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AN INTEGRATED APPROACH FOR THE CHARACTERIZATION OF GROUNDWATER QUALITY USING MULTIVARIATE STATISTICAL TECHNIQUES AND SPATIAL ANALYSIS

S. Geetha[1], M. Dharmendirakumar[2] and J. Sunil[3*]

[1]Department of Applied Science and Technology, AC Tech, Anna University, Chennai, India
[2]Department of Applied Science and Technology, AC Tech, Anna University, Chennai, India
[3]Department of Mechanical Engineering, Annai Vailankanni College of Engineering, Kanyakumari, India

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ABSTRACT. Ground water accessed via wells in areas of Tiruvallur district of the southern Indian state of Tamil Nadu has been a subject to increase sea-water intrusion. The present study highlights the potable water crisis in the northern district evaluated using GIS-assisted determination of water quality parameters across fifty sampling sites. The most informative parameters evaluated within this study were TDS, EC, TH, Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} while parameters such as pH, CO_3^{2-}, etc. had limited correlated significance to water quality. The total dissolved solids (TDS) and electrical conductivity (EC) determined in the study area indicated significantly elevated levels across the sampling sites. Weighted arithmetical indexing (WAI) of the water quality parameters indicated 30 out of 50 water sources meet the tolerance limits for both drinking and irrigation. Based on BIS standards, only 13 sites met acceptable limits for safe drinking water. Principal component analysis and piper plot analysis revealed a significant involvement of Mg^{2+}, Na^+, Cl^- and SO_4^{2-} in the impairment of water quality, particularly in the coastal zones. Spatial hydro-chemical profiles developed in this study reveal 'hot-spots' of sea-water tainted water sources, and the hydro-chemical dominance of alkali earth components. Altogether, the study findings indicate a widening water crisis on top of over-exploited water resources and discuss possible factors and remedial steps in addressing the situation.

KEY WORDS: Ground water, Principal component analysis, Piper Plot, Water quality index, Irrigation suitability

INTRODUCTION

Incremental exploitation of ground water resources on account of growing human population and activities is further compounded in crisis with a worsening quality of accessible water [1-3]. As observed increasingly across the developing world, over-exploitation of ground water has led to retreating of the water table deeper in the ground; this phenomenon is further associated with increasing content of total dissolved solids in the water, frequently linked to leaching of minerals from lower strata of rocks. In addition to this, surface run-offs from agricultural land, direct input from human activity (construction/industry) also drive TDS in ground water. The ability to sustain human growth and agriculture is directly related to maintenance of acceptable water sources [4]. The growing need and depleting resource for irrigation water is confounded by diminishing water quality in parts of the country and demonstrated in the present study conducted in the northern Tiruvallur district within the southern Indian state of Tamil Nadu. The study area, comprising of five administrative blocks borders the Bay of Bengal on the eastern front. To the north of this territory lies the Pulicat lagoon, which experiences periods of hyper-salinity due to pronounced evaporation and land development [5]. Over the last decade, water quality reports in the region have accentuated a diminished access to usable water in the Minjur block, which contains critical to semi-critical water reserves [6, 7]. While the salinity of the water is discussed, it is unclear how the hydro-geo-chemical patterns impact the local region. The extended disadvantages of using drinking water with elevated levels of TDS and salt is often manifested as gastric disturbances and according to a scientific report, an increase in cardiovascular conditions [8].

*Corresponding author. E-mail: sunil0520@gmail.com

The present study is thus a direct independent attempt to evaluate the ground water quality and derivative usability indices in the north Tiruvallur district comprising the blocks Minjur, Gummidipoondi, Ellapuram, Sholavaram and Puzhal. Earlier studies have evaluated lower district areas with a general consensus depicting mostly safe water indices for both drinking and irrigation, at least based on standardized weighted arithmetic index [6, 9]. An insightful interpretation of the data, specially taking into consideration the principal components is required. Furthermore, discussion is warranted, taking into consideration the water quality indices and the long term impact of following locally accepted norms which exceed safety limits as assessed by national and international health agencies. The broad purposes of the current investigation were (1) to provide an overview of present groundwater quality and (2) to determine spatial distribution of groundwater quality parameters such as electrical conductivity (EC), chloride (Cl^-), sodium (Na^+), bicarbonates (HCO_3^-), and sodium adsorption ratio SAR concentrations, and (3) to map irrigation water quality index (IWQI) in the study area in order to identify places with the best quality for irrigation within the study area by using geographical information system (GIS) and geo-statistical techniques. To this effect, the work presented here hypothesizes (A) water quality indices (both drinking and irrigation water) are severely impacted, at least in part in the study area, (B) water quality characterized by high-TDS, high-cation type water, particularly at the coastal water resources, and (C) coastal water resources are largely affected by sea-water intrusion, in part due to close proximity of salt-water sources. Yet, largely, the unaffected resources are suitable for irrigation and to a major extent for drinking.

The study design will involve multivariate analysis to effectively gauge water quality with multiple indices and determine their level of consensus. Multivariate statistical analysis like correlation analysis (CA), principal component analysis (PCA), cluster analysis and piper plot can be used to characterize and evaluate the temporal and spatial variations of groundwater quality from complicated datasets [8]. Hydro-geochemical study involves presentation of geochemical data in the form of graphical charts like piper diagrams to assess the geochemical processes controlling the water chemistry and to delineate variation in hydro-chemical [10, 11]. Water quality index (WQI) developed by the national sanitation foundation (NSF) is applied here as a standard index for assessment of the water quality and also as a technique of rating water quality [NSFWQI]. Parameters are weighted according to their perceived importance to overall water quality and the index is calculated as the weighted average of all observations of interest [12, 13]. Groundwater quality was assessed for drinking and irrigation purposes using sodium adsorption ratio (SAR), soluble sodium percentage (%Na), permeability index (PI), entropy weighted water quality index (EWQI). These indices serve as a tool to convert a large set of data into a much reduced and translational-informative form. The study focuses on the application of geographical information system (GIS) and geo-statistical approach for the determination of spatial distribution of groundwater quality parameters. Furthermore, the approach will also be utilized for mapping irrigation water quality indices to identify places to aid in the decision to access the best quality for irrigation within the study area. Broadly, the present study provides an overview of the contemporary quality of the groundwater in the study area to report its suitability for drinking and irrigation purposes, which is an urgent but unmet need. The study would be of vital interest for the decision-makers in water resource management, public health, and ecosystem protection, given the emerging water crisis and unmitigated sea-water intrusion issue.

EXPERIMENTAL

Description of the study area

The study area covers the coastal blocks of Tiruvallur district, Tamilnadu, India. Geographically, it is located in the North Eastern part of Tamil Nadu between 12°15' and 13°25' N to 13°08' N and 79°53' E to 80°20' E. The study covers an area of 1278 sq km. The annual mean minimum and maximum temperature are 24.3 °C and 32.9 °C. The humidity is usually in the range of 58%

to 84%. Rainfall data analysis shows that the normal annual rainfall varies from 950 mm to 1150 mm. It may be noted that the area gets more rainfall during the North East Monsoon though it gets the influence of South West Monsoon (June - September) and North West Monsoon (October - December). The types of soil, predominantly found are red non-calcareous and coastal alluvial. Also, the soil found in the coastal region is of the erinaceous type (sandy). Seasonal rivers like Kosasthalaiyar, Araniar and Buckhingham Canal are flowing through the area and their drainage pattern is generally dendrite. Since these seasonal rivers are not sufficient, irrigation through tanks, tube wells and open wells are very common. Ground water occurs under phreatic to semi-confined conditions in the inter-granular pore spaces in sands and sandstones and the bedding planes and thin fractures in shale [13].

