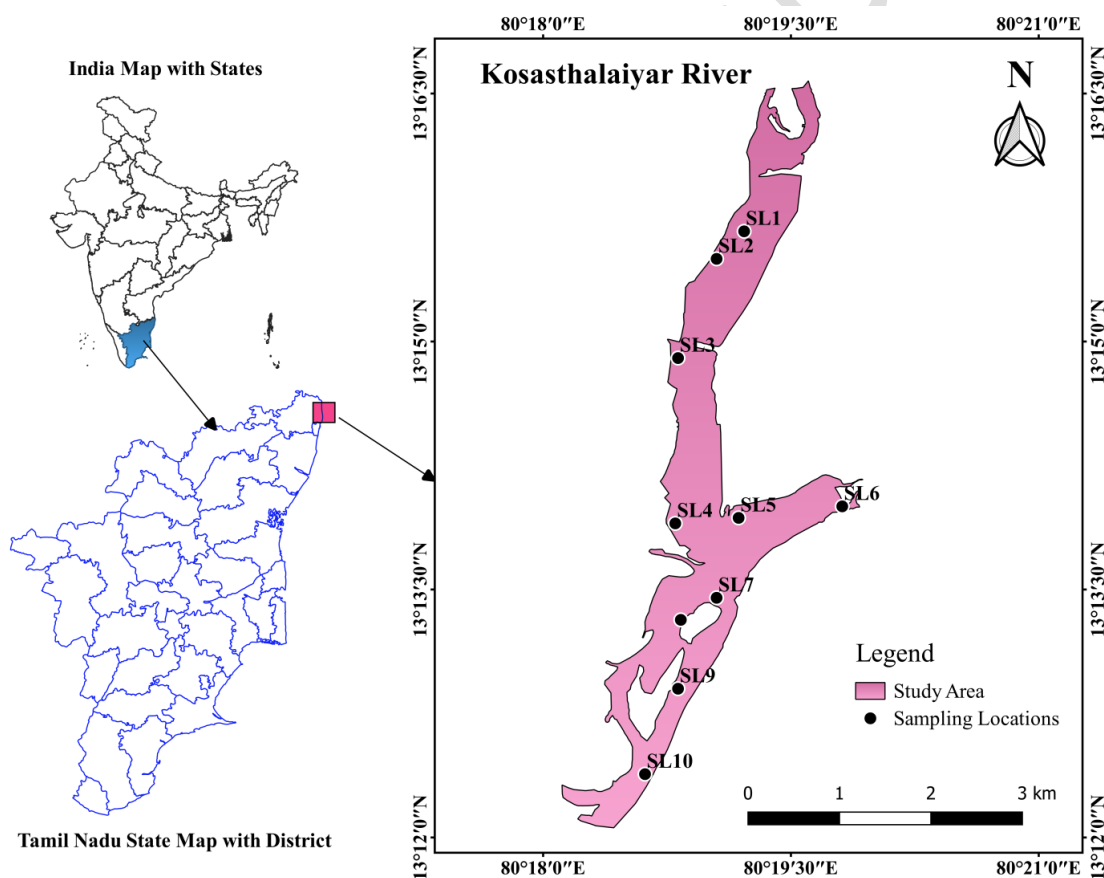
sanghitasens390@gmail.com

Karuppasamy Sudalaimuthu

Department of Civil Engineering, SRM Institute of Science and Technology, Kattankulathur-603203, Tamilnadu

karuppasamysudalaimuthu345@gmail.com

GRAPHICAL ABSTRACT



Abstract: The increasing industrialization and urbanization in recent times has led to a significant increase in heavy metal pollution in soil and sediment. The present study aims to evaluate the heavy metal contamination (HmC) in surface sediments collected from the Kosasthalaiyar River located between latitudes 13°12'03"N and 13°16'34"N and longitudes 80°18'6"E and 80°19'56"E. Ten sampling locations were selected in the study area and samples

of surface sediments were collected and analyzed for 16 geochemical and heavy metal parameters, including Silver (Ag), Aluminium (Al), Calcium (Ca), Cadmium (Cd), Chloride, Cobalt (Co), Total Chromium (Cr), Copper (Cu), Mercury (Hg), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Lead (Pb), Silica (Si), Titanium (Ti), and Zinc (Zn). The study aims to determine the potential environmental hazards of heavy metals in the sediment through calculation of the potential environmental hazard index (RI). Assess the impact of human activities on HmC in the surface sediments using four pollution indices: the Geo-accumulation index (Igeo), the Contaminant factor (CF), the degree of contamination (DC), the potential contamination index (PCI), and the pollution load index (PLI) and Conduct a human health risk assessment (HHRA) of heavy metals in the sediment. The study results will provide insight into the contamination levels and help inform measures for controlling pollution and promoting sustainability in the area.

Keywords: Heavy metals (Hm's), Kosastalayar River, pollution indices, human health risk assessment (HHRA).

1. Introduction

Rivers are strategically important waterways worldwide, providing significant contributions to domestic, industrial, and agricultural water requirements; they play an essential role in coordinating and organizing the landscape. Rivers are the main route for heavy metal (Hm) transport because they can carry heavy metals (Hm's) from hundreds of kilometers across waterways in a relatively short period (Patel et al. 2018). As a result, contaminants of Hm's with high concentrations are continuously discharged into the river and marine aquatic systems (Li et al. 2022). Sediment analysis plays an essential role in determining the concentration of metals in many aquatic ecosystems, surface integration of dissolved Hm's, spatial distribution, sedimentation, behaviors of Hm's and re-suspension, as well as determining the patterns of pollution in ecosystems (Singh et al. 2020; Li et al. 2022).

Hm's are persistent and bio-accumulating environmental pollutants, and their toxicity is processed by metal structures such as metal-organic compounds (Patel et al. 2018; Navarrete-Rodríguez et al. 2020). The toxic heavy metal pollutants/ contamination (HmC) in the surface aquatic and marine ecosystems result from various natural and anthropological sources. Natural factors include weathering actions of rocks and soils, atmospheric precipitation, and aeolian sediments (Chandrasekaran et al. 2015; Perumal et al. 2021). However, Hm's also can enter ecosystems from anthropological sources such as industrial effluents, household sewage, excess utilization of fertilizers–pesticide on agro-lands, fossil fuel combustion, and atmospheric sedimentation, and have a higher impact on the accumulation of HmC in the marine and aquatic environment (Chandrasekaran et al. 2015; Patel et al. 2018; Perumal et al. 2021). Therefore, the Hm levels in the sediment are an essential gauge for observing the quality of the environment.

Many contaminants, along with significant metals, can cause biological hazards or sub-lethal effects to aquatic organisms due to toxicity, and the behavior of Hm's is still not fully understood (Chandrasekaran et al. 2015; Huang et al. 2020; Singh et al. 2020; Iordache et al. 2022). The solubility, distribution, and kinetic effect of Hm's in sediments depend on the sequence of physical and chemical properties such as seasonal variations, sediment texture, pH, organic matter, Eh, DO, redox potential, chelating agents, etc. (Chandrasekaran et al. 2015; Patel et al. 2018; Navarrete-Rodríguez et al. 2020). In addition, the metals are absorbed from the water

columns on the surface of the particles and settle in them (Karthikeyan et al. 2020). Therefore, it is vital activity to keep on track of the distribution of these pollutants and their levels of pollution, develop a mechanism for accumulating and transporting these harmful pollutants into the aquatic environment, and obtain information essential for the monitoring, conservation, and sustainable use of coastal ecosystem (Perumal et al. 2021).

The Hm concentrations in rivers are generally lower in the upper reaches than in the lower due to downward accumulation. However, due to different sources of anthropological inputs, such concentrations may not always be the same throughout the river system, varying from site to site (Patel et al. 2018). Physico-chemical analysis of typical Earth materials such as suspended particles, sediments, and water is a direct approach and is widely used by many researchers (Nobi et al. 2010; Sundararajan and Srinivasalu 2010; Balamurugan et al. 2011, 2020b, a; Jesudhas et al. 2017, 2022; N. et al. 2018; Johnny et al. 2018; Kader and Narayan Sinha 2018; Adjiri et al. 2019; Fabbrocino et al. 2019; Calmuc et al. 2021) as such approach can reveal the hydrogeochemistry, water quality, health risk and status of HmC in the environment. Various pollution indices such as the CF (contamination factor), DC (degree of contamination), Ecological risk factor, enrichment factor, etc., and Environmental quality indices, Igeo (geo-accumulation index), PLI (pollution load index), and PERI (Potential ecological risk index) using local background data have been developed to estimate the pollutant source and HmC levels in water systems (Kader and Narayan Sinha 2018; Patel et al. 2018; Sreenivasulu et al. 2018; Gyamfi et al. 2019; Karthikeyan et al. 2020; Singh et al. 2020; Calmuc et al. 2021). In recent years, studies of sedimentary beds have found an increase in the number of Hm's. Furthermore, Many studies have revealed that the sediments in the river basin are highly polluted by such Hm's (Chakraborty et al. 2014; Chowdhury and Maiti 2016; Kader and Narayan Sinha 2018; Sankar et al. 2018; Sreenivasulu et al. 2018; Navarrete-Rodríguez et al. 2020), so this has become a significant concern for researchers and decision-makers (Nobi et al. 2010; Banerjee et al. 2012; Huang et al. 2020; Astatkie et al. 2021; Iordache et al. 2022; Li et al. 2022). Therefore, an estimate of the Hm distribution in the surface sediments would help determine the level of pollution in the aquatic ecosystem of the East Coast of South India.

