Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 13	No. 1	pp. 101-106	2014

Original Research Paper

Evaluation of Effect of Calcium on Scale Formation and Corrosivity of Groundwater Using GIS

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 16-7-2013
Accepted: 29-9-2013

Key Words:
Groundwater quality
Scale formation
Corrosion,
Langelier Saturation Index
Ryznar Saturation Index

ABSTRACT

The ancient Thanjavur population located in delta of River Cauvery had been dependent on surface water for drinking until recently, wherein there is an incremental rise in augmented bore-well water supply. Incidentally, there have been observations of moderate to high scale formations by the groundwater during domestic heating, as well as consistently high record of kidney-stone (mostly calcium oxalates) occurrence in the city and its suburbs. The present work focuses on calcium content, its desirability level and the corrosion/scaling coefficients. One hundred two (102) samples were collected prior to monsoon season in the year 2008 from the study area for study of various physico-chemical parameters. In order to estimate scalability and corrosivity, two standard indices (namely Langelier Saturation Index and Ryznar Saturation Index) were used. GIS has been used to develop integrated maps for demarcating zones of different calcium concentrations in groundwater and its relation with scale and corrosion formation tendencies.

INTRODUCTION

Due to inadequacy of surface water resources for domestic as well as industrial purposes, demand for groundwater has been increasing day by day in all cities of India. Groundwater sources range over a broad spectrum of physico-chemical properties (Davies & De Wiest 1966, Gibbs 1970, Todd 1980). Scaling and corrosion are known to be the most prominent effects on materials that are used in the industries, piping system, domestic utensils, etc. Hard water mineral deposits or scaling is the precipitation of minerals (Evans 1926, Rachid et al. 2010). In fact, the scaling often clogs the pipeline and decreases the life of the water-treatment equipment, breakdowns in boilers, cooling towers and other water-handling equipments (Hem 1991). In domestic settings, the hardness of water is often indicated by the non-formation of suds when soap is agitated in the water sample. Scaling is known to be caused by multivalent cations, usually bivalent cations (Ca^{2+} and Mg^{2+}). These ions enter a water supply by leaching from minerals within an aquifer, predominant minerals being calcite and gypsum (Loewenthal et al. 2003).

Corrosion is commonly known as the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings (identified to be electrochemical oxidation of metals in reaction with an oxidant such as oxygen) (Saricimen et al. 2010). Formation of an oxide(s) and or salt(s) of the metals surface are the end results of corrosion damaging the metals (Jones 1992).

Factors causing corrosion and scale-formation include acidity, high chloride concentration, dissolved oxygen, temperature, pH and concentrations of HCO_3^-, CO_3^{2-}, Ca^{2+} and Mg^{2+} (Aiman & Enab 2007, Snoneyink & Jenkins 1980, Wranglen 1985). To evaluate the scale formation and corrosivity potential of water, so many indices are available although Langelier Saturation Index (LSI) and Ryzner Saturation Index (RSI) are the more commonly used $CaCO_3$ saturation indices. LSI determines whether water has tendency to precipitate or dissolve $CaCO_3$ and RSI estimates the quantity of the precipitated or dissolved amount of $CaCO_3$. It is believed that supersaturated waters are scale forming whereas undersaturated waters are corrosive (Gupta et al. 2011).

In Thanjavur city, water supply requirements were met by Vennar river and Vadavur river (distributaries of River Cauvery diverted after Grand Anicut) for past many years. However, in recent years, domestic water demand of the city has been increasing due to the growth of population, institutional as well as commercial sectors within the city, to augment which, the city municipality has dug 32 new deep bore wells in and around the city since last three decades, although neither the surface water nor the groundwater has been treated before supplying for distribution in the city (TNUIFL 2007). Although, with increasing sanitary awareness, in many of the houses in various residential colonies, the city water has been boiled and cooled before drinking by individual householder at their own initiatives to avoid drinking hard water, yet a good proportion of the residential population is still getting increasingly affected by health problems (most commonly, kidney stones) over past few years. This paper is aimed at finding effects of calcium contents of groundwater on scale formation and corrosivity using LSI and RSI indices so as to develop an integrated groundwater quality map for demarcating the scaling and corrosive zones of Thanjavur city developed using Geographical Information System (GIS), as a guideline for the residents in exercising care and suitable level of treatment (esp. corrosivity and scaling) before consumption.

