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PositiveImpactonthequality of Groundwater In Chennai CoastalAquiferDueToTheCloudBurstDuringDecember2015

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Abstract: *The over dependence of groundwater for drinking requirements is a unique feature in Tamilnadu due to the increasing population, and the increasing demand in agricultural and industrial sectors as well, causing coastal groundwater at many places to be contaminated.Duringeach season,fiftyfive groundwater samples were collectedfor three consecutive seasonsto taking to165 samples, during post monsoon in January 2015, pre monsoon in June 2015 and after floods post monsoon in January2016.The groundwater parameters such as pH, EC, TDS,* Ca^+, Mg^+, Na^+, K^+, Cl^-, HCO^{3-}, SO_4 *and* NO_3 *were determined for all three seasons. Comparing BIS (2012), Na, Ca, Mg, and K; Cl,* HCO_3,SO_4 *and* NO_3 *concentrations were above permissible limit in most of the samples, indicating contamination in groundwater for drinking and other domestic purposes in the study area. Total dissolved solids (TDS) and Electrical Conductivity (EC) are being observed to be above permissible limit in some locations and they are unfit for drinking purpose and moderately useful for other domestic purposes. At several locations the groundwater is not suitable for drinking and domestic due to industrial activities and urbanization but overall the quality of groundwater is enriched due to the sudden cloud burst of December 2015. Chennai Metrocity experienced more than 40 cm rainfall within two days due to cloudburst. The results of the analyses were interpreted to know thegroundwater chemistry and quality.*

Key Words: *Groundwater quality,Spatialdistribution,TDS classification, SARdiagram,Molar ratios.*

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I. Introduction

Hydrogeochemical study is useful to identify the processes that are responsible for groundwater chemistry and many problems normally arise due to indiscriminate use of ground water over long periods. This includes problems such as water logging, sea water intrusion in coastal aquifer, critical lowering of water table, land subsidence and water quality deterioration. The coastal aquifers have impact from seawater intrusion both by the natural processes and anthropogenic activities like, over-abstraction, urbanization and agricultural activities (Ozler 2003, Balasubramanian*et al* 2017). It is aggravated normally by the influence of local aquifer characteristics and heterogeneities. Saline water is the most common type of pollution in fresh ground water (Todd 1980).

Hydrogeochemical data helps in estimating the extension of mixing, the circulating pathways and residence time of groundwater (Edmunds 1995). The type and concentration of salts in groundwater depend on the geological environment and movement of groundwater (Ragunath 1987). Salt water intrusion is a major hazard in the coastal aquifers in different parts of India especially, in Tamilnadu. Over-exploitation of groundwater from such coastal aquifers to meet the increasing demand accelerates the progress of seawater further towards the land. This will lead to the abandoning of production wells due to contamination of groundwater owing to the mixing of seawater. Every human activity uses chemicals and generates wastes, be they industrial, agricultural or domestic. Often these chemicals and wastes make their way to the groundwater, for example, domestic fertilizers carried with rainfall down through the soil to the water table, industrial storage tanks leaking fluids onto the ground and then leaching to the groundwater. Several regions in India have encountered degradation in groundwater quality due to rapid urbanization and an exponential increase in population (Ramesh and Elango 2005; Brindha and Elango 2010; Brindha*et al* 2011; Sridhar *et al* 2015 and Balasubramanian*et al* 2016).

II. Study Area

The study area covers the northeast coast of Chennai region consisting of coastal groundwater at Ennore that comes under Thiruvallur district of Tamil Nadu. The study area is located on northeast coast of Chennai Metropolitan City. It covers an area of 250 sq km that falls between 13°4'N and 13°12′N latitude and from 80°16'E to 80º24′E″ longitude as shown in **Fig. 1**.Ennore Creek is located in the northern part and the main source of pollution input to Ennore Creek is through the discharge of waste water effluents, leachates, chemicals, paints, fertilizers and petroleum refining industries located in the northern part of the city limits.Ennore coast consists of alluvial tracts, beach dunes, tidal flats and creek in the eastern part. The geology of Chennai comprises mostly clay, shale and sandstone. The total area of the creek is 2.25 sq km. coovum river in the central part, Adayar river in southern part and traverse into the Bay of Bengal. In the study area, Ennore coasts, completely receives the major amount of untreated domestic sewage from Royapuram area.

