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A GIS-based assessment of water quality pollution indices for heavy metal contamination in Tuticorin Corporation, Tamilnadu, India

S. Selvam[1] · S. Venkatramanan[2] · C. Singaraja[3]

Abstract The present study was conducted to evaluate the metal pollution of groundwater in the vicinity of Tuticorin Corporation in Tamilnadu State, India, used by various pollution indices such as heavy metal pollution index (HPI), heavy metal evaluation index (HEI), and degree of contamination (DOC). Thirty-six groundwater samples were collected during the summer season (May 2013) and the concentration of metals Al, Cr, Fe, Cu, Mn, Ni, Zn, Cd, and Pb was analyzed. Consequences exhibited that groundwater was contaminated with Mn (59.12 ppb), Cu (162.41 ppb), Pb (196.15 ppb), Cr (187.12 ppb), and Cd (10.11 ppb). Correlation and factor analysis revealed that the sources of metals in groundwater in the study area are the same, and it may due to the leachates from the nearby sewage farm, industrial activity (State Industries Promotion Corporation of Tamil Nadu Limited (SIPCOT)), Buckle canal, and solid wastes dumped in the residential area. Groundwater pollution indices of HPI, HEI, and DOC revealed that most of groundwater samples belonged to the medium to high zones, which was adjacent to the polluted Buckle canal, SIPCOT industrial waste, and sewage fish farm in the coastal area. The present study points out that the metal pollution causes the degradation of groundwater quality around Tuticorin coastal corporation. These study results will be very helpful for sustainable management of groundwater resources, and they will enable planners and policymakers to evolve a strategy to solve similar problems elsewhere.

Keywords Heavy metals · HPI · HEI · DOC · Tuticorin

Introduction

Water is the most important natural resource utilized for drinking, irrigation, and industrial purposes in various areas. Water is not only the most important essential constituent of all animals, plants, and other organisms but also the pivotal for the survivability of mankind in the biosphere. Groundwater occurs almost everywhere beneath the earth surface not only in a single widespread aquifer but also in thousands of local aquifer systems. Several factors such as climate, characteristics of soil, circulation of groundwater through rock types, topography of the area, intrusion of saline water in coastal areas, human activities on the ground, etc. posses several effects on the quality of water (Agarwal et al. 2013). Safe and good-quality drinking water is the basis for good human health. Water provides some elements, but when polluted, it may be dangerous to human health and cause diseases such as various cancers, adverse reproductive outcomes, cardiovascular disease, and neurological disease (Chidambaram et al. 2007a; Srinivasamoorthy et al. 2008; Magesh and Chandrasekar 2012; Singaraja et al. 2012a; Selvam et al. 2013a).

Water contaminated from industrial effluents, pesticides, fertilizers, and detergents finds its way into lakes, streams, rivers, oceans, and other water bodies and adds toxic substances into these aquatic systems. The problem of environmental pollution due to toxic metals has raised widespread concerns in different parts of the world, and results reported by various agencies have been alarming. "Heavy metals" is a collective term which applies to the group of the metals and

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metalloids with atomic density greater than 4 g/cm^3 (Hutton and Symon 1986; Nriagu and Pacyna 1988). However, being heavy metal has little to do with density but concerns chemical properties. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), and platinum group elements. The main sources of heavy metal pollution are agricultural runoff, sewage, and discharges of untreated and semi-treated effluents from metal-related industries such as metal electroplating, manufacturing of batteries, circuit boards, and car repair. Road is also one of the largest sources of heavy metals (Farmaki and Thomaidis 2008; Magesh et al. 2011; Selvam et al. 2013b). Some heavy metals such as Cu, Fe, Mn, Ni, and Zn are compulsory micronutrients for flora–fauna and microbes. Besides, metals like Cd, Cr, and Pb are harmful beyond a certain limit. Therefore, the heavy metal concentration in drinking water should be kept in low ppb range. One of the most hazardous trace metals found in drinking water is arsenic (As) being both toxic and carcinogenic. In very small quantities, even Cr and Ni are required in the body. However, some other metals like As, Cd, Pb, and methylated mercury have been reported to have no known importance in human biochemistry and physiology, and consumption even at very low concentrations can be toxic. Even for those that have bioimportance, dietary intakes have to be within regulatory limits as excesses may result in poisoning or toxicity (Fosmire 1990; Nolan 2003; Young 2005; Chidambaram et al. 2007b; Srinivasamoorthy et al. 2011; Selvam et al. 2013c; Singaraja et al. 2015; Venkatramanan et al. 2014).

As the population of Tuticorin Corporation continues to rise, human activities like soil fertility remediation by fertilizer application, indiscriminate refuse, waste disposal and the use of septic tanks, soak away pits, and pit latrines are on the increases as well. These activities are capable of producing toxic leachates which percolate into porous geological stratum accommodating groundwater, thereby contaminating groundwater as well (Mondal et al. 2010; Singaraja et al. 2012b; Selvam et al. 2014a; Antony Ravindran and Selvam 2014). Borehole water serves as the major source of drinking water in the local population of Tuticorin Corporation, since only very few households can afford and rely on treated and purified bottle water. This practice places commercial value on a relatively noncommercial commodity (groundwater), thereby neglecting quality and professional considerations and in the process risking public health, all in a bid to maximize profit.

It is expected that this research can contribute to the identification of heavy metal contamination sources and origins and to the effective conservation and management of groundwater in Tuticorin Corporation, Southern Tamilnadu. It applied both the conventional statistical methods and geographic information system (GIS) to develop the source of heavy metal contamination.