STUDY AREA

The city of Thanjavur (total geographical area 36 km^2; located between latitudes of 10°44'54.88' N to 10°48'05.25' N and longitudes of 79°06'10.04' E to 79°09'24.38' E; at an average elevation of 57 metres above mean sea level) is an important agricultural centre located besides the Cauvery delta, known as the "rice bowl" of Tamil Nadu in southern India. It is situated at a distance of 314 km south-west of Chennai and 56 km east of Tiruchirapalli. Although most of Thanjavur district is a level-plain watered by the Cauvery and tributaries, the taluk of Thanjavur is made up mostly of barren uplands sloping towards the east. To the south of Thanjavur town, is the Vallam tableland, a small plateau interspersed at regular intervals by ridges of sandstone. Lithologically, Thanjavur region consists of laterite, sand, sandstone, gravels and patches of kankar formations, which belong to tertiary to recent age. The area is generally undulating upland formed with red laterite gravelly sandy loam soil. The urban agglomeration with a population of 290,732 as per Census of India, 2011 (Census of India 2001) encompasses Vallam to Mariamman Koil (west-east) and Vayalur to the Air Force Station (north-south), with the Grand Anicut Canal (Pudhaaru), Vadavur and Vennar rivers flow across the city. The average temperature in the city varying between 32.5°C and 36.6°C. 23.5°C and 22.8°C were measured in summer and winter respectively and the average rainfall is 111.37 mm. The major crops are paddy, sugarcane, coconut, plantain, etc. Study area is shown in Fig. 1.

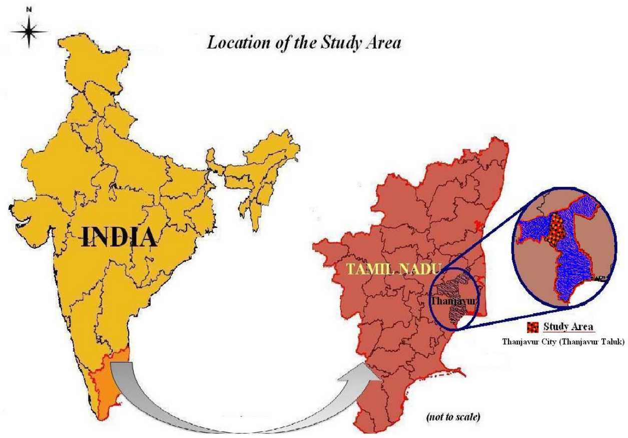


Fig. 1: Study area of Thanjavur city with administrative boundaries.

