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Pollution Status of Groundwater Resources Through Hydrochemical Characteristics - A Case Study From Southern India

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Abstract

Mayiladuthurai is situated on the banks of river Cauveri. This research work aims to determine the quality of water which were collected from twenty groundwater sources. From the identified twenty locations, water samples were collected. The sampling stations include three taluks in the Mayiladuthurai district. The samples were analysed for various physicochemical qualities of water and compared with BIS & WHO standards. Frequency histogram and statistical analysis were applied to analyse the obtained data. Results of hydrochemistry revealed the dominance of hardness, magnesium and fluoride ions. The present investigation of hydrochemistry concludes that the drinking nature of the analyzed samples was very weak quality-wise and could not be used for drinking as such. Besides, fluoride ion related health problems were raised in some packets of the study area. The analytical report reveals that the quality of water has deteriorated and this may have a severe impact on human beings and other organisms in the study area.

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1. Introduction

The only source of fresh water and safety drinking water is ground water due to industrialization and modernization activities. Naturally groundwater is present in the body segments of rocks. According to the geological nature of the region, the chemical salts present in the ground water differ. Due to the accumulation time length differs, the salt content available in ground water becomes lower or higher [1-2].

To identify the quality of ground water resources of the samples, hydro chemical analyses was carried out. The statistical tools help to get a better understanding of the real nature of ground water resources. Then to identify various reasons caused for the changes of the quality of ground water, ground water chemistry is highly supported. It is also helpful to study the origin and possible mechanisms of contamination processes [3]. Then to draw up adequate management plans to guard the contamination of resources, hydrochemistry is highly supportive. Therefore, it is completely examined to know the status and identify the pollutants available in the ground water of the

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study area.

2. Materials and methods

2.1. About the study area

Mayiladuthurai is a new district of Tamil Nadu is one of the commercial places and fast developing cities in Tamil Nadu. Its surroundings are mostly cultivated lands. The residents mostly depend on groundwater for their cultivation, domestic and industrial purposes. In this study area 19 bore wells and one open well were selected for collecting water samples during the study period. Latitudes 11° 6′35″ of North and longitudes 79° 39′0″of East covers the three taluks namely Sirkazhi, Kuttalam and Mayiladuthurai. All the 20 groundwater sampling points were given in Fig. 1. The names of sample collecting stations were tabulated in Table 1. They were separated into three, namely profile A, profile B and profile C. In profile A, 6 sampling stations were selected from Kuthalam and Mayiladuthurai taluks and in profile B, 7 sampling stations were selected from Mayiladuthurai taluk. In profile C, 7 sampling stations were selected from Mayiladuthurai and Sirkazhi taluks.

The study and analyses were carried out from January 2021 to December 2021. During the study period, every month a study was conducted. Totally 240 samples were received from the stations. The physical qualities of all the 240 samples were appraised immediately after collecting the water with the help of some calibrated digital equipment. The chemical characteristics of water samples were determined by using methods recommended by APHA(1995) and BIS(1991).

Acid titration was used to identify the total alkalinity amount. Elements like calcium, magnesium and total hardness were measured with the help of the EDTA complexometric titration method. Argentometric titration was utilized to calculate chloride ions. The turbidity spectrometric technique was applied for measuring sulphate ions. SPADNS spectrometric technique was used to measure fluoride content. Brucine sulphate spectrometric tool was taken into account for measuring nitrate ion concentration. Flame photometry has been utilized to identify sodium and potassium ions.

Table 1. Details of groundwater sampling stations in the study area

S. No	Sampling stations	Source of water
Profile A		
S-1	Kuthalam	Open well
S-2	Sethrabalapuram	Bore well
S-3	Arayapuram	Bore well
S-4	Malliyam	Borewell
S-5	Mahadhanapuram	Bore well
S-6	Moovalur	Borewell
Profile B		
S-7	Sitharkadu	Bore well
S-8	Mayiladuthurai Pookadai Street	Borewell
S-9	Mayiladuthurai Koranadu	Borewell
S-10	Mayiladuthurai Mahadhana Street	Borewell
S-11	Thiruvazhandur	Borewell
S-12	Mayiladuthurai Coconut tree street	Borewell
S-13	Senthangudi	Bore well
Profile C		
S-14	Nagangudi	Bore well
S-15	Lakshmipuram	Bore well
S-16	Uluthukuppai	Bore well
S-17	S.S. Nallur	Borewell
S-18	Thirunanriyur	Borewell
S-19	Keezha Athukudi	Borewell
S-20	Mela Athukudi	Bore well