Study area

Tuticorin is located strategically close to the east–west international sea routes on the southeast coast of India. It is a coastal town with a sea port and has been recently upgraded as corporation. Tuticorin was established as a municipality in 1866. It attained the status of corporation on 5 August 2008 after 142 years. The study area covers a geographical area of 154 km^2 and lies between 8° 43′–8° 51′ N latitude and 78° 5′–78° 10′ E longitude (Fig. 1). The population is mainly engaged in agriculture. Numerous salt pans, salt-based industries, and marine chemical industries are located in this zone. The city was industrially developed after the construction of the port and became district headquarters in the year 1986. After the formation of the district headquarters, the economic development was boosted and began to develop rapidly. Therefore, the urban expansion takes place in the different parts of the city during the study period. This farm which is approximately 40 ha is totally dedicated to all-year-round agricultural production with a few population of nomads and agriculturists settled within the area. Common crops such as tomatoes, garden eggs, pepper, spinach, cassava, and other vegetable/leguminous crops are grown in the dry season, while crops like rice, sugarcane, maize, and guinea corn are also mixed with the above crops in the rainy season (Selvam et al. 2014b). In the rest of the study area, industries manufacturing chemicals, salt, flower dying, copper wire, copper alloy, alkali chemicals and fertilizers, petrochemicals and plastics, heavy water, chemical dying, and bleaching dispose industrial and hazardous wastes nearby agricultural lands which craft a major threat to the adjoining groundwater environment. Topographic elevation varies from 0 (near the coastline) to 27 m (msl) in the western part of the study area. The slope is gentle in the western and the central part; further, it is nearly flat in the eastern part (Selvam et al. 2014c).

Geology and hydrology

The study area consists of 90 % of sedimentary rocks of Tertiary to Recent age comprising shell limestone and sand, Tuffaceous Kankar, sand (aeolian deposits), etc., and the remaining area is covered by mixed and composite gneiss of Proterozoic age of crystalline rocks (Fig. 1). The sedimentary rocks are fine to medium grained, hard, compact, and fossiliferous with shells of gastropods and pelecypods. The thickness of the strata varies from place to place, from a few meters to more than 20 m. The formation extends in the NE–SW direction dipping SE with low angles. Sand admixed with clay is the major formation making the aquifer media. The coastal study area is underlined by loose-textured coarse calcareous grits and shell limestone of sub-recent age. Rocks are horizontally bedded with a low dip of 10° to 15° SE. The Archaean groups
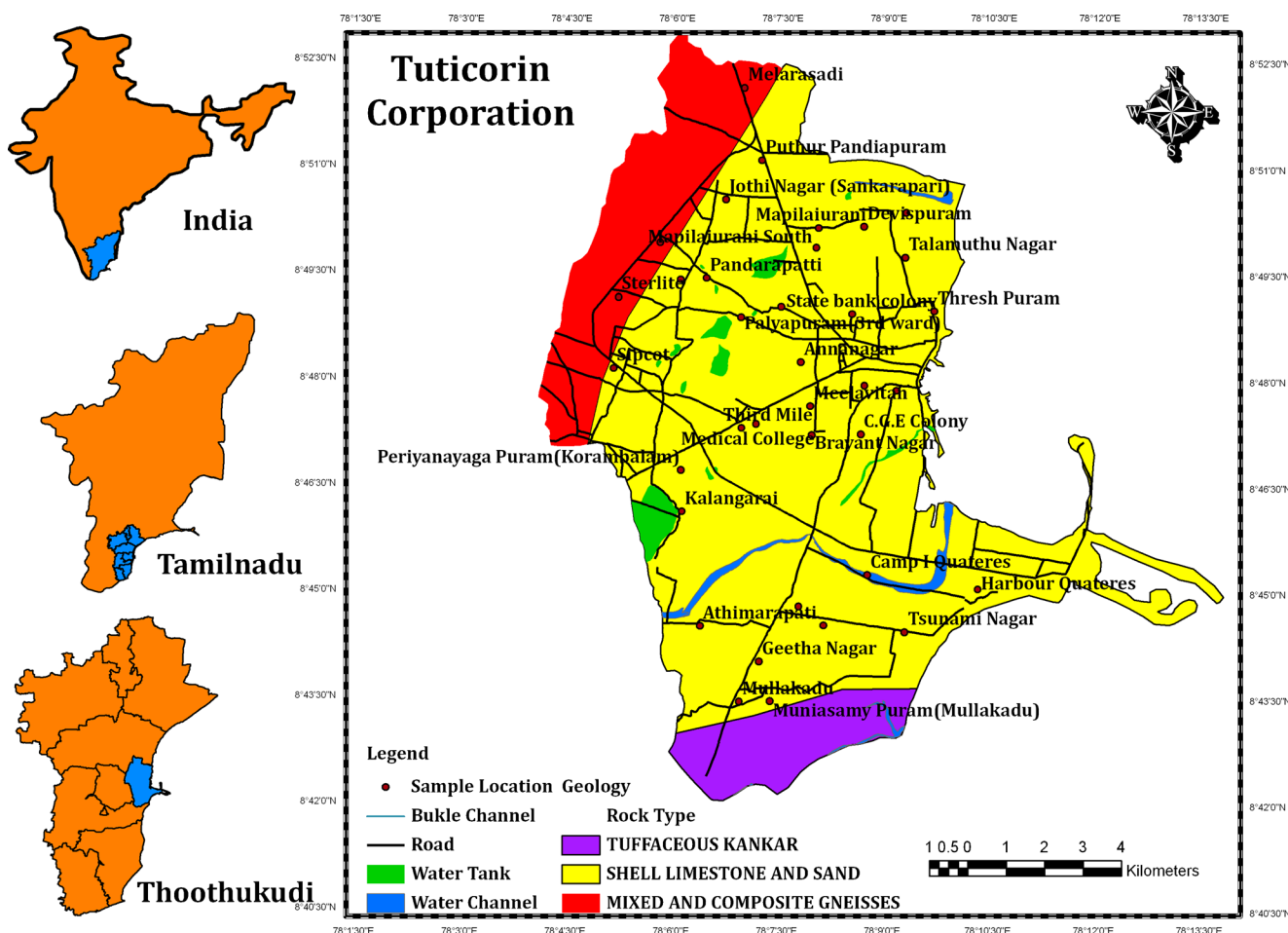
Fig. 1 Map of geology with sample location of the study area

of formations are crystalline, metamorphic, and finely foliated with a general NW–SE trend (Balasubramanaian et al. 1993; Selvam et al. 2014d). The area is covered with black soils in the western part (Sankarapari area), red soil (sandy loam to sandy soil) in the central part, and alluvial sandy soils (coastal area) in the eastern part (Fig. 2). Thickness of soil is 3 m and the sandy soils originated from sandstones with low soil moisture retention. Alluvium soils of wind-blown sands and shells are setup by beach sand and coastal dunes, which have very low soil moisture retention. Aquifer systems of the district are established by unconsolidated and semi-consolidated formations of weathered and fractured crystalline rocks. Porous formation of the district exhibits sandstones of Tertiary age, while recent formations containing sands, clays, and gravels are confined to major drainage courses in the district. The maximum thickness of alluvium is 45.0 m bgl, whereas the average thickness is about 25.0 m (Selvam 2012).