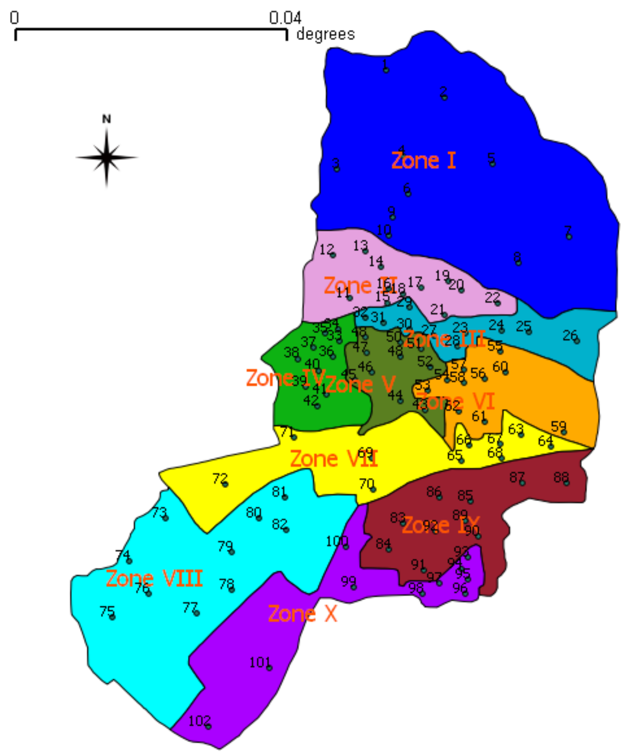


Fig. 2: Sample locations (Bore wells) in Thanjavur city.

MATERIALS AND METHODS

Thanjavur city is divided into ten zones based on Panchayat wards. Water samples were collected from each zone in pre-monsoon season in the year 2008.

Groundwater samples collection and testing: Water samples were collected in pre-monsoon season in the year 2008 from 102 different bore wells within the city, with a minimum of ten samples from each of the ten zones of the city . Fig. 2 shows the sample locations (bore wells) within city boundary. Collected samples were tested for various physico-chemical parameters, as per the standard methods (BIS 1991, ISI 1983, WHO 1984) for examination of water in Regional water testing laboratory, (Tamil Nadu Water Supply and Drainage) TWAD Board, Thanjavur. The physical parameters studied include total dissolved solids (TDS), electrical conductivity (EC) and temperature, whereas the chemical parameters included pH, calcium hardness and total alkalinity.

Evaluation of statistical compatibility of the estimated water quality parameters: The various water quality data (calcium content, LSI and RSI) estimated were analysed for their descriptive statistics with respect to the corresponding zones, using IBM SPSS Statistics (version 20.0.0, 2011). The parameters were presented in terms of box plot to compare the central tendencies, dispersions, range and the outliers.

Calculation of Indices

(i) Langelier Saturation Index (LSI): This indicates the driving force for scale formation and growth in terms of pH as a master variable. It is purely an equilibrium index and deals only with the thermodynamic driving force for calcium carbonate scale formation and growth, and thus provides no indication of how much scale or calcium carbonate that actually precipitates to bring water to equilibrium (Langelier 1936).

If LSI is negative: No potential to scale, water will dissolve $CaCO_3$.

If LSI is positive: Scale can be formed and $CaCO_3$ precipitation may occur.

If LSI is close to zero: Borderline scale potential.

In order to calculate the LSI, it is necessary to know the total alkalinity (mg/L as $CaCO_3$), the calcium hardness (mg/L as $CaCO_3$), the total dissolved solids (mg/L TDS), the actual pH and the temperature of the water (°C) (Ramachandramoorthy et al. 2010).

LSI is defined as:

(1) LSI = pH – pHs

pH is the measured water pH.

pHs is the pH at saturation in calcite or calcium carbonate and is defined as:

(2) pHs = (9.3 + A + B) – (C + D)

Where,

(3) $A = (\log_{10} [TDS] - 1)/10$

(4) $B = -13.12 \times \log_{10} (^{o}C + 273) + 34.55$

(5) $C = \log_{10} [CaH \text{ as } CaCO_3] - 0.4$

(6) $D = \log_{10} [\text{Total Alkalinity as } CaCO_3]$.

From the analysed data LSI is calculated using equations (1) to (6).

The use of the equation developed by Langelier made it possible to predict the tendency of natural or conditioned water to deposit calcium carbonate or to dissolve calcium carbonate. Thus, it is useful in predicting the scaling or corrosive tendencies of the water (Kemmer 1979, Melidis et al. 2007). If the water dissolves calcium carbonate, the water is corrosive and has a negative value, if the water deposits calcium carbonate, it has a scaling tendency and a positive value. Interpretation of LSI test results is given in Table 1.

Table 1: Interpretation of Langelier Saturation Index (LSI) test results.