Due to the high urban and industrial growth rate in the study area, the excess pollutants discharged into the Kosasthalaiyar River (KR) lead to ecological degradation. These pollutants can be absorbed or accumulate in the sediments and move into aquatic life. According to the available literature, there is no long-term monitoring study on Hm pollution on the riverbank. The study region is lying between the latitude $13^{\circ} 12' 03.53168''$ – $13^{\circ} 16' 34.60671''$ N and longitude $80^{\circ} 18' 6.85765''$ – $80^{\circ} 19' 56.16288''$ E. The present study attempts to understand the HmC in the sediments of the KR basin in Tamil Nadu, India, through field samples. KR is one of the three rivers flowing through Chennai and is also known as Kortalaiyar. The length of the river in the metropolitan area of Chennai is 16 km out of its total length of 136 km. KR is produced near Pallipattu in the Thiruvallur district and flows into the sea at Ennore creek. The mainstream of this river flows through the Poondi reservoir. The KR bed is 150 to 250 m wide and has a total catchment area of 3,757 km². The normal river discharge capacity is 110,000 m³ / s, and the expected flood discharge capacity is approximately 125,000 m³ / s (Bhuvana 2016). This study will assist the authorities concerned in ensuring the presence of Hm's in the study area and will act as the foundation for mitigation measures. Furthermore, the HmC levels of the study area can be constantly monitored to protect the human community and biodiversity.

Therefore, the pollution indices calculation method is appropriate for evaluating Hm concentrations and their toxicity (Calmuc et al. 2021).

The scientific novelty of this study is indicated by the geographical importance of the study area, as different types of HmC sources are located close to the study area. Meanwhile, this region has not yet calculated human health risk assessment (HHRA) and advanced studies on these types of pollution indices. Therefore, various important specific pollution indices were used and tested to achieve the objectives of the study, namely the geo-accumulation index (I_{geo}), the contamination factor (CF), the degree of contamination (DC), the pollution load index (PLI), the potential contamination index (PCI) and potential ecological risk code (PERI).

One of the drawbacks of existing methodologies for monitoring heavy metal (Hm) pollution on riverbanks is the lack of long-term studies. This means that there is a lack of data on how Hm pollution levels change over time, and how they are affected by various factors such as seasonal changes and anthropogenic activities. Another drawback is that the existing methodologies may rely on point-based sampling methods, which only provide a snapshot of pollution levels at specific locations, and may not accurately reflect the overall level of pollution in the area. Additionally, they may not take into account the dynamic nature of Hm pollution, which can change rapidly and unpredictably. As a result of these drawbacks, existing methodologies may not be able to provide a comprehensive understanding of Hm pollution on riverbanks, and may not be able to identify key sources of pollution or inform effective management and mitigation strategies.

This study aims to assess the levels and sources of heavy metal pollution in the Kosasthalaiyar River and Ennore Creek. The study will use a geo-statistical approach, which combines spatial analysis and statistical methods, to evaluate the pollution levels and identify the sources of contamination. The area of focus is the Kosasthalaiyar River near Ennore Creek, which is known to have high levels of urban and industrial growth and potential for heavy metal pollution due to discharge of pollutants from these activities. The research aims to provide a comprehensive understanding of the heavy metal pollution in the area and inform effective management and remediation strategies to protect the ecosystem, aquatic life and human health as well as compliance with regulations.

The use of spatial autocorrelation, which refers to the similarity of values at nearby locations, in order to model and predict the distribution of a variable of interest. The use of spatial interpolation techniques, such as kriging, to estimate values at unsampled locations based on measurements from a set of sampled locations. The geostatistical models, such as the Gaussian process, to model the spatial structure of the data, and account for the uncertainty associated with the estimate. The estimation, such as variography, semivariography and kriging to examine the spatial structure and to predict the spatial continuity at unsampled points

Limitations included the methods of analysis used in the study may not be able to detect all heavy metals present in the samples, which could lead to an underestimation of pollution levels.

The study did not consider other anthropogenic activities that could contribute to heavy metal pollution, such as mining or agricultural practices.

The analysis and evaluation of heavy metal pollution in the Kosasthalaiyar River near Ennore Creek is based on several advantages offered by this approach.

Spatial Autocorrelation: Geostatistics is able to take into account the spatial autocorrelation present in environmental data, meaning that values of heavy metal concentrations at nearby locations are likely to be similar.

Interpolation: By using geostatistics, it's possible to use the information from sample locations and interpolate the data to other unsampled locations, making it possible to estimate the heavy metal concentrations in the whole study area.

Uncertainty: Geostatistics incorporates the uncertainty associated with the estimates, making it possible to provide a range of possible values for heavy metal concentrations at unsampled locations, rather than a single estimate.

Modeling: Geostatistics makes it possible to model the spatial structure of the data, to better understand the underlying processes that are affecting the heavy metal concentrations and predicting the spatial continuity.

Data Efficiency: Geostatistics allows for efficient use of data, as it does not require a dense sampling design and it can help to avoid biasness in sampling.

Human health risk assessment : It can be used as a supplementary method to evaluate the human health risk associated with heavy metal pollution in river sediments.

MOTIVATION:

The motivation behind the research was driven by the need to understand and address the negative impacts of heavy metal pollution on the environment and human health. The study area has seen significant urban and industrial growth, leading to an increase in pollutants being discharged into the Kosasthalaiyar River (KR), resulting in ecological degradation. The pollutants can accumulate in the sediments and move into aquatic life which can have severe effects. Despite the potential impacts, there has been no long-term monitoring study on heavy metal pollution in the KR and its immediate surroundings. Therefore, the study's goal is to assess the heavy metal pollution levels and sources of contamination in the KR and Ennore Creek using a geo-statistical approach, in order to inform effective management and remediation efforts that ultimately will lead to the protection of the aquatic life and human health as well as compliance with regulations.

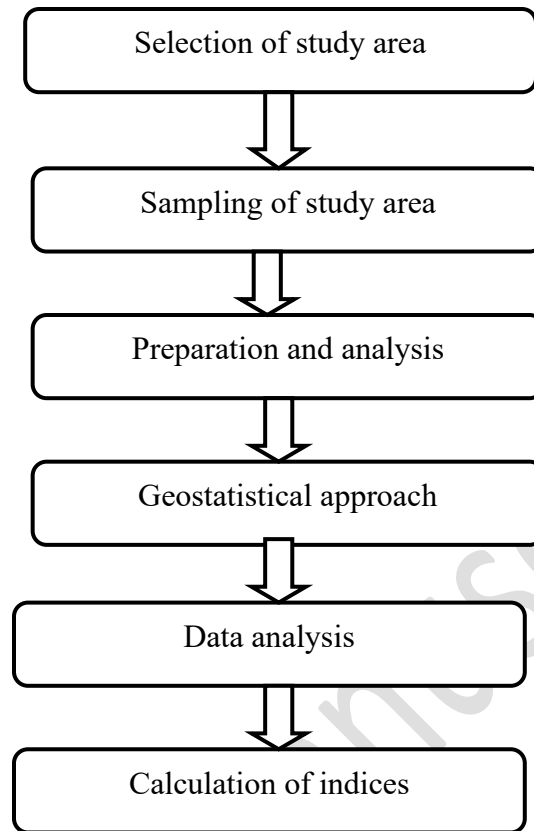


Figure 1: flow diagram of proposed scheme

The analysis and evaluation of heavy metal pollution in the Kosasthalaiyar River near Ennore Creek using a geostatistical approach would involve several specific methods and procedures.

Sampling Design: The study would involve selecting appropriate sampling locations along the river, taking into account factors such as proximity to sources of pollution and potential variability in heavy metal concentrations. A random sampling design can be used, or a sampling design that's more adaptive to the study area can be chosen.

Sample Collection: The samples of surface sediments would be collected at each sampling location, and appropriate measures would be taken to ensure the integrity and representativeness of the samples.

Sample Analysis: The collected samples would then be analyzed for a range of heavy metal parameters, such as Silver (Ag), Aluminium (Al), Calcium (Ca), Cadmium (Cd), Chloride, Cobalt (Co), Total Chromium (Cr), Copper (Cu), Mercury (Hg), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Lead (Pb), Silica (Si), Titanium (Ti), and Zinc (Zn). A variety of analytical techniques can be used for this step, such as atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, or X-ray fluorescence.