2.2. Description of the Profiles

2.2.1. Profile A

Profile A is located on the Cauvery river bed which goes north up to Kollidam then it flows clockwise towards Poompuhar, were situated in the Bay of Bengal. Several small scale industries, rubber industries, brick manufacturing and Oil and Natural Gas Corporation(ONGC) power plant are situated around profile A. A few kilometres away from profile A many silk industries are situated. The effluents of these industries are directly discharged into the land and finally, it reaches the river.

2.2.2. Profile B

Profile B is positioned towards the northeast of profile A. In all these areas Cauvery river plays the main source for agricultural purposes and on the river bed found the gas plants at different stages. Municipal solid waste dump sites are located, from which open-air combustion is taking place regularly. The area is a flourishing commercial central place in the district. This profile has many temporary water storage ponds. These are depending on the rainy season and rain water. Similarly, surface water channels get a large huge amount of discharges and sewage unwanted water all through the year. These ponds receive impurities from the city, and industrial left-over. The nearby agricultural excess water is also mixing these ponds during the rainy season.

2.2.3. Profile C

Profile C is located again towards the northeast of profile B and it is also on the river bed of Cauvery. So mostly fertile lands are found here. To the inhabitants of this area agricultural activity supports a lot.

The leading industrial setups in these places are weaving, rubber, brick making, earthenware, and food and soap manufacturing. Sawmills, gas stations and auto-repair workshops are located frequently in the research paper region. And in this region, many ponds are found and they are seasonal. Open sewage water is discharged into the ponds through canals.