Sl. No.	Index	Appearance
1	-4.0	Very Severe Corrosion
2	-3.0	Severe Corrosion
3	-2.0	Moderate Corrosion
4	-1.0	Mild Corrosion
5	-0.5	Slight Corrosion
6	0.0	Balanced
7	0.5	Faint Scaling
8	1.0	Slight Scaling
9	2.0	Mild Scaling
10	3.0	Moderate Scaling
11	4.0	Severe Scaling

Table 2: Interpretation of Ryzner Saturation Index (RSI) test results.

Sl. No.	Index	Appearance
1	4.0-5.0 (<4.0)	Severe Scaling
2	5.0-6.0	Moderate Scaling
3	6.0-7.0	Little Scaling
4	7.0-7.5	Slight Corrosion
5	7.5-9.0	Moderate Corrosion
6	9.0 and above	Severe Corrosion

(ii) Ryznar Saturation Index: The Ryznar Saturation Index is an empirical method for predicting scaling tendencies of water based on a study of operating results with water of various saturation indices (Ryznar 1936).

RSI = 2 pHs – pH

Where, pHs is Langelier's saturation pH

This index is often used in combination with the LSI to improve the accuracy in predicting the scaling or corrosion tendencies of water. Interpretation of RSI test results is given in Table 2.

Preparation of the base map: For GIS study, the required base map was prepared using topo-sheet (obtained from Survey of India) as well as the Thanjavur town map, taluk map and district map of scales 1:12,800, 1: 75,000 and 1:2,50,000, respectively (all these three maps obtained from director of survey of land records, Madras, 2003). The maps were georeferenced using Quantum GIS (version 1.7.2) after collecting the co-ordinates using GPS (Trimble Juno SB). The georeferenced map was digitized for preparing based map. The point-features (groundwater sampling locations) and polygon-features (boundaries), were extracted in the form of shape files for further studies.

Using the various selected water quality parameters (calcium content, Corrosivity and scalability indices) contouring was carried out. Based on the intersection of these pa-

