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Fluoride contamination of groundwater in a coastal region – a growing environmental pollution threat

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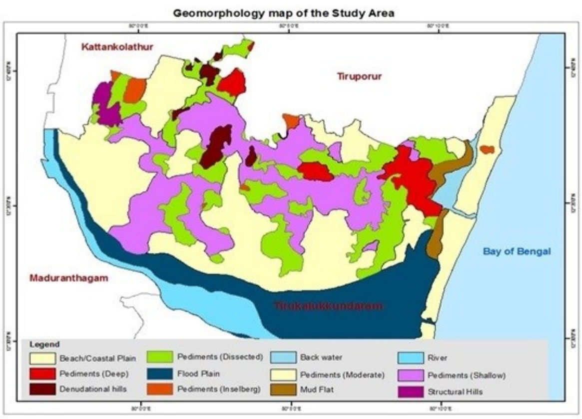
Graphical abstract



Abstract

The research work's main objective is to correctly examine and find out the proper hydro-geochemistry of groundwater during the dry and wet seasons and hence evaluate it's quality in India, Tamil Nadu state's Thirukkazhukundram Block. Data from two seasons-the "Pre-monsoon" in August 2016 and the "Post-monsoon" in February 2017-have just been used to do subjective assessments of the chemical composition of the underground water. The results of a thorough geochemical investigation of the subsurface zone are given. Gibbs emphasizes that the majority of samples in both seasons are dominated by evaporation and weathering mechanism sector. The majority of the sample's mixed water type is interpreted hydro-chemically in accordance with Piper's classification. According to the Wilcox diagram, the majority of PRM and POM samples fall into the group of "very good to good and good to permissible." The USSL diagram shows that just 23% of the samples for the C1-S1 type were collected during POM. 23% samples align under C2-S1 during PRM and 57% fall under C2-S1 during POM for. It was noted that 67% and 20% of the samples accounted under C3-S1type respectively, for POM and PRM. The C4-S1type is in PRM only, as of 13% of the samples. The irrigation quality of the groundwater samples showed that they were basically suitable for the very same purpose. Fluoride contamination in groundwater has nowadays become a slowly creeping issue in the study area. Steps need to be taken promptly to avert the resulting human health hazard on account of this pollution, in due course of time. Using ArcGIS 10.0, the groundwater quality chart was produced. Using inverse distance weighting, the regional distribution of groundwater quality measurements was interpolated. The findings of this study highlight the significance of creating techniques for managing aquifer systems.

Keywords: Hydrogeochemistry, water quality, aquachem, Gibb's plot, Wilcox diagram

1. Introduction

Depending on how it is utilized and exhausted, subsurface water can be categorized as either a renewable or non-renewable resource. One-third of the world's population, uses excessive amounts of subsurface water. Groundwater is the main source of domestic subsurface resources in both urban and rural India (Nagamani *et al.*, 2021; Amuthini Sambhavi *et al.*, 2018). The two most crucial factors are the lack of consumable surface water and the widely held belief that lithological water is safer and cleaner than plane water due to the shielding properties of the earth's upper surface. India is dealing with serious climate change, just like many other developing nations. India's water supply is particularly vulnerable to pollution because of its large population and developing economy. Anthropogenic activity is causing a deterioration in the quality of underlying water resources (Amuthini Sambhavi *et al.*, 2021). As the undergroundwater migrates from recharge to discharge, a number of hydrogeochemical procedures alter its chemical framework (Glover *et al.*, 2012). GIS can be an eminent tool for drawing solutions for problems involving water resources, for evaluating water quality and managing water resources (Gnanachandrasamy *et al.*, 2012; Anitha *et al.*, 2011).

Understanding the nature of the water is necessary to decide whether it is suitable for usage in various applications. The categorization of groundwater quality of hard rock aquifer of Gadilam river was performed by (Aravindan *et al.*, in 2004; Kalpana *et al.*, 2018). Keesari *et al.,* 2014; Mukesh Kumar Mahato *et al.,* 2016; Krishna *et al,* 2009; Pandian K., and Sankar 2007; Selvam *et al.*, 2018; Sharma *et al.,* 2017; Sreedevi 2004; Subba Rao 2002; Venkatramanan *et al.,* 2017 also carried out groundwater related research studies. The study taken up by Eaton F.M., 1950 is really helpful in my research dealing with water quality.

Tamil Nadu is one of India's most important agricultural state despite having limited water resources. There are no perennial rivers in the state. The rivers that flow through this area are mostly seasonal and come from the adjacent states. The state has 61 large reservoirs and more than 39,202 larger and smaller tanks, all of which are fully utilized for human, industrial, and agricultural purposes. Because surface water sources are shrinking, developers have shifted to groundwater resources as a contingency or alternative supply source. The deterioration of groundwater quality in Tamil Nadu's Thirukkazhukundram Block is one of the sources of numerous problems, viz. serious diseases, decreased crop yield etc. As a result, the current investigation was carried out in the southern part of Thirukkazhukundram Block to determine the nature of groundwater for drinking and irrigation purposes. The hydro-geological condition of the review region is the primary cause responsible for this fluoride contamination, which needs to be addressed right away to prevent a health risk to the general population over time. The fitness and disinfection agency incharge of the residents' health and waterworks will use the study's findings to help establish corrective action. Therefore, when inventing any creative ideas, groundwater is seriously evaluated. Recently, groundwater resource appraisal has witnessed an increase in the usage of the Geographic Information System (GIS) (Burri *et al.*, 2019). In a database called a "geographic information system," or "GIS," spatial data is recorded and structured. They can gather and produce map data. They are also capable of carrying out a variety of model calculations or evaluations.