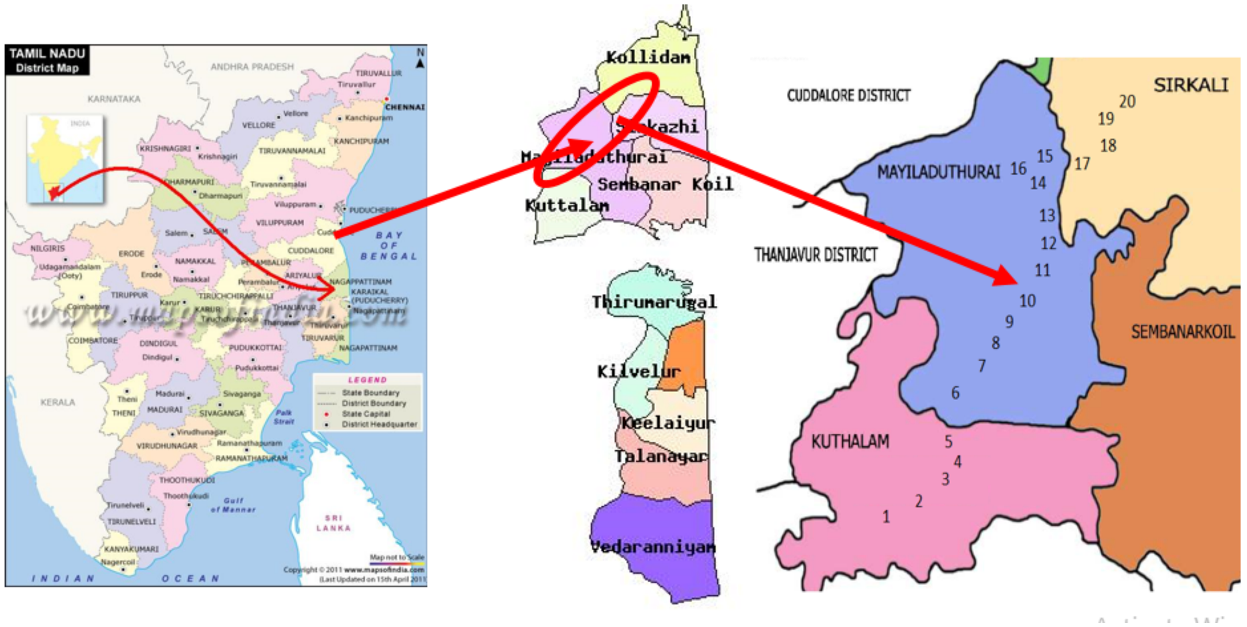

Figure 1. The map of the study area with groundwater sampling stations

2.3. Accuracy of analysis

The ionic balance is one of the most common ways to check for analytical errors. Water is electrically neutral, so the addition of major cations should equal the addition of the anions. Major ions like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+},(HCO_3^{-} + CO_3^{2-}), Cl^{-}, SO_4^{2-} and NO_3^{-} were taken into account in this analysis since these ions contribute more than 95% of ions in water.

$$\text{Ionic balance error (\%)} = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}} \times 100$$

2.4. Statistical analysis

A statistical tool namely MS Excel-2007 is used to analyze the obtained results of the analysis.

2.5. Descriptive statistics

Minimum, maximum, median, standard deviation and coefficient of variation values are helpful, to sum up, the obtained results.

2.6. Graphical representation

In this paper, the characteristics results of groundwater samples are graphically represented with a percentage frequency histogram which is to interpret the quality of samples in high quantum. In the present study, the data of each parameter are categorized into class intervals based on their values or permissible limits. The frequency was enumerated for those class intervals. The frequency of each class interval was further changed into frequency percentage to represent the data. From the percentage frequency value, a histogram was formed for each parameter to interpret the quality based on their guideline value.

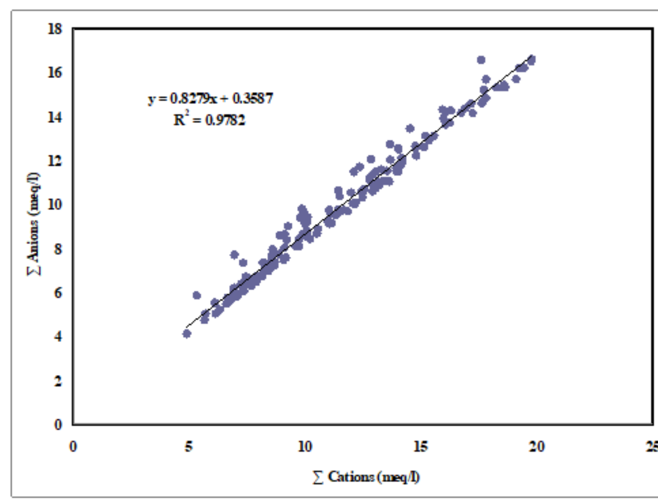

Figure 2. Scatter plot represents the relationship of total cations with total anions

3. Results and discussion

3.1. Accuracy of analysis

The accuracy of this chemical analysis in the hydro-chemistry of groundwater samples was checked with Ionic balance Error (IBE) and relation of total cations (TZ^{+}) & anions (TZ^{-}) with the measured Electrical Conductance (EC) which is presented in Fig. 2. From the obtained values, the Ionic Balance Errors were within ± 10 %. A perusal of Fig. 2. indicates that total cations values were increased with the increasing values of total anions with a correlation coefficient (R^2) value of 0.9782.

3.2. Physical and chemical properties of the selected resources

Analytical results are obtained for the physical and chemical properties of the selected groundwater samples were put into comparison with guideline values, the guideline value is given by [4], and [5] for identifying the samples for drinking purpose usage. (Table 2.) describes the guideline values. The statistical summary of the analyzed physical and chemical parameters were tabulated in Tables 3 -5

3.3. Physical characteristics of groundwater resources

3.3.1. pH –

From the percentage frequency histogram [Fig. 3] of the physical property pH, all of the samples were alkaline and desirable for drinking purposes in the range of 6.5 – 8.5. The data on pH values (Tables 3 - 5) indicated that groundwater samples were collected from all the profiles namely A, B and C. Median value obtained for pH is7.6.

Groundwater should meet the standards and guideline values to make it suitable for drinking. Because when it is used as drinking water, it gives excellent support for functioning good metabolic activities in human beings. The quality speaks in the industrial usage too. Generally, pH values of natural water lie between 4.5 and 9.0. In this study, pH values in the most of samples oscillated between the pH values of 6.5 – 8.5. As per the guidelines, this range is suitable for drinking purposes.

