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Identification of Surface Water Contamination Zones and its Sources on Mahanadi River, Odisha Using Entropy-Based WQI and MCDM Techniques

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Abstract

Information entropy, geographic information systems (GIS), and an examination of the use of TOPSIS and ELECTRE as multi-objective decision-making tools, this study demonstrates an integrated approach to investigating surface water quality for drinking purposes and applying it to the Mahanadi River in Odisha. 19 distinct locations and 20 physicochemical factors were examined for this aim over a 7-year period (2016-2023). EWQI's classification depicts 84.21% of the samples belongs to good category, 10.53% falls under the poor group, and eventually, 5.26% belongs to extremely poor class. To classify different levels of pollution, multivariate statistical analysis framework namely, Principal Component Analysis (PCA), Cluster Analysis (CA) and Discriminant Analysis (DA) were implemented in the on-going work. In case of CA, the results suggests that by separating the locations into three major groupings, such as relatively more polluting, medium-polluted, and less polluted locations, it depicts site similarity. Also, DA analysis highlights the linkages between the stations. PC could provide a good explanation for 93.92 % total fluctuation in the water quality. In addition, this study clearly justifies the effectiveness of all finding’s outcomes discussed above by the application of TOPSIS and ELECTRE in prioritizing decisions, based on their comparative levels of pollution. Spatial variation maps of all water quality parameters and all methods illustrated above specify that St. (8), (9) and (19) have poor water quality. Leaching, organic, and natural pollutants, industrial and home waste water, soil erosion and weathering, have all been identified as major contributors to river water pollution.

Keywords

Information entropy, GIS, ELECTRE, Mahanadi River, Multivariate analysis, TOPSIS

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1. Introduction

The most significant freshwater sources that are readily usable by humans are rivers [1]. Additionally, it serves as a landfill for industrial and human garbage [2]. This led to river contamination, which has elevated it to the top of the environmental worries list [3]. Despite the fact that this resource can be replenished, rapid grow of commercial institutions, rise in population and industrialization that creates tremendous pressure on the water supply [4]. Among the most fundamental sources of water on the globe is surface water, which is used for essential purposes like drinking, agriculture, and industry [5]. In addition, the quality has declined due to the overuse of water resources and the exponential growth in population [6]. Unregulated household, agricultural, and industrial activity pollution exists in developing nations [7]. In light of this, it is crucial to evaluate and keep track of the water quality of the accessible resources, which are mostly used for drinking [8]. Too far, a variety of methods and criteria have been generated to provide water quality metrics. All agree that the Water Quality Index (WQI) is an important strategy for categorizing and regulating the aquatic environment [9]. Recently, methods for measuring water quality indexes have been devised and hence, it is a crucial component in the grading and maintenance of surface water quality [10]. Entropy WQI's representation of water quality enables a better assessment of the circumstances of water quality in various locations and, as a result, a better allocation of resources to the areas that need them the most [11]. Entropy theory has been utilized frequently over the past ten years to analyze water quality and has been found to be more accurate than other indexing techniques [12]. The literature shows that the entropy weighted method has been frequently used [13]. Geographical Information System (GIS) is a crucial tool for mapping the quality of surface water nowadays [14]. These programs include geographical analysis and its capabilities, that can handle massive amounts of data [15]. Numerous research has been carried out to evaluate water quality utilizing WQI within a GIS framework [16]. Additionally, GIS-based mapping and IDW are crucial for resource management that is sustainable [17]. An effective method for analyzing the characteristics of physicochemical parameters and figuring out how they relate to one another is multivariate statistical analysis (MSA) [18, 19]. A robust data mining approach called hierarchical cluster analysis (HCA) is applied to categorize elements are that are grouped based on the degree to which their qualities resemble one another [20]. The statistical method known as discriminant analysis (DA), which is based on regression, that enables us to create discriminant functions and it’s expressed in the form of DFs [21]. It is observed that a linear mixture of unrelated variables called a DF makes a distinction between different dependent variable categories [22]. A helpful method for clarifying large data sets in complex formats and minimizing process distortion is principal component analysis (PCA). It also motivates us to be alert to factors that could lead to pollution or have an impact on the quality of the water [23]. Recently, models using multi-criteria decision-making techniques and growing computer technology have been created and used to create programs for rehabilitation and damage analyses in wastewater systems [24]. For multi-criteria analysis, a most prominent method termed as “Elimination and Choice Expressing Reality (ELECTRE)”, which is referred to be called as outranking method, is an appropriate way for selecting between choices [25]. One of the most effective and precise models of multi-index decision making used by planners is referred as “Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS)” [26]. These two techniques are predicated on the assumption that the chosen alternative must be as near to the most ideal positive value, which considered as the best option and in second case, it is as far away from the most unfavorable solution i.e., the worst option [27]. As far as the author is aware, no single study evaluates the quality of drinking water using an integrated strategy based on WQI, multivariate, and MCDM techniques for the river basin. Therefore, the key objective of the current research is to assess the topographic water quality in Mahanadi River Basin (MRB), to provide a realistic perspective and understanding of the overall water quality in this region.

2. Study Area

It is widely believed that the "Mahanadi River" is one of the pivotal rivers that flow from west to east before emptying into the Bay of Bengal. Generally, the basin lies encompassed within the geographical coordinates of 80°30’ to 86°50’ East longitudes and 19°20’ to 23°35’ latitudes. The river empties into a region of 141600 km^2 which pertains to 4% of the total geographical area of the country [28]. Out of its total length of 851 km, 494 km of it runs primarily in the State of Odisha. The drainage basin has an average elevation of 426 m, a high elevation of 877 m, and a minimum height of 193 m. It is seen that the average annual rainfall is 1572 mm, of which the southeast monsoon, which lasts from mid-June to mid-October, contributes 70% of the total. A tropical monsoon climate with average annual temperatures ranging from 15.8°C to 28.7°C is evident from the river basin. The river experiences cyclonic storms and seasonal rainfall because it flows through a tropical zone. Red, yellow, mixed red & laterite soils are the two main types of soil in the basin [29]. Agriculture is evidently the backbone of the basin's economy and a necessity for human survival. Rice, oilseed, and sugarcane are the three main crops connected to this river. During the southwest monsoon season, it refers mostly to a coast that is wave-dominated, whereas during the non-monsoon season, it is mixed wave and tide-dominated. Locations and layout of the 19 quality monitoring points can be found in Figure 1.

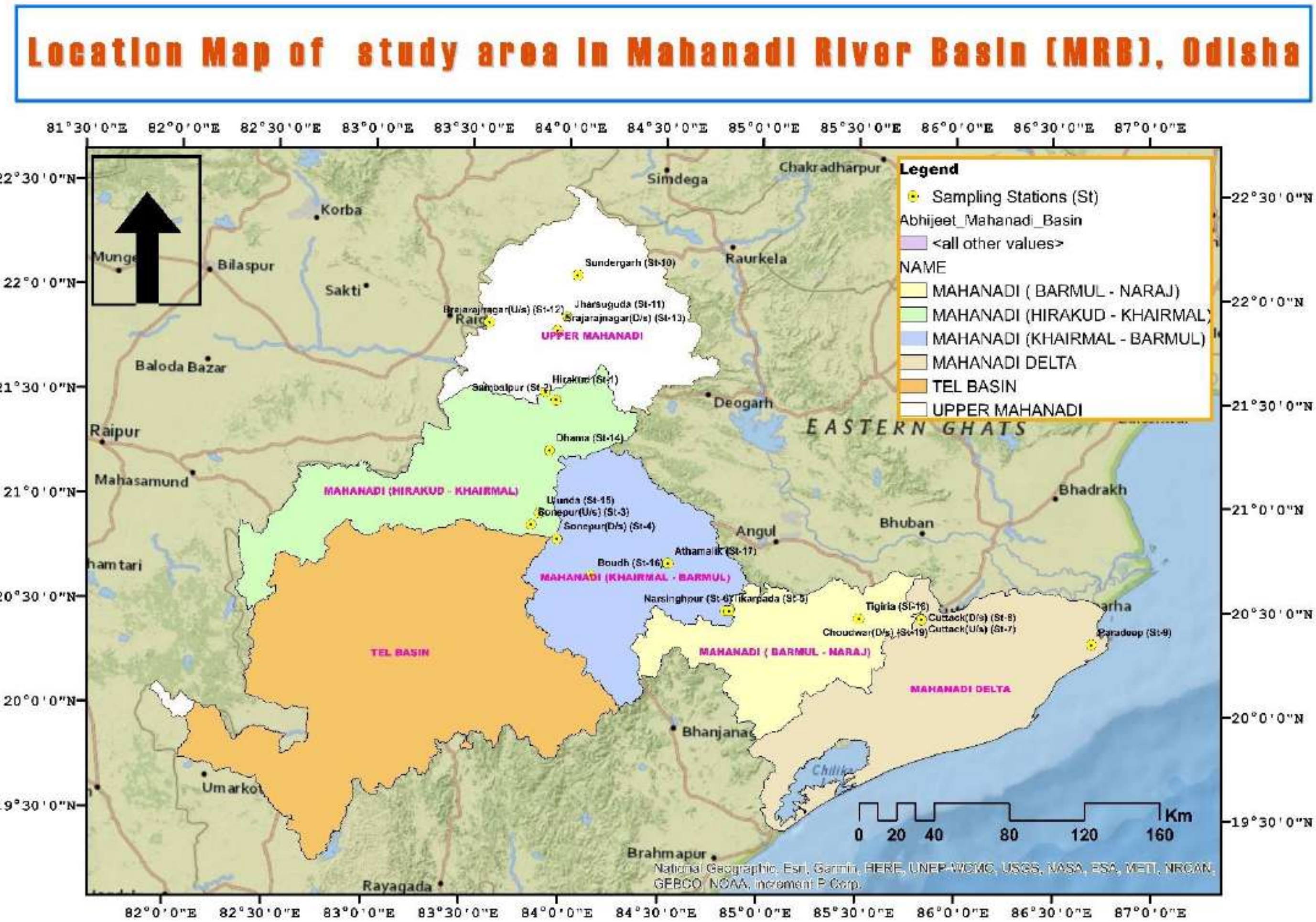


Fig. 1. Location of the study area, Mahanadi watershed of Odisha, India

3. Sampling Methodology

Grab samples were taken at a depth of around 0.3 meters below the surface of the river from the Mahanadi basin and its tributaries. To track the places designated for water quality evaluation, the State