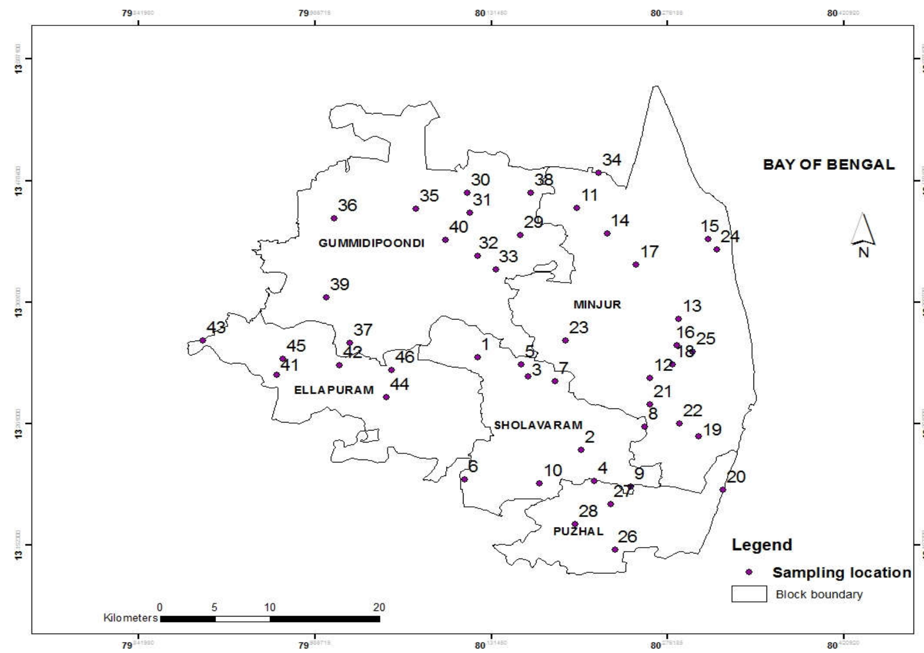


Figure 1. Ground water sampling locations of the coastal blocks of Tiruvallur district, India.

Sampling and analytical methods

A field survey was conducted and water samples were collected from 50 wells as identified in Figure 1. The samples were collected during the Premonsoon season. The water samples were analysed in laboratory for different physiochemical parameters (such as pH, electrical conductivity, total dissolved solids, total hardness, calcium, magnesium, potassium, sodium, chlorides, sulphates, nitrate, fluoride, carbonates and bicarbonates). The sample collection bottles (high-density polyethylene, HDPE), each with a capacity of one litre, were thoroughly washed with diluted HNO_3 acid, and then with distilled water. Next, the bottles were sterilized under aseptic conditions to avoid unpredictable contamination and subsequent changes in the properties of the groundwater. The collected groundwater samples were transported to the laboratory on the same day. Calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-) and chloride (Cl^-) were analyzed by volumetric titration methods, sodium (Na^+) and potassium (K^+) were measured with the flame photometer, sulfate (SO_4^{2-}), and nitrate (NO_3^-) were using spectrophotometric technique as per the methods described by the American Public Health Association [14]. All parameters are expressed as mg/L except for pH (absolute units) and electrical conductivity (µS/cm). The collection, preservation, transportation and analysis of water samples were carried out according to the standard methods described in APHA [14]. pH, EC and TDS were measured immediately after sampling at the sample collection site using a water analysis kit. Sodium (Na^+) and potassium (K^+) were analyzed by flame photometer; calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically using EDTA standard solution. Bicarbonate (HCO_3^-) was estimated by titration with H_2SO_4 standard solution. Chloride (Cl^-) was determined by titrating against $AgNO_3$ standard solution and sulfate (SO_4^-) using spectrophotometer. Nitrate and fluoride were also determined using a spectrophotometer in the laboratory. The analytical precision for the measurements of ions was determined by calculating the ionic balance error that varied between 5 and 8% [3, 4, 13-14]. The experimental values are compared with standard values recommended by World Health Organization (WHO) and Bureau of Indian Standards (BIS).

Statistical analysis

Multivariate statistical correlation matrix was determined between all parameters using statistical package for the social sciences (SPSS) software for Pearson's correlation analysis. Principal component analysis and dependent statistical determinations were carried out with Data tab Statistics Calculator (Data tab, Graz Austria) [10-11]. Principal component analysis (PCA) was used to analyse each element's association and reduce the number of parameters, making water quality testing easier in each sampling site. Cluster analysis was carried out using ClustVis for visualizing clusters in multivariate data [15]. Hydro-chemical facies was determined by the piper diagram [16-17]. Doneen plot analysis for calculating suitability of water for irrigation was carried out using meq/L values for Mg^{2+}, Ca^{2+}, Na^+ and HCO_3^- [18, 19].

Water quality index (WQI)

Water quality index (WQI) reflects the gross influence of various measured water components on the overall quality of water. The quality of water varies with time and geography, depending on the relative concentrations of different constituents and indicators of water quality parameters. Accordingly, appropriate parameters have been identified and evaluated to measure WQI reliably. In this study, the parameters considered for the suitability of water for domestic purposes are pH, total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), chloride (Cl^-), total dissolved solids (TDS), total nitrates (NO_2^-,NO_3^-), sulfate (SO_4^-) and fluoride (F). Similarly, the irrigation suitability of groundwater was examined based on sodium adsorption ratio (SAR) in associated with electrical conductivity (EC), sodium (Na^+), chloride (Cl^-), and bicarbonate (HCO_3^-). Additionally, derivative indices of Kelly's ratio (KR), magnesium adsorption ratio (MgR) were also determined and employed in evaluating quality indices for the sampled water.

Water quality index calculation

The water quality index (WQI) is a single figure that can be easily calculated and used to describe the overall quality of water bodies utilised for various purposes. WQI was calculated by adopting weighted arithmetical index method, briefly described here, a weight is assigned to the determined parameters significant to its relative importance (w_i); the maximum weight assigned is 5 and minimum is 1. The maximum intensity was assigned to parameters that root to severe damages to men and material and minimum weight is assigned for significantly less impact parameter. The relative weights (RW_i) are calculated as per the formula

$$\mathrm{R}W_i = \frac{\mathrm{w_i}}{\sum_{\mathrm{i}}^{\mathrm{n}} \mathrm{w_i}} \tag{1}$$

where, n is the number of parameters being assessed by WQI. Each parameter is assigned a quality rating scale (qi) as per the formula

$$q_i = \frac{e_i - W_i}{b_i - v_i} \times 100 \quad (2)$$

where, e_i is the value of each parameter as observed experimentally, v_i is the base value for each parameter (0 for all parameters except pH) and b_i is the standard value as recommended by BIS [20]. The sub-index (S.I.i) of each parameter for a place is thus calculated as

$$\mathrm{S}.l_i = q_i \times \mathrm{R}W_i \quad (3)$$

WQI of each station is calculated as

$$\mathrm{WQI} = \sum_1^n \mathrm{S}.l_i \quad (4)$$

Finally, the computed WQI values are usually classified into five categories as excellent water, good water, poor water, very poor water and unfit water for drinking purposes [21].