III. Methodology

In the study area 165 groundwater samples were collected during the post monsoon January 2015, pre monsoon June 2015 and post monsoon January 2016 from bore wells to assess groundwater quality. It covers an area of 250 sq km that falls between 13°4'N and 13º12′N latitude and from 80°16'E to 80º24′E″ longitude. They were analyzed to establish chemical characteristics of groundwater. The chemical characteristics comprise major cations and anions like Na, K, Ca, Mg, SO_4, HCO_3 and Clincluding the measurement of pH and EC. pH were measured using a portable pH meter, EC were measured be means of an Electrode at the time collection of sample in the field itself, and TDS were determined by calculation method . With respect to cations and anion analyzed in laboratory using 883 Basic IC (Ion Chromatography) instrument.Bicarbonate was done by volumetric method. APHA (1998) procedures were followed for the above mentioned analyses. The suitability of groundwater for agricultural and domestic purposes was evaluated by comparing the values of different water quality parameters with those of the Bureau of Indians Standards (BIS 2012) values for drinking water.

IV. Results

Suitability of groundwater for drinking and domestic purposes is determined keeping in view the effect of various chemical constituents in water on the human beings. Though many ions are very essential for the growth of human, but when present in excess, have an adverse effect on the human body (CGWB, 2013). The quality standards for drinking water have been specified by BIS (2012). The major ions (Ca, Mg, Na, K, HCO_3, SO_4, Cl) and the important physical and chemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), and total hardness (TH) were determined for the suitability of groundwater in the study area. Due to heavy rainfall during December 2015 (cloud burst) the aquifer in the study area is being recharged and some portions of aquifer escape from the seawater intrusion that are being reflected in the results.

V. Discussion

5.1 Hydrogen Ion Concentration (pH)

The pH indicates the strength of the water to react with the acidic or alkaline nature. In the study area, pH is ranging from 6.7 to 8 during post- monsoon (January 2015), from 6.48 to 7.74 during pre- monsoon (June 2015) and from 6.48 to 7.8 during post-monsoon (January 2016), respectively as shown in **Fig. 2**.Due to heavy rainfall most of the locations are being recharged from rainwater during post-monsoon of January 2016. The permissible limit of pH for drinking purpose is from 6.5 to 8.5 (BIS 2012). The reported values are within the permissible limit for the study area during all the seasons. The groundwater of the study area is alkaline nature. Most of the biological processes and biochemical reactions are pH dependent. pH is considered as an indicator of overall productivity that causes habitat diversity (Minns 1989).

5.2 Electrical Conductivity (EC)

The ability of groundwater to conduct an electric current is measured by its electrical conductivity. It is an approximate measure or indicator of ionic concentration. It depends on temperature, ionic concentration and type of ions present. For groundwater, an EC of 300 µS/cm suggests a pollution problem, while values as high as 1500 µS/cm may be acceptable for drinking purpose.

In the study area, EC value ranges from 822 to 5960 µS/cm during post-monsoon (January 2015),from546 to 5750 µS/cm during pre-monsoon (June 2015) and from 396 to 5860 µS/cm during post-monsoon (January 2016). The spatial distribution of EC is found to be above the permissible limit in the Northern, Northeastern coastal environment of the study area as shown in **Fig. 3**. Larger variation in EC is attributed to saline water sources, mineral dissolution and inflow of pollutants from anthropogenic activities (Srinivasamoorthy*et al* 2011). According to BIS (2012), the permissible limit of EC for drinking water is 1500 µS/cm. In coastal streams or estuaries, salt water often mixes with fresh water. The addition of salt water greatly increases conductivity. In the study area, high conductivity was observed in most of the groundwater samples and this may be attributed to high sodium and chloride content in groundwater as the study area is a coastal plain, where saline water mixes with fresh water in terms of seawater intrusion. Due to the heavy rainfall during December 2015 (cloud burst), most of the locations had recharging from rainwater such that the EC lowers during post-monsoon (January 2016). The concentration of salinity diluted in some of the locations in the study area.