Spatial Interpolation: The data would be analyzed using geostatistical methods such as kriging to interpolate heavy metal concentrations at unsampled locations and to provide an estimate of uncertainty associated with the predictions.

Data Analysis: The data would be analyzed to calculate various pollution indices such as potential environmental hazard index (RI), the Geo-accumulation index (Igeo), the Contaminant factor (CF), the degree of contamination (DC), the potential contamination index (PCI), and the pollution load index (PLI)

Human health risk assessment: The data would be used to conduct a human health risk assessment (HHRA) of heavy metals in the sediment.

Interpretation and Conclusion: The results of the analysis and evaluation would be interpreted and conclusions would be drawn about the level and distribution of heavy metal pollution in the Kosasthalaiyar River near Ennore Creek, and about the sources and causes of pollution.

Remediation and mitigation measures: Based on the results of the study, appropriate remediation and mitigation measures can be proposed to control or reduce heavy metal pollution in the area.

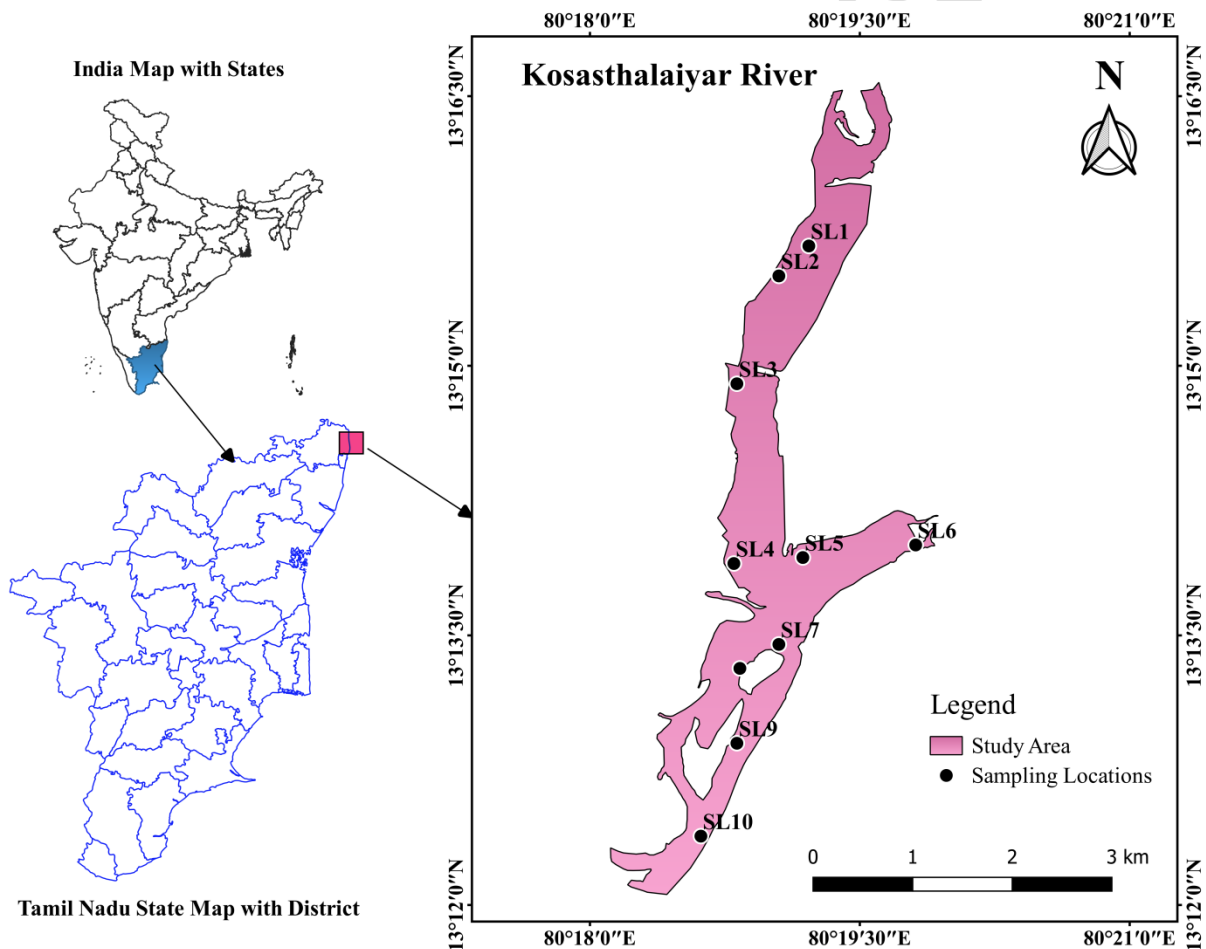


Figure 2 shows the Geographical location of the study area with sampling locations.

The study area is located along the Kosasthalaiyar River near Ennore Creek in the state of Tamil Nadu, India. Sampling locations were selected at various points along the river including upstream, downstream, and at the confluence of tributaries near the Ennore Creek.

2. Materials and Methodology

Samples of surface sediments collected at 10 sample sites selected in the study area during the pre-monsoon season were subjected to laboratory testing following USEPA 3050B and APHA 23RD EDITION protocol. 16 geochemical and Hm parameters were identified, and laboratory tests were conducted according to the standard test procedures. The tested parameters were copper (Cu), manganese (Mn), zinc (Zn), Total Chromium (Cr); (Hg), Lead (Pb), Nickel (Ni), Aluminum (Al), Calcium (Ca), Silica (Si), Titanium (Ti), Silver (Ag), Cobalt (Co), Cadmium (Cd), Molybdenum (Mo), and chloride. Concentrations of mercury (Hg), titanium (Ti), and silver (Ag) in this study area are below the detectable range.

2.1 The contamination factor (CF)

CF is another effective method to evaluate the HmC level in sediments using the background reference value (B_n) in the study area. It also represents the effects and contribution of each Hm ion in the sediments. The classifications of CF values are less than 1 is low contaminated, 1 to 3 is reasonably contaminated, 3 to 6 is considerable contamination, and greater than 6 is high and very highly contaminated sediments. The following is used to calculate the CF:

$$CF = \frac{C_n}{B_n}$$

2.2 Geo-accumulation index (I_{geo})

Muller 1969 developed the I_{geo} equation to identify the HmC in sediments. It is a more effective method to calculate the contamination level using reference values recorded in the same zone in previous studies. The recorded concentration of Hm (C_n) in sediment and B_n is the reference value of the particular Hm in the study region. The classification of contamination level in sediments is the value of I_{geo} less than equal to 0 is uncontaminated, 0 to 1 is uncontaminated to moderately contaminated, 1 to 2 is moderately contaminated, 2 to 3 is moderate to highly contaminated, greater than 4 highly to extremely contaminated and greater than 5 significantly contaminated. The following formula is used to calculate I_{geo} :

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5 \times B_i} \right]$$

2.3 The degree of contamination (Cd)

Hakanson 1980 developed the degree of contamination equation to simplify the contamination impact in the study region. It is the sum of the CF in the same region. It helps to recognize the quantitative impact of each HmC in the current region. Hakanson proposed its classification as an index value less than 6 is a low Cd, 6 to 12 is a moderate Cd, 12 to 24 is a considerable Cd, and greater than 24 is a high-level Cd. The following formula is used to calculate the Cd value:

$$C_d = \sum_{i=1}^{i=n} CF$$

2.4 The pollution load index (PLI)

Tomlinson et al. 1980 proposed the PLI equation to examine the contamination in the study region by comparing the level of contamination in the sites. PLI is calculated by taking the square root of the product of all CFs in the study region, where we already calculated in the same region. The classification of PLI value less than 1 is no elemental pollution and greater than 1 is the presence of pollution. The following was used to calculate the PLI

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times CF_4 \times CF_5 \times CF_6 \dots}$$