Pollution Control Board, Odisha, are used for collecting water quality data. 19 monitoring sites were used as the reference sample in these tests of quality assessment, which were conducted on a regular basis from 2016 to 2023. Using the standard methods for analyzing water and wastewater, water quality samples and analysis were carried out at every point along the river as per [29]. The sites were picked in order to evaluate the effects on water of household, industrial, and mining operations in the basin. Prior to use, high density polyethylene sample bottles were repeatedly rinsed with double distilled water after being immersed in % HNO_3 for 24 hours. 20 water quality parameters namely boron (B^+), biochemical oxygen demand (BOD), total coliform (TC), sodium adsorption ratio (SAR), chloride (Cl^-), ammoniacal nitrogen (NH_3-N), iron (Fe^{2+}), nitrate (NO_3^-), fluoride (F^-), sulphate (SO_4^{2-}), total suspended solids (TSS), free ammonia (free-NH_3), total dissolved solids (TDS), pH, dissolved oxygen (DO), total hardness (TH), electrical conductivity (EC) alkalinity (Al), chemical oxygen demand (COD), and Total Kjeldahl nitrogen (TKN) were used in this investigation. Following sample collection, the onboard measurements of pH and EC as well as fixation of DO were performed. Other parameters other than pH, EC, and DO were analyzed in accordance with accepted practices [29]. Using Winkler's technique, DO and BOD were measured. Through thorough standardization, procedural blank measurements, spiked samples, and duplicate samples, the analytical data quality was guaranteed. The dilutions were performed using deionized water. The standards-based methodologies' recommendations for quality control were followed. Standard reference materials (SRM) evaluated the precision and consistency of the procedure. In addition, the data accuracy was verified by the charge balance error (CBE) of the major ions in all samples, falling within ± 10% and the following formula given as,

$$CBE = \{\Sigma \text{ Cations} - \Sigma \text{ Anions}/ \Sigma \text{ Cations} + \Sigma \text{ Anions}\} \times 100.$$

4. Methodology

Multiple surface water quality assessment techniques have been widely employed by researchers in the literature [30]. A scientific method that also takes into account the unpredictability of water quality measures is entropy weight [1]. As a result, it is a useful method of presenting uncertainty and probability. Entropy water quality indexes is an enhancement in compared to traditional WQIs, that exhibits on assigning weights to characteristics, based on subjective evaluations and professional opinion [31]. The higher the score, the more each type of pollution or component contributed, and the poorer the water quality was [32]. The following steps are used to calculate entropy weights: Data Normalization is calculated from the following Eqn. (1)

$$v_{ij} = a_{ij} / a_{1j} + \ldots\ldots + a_{mj} \tag{1}$$

for all j belongs to {1, …., c}, where a_{ij} talks about concentration of j^{th} parameter at i^{th} sampling period and ‘c’ stands to be total number of parameters. Furthermore, total number of sampling periods is expressed as ‘m’. Information entropy is suggested by [1], and it is given in Eqn. (2).

$$E_j = -(1/\ln m) \times \Sigma\, v_{ij} \times \ln v_{ij} \tag{2}$$

Weight determination expressed as (w_j) is calculated by Eqn. (3) as

$$w_j = d_j / (d_1 + \ldots + d_c) \tag{3}$$

where, $d_j = 1-E_j$. In case of Quality rating scale, each parameter has given the following Eqn. (4) as

$$Q_j = (C_j/S_i) \times 100 \tag{4}$$

where C_j = measured concentration of the parameter. Thus, EWQI was calculated by Eqn. (5).

$$EWQI = \Sigma\, w_j \times Q_j \quad (5)$$

Following this, its classification is differentiated into five classes, namely, a EWQI value <50, referred as excellent <50, score between 50 and 100, signifies good class, average class varied in a range of 100 to 150, value in a range of 150-200, classify poor water, and finally, >200 graded as extremely poor water [33, 34].

[35] proposed and created the multi-criteria decision-making process known as TOPSIS. It serves as a useful tool for selecting a variety of options by calculating the Euclidean distances between a desired ideal best and an undesirable ideal worst. Based on entropy weights and user-defined criteria, TOPSIS computes a weighted normalized matrix in the presence of uncertainty [35]. It is possible to obtain the normalized decision matrix (NDM), presented in Eqn. (6), which represents the relative performance of the alternatives.

$$NDM = R_{ij} = a_{ij} / (\Sigma\, a_{ij}^{2})^{1/2} \tag{6}$$

The ideal best (IB) and the ideal worst (IW) of the alternatives were estimated in Eqn. (7)

$$IB = A_{+} = \{V_1 +, V_2 + \ldots., V_n^{+}\} \text{ and,}$$

$$IW = A_{-} = \{V_1 -, V_2 - \ldots\ldots, V_n^{-}\} \tag{7}$$

The distance between the positive (d_i^{+}) and negative (d_i^{-}) ideal alternatives is represented in Eqn. (8) as follows:

$$d_i^{+} = \{\Sigma\, (v_{ij} - v_j^{+})^2\}^{1/2} \text{ and } d_i^{-} = \{\Sigma\, (v_{ij} - v_j^{-})^2\}^{1/2} \tag{8}$$

The closeness coefficient (CC) of each alternative was computed as follows in Eqn. (9):

$$CC_i^{+} = d_i^{-} / (d_i^{-} + d_i^{+}) \tag{9}$$

Finally, the possibilities were ordered by their closeness coefficients.

Another approach namely, ELECTRE is software for making multi-criteria decisions that enables the best ranking to be made by fusing the weight of a criterion with data, both numerical and subjective [36]. The initial matrix, containing the alternative data, was built and expressed as a normalized decision matrix (X_{ij}). The Eqn. (10) containing weighted normalized decision matrix (V) given as

$$V = R \times W = \begin{matrix} V11 \ldots\ldots & V1n \\ V1m \ldots.. & Vmn \end{matrix} \tag{10}$$

It is created by multiplying the component parts of the decision matrix normalized by the constants of the weight of the factor [37]. However, these weights and rankings are compared to determine the superior and inferior sets, which are determined using the equations suggested by [38]. The links between alternatives' relative distances in Eqn. (11), can be enhanced through calculation by the net superior (C_{net}) and inferior (D_{net}) indices for each alternative

where,

$$C_{net} = \Sigma\, C_{pq} - \Sigma\, C_{qp} \text{ and } D_{net} = \Sigma\, D_{pq} - \Sigma\, D_{qp} \tag{11}$$

The correlational analysis (CA), principal component analysis (PCA), and hierarchical cluster analysis (HCA) techniques were also used in the current work in addition to the aforementioned methods. These strategies encourage the use of powerful data classification tools and practical visualization techniques to locate the source of pollution in surface water [1]. To investigate the spatial heterogeneity, HCA was used to group together similar sampling sites based on correlation coefficients as indicators of similarity [39]. It employs Ward's approach as a linkage algorithm and Euclidean distance as ‘a measure of similarity’. The Euclidean distance calculates how far apart two observations are geometrically. However, Ward's technique was used to standardize the data before creating the 2-D dendrogram diagram [40]. The main goal of DA is to create discriminant functions, which are nothing more than a linear combination of discriminating factors that allow for the best possible discrimination between the categories of the dependent variable. If the DA is trustworthy for the given set of data, a classification table that is both accurately and erroneously calculated will produce a high accuracy percentage. For each group, the DA approach creates a discriminant function that operates depending on the original data as indicated in equation, which is represented in Eqn. (12) as

$$f(G_i) = k_i + \Sigma\, w_j \times p_j \tag{12}$$

The term 'i' refers to 'various groups i.e., G', while k_i stands for 'constant inherent to each group', n depicts to 'pertinent parameters' and finally, w_j is said to be the 'weight coefficient'. PCA has the advantage of reducing the number of variables to a smaller number of factors, which can then be used to sort variables and clusters of data based on these factors. The parts that make up the principal components (PCs) are arranged in a descending order and contribute less to the total variability [41]. The primary variables influencing water quality are identified using the weighted correlation coefficient. Liu et al. (2003) categorizes factor loadings as strong, moderate and weak according to the total values of >0.75, 0.75-0.50 and 0.50-0.30 respectively [42]. The computations were finally performed using the correlation matrix of the rearranged chemical components. These statistical methods support effective data classification tools and practical visualization strategies for locating the source of pollution in surface water.

5. Results and Discussions

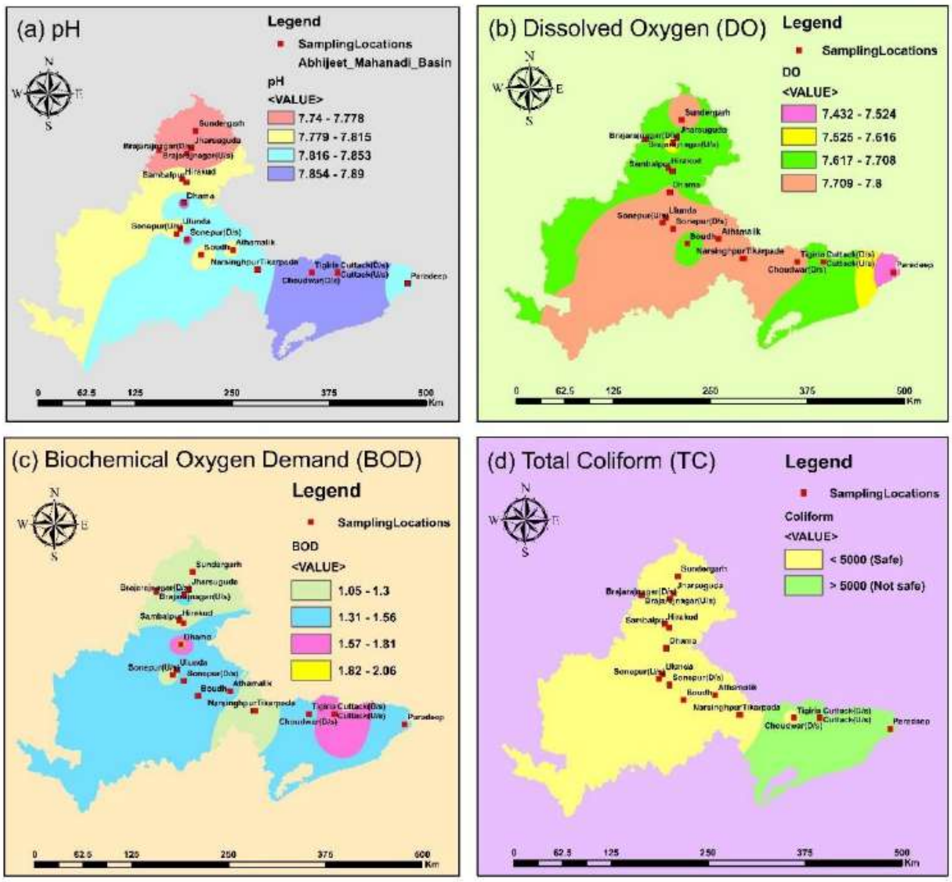
In Table 1, the descriptive statics of the monitored physicochemical parameters at a total of nineteen sampling sites of the Mahanadi River are displayed.