5.3 Total Dissolved Solids

Total dissolved solids (TDS) comprise inorganic salt and small amounts of organic matter that are dissolved in water. The desirable limit of Total Dissolved Solids in groundwater is from 500 to 2000 mg/l for drinking water. The potability of water decreases when the concentration exceeds these limits. According to Davis and De Wiest (1996) **(Table 1)** classification of groundwater based on TDS is shown in **Fig. 4a**,where 38% are permissible for drinking, 53% suitable for irrigation and 9% are unfit for drinking and irrigation purpose in pre monsoon season (June 2015), 5% of the total groundwater samples are suitable for drinking, 46% permissible for drinking, 42% suitable for irrigation and 7% unfit for drinking and irrigation purpose in pre monsoon season (June 2015), 7% of the total groundwater samples are suitable for drinking, 27% permissible for drinking, 60% suitable for irrigation and 5% unfit for drinking and irrigation purpose in post monsoon season (January 2016). In the study area, TDS ranges from 536 to 3814 mg/l during post-monsoon (January 2015), from 349 to 3680 mg/l during pre-monsoon (June 2015) and from 253 to 3750 mg/l during post-monsoon (January 2016). Spatial distribution of TDS is found to be above the permissible limit in Parrys corner, Royapuram, Railway colony and Attipattuputhunagar of the study area. Due to heavy rainfall during December 2015 (cloud burst), most of the locations had recharging from rainwater such that the TDS lowers during post-monsoon (January 2016). In the Northeastern part of the study area, the higher values of TDS is due to seawater intrusion from nearby coastal area and the influence of brackish water of Buckingham canal that parallels the coast as shown in **Fig. 4**. In the study area, during pre and post monsoon seasons, the groundwater is mostly affected by natural sources like, sewage, urban run-off, industrial wastewater and chemicals used in the water treatment process, and natural environmental features such as sea water intrusion, but other sources may include: storm water, agricultural runoff, and point/non-point wastewater discharges.

5.4 Total Hardness

Hard water is water with a high mineral content. Hardness is defined as the presence of alkaline earth metals and other polyvalent cations. Generally, most of the groundwater is rich in Calcium and Magnesium ions. These ions react with soap and form precipitate thus, preventing foam formation. This type of water is called hard water. Hardness caused by bicarbonate, termed as 'Carbonate hardness', can be removed by boiling and also known as 'Temporary Hardness'. 'Non-carbonate Hardness', caused by Chloride and Sulphate, which cannot be removed by boiling is known as 'Permanent Hardness'.According to Sawer and McCarty (1967) (**Table 2**) classification of groundwater based on TH mg/L, 25% belongs to hard, 75% belongs to very hard in post monsoon season (January 2015), 23% belongs to moderately hard, 42% belongs to hard, 35% belongs to very hard in pre monsoon season (June 2015), 4% belongs to moderately hard, 15% belongs to hard, 81% belongs to very hard in post monsoon season (January 2016). In the study area, TH value ranges from 225 to 1100 mg/l during post-monsoon (January 2015), from 89 to 1148 mg/l during pre-monsoon (June 2015) and from 81 to 1548 mg/l during post-monsoon (January 2016). In post monsoon most of the samples above permissible limit in Northern east of the study area as shown in **Fig. 5**. According to BIS (2012) have specified 200 mg/l as the acceptable limit and 600 mg/l as the maximum permissible limit for drinking water.So most of the samples affected by backwaters and domestic pollution.December 2015 floods increased the total hardness due to merging of local canals and stagnant water in northeastern part of the study area.

VI. Chemical Parameters

The minimum, maximum and average for Post monsoon 2015 to 2016 and Pre monsoon 2015 groundwater samples physico-chemical parameters given below in **Table 3**.

6.1 Calcium

Calcium is a key element in many geochemical processes. Different minerals like, gypsum, anhydrite, dolomite, calcite and aragonite serve as primary sources for calcium ion in water. According to BIS (2012) guidelines, Ca in drinking water should be between 75 mg/l and 200 mg/l.

Calcium in the study area varied from 22 to 280 mg/l during post-monsoon (January 2015), from 12 to 132 mg/l during pre-monsoon (June 2015) and from 13 to 201 mg/l during post-monsoon (January 2016). Due to recharge of heavy rainfall during December 2015 (cloud burst), Ca becomes within permissible limit in Northern and Northeastern part of the study area during post-monsoon (January 2016) as shown in **Fig. 6**. Calcium is the most dominant natural element. The origin of calcium may be due to the dissolution of precipitation of $CaCO_3$ and $CaMg(CO_3)_2$ during recharge (Lakshmanan*et al* 2003). Another main source of calcium is due to rapid industrialization and urbanization in the study area that contribute high concentration of calcium in the groundwater. It may block the absorption of heavy metals in the body and is thought to increase bone mass.

6.2 Magnesium

The principal sources of magnesium in natural waters are various kinds of rocks while sewage and industrial wastes are also important contributors of magnesium. The values of magnesium concentration in the study area ranges from 17 to 109 mg/l with an average value of 42 mg/l during post-monsoon (January 2015) from 7 to 199 mg/l with an average value of 33 mg/l during pre-monsoon (June 2015); and from 12 to 277 mg/l with an average value of 64 mg/l during post-monsoon (January 2016). Due to heavy rainfall during December 2015 (cloud burst), Mg becomes within the permissible limit in north and southern part of the study area during post-monsoon (January 2016) as shown in **Fig. 7**. Magnesium is an essential ion for functioning of cells in enzyme activation, but at higher concentration, it is considered as laxative agent, while deficiency may cause structural and functional changes in human beings.