Evaluation of irrigation water quality

The irrigational water quality of the collected samples was assessed using water quality indices such as SAR (sodium absorption ratio) is an important parameter for determination of suitability of irrigation water [19]. Sodium hazard of irrigation water can be well understood by knowing SAR value which is calculated by the following formula,

$$\mathrm{SAR} = \frac{\mathrm{Na^+}}{\sqrt{\frac{\mathrm{Ca^{2+} + Mg^{2+}}}{2}}} \quad (5)$$

where, all ionic concentrations are expressed in meq/L. Other indices of value for assessment of irrigation water quality are figures such as permeability index (PI) (Doneen plot), Kelly's ratio (KR), magnesium ratio (MgR) and soluble sodium ratio (SSP) [19, 22-25]. Permeability index in conjugation with a Doneen plot (total ionic content vs PI) provides a numeric and visual guide to rating of water quality for the purpose of irrigation. PI is instrumental in the ability of water to access the rooting depths of crops; a poor PI score (<25%; Class III) is indicative of unsuitable water for irrigation. For sandy/loam type soils (as is the case in the present study case), a class I cut-off of 63% permeability is recommended in WQ evaluation [25]. Doneen defines PI as follows,

$$\mathrm{PI} = \frac{\mathrm{Na^+} + \sqrt{\mathrm{HCO_3}^-}}{(\mathrm{Na^+ + Ca^{2+} + Mg^{2+}})} \times 100 \quad (6)$$

Kelly's ratio calculated here is a valuable tool to assess sodium content of water and indirectly the site soil as a proportion function of alkaline earth ions (calcium and magnesium). Kelly's ratio is calculated as,

$$\mathrm{KR} = \frac{\mathrm{Na^+}}{(\mathrm{Ca^{2+} + Mg^{2+}})} \quad (7)$$

The ratio is a non-reductive expression of sodium proportion unlike the SAR. Being a more direct function of proportion, the KR value of 1 is considered a threshold and all water samples with values greater than 1 are considered unsuitable for irrigation. Magnesium Ratio or magnesium hazard, as it is also known is a function of magnesium to the total magnesium and calcium content of the water sample. Larger proportions of magnesium adversely affect crop growth due to increased alkalinity, hence a ratio greater than 50% is considered deleterious for irrigation purpose. MgR is calculated here as,

$$\mathrm{MgR} = \frac{\mathrm{Mg^{2+}}}{(\mathrm{Ca^{2+} + Mg^{2+}})} \times 100 \quad (8)$$

Soluble sodium percent is an indicator for relative sodium proportion, which is considered an exchangeable equivalent to Ca^{2+} and Mg^{2+} in clay-type soil. The implication drawn from the number is the relative sodium loading which may exaggerate precipitation, turbidity and general water quality for irrigation [26]. A value greater than 50% is considered as unsuitable for the purpose of irrigation. SSP is calculated here as,

$$SSP = \frac{(Na^{+} + K^{+})}{(Na^{+} + K^{+} + Ca^{2+} + Mg^{2+})} \times 100 \quad (9)$$

RESULTS AND DISCUSSION

Statistical analysis of groundwater

Hydro-chemical characteristics are major features with which to resolve the suitability of groundwater for various purposes [6, 19, 25] The physiochemical parameters of water samples were studied and descriptive statistical data of groundwater parameters provided in Table 1 with basic sample statistics. The World Health Organization (WHO) and BIS (IS 10500-2012) drinking water standards are also presented in Table 1 for subsequent analogy [8, 20]. The snapshot that emerges from this simple data provides the overview of the general water quality in the northern Tiruvallur district which is the subject of this study.

Table 1. Gross statistics of Tiruvallur (TN) groundwater parameters.

Parameter	Mean	Min	Max	Standard deviation	BIS standards (IS10500-2012)	WHO standards (2017)
pH	7.84	7.30	8.50	0.26	6.5-8.5	6.5-8.5
EC	1849	440	9020	1615	-	1500
TDS	1103	326	5384	1004	500	500
TH	456	120	2860	424	300	100
Ca^{2+}	89.0	21.0	724	102	75.0	75.0
Mg^{2+}	53.5	6.00	364	55.4	30.0	50.0
Na^{+}	237	28.0	1533	264	-	200
K^{+}	20.1	1.00	94.0	18.0	-	12.0
CO_3^{2-}	0.52	0.00	5.40	1.05	-	-
HCO_3^{-}	270	48.7	782	137	-	500
Cl_{-}	412	42.0	3268	547	250	250
SO_4^{2-}	86.6	11.0	522	89.9	200	250
$NO_3^{-} + NO_2^{-}$	14.6	2.00	74.0	18.4	45.0	45.0
F^{-}	0.40	0.00	1.32	0.33	1.00	1.50

All parameters are in mg/L, except for pH which is in standard units and EC electrical conductivity, in µS/cm. n = 50.

Water pH dictates the growth of crops, especially when it is heavily influenced by the aquifer chemical composition [6, 19]. The pH of the groundwater in the study area varies from 7.30 to 8.5 with an average value of 7.84, denoting very mild alkaline nature of the water, well within the permissible limits as laid down by water management authorities. It should be noted that the pH values depict the least variance among all the data measured in this study. The electrochemical conductivity assessment reveals the concentration of ionized substances in water and likely hardness and other mineral contamination. The EC values varied from 440 µS/cm to 9020 µS/cm with an average value of 1848 µS/cm. EC is used to depict salinity in water samples. The high variance in EC values maybe explained by the virtue of processes like sea water intrusion, mineral dissolution from the subterranean water cisterns, over ground soil exchange, etc. [27, 28]. The nearly twenty-fold variation between the various sampling sites strongly annotates the uniqueness of the water stores, belying the proximity in quality suggested by the pH balance data.