3.3.2. Electrical Conductance (EC) –

The obtained results (Tables 3-5) revealed that groundwater samples collected in this study were a fresh category, which fluctuated between 0.36 and 1.93 dS/m in the profile A, 0.36to 2.39 dS/m in the profile B and 0.45 to 2.20 dS/m in the profile C. The results of EC values are plotted in a percentage frequency histogram [Fig. 4]. According to Fig. 4. about 45.8% of groundwater samples from profile A, 53.6% of groundwater samples from profile B and 50.0% of groundwater samples from profile C were in the desirable range (<1 dS/m). About 54.2% of groundwater samples from profile A, 46.4% of groundwater samples from profile B and 50.0% of groundwater samples from profile C were in the acceptable range of EC (1 - 3 dS/m).

The presence of salt content reflects in the form of electrical conductivity. Usually, the salts are present in the form of ions. The ionic strength of water is greatly influencing the electrical conductivity of water. The electrical conductivity value easily informs the number of salts present in the particular sample. From the results of the physical and chemical investigation in the research work, it is noted that most of the samples used in the study are within the acceptable limit of EC value, and suitable for drinking purposes. From the obtained results, S-8 of profile B showed a higher value of EC (2.39 dS/m) and this may be due to the surface contamination, farming activity and developed engineering activities which release massive quantities of their waste products into the ground.

3.3.3. Total Dissolved Solids –

TDS values give better support to classifying the samples into different types. For classification, the physical and chemical properties of samples are very much important [2, 6]. Fig. 5 explains the percentage frequency histogram for TDS values.

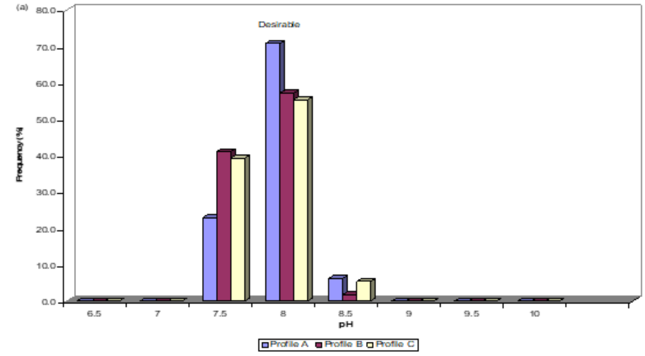

Figure 3. Percentage frequency histogram of pH

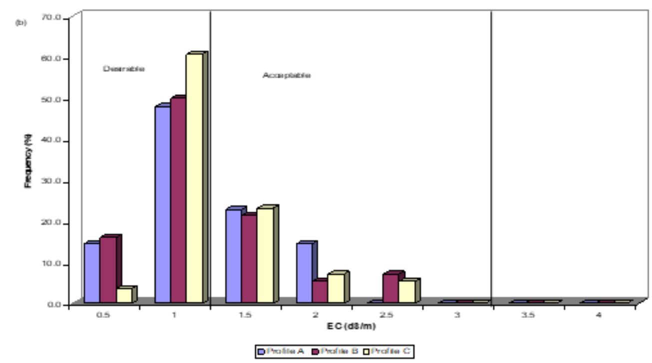

Figure 4. Percentage frequency histogram of EC values in the groundwater samples collected from the study area

According to Fig. 5, 33.3% of the water samples from profile A, 50.0% of the water samples from profile B and 42.9% of the water samples from profile C exhibited a desirable level (< 500 mg/l) of TDS. 66.7% of the groundwater samples from profile A, 50.0% of water samples from profile B and 57.1% of water samples from profile C were in the acceptable range (500- 1500 mg/l) of TDS. In addition, all samples collected for this study did not exceed the allowed scale of guideline value (>1500 mg/l) for drinking water quality. It means that the collected water samples can be used for drinking purposes according to the TDS value.