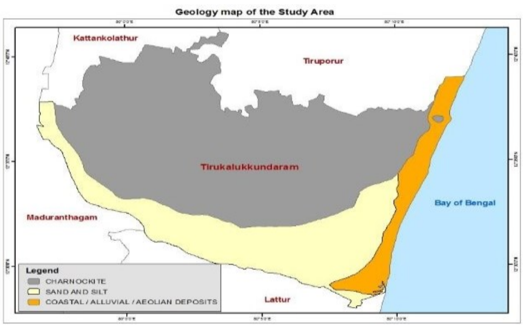


Figure 1. Geology map of Thirukkazhukundram block

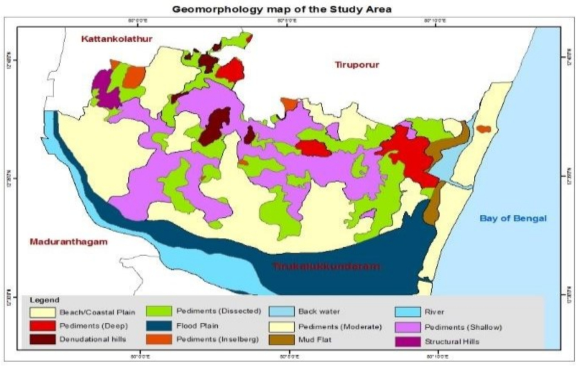


Figure 2. Geomorphology map of Thirukkazhukundram Block

2. Method and materials

The deterioration of groundwater quality in Tamil Nadu's Thirukkazhukundram Block is one of the reasons for many human health issues, lack of healthy agricultural crops, reduced crop yield etc. In order to identify the sort of underground water that is acceptable for irrigation and drinking, the current examination was carried out in the southern part of Thirukkazhukundram Block. Geology map of Thirukkazhukundram block Figure 1 Geomorphology map of Thirukkazhukundram Block (Figure 2). Thirukkazhukundram Block's Dug and Bore wells' water samples were taken from 30 villages in the "dry season" of August 2016 and in the "wet period" of February 2017. Thirty water samples were investigated in August 2016 (Figure 1), and the water composition of the same areas was once more evaluated in February 2017 to determine the water samples nature due to seasonal changes. Using conventional analysis procedures assured by (APHA), the specimens' suitability for various purposes was assessed. Clean 250 mL plastic bottles were utilized to collect the water samples. Bottles were three times rinsed with groundwater before sampling. After 10 minutes of extraction, bore well water samples were filled. The well had its soil water removed. The samples were brought to the lab to be tested at 5°C using a cooled ice box. According to "APHA 1998" standards, tests for various chemical parameters of the samples were undertaken within 24 hours. Using the ArcGIS 10.0 programme, thematic maps of waterquality were produced for the chemical parameters. The prediction is supported by the Piper plot, Gibbs and Wilcox diagram, and USSL diagram format produced by the Aquachem software.

3. Results and discussion

It is possible to do research on the effects of seasonal fluctuations on the suitability of groundwater for human intake, domestic use, and agricultural use. Chemical analysis of water samples collected in the Thirukkazhukundram Block during the dry (PRM) and wet (POM) seasons produced statistical data that are given in Tables 1a and 1b.

Table 1a. Premonsoon Major ion (ppm) concentrations of groundwater in Thirukkazhukundram Block

S.No	Location	pH	EC	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4	F	TH
1	Nenmeli	8.1	746.21	529.81	50.21	24.12	62.14	18.21	266.2	64.12	44.12	0.86	224.52
2	Thirumani	7.6	650.85	462.10	38.12	29.12	43.21	10.21	242.12	60.14	38.44	0.69	214.92
3	Alagusamudram	7.6	773.97	549.52	51.23	12.24	96.24	8.21	154.12	132.1	88.12	0.84	178.18
4	Keerapakkam	7.8	2402.5	1705.79	175.3	85.14	202.2	45.12	503.65	388.2	302.2	0.56	787.56
5	Mosivakkam	7.5	1086.2	771.21	53.21	48.15	76.12	22.11	411.4	76.21	83.85	0.74	330.87
6	Thazhambedu	7.8	1617.4	1148.38	86.21	34.52	176.3	38.21	355.12	268.2	188.1	0.63	357.13
7	Manapakkam	7.8	2740.2	1945.56	191.6	62.31	232.1	92.14	532.21	438.1	386.1	1.36	734.32
8	Kuzhipanthandalam	7.9	1108.2	786.80	76.58	36.21	102.6	14.25	285.36	175.2	89.32	1.44	340.05
9	Pulikundram	7.8	2126.2	1509.59	104.2	99.12	220.4	53.21	386.54	385.4	259.1	1.47	667.88
10	Mamallapuram	8.2	748.04	531.11	45.26	21.23	86.25	13.25	172.56	102.2	88.54	0.95	200.27
11	Ponvilayantha-kalathur	7.2	2036.5	1445.94	141.2	55.23	205.3	33.12	402.23	342.5	261.2	1.36	579.61
12	Thirukazhu-kundram	7.7	2766.5	1964.20	185.3	104	265.3	74.25	525.13	475.2	328.7	1.47	890.13
13	Igai	7.7	1084.6	770.07	90.23	22.12	83.21	11.52	314.6	145.2	99.65	0.69	316.14
14	Navalur	7.6	922.92	655.27	75.26	13.26	88.23	24.15	208.14	138.5	102.2	0.95	242.33
15	Kadambadi	7.8	676	479.96	48.41	11.23	76.23	12.24	149.25	88.12	88.21	1.36	166.99
16	Salur	7.7	1011.1	717.91	56.21	29.12	124.2	19.45	221.23	155.4	103.2	1.44	260.06
17	Pattikadu	7.7	1127	800.15	68.14	41	101.2	25	231.41	202.3	124.2	1.36	338.7
18	Thathalur	7.8	977.59	694.09	64.21	27.52	82.41	19.23	314.6	108.4	76.49	1.42	273.43
19	Amaipakkam	7.7	935.27	664.04	62.12	11.41	102.5	22.41	203.21	154.2	102.5	1.36	201.94
20	Kunnathur	7.9	1363.2	967.84	92.52	45.12	102.1	23.21	459.8	150.2	90.38	1.36	416.48
21	Veerapuram	7.7	1260.7	895.11	78.12	34.21	135.2	39.12	288.52	168.2	145.2	0.95	335.67
22	Kilapakkam	7.7	2647.1	1879.46	201.2	92.51	235.2	65.21	607.41	435.3	235.1	1.42	882.7
23	Neikuppi	7.8	830.55	589.69	55.23	26.12	65.21	23.45	188.41	124.6	101.2	1.86	245.27
24	Vilagam	7.9	1797.1	1275.95	155.2	61.23	265.4	36.21	402.12	224.5	124.6	1.36	639.23
25	Pandur	7.6	729.48	517.93	50.12	13.23	88.12	15.23	165.23	105.2	75.14	1.33	179.48
26	Saduranga-patnam	7.5	1186.8	842.64	65.21	29	145.2	30.12	303.21	164.2	102.3	1.42	282.02
27	Lathur	7.6	1523.1	1081.37	114.2	35.62	151.2	32.12	401.26	204.2	135.1	1.36	431.56
28	Irumbilicheri	7.9	1158.9	822.83	76.23	38.31	109.1	23.56	301.23	151.2	121.1	1.44	347.82
29	Nallathur	7.3	671.01	476.42	30.35	14.28	85.63	22.61	175.21	88.23	56.23	1.42	134.48
30	Voyalur	7.3	616.94	438.03	32.21	22.41	52.12	26.23	169.4	88.41	46.13	0.94	172.57

Table 1b. Postmonsoon Major ion (ppm) concentrations of groundwater in Thirukkazhukundram Block