Total dissolved solids (TDS) represent different ions like carbonates, bicarbonates, chlorides, sulfate, phosphate, calcium, magnesium, sodium and potassium. The TDS ranges from 326 to 5384 mg/L, with a mean of 1103 mg/L. The occurrence of high TDS can be due to varied reasons, but it is frequently attributed to the dominance of environmental pollution like percolation of channel water containing solids, agricultural wastes, and industrial seepages, especially in nations such as India. TDS is also influenced by the leaching of rocks occurring at the water source. Infrequently, TDS can be attributed to water content by virtue of its source, such as the ocean, hyper saline lake, etc. [29, 30]. TH ranged from 120 to 2860 mg/L, with an average of 456 mg/L. Not unlike EC, TH data points vary over a twenty-fold difference. Similar to water sources with a large amount of clay, or origins from dolomite rock holding areas, the high and highly variable TH could be likely due to the presence of Ca^{2+} and Mg^{2+}, which are prevalent cations in the study area. While the very large content may not be explained by clay or rock strata leaching alone, other sources of Ca and Mg may occur naturally [32, 33]. The cations concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} vary significantly, with the mean values of 89.0, 53.5, 236 and 20.1 mg/L, respectively. The mean concentration of the cations is higher than the permissible limit suggested by BIS and WHO. The higher values of calcium and magnesium ions present in the groundwater are possibly due to the leaching of rock-forming silicates, limestone, dolomite, gypsum and anhydrides [26, 30, 34]. Leaching of soil introduces salt to the water and is a leading cause for high concentration of sodium ions at least in hinterland water sources. Seawater percolation in the coastal is the aquifers account for high sodium content. The measured dominance of cations is in the following order: $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$. This observation is concurrent with subsequently determined statistical correlations, as demonstrated further on. In a similar fashion, the anionic concentrations of CO_3^{-}, HCO_3^{-}, Cl^{-}, SO_4^{2-}, nitric/nitrous species (NO_2^{-}, NO_3^{-}) and F varies significantly, depending on the anion with the mean value of 0.52, 270, 412, 86.6, 14.6, 0.40 mg/L, respectively. As noted, Cl^{-} variance coincides with Na^{+} statistics. The alkalinity of the groundwater is on occasion driven by bicarbonates, however given the low bicarbonate and carbonate content it is unlikely that pH in influenced by these ionic species. Based on earlier studies, the carbonates and bicarbonates originate from dissolved salts, weathering of silicate rocks, dissolved carbon dioxide, etc. [35]. Chloride is one of the most prevailing ion in the groundwater samples. Elevated Cl^{-} levels are usually accounted for as a result of progressive stalinization, industrial effluents, chemical fertilizers and irrigation return flow, but in the current scenario, given low SO_4^{2-} levels, fertilizer run-off may likely be eliminated as a source of contamination [36, 37]. The chlorides moves conveniently with the soil water, gets absorbed by crops, moves inside the transpiration stream and accumulates within the leaves. Input of chloride beyond the crop tolerance limits lead to leaf burns and drying of leaf tissues [38]. In human, excess intake of Cl^{-} can bring about hypertension and renal stones due to chronic use. The amount of fluoride in the groundwater is within the permissible limit. The dominance of anions within this study is in the following order: $Cl^{-} > HCO_3^{-} > SO_4^{2-} > (NO_2^{-} + NO_3^{-})$.

Other indices that reflect the potential effect on crops by the water used for irrigation are potential salinity and the Doneen plot for permeability [24, 25]. Potential salinity is an informative index which can be used to determine if salt laden water will have an impact on irrigation and whether such an eventuality needs to be countered with adaptive agricultural practices. Briefly, the potential salinity plot describes a threshold (15 meq/L) of saline species under which crops are not impacted negatively by prevalent salinity of the water. With increasing salinity (15–35 meq/L), salt content of the water and soil does in fact, affect crops. Such a phenomenon dictates the rotation of moderately salt tolerant crop species. Above 35 meq/L PS, salinity approaching sea water contamination, more salt tolerant crops would be recommended to maintain agriculture, to overcome the arability challenge from the salt influx. The study depicted in Figure 2 reveals a majority of the water sampled to be from sources with acceptable PS. Crop strategies do not require modification in this scenario, however roughly 8 sampling sites indicate moderate to severe salt stress. In this case, a paradigm shift would be indicated for planting crops. Of note, the Central Salt Research Institute (Gujrat), is developing plant species such as tobacco which are genetically altered to tolerate salt stress [40, 41]. Such plants would be a good alternative to regio-specific crop rotation strategies.

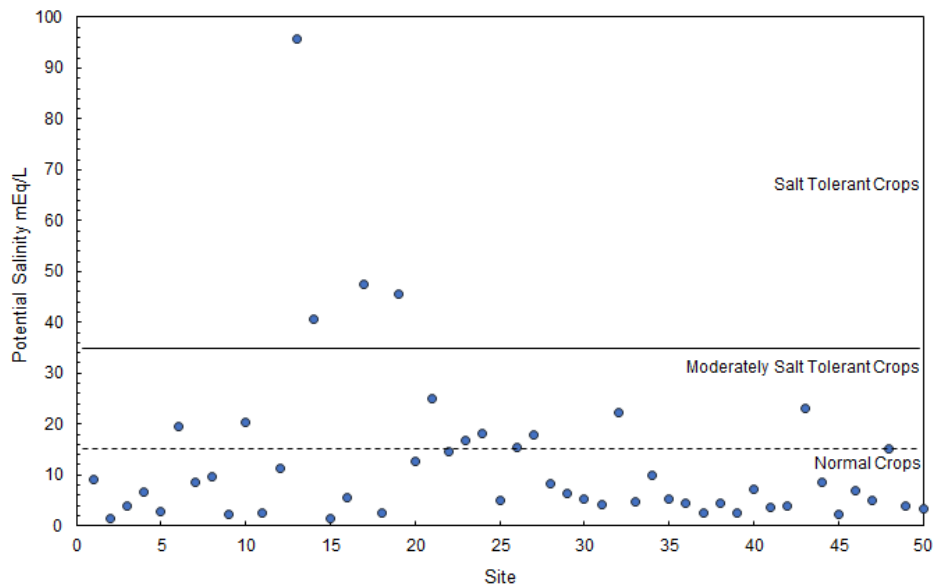


Figure 2. Potential salinity calculated from wqi parameters and impact upon crops.

Analogous WQ index to SAR, SSP and KR is a function known as the Doneen plot. It takes into account the calculated permeability index of the study sites and presents a comparative picture with regards to the ionic strength of the water involving the solutes in consideration [19, 25]. The permeability index calculated from Na^+, Ca^{2+}, Mg^{2+} and HCO_3^- content is reflective of the ability of the sampled water to permeate the soil. The higher the permeability, the easier the water can reach the 'rooting' depths of crops. Due to the interplay between Na^+, Ca^{2+}, Mg^{2+}, the properties of the soil can be negatively impacted to affect permeation. The Doneen plot as seen in Figure 3 explores the relationship between the gross ionic strength of the water sample and its estimated permeability. In the present work, water resources being investigated are present in geographical pocket with mostly sandy type soil, which also impacts permeation. To account for this fact, Doneen classification is chosen on the grounds of permeability.

As observed, while 8 water sites are considered fair – acceptable for irrigation, 6 are classified as unacceptable. The majority of the water sources (36) are generally safe and considered good for irrigation.

Multivariate statistical analysis

Multivariate statistical strategies are invaluable in drawing insight and latent information from large data pools. Correlation analysis (CA), principal component analysis (PCA) and hierarchical cluster analysis (HCA) provide pertinent information about contributing factors, primary components of large variance, association between multiple components [10, 11].