The average annual rainfall of this study area is 877 mm. The NE monsoon contributing 65.4 % of annual rainfall is the major component of recharge into the aquifer. The total number of rainy days in a year is only 38.5. Rainfall data from seven stations over the period of 2000–2010 were utilized,

and a perusal of the data shows that the normal rainfall varies from 599 to 749 mm, which is far less than that of the state average (942.8 mm). The contribution of the SW monsoon is only 8.06 % (Selvam 2014).The maximum and minimum rainfall was observed during November and June, respectively. Hydrological characteristics of this coastal belt consist of two major geological formations such as shell limestone and aeolian deposits. Groundwater occurs in confined and semi-confined condition. Hydraulic properties of these aquifers are exhibited in vertical and horizontal dimensions. The depth of the water table varies from 1 to 10 m bgl in post-monsoon and 2 to 15 m bgl in pre-monsoon. The mean maximum and minimum temperature was noted in 37.6 °C (June) and 19.9 °C (January), respectively. During the NE monsoon, the temperature came down to 22.30 °C corresponding to a heavy downpour. The temperature is relatively high and increases the rate of evaporation of the surface water and also the actual evapotranspiration, which is nearly equal to that of the annual precipitation (Balasubramanaian et al. 1993; Selvam et al. 2014e). Based on the scanty contribution of rainfall over recharge into the groundwater system, it is expected to be very less.

Fig. 2 Soil map of the Tuticorin Corporation
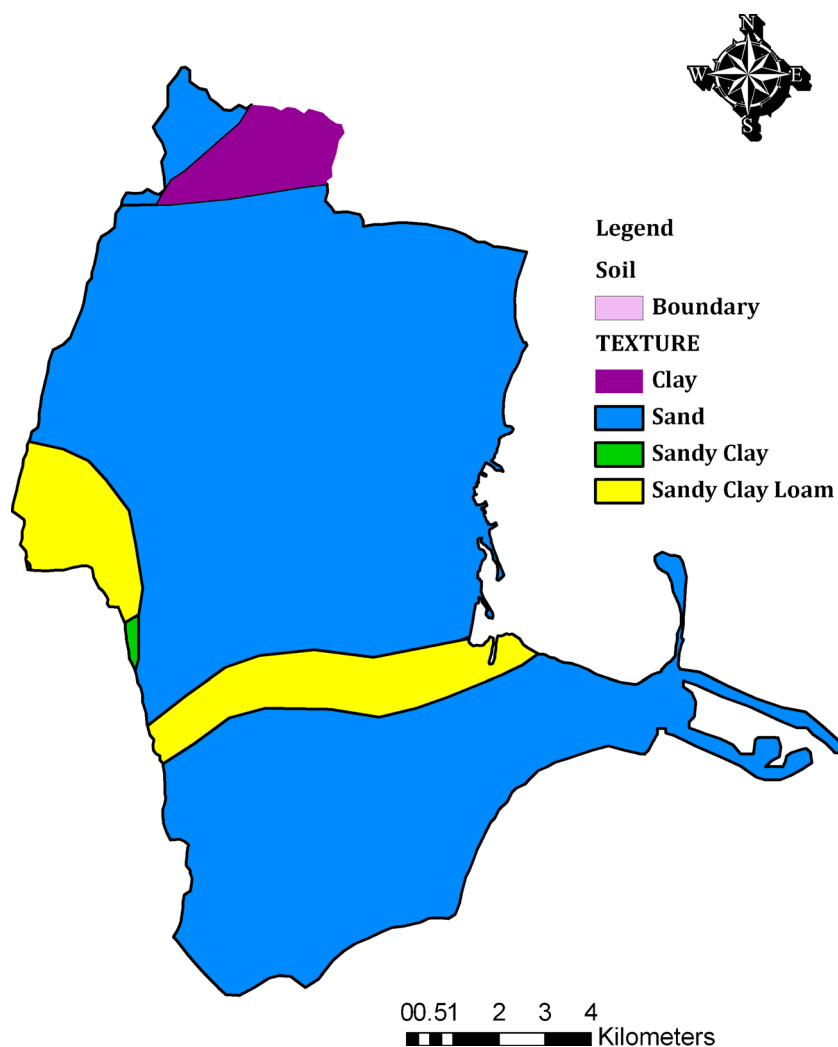
Materials and methods

Groundwater sampling and analysis

Thirty-six groundwater samples were gathered in the year of 2013 (Fig. 1). Groundwater sampling design was followed by Geological Survey Toposheets (No. 58L/1&5, 58L/2) to identify the drilled bore well sites of the study area. Groundwater of drilled wells was sampled from the taps of water users after pumping for about 10 min to remove stagnant water. Groundwater samples were collected from high-quality polyethylene bottles through 0.45-μm cellulose nitric membrane filter to eliminate suspended materials. Methods of sample collection and analysis were followed according to the American Public Health Association (APHA 1995). Most of the borehole wells were developed in bedrock, and the depth of the boreholes ranged between 20 and 250 m. The diameters of the borehole wells were 5–8 in. Groundwater samples for the analysis of metal components were

acidified to pH<2.0 in the field. All samples were stored in ice chests at 4 °C and transported directly to the laboratory, where they were analyzed within 2 weeks. pH, electrical conductivity (EC), and DO were measured in the field using portable instruments. The groundwater samples were brought to the analytical laboratories of the National Geophysical Research Laboratory (Hyderabad). Each of the thoroughly mixed water samples was filtered using Whatman filter paper no.42, and laboratory samples were collected in 1-l containers, acidified with nitric acid (AR grade) to pH 2 (0.2 % v/v) and stored for further analysis (Balaram 1993), and then processed for analysis of elements using an inductively coupled plasma–mass spectrometry (ICP–MS) model ELAN DRC II, PerkinElmer Sciex® Instrument, USA. Filtered water samples were directly introduced into an ICP–MS instrument by conventional pneumatic nebulization, using a peristaltic pump with a solution uptake rate of about 1 ml/min. The nebulizer gas flow, sample uptake rate detector voltages, and lens voltage were optimized for a

sensitivity of about 50,000 counts/s for 1 ng/ml solution of In. The instrumental and data acquisition parameters are given in Balaram ([1993]). Calibration was performed using the certified reference material NIST 1640 (National Institute of Standards and Technology, USA), in order to minimize matrix and other associated interference effects. Certified reference material for trace elements SLRS-4 (National Research Council, Canada) was analyzed as an unknown to check the precision and accuracy of the analysis. Blanks were analyzed along with samples and corrections were carried out accordingly. Accuracy of quality assurance (QA) was measured by pointed samples with known concentrations of solutes, and precision was checked by blind duplicate samples from the same site. This is to verify that refinement procedures and laboratory protocols were acceptable (Koterba et al. [1995]; Forstner and Wittman [1981]). The relative standard deviation (RSD) was found to be better than 6 % in the majority of the cases, which indicates that the precision of the analysis is reasonably good. The analyses were carried out for the elements particularly heavy metals, potentially toxic elements (PTEs), and other trace elements and major cations.