6.3 Sodium

Sodium is the sixth most abundant mobile element on the earth and soluble in groundwater. In groundwater, sodium originates from natural and anthropogenic sources. In the study area, Na value ranges from 55 to 890 mg/l with an average value of 210 mg/l during post-monsoon (January 2015), from 55 to 2125 mg/l with an average value of 271 mg/l during pre-monsoon (June 2015); and from 46 to 612 mg/l with an average value of 260 mg/l during post-monsoon (January 2016). Spatial distribution of Sodium is found to be above the permissible limit in the, North, Northeastern and Central part of the study area during all the seasons as shown in **Fig. 8**. Due to heavy rainfall during December 2015 (cloud burst), Na becomes above permissible limit in Northeastern part of the study area but at the same time the concentration of sodium diluted from the groundwater in many part of the location during post-monsoon (January 2016). Higher sodium concentration was observed in Northeastern and central part of the study area, due to seawater intrusion from the nearby coastal environment. Ennore creek and the influence of Buckingham canal along the coastal region (Sridhar *et al* 2015: Balasubramanian*et al* 2016) being the other cause. Brackish water that infilters into the aquifers, saltwater intrusion into wells in coastal areas, groundwater pollution by sewage effluent and infiltration of leachate from landfills or industrial sites are the main attributes for higher concentration of Na in Northeastern and Central part of the study area. Increased intake of sodium may cause problem, such as heart disease and kidney malfunction.

6.4 Potassium

Potassium (K) is an element commonly found in soils and rocks. Potassium in groundwater is generally low due to its lesser mobility (Herman Bouwer 1978). The potassium concentration variedfrom 2 to 104mg/l with an average value of 29 mg/l during post-monsoon (January 2015), from 8 to 77 mg/l with an average value of 19 mg/l during pre-monsoon (June 2015); and from 2 to 128 mg/l with an average value of 23 mg/l during post-monsoon (January 2016). Spatial distribution of Potassium is found to be above the permissible limit in North and Northeastern part of the study area during all the seasons as shown in **Fig. 9.** Due to heavy rainfall during December 2015 (cloud burst), K becomes within the permissible limit in northern and southern part of the study area during post-monsoon (January 2016).In the study area, the source of potassium is from leaching of fertilizer and sea water ingress. Potassium is an essential nutrient for humans. But, excessive intake of K will lead to diseases related to heart and kidney.

6.5 ANIONS

6.5.1Chloride

Chloride (Cl^-) is a negative ion of the element chlorine (Cl) and is widely distributed in the environment. It is present in water, soil, rock, and many foods. Chloride indicates contamination due to animal and human waste. Chloride is a common constituent of all natural water and is generally not classified as harmful constituent (Jayanta and Siba 2009). Anthropogenic sources of Cl in groundwater might also be due to the influences of irrigation-return flows and chemical fertilizers (SubbaRao*et al* 2012). Bureau of Indian Standard (BIS) classified 250 mg/l as the desirable and 1000 mg/l as the permissible limit for drinking water purpose. In the study area, Chloride value ranges from 120 to 1670 mg/l with an average value of 411 mg/l during post-monsoon (January 2015), from 102 to 4182 mg/l with an average value of 440 mg/l during pre-monsoon (June 2015); and from 98 to 1464 mg/l with an average value of 415 mg/l during post-monsoon (January 2016), respectively. Spatial distribution of Chloride illustrates that the northeastern, and northern part of the study area have concentration above the permissible limit during all the seasons as shown in **Fig. 10.** Due to heavy rainfall during December 2015 (cloud burst), Cl becomes within the permissible limit in northern part of the study area during post-monsoon (January 2016). In the study area, the higher concentration of Cl is attributed to seawater intrusion and irrigation return flow (Jeevanandam*et al* 2012). Anthropogenic activities can locally affect chloride concentrations in ground water. Some anthropogenic factors commonly cited as influences on chloride levels in water include road salting during the winter, improper disposal of oil-field brines, contamination from sewage, and contamination from various types of industrial wastes (Hem 1985, 1993).