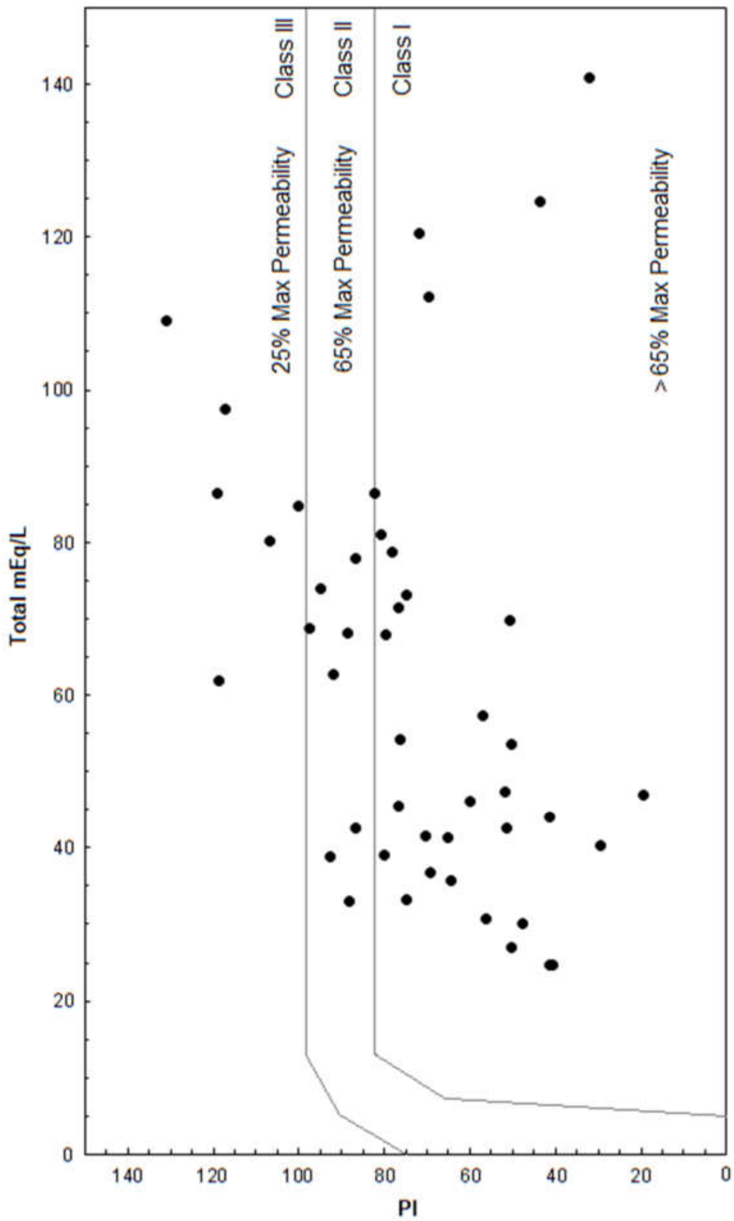


Figure 3. Doneen plot to assess suitability of water source for irrigation.

Pearson's correlation matrix methodology is used to assess the extent to which two or more variables are statistically associated. The correlation matrix is accomplished by SPSS Software for fourteen parameters and values of the correlation coefficient are shown in Table 2. The correlation coefficient of <0.5 indicate poor correlation. High significance of association is indicated by high values (>0.9) and are indicated. A strong correlation exists between Cl^- with Na^+ (0.97), Mg^{2+} (0.93), Ca^{2+} (0.90), EC (0.98), TH (0.91) and TDS (0.89) indicating the leaching of secondary salts and sea water intrusion. Significant correlation is demonstrated between EC with Na^+ (0.98), TDS (0.92), Mg^+ (0.91) which implies significant impact of these ions in driving the salt content of the water samples. The data also implicates TDS in driving electrical conductivity in water samples in majority of the samples. Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} are associated with TDS with high correlation coefficients 0.91, 0.84, 0.73, 0.89 and 0.76, respectively, although the correlation of Ca^{2+} and SO_4^{2-} appears to be lower than that for Na^+, Mg^{2+} and Cl^-.

Table 2. Pearson correlation matrix of the study area.

	pH	EC	TDS	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^- + NO_2^-	F^-
pH	1													
EC	-0.101	1												
TDS	-0.205	0.920**	1											
TH	-0.012	0.897**	0.798**	1										
Ca^{2+}	-0.027	0.849**	0.736**	0.941**	1									
Mg^{2+}	-0.113	0.919**	0.848**	0.903**	0.876**	1								
Na^+	-0.096	0.981**	0.900**	0.865**	0.836**	0.885**	1							
K^+	-0.026	0.249	0.243	0.069	-0.007	0.118	0.229	1						
CO_3^{2-}	0.099	0.099	0.111	-0.027	-0.046	0.013	0.102	0.816**	1					
HCO_3^-	-0.200	0.127	0.171	-0.083	-0.224	-0.012	0.159	0.236	0.000	1				
Cl^-	-0.102	0.984**	0.890**	0.919**	0.902**	0.937**	0.971**	0.186	0.081	0.000	1			
SO_4^{2-}	0.039	0.767**	0.714**	0.643**	0.591**	0.713**	0.694**	0.120	-0.010	-0.021	0.731**	1		
NO_3^- + NO_2^-	-0.193	0.159	0.297	0.082	0.055	0.041	0.185	0.138	0.063	0.304	0.110	0.008	1	
F^-	-0.258	0.309	0.265	0.307*	0.281	0.351	0.347	-0.017	-0.009	0.187	0.323	0.034	0.259	1

Values represent Pearson's correlation coefficients with appropriate sign (+/-). Significance is indicated by asterisks, ** (> 0.5).

The correlation coefficients of TH with Ca^{2+} (0.94) and Mg^{2+} (0.90) are particularly significant here, since these minerals are frequently associated with hardness of water. The pH has a negative correlation with most of the parameters as described earlier suggesting a diminished alkaline influence of the earth metal ions found abundantly in the water samples in the study.

Principal component analysis

The covariance of the parameters based on Pearson's matrix was also determined. The matrix forms the basis of the principal component analysis and utilizes the covariance values to establish principal component data groups. The eigen values and vectors determined from the covariance matrix yield three principal components, as shown in Table 3. As seen in Table 3, PC analysis classifies component 1 as the one with the most variance or 'information'. As mentioned earlier, TDS, EC, TH, cations correlate strongly with each other and demonstrate high variation in data. Consequently, the high eigen values corresponding to these parameters are grouped within principal component 1, followed by much smaller eigen values for the same parameters being grouped into subsequent principal component groups. Thus, we may interpret from the data that while water quality parameters such as K^+, NO_2^-/NO_3^- species, F^-, HCO_3^-, CO_3^{2-} and pH score very low in the PCA and hence are insignificant as primary contributory factors to the quality of the water. On the other hand, the very high values for TDS, EC, TH, Na^+, Ca^{2+}, Mg^{2+} and to some extent SO_4^- as well implicate them as strong factors in the overall composition and quality of ground water from the study area. Further, Table 3 provides the explained variance for each principal component (group). The explained variance is an indicator of degree of information which accounts for the impact on water quality as tested in the study area. Of the calculated 14 principal component (groups), the first group, predictably has the largest amount of variance which exponentially decreases with subsequent components. Thus, component 1 accounts for over 50% of the determined variance, followed by components 2, 3, etc. Kaiser's criterion applied to the data allowed for determining that statistically relevant principal components are restricted to the first three components [42]. Eigen values lower than 1 is considered insignificant contributors to variance.

Table 3. Principal component analysis for study area water samples.