Heavy metal evaluation index (HEI)

HEI gives an overall quality of the water with respect to heavy metals (Edet and Offiong [2002]) and is expressed as follows:

$$HEI = \sum_{i=1}^{n} \frac{H_c}{H_{mac}}$$

where H_c and H_{mac} are the monitored value and maximum admissible concentration (MAC) of the ith parameter, respectively.

Heavy metal pollution index (HPI)

The HPI method was developed by assigning a rating or weightage (Wi) for each chosen parameter and selecting the pollution parameter on which the index was to be based. The rating is an arbitrary value between 0 and 1, and its selection reflects the relative importance of individual quality considerations. It can be defined as inversely proportional to the recommended standard (Si) for each parameter (Horton [1965]; Reddy [1995]; Mohan et al. [1996]).

In this study, the concentration limits (i.e., the highest permissible value for drinking water (Si) and maximum desirable value (Ii) for each parameter) were taken from the international WHO standard. The uppermost permissive value for drinking water (Si) refers to the maximum allowable concentration in drinking water in the absence of any alternate water source. The desirable maximum value (Ii) indicates the standard limits for the same parameters in drinking water.

The HPI, assigning a rating or weightage (Wi) for each selected parameter, is determined using the expression below (Mohan et al. [1996]).

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}$$

where Q_i and W_i are the sub-index and unit weight of the width parameter, respectively, and n is the number of parameters considered. The sub-index (Q_i) is calculated by

$$Q_i = \sum_{i=1}^{n} \frac{\{M_i(-)l_i\}}{S_i - l_i} \times 100$$

where M_i, I_i, and S_i are the monitored heavy metal, ideal, and standard values of the ith parameter, respectively. The sign $(-)$ indicates numerical difference of the two values, ignoring the algebraic sign.

Degree of contamination (DOC)

The contamination index (C_d) summarizes the combined effects of several quality parameters considered harmful to household water (Backman et al. [1997]) and is calculated as follows:

$$Cd = \sum_{i=1}^{n} C_{fi}$$

where

$$Cd = \sum_{i=1}^{n} C_{fi}$$

$C_{fi} = (C_{Ai}/C_{Ni}) - 1$; C_{fi}, C_{Ai}, and C_{Ni} represent the contamination factor, analytical value, and upper permissible concentration of the ith component, respectively, and N denotes the "normative value." Here, C_{Ni} is taken as MAC.

Geostatistical analysis

The experimental data were subjected to statistical analysis using SPSS software (version 17.0 for Windows). Pearson's product-moment correlation matrix was used to identify the relationship among element pairs. After computation of the correlation matrix and to identify the interrelationship, all pairs of constituents were determined. Factor analysis is a widely used statistical technique in groundwater studies because it reduces the number of variables and enables the detection of structure in the relationships between variables. Principal component analysis was used to infer the hypothetical sources of heavy metals. Exploratory factor analysis was performed by varimax rotation (Howitt and Cramer [2005];

Table 1 Well inventory and chemical characteristics in the study area

Well no.	Location name	Latitude	Longitude	PRM		
				Total depth (m)	Depth to water table (m)	pH
1	Mullakadu	78.1158	8.7241	12	7	7.8
2	Muniasamy Puram	78.123	8.7243	13.6	11.4	7.8
3	Geetha Nagar	78.1204	8.7335	13	8.7	7.4
4	Athimarapati	78.1064	8.7418	10.3	7.1	7.8
5	Susai Nagar	78.1356	8.7421	19.3	15.4	7.4
6	Tsunami Nagar	78.1548	8.7407	13.6	9.5	7.7
7	Harbour Quateres	78.1721	8.7509	9.2	5.5	7.7
8	Camp I Quateres	78.1459	8.7541	19.6	13.1	7.6
9	Muthiapuram	78.1297	8.7466	19	16	7.4
10	Periyanayaga Puram	78.1016	8.7785	19.6	11.3	7.6
11	Medical College	78.1193	8.7895	18	12	7.6
12	Brayant Nagar	78.1325	8.7869	16	13	7.7
13	C.G.E Colony	78.1441	8.7872	22	17.5	7.7
14	Fisher Colony	78.1525	8.7975	15.3	9	7.9
15	Shunmugapuram	78.1449	8.7987	16	8	7.4
16	Annanagar	78.1298	8.8041	9.3	5	7.5
17	Third Mile	78.1159	8.7885	16.3	10.2	7.8
18	Meelavitan	78.1321	8.7937	19.8	15	7.1
19	SIPCOT	78.0855	8.8024	29.5	25	7.8
20	Sterlite	78.0866	8.8192	70	30	8.8
21	Jothi Nagar	78.1118	8.8423	50	28	10.2
22	Melarasadi	78.1161	8.8686	29	22	7.5
23	Puthur Pandiapuram	78.1203	8.8516	32.3	19	8
24	Mapilaiurani	78.1338	8.8357	16.9	9.5	8.1
25	Devispuram	78.1445	8.8361	46	18.5	7.5
26	Siluvaipatti	78.1545	8.8395	18	15	7.4
27	Talamuthu Nagar	78.1544	8.8289	20.3	13	7.7
28	Thresh Puram	78.1613	8.8163	16.3	7.3	7.8
29	State bank colony	78.1419	8.8155	16.3	4.4	7.5
30	Mapilaiurani South	78.1333	8.8311	9.6	5.5	7.5
31	Ayya samy street	78.1251	8.8172	16.3	8	8
32	Palyapuram	78.1156	8.8146	19.6	8.1	7.9
33	Pandarapatti	78.1074	8.8237	49	27	7.9
34	Vijay Company	78.0964	8.832	76	15	7.9
35	Sankarperi Entrance	78.1012	8.8233	19.3	15	7.5
36	Kalangarai	78.1019	8.7688	25.4	11.2	7.9

Tariq et al. 2012; Venkatramanan et al. 2012, 2013; Selvam 2015), which minimized the number of variables with a high loading on each component, thereby facilitating the interpretation of principle component analysis results.