6.5.2 Bicarbonate

Bicarbonate represents the major sum of alkalinity. Alkalinity in water is the measure of its capacity of neutralization. It is formed mainly due to the action of atmospheric CO_2 and CO_2 released from organic decomposition. Bicarbonate is the major source for alkalinity of groundwater and responsible for the buffering capacity of water. In the study area, bicarbonate value ranges from 109 to 732 mg/l with an average value of 374 mg/l during post-monsoon (January 2015), from 67 to 652 mg/l with an average value of 221 mg/l during pre-monsoon (June 2015); and from 85 to 579 mg/l with an average value of 299 mg/l during post-monsoon (January 2016), respectively. Spatial distribution of HCO_3 concentration is within the permissible limit of BIS (2012) but at some locations it is above the permissible limit in the study area as shown in **Fig. 11.**Due to heavy rainfall during December 2015 (cloud burst), HCO_3 becomes within the permissible limit in central part of the study area during post-monsoon (January 2016).The primary source of carbonate and bicarbonate ions in groundwater is due to dissolution of the carbon dioxide in rain, which when enters the soil dissolves groundwater. Decay of organic matters also releases carbon dioxide for dissolution. The source of bicarbonate may be due to saline water intrusion from the nearby coastal area and due to the canal recharge that increases the bicarbonate content in the groundwater.

6.5.3 Sulphate

Sulphate (SO_4) is a combination of sulphur (S) and oxygen (O). It occurs naturally in soils and rock formations. Sulphate is one of the major anion found in groundwater and normally its concentration levels would be less than that of chloride and bicarbonate because of solubility controls. BIS (2012) have been classified 200 mg/l as the desirable limit and 400 mg/l as the permissible limit for drinking water purpose. In the study area, sulphate concentration ranges from 3.9 to 222 mg/l with an average value of 35 mg/l during post-monsoon (January 2015), from 14.3 to 121 mg/l with an average value of 36 mg/l during pre-monsoon (June 2015); and from 30 to 423 mg/l with an average value of 158 mg/l during post-monsoon (January 2016), respectively. Spatial distribution of SO_4 illustrates that the northeastern part of the study area shows above the permissible limit during January 2016 as shown in **Fig. 13.** Due to heavy rainfall during December 2015 (cloud burst), SO_4 becomes within the permissible limit in southern part and western part of the study area during post-monsoon (January 2016).Man-made sources include industrial discharge and deposition from burning of fossil fuels. The other sources of this ion in the aquifer may also be due to bacterial fixation, impact of fertilizers, tannery and other anthropogenic sources (Chidambaram *et al* 2012).

6.5.4 Nitrate

Nitrate is the important indicators of anthropogenic sources of pollution. The average concentration of nitrate in rain water is only 0.2 ppm and hence, its average concentration in groundwater remains below 5 ppm. The main contribution of nitrate is from decaying of organic matters, sewage wastes and the application of fertilizers. In the study area, Nitrate concentration ranges from 10 to 81 mg/l with an average value of 21 mg/l during post-monsoon (January 2015) from 12 to 129 mg/l with an average value of 26 mg/l during pre-monsoon (June 2015); and from 2 to 193 mg/l with an average value of 69 mg/l during post-monsoon (January 2016), respectively.Spatial distribution of NO_3 concentration at most of the locations are above the permissible limit (BIS 2012) for drinking purpose during June 2014 and January 2016 season in the study area as shown in**Fig. 13**. Due to heavy rainfall during December 2015 (cloud burst), water was stagnant for weeks together made the concentration of NO_3 above the permissible limit in the study area during post-monsoon (January 2016). The high concentration of nitrate in the water may lead to death of infants due to ‘‘methemoglobinemia’’ or blue baby disease and gastric carcinomas. Nitrate in groundwater mainly originates from surface contamination sources. Nitrate (>300 mg/l) poisoning may result in the death of livestock (animal deaths) consuming water (Canter 1997).

7 SODIUM ABSORPTION RATIO (SAR) AND USSL DIAGRAM

The alkali or sodium hazard to groundwater is found by determining the sodium absorption ratio (SAR). The SAR is calculated using the following formula (Karnath 1987):

$$SAR= Na^{+}/\sqrt{Ca^{2+}+Mg^{2+}/ 2}$$

The salinity hazard to groundwater is measured with its electrical conductivity (EC). The salinity in the groundwater originates mainly due to weathering of rocks, leaching from the top soil, and some anthropogenic activity along with climate having a influence.

The classification of water samples of the study area based on SAR are given in **Table 4**, Based on Richards (1954) classification, during post monsoon (January 2015) season, 20%, 30%, 36% and 14% of samples fall in “Excellent”, “Good”, “Fair” and “Poor” categories but in pre-monsoon (June 2015) period, 4%, 14%, 37%, and 44% of samples fall in “Excellent”, “Good”, “Fair”, and “Poor” categories, and during post monsoon (January 2016) season, 10%, 34%, 28%, and 28% of samples fall in “Excellent”, “Good”, “Fair”, and “Poor” categories. Based on the SAR classification most of the groundwater samples fall in “Fair” category due to high industrial pumping area, untreated wastewater and saline water intrusion.