2.5 The potential contamination index (PCI)

The PCI is another method to evaluate the concentration of Hm presence in the sediments. The ratio of the maximum concentration of Hm (C_{max}) and the background value of respective Hm (B_n) describe the potential contamination index of the study region. The classification of PCI values is less than 1 is low contamination, 1 to 3 is reasonable contamination, and greater than 3 is severe contamination. The following formula is used to calculate PCI:

$$PCI = \frac{C_{max}}{B_n}$$

2.6 Potential ecological risk (PERI)

Hakanson 1980 proposed the PERI to evaluate the detrimental impact of the Hm's in the sediments. The PERI value indicates the ecological sensitivity of each Hm concentration. The PERI value was calculated from the contamination factor and toxic response coefficient of each Hm. A value of PERI less than 95 is a low potential risk, 95 to 190 is a moderate risk, 190 to 380 is a considerable risk, and greater than 380 is a very high risk. It is calculated using the following formula:

$$PERI = \sum P_n$$

$$P_n = T_n \times CF_n$$

2.7 Human health risk evaluation

Human population and human health are the most significant factor in assessing sediment HmC. Recent research described that humans are highly exposed to HmC and increased the impact of carcinogenic and non-carcinogenic risks on human health. The United States Environmental Protection Agency recommendations are followed to calculate the risk assessment in the study area. The three values of Chronic daily intake $CDI_{ingestion}$, $CDI_{inhalation}$, and CDI_{dermal} are more significant values that were calculated to identify cancer and non-cancer disease related to HmC. The reference values for CDI calculation are given in Table 1. The following formula was used to find the values:

$$CDI_{ingest} = \frac{C \times IR \times EF \times ED \times CF}{BW \times AT}$$

$$CDI_{inhalation} = \frac{C \times InhR \times EF \times ET \times ED}{PEF \times BW \times AT}$$

$$CDI_{dermal} = \frac{C \times SA \times AF \times ABS \times ED \times EF \times CF}{BW \times AT}$$

Table 1. Adopted CDI reference values (source: Amit Kumar et al. 2020)

S.	Parameter	Units	Adult	Children
01.	ABS (Absorption factor)	Unit less	0.001	0.001
02.	AF (Soil to skin adherence factor)	mg cm ⁻²	0.07	0.2
03.	ATc (Average time for carcinogenic)	Days	365 x 70	365 x 70
04.	ATnc (Average time for non-carcinogenic risk)	Days	365 x 35	365 x 35
05.	BW (Body weight)	Kg	70	15
06.	CF (Conversion Factor)	mg day ⁻¹	10 ⁻⁶	10 ⁻⁶
07.	ED (Exposure duration)	Years	35	6
08.	EF (Exposure frequency)	Days Years ⁻¹	312	200
09.	ET (Exposure time)	h day ⁻¹	8	4
10.	InhR (Inhalation Rate)	m ³ h ⁻¹	1.56	1.2
11.	IR (Ingestion rate of soil)	mg day ⁻¹	100	200
12.	PEF (Particle emission factor)	mg kg ⁻¹	1.36 x 10 ⁹	1.36 x 10 ⁹
13.	SA (Skin surface area available for contact)	cm ²	6032	2373

Where C – concentration of Hm's in sediments (mg kg⁻¹).

$$HQ = \frac{CDI}{RfD}$$

$$HI = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{der}$$

3. Result and discussion

3.1 Manganese

Manganese is one of the most predominant Hm's presents in the sediment naturally, rocks of sedimentary and hydrothermal sedimentary genesis (Santamaria and Sulsky 2010; Haqueetla. 2022). In the present study, manganese ranges from 78.6 to 110mg/kg with a mean of 93.12mg/kg. The sampling sites S1, 2, and 3 are recorded as having a higher concentration of manganese in the investigation zone. The spatial analysis revealed that a lower concentration of manganese was recorded in the northern part and southwest part, higher manganese level was

recorded in the northern lump of the concerned KR (Fig 2a). The excess concentration of manganese in the sediments is easily transferred to the human body, and it will cause damage to the lungs, liver, and kidneys.

3.2 Copper

In general, copper is the most crucial plant growth and development micronutrient. In addition, it helps to increase plants' photosynthesis process and respiration (Angelaki et al. 2022; Scott-Fordsmand et al. 2022). In this study, copper concentration varies from 8.65 to 18.9 mg/kg with a mean of 13.30 mg/kg. The elevated concentration of copper was recorded in S4, S1, S2, and S10 sampling sites. The spatial analysis revealed that the lower concentration of copper was recorded in the southern and southwest parts, while the higher concentration of copper was recorded in the eastern and northern sides of the study area (Fig 2b). The elevated concentration of copper causes serious health issues on human health such as bone disease, nervous system malfunctioning, and immune system problems.

3.3 Zinc

In improper disposal of municipal waste, zinc-containing waste from industries and electrical utilities are the primary source of zinc concentration in soil and groundwater (Chen et al. 2022; Maqsood et al. 2022). In the study region, zinc levels vary from 18.6 to 42.3 mg/kg, averaging 31.5 mg/kg. The sampling sites S2, S7, S8, and S9, have recorded a higher zinc concentration in sediments. The spatial analysis revealed that the lower concentration of zinc was recorded in the northern part, and the higher concentration of zinc was recorded in the eastern and southern parts of the study area (Fig 2c). The higher zinc concentration causes vomiting, diarrhea, and abdominal pain in human health.

3.4 Lead

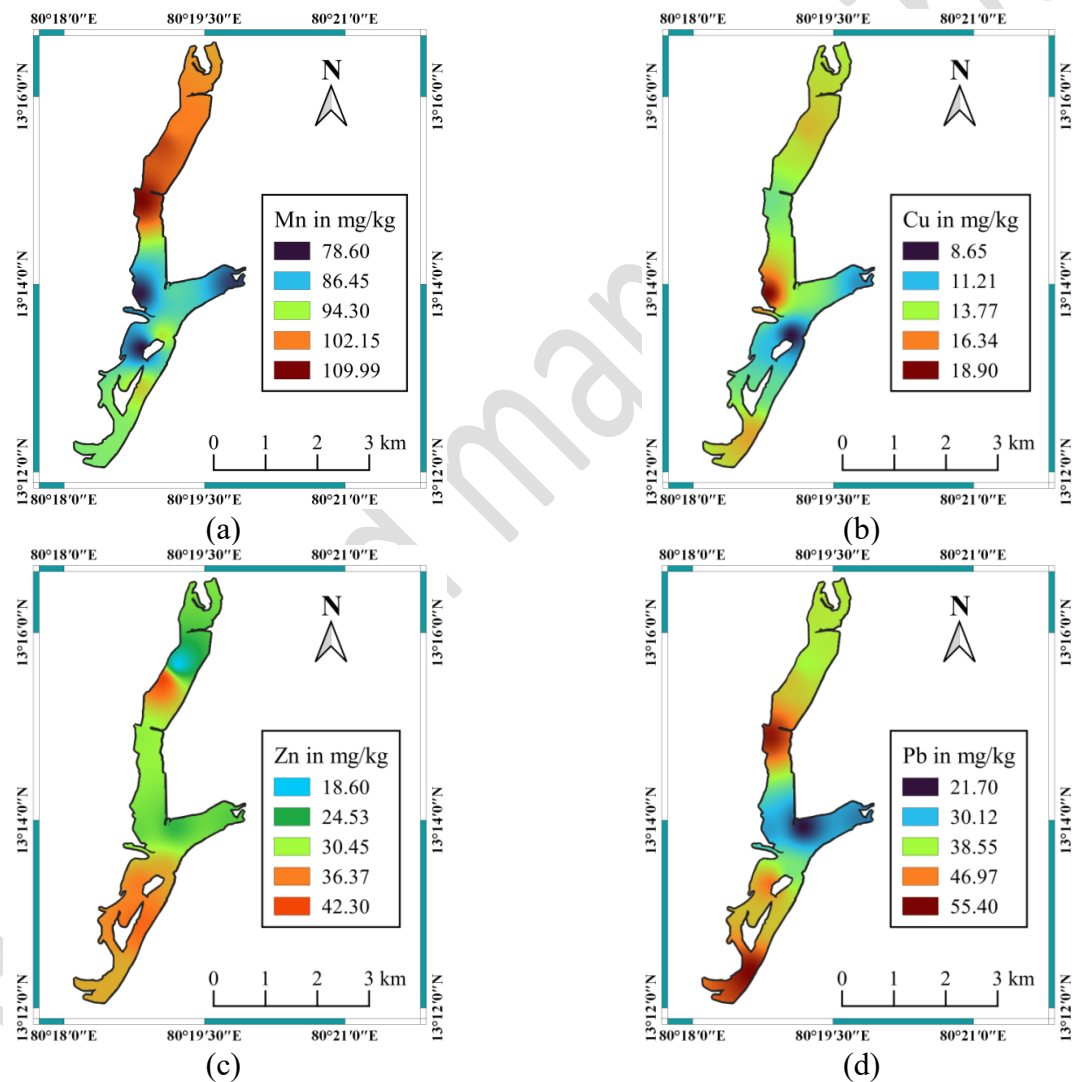
Lead is a naturally occurring mineral in sediments with a combination of igneous, metamorphic, and sedimentary rock (Ma et al 2022; Schmidt et al. 2022). The lead concentration in the study region ranged from 21.7 to 55.4 mg/kg with a mean of 39.37 mg/kg. The higher lead concentration was recorded in sampling sites S3, S10, and S8. The spatial analysis revealed that the lower lead concentration was recorded in the southern and southwest parts, and the higher lead concentration was recorded in the eastern and northern lump of the mentioned study area (Fig 2d). The excess concentration of lead cause root and plant growth problem, reduce chlorophyll production in plants and also affects the water and protein content in the plants. It will also cause human health such as brain damage, kidney problem, anemia, and weakness.