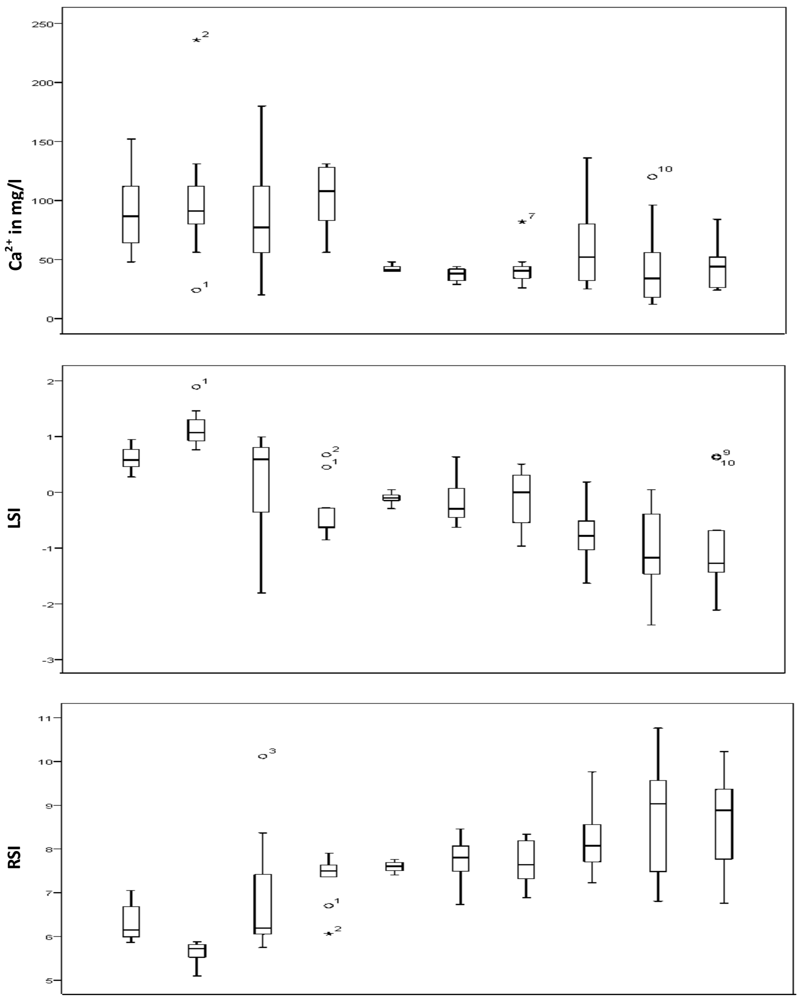


Fig. 3: Box plots for Ca^{+2} (mg/L), LSI and RSI of the samples.

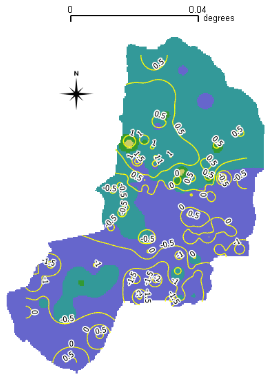
rameters the natural classification for each of the parameters was obtained, which were used for querying to estimate various relationships between the calcium content and the Corrosivity/scalability indices.

RESULTS AND DISCUSSION

Evaluation of calcium, corrosivity and scalability distribution pattern: Since the zones are divided based on the population density and natural boundaries rather than geographical area coverage, distribution of samples (although taken at least ten in number in each of the zones) appears to be clustered towards the central as well as south-eastern regions (Fig. 2). The box plots (Fig. 3) clearly indicate that zone 5 shows the smallest range in all the three characteristics i.e., Ca^{2+}, LSI and RSI. So far as highest range is concerned, it is zones 3 and 7 for calcium and zones 3 and 8 for LSI and RSI.

Outliers are observed to be few in numbers with maximum variation for calcium in zone 2, LSI in zone 10 and RSI in zone 4. The means of these distributions are more or less representing central tendencies of the data except in case of zones 3 and 9 (and sometimes zone 10). As indicated from Fig. 2, zones 4, 5 and 6 are fairly smaller compared to rest of the town and their variation among the sample mean is minimum. This means that the geographical size of the zone does not seem to affect the non-homogeneity of the data.

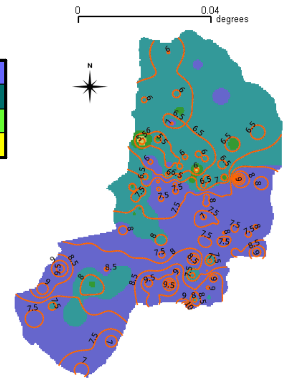
Variation of calcium content with corrosive or scaling indices: As referred to in the preceding paragraphs (Figs. 4 and 5) the calcium distribution was found to be higher in few patches in northern half of the study area surrounded by moderate calcium in the north and lowest calcium towards south. The contours of LSI and RSI show different trajectories. The LSI values show almost equal distribution of positive and negative values at northern and southern part of the



Legend

<75 mg/l (Lowest Ca)	Blue
75 – 125 mg/l (Low Ca)	Light Green
125 – 175 (Moderate)	Green
175 – 240 (High Ca)	Yellow

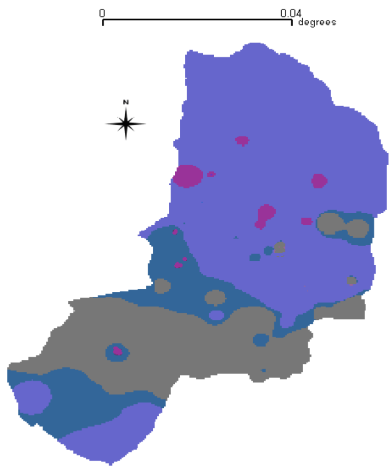
Fig. 4: Ca (mg/L) distribution with LSI contours.