The classification of groundwater for irrigation purpose based on the USSL diagram in the study area is shown in **Fig. 14 (a, b and c)**and the percentage of samples that fall in combination of sodium and salinity is presented in **Table 5.**

The SAR and EC values of water samples of the study area are plotted in diagram suggested by the U.S. Salinity Laboratory (1954) for evaluating suitability of waters for irrigation purpose as shown in **Fig. 14 (a, b and c**). In this diagram, waters of the study area are classified into C1, C2, C3 and C4 types on the basis of salinity hazard and S1, S2, S3 and S4 types on the basis of sodium hazard.

Based on USSL diagram, the water samples of the study area fall in,

a) C3S1 (High salinity with low sodium) category, with the following percentages of samples at various periods: 49% post-monsoon (January 2015), 20% pre-monsoon (June 2015), 51% post-monsoon (January 2016).

b) C3S2 (high salinity with medium sodium) category, with the following percentages of samples at various periods: 16% post-monsoon (January 2015), 50% pre-monsoon (June 2015), 9% post-monsoon (January 2016).

c) C4S2 (High salinity with medium sodium) category, with the following percentages of samples at various periods: 31% post-monsoon (January 2015), 5% pre-monsoon (June 2015), 18% post-monsoon (January 2016).

d) C4S3 (Very High salinity with High sodium) category, with the following percentages of samples at various periods: 0% post-monsoon (January 2015), 11% pre-monsoon (June 2015), 11% post-monsoon (January 2016).

e) A few of the water samples fall in C4S1 (very high salinity with low sodium) and C2S1 (medium salinity with low sodium) category during some of the seasons; C3S3 (high salinity and high sodium) and C4S4 (very high salinity and very high sodium) in only one season.

It is observed that most of the water samples fall in C3S1 (high salinity with low sodium), some of the samples fall in C3S2 (high salinity with medium sodium), category of the study area and these waters can be used for irrigation and domestic purposes. Few samples fall in C3S3, C4S1, C4S2, C4S3 and C4S4 are the poor groundwater that is not suitable for irrigation purpose and domestic purpose also. These sample locations are nearer to the Coovumriver and along the coastal area. USSL diagram confirms that the groundwater is being affected by industrial untreated water and saline water intrusion in the study area especially, in northeastern region where industries are located as well as near the coast. Some of the samples fall in C4S1, C4S2 and C4S3 are “unsuitable” for irrigation that are being attributed to agricultural wastes, industrial effluents and urban activities apart from seawater intrusion in the study area (Balasubramanian*et al* 2016).

VII. Wilcox’s Diagram

Wilcox (1955), elaborated the method for determination of suitability of groundwater for agricultural use is by calculating Na^+ percentage because Na^+ reacts with soil to reduce its permeability (Todd 1980, Janardhana 2007). Sodium content is usually expressed in terms of percent sodium or soluble-sodium percentage (% Na). Sodium content expressed in terms of sodium percentage or soluble sodium percentage is defined as:

$$Na\% = (Na + K) \times 100 / (Ca + Mg + Na + K)$$

All the concentrations are expressed in meq/L. Sodium concentration is important in classifying irrigation water because sodium causes an increase in the hardness of the soil due to its tendency to be absorbed by clay particles, displacing magnesium and calcium ions, when high in irrigation water. When the concentration of sodium is high in irrigation water, sodium ions tend to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process reduces the permeability and results in soil with poor internal drainage (Tijani 1994). Hence, air and water circulation is restricted during wet conditions and such soils become usually hard when dry (Saleh*et al* 1999).

Wilcox's diagram (Wilcox 1955), is drawn for the classification of groundwater for irrigation, wherein EC is plotted against %Na as shown in **Fig. 15 a and b,** and the inferences are tabulated in **Table 6.**

According to the Wilcox plot, the groundwater of the study area is being classified as:

a) 51%, 18%, 22% and 9% of the water samples fall in "Good to Permissible", "Permissible to Doubtful", "Doubtful to Unsuitable", and "Unsuitable" categories, respectively during post-monsoon, January 2015.

b) 10%, 5%, 50%, 25% and 10% of the water samples fall in "Excellent to Good", "Good to Permissible", "Permissible to Doubtful", "Doubtful to Unsuitable", and "Unsuitable" categories, respectively during pre-monsoon, June 2015.

c) 10%, 40%, 10%, 30% and 10% of the water samples fall in "Excellent to Good", "Good to Permissible", "Permissible to Doubtful", "Doubtful to Unsuitable", and "Unsuitable" categories respectively during pre-monsoon, January 2016.