Table 1. The values of the parameters analyzed by sampling the stations

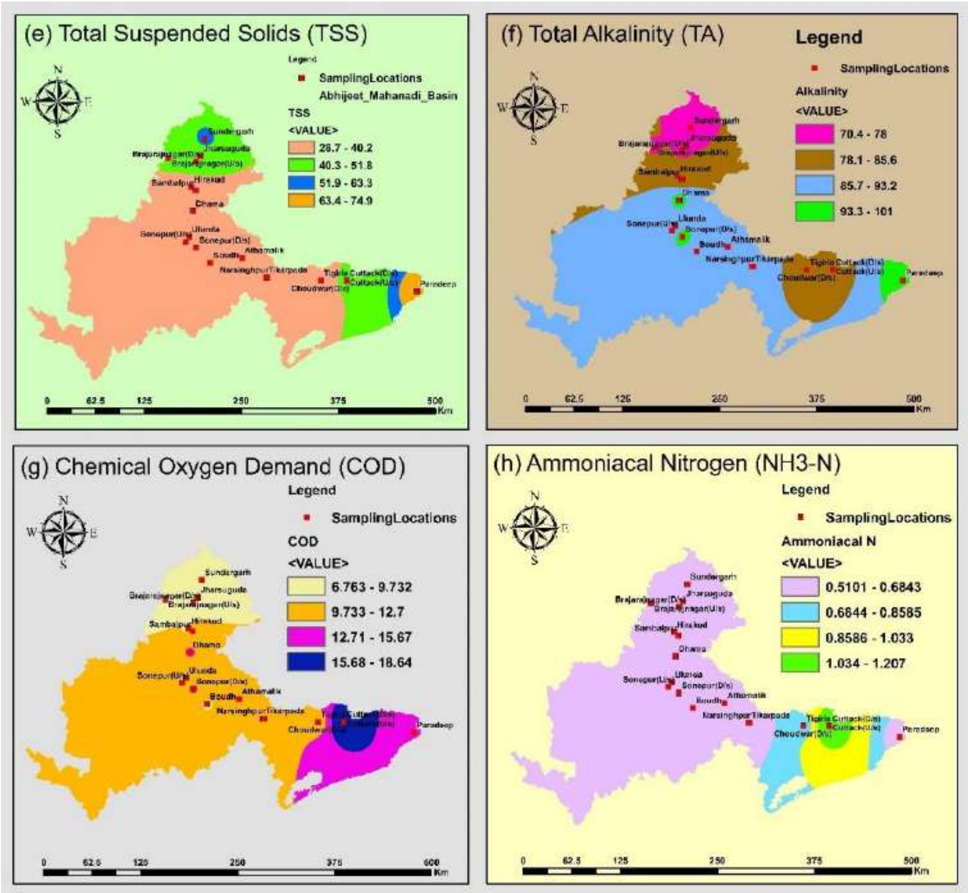
Parameters	Range (Minimum-Maximum)	Standard Deviation (SD)
pH	7.7-7.9	0.05
DO	7.2-7.8	0.14
BOD	1.05- 2.4	0.34
TC	1212.4-42529.20	9193.97
TSS	28.6-74.9	11.56
Alkalinity	70.4-100.9	8.24
COD	6.7-21.8	3.96
NH_3-N	0.5-1.9	0.31
Free NH_3	0.02-0.06	0.01
TKN	3.2-11.8	2.07
EC	138.1-7779.3	1743.33
SAR	0.4-16.5	3.69
B	0.03-0.5	0.12
TDS	82.3-13230.6	3007.19
TH	51.2-2195.2	486.60
Cl^-	9.6-4904.9	1122.58
SO_4^{2-}	4.9-376.0	84.68
F^-	0.26-1	0.17
NO_3^-	1.2-2.7	0.41
Fe^{2+}	0.6-2.6	0.46

The nutritional absorption and bioavailability of nutrients and toxic metals, are generally determined by the water's pH. [43]. The pH of the river (7.7–7.9) was found to be within the range of 6.5–8.5 recommended by [44]. Another crucial metric that reveals the health of an aquatic habitat is DO. The river water's DO concentration (7.2–7.8) during the sampling period was higher than 6.0 mg/. Due to the river's ability to purify itself, reaeration occurs along its length, which can be used to support the growth in DO levels [45]. The amount of organic contamination brought on by an overabundance of organic materials has historically been gauged by the BOD levels of rivers. The majority of the locations' readings (1.0–2.4) were found to be within the WHO-threshold limit of 5 mg/l, which is the acceptable limit (2012). The existence of more coliforms in water is typically a result of water contamination. Its value in the current study is provided in MPN/100 ml and ranges from 1212-42529. The acceptable upper limit is 5000 MPN/100 ml. According to reports, waste waters close to industry, municipal sewage systems, or hospitals are to account for the greatest levels of this group of bacteria detected in St-8, 9 and 10. The TSS result was within the range of (28.6-74.9 mg/l), which is the threshold value. It has an impact on aquatic life. Clay and silts, as well as biological solids like bacteria and algae cells, were the main sources of TSS. Alkalinity is the water's ability to buffer acids and keep the pH level steady. Alkalinity is a term used to describe a solution's ability to react with a solute and neutralize an acid [46]. Hence, as per [44], this parameter established an acceptable limit of 200 mg/l. The results in the samples that were taken ranged from 70.4 to 100.9 mg/l. Aquatic ecosystem resources are evaluated using COD as a main criterion since it shows the quantity of organic contaminants that deplete oxygen in the water body [47]. The value in the study region varied from 6.7 to 21.88 mg/l, satisfying the WHO's 30 mg/l threshold. NH_3-N is a signal for residential sewage and mineral composition pollution. The value was between 0.5 to 1.93 mg/l, which is well within the 2 mg/l WHO standards. Free NH_3 reveals that home sewage and hydrochemistry associated with minerals were the main sources of the contamination, primarily from the outflow of waste water from Pulping processes, household waste, and metal manufacturing waste crossing the river near the coastline. The sampling sites' free NH_3 concentrations span between 0.02-0.06 mg/l. The threshold value is 2 mg/l. The origin of indicator i.e., TKN often denotes incomplete organic matter degradation processes and is a reliable sign of river contamination from urban effluents [48]. The TKN ranged from 3.28 to 11.80 mg/l. As per [44], it suggests that the threshold value is taken as 5 mg/l. Ammonium ion species were found in the water in St-8 and St-9 (areas with higher TKN values), which were attributed to the nitrogen cycle, domestic effluents (urea), and urban runoff [49]. EC denotes the total ions in dissolved form that are present in the water and are affected by different effluent discharges into the river [50]. Along the locations, conductivity varied between 138.1 and 7779.3 µS/cm. Higher levels were seen in St-9, which could be attributed to port operations, shipping, and agricultural practices. The amount of salt absorbed by soil and the SAR of irrigation water are significantly correlated. High levels of Na^+ salts in soil damage its physical state and texture, making it difficult to cultivate [51]. SAR levels were determined to be 0.41–16.59, which meets the WHO threshold of 20 meq/l. Therefore, irrigation is feasible at all places. At low concentrations, boron is a necessary element for plant growth; but, at greater amounts, boron becomes harmful. Boron concentrations ranged from 0.03-0.55 mg/l, indicating that the water is suitable for irrigation and drinking. TDS may be caused by rainfall, surface runoff, river water flow, and bank and riverbed erosion, according to observations. Its values fluctuated in the current work, is around a range between 82 and 13230 mg/l. All samples belong to freshwater category as per [44] i.e., 100 mg/l except St-9. The addition of ions from the source rocks and also the longer residence time of surface water in contact with the aquifer system are responsible for the greater TDS in St-9. The maximum permitted level of TH is 600 mg/l, and the ideal level for consumption is around 300 mg/l, according to WHO guidelines. Throughout the investigation period, it varied between 51.2-295.2 mg/l. The hard water found in St-9 is to blame for aesthetic concerns because it has a disagreeable taste and makes soap less effective at producing scale on plumbing fixtures and in pipes [52].

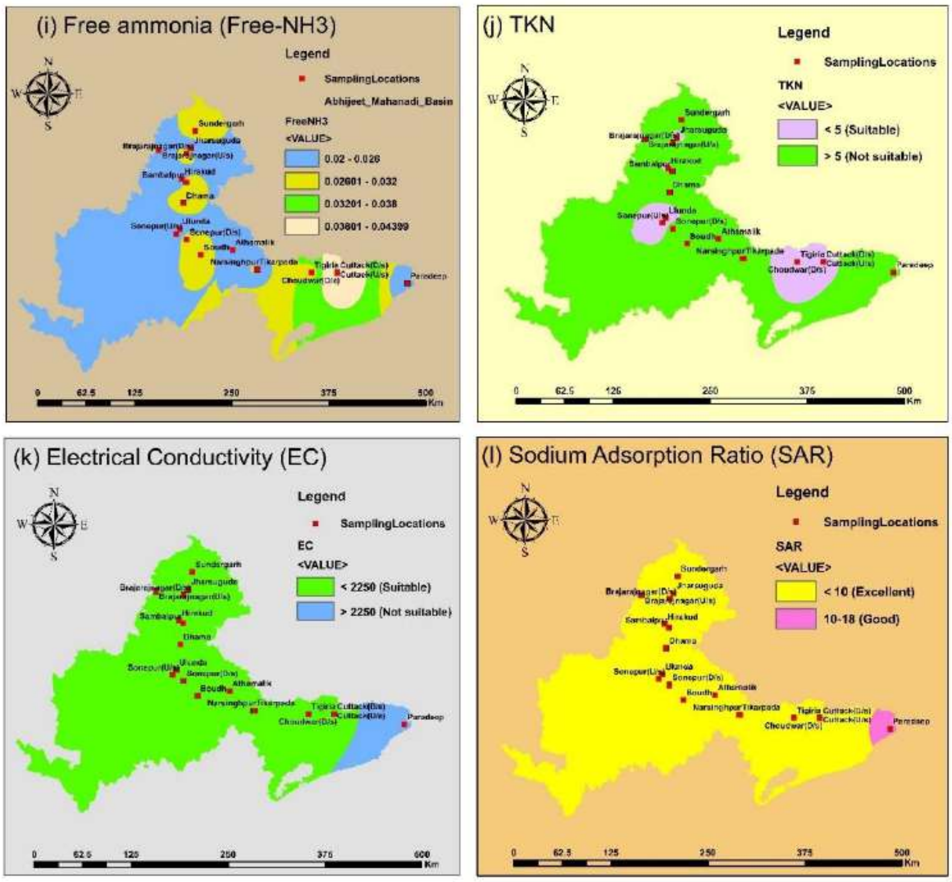
Cl- is used in the treatment of water to eliminate bacteria, parasites, viruses, and microorganisms by neutralizing and oxidizing them [1]. Except for the St-9 location, all of the water samples included in this investigation has Cl- concentrations below the permissible limit of 250 mg/l. The key factor at the St-9 site is efficient leaching from the topsoil caused by domestic and industrial activity, as well as dry temperatures [53]. For surface water, however, the quantities of SO_4^{2-} that we have measured range from 4.97 to 376.07 mg/l. Accordingly, we may consider the current levels to be safe for use based on the WHO's 200 mg/l standard. Due to industrial Sulphur gas emissions, which oxidize and enter the aquifer matrix after precipitation, SO_4^{2-} levels are greater in St-9 [54]. The earth's crust contains the naturally occurring element F^-, which is extremely hazardous to freshwater aquatic life. According to reports, industrial sites like brick kilns and fertilizer are potential sources of F^- near the surface. The maximum permitted level is 1 mg/l. The magnitude of the measurement was 0.26 to 1.0 mg/l, indicating that all sampling points are within the acceptable range. Natural ions called NO_3^- play a vital role in the nitrogen cycle. However, because it causes methemoglobinemia in infants under 6 months of age, the ion in surface water is undesirable [54]. Surface water has a NO_3^- concentration that ranges from 1.29 to 2.70 mg/l. The recommended limit for drinking water is 45 mg/l, according to [44]. Since Fe^{2+} helps in blood flow, it is not thought that the concentration found poses a health risk. It aids in the blood's ability to carry oxygen. According to WHO recommendations, the ideal level of Fe^{2+} is 3 mg/l. The research area's Fe^{2+} concentration was 0.6-2.61 mg/l, which is below the threshold criteria. The determining factor in the study area's cation dominance hierarchy is $Fe^{2+} > B^+$, whereas the anions is $Cl^- > SO_4^{2-} > NO_3^- > F^-$. Figures 2a–t shows the results of the spatial map display of all parameters using IDW interpolation in ArcGIS 10.5.