S.No	Location	pH	EC	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4	F	TH
1	Nenmeli	7.96	272.06	193.16	26	8.14	18.15	5.12	77.12	33.14	20.41	0.00	98.36
2	Thirumani	7.69	215.89	153.28	18	6.12	16.12	6.41	61.23	28.14	15.12	0.00	70.09
3	Alagusamudram	7.92	200.39	142.28	17.25	4.12	13.21	5.14	63.21	24.56	14.15	0.45	59.99
4	Keerapakkam	7.83	883.3	627.14	50.12	16.24	103.3	22.14	205.1	134.6	92.14	0.36	191.9
5	Mosivakkam	7.03	509.15	361.50	41	12.12	43.8	12.41	131.2	91.23	23.45	0.44	152.2
6	Thazhambedu	7.42	367.1	260.64	26.31	13.24	24.15	9.24	110.1	55.12	20.14	0.84	120.1
7	Manapakkam	7.84	1098.3	779.78	75.14	26.24	131.2	18.24	244.2	175.2	102.1	0.69	295.4
8	Kuzhipan-thandalam	7.29	241.38	171.38	16.24	4.25	23.45	5.26	68.45	33.12	18.42	0.74	58.01
9	Pulikundram	7.84	1219.4	865.78	86.23	31.42	133.2	25.41	291.1	161.2	135.2	1.36	344.4
10	Mamallapuram	7.33	100.79	71.56	8.21	1.23	10.24	1.23	30.12	10.23	6.52	0.00	25.54
11	Ponvilayantha-kalathur	7.65	670.08	475.76	52.41	18.24	66.21	18.24	155.2	124.1	35.42	0.86	205.8
12	Thirukazhu-kundram	7.45	1104.8	784.38	77.45	31.24	116.2	26.24	241.3	161.2	124.6	0.68	321.8
13	Igai	7.29	512.06	363.56	30.12	18.12	46.72	12.14	115.9	102.1	32.14	0.44	149.7
14	Navalur	7.5	332.03	235.74	25.41	8.12	26.51	10.23	81.24	64.12	18.24	0.36	96.81
15	Kadambadi	7.61	236.99	168.26	21.14	6.42	18.98	5.12	55.12	45.21	12.14	0.84	79.16
16	Salur	7.55	373.94	265.50	30.12	8.24	38.12	10.12	83.12	68.12	25.41	0.79	109.1
17	Pattikadu	8.09	312.34	221.76	26.15	8.96	24.12	7.29	98.12	36.12	18.12	1.36	102.1
18	Thathalur	7.54	466.08	330.92	22	18.32	45.21	11.10	118.2	88.21	21.41	0.42	130.3
19	Amaipakkam	7.61	368	261.28	20.12	16.21	30.12	11.20	101.2	55.12	20.14	0.87	116.9

20	Kunnathur	7.84	495.89	352.08	43.12	10.12	34.12	9.21	151.2	65.12	38.12	0.96	149.2
21	Veerapuram	7.33	523.38	371.60	44.12	12.14	36.21	11.23	152.2	66.14	41.23	0.41	160
22	Kilapakkam	7.48	1079.7	766.62	55.26	32.14	136.2	25.12	236.1	174.2	100.2	0.36	270.1
23	Neikuppi	7.35	227.18	161.30	7.84	3.24	31.26	8.21	66.32	31.02	12.26	1.25	32.89
24	Vilagam	7.05	617.01	438.08	48.12	26.12	74.21	10.12	165.1	78.12	31.23	0.84	227.5
25	Pandur	7.94	458.73	325.70	21.12	12.14	60.21	7.31	134.1	63.21	26.24	0.45	102.6
26	Sadurangapatnam	7.33	621.89	441.54	26.35	13.56	75.26	12.35	161.2	92.31	55.21	0.36	121.5
27	Lathur	7.7	551.41	391.50	23.14	12.41	66.23	10.23	135.2	102.3	36.21	0.64	108.8
28	Irumbilicheri	7.57	682.96	484.90	55.24	15.21	72.14	12.14	161.2	124.4	42.14	0.74	200.4
29	Nallathur	7.34	796.62	565.60	35.12	14.26	120.1	15.26	172.3	135.1	66.12	0.00	146.3
30	Voyalur	7.53	213.83	151.82	16.24	7.89	15.21	2.31	66.21	26.32	15.23	0.00	72.98

3.1. pH

H is Hydrogen ion activity. The pH of natural water is very often directed by the carbon-dioxide- bicarbonate-carbonate system. The pH value 7 denotes the natural water or it could be understood that there is a default balance between dissociated hydrogen and hydroxyl ions. Excess hydrogen ion indicates an acid solution with pH < 7 and excess hydroxyl ion infers a basic solution with pH > 7.pH varies between 7.2 and 8.2 with a mean of 7.71 during PRM. For POM, the pH variation is between 7 and 8.1 with an average 7.6.WHO standard comparison interprets that pH values are cent percent wellwithin the permissible limits during both PRM and POM.

3.2. Electrical conductivity (EC)

Electrical conductance, is the foremost possibility of any substance to transmit an electric current. Specific electricalconductanceistheconductance of a material of unit length and unit cross section at a stated temperature. The ionic simulation is relatedto the molecular weight and electrical charge of the solute and fluctuates with temperature. For dry and wet monsoon water samples, respectively, the electrical conductivity (EC) value variation ranges from 616.9 to 2766 µs with an average of 1311 µs and from 100.8 to 1219µs with an average of 533.5µs.

3.3. Total dissolved solids (TDS)

The quantity of all dissolved gases, colloids, cations, and anions in organic compounds is measured astotal dissolved solids (TDS). Figures 3a and 3b show that it fluctuates between 438 and 1964 mg/l during PRM with mean being 931 mg/l and between 72 and 866 mg/l with 379 mg/l as mean during POM.

Due to the geological mixing of salts in a soil profile and the elevation in the water table, water samples collected after monsoons typically have greater electrical conductivity than samples collected during the dry season. Salts are encased in the pores and fissures of the clay during the monsoon season and released with the groundwater. According to Hundal and Khurana, this causes rainy season waters to have higher TDS and EC concentration levels than pre-monsoon waters (2013).

4. Chemical parameters that affect the water's quality

4.1. Calcium (Ca)

Calcium concentration simply fluctuates starting from 30 up to 201mg/l with 87mg/l as an average during PRM while it ranges from 8 to 86mg/l with an average 36mg/l during POM. Examination of anions and cations, along with cross-examination of geology and land-use data, may provide vital facts about the interplay of pure water and associated processes in indestructible terrain and the hydrogeochemical informations will aid in forming apt plans to take care of the aquifer and hence put forth remedial measures to safeguard the contaminated groundwater, Elango *et al.*, 2003; James and Sajil Kumar; 2016; Subramani *et al.*, 2010.According to WHO guidelines in 2011, the permissible levelis between 75 and 200 mg/l. 50% of samples have values < 75 mg/l in the pre-monsoon and post- monsoon slots. Only samples from the villages of Manapakkam, Pulikundram, and Thirukazhukundram had values above 75mg/l; all other samples had values below the required level.