Most of the groundwater samples fall in "Excellent to Good", "Good to Permissible" and "Permissible to Doubtful", categories and they are fit for irrigation purpose. Some of the samples that fall in "Doubtful to Unsuitable" category can be used for salt water tolerant crops.

The samples that fall in "unsuitable" category are not fit for irrigation purpose, and they are either polluted by sea water intrusion or by effluents discharged from adjoining industries (Sridhar *et al* 2015) and very few groundwater samples show abnormal values during pre and post monsoon, due to high salinity.

VIII. Gibb's Plot

Gibbs (1970) proposed a diagram to understand the relationship of the chemical components of water from their respective aquifer lithologies. Three distinct fields such as precipitation, evaporation and rock water interaction, can be identified form Gibb's plot.

The chemical composition of groundwater is the imprints of the rock water interaction and chemical processes. So, groundwater chemistry can be used to identify the rock water interaction or chemical processes. Gibb's (1970) plots are drawn using TDS vs. Na+K/(Na+Ca+K) and TDS vs. Cl/(Cl+HCO_3). Viswanathaiah*et al* (1978) interpreted the rock water interaction in the groundwater chemistry of Karnataka. Rengarajan and Balasubramanian (1990), Sathyamoorthy (1991), Edwin Moses (1994), and Sreedevi (2004) have reported hydrogeochemical process based on Gibb's plot from various parts of India.

According to the Gibb's diagram, for the study area, most of the samples fall in "evaporation" field as well as in the field of anthropogenic activity. In the cations plot, illustrated in **Fig. 16a and b,** most of the water samples fall in "evaporation" and "anthropogenic" field during January 2015 and June 2015 seasons. During January 2016, most of the samples fall in "anthropogenic" and some of the samples fall in "rock-water interaction" field due to dilution of groundwater caused during December 2015 unpredictable floods in the study area. In the anions plot **Fig. 16 a**, most of the water samples indicate "evaporation" field in January 2015 seasons and some of the samples fall in "anthropogenic" activity. **Fig. 16 b** shows that during June 2015 and January 2016 water samples fall in "anthropogenic" activity and few samples fall in the field of "evaporation". Evaporation indicates increase in salinity by increasing Na and Cl in relation to increase in TDS (Gupta *et al* 2008).

IX. Sea Water Intrusion Na/Cl (Molar Ratio)

Effects of seawater intrusion have been evaluated by studying a series of ionic ratios (Petalas and Diamantis 1999; Sanchez Martos*et al* 1999, 2002; Vengosh*et al* 2002; El Moujabber*et al* 2006). Conservative seawater–fresh water mixing is expected to show a linear increase in Na and Cl (Sanchez Martos*et al* 1999). Ratio values of groundwater less than the seawater ratio 0.86 indicates that fresh groundwater was contaminated with the saline waters. The threshold value of Cl^-concentration is 63mg/l. Moles ratios of Na^+/Cl^- versus Cl^- concentrations indicate that ratio values of groundwater falling near the seawater ratio (0.86) indicate that fresh groundwater were contaminated with the saline waters.

Maximum values close to the seawater ratio indicate recent simple mixing of groundwater with seawater (Mercado 1985). Very high Na/Cl ratios may be indicative of anthropogenic contamination, like fertilizers (Jones *et al* 1999).

In the study area, Na^+/Cl^- molar ratio ranges from 0.39 to 1.94 during post-monsoon (January 2015) and from 0.33 to 3.5 during pre-monsoon (June 2015) and from 0.41 to 2.35 during post-monsoon (January 2016). Ratios less than the seawater ratio (0.86) indicate that fresh groundwater was contaminated with the seawater, where inverse cation exchange occurs and Na^+ is taken by the exchanger. The ratio diagram (**Fig. 17a and b)** shows that the majority of the samples fall in saline water contamination in the study area.

The calculated Na^+/Cl^- molar ratios (**Table 7)** show that 32%, 28% and 32% of samples fall in "Recommended limit" for agriculture (Cl = 250mgl)" during January 2015, June 2015 and January 2016, while

68%, 72% and 67% of samples show that the values fall in "Affected by saline water" category, thus, indicating recent simple mixing of seawater (Mercado 1985).

Intrusion can affect the quality of water not only at the pumping well sites, but also at other well sites, and undeveloped portions of the aquifer. According to Na/Cl ratio most of the groundwater is being affected by seawater intrusion due to over exploitation of groundwater during pre monsoon season and few samples show recharge from precipitation during post monsoon seasons in the study area. The groundwater affected by anthropogenic activity are due to improper drainage systems and regulation not followed by the industrial waste water discharge systems in the study area.