3.5 Nickel

In the study area, nickel varied from 9.8 to 24.6 mg/kg with a mean of 16.73 mg/kg. The higher concentration was recorded in sampling sites such as S3, S8, and S4. The spatial analysis revealed that the lower nickel concentration was recorded in the southern and southwest lump, and the higher concentration of nickel was recorded in the eastern and northern parts of the study area (Fig 2e). The higher level of nickel in sediments affects human health and cause allergy, kidney diseases, lung fibrosis, cardiovascular problem, and nasal cancer. The primary reason for nickel in sediments are anthropogenic activities, namely mining smelting, organic amendments, sewage sludge disposal, and compost-based sludge disposal (Wei et al. 2022; Dieu et al. 2022).

3.6 Aluminum

Aluminum is not a harmful Hm present in sediments with various bonds with clay particles and organic matter (Fernandes et al. 2021). The aluminum concentration in the prevailing study region ranged from 0.62 to 1.24 mg/kg with a mean of 0.91 mg/kg. The higher concentration was recorded in the S1, S2, S3, and S9 sampling sites. The spatial analysis revealed that the lower aluminum concentration was recorded in the northern and southeast parts, and the higher aluminum concentration was recorded in the western and northern parts of the concerned study area (Fig 2f). Continuous exposure of aluminum contaminated sediments causes lung diseases, abnormal chest problems, central nervous system damage, and heart problem (Alamdari et al. 2022)



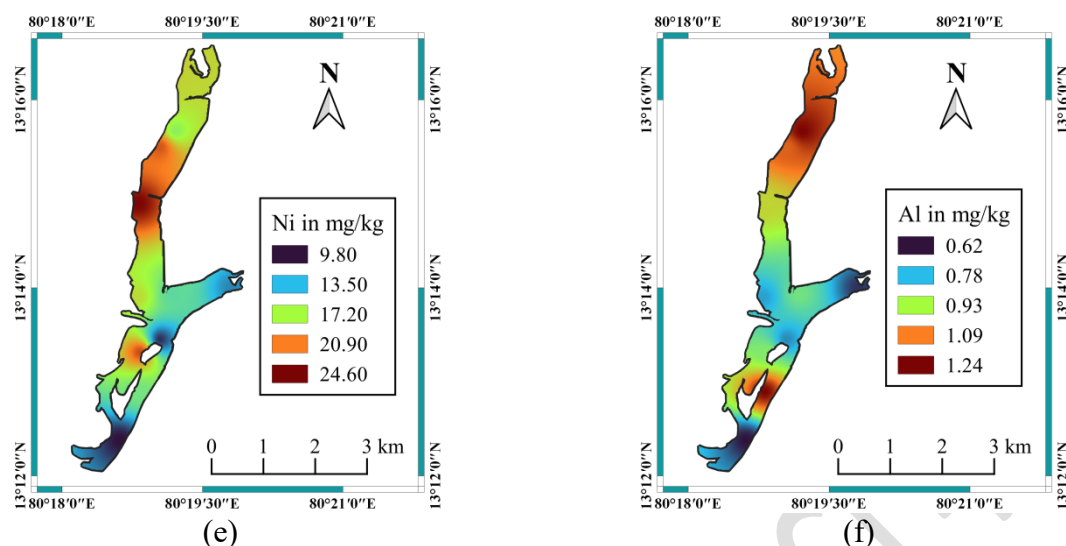


Figure 2 Spatial analysis of a) Manganese b) Copper c) Zinc d) Lead e) Nickel f) Aluminum

3.7 Calcium

Calcium naturally occurs in the rock sedimentary layer and soil. The allowable concentration of calcium present in the soil help to enhance the growth of plants, and it acts as the primary nutrient for all crops (Noolu et al. 2021; Das et al. 2022). The calcium concentration in this region ranged between 89.6 to 175 mg/kg, with a mean of 138.16 mg/kg. The higher concentration was logged in the S4, S2, S6, and S10 sampling sites. The spatial analysis revealed that the low level of calcium was logged in the southern part and north-west parts, and the high calcium was logged in the southern-east part of the study area (Fig 3a).

3.8 Silica

The presence of silica in sediments and soil helps strengthen the plant's cells and reduce water loss in agriculture. It also increases the plant tolerance, frost, and lodging action on the plants (Brand et al. 2021; Barbhuiya et al. 2021). In general, sandy soil contain a higher percentage of silica content. The concentration of silica in this region ranged between 4.1 to 6.2 mg/kg with a mean of 5.49 mg/kg. The higher concentration was recorded in the S3, S4, S5, and S9 sampling sites. The spatial analysis revealed that the lower silica concentration was recorded in the southern and southwest parts, while the higher concentration of silica was recorded in the eastern and northern parts of this region (Fig 3b).

3.9 Cobalt

Cobalt is a significant element in soil that plays a critical role in the plant growth and photosynthesis process. It is necessary for stem thickness, growth, and expanding leaf discs (Banerjee et al. 2021; Dieu et al. 2022). The concentration of cobalt in the study region ranged from 0.05 to 0.14 mg/kg with a mean of 0.089 mg/kg. The higher concentration was recorded in the S1, S2, S3, and S9 sampling sites. The spatial analysis revealed that the lower concentration of cobalt was recorded in the southern and southwest lump, and the higher concentration of cobalt was recorded in the eastern and northern parts of the study area (Fig 3c).

3.10 Cadmium

Cadmium is another important element to investigate the contamination of sediments in the river bed and basin. Urbanization and industrialization are the primary reason for the cadmium contamination in soil. It will affect plant growth and intensively affect agriculture practices (Yang et al. 2022; Kumar et al. 2022). The cadmium concentration in this region varies from 1.25 to 2.78mg/kg, with a mean of 1.83 mg/kg. The higher concentration was logged in the S1, S2, S3, and S9 sampling sites. The spatial analysis revealed that a lower cadmium concentration was logged in the northern and southeast parts, and a higher cadmium concentration was logged in the eastern part of the study area (Fig 3d).

3.11 Molybdenum

Molybdenum is an element rich in coastal sediments, followed by copper concentration. Molybdenum is a Hm-strong chalcophile element forming several minerals, including molybdenite (Hui et al. 2021). In the study area, molybdenum concentration ranges from 0.34 to 0.69 with a mean of 0.478. A higher Mo was recorded in the two-sampling sites, S1 and S4. The spatial analysis revealed that the lower concentration of Mo was logged in the north-west part and southern parts, higher level of Mo was logged in the north and eastern parts of this area (Fig. 3e). The elevated concentration of Mo in sediments affects the plant growth, depressed tillering and leaves are turning to yellow color (Han et al. 2019)

3.12 Chloride

Chloride is the more important parameter in assessing the potential risk of Hm concentration in the ecological field (Hammam et al. 2020). In this region, chloride concentration ranged between 3800 to 6100 mg/l, averaging 5310 mg/l. More chloride concentration was recorded in S7, S3, S4, and S5 sampling sites. The spatial analysis revealed that the lower chloride concentration was recorded in the southern and southwest parts, and the higher concentration of chloride was recorded in the eastern and northern parts of the study area (Fig 3f). The elevated concentration of chloride cause burning pain, redness, and blister on the skin and also affects the throat, nose, and eyes (Xiao et al. 2022).

3.13 Chromium

An increase in nitrification and denitrification is the predominant process for high chromium contamination in soil (Borah et al. 2018; Khan et al. 2020). It reduces the bacterial community in the soil and increases the chromium concentration. The chemical level of Chromium in this region ranged from 25.8 to 94.5mg/kg with a mean of 59.23 mg/kg. The higher concentration was recorded in the S1, S3, S4, and S10 sampling sites. The spatial analysis revealed that the lower concentration of Chromium was recorded in the southern and southwest parts, and the higher concentration of Chromium was recorded in the eastern and northern parts of the study region (Fig 4).