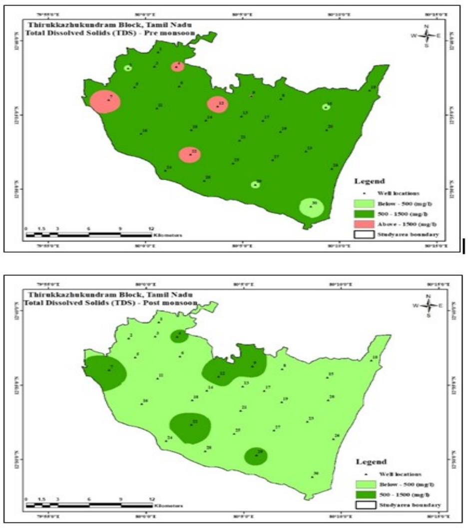


Figure 3. (a and b) TDS–Premonsoon, Post-monsoon waters of Thirukkazhukundram Block

4.2. Magnesium (Mg)

Magnesium is the second superior cation in the research block (Mg). The concentration varies during PRM from 11 to 104 mg/l with a mean of 39 mg/l, according to the analytical database utilised for the study block. In comparison, it fluctuates between 1 and 32 mg/l with 14 mg/l being the average during POM (Tables 1a and 1b). Magnesium's restricted range is 30-150mg/l according to the WHO standard. Only fivesamples are in the appropriate range during POM seasons, compared to six samples during PRM with levels below 15 mg/l.

4.3. Sodium (Na)

In groundwater, sodium (Na) predominates over potassium (K). Tables 1a & 1b demonstrate that sodium content ranges between 10 and 136 mg/l during the wet period, with mean being 56 mg/l, and between43 and 265 mg/l with mean being 129 mg/l during the dry period. 50-200mg/l is the sodium WHO recommended range. Na concentrations in seven villages in the central and southern regions of the Thirukkazhukundram block are greater than what is allowed during PRM. Na concentrations during POM, however, are only within the acceptable range in 12 settlements, while they are below the acceptable level in the remaining villages. The north, middle, and bottom portions of the block are covered by the communities with admitted range.

4.4. Potassium (K)

In the case of potassium, PRM's concentration range is 8–92 mg/l with mean being 30 mg/l, POM's concentration fluctuation is from 1-26 mg/l with mean being 12 mg/l. Except for three samples, rest ofthe samples surpass the permitted limit, although only at concentrations less than 10mg/l during PRM. Only 11 samples are deemed acceptable in the case of POM.

4.5. Carbonates and bicarbonates (CO_3 and HCO_3)

Bicarbonates, carbonates, and hydroxides control the alkalinity of natural water. The pH of the water and other factors affect how many of these anions are present in a given percentage. During PRM and POM, the carbonate ion concentration is zero. In the dry period, the bicarbonate ion concentration fluctuates between 149 and 607 mg/l and mean is found to be 311 mg/l, and during the wet season, it fluctuates between 30 and 291 mg/l and a mean of 133 mg/l is noted (Tables 1a & 1b). HCO_3 ions are present in Kilapakkam at a concentration of 607 mg/l. Water testing from the remaining towns primarily shows admitted bicarbonate concentrations. 200–500 mg/l of bicarbonate is recommended by the WHO.

4.6. Sulphate (SO_4)

Sulphate is a common component of groundwater due to weathering of the soil and rocks, atmosphericprecipitation, dry fallout, and artificial inputs such Magnesium fertiliser use. The WHO has establisheda safe maximum limit of 400 mg/l and a suggested threshold of 250 mg/l. Tables 1a & 1b provide the concentration ranges for PRM and POM. Sulphate, which are 38 to 386 mg/l and 7 to 135 mg/l, respectively, and average values arrived at respectively are 136 mg/l and 43 mg/l.

4.7. Chloride (Cl)

Chloride is more detrimental to plants than sulphate, making it the best pollution indicator and the mostdifficult anion for irrigation. According to Herman Bouwer, igneous rocks hardly ever cause water to become chlorinated in 1978. Water chloride is a potent oxidising agent that uses oxygen to gradually degrade water. Chloride improves conductivity, while calcium and magnesium enhance water corrosiveness, affecting metallic equipment. During the dry season, the chloride content ranges from 60 to 475 mg/l with mean being 193 mg/l, while during the rainy period, it fluctuates from 10 to 175 mg/l and an average of 82 mg/l is noted. According to Tables 1a & 1b, the WHO admission range for chlorideis 250–600 mg/l.

4.8. Fluoride (F)

The fluoride-rich groundwater occurence in this area could be attributed to fluoride being released from fluoride-bearing minerals in the study area's rocks. Such minerals are fluorite (CaF_2) and fluorapatite $Ca_5(PO_4)_3F$ in carbonatite intrusions, hornblende $Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$ and biotite $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$and fluorapatite $Ca_5 (PO_4)_3 F$ in carbonatite intrusions, hornblende $Ca_2 (Mg, Fe,Al)_5 (Al,Si)_8 O_{22} (OH,F)_2$ and biotite $K (Mg,Fe)_3 (AlSi_3O_{10}) (F,OH)_2$ in gneisses. The content of Fluoride within fluorite mineral is 48.67 percent, is 3.77 percent in fluorapatite, and finally, it's 2.9 percent and 1.1 percent in hornblende and biotite, respectively. Fluoride leaching is influenced surely by the alkaline character of the groundwater. Groundwater alkalinity is caused by the leaching of organic matter from the soil layer as well as the silicate minerals weathering. The heightened level of fluoride is on account of the dissolution of fluoride from fluoride-filled minerals such as fluorite, biotite,hornblende, and fluorapatite, as well as the ion exchange process in the worn out and seriously fracturedaquifer system. Fluoride-