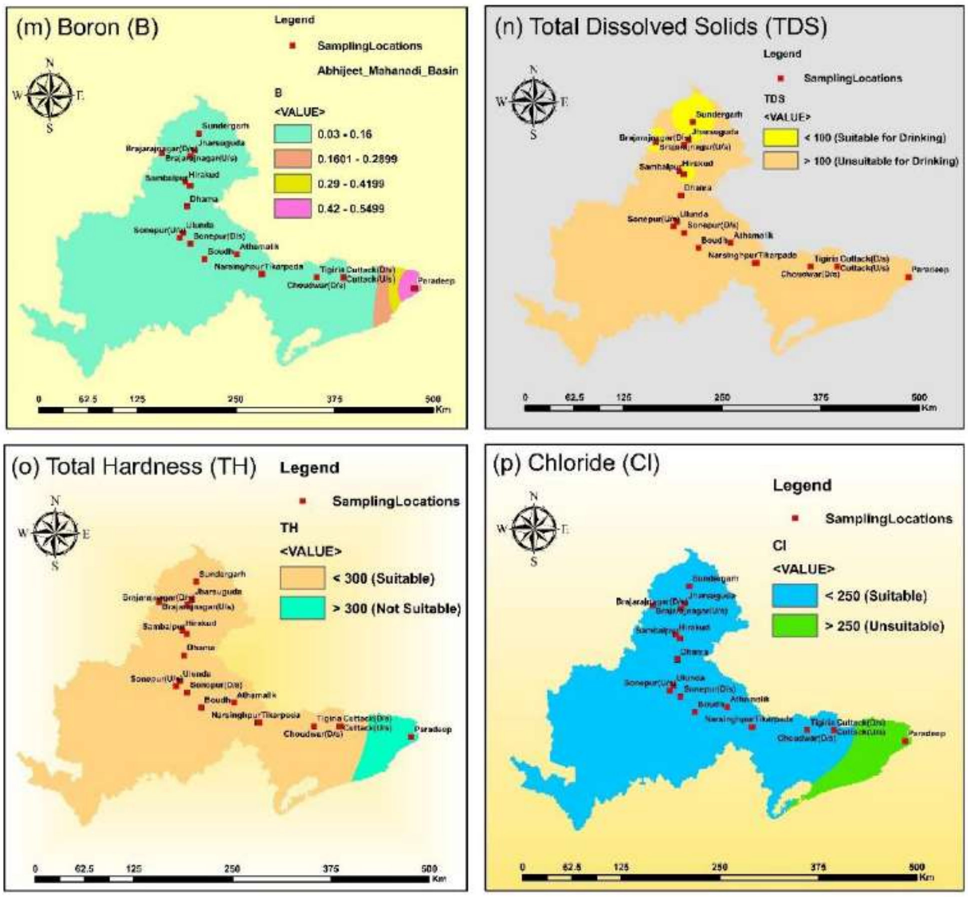
(a) pH, (b) DO, (c) BOD and (d) TC



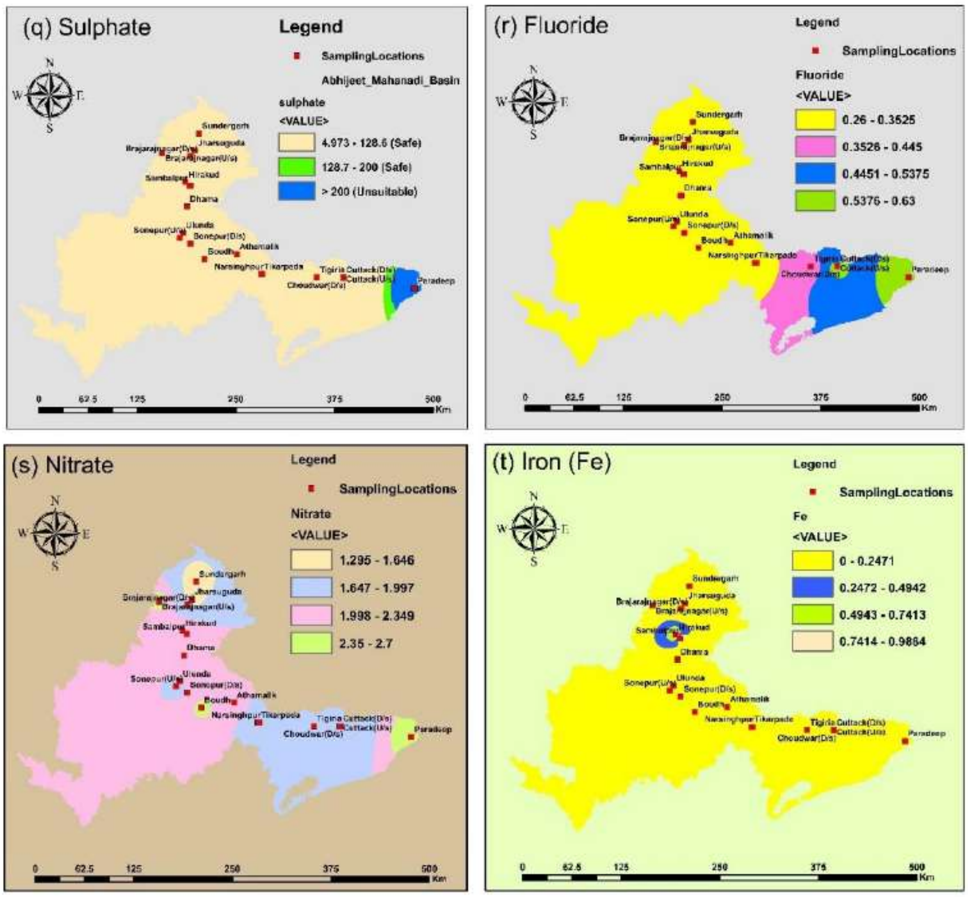
(e) TSS, (f) TA, (g) COD and (h) NH_3-N



(i) Free-NH_3, (j) TKN, (k) EC and (l) SAR



(m) Boron, (n) TDS, (o) TH and (p) Cl^-



(q) SO_4^{2-}, (r) F^-, (s) NO_3^- and (t) Fe^{2+}

Fig. 2. Distribution of spatial maps

The methodology section of this research provides a detailed explanation of the EWQI calculation. The EWQI ranged from 14.6 to 1065.2 in the research area, which represents excellent to extremely poor categories. However, in the upstream portions close to the sample sites, the water quality improved. The St-(9), (19) and (8) sample sites consistently displayed unsatisfactory water quality. A little over 84.21 % locations show good conditions, 10.53 % showed poor conditions and 5.26 % locations (1 place) showed extremely poor water conditions. The higher values of EWQI at site 9 were attributed to Cl^-, SAR, TH, EC, TKN, TDS, TC and SO_4^{2-}. This shows about detrimental effect on human activity towards the quality of potable water. Table 2 displays the EWQI values for each sample based on the WHO drinking water quality standard. Figure 3 illustrates how the severely contaminated areas were generally visualized using 3D spatial analysis. Weights, on the other hand, are the results of data normalization in MCDMs. Priority ranks of the relevant sampling locations were established using ELECTRE and TOPSIS, and their findings were compared (Dell' Aira et al. 2021). This was done after calculating the factor weight coefficients from the EWQI. All of the physical and chemical water quality characteristics were subjected to each methodology in order to create overall rankings, with the highest rank for each time denoting the most polluting sampling point. The priority ranks as well as performance score (PS) are shown in Table 2. The results in case of both methods, the station 9 is placed in the category of most polluted site with the rank of 1 on account of greater value containing TH, SAR, Cl^-, TDS, SO_4^{2-}, TKN, EC, and TC, which were also higher than their desirable concentration and highest among all the locations. Furthermore, it was clear that the locations 8 and 19 had poor water quality because they had the second and third highest EWQI scores. High TKN and EC levels were also present. The cause could be the subsequent release of pollution in the river's downstream zone as a result of sewage, agricultural, and leachate drainage systems (Islam et al. 2020). Figures 4 and 5 display the created interpolated map. Therefore, using MCDMs like TOPSIS and ELECTRE showed effective in prioritizing sampling locations based on their degree of pollution/contamination levels and in calculating current ranks with high accuracy for samples.