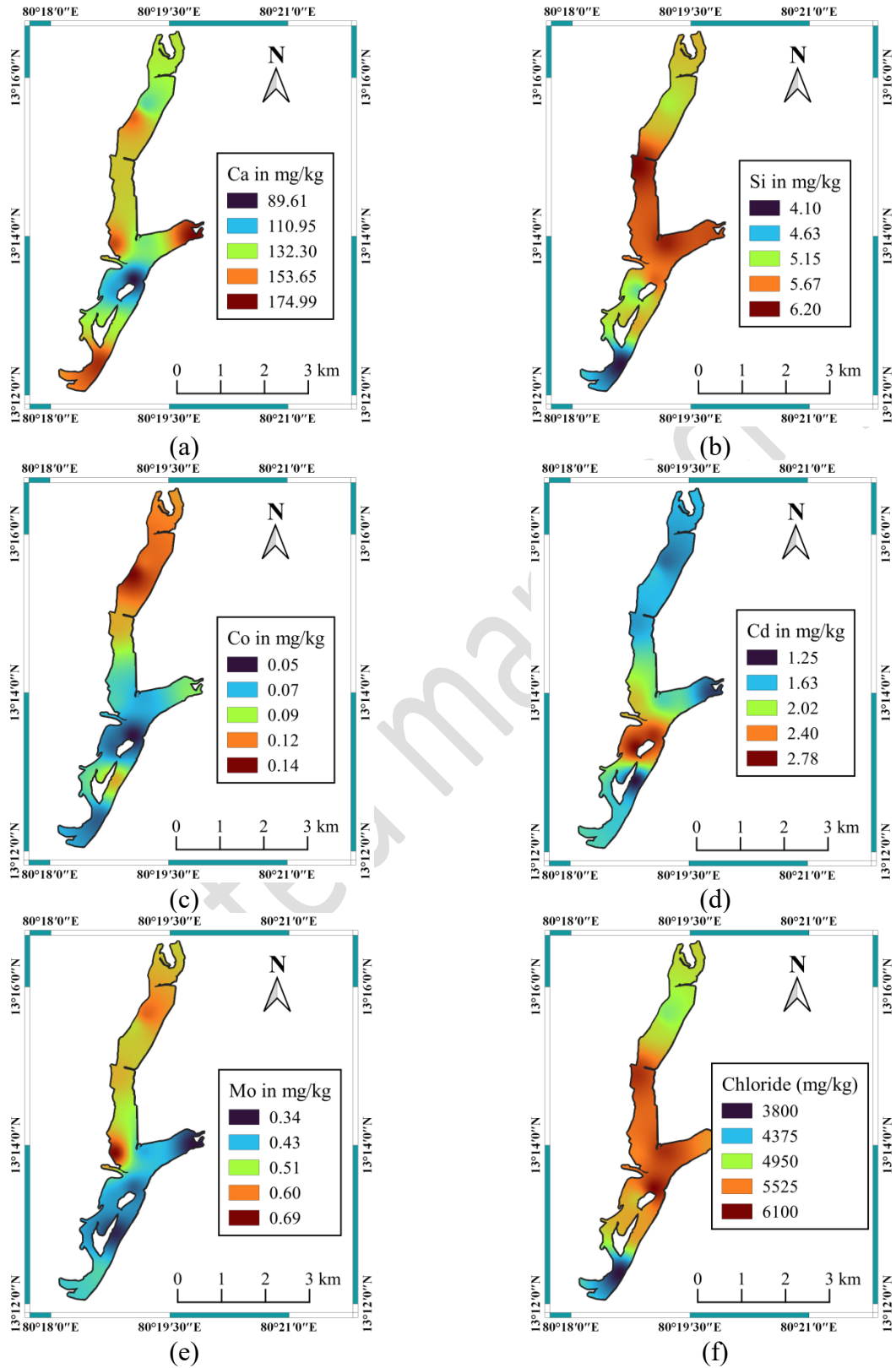


Figure 3 Spatial analysis of a) Calcium, b) Silica, c) Cobalt, d) Cadmium, e) Molybdenum f) Chloride

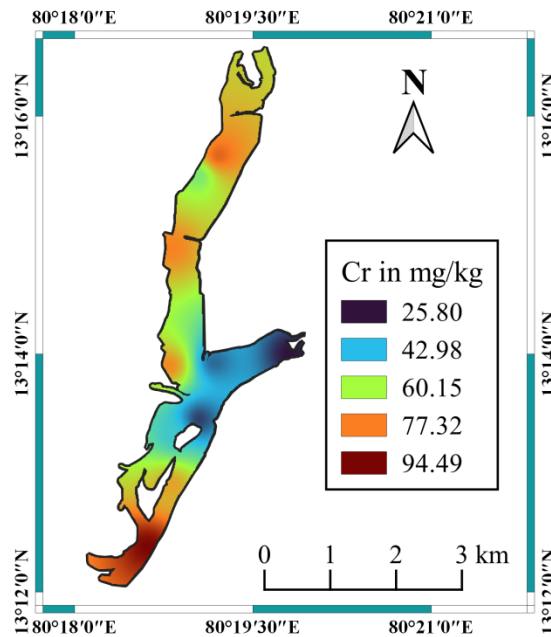


Figure 4 Spatial analysis of Chromium

4. Heavy metal accumulation evaluation

In the present study, detailed heavy accumulation was evaluated and spatially analyzed in the contaminated zone by following the inverse distance weighted method in QGIS. The contamination factor for each element revealed that all the sample locations were moderately contaminated by Hm's such as Mn, Cu, Zn, Pb, Ni, Al, Ca, Si, Co, Cd, and Mo. The contamination factor for Chromium revealed that 80% of samples were moderately contaminated, and 20% of samples were considerably contaminated in the study region (Table.2 and 3). The spatial analysis of the contamination factor for each element is shown in Fig.6. It also revealed that 100% of the sample location were moderately contaminated except for Chromium. The southern part of the study region was identified as considerably contaminated with chromium elements.

The results of geo accumulation(Igeo) index for each elements revealed that 100% of the sample location were unpolluted with reference to manganese elements, 50% of the sample were unpolluted and 50 % of the sample location were unpolluted to moderately polluted due to copper elements, 40% of the sample were unpolluted and 60 % of the sample location were unpolluted to moderately polluted due to zinc contamination, 40% of the sample were unpolluted and 60 % of the sample location were unpolluted to moderately polluted due to zinc contamination, 30% of the sample were unpolluted and 70 % of the sample location were unpolluted to moderately polluted due to chromium contamination, 30% of the sample were unpolluted and 70 % of the sample location were unpolluted to moderately polluted due to lead contamination, 30% of the sample were unpolluted and 70 % of the sample location were unpolluted to moderately polluted due to nickel contamination, 60% of the sample were

unpolluted and 40 % of the sample location were unpolluted to moderately polluted due to aluminum contamination, 50% of the sample were unpolluted and 50 % of the sample location were unpolluted to moderately polluted due to calcium contamination, 90% of the sample were unpolluted and 10 % of the sample location were unpolluted to moderately polluted due to silica contamination, 40% of the sample were unpolluted and 60 % of the sample location were unpolluted to moderately polluted due to cobalt contamination, 70% of the sample were unpolluted and 30 % of the sample location were unpolluted to moderately polluted due to cadmium contamination, 60% of the sample were unpolluted and 40 % of the sample location were unpolluted to moderately polluted due to aluminum contamination (Table.2 and 4). The spatial analysis of Igeo revealed that the south-west and southern part of the study region was identified as unpolluted, and the northern and east part of the study area was identified as unpolluted to moderately polluted zone (Fig.7). The result of the pollution load index for all elements revealed that the value of PLI greater than 1 and it indicates that presence of pollution in the region (Table.5). The CD results revealed that the contaminated of Mn, Cu, Al, Ca, Si, Cd, and Mo were identified as reasonable contamination (Cd value ranges from 8 to 16), the degree of contamination of Zn, Cr, Pb, Ni, and Co were identified as considerable contaminated elements and the value ranges from 16 to 32 (Table.5). The potential contamination index results shows that all the sample location fell under the reasonable contamination ($1 < PCI < 3$) for all the Hm elements. The potential ecological risk for Mn, Cu, Zn, Cr, Pb, Ni, and Co divulged that low potential ecological risk ($PERI < 95$), PERI value for Cd greater than 350, and it is a very high ecological risk, PERI value for Mo range between 190 to 380 and it is the considerable ecological risk (Table.5).

4.1 Human health risk evaluation

The pathways of sediment contamination exposure (children and adults) chosen were ingestion, inhalation, and dermal contact for the selected parameter in the concerned study area were calculated and existing in Table.6. The sum of the $HQ_{\text{ingestion}}$, $HQ_{\text{inhalation}}$, and HQ_{dermal} is equal to the total hazards index. The manganese hazards index value for children varies from $6.41E-03$ to $8.98E-03$ with a mean of $7.60E-03$, and for adults, the value ranges from $6.89E-04$ to $9.64E-04$ with a mean of $8.16E-04$. The nickel hazards index value for children varies from $5.60E-03$ to $1.41E-02$ with a mean of $9.56E-03$, and for adults, the value ranges from $6.01E-04$ to $2.15E-01$ with a mean of $1.03E-03$. The cadmium hazards index value for children varies from $2.86E-02$ to $6.35E-02$ with a mean of $4.20E-02$, and for adults, the value ranges from $3.07E-03$ to $6.82E-03$ with a mean of $4.50E-03$. The molybdenum hazards index value for children varies from $7.77E-04$ to $1.58E-03$ with a mean of $1.09E-03$, and for adults, the value ranges from $8.34E-05$ to $1.69E-04$ with a mean of $1.17E-04$. The chromium hazards index value for children varies from $9.83E-02$ to $3.60E-01$ with a mean of $2.26E-01$, and for adults, the value ranges from $1.05E-02$ to $3.86E-02$ with a mean of $2.42E-02$. The zinc hazards index value for children varies from $7.08E-04$ to $1.61E-03$ with a mean of $1.20E-03$, and for adults, the value ranges from $7.60E-05$ to $1.73E-04$ with a mean of $1.29E-04$. The results show that the human health risk is very low for the selected parameter in the study region (Table.6).