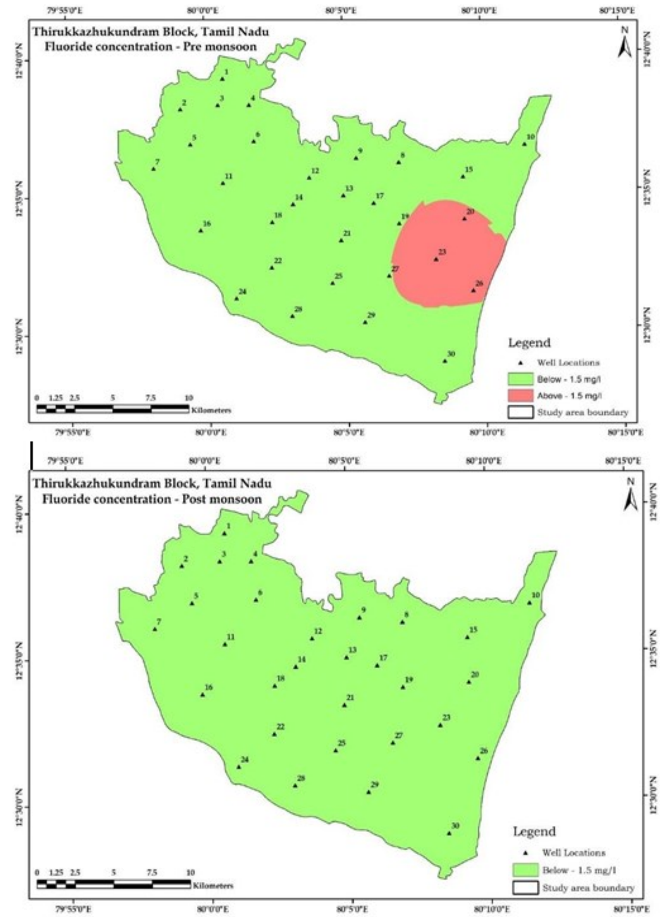


Figure 4. (a and b) Spatial Distribution of Fluoride – Pre-Monsoon

containing minerals include fluorite, granite, gneisses, and pegmatite. For instance, rock types with significant fluoride contamination include granite, gneisses, basalts, dolerites, quartzites, pegmatites, hornblende, syenites, biotite, muscovite, fluorite, fluoromica, cryolite, villanite, etc (Saxena & Ahmed in 2001). Three to four strata, comprising the gneiss or charnockite bedrock, sedimentary lithology, fractured gneissic or charnockite rocks, and finally diluvium on top, define the research region. According to Raju *et al.*, in 2009, it is unusual for alluvial zones to undergo changes inwater level and fluoride pollution below the surface. The most recently built wells and subsurface waterbodies dry up during the pre-monsoon season. The interaction of soil and water speeds up the enrichment process and hastens the water table's decline. There is no doubt that excessive groundwater pumping is a factor in the fluoride's unintentional and gradual infiltration into the flowing underground water. The study area's Fluoride levels range from 0.56 mg/L to 1.86 mg/L during the pre-monsoon period and 0 to 1.36 mg/L during the post-monsoon periods, with only three samples above the WHO's permitted value of 1.5 mg/L. Neikuppi alone suffers a dry period fluoride pollution of nearly 2mg/l which is beyond the accepted limit as per the WHO standards. Figures 4a and 4b depict the pre and post monsoon spatial fluoride distribution maps, respectively. Fluoride poisoning in drinking water causes health concerns. As the entire community's domestic needs are met by the groundwater in my research region, it is surely vital to establish precautious steps to avoid fluoride pollution, which could cause skeletal and dental fluorosis and pose a major threat to the next generation.

4.9. Fluoride's negative effects on health

In Reproductive system, (Naseem *et al.*, in 2016) fertility rate is curtailed in females and in males, testosterone reduction, follicle stimulating hormones and inhibin-B quantity diminution is prominent (Ortiz-Pérez *et al.*, in 2003). Fluoride also seriously damages the morphology and motility of male sperm, claim Chinoy & Narayana (1994). IQ and cognitive capacity attrition is influenced by neurobehavioural variables, according to (Trivedi *et al.*, 2007 and Choi *et al.*, 2012). The mental development of children is damaged. According to Grandjean and Landrigan, neurotoxicity affects children's developing brains (2006). Energy requirement of central nervous system takes place by affecting the glycolysis cycle according to (Valdez-Jiménez *et al.*, 2011). As per Spittle, fluoride has an impact on how proteins and enzymes function, how the brain works, and how faulty memory and cognition occurs (1994). According to Dementia USEPA 2009, abnormal fluoride concentrations can affect mental and emotional problems as well as cognition. Visuospatial skills as well as metabolic functions are undoubtedly impacted (Calderon *et al.*, 2000). Taking up cardiovascular system, High fluoride intake, according to Xu *et al.*, 1997, can result in oxidative stress that promotes inflammatory mechanisms, atherosclerosis, vascular stiffness and myocardial cell damage, Bradycardia, abnormal heart rhythms, reduced myocardial function, Hypothyroidism, diabetes mellitus and obesity. Nureddin2018 causes both hypercalcemia and hypocalcemia. A few of the typical gastrointestinal adverse effects, according to Pratusha *et al.*, 2011 include the missing of the mucus layer, hyperaemia, oedema, haemorrhage, and perforation of the lining in the stomach. Beginning to manifest are nausea, vomiting, and stomach discomfort (Nabavi *et al.*, 2013). Insufficient fluoride intake, according to Kheradpisheh *et al.*, 2018, produces endocrine system-based effects that result in structural changes and thyroid gland dysfunctions. In addition, secondary hyperparathyroidism, reduced glucose tolerance, and increased parathyroid and calcitonin activity were found by Doull *et al.*, in 2006. In the case of renal system, a fluoride concentration anomaly increases the risk of stones in kidney, claim Doull *et al.*, in 2006. The pathogenicity, histology, and metabolism of the glomeruli vary as found by Bouaziz *et al.*, 2006.

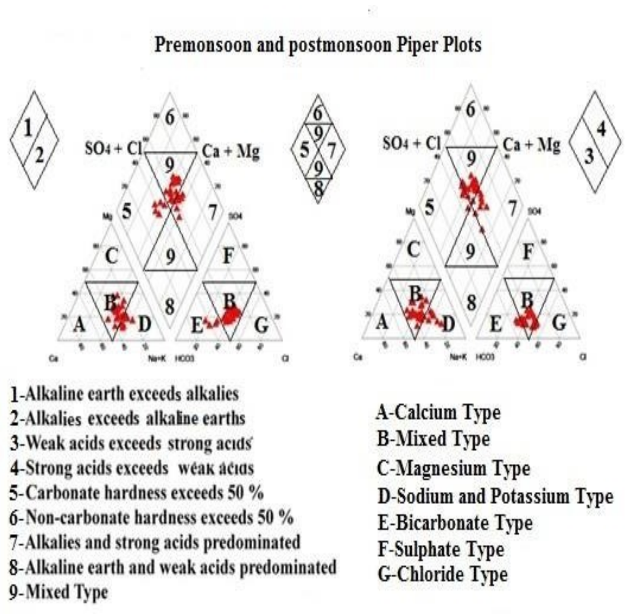


Figure 5. (a and b) Premonsoon and Postmonsoon Piper Plots

5. Groundwater types

One approach to do this is to compare the quality of the water using a trilinear Piper diagram. Aghazadeh & Mogaddam (2010) has also used this in his study. Finding the water facies is the first step in figuring out how groundwater forms. The trilinear diagram developed by Piper in 1944, which displays concentrations of the major cations and anions in the groundwater, can be utilized to illustrate the geochemical evolution of undergroundwater. Each of the bottom triangle fields and the center diamond-shaped field is divided into three sections. The integration of substantial ions is the only thing that happens in all three sectors. The plots (Figures 5a & 5b) indicate that the majority of groundwater specimens obtained in the dry season align into the mixed type of water category, followed by the alkalis strong acids predominated type of water category, and carbonate hardness surpasses the national average (50%). The POM has a similar pattern, with the majority of specimens falling under the mixed type of watercategory, followed by the alkalies and strong acids predominated category. Na, Cl, and Mg are continuously mixed throughout the year's five seasons, with just a few representations of HCO_3 and calcium. As a result, chemical weathering, followed closely by penetration, leaching, evaporation, saltwater intrusion, and human activities, controls the region's groundwater chemistry.