Table 2. Suitability of surface water for drinking needs based on entropy WQI, TOPSIS and ELECTRE

Sample No	EWQI	Rank	Water type	TOPSIS (PS/P_i^*)	Rank	ELECTRE (PS/C_a)	Rank
St-1	15.7	16	Excellent	0.006	18	0.025	16
St-2	18.4	9	Excellent	0.013	6	0.030	9
St-3	16.2	15	Excellent	0.005	19	0.025	15
St-4	19.9	5	Excellent	0.011	10	0.031	6
St-5	18.6	8	Excellent	0.010	11	0.029	11
St-6	19.5	6	Excellent	0.012	9	0.029	10
St-7	17.6	12	Excellent	0.009	14	0.028	12
St-8	196.0	2	Poor	0.132	2	0.074	2
St-9	1065.2	1	Extremely Poor	0.887	1	0.959	1
St-10	15.0	18	Excellent	0.008	15	0.025	17
St-11	15.1	17	Excellent	0.007	16	0.024	19
St-12	14.6	19	Excellent	0.006	17	0.025	18
St-13	16.9	13	Excellent	0.009	12	0.027	13
St-14	20.0	4	Excellent	0.012	8	0.030	7
St-15	16.3	14	Excellent	0.009	13	0.027	14
St-16	18.4	10	Excellent	0.016	4	0.031	4
St-17	19.5	7	Excellent	0.013	7	0.030	8
St-18	17.9	11	Excellent	0.014	5	0.031	5
St-19	152.0	3	Poor	0.034	3	0.046	3

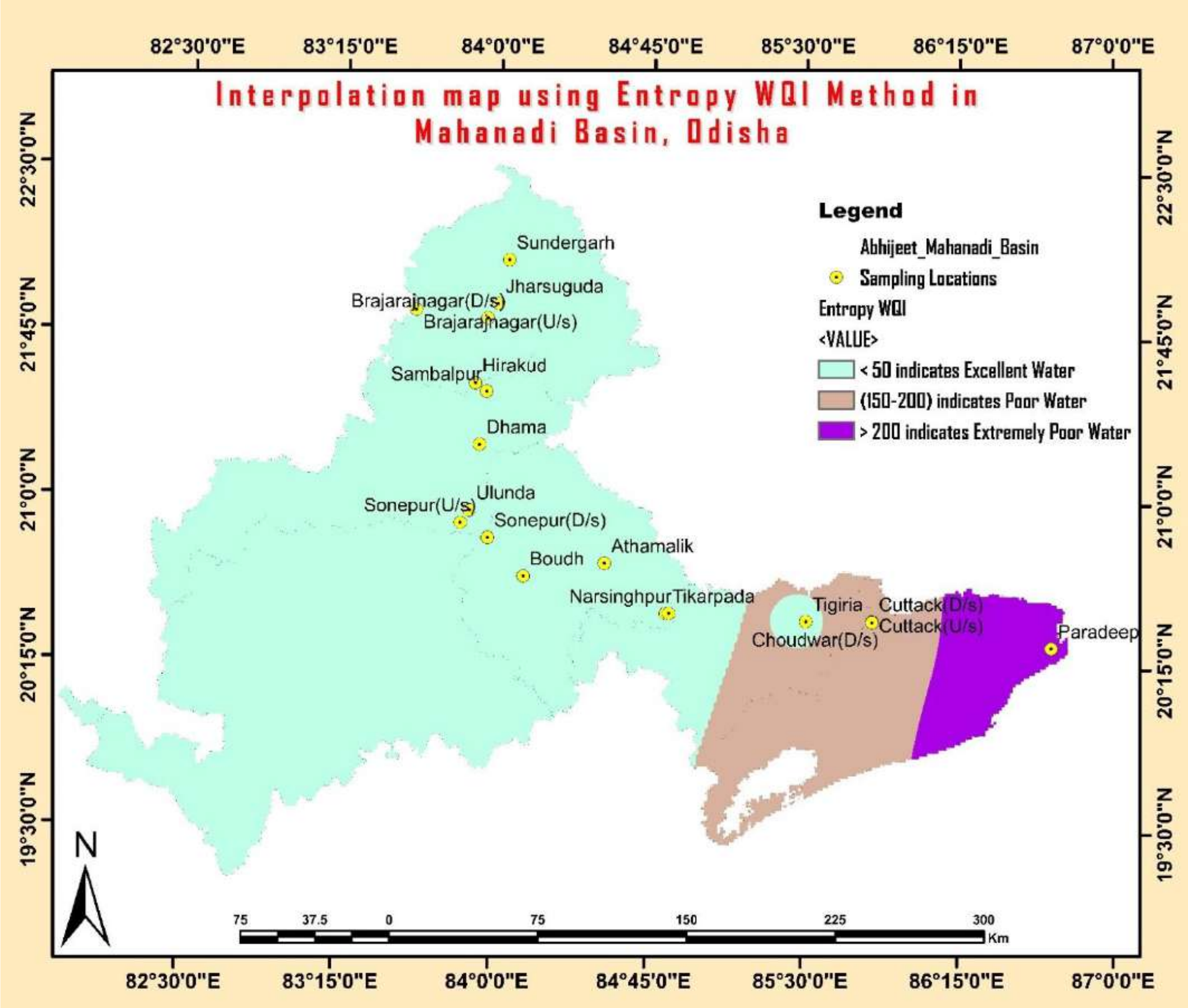


Fig. 3. EWQI map of surface water sample points at the study area

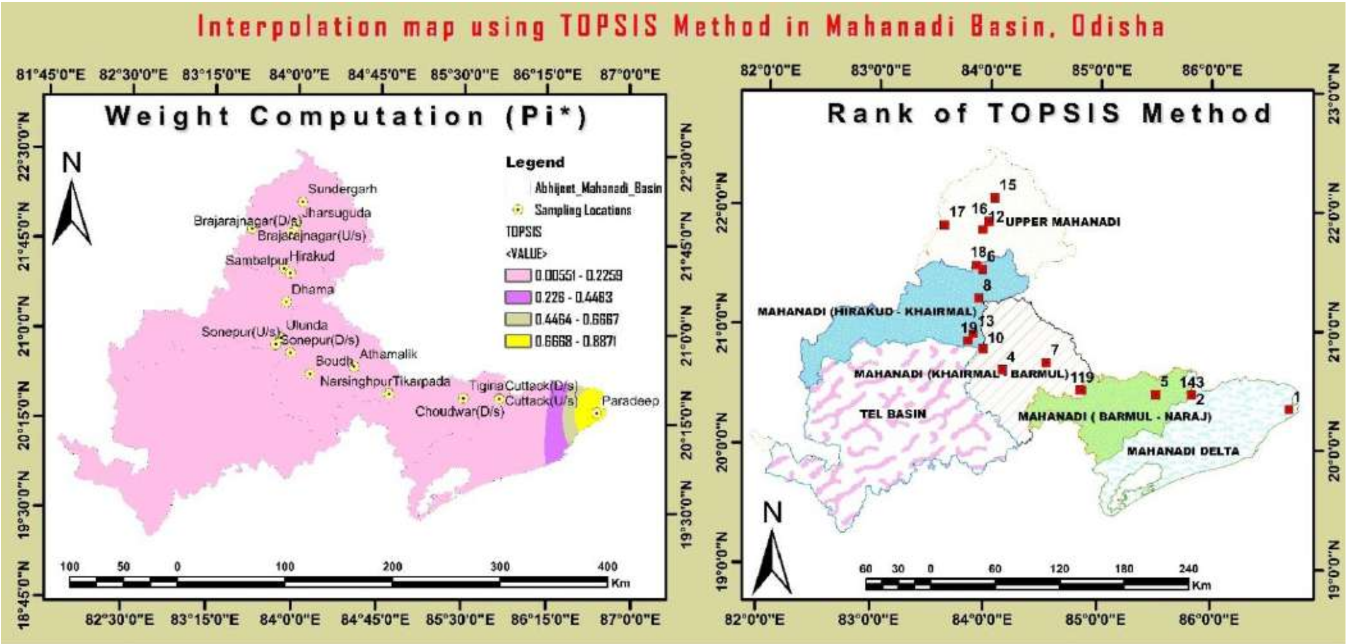


Fig. 4. TOPSIS map of surface water sample points at the study area

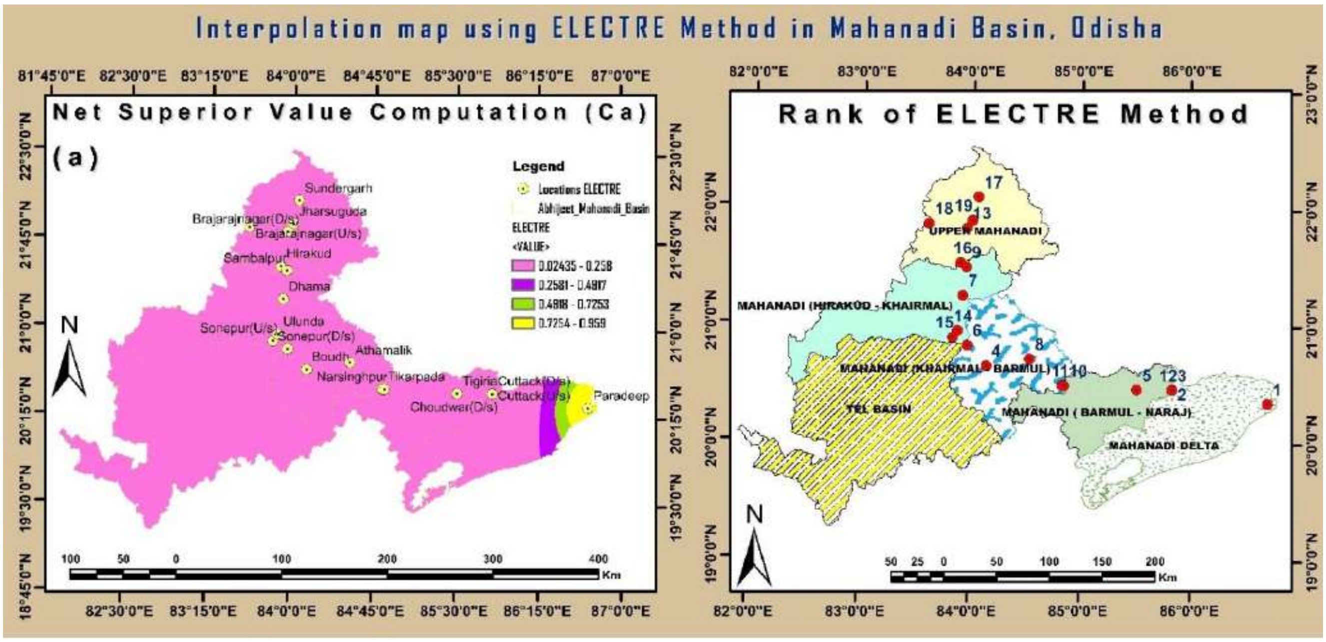
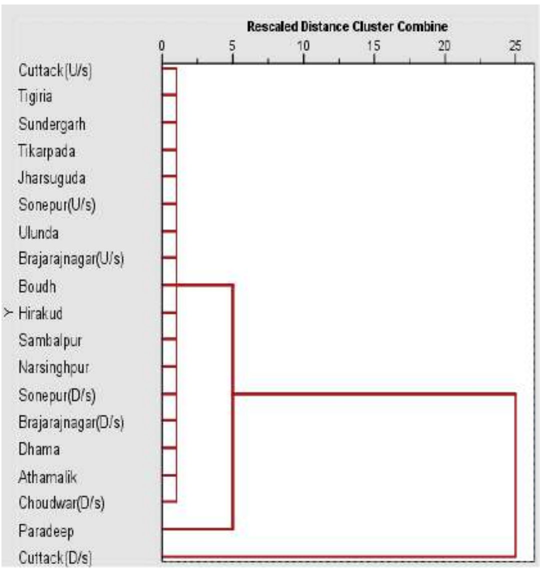
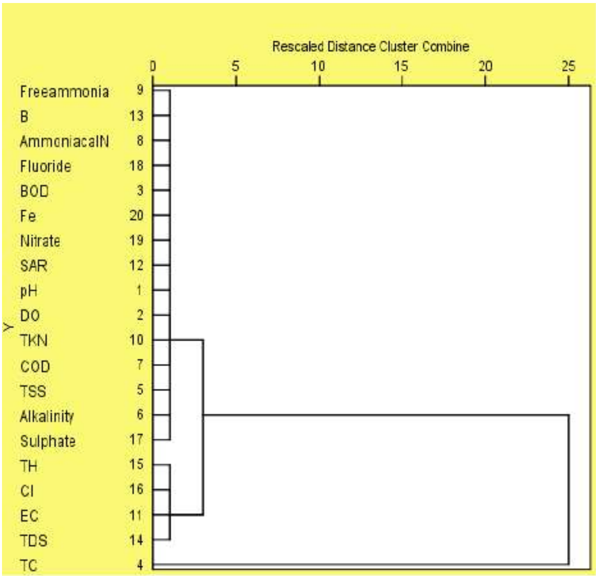