Legend

<75 (Lowest Ca)	Blue
75 – 125 (Low Ca)	Light Green
125 – 175 (Moderate Ca)	Green
175 – 240 (High Ca)	Yellow

Fig. 5: Ca (mg/L) distributions with RSI contours.



Color & Name	Interpretation
Blue	Moderate Ca, mild scaling and moderate corrosion
Teal	Moderate Ca, faint scaling and moderate corrosion
Red	High Ca, faint scaling and moderate corrosion
Brown	Moderate Ca, faint scaling and severe corrosion

Fig. 6: Integrated Ca, LSI and RSI distributions map.

study area respectively with segments of reverse patches on opposite sides. However, the RSI values vary from 6 to 7 in entire northern part and southernmost part of the study area whereas a narrow fringe of higher values up to 9.5 is being observed in the intermediate zones separating the above mentioned zones, with sporadic exceptions of high RSI pockets.

Delineations of calcium, corrosivity and scalability zones: Based on super imposition of calcium, LSI and RSI, an integrated thematic map was prepared as shown in Fig. 6. Observed calcium content is shown in Fig. 3 using box plots for the zones 1 to 10 with minimum, maximum, lower quartile, upper quartile and median. 240 mg/L and 12 mg/L have been observed as the highest and lowest concentrations of calcium during the pre-monsoon season of Thanjavur city. Zones 2 and 6 samples are presented showing highest and lowest median concentrations respectively, compared to other zones. Zones 1 to 4 present the median calcium contents more than 75 mg/L (desirable level as per the BIS standards). Box plots were also drawn for calculated LSI and RSI values (Fig. 3). The median values of LSI in zones 1 to 3 are found to be higher than zero and indicating that these zones are prone to slight to moderate scale formation tendencies. Zones 4 to 7 indicate slight to moderate corrosion level whereas zones 8 to 10 show the tendency of moderate to severe corrosion.

Figs. 4 and 5 depict classification of lowest Ca (<75 mg/L), low Ca (75-125 mg/L), moderate Ca (125-175 mg/L) and high Ca (175-240 mg/L). Fig. 6 gives classification of moderate Ca, mild scaling and moderate corrosion-blue colour, moderate Ca, faint scaling and moderate corrosion-teal colour, high Ca, faint scaling and moderate corrosion-red colour and moderate Ca, faint scaling and severe corrosion-brown colour. As indicated from the diagram, most part of the study area is occupied by moderate Ca and moderate to high corrosion, with a small patches of high calcium and moderate corrosion (Fig. 6), interspersed relatively more on the northern region of the area than the southern. These are the regions suggested to be unsuitable for untreated groundwater consumption. The next in the priority of unsuitability (moderate calcium and severe corrosion) is the brown regions (Fig. 6) located towards the southern part of the study area and localized patches in the north-eastern region. By and large most part of the northern region and the southernmost fringe of the study area (with few sporadic patches) are moderate with respect to calcium as well as corrosion, with faint to mild scaling, representing relatively better water quality with regard to potability. Accordingly, the treatment method to be employed and future exploration of bore/dug-well sites need to be decided based on the zonal delineation presented herewith, for better public health and safety.

CONCLUSIONS

As per the studies carried out, it is evident that for potability consideration, not only the calcium content of the water, but its corrosivity and scale-forming capacities need to be considered, which are the functions of other soluble ions present in the water (as defined in text). Secondly, various corrosivity indices show variability with regard to their estimate, by virtue of the parameters used and hence superimposition of the indices can be used to generate range of variability of the zones (for example, high - when both indices show high values, moderate - when only one of the indices show higher values and low - when both of the indices show low values). Finally, based on water quality (here, calcium content) and their reactivity (here, corrosivity and scale-forming ability), the technique of delineation of the zones would help not only in designing the specific treatment strategies for groundwater procured from the bore/dug-well in the vulnerable zones, but also to plan for future exploration sites, and sometimes, even redesigning the land-use pattern and landscaping of the area, with regard to habitation, agriculture, drainage and so forth.

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