Concept of IDW

The base map of the Tuticorin area was digitized from survey of India toposheet using ArcGIS 9.3 software. The precise locations of sampling points were determined in the field using GARMIN 12-Channel GPS and the exact longitudes and latitudes of sampling points are imported in the GIS platform. The spatial distribution for groundwater quality parameters like HEI, HPI, and DOC was done with the help of spatial analyst modules in ArcGIS 9.3 software. Inverse distance weighted (IDW) interpolation technique was used for spatial modeling. IDW interpolation determines cell values using a linearly weighted combination of a set of sample

Table 2 Statistical measures such as minimum, maximum, average, and standard deviation in the pre- and post-monsoon period

Water quality parameters	Units	Minimum concentration	Maximum concentration	Average	SD
General ions					
pH	–	7.1	10.2	7.6	7.8
EC	μS/cm	350	19100	4887.778	4332.83
TDS	mg/l	530	10200	3016.111	2426.35
Metal ions					
Al	ppb	92.21	560.00	249.36	223.3
Cd	ppb	9.00	49.00	10.11	9.32
Cr	ppb	50.84	320.00	187.12	101.3
Cu	ppb	51.00	313.00	162.41	98.36
Fe	ppb	42.00	198.00	124.54	89.63
Mn	ppb	23.00	96.42	59.12	41.32
Ni	Ppb	315.65	7.50	107.29	91.25
Pb	Ppb	63.00	704.00	196.15	102.63
Zn	Ppb	39.00	413.00	159.40	123.25
Calculated pollution					
HEI	–	7.89	44.3	29.55	–
HPI	–	25.03	289.62	103.10	–
DOC	–	0.56	10.56	4.56	–

points. The weight is a function of inverse distance. Further, an input point is from the output cell location, the less importance it has in the calculation of the output value. The output value for a cell using IDW is limited to the range of the input values used to interpolate. Because the IDW is a weighted distance average, the average cannot be greater than the highest or less than the lowest input. Therefore, it cannot create ridges or valleys if these extremes have not already been sampled. Also, because of the averaging, the output surface will not pass through the sample points. The best results from IDW are obtained when sampling is sufficiently dense to represent the local variation that needs to be simulated. Thus, the IDW technique is ideal for analysis in respect of water quality data from various sampling points densely spread out. If the sampling of input points is sparse or very uneven, the results may not adequately represent the desired surface.

Results and discussion

The metal concentrations of the groundwater samples in the pre-monsoon period were statistically analyzed, and the results such as well inventory, maximum, minimum, average,

Fig. 3 Taxonomy of groundwater samples based on the plot of metal load and pH
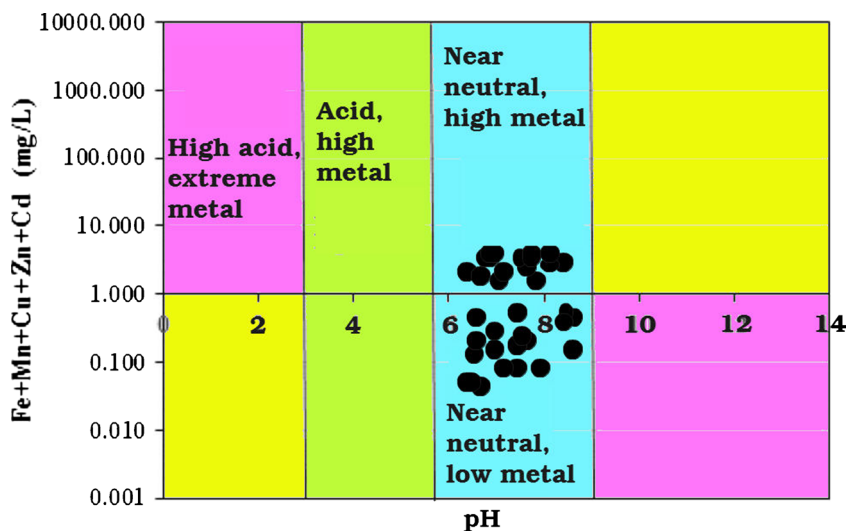
Table 3 Categorization of groundwater quality of the study area on modified categories of pollution indices

Index method	Group	Scale of pollution	Number of samples fall in the limit	Percentage of samples fall on the limits
HEI	<10	Low	20	57
	10–20	Medium	07	20
	>20	High	09	23
HPI	<90	Low	11	30
	90–180	Medium	16	42
	>180	High	09	28
DOC	<1	Low	20	55
	1–3	Medium	07	20
	>3	High	09	25

and standard deviation parameters are given in Tables 1 and 2. To determine the distribution pattern of the concentration of different elements and to demarcate higher concentration zones, contour maps for various elements were generated with the use of the ArcGIS 9.3 software. The negative logarithm of hydrogen ion concentration (pH) ranged from 7.1 to 10.2 in pre-monsoon, which indicates that it is slightly alkaline in nature and is between the maxi owners of boreholes within the city to commercialize the boreholes, which many of the residents patronize due to its affordability, mum permissible limits of WHO standards. EC ranged between 350 and 19, 100 μs/cm in pre-monsoon. Higher concentration of EC was