	Component			Explained variance		
	1	2	3	Total	% of variance	Accumulated %
TDS	0.92	0.14	0.088	7.11	50.78	50.78
$NO_3^- + NO_2^-$	0.17	0.44	0.49	1.98	14.12	64.9
Ca^{2+}	0.89	-0.28	-0.09	1.65	11	76.7
Mg^{2+}	0.95	-0.11	-0.01	0.9	8	83.11
Na^+	0.97	0.07	0.02	0.81	5.76	88.87
K^+	0.2	0.84	-0.41	0.7	4.97	93.84
Cl^-	0.99	-0.04	-0.04	0.38	2.7	96.54
SO_4^{2-}	0.76	-0.12	-0.18	0.16	1.14	97.68
CO_3^{2-}	0.08	0.75	-0.54	0.11	0.76	98.44
F^-	0.36	0.14	-0.53	0.1	0.7	99.14
EC	0.99	0.05	-0.02	0.07	0.5	99.63
TH	0.93	-0.18	-0.05	0.04	0.27	99.9
pH	-0.11	-0.21	-0.6	0.01	0.07	99.98
HCO_3^-	0.05	0.54	0.49	0	0.02	100

Hierarchical cluster analysis

Primary data from the analysis of the water samples yielded precise values for indicated water quality parameters. While TDS, EC, TH, pH are dependant variables which rely on levels of the various ionic species present in the water, the ionic species may be investigated for mutual associations based on water source. Such a determination involves cluster analysis of linked groups. Hierarchical cluster analysis as shown in Figure 4 demonstrate the linking distance between the various groups to indicate close association.

The statistical cluster analysis program uses correlation statistics to cluster the data into a two-dimensional hierarchical cluster dendogram. The top dendogram clusters the ionic components while the left dendogram depicts a more complex dendogram clustering the fifty sampling sites based on their correlated traits. Parameters with lowest correlation scores (HCO_3^-, F^-) were eliminated from cluster analysis to refine the output. It should be noted that Cl^- and Na^+ followed by Ca^{2+} demonstrate the highest correlation statistics in the heat map. Clustering of water source sites is based on correlation of compositions. For instance, the co-clustering of sites 13 and 17 is observed within a small subset of clusters. It is noteworthy that these sites are roughly similar in context of elevated TDS, EC and TH. The clustering driven by ionic correlations appears to generate cluster 'clads' of comparable WQI features.

Piper plot analysis

Piper plot or diagram is used in the present study to fit data from tested water sources into a diamond cross-plot to develop a feature-rich depiction of water quality in terms of its relative composition [16]. The study reveals an inclination of the water samples towards the Na-Cl type. Of the data pool, site 13 has the most pronounced features in terms of TDS, EC, TH, Na^+ and Cl^-

content. The data from site 13 is annotated as a red circle to highlight the functionality of the piper plots in Figure 5. The Piper plot further delineates the composition of tested water samples into its cationic and anionic species. The relative proportions of the ionic species are spatially distributed based on the tri-linear plot coordinates leading to a chemical signature which identifies the primary chemical drivers in the water sample. For instance, the cationic triangle reveals the majority of the water samples to be of the Na-K type.

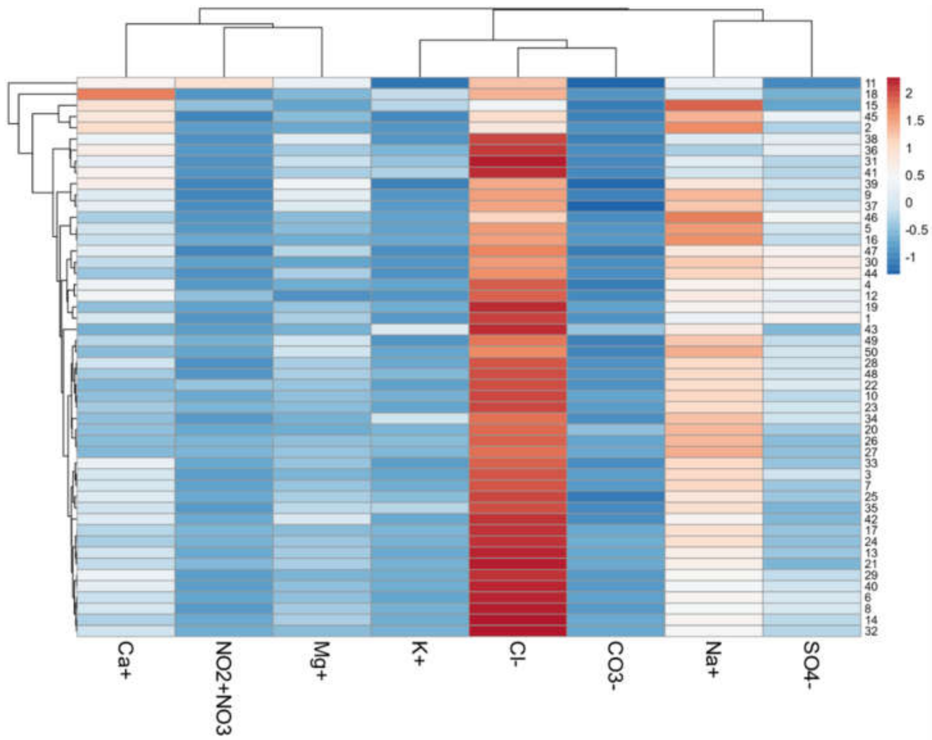


Figure 4. Hierarchical cluster dendogram. Inset heat map legend depicts correlation coefficients (red, high correlation > blue, low correlation).

Due to the relative proportions of Ca^{2+} and Mg^{2+}, samples like those from site 13 appear normally distributed in the middle of the cationic cluster. The anionic triangle plot denotes the Cl-type predominance in the water samples. Taken together, the piper plot is unequivocal in pinpointing the effective composition of the water samples, which is saline in nature. Sea water intrusion could account for the very strong Na-Cl signature in majority of the water samples, especially from the Minjur block [43].

Water quality index (WQI)

Based on thorough earlier studies, relevant water quality parameters were analysed and a sustainability evaluation was done. Table 6 exhibit the values of WQI of the study area and its suitability. The computed WQI values ranges from 37.9 to 299 as depicted in Table 4. 62.5% of the water samples signify as excellent to good water quality classes so these can be considered suitable as potable water. Remaining 37.5% of the samples collected falls on poor, very poor and unsuitable classes which were accounted to be unfit for consumption. The reason for this can be due to the over exploitation of ground water, domination of agricultural activities, leaching of ions to even discharge of effluents from domestic and industrial sources. The groundwater quality is classified based on DWQI range such as less than 50, 50 to 100, 100 to 200, 200-300, higher than 300 into excellent, good, poor, very poor and unsuitable, respectively.

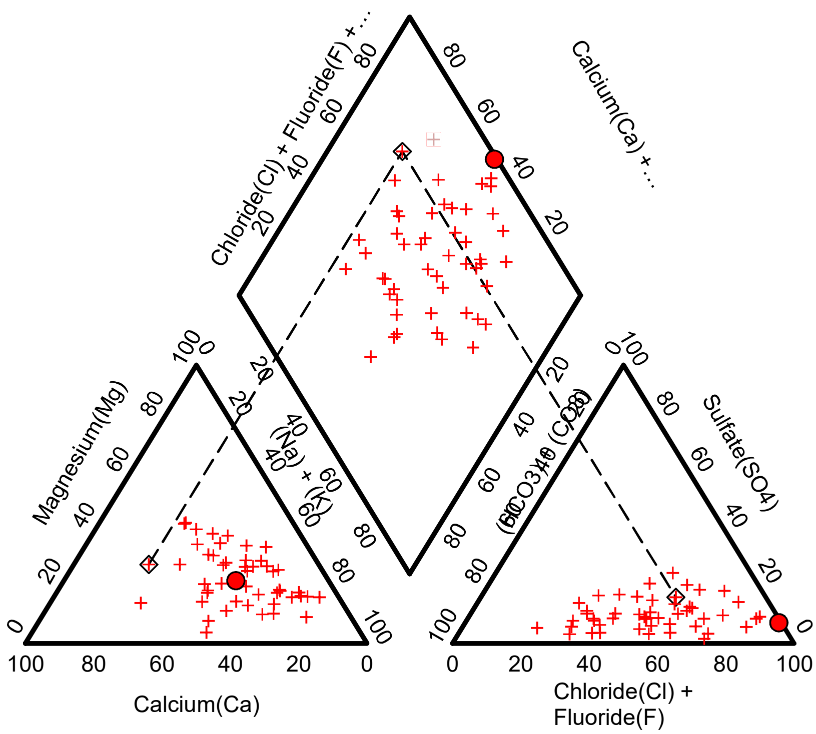


Figure 5. Piper plot to study broad hydro-chemical compositions of water.