Table 2a. Premonsoon Chemical parameters of groundwater samples in Thirukkazhukundram Block

S.No	Locations	Naper	SAR	RSC	PI	KR	MH	RSBC	PS	TH	CR
1	Nenmeli	41.4	1.8	-0.1	66.6	0.6	44.2	1.9	2.3	224.5	0.7
2	Thirumani	33.2	1.3	-0.3	62.7	0.44	55.7	2.1	2.1	214.9	0.7
3	Alagusamudram	55.2	3.1	-1	74.5	1.17	28.3	-0	4.6	178.2	2.5
4	Keerapakkam	38.7	3.1	-7.5	47.5	0.56	44.5	-0	14	787.6	2.3
5	Mosivakkam	36.9	1.8	0.13	59.5	0.5	59.9	4.1	3	330.9	0.6
6	Thazhambedu	54.8	4.1	-1.3	68.1	1.07	39.8	1.5	9.5	357.1	2.2
7	Manapakkam	45.9	3.7	-6	52.7	0.69	34.9	-1	16	734.3	2.5
8	Kuzhipanthandalam	41.5	2.4	-2.1	58.8	0.66	43.8	0.9	5.9	340.1	1.7
9	Pulikundram	45	3.7	-7	52.7	0.72	61.1	1.1	14	667.9	2.9
10	Mamallapuram	50.5	2.7	-1.2	70	0.94	43.6	0.6	3.8	200.3	1.8
11	Ponvilayanthakalathur	45.8	3.7	-5	56	0.77	39.2	-0	12	579.6	2.5
12	Thirukazhukundram	43	3.9	-9.2	49.3	0.65	48.1	-1	17	890.1	2.6
13	Igai	38.2	2	-1.2	59.2	0.57	28.8	0.7	5.1	316.1	1.3
14	Navalur	47.9	2.5	-1.4	65.5	0.79	22.5	-0	5	242.3	1.9
15	Kadambadi	52.1	2.6	-0.9	73.3	0.99	27.7	0	3.4	167	1.8
16	Salur	53.2	3.4	-1.6	68.9	1.04	46.1	0.8	5.5	260.1	2
17	Pattikadu	42.7	2.4	-3	56.8	0.65	49.8	0.4	7	338.7	2.5
18	Thathalur	42.7	2.2	-0.3	64.7	0.66	41.4	2	3.9	273.4	1
19	Amaipakkam	55.5	3.1	-0.7	73.9	1.1	23.2	0.2	5.4	201.9	2.2
20	Kunnathur	37.7	2.2	-0.8	56.3	0.53	44.6	2.9	5.2	416.5	0.9
21	Veerapuram	50.6	3.2	-2	64	0.88	41.9	0.8	6.3	335.7	1.7
22	Kilapakkam	40.3	3.4	-7.7	48	0.58	43.1	-0	15	882.7	2
23	Neikuppi	41.2	1.8	-1.8	59.3	0.58	43.8	0.3	4.6	245.3	2
24	Vilagam	49.4	4.6	-6.2	58	0.9	39.4	-1	7.6	639.2	1.6
25	Pandur	54.1	2.9	-0.9	73.8	1.07	30.3	0.2	3.8	179.5	1.8
26	Sadurangapatnam	55.7	3.8	-0.7	71.5	1.12	42.3	1.7	5.7	282	1.5
27	Lattur	46.2	3.2	-2.1	60.1	0.76	34	0.9	7.2	431.6	1.5
28	Irumbilicheri	43.5	2.5	-2	59.5	0.68	45.3	1.1	5.5	347.8	1.5
29	Nallathur	61.5	3.2	0.18	84.5	1.38	43.7	1.4	3.1	134.5	1.4
30	Voyalur	46	1.7	-0.7	68.8	0.66	53.4	1.2	3	172.6	1.4

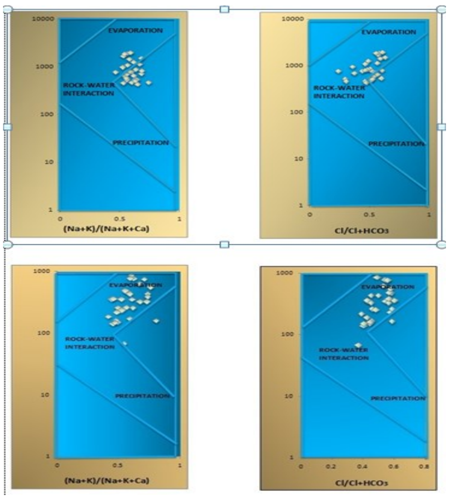


Figure 6. (a and b) Premonsoon Gibb's Plot

6. Mechanism controlling groundwater chemistry

To help people grasp the connection between the lithology of the aquifers that contain the fluids and their chemical composition, Gibbs offered a visual representa-tion in 1970. Three separate realms, including evapora-tion, weathering, and precipitation dominance, are depic-ted in the Gibbs diagram (Figures. 6a & 6b). The corresponding total dissolved solids (TDS) values for each of the specimens have been plotted against the Gibbs ratio I for the anion, Cl/Cl+HCO3, and ratio II for the cation, Na+K/(Na+K+Ca). Only a few samples are discovered in the evaporation zone throughout the PRM and POM seasons, with the vast majority of specimens being discovered in the rock dominance zone. Despite the fact that the evaporation zone also contains some representations from both seasons, the anions show a similar pattern. The image highlights the crucial part that the weathering rocks play in regulating groundwater chemistry.

7. Quality of water for irrigation

The concentration of various chemical components in groundwater determines its value for agricultural use. According to Todd (2007), salts can hinder plant growth in two different ways: physically by limiting water absorption through osmotic processes, or chemically by inducing metabolic reactions that are similar to those caused by toxic substances. The suitability of irrigation water is influenced by a number of chemical elements, including total dissolved salts, (EC), (RSC), and (SAR).Problems with salinity and alkalinity arise in irrigation water. There are numerous techniques to classify the quality of irrigation water. Thirukkazhukundram Block water samples were categorized using three different methods suggested by separate researchers.

The physical properties of soil are harmed by excesses of carbonate and sodium bicarbonate over calcium and magnesium, which results in the decomposition of organic materials and, when the soil has dried, leaves a black mark on the surface. This can be evaluated using the format (Tables 2a & 2b) shown below (Ragunath 1987):

$$RSC = (Ca + HCO_3) - (Ca + Mg) \quad (1)$$

When all ionic concentrations are put up in meq L^{-1} units.