Fig. 4 Spatial distribution of HEI pollution indices of groundwater samples
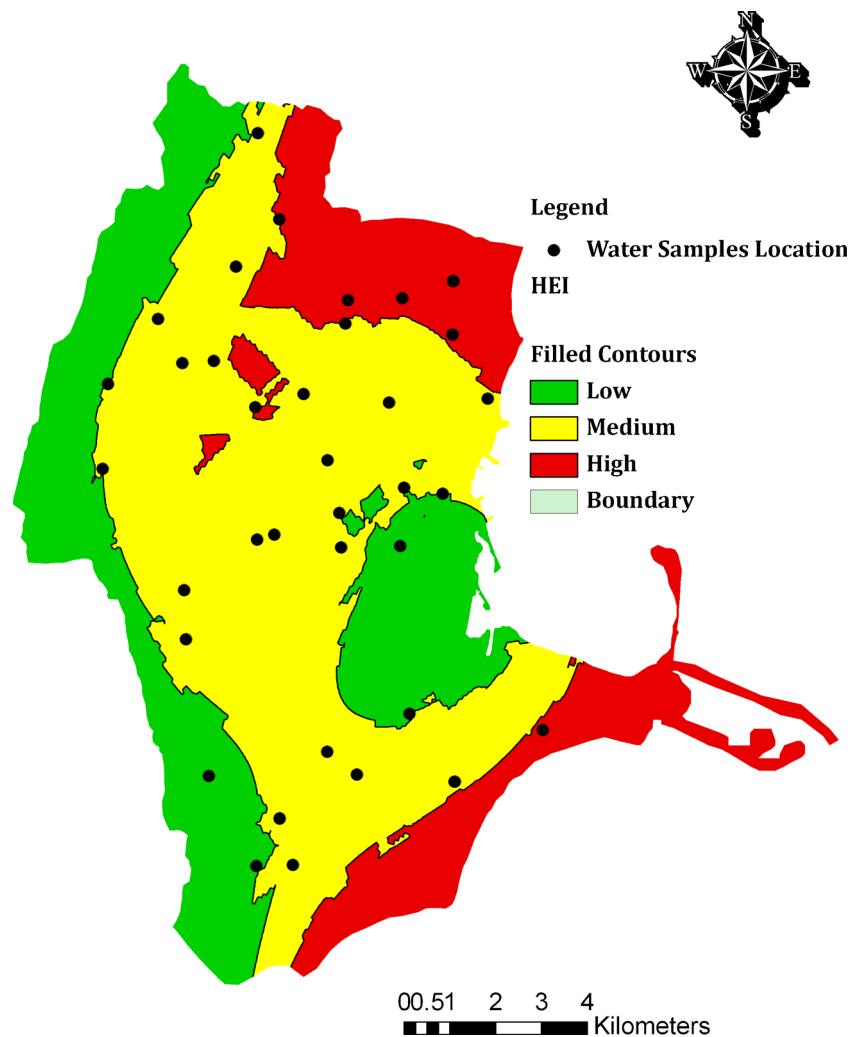
observed in the N–W portion because it is greatly influenced by seawater intrusion and human activity. The level of DO (2.7–8.6 mg/l) in groundwater samples is more or less low, and it could infer the presence of pollutants that consume the oxygen in water (Akinbile and Yusoff 2011).The mean metal concentration in groundwater samples followed a descending order as follows: Cr > Cu >Pb> Fe > Zn > Ni >Mn> Cd. The bond between metal loads (Fe + Mn + Cu + Zn + Cd) and pH for the groundwater samples is shown in Fig. 3, and 70 % of the samples were plotted in the field of near-neutral and low metal sector and the remaining 30 % of the samples fall in near-neutral and high metal sector. The metal contaminations were increased by various chemical industries and human activity (Caboi et al. 1999; Venkatramanan et al. 2014).

Pollution indices

Assessments of water quality pollution were carried out by heavy metals of groundwater samples (Edet and Offiong 2002). The study area was classified into three categories such as low (<10), medium (10–20), and high (>20) categories (Table 3). HEI values ranged from 7.89 to 44.3. Based on the HEI distribution, 57 % of the samples fall in a low-pollution zone, and the remaining 43 % of the groundwater samples are included in medium and high-pollution zones. The medium and high-pollution zones are located at the N–E and S–E parts of the study area. High concentration of HEI in the pollution indices is due to leaching of industrial waste from soil and also to anthropogenic activities (Fig. 4).

HPI values of all groundwater samples were calculated using MAC (maximum acceptable concentration) (Siegel 2002). The heavy metal evaluation index was used for a better understanding of the pollution indices. The values are useful to assess the groundwater quality in each sample point. The study area was classified into three zones according to HPI values, that is, low (<90), medium (90–180), and high (>180) categories (Table 3). The HPI value ranged between 25.03 and 289.62. According to HPI distribution (Fig. 5), 30 and 42 % of the samples fall in low

Fig. 5 Spatial distribution of HPI pollution indices of groundwater samples
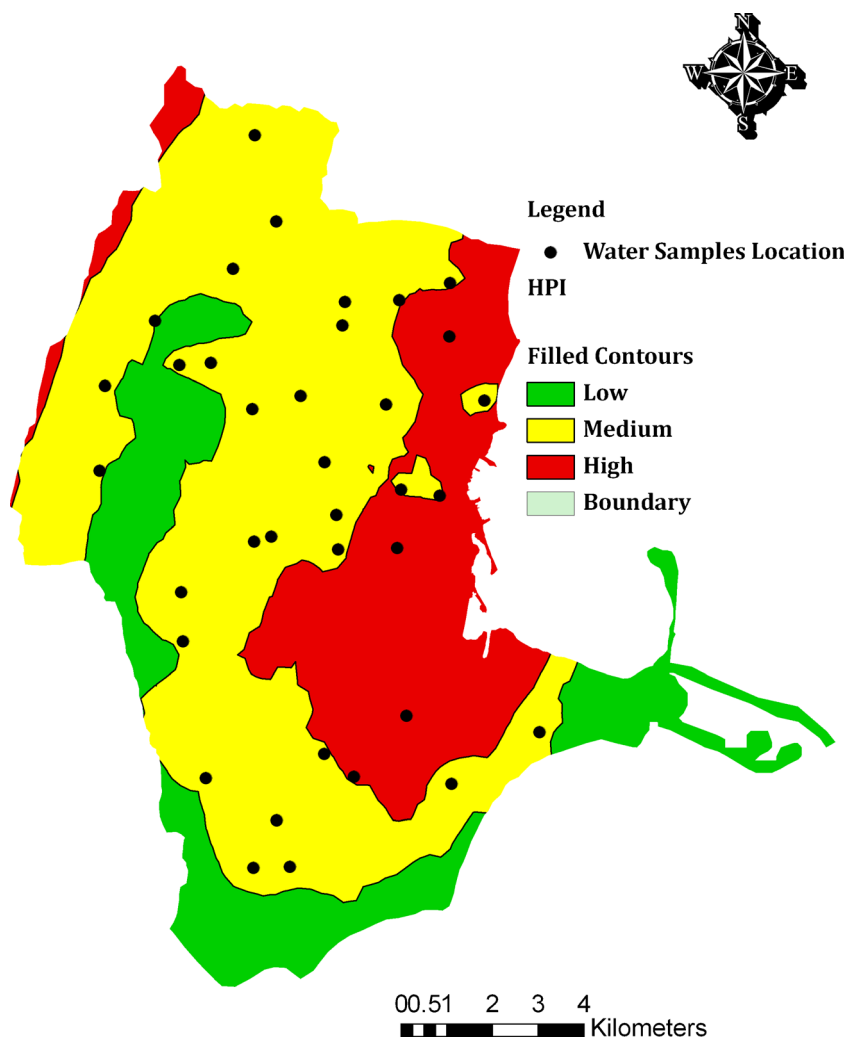
and medium-pollution zones, respectively, and the remaining 28 % of samples were above the critical limit of 100 proposed by Prasad and Bose (2001). As per HPI values, medium and high categories are considered as polluted groundwater, and these sampling points are located near the sea and the State Industries Promotion Corporation of Tamil Nadu Limited (SIPCOT) industrial area. Moreover, the metals contaminated by seawater intrusion, industrial waste, and sewage leaked from sewers.