However, there are 15 water sources which are not considered ideal and 4 sites which are entirely unsafe for human use. Note water from site 13 is classified as the worst quality of water, concurring with its extremely high TDS and salinity.

Irrigation suitability

The earlier discussion on irrigation suitability of the water resources in the northern district of Tiruvallur divulged details on specific aspects of the water samples in terms of their composition and the contemporary norms for irrigation suitability. Here we discuss broadly the ground reality of the irrigation suitability of the water sources in the study area. As noted earlier, depending on the WQ index used, a majority of the water samples were either deemed acceptable or unsuitable for irrigation use. Although SSP and KR are broad strokes of threshold classifications and may be subject to case-wise interpretation [25]. To aid this, the various indices need to be considered in concert. Based on SAR and SSP, at least half of the water sites can be considered 'irrigation-competent'. Potential Salinity determined for the water samples indicate only a handful of the sites experience a severe salt stress (sites 13, 14, 17, 19). While 11 sites have a marginal salinity issue, the vast majority may be considered as acceptable sources of irrigation water. Finally, the Doneen plot specifically identifies sites which do not meet the criteria of achieving at least 65% permeability. While other indices allow single components to dominate the index and drive the decision-making process, Doneen plot circumvents such an ionic dominance by factoring in the gross ionic load in the sample. Thus, site 13 with its extremely large Na component is balanced by the content of other ions. The interpretation in this context allows site 13 to be included in the acceptable water sources, despite its high salinity. Like the Kelly's ratio analysis, the weighing of a single WQ index appears to be at the risk of flawed interpretation. It has to be borne in mind that all the indices were developed with a specific function in focus, with the broad aim to classify a specific feature and not the general water quality at large. According to the Doneen classification [19, 25], water sources from sites 22, 23, 26, 34, 46 and 49 are compromised in their ability to irrigate safely.

Table 4. WQI for human consumption.

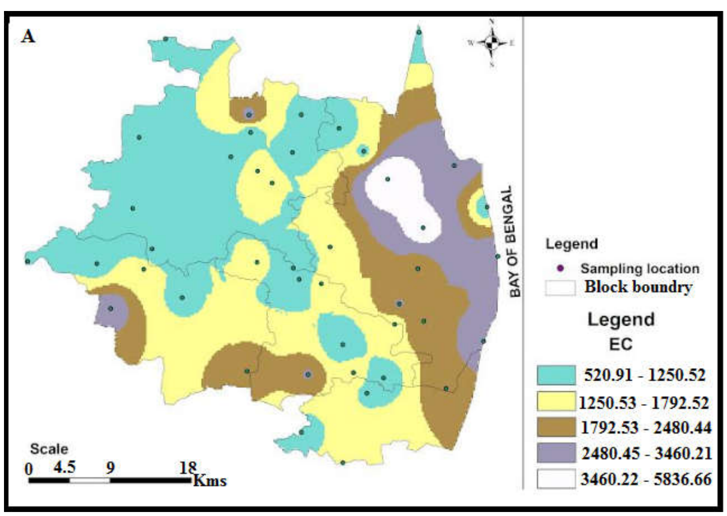
Sample No.	DWQI	Type of classification	Sample No.	DWQI	Type of classification
1	47.19	Excellent water	26	58.12	Good water
2	55.31	Excellent water	27	60.17	Good water
3	24.10	Excellent water	28	42.24	Excellent water
4	45.51	Excellent water	29	31.25	Excellent water
5	21.98	Excellent water	30	24.78	Excellent water
6	50.68	Good water	31	24.04	Excellent water
7	37.57	Excellent water	32	49.41	Good water
8	33.42	Excellent water	33	37.76	Excellent water
9	25.50	Excellent water	34	39.31	Excellent water
10	51.90	Good water	35	34.75	Excellent water
11	34.92	Excellent water	36	23.48	Excellent water
12	47.75	Good water	37	27.85	Excellent water
13	198.5	Very poor water	38	26.21	Excellent water
14	84.41	Poor water	39	27.81	Excellent water
15	21.95	Excellent water	40	28.01	Excellent water
16	30.15	Excellent water	41	21.95	Excellent water
17	111.1	Poor water	42	25.97	Excellent water
18	25.54	Excellent water	43	59.07	Good water
19	96.51	Poor water	44	37.23	Excellent water
20	42.69	Good water	45	25.31	Excellent water
21	73.15	Good water	46	40.10	Good water
22	69.34	Good water	47	30.49	Excellent water
23	56.62	Good water	48	51.28	Good water
24	52.80	Good water	49	32.22	Excellent water
25	40.87	Excellent water	50	31.42	Excellent water

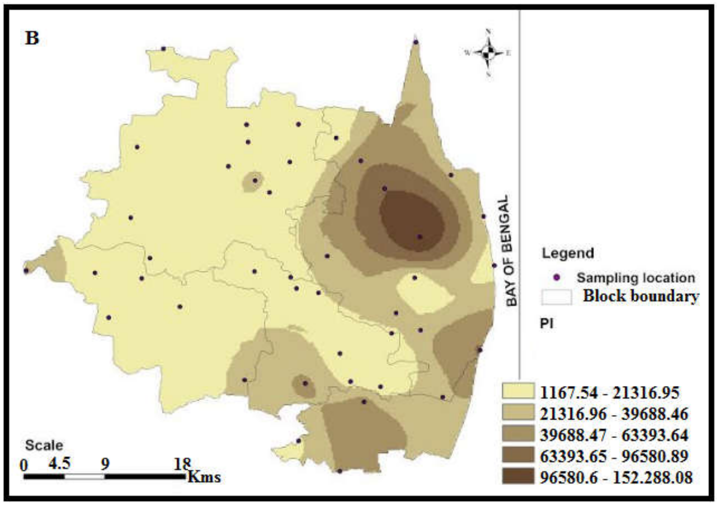
The phenomenon of sea-water intrusion and its downstream effects in alteration of water quality parameters renders it complex to be interpreted, especially since the norms are not designed to factor sea-water contamination. A modified approach to reliably interpret statistical information is hence required. Such a modified interpretation could be invaluable in studying coastal area agriculture as well. In the present context, we draw an average consensus of the various indices calculated. A majority of the water sources are deemed safe for irrigation, while the practical threat of sea water contamination renders sites like number 13, 17, 19 unusable. Magnesium hazard and other potential indicators are virtually absent in the current study, low levels of nitrogen species and sulphates indicate very low degree of fertilizer contamination [45]. The usability of water is almost complete dictated by the degree of sea-water intrusion.