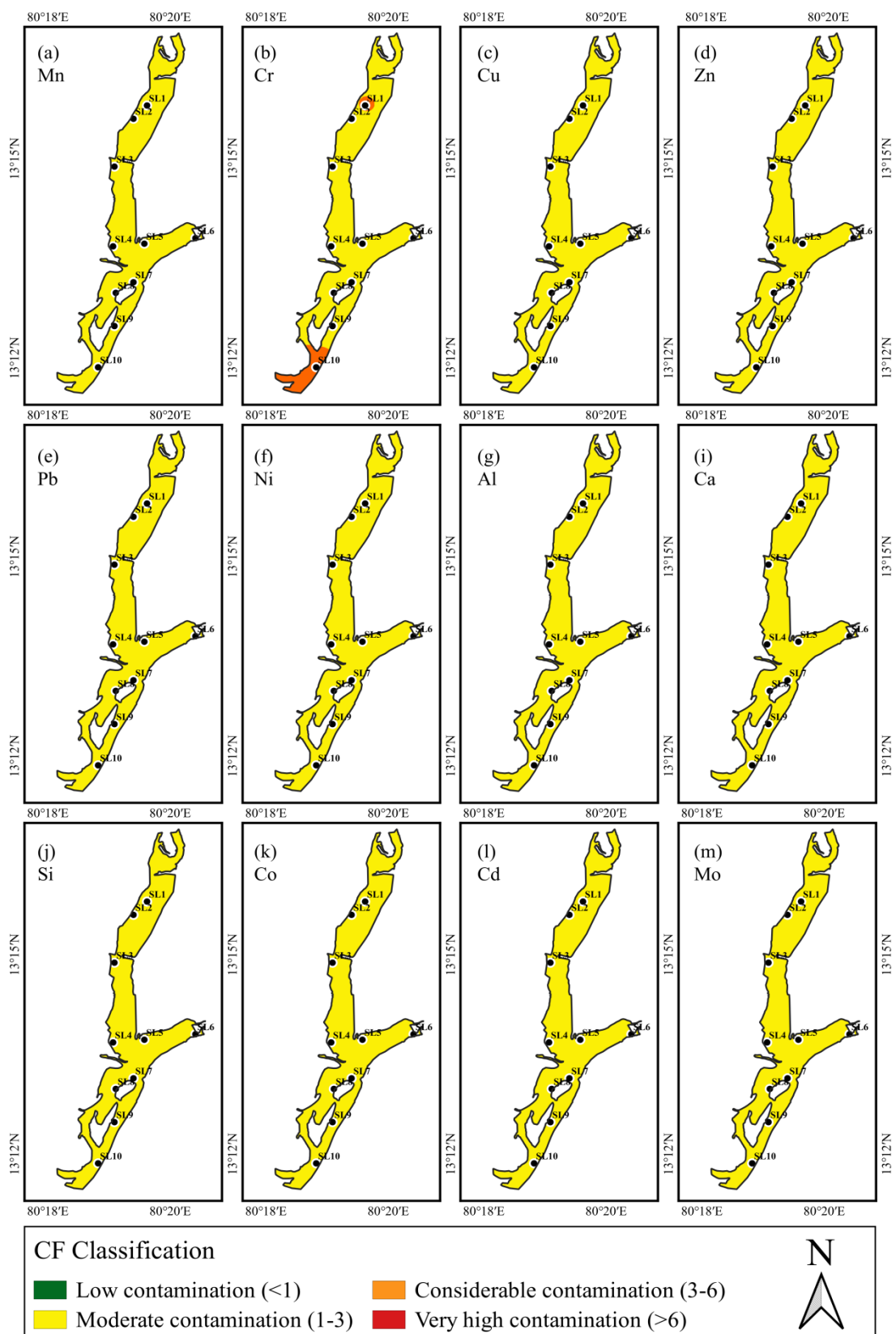


Figure 6 Spatial analysis of contamination factor for twelve Hm elements

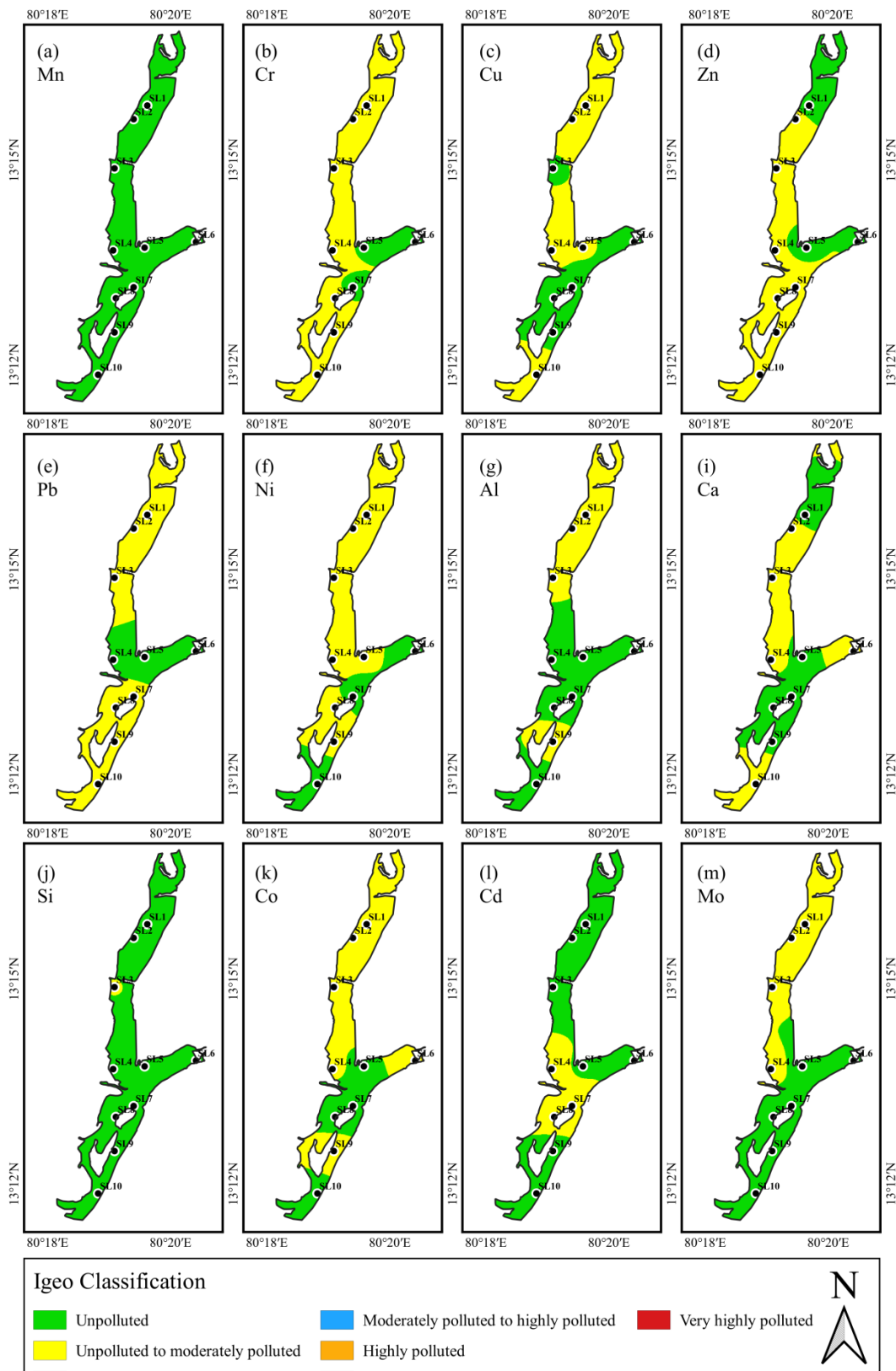


Figure 7 Spatial analysis of Igeo for twelve Hm elements

Table.2 Description of Index classification of Hm accumulation in the study region

[illegible]

Table.3 Shows the contamination factor values for the geochemical parameters.