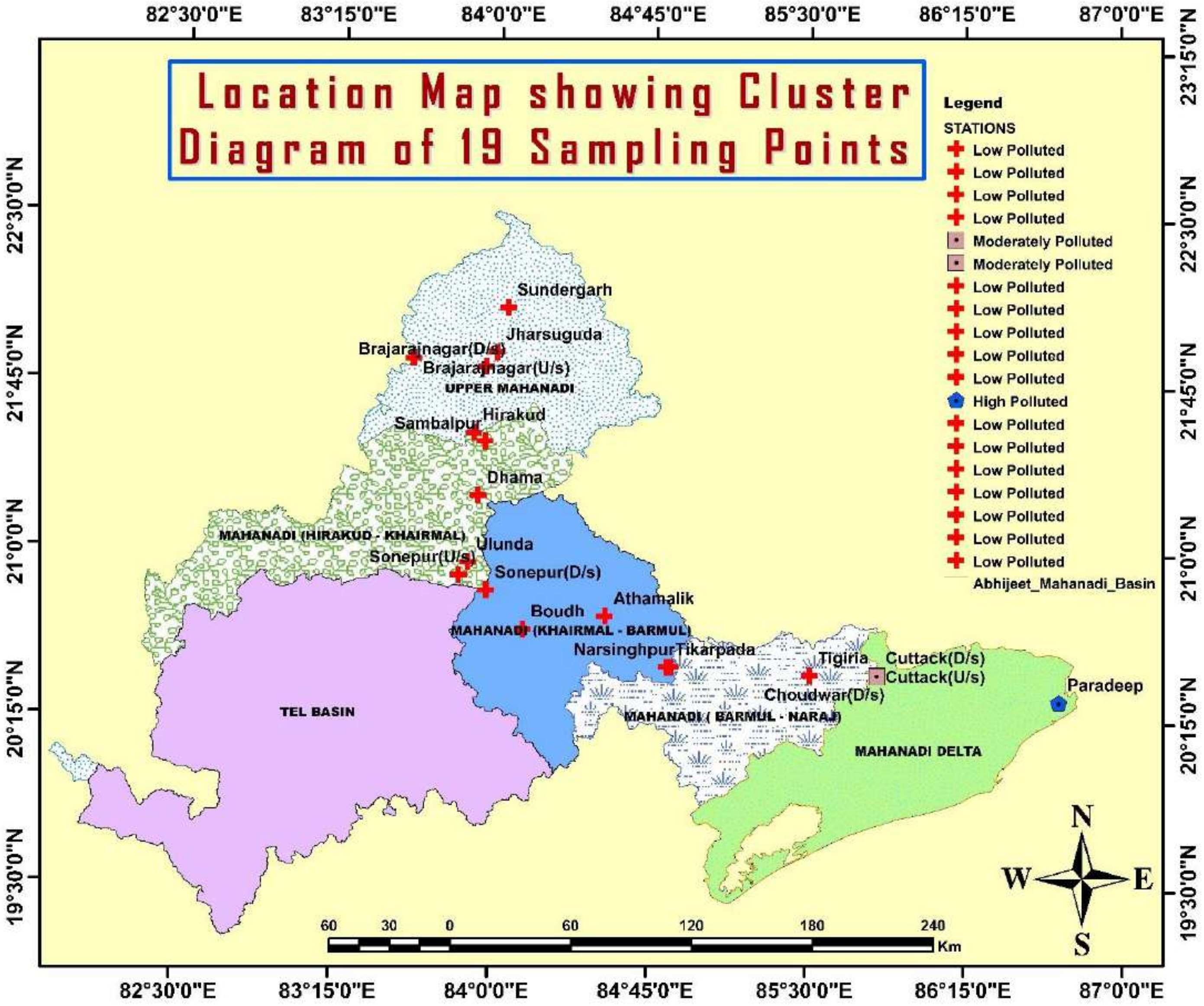
Fig. 5. ELECTRE map of surface water sample points at the study area

Using MATLAB software, the data matrix was once more examined using Cluster Analysis (Hierarchical Tree Clustering, Rescaled distance cluster combine analysis). HCA was applied to the 19 sampling sites using 20 variables [55]. As a result of the dominating ions and sites existing in the research region, three separate clusters or groupings of the data were found and categorized as dendrograms in Figures 6(a), (b), and (c). In the present investigation, Cluster 3 includes EC, TDS, TH and Cl^-. It is affected mainly by salinity factor due to mineral dissolution. TC is the only parameter that covered by Cluster 2, includes toxic anthropogenic fecal coliform bacteria. Coliform is a good sign of fecal pollution when found in water bodies [56]. The Cluster 1 consists of further 15 variables, which probably derived from anthropogenic activities. Following this, dendrogram view of all sites represents, that shows Cluster 1 comprises of 16 testing places, in which all sites belong to 'excellent-good water' quality. Hence, this cluster is categorized as 'low polluted zone'. However, cluster 2 consisting of two sample sites namely St-(19) and (8). These samples depict 'poor water' status. So, this group of objects is known as 'moderately polluted' zone. St-(9) points towards Cluster 3. This cluster illustrates very poor water because of higher concentration of SO_4^{2-}, TH, TKN, Cl^-, and TC. Hence, it is known as high polluted zone. This demonstrates that the surface water chemistry in the examined area is controlled by a combination of human operations, leakage, and dissolution [57].





(a) (b)



(c)

Fig. 6. Dendrogram showing results (a) Sampling Sites, (b) Physicochemical parameters and (c) Spatial distributions of HCA for 19 sampling points

DA was carried out with the constraint that it would be useful in identifying naturally banded or clustered water sample sites. The clusters based on CA were used to examine the variation. Two modes—Standard mode and Stepwise mode—are used to carry out this technique in the current investigation. For the creation of discriminating functions, standard mode incorporates all the predictive factors (DFs). When there are numerous predicting variables, the stepwise approach is useful. These two modes were employed in the construction of discriminant functions (DFs), and Tables 3, 4, and 5 shows the classification outcomes as a result, in this ongoing research. Wilk's Lambda (λ) indicates the case-by-case grouping function's capacity for discrimination. λ equals to 1 signifies equal group means. On the other hand, a small λ demonstrates that group means appear to be different and that within-group variability is minimal compared to overall variability. The values of each discriminant function's i.e., 'Wilk's lambda' and 'Chi-Square' ranged from 0.063-0.33 and 63.01-286.33, respectively, demonstrating the validity and reliability of the spatial discriminant technique. Additionally, the p-level value was less than 0.01, demonstrating the validity and efficacy of the time DA. Using 20 and 10 factors, respectively, standard mode and stepwise mode were able to reach discriminant accuracy rates of 100 and 97.92%. The final outcomes suggests that 10 indicators namely (EC, SAR, TKN, TDS, TH, TC, Cl^-, SO_4^{2-} and Fe^{2+}) were shown to be the most effective discriminant (predictive) variables for describing the variation in water quality in three groups. These indicators are regarded as crucial differentiating factors that explain the regional variance in water quality. Since TC in water is caused by sanitary contamination, it should be protected at these locations by taking steps to lessen or eliminate the causes of pollution. It is evident that there is a large excess in values virtually everywhere throughout the course of the river. High concentrations of TKN, which strongly depart from the threshold values, are commonly obtained from fertilizers or waste water leaks in water sources. The areas with the highest levels of pollution (St-8, 9 & 19) are those that are most influenced by point source pollution releases, which make the pollution there worse than it is elsewhere. As a result, DA reduced the vast data's dimensionality and defined a small number of indicator variables responsible for fluctuation in water quality. Figure 7 displays the values of the discriminant scores.

Table 3. Results of spatial-DA for spatial variation

Mode	DFs	Canonical Relation (R)	Eigen value	Wilk's lambda	Chi-square	P-value (sig)
Standard	1	0.99	2.156	0.063	286.33	0
	2	0.98	2.143	0.328	73.612	0
Stepwise	1	0.95	2.121	0.064	280.116	0
	2	0.91	2.099	0.33	63.012	0

Table 4. Description of Classification functions (CFs)

Indicator	Standard Mode			Stepwise Mode		
	LP	MP	HP	LP	MP	HP
pH	269.1000	265.7000	261.0000			
DO	17.0000	16.3000	17.3000			
BOD	23.1320	21.7800	21.8910			
TC	7.2100	2.1920	1.5670	7.876	3.111	3.234
TSS	-51.2300	-42.1230	-8.6780			
Alkalinity	-0.0310	-0.0430	-0.0330			
COD	1.1000	1.0000	0.8000			
NH_3-N	21.5000	21.3000	21.0000			
Free NH_3	-1.2100	-3.3320	-5.6780			
TKN	6.8910	21.3410	21.8910	-6.6660	15.4230	46.5670
EC	0.8790	2.1230	4.3450	-33.2110	-28.9810	4.1110
SAR	-6.2310	-6.5670	-6.5450	0.3230	-0.5554	-0.9800
B						
TDS	-2.4560	-2.1230	-1.2340	-2.0090	-4.3450	-7.6780
TH	-6.3450	-6.3320	-2.1230	-0.0050	-0.0120	-0.0110
Cl^-	-0.0800	-0.0100	-0.0110	-0.8760	-0.7760	0.4320
SO_4^{2-}	-2.3410	-2.3210	-0.9980	-3.2220	-2.1110	-0.7760
F	6.7860	4.2340	1.2350			
NO_3^-	-0.9230	-16.2310	-41.2100			
Fe^{2+}	-0.4230	-0.3330	-0.4110	-0.4560	-0.5550	-0.6640
(Constant)	-42.31	-56.87	-81.39	-28.56	-55.31	-88.61