Table 2b. Postmonsoon Chemical parameters of groundwater samples in Thirukkazhukundram Block

S.No	Locations	Na%	SAR	RSC	PI	KR	MH	RSBC	PS	TH	CR
1	Nenmeli	31.9	0.8	-0.7	69.4	0.4	34	-0.03	1.1	98.4	1.2
2	Thirumani	38.2	0.84	-0.4	81	0.5	35.9	0.105	1	70.1	1.3
3	Alagusamudram	37	0.74	-0.16	89.7	0.48	28.3	0.175	0.8	60	1.1
4	Keerapakkam	56.9	3.24	-0.48	75.9	1.17	34.8	0.861	4.8	192	1.9
5	Mosivakkam	42.2	1.54	-0.89	68.1	0.63	32.8	0.105	2.8	152	1.8
6	Thazhambedu	34.9	0.96	-0.6	69.3	0.44	45.4	0.492	1.8	120	1.3
7	Manapakkam	51.1	3.32	-1.91	66.4	0.97	36.5	0.252	6	295	2
8	Kuzhipanthandalam	49.9	1.34	-0.04	95.4	0.88	30.1	0.312	1.1	58	1.4
9	Pulikundram	48.3	3.12	-2.12	62.9	0.84	37.5	0.469	6	344	1.6
10	Mamallapuram	48.3	0.88	-0.02	120	0.87	19.8	0.084	0.4	25.5	1
11	Ponvilayanthakalathur	44.8	2.01	-1.57	64	0.7	36.5	-0.07	3.9	206	2.1
12	Thirukazhukundram	47.1	2.82	-2.48	61.3	0.79	39.9	0.089	5.8	322	2
13	Igai	43.9	1.66	-1.09	67.9	0.68	49.8	0.397	3.2	150	2.3
14	Navalur	42.2	1.17	-0.6	74.7	0.6	34.5	0.064	2	96.8	2.1
15	Kadambadi	37.7	0.93	-0.68	73.7	0.52	33.4	-0.15	1.4	79.2	2.1
16	Salur	46.8	1.59	-0.82	73.6	0.76	31.1	-0.14	2.2	109	2.2
17	Pattikadu	37.7	1.04	-0.43	75	0.51	36.1	0.303	1.2	102	1
18	Thathalur	46.3	1.72	-0.67	73.5	0.75	57.9	0.84	2.7	130	1.9
19	Amaipakkam	40.6	1.21	-0.68	71.2	0.56	57.1	0.655	1.8	117	1.5
20	Kunnathur	36.6	1.22	-0.51	68.4	0.5	27.9	0.327	2.2	149	1.2
21	Veerapuram	36.8	1.25	-0.71	66.1	0.49	31.2	0.293	2.3	160	1.2
22	Kilapakkam	54.9	3.61	-1.53	69.7	1.1	49	1.113	6	270	2.1
23	Neikuppi	70.5	2.37	0.43	119	2.07	40.5	0.696	1	32.9	1.3
24	Vilagam	43.4	2.14	-1.84	62.6	0.71	47.2	0.305	2.5	228	1.3
25	Pandur	57.8	2.59	0.15	87.8	1.28	48.7	1.144	2.1	103	1.3
26	Sadurangapatnam	59.6	2.97	0.21	85.9	1.35	45.9	1.328	3.2	122	1.6
27	Lathur	59.1	2.76	0.04	86.4	1.32	46.9	1.061	3.3	109	2
28	Irumbilicheri	46.2	2.22	-1.37	66.7	0.78	31.2	-0.11	3.9	200	2
29	Nallathur	65.7	4.32	-0.1	84.7	1.79	40.1	1.072	4.5	146	2.2
30	Voyalur	33.1	0.77	-0.37	80.3	0.45	44.5	0.275	0.9	73	1.1

Table 3. Grades of groundwater samples for irrigation purpose based on various indices

Parameters	Range	Water class	Sample Nos. Samples (%)			
			PRM	POM	PRM	POM
EC	< 250	Excellent	-	7	-	23
	250-750	Good	7	17	23	57
	750-2250	Permissible	19	6	63	20
	>2250	Doubtful	4	-	-	13
SAR	0–10	Excellent	30	30	100	100
	10–18	Good	-	-	-	-
	18–26	Doubtful	-	-	-	-
	>26	Unsuitable	-	-	-	-
RSC	< 1.25	Good	30	30	100	100

	1.25–2.5	Doubtful	-	-	-	-
	>2.5	Unsuitable	-	-	-	-
KR	<1	Suitable	16	16	53	53
	>1	Unsuitable	14	14	47	47
SSP	< 50	Good	23	23	77	77
	> 50	Unsuitable	7	7	23	23
MH	< 50	Suitable	26	28	87	93
	50.00	Unsuitable	4	2	13	7
Na%	< 20	Excellent	-	-	-	-
	20–40	Good	5	9	17	30
	40–60	Permissible	24	19	80	63
	60–80	Doubtful	1	2	3	7
	> 80	Unsuitable	-	-	-	-
TH	< 75	Soft	-	6	-	20
	75–150	Moderate	1	14	3	47
	150–300 Hard	13	8	43	27	
	> 300	Very Hard	16	2	53	7

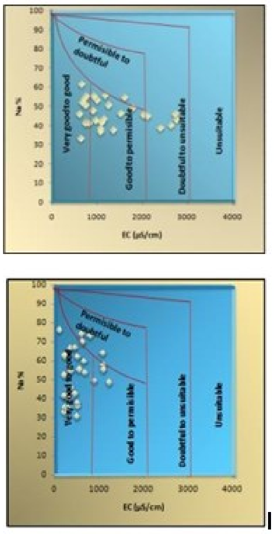


Figure 7. (a and b) Premonsoon and Post-monsoon water analysis results in Wilcox diagram

8. Wilcox diagram

According to Wilcox in 1955, the Wilcox diagram is used to evaluate agricultural waters based on their salinity and EC. While saline soils tend to have chloride or sulphate anion as the dominant anion, alkali soils have a high salt content and a majority carbonate anion. According to Todd (2007), there is no proof that either kind of sodium-enriched soil encourages plant growth. The following formula represents the proportion of sodium, often known as the soluble sodium percentage (Tables 2a & 2b):

$$Na\% = Na \times 100/(Ca + Mg + Na + K) \quad (2)$$

The meq L^{-1} represents the total ionic concentrations in the scenario.

Based on the correlation between the Na% and E.C. values, the PRM Wilcox diagram (Figures 7a & 7b) determines the kind of water. Only 3% of the samples are noted as possibly falling into the questionable category, whereas 81% of the samples are graded as acceptable and 17% as good. Only 7% of the samples in POMare regarded dubious, 30% are good, and 63% are deemed acceptable. Mg^{2+} and Ca^{2+} ions were replacedby absorbed clay particles in irrigation water with a high salt content. The increased concentrations of salt and chloride in groundwater are most likely the result of the weathering of feldspar. This procedure of exchanging Na in water for Ca^{2+} and Mg^{2+} in soil decreases perviousness and ultimately ends up in soil with inferior internal drainage. The water had surplus of carbonate and bicarbonate concentration over the alkaline earth, particularly calcium and magnesium, above permissible limits, affecting cultivation (Richards 1954, and Eaton 1950). Table 3 shows that during both seasons, 100% of the samples fall under suitable category for agriculture purposes. This implies that soil salts may very well be dissolved by rainfall, rendering the groundwater suitable for irrigation.

$$SAR = \frac{Na}{\sqrt{Ca + Mg / 2}} \quad (3)$$

When all ionic concentrations are measured in meq L^{-1} units.