The study area was classified into three zones according to DOC values, that is, low (<1), medium (1–3), and high (>3) categories (Table 3). The value of DOC in the groundwater varies from 0.56 to 10.56, with an average of 4.56. According to DOC distribution (Fig. 6), 55 % of the samples fall in a medium zone, 20 % in a low zone, and 25 % in a high-pollution zone. High-pollution zones were located near residential areas, the subway, or the buckle channel effluents. Groundwater in this zone was affected by sewage waste and small-scale industries (Bhuiyan et al. 2010; Prasanna et al. 2012; Venkatramanan et al. 2014).

Geometry of factor analysis

Factor analysis is a useful tool to define the factors that impact on the groundwater quality and its hydrochemical processes. The results of this operation are high factor loadings (close to 1 or −1) obtained for the variables correlated in each factor and low factor loadings (close to 0) obtained for the remaining variables. The number of factors which is the best variance of the analyzed data with eigenvalue of >1 exhibits reasonable interpretation. There are five factors explaining 75.40 % of the total variance of the original data set, which is sufficient enough to give a good idea of data structure (Table 4).

The first factor obtained explains the biggest part of variance; it accounts for 41 % of the total variance and 8.1 of the eigenvalue. High factor loadings indicate strong relationship between the variable and the factor describing this variable. This factor has high loadings with DO, Fe, Ni, and Zn (0.90, 0.83, 0.85, and 0.60, respectively) and moderate loadings with Cd (0.42). Components in factor 1 are derived from mixed sources due to chemical induction of SIPCOT infiltration of

Fig. 6 Spatial distribution of DOC pollution indices of groundwater samples
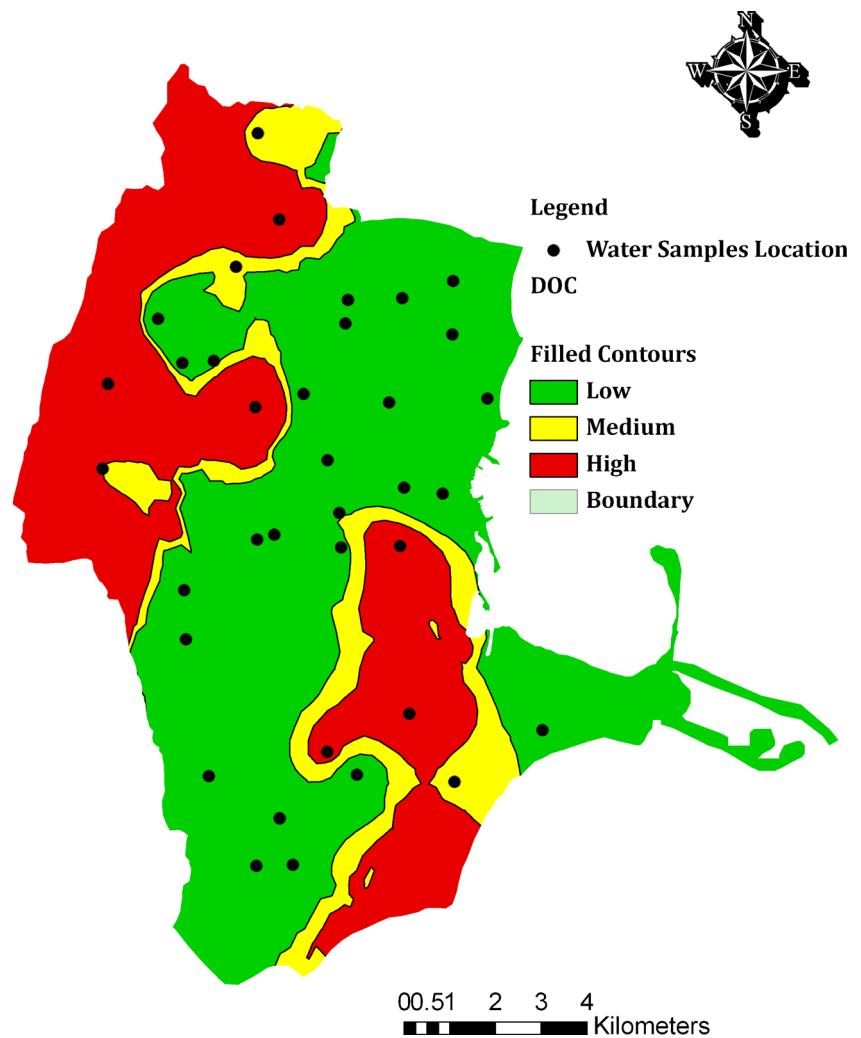
Table 4 Varimax-rotated principal component analysis for the heavy metal concentration in samples