Table 5. Classification matrix for discriminant analysis of spatial variation

Pre-identified Clusters	% Count	LP	MP	HP
Standard mode				
LP	100.00	16	0	0
MP	100.00	0	2	0
HP	100.00	0	0	1
Total	100.00	16	2	1
Stepwise mode				
LP	93.75	15	1	0
MP	100.00	0	2	0
HP	100.00	0	0	1
Total	97.92	15	3	1

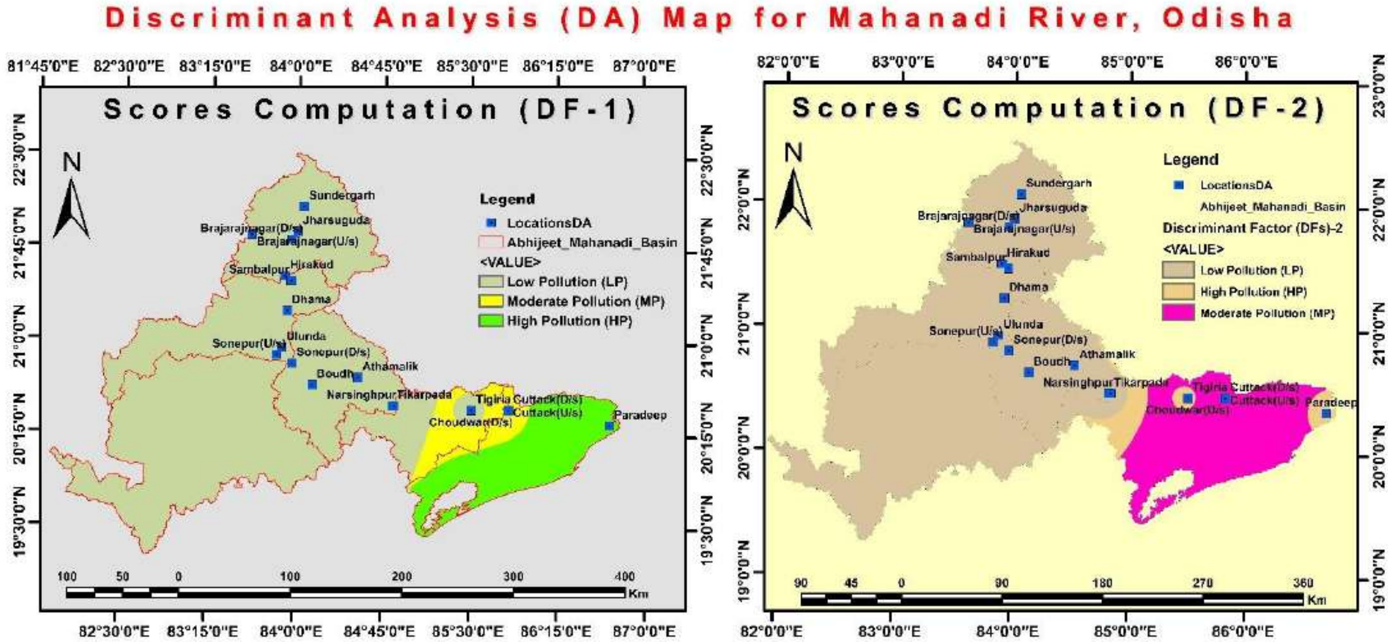


Fig. 7. Discriminant analysis of surface water sample points at the site area

PCA has been applied in the research region for the connection of chemical compositions, specified by a single or many variable loadings on the component that helps in determining the surface water quality. To Calculate the number of PCs required to fully uncover the internal data structure, a scree plot was utilized [58]. It is shown in Figure 8 and is used to define the point of inflection on the curve. After the fifth eigenvalue, which denotes the dominance of five components in the water chemistry, the slope drops off from the scree plot. Five principal components (PCs) were derived from the original data set based on the eigen value greater than 1, and these five PCs accounted for 93.91 %. PC1 consists of 47.68% variance in the dataset with high loadings of ‘TH, SO_4^{2-}, EC, TDS, Cl^-, SAR, B, TSS and TKN’. Reversible electron transfer and carbonate degradation produce EC. Cl^- is produced by the leaching of industrial effluents and longer surface water migration distances [59]. Site sanitation and nutrient contamination from an unsewered urban context explain TKN loading. There is a 20.40 % variation in PC2 that shows considerable COD, free NH_3, and NH_3-N loadings [60, 61]. It might be attributable to human activities like runoff from farmers' excessive fertilizer use or clothes washing along the basin's borders. These ions originate from human activity in the research area. PC3, which further clarifies 11.19% of the entire variance, includes positive loadings of F^- and DO while TC and BOD belongs to moderate loadings. Commercial trash, landfill dumping, and untreated sewage water are the prominent F^- sources [62]. DO indicate that the river was well oxygenated [63]. TC and BOD appear to be caused by the impacts of both human induced practices and scheme of partial ecological restoration [64]. This component is associated with sub-surface activities. Component 4 (PC4) accounts for 8.67% of the entire variance, which comprises of parameters like TA and NO_3^-. Leaching of fertilizer from fertilizer from agricultural land results in higher loading. It is well associated with external activities [65]. A 5.96% of variance with moderate loading of pH and negative loaded with NO_3^- in PC5, that originates from urban and agricultural activities [66]. In addition, pH change may be due to the characteristics of waste water and sea water. Seasonal variability affects the river water quality as the rise and fall in temperature (influenced by changes in season) affects the pH of water [67]. In Table 6, eigenvalues for various parameters, such as cumulative percentage variance and % changes/variances, are displayed. Positive PCA results (Figure 9) imply that the factor scores (FS), which are heavily loaded on a certain component, have an impact on the water sample, whereas negative PCA results imply that these parameters have little to no impact on water quality [68]. They are frequently acquired using the regression method [69]. This phase was performed in order to better understand the factor distribution scores in Figure 9 and Table 7. Consequently, the combined geogenic and anthropogenic activity that takes place throughout the region is represented by the score FS-1 [70]. FS-2 mostly depicts a natural process (salinity component). The outcomes of human actions are depicted in FS-3. According to [71]), FS-4 had an impact on the contamination caused by urban liquid waste discharges. Human-caused factors (agrochemicals and domestic sewage) according to the FS-5, affect the water quality [72, 73]. In conclusion, this approach assists in extracting data sets that contain information on the sources of ions and factors that affect the quality of surface water (Figure 10).

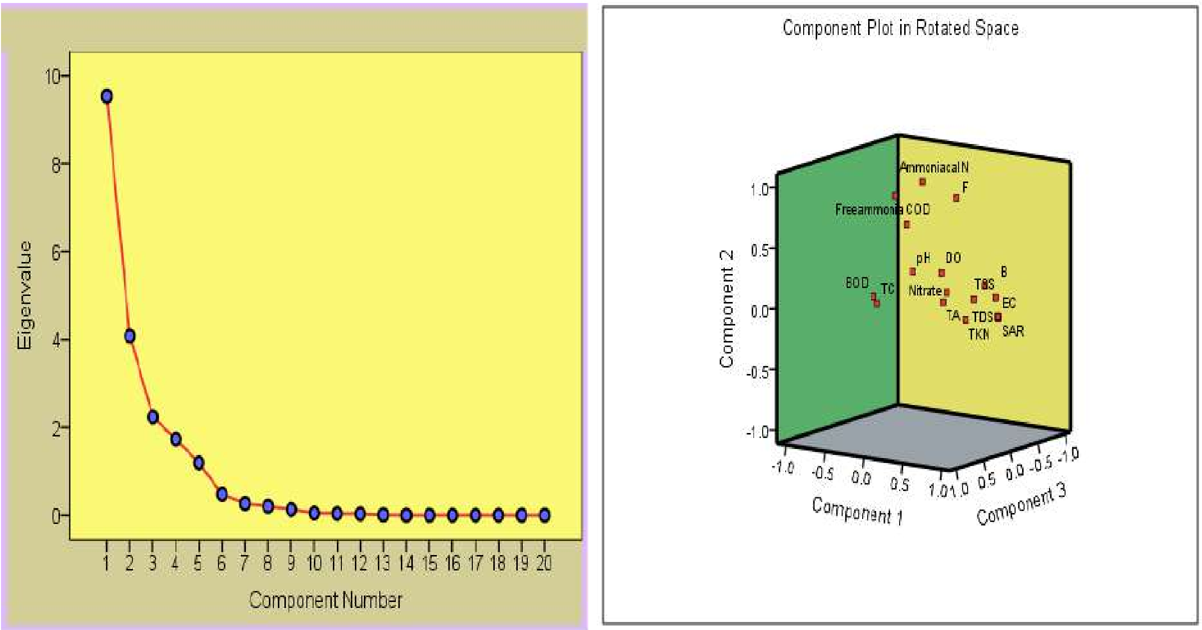


Fig. 8. Scree and loading plot of variance of PCs

Table 6. Results of loadings on significant PCs

Parameters	Principal Component (PC)				
	1	2	3	4	5
pH	0.10	0.63	0.02	0.30	0.65
DO	-0.52	-0.19	0.75	0.16	0.24
BOD	0.16	0.67	-0.62	0.15	0.03
TC	0.21	0.58	-0.71	-0.19	0.10
TSS	0.78	-0.10	-0.08	-0.56	-0.08
Alkalinity	0.48	0.28	-0.01	0.76	0.07
COD	0.37	0.91	-0.02	0.07	-0.06
NH_3-N	0.07	0.77	0.55	-0.22	-0.17
Free NH_3	-0.03	0.88	0.23	-0.32	-0.14
TKN	0.76	-0.15	-0.20	-0.14	-0.30
EC	0.98	-0.17	0.05	0.05	0.07
SAR	0.98	-0.18	0.04	0.04	0.07
B	0.98	-0.03	0.13	0.05	0.02
TDS	0.98	-0.17	0.05	0.05	0.07
TH	0.98	-0.15	0.05	0.06	0.07
Cl^-	0.98	-0.17	0.05	0.04	0.07
SO_4^{2-}	0.98	-0.16	0.05	0.05	0.08
F	0.47	0.62	0.58	-0.04	-0.16
NO_3^-	0.47	0.05	0.06	0.52	-0.61
Fe^{2+}	0.71	-0.01	0.17	-0.45	0.33
Eigen value	9.54	4.08	2.24	1.73	1.19
% Of variance	47.69	20.41	11.19	8.67	5.96
Cumulative%	47.69	68.10	79.28	87.95	93.92