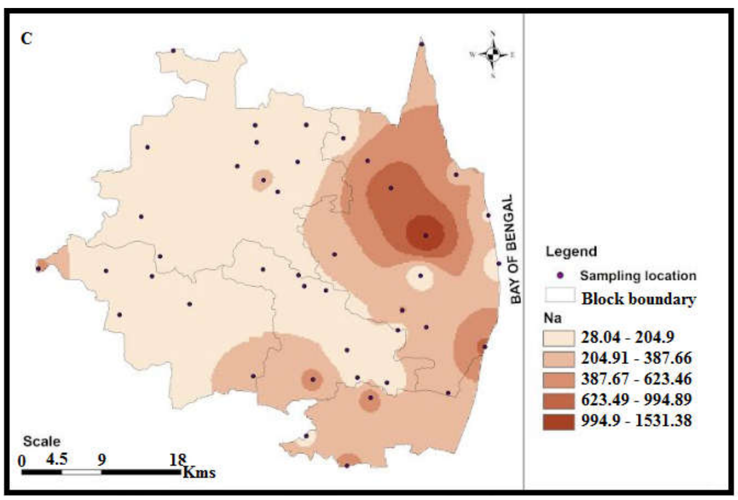
Spatial analysis of hydrochemical features

The geo-spatial mapping of hydro-chemical traits as accomplished in this study helps to generate high-quality cartographical data which are used in conjunction with statistical interpretation here to better express the hydro-chemical signature of water sources in the study area. Figure 6 shows the panel of GIS-assisted hydro-chemical mapping of the northern Tiruvallur district. The panel depicts (left to right) in the top row – the zone map of the study area, maps of TDS, EC and in the bottom row – maps of PI, Na^+ and Cl^-. As discussed extensively, the TDS is a potent indicator of dissolved content of the water samples [46]. Ionic species register heavily in the TDS composition as evidenced by its high conductance and strong correlation coefficients with Ca^{2+}, Mg^{2+}, Na^+, Cl^- and SO_4^{2-}. The region surrounding site 13 shows a remarkable intensification of TDS which gradually spreads out in the area. Secondary sites are around site 19 to the bottom of the study area. Similarly, sites 13 and 17 are implicated again for very high electrical conductance readings. While arguably generated by the hyper-saline water, pockets of high EC are seen at multiple locations away from the coast or the Pulicat Lake towards the north.

Significantly, the geo-patterns of Na and PI form resembling distributions. The core pattern of high value zones are maintained throughout the panel images, especially for Na^+, Cl^- and PI. The resemblance of the patterns could be attributed to interdependence such as TDS and PI being a function of Na^2. Cl^{2-} and Na^- has similar core patterns, which based on the piper plot is suggestive of NaCl dominance in the vicinity of site 13 and 17. The high salinity is in turn attributed to sea-water intrusion as well as estuary back-flow from the northern hyper-saline Pulicat Lake. The estuary allows hyper-saline waters, at least in the pre-monsoon period to penetrate the land in the indicated areas. Extensive studies are required to map the precise mechanism, geo-patterns and extent of sea-water intrusion such as the investigation carried out by Saxena, et al using strontium and boron [47].




B
BAY OF BENGAL
Legend
Sampling location
Block boundary
PI
1167.54 - 21316.95
21316.96 - 39688.46
39688.47 - 63393.64
63393.65 - 96580.89
96580.6 - 152.288.08
Scale
0 4.5 9 18 Kms


C
BAY OF BENGAL
Legend
Sampling location
Block boundary
Na
28.04 - 204.9
204.91 - 387.66
387.67 - 623.46
623.49 - 994.89
994.9 - 1531.38
Scale
0 4.5 9 18 Kms

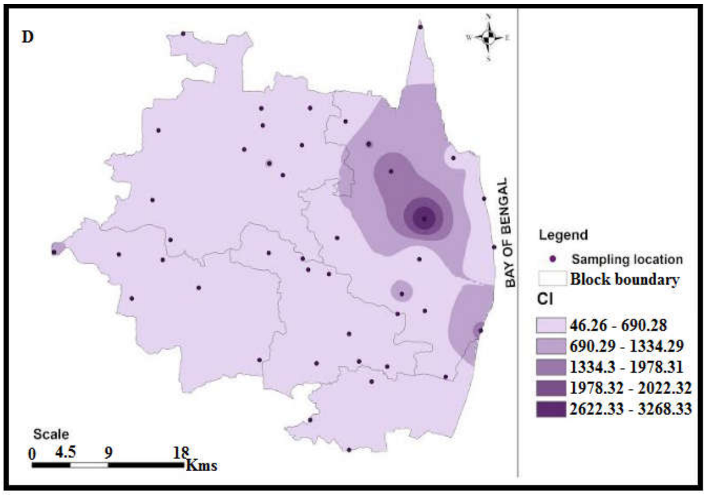


Figure 6. Spatial mapping of hydro-chemical features. (A) EC distribution map, (B) PI distribution map, (C) Na distribution map and (D) K distribution map.

Thus, an image emerges implicating a spill-over of sea water into the water resources of Tiruvallur district along the coastline and towards the north along the lake Pulicat. The groundwater runs a high probability risk of getting contaminated by sea water and in some cases, with evidenced intermixing. Water from Minjur block is not claimed as drinking water for urban use since 2017, instead waterproof reservoir tanks are being increasingly used to prevent the phenomenon. However, the question of usability of groundwater for irrigation still persists. As discussed here, the general consensus although not unanimous, suggests the use of ground water for drinking and irrigation, except in certain sites. The primary hazard for agricultural activity is NaCl; hence the use of salt-tolerant plant varieties is indicated. Cross-disciplinary studies may be undertaken to explore salt water irrigation and cultivation methodologies [47]. While desalination is an expensive approach for irrigation, it may still provide much needed relief to the local population.

CONCLUSION

The present study effectively evaluates and compares the water quality of water sources across fifty sites in the state of Tamil Nadu. The coastal block of Minjur has been implicated lately as a critical water resource and at the threat of hyper-salinity. A systematic evaluative and statistical approach has identified principal components comprising of the fourteen distinct water quality parameters measured in each of the fifty water samples. A basic statistical approach implicates TDS, EC, TH, Na and Cl as potent input to the water quality. The measured dominance of cations is in the following order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, while the dominance of anions is in the order: $Cl^- > HCO_3^- > SO_4^{2-} > (NO_2^- + NO_3^-)$. More specifically, the multivariate analysis conducted here pinpoints the challenging nature of the water sources. The statistical treatment identifies NaCl as a primary contaminant of the water sources in most cases, implicating sea-water intrusion at many test sites. The multivariate analyses provide a complex output with regards to irrigation-suitability of water, largely owing to the large mineral content of the water, however a consensus-drawing inference allows fair evaluation of the samples and allows for identification of salt-stress regions.

The water sources in Tiruvallur district are largely irrigation-suitable, except for hot-spots with hyper-saline water, unsafe for irrigation and drinking. Additional administrative support is warranted in this scenario, with efforts required to combat the sea-water intrusion of ground water and for providing support for agricultural activities in the hyper-saline zones.

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