Parameters	Factors				
	1	2	3	4	5
pH	−.693	−.149	−.320	−.049	.297
EC	.136	−.184	−.479	.663	.147
DO	.908	.121	.090	−.025	.140
Al	.245	.629	−.105	−.089	.216
Cr	−.044	.473	.764	−.069	−.258
Mn	−.582	.596	.429	−.140	−.066
Fe	.831	.392	−.055	−.134	.112
Ni	.859	.326	-.115	.189	.008
Cu	−.894	.226	.068	.028	.155
Zn	.608	.069	.158	−.098	.442
Cd	.428	.501	−.472	.739	−.290
Pb	−.209	.731	−.448	.224	−.122
Total	8.124	2.335	1.844	1.537	1.241
% of variance	40.622	11.676	9.218	7.684	6.204
Cumulative %	40.622	52.298	61.516	69.200	75.404

landfill leachate or municipal sewage to the surrounding aquifers. The second factor accounts for 11.6 % of the total variance and 2.3 of the eigenvalue; it has high loadings with Al, Cr, Mn, and Pb (0.62, 0. 47, 0.59, and 0.73). This indicates that the influence of human activity is one of the most important factors controlling groundwater chemistry of this study area. This factor corresponds to the role of unwise use of lead materials and phosphate fertilizers. However, the spatial distribution of contamination observed in the aquifer suggested that the main contamination sources came from the industrial and agricultural activities. Factor 2 is loaded on Pb and Al, which are derived from western part of the study area along the SIPCOT chemical industrial effect. The higher

concentration of Pb in groundwater indicates that it is discharge from industrial effluents of SIPCOT and human activity.

The third factor accounts for 9.2 % of the total variance and 1.8 of the eigenvalue; there are high loadings for Cr (0.76) and moderate loading with Mn (0.42). This is denoted as waste disposal, petroleum, carbon consumption, and agricultural practices. The fourth factor accounts for 7.6 % of the total variance and 1.5 of the eigenvalue; it has high loading with Cd (0.73) and moderate loading with EC (0.66). The contamination of this metal in groundwater is due to the dissolution and corrosion from household plumbing systems. A higher concentration of EC in this study area may be derived from seawater intrusion and anthropogenic sources such as fossil fuel consumption and the industrial production, use, and disposal of nickel compounds and alloys (Kasprzak et al. 2003). The fifth factor exhibits high loading of Zn (0.44) and moderate loading of pH (0.29), which occurred under alkaline conditions. It accounts for 6.2 % of the total variance and 1.2 of the eigenvalue. Despite, the little occurrence of Zn in nature, it is also emitted through effluents of many commercial industries during smelting (metal processing) activities. A higher Zn concentration in downstream was attributed to the greatest frequency of nearby sources like hazardous waste sites, industrial areas such as lead smelters, and the emission of industrial effluents through the transmission of iron pipes; municipal sewages are the more concentrated sources of zinc in the water (Cole et al. 1984) as this is represented near the SIPCOT region.

Geometry of correlation matrix

Pearson's correlation coefficient matrices for the analyzed parameters of individual metals are presented in Table 5. The statistically significant level is $p<0.01$. Correlation matrix

Table 5 Correlation coefficients for parameters of groundwater samples

	pH	EC	DO	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
pH	1											
EC	−0.02	1										
DO	0.12	0.09	1									
Al	−0.22	0.02	0.09	1								
Cd	**0.66**	0.17	**0.78**	**0.62**	1							
Cr	0.03	0.18	0.12	0.23	0.01	1						
Cu	0.12	0.21	0.33	−0.11	**0.33**	**0.44**	1					
Fe	−0.45	0.12	0.25	−0.23	0.15	−0.11	0.22	1				
Mn	−0.22	**0.44**	−0.22	−0.33	−0.22	0.21	**0.31**	0.12	1			
Ni	0.16	−0.12	−0.15	0.12	−0.33	0.14	−.23	−0.11	0.23	1		
Pb	**0.65**	−0.56	0.39	0.16	0.15	0.09	−0.11	0.11	**0.45**	**0.58**	1	
Zn	0.22	−0.12	0.33	0.29	0.22	−0.22	−0.03	0.14	0.05	0.06	0.02	1

Significant values are in bold

exhibits that pH and Cd and pH and Pb may have the same potential contamination source, with a correlation coefficient of 0.66 ($p<0.01$) and 0.65 ($p<0.01$), respectively. Meanwhile, EC and Mn have a correlation coefficient of 0.44 ($p<0.01$), and furthermore, significant correlation is exhibited between DO and Cd, Al and Cd, Cd and Cu, Cr and Cu, Cu and Mn, Mn and Pb, Ni and Pb shows good correlations with respective correlation coefficient (r) values of 0.78, 0.62, 0.33, 0.44, 0.31, 0.45, and 0.58, respectively. However, Fe shows very low correlations with other variables, indicating the possibility of different source to the other trace elements. As can be seen from Table 5, the absence of correlation between these heavy metals illustrates that the metals are not controlled by a single factor. These associations of metals clearly indicate that the groundwater has assimilated various contaminants from the processes of chemical industries and landfill leachate/ municipal sewage systems (Tariq et al. 2010). The significant correlations among the metals of Mn, Cu, Pb, and Cd revealed that they may have originated from common sources, preferably from industrial activities.

Conclusion

This work aimed at analyzing the metal pollution status and identifying the correlations between these examined metals in groundwater of Tuticorin Corporation. Results of this present research clearly demonstrated that the metal content in the groundwater was highly polluted by industrial and human activity. Groundwater eminence in the study area was influenced by various kinds of contamination sources such as SIPCOT industrial wastes, sewage-leaked sewers, groundwater discharged from the subway, and seawater intrusion. The bond between metal loads (Fe + Mn + Cu + Zn + Cd) and pH for the groundwater quality exhibits near-neutral and low metal sector and the remaining 30 % fall in the near-neutral and high metal sector. Regarding the pollution indices of HPI, HEI, and DOC, it indicates that it is 28, 23, and 25 %, respectively, and it is highly polluted due to industries' leachates and municipal sewage system. A remarkable spatial distribution of this HPI, HEI, and DOC concentration was found to be increased from northwest to western part of the study area because of the SIPCOT industrial effluent. The geometric factor analysis and Pearson's correlation matrix suggest that the Mn, Cu, Pb, Cr, and Cd metals clearly indicate that the groundwater has integrated with various contaminant processes of chemical industries and landfill leachate or municipal sewage system. But, factor 4 of EC was mainly derived from seawater intrusion and irrigation runoff. The recommendation of this present research suggested that the government should adopt some treatment technologies (Central effluent treatment plant and Iron oxyhydroxides and the adsorption/co-precipitation removal mechanism) to minimize these heavy metal contaminations in groundwater for safe drinking and other public utilities.

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