Table 7. Factor Scores in each sample

Site No.	FS1	FS2	FS3	FS4	FS5
St-1	-1.28	-1.26	-0.03	0.15	-0.27
St-2	-0.47	-0.39	-0.63	0.51	-1.64
St-3	-1.56	-1.09	0.31	1.11	0.34
St-4	-0.58	1.10	0.04	1.61	0.52
St-5	-0.79	-0.71	0.39	-0.21	0.87
St-6	-0.74	-0.40	0.32	0.85	0.77
St-7	-1.31	0.47	1.02	-0.88	2.54
St-8	0.89	4.38	-4.69	-1.00	0.59
St-9	12.46	-1.37	0.29	0.20	0.33
St-10	-0.67	-1.77	0.33	-3.22	0.17
St-11	-1.59	-1.99	-0.01	-1.38	0.40
St-12	-0.82	-1.97	0.07	-0.38	-1.64
St-13	-0.31	-0.89	-1.23	-1.41	-1.58
St-14	-0.54	1.42	-0.49	2.13	-0.11
St-15	-1.38	-0.88	-0.07	1.58	-0.38
St-16	-0.37	-0.54	-0.22	0.72	-0.85
St-17	-0.64	-0.34	0.02	0.99	-0.07
St-18	-1.05	0.58	0.75	-0.33	1.26
St-19	0.75	5.67	3.82	-1.02	-1.26

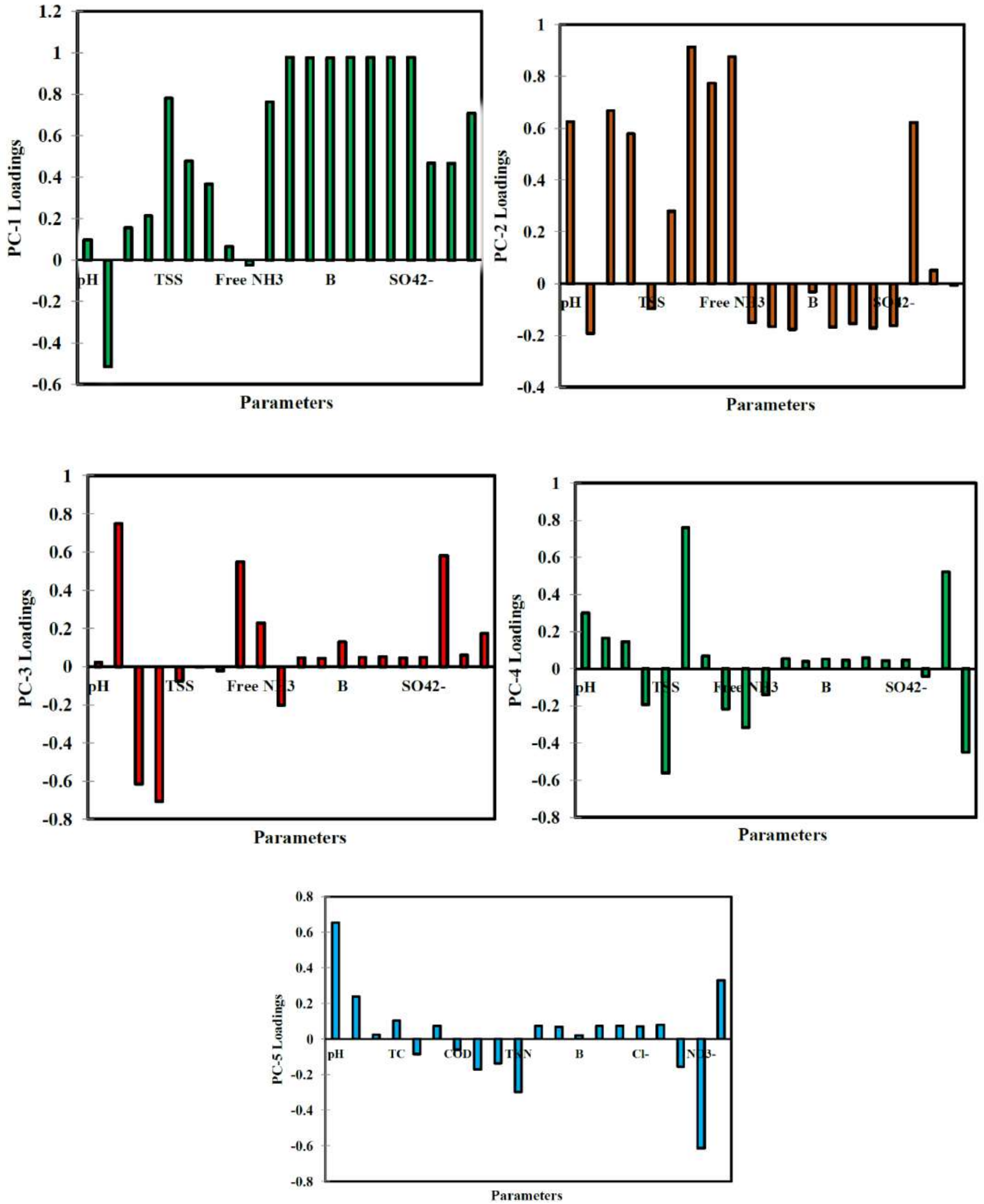


Fig. 9. Variation of 1st to 5th surface water factors extracted by PCA

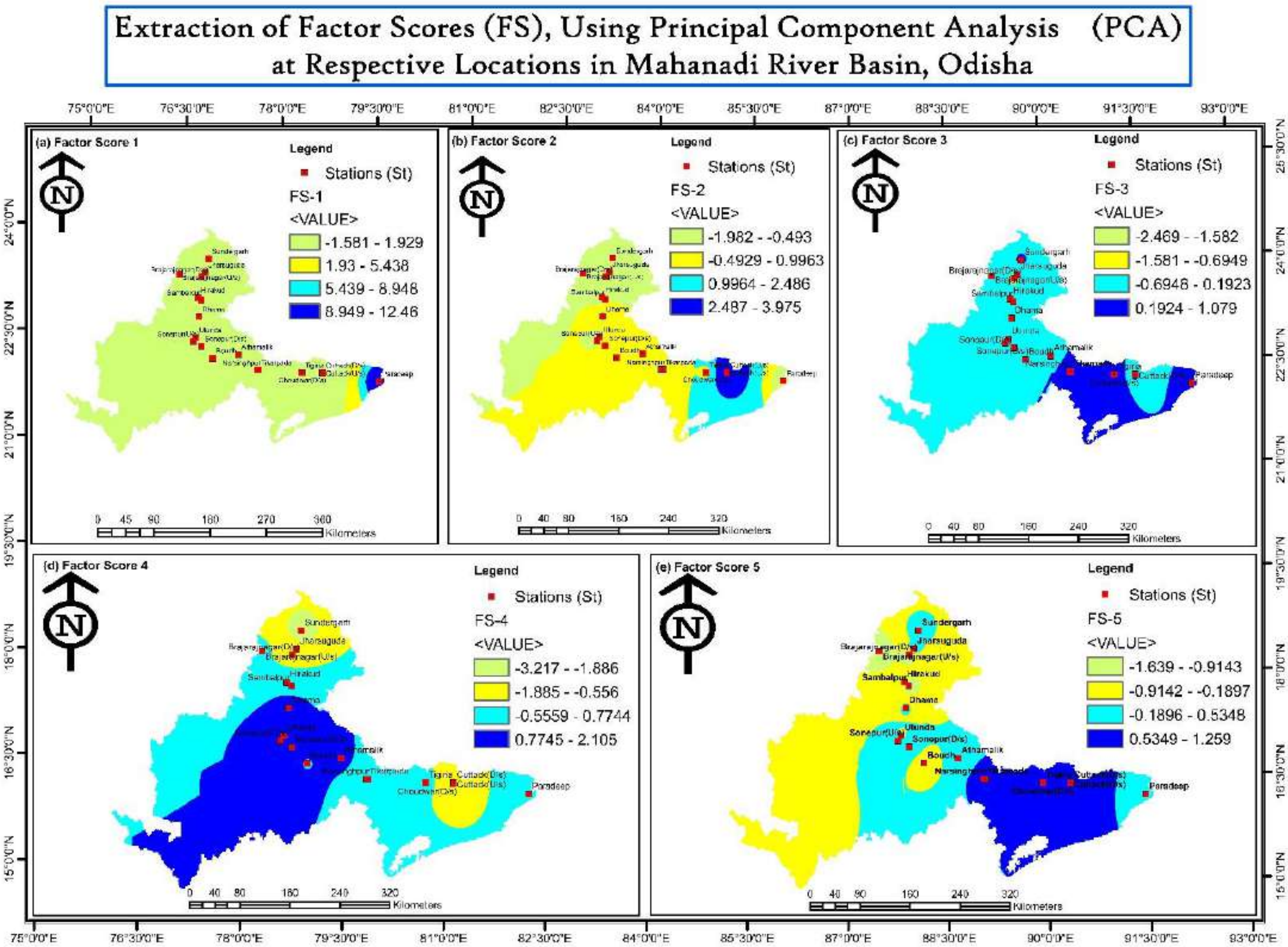


Fig. 10. Geo-spatial distribution of factor scores/loadings using GIS

6. Conclusion

The study has defined the surface water identification for human consumption and agriculture/farming uses, in the Mahanadi Basin, Odisha. In this study, applying multivariate statistical analysis techniques, the contributions of numerous likely sources to each water quality feature were allocated, such as CA, DA, and PCA, as well as MCDMs like ELECTRE and TOPSIS. A set of 20 water quality variables comprising 19 test sites over a 7-year period (2016-2023) was used for this. The study of EWQI reveals that the water quality is polluted at St-(8), (9) and (19) and not fit for drinking purpose, even though the local people are drinking. The high EWQI values at St. (9) were due to the high value of TC, TKN, EC, TDS, Cl^-, SO_4^{2-}, NO_3^- and Fe^{2+}. Seasonal fluctuations, agricultural practices, and other human-caused activities may be too responsible for this. On the basis of comparisons between the attributes of the river water quality, CA grouped the sampling places into 3 major classes. One of the explanations could be that industrial and domestic wastewater effluent emissions were often kept at a level that was relatively constant over the whole period. The best outcomes for spatial analysis come from DA. It used only 10 parameters (TC, TKN, EC, SAR, TDS, TH, Cl^-, SO_4^{2-} and Fe^{2+}) were shown to be the most accurate predictors (discriminant variables) of the heterogeneity of water quality in three clusters in stepwise method. It may be determined that the main causes of river water contamination are fluxes of point sources from human - caused climate change spurred on by the release of industrial, residential, and agricultural trash. According to the PCA analysis, five factors accounted for around 93.92 % of the variations in the dataset across the entire time period. The PCA results showed that the level of pollution increases as you move downstream. MCDMs were incorporated to examine the geospatial distribution of the relative water quality in relation to physicochemical characteristics. The developed TOPSIS and ELECTRE was applied on the dataset and ranked the St-9 as the most contaminated sampling point on the degree of performance score/closeness coefficients, followed by 2nd (St-8) and 3rd (St-19). Last but not least, the study has supported the viability and dependability of EWQI, MCDM, and multivariate statistical approaches for data analysis and justification from surface water quality analysis. More investigation would be needed to accurately evaluate the changes in other water quality parameters, which were not included in this current study, as well as the unidentified sources of contamination.

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