Samples	Geoaccumulation Index (igeo) of test parameters											
	Mn	Cu	Zn	Cr	Pb	Ni	Al	Ca	Si	Co	Cd	Mo
SL-01	-0.063	0.069	-0.176	0.319	0.074	0.050	0.125	-0.049	-0.073	0.204	-0.112	0.085
SL-02	-0.046	0.042	0.181	0.151	0.116	0.177	0.081	0.070	-0.056	0.271	-0.048	0.025
SL-03	-0.030	-0.009	0.026	0.298	0.221	0.224	0.023	0.024	0.004	0.166	-0.083	0.048
SL-04	-0.174	0.163	-0.002	0.292	-0.056	0.093	-0.093	0.084	-0.025	0.028	0.071	0.131
SL-05	-0.119	0.014	-0.041	-0.046	-0.176	0.012	-0.029	-0.031	-0.004	-0.030	-0.030	-0.084
SL-06	-0.166	-0.092	-0.016	-0.176	-0.084	-0.077	-0.156	0.115	-0.018	0.079	-0.146	-0.176
SL-07	-0.091	-0.176	0.093	-0.103	0.039	-0.146	-0.105	-0.176	-0.025	-0.176	0.152	-0.128
SL-08	-0.176	-0.060	0.119	0.077	0.167	0.183	-0.019	-0.099	-0.099	-0.097	0.171	-0.095
SL-09	-0.083	-0.016	0.144	0.271	0.116	0.031	0.125	-0.001	-0.049	0.166	-0.176	-0.164
SL-10	-0.106	0.080	0.088	0.388	0.231	-0.176	-0.176	0.097	-0.176	-0.097	-0.045	-0.045

Table.4 Shows the contamination factor values for the geochemical parameters.

Sample Locations	Contamination Factor Values of Test Parameters											
	Mn	CU	Zn	Cr	Pb	Ni	Al	Ca	Si	Co	Cd	Mo
SL-01	1.298	1.757	1.000	3.128	1.779	1.684	2.000	1.339	1.268	2.400	1.160	1.824
SL-02	1.349	1.653	2.274	2.124	1.959	2.255	1.806	1.763	1.317	2.800	1.344	1.588
SL-03	1.399	1.468	1.591	2.981	2.498	2.510	1.581	1.585	1.512	2.200	1.240	1.676
SL-04	1.004	2.185	1.495	2.938	1.318	1.857	1.210	1.819	1.415	1.600	1.768	2.029
SL-05	1.141	1.549	1.366	1.349	1.000	1.541	1.403	1.395	1.488	1.400	1.400	1.235
SL-06	1.024	1.214	1.446	1.000	1.235	1.255	1.048	1.953	1.439	1.800	1.072	1.000
SL-07	1.218	1.000	1.860	1.182	1.641	1.071	1.177	1.000	1.415	1.000	2.128	1.118
SL-08	1.000	1.306	1.973	1.791	2.203	2.286	1.435	1.194	1.195	1.200	2.224	1.206
SL-09	1.239	1.445	2.091	2.802	1.959	1.612	2.000	1.496	1.341	2.200	1.000	1.029
SL-10	1.176	1.803	1.839	3.663	2.553	1.000	1.000	1.875	1.000	1.200	1.352	1.353

Table.5 Shows the major pollution indexes with contamination classification

Parameter	Index Value							
	PLI	Pollution Class	DC	Pollution Class	PCI	Pollution Class	PERI	Pollution Class
Mn	1.177	Pollution Presence	11.847	Reasonable Contamination	1.399	Reasonable Contamination	11.847	Low potential ecological risk
Cu	1.505	Pollution Presence	15.382	Reasonable Contamination	2.185	Reasonable Contamination	76.908	Low potential ecological risk
Zn	1.651	Pollution Presence	16.935	Considerable Contamination	2.274	Reasonable Contamination	16.935	Low potential ecological risk
Cr	2.105	Pollution Presence	22.957	Considerable Contamination	3.663	Severe Contamination	45.915	Low potential ecological risk
Pb	1.741	Pollution Presence	18.143	Considerable Contamination	2.553	Reasonable Contamination	90.714	Low potential ecological risk
Ni	1.633	Pollution Presence	17.071	Considerable Contamination	2.510	Reasonable Contamination	85.357	Low potential ecological risk
Al	1.424	Pollution Presence	14.661	Reasonable Contamination	2.000	Reasonable Contamination	NA	-
Ca	1.511	Pollution Presence	15.420	Reasonable Contamination	1.953	Reasonable Contamination	NA	-
Si	1.330	Pollution Presence	13.390	Reasonable Contamination	1.512	Reasonable Contamination	NA	-
Co	1.689	Pollution Presence	17.800	Considerable Contamination	2.800	Reasonable Contamination	89.000	Low potential ecological risk
Cd	1.418	Pollution Presence	14.688	Reasonable Contamination	2.224	Reasonable Contamination	440.640	Very high ecological risk
Mo	1.367	Pollution Presence	14.059	Reasonable Contamination	2.029	Reasonable Contamination	253.059	Considerable ecological risk

Table.6 Hazards index value for Hm accumulation in the study area

Children						Adult					
Mn	Ni	Cd	Mo	Cr	Zn	Mn	Ni	Cd	Mo	Cr	Zn
8.32E-03	9.43E-03	3.31E-02	1.42E-03	3.07E-01	7.08E-04	8.94E-04	1.01E-03	3.56E-03	1.52E-04	3.30E-02	7.60E-05
8.65E-03	1.26E-02	3.84E-02	1.23E-03	2.09E-01	1.61E-03	9.29E-04	1.36E-03	4.12E-03	1.32E-04	2.24E-02	1.73E-04
8.98E-03	1.41E-02	3.54E-02	1.30E-03	2.93E-01	1.13E-03	9.64E-04	1.51E-03	3.80E-03	1.40E-04	3.14E-02	1.21E-04
6.44E-03	1.04E-02	5.05E-02	1.58E-03	2.89E-01	1.06E-03	6.91E-04	1.12E-03	5.42E-03	1.69E-04	3.10E-02	1.14E-04
7.32E-03	8.63E-03	4.00E-02	9.60E-04	1.33E-01	9.67E-04	7.86E-04	9.26E-04	4.29E-03	1.03E-04	1.42E-02	1.04E-04
6.57E-03	7.03E-03	3.06E-02	7.77E-04	9.83E-02	1.02E-03	7.05E-04	7.54E-04	3.29E-03	8.34E-05	1.05E-02	1.10E-04
7.81E-03	6.00E-03	6.08E-02	8.68E-04	1.16E-01	1.32E-03	8.38E-04	6.44E-04	6.52E-03	9.32E-05	1.25E-02	1.41E-04
6.41E-03	1.28E-02	6.35E-02	9.37E-04	1.76E-01	1.40E-03	6.89E-04	1.37E-03	6.82E-03	1.01E-04	1.89E-02	1.50E-04
7.95E-03	9.03E-03	2.86E-02	8.00E-04	2.75E-01	1.48E-03	8.53E-04	9.69E-04	3.07E-03	8.58E-05	2.96E-02	1.59E-04
7.54E-03	5.60E-03	3.86E-02	1.05E-03	3.60E-01	1.30E-03	8.09E-04	6.01E-04	4.15E-03	1.13E-04	3.86E-02	1.40E-04

5. Conclusion

The present study was directed in the northern part of Tamil Nadu, India, to assess the ecological risk and human health risk hazards such as carcinogenic and non-carcinogenic risk evaluation using sixteen various sediments elements. The ecological risk assessment results concluded that cadmium, Chromium, and molybdenum are notable elements that are the primary reason for ecological risk impact in the study region. The ecological indices revealed that the presence of pollution had been identified, and the contamination level is in the initial stage. The present contamination factors such as municipal waste disposal, industrial activities, and human activities are continuing in the future and it causes serious ecological risks in this present region. The HHRA results show that very low level of risk for human health in the study region. But the presence of contamination may be affecting the plant growth and agriculture activities in and around the study region. Such assessments provide important information to policy-makers, environmental activists, and foresters to mitigate the potential risk of alluvial pollution in humans, ecology, and the environment and take precautionary mitigation measures.

The choice of using a geostatistical approach in the analysis and evaluation of heavy metal pollution in the Kosasthalaiyar River near Ennore Creek is based on its ability to handle spatial data and incorporate spatial autocorrelation, its ability to interpolate and estimate heavy metal concentrations in unsampled locations, its ability to model the spatial structure of the data, and its ability to evaluate the uncertainty and human health risk associated with heavy metal pollution.

Author contributions

Sanghita Sen performed the experimental design, sampling campaigns, and water quality analysis and prepared the manuscript text. Karuppasamy Sudalaimuthu performed the literature review and the model configuration, analyzed and interpreted the data and results, and prepared the manuscript text.

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Conflict of Interest

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication, falsification, double publication and, or submission, and redundancy, have been entirely witnessed by the authors.

Declaration:

Ethics Approval and Consent to Participate:

No participation of humans takes place in this implementation process

Human and Animal Rights:

No violation of Human and Animal Rights is involved.

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