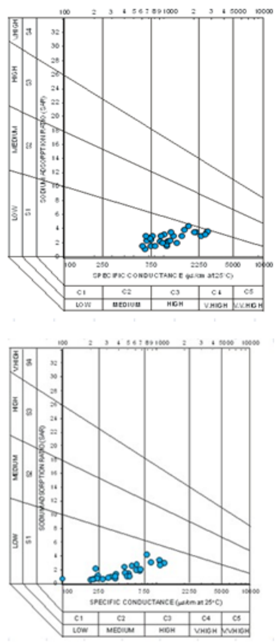


Figure 8. (a and b) Pre-monsoon USSL diagram

The US Salinity Diagram is used to place SAR and EC, establishing the Richards' irrigation classification system (1954) (Figures 8a and 8b). Salinity (C1, C2, C3, and C4) and sodium risk (S1, S2, S3, and S4) are used to categorize waters. According to the US salinity chart (Table 4), for C1-S1 type we have 23% of the samples only during postmonsoon. For C2-S1 we have 23% during premonsoon and 57% during postmonsoon. C3-S1 is found to have 67% during premonsoon and 20% during postmonsoon. Finally, for C4-S1 we have 13%, only for premonsoon.

From the Karl Pearson's correlation coefficient measurement (Table 5a &5b), it is inferred that good correlation existsbetween Ca-Mg, Ca-Na, Mg-Na, Ca-K, Mg-K, Na-K, Ca-HCO_3, Mg-HCO_3, Na-HCO_3, K-HCO_3, Ca- Cl, Mg-Cl, Na-Cl, K-Cl, HCO_3-Cl, Ca-SO_4, Mg-SO_4, Na-SO_4, K-SO_4, HCO_3- SO_4, Cl- SO_4. As found from the correlations, the chloride ion is very well correlated with all the cations on account of the majorcontributions of the study block, viz. secondary leaches' infiltration, chemical weathering, and anthropogenic impact.

9. Statistical analysis

Table 4. Groundwater classification based on USSL diagram

	No. of Samples	
Category	**Premonsoon**	**Postmonsoon**
C1-S1		2, 3, 8, 10, 15, 23, 30
C2-S1	1, 2, 10, 15, 25, 29, 30	1, 5, 6, 11, 13, 14, 16, 17, 18, 19, 20, 21, 24, 25, 26, 27, 28
C3-S1	3, 5, 6, 8, 9, 11, 13, 14, 16, 17, 18, 19, 20, 21, 23, 24, 26, 27, 28	4, 7, 9, 12, 22, 29
C4-S1	4, 7, 12, 22	

Table 5a. Pre Monsoon Correlation Analysis

	pH	EC	TDS	Ca	Mg	Na	K	HCO3	Cl	SO4	F
pH	1										
EC	0.045	1									
TDS	0.045	1	1								
Ca	0.083	0.961	0.961	1							
Mg	0.092	0.902	0.902	0.824	1						
Na	0.036	0.926	0.926	0.897	0.823	1					
K	0.002	0.903	0.903	0.834	0.782	0.824	1				
HCO3	0.081	0.906	0.906	0.889	0.851	0.772	0.772	1			
Cl	0.006	0.972	0.972	0.914	0.871	0.909	0.887	0.797	1		
SO4	0.013	0.94	0.94	0.872	0.798	0.849	0.894	0.752	0.958	1	
F	0.042	0.124	0.155	0.240	0.135	0.147	0.032	0.425	0.354	0.004	1

Table 5b. Post Monsoon Correlation Analysis

	pH	EC	TDS	Ca	Mg	Na	K	HCO3	Cl	SO4	F
pH	1										
EC	0.043	1									
TDS	0.043	1	1								
Ca	0.084	0.915	0.915	1							
Mg	-0.05	0.902	0.902	0.844	1						
Na	0.009	0.966	0.966	0.809	0.845	1					
K	0.012	0.941	0.941	0.852	0.861	0.888	1				
HCO3	0.072	0.984	0.984	0.916	0.896	0.934	0.91	1			
Cl	-0.01	0.966	0.966	0.856	0.864	0.945	0.926	0.923	1		
SO4	0.124	0.955	0.955	0.875	0.823	0.918	0.91	0.935	0.878	1	
F	0.072	0.142	0.142	0.240	0.134	0.102	0.121	0.042	0.243	0.014	1

10. Conclusion

Several areas across Thirukkazhukundram had their water quality inspected and assessed. The Thirukkazhukundram Block's wells were therefore surveyed for groundwater samples. The physical and chemical properties of the groundwater samples were examined to ascertain whether they were appropriate for irrigation and drinking. The pH levels during PRM and POM are within the permitted ranges as per the 2011 WHO standard. When the salts in a soil profile geologically mixed as a result ofthe monsoon season's rise in the water table, the electrical conductivity of water samples taken later than those taken earlier was higher. The levels of salt and chloride ions in the water during both seasonsindicated that people were exceeding the aforementioned water restrictions. It might be brought on by seawater seeping into the coastal aquifer, according to some theories. To stop the emergence of these conditions, the coastal aquifers in the study area must be maintained sustainably.

According to Gibbs' findings for both seasons, the evaporation and weathering process sector accounts for the majority of samples. The majority of the samples, in accordance with Piper's classification, consist of mixed water.The bulk of PRM and POM samples, respectively, fall within the very good to good and good to permitted categories, according to the Wilcox diagram. USSL diagram signifies that for C1-S1 type wehave 23% of the samples only during post-monsoon. For C2-S1 we have 23% during pre-monsoon and57% during postmonsoon. C3-S1 is found to have 67% during pre-monsoon and 20% during post-monsoon. Finally, for C4-S1, we have 13%, only for pre-monsoon. The irrigation quality of the groundwater samples showed that they were basically suitable for agricultural usage. More deep boreholes are still being drilled in the research area to supply the area's resources for agricultural and general use. It has, however, been curtailed or ceased in order to safeguard the environment. Regular groundwater condition monitoring and strategy development are crucial for preventing further deterioration of water quality. As water treatment programs are being implemented slowly, fluoride in groundwater seems to represent a reasonable concern when levels exceed allowable limits. Also, the majority people uses groundwater exclusively for drinking and other domestic tasks. The bulk of peopleonly have limited access to water. Assured concern can only check that the fluoride content doesn't gobeyond the authorized level and that the required precautions are put at right intervals to preserve the life that currently exists in this specific location due to the numerous health risks that can emerge fromabnormal high fluoride concentrations.

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