X. Seawater Intrusion Cl^-/Hco_3^- (Molar Ratio)

In the seawater, Cl^- is the dominant ion but it is available in small quantities in groundwater, while HCO_3^- is available in large quantities in groundwater but in medium quantities in seawater. In the study area, Cl^-/HCO_3^- molar ratio ranges from 0.49 to 11.8 during post-monsoon (January 2015) and from 0.32 to 10.28 during pre-monsoon (June 2015) and from 0.68 to 12.8 during post-monsoon (January 2016). The Cl/ (HCO_3+CO_3) known as Simpson's ratio is important as for seawater intrusion is concerned (El Moujabber*et al* 2006).

Classification of groundwater for $Cl^-/$ (HCO_3+CO_3) Simpson's ratio, is presented in **Table 8.** During post-monsoon (January 2015) season, 41%, 30%, 14% and 14% samples fall in "Slightly affected by sea water", "Moderately affected by seawater intrusion", "Injuriously contaminated by sea water" and "Severely affected by sea water" categories for seawater intrusion; during pre-monsoon (June 2015) season, 10%, 40%, 28% and 20% samples fall in "Slightly affected by sea water", "Moderately affected by seawater intrusion", "Injuriously contaminated by sea water" and "Severely affected by sea water" categories for seawater intrusion and post-monsoon (January 2016) season, 26%, 44%, 16% and 12% samples fall in "Slightly affected by sea water", "Moderately affected by seawater intrusion", "Injuriously contaminated by sea water" and "Severely affected by sea water" categories for seawater intrusion. The Cl/ (HCO_3+CO_3) ratio shows a positive linear relationship (**Fig. 18a and b)** with Cl^- concentration indicating simple mixing with sea water (Singaraja*et al* 2014). The $Cl/(HCO_3+CO_3)$ ratio indicate that the bore wells close to the coastline have much higher molar ratios than the boreholes drilled away from the coastline.

$Cl/(HCO_3+CO_3)$ ratio indicate most of the samples are affected by salinity in northern eastern part of the study area, where overexploitation of groundwater is seen for industrial and domestic purposes. Some of the locations, especially, southern part of the study area is being recharged by precipitation during rainy season.

XI. Conclusion

The spatial distribution of EC is found to be above the permissible limit in the Northern, Northeastern coastal regions. Spatial distribution of TDS is found to be above the permissible limit in Parrys corner, Royapuram, Railway colony and Attipattuputhunagar of the study area due to seawater intrusion and anthropogenic activities. Results show that the spatial distribution of Total hardness is found to be above the permissible limit in the, Northeastern part and some of the central regions. Calcium concentration is within permissible limit in the regions. Magnesium concentration shows that it is high in the Northeastern regions because of coastal environment. Sodium is found to be above the permissible limit in the North, Northeastern and Central regions. Potassium is found to be above the permissible limit in North and Northeastern regions very near to the coastal region. Chloride illustrates that the northeastern, and northern region have concentration above the permissible limit during all the seasons. HCO_3 concentration is within the permissible limit of BIS (2012) but at some locations it is above the permissible limit.SO_4 illustrates that the northeastern region shows above the permissible limit in the coastal region. NO_3concentration at most of the locations are above the permissible limit (BIS 2012) for drinking purpose during June 2015 and January 2016 seasons.USSL diagram confirms that the groundwater is being affected by industrial untreated water and saline water intrusion in the study area especially, in northeastern region where industries are located as well as near the coast. Most of the groundwater samples fall in Wilcox diagram "Excellent to Good", "Good to Permissible" and "Permissible to Doubtful", categories and they are fit for irrigation purpose. Some of the samples that fall in "Doubtful to Unsuitable" category can be used for salt water tolerant crops. Evaporation indicates increase in salinity by increasing Na and Cl in relation to increase in TDS. According to Na/Cl ratio most of the groundwater is being affected by seawater intrusion due to over exploitation of groundwater during pre monsoon season and few samples show recharge from precipitation during post monsoon seasons in the study area.$Cl/(HCO_3+CO_3)$ ratio indicate most of the samples are affected by salinity in northern eastern part of the study area, where overexploitation of groundwater is seen for industrial and domestic purposes. Some of the locations, especially, southern part of the study area is being recharged by precipitation during rainy season. Most of the place water stagnant and mixed with sewage water and contaminated the groundwater in the study area due sudden cloudburst during December 2015 in Chennai, at the same time most of the locations groundwater quality can be improve and diluted from the salinity due to heavy rain in Chennai region and surrounding coastal environment.

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