Numerous salts are present in the naturally available water. The

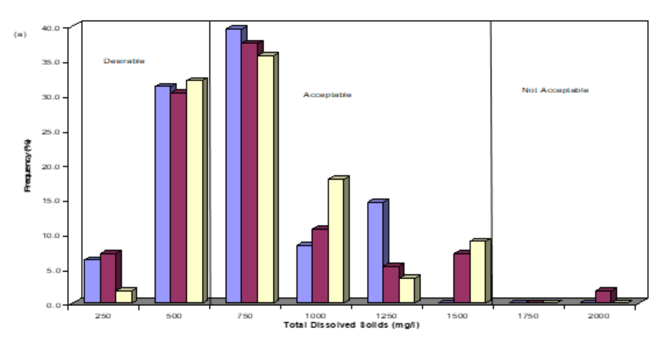

Figure 5. Percentage frequency histogram of TDS

Table 2. Guideline values for drinking water quality

Substance or Characteristics	BIS (2003)		WHO (2006b)	
	Desirable	Max. acceptable	Permissible	Max. acceptable
pH	6.5 – 8.5	No relax.	6.5 – 8.5	6.5 – 9.2
EC (dS/m)	1	3	-	-
TDS (mg/l)	500	1500	500	1500
Total Alkalinity (as $CaCO_3$), mg/l	200	600	500	-
Total hardness (as $CaCO_3$), mg/l	300	600	200	500
Calcium (as Ca), mg/l	75	200	-	-
Magnesium (as Mg), mg/l	30	100	-	-
Sodium (as Na), mg/l	-	-	-	200
Potassium (as K), mg/l	-	-	-	-
Chloride (as Cl), mg/l	250	1000	250	600
Fluoride (as F), mg/l	1.0	1.5	-	1.5
Sulphate (as SO_4), mg/l	200	400	250	500
Nitrate (as NO_3), mg/l	45	No relax.	-	50
Phosphate (as PO_4), mg/l	-	-	-	-

Table 3. Summary statistics of Physico-chemical characteristics of groundwater samples collected in the Profile A

Parameters	**Unit**	**N** [a]	**Min.**	**Max.**	**Mean**	**Median**	**SD**	**CV**
pH	-	240	7.4	8.0	7.7	7.6	0.17	0.022
Electrical Conductivity	(dS/m)	240	0.36	1.93	1.12	1.08	0.54	0.482
TDS	(mg/l)	240	230.33	1233.33	719.50	693.25	347.22	0.483
Sodium	(mg/l)	240	18.00	35.00	27.09	27.00	4.09	0.151
Potassium	(mg/l)	240	0.12	0.27	0.22	0.22	0.04	0.174
Carbonate	(mg/l)	240	0.00	0.40	0.05	0.00	0.10	2.085
Bicarbonate	(mg/l)	240	125.50	400.80	262.30	257.90	82.37	0.314
Total Alkalinity	(mg/l)	240	125.70	400.80	262.35	257.98	82.34	0.314
Total Hardness	(mg/l)	240	206.07	828.90	512.45	525.17	194.83	0.380
Calcium	(mg/l)	240	38.00	155.00	104.31	110.75	36.68	0.352
Magnesium	(mg/l)	240	27.00	110.33	61.19	59.38	26.08	0.426
Chloride	(mg/l)	240	56.00	195.80	138.07	148.00	46.47	0.337
Sulphate	(mg/l)	240	22.33	139.80	76.29	68.63	42.04	0.551
Fluoride	(mg/l)	240	1.96	5.13	3.08	3.01	1.12	0.363
Nitrate	(mg/l)	240	0.06	0.61	0.26	0.22	0.18	0.687
Phosphate	(mg/l)	240	0.02	0.07	0.05	0.04	0.02	0.407
SAR	(mg/l)	240	0.36	0.83	0.55	0.54	0.15	0.263

[a] N – No. of samples [(20 sampling stations × 12 months) = 240], SD – Standard Deviation, CV – Co-efficient of variation, SAR- Sodium Adsorption Ratio

Table 4. Summary statistics of Physico-chemical characteristics of groundwater samples collected in the Profile B

Parameters	Unit	N [a]	Min.	Max.	Mean	Median	SD	CV
pH	-	240	7.2	7.8	7.6	7.6	0.16	0.021
Electrical Conductivity	(dS/m)	240	0.36	2.39	1.07	0.81	0.64	0.594
TDS	(mg/l)	240	228.33	1314.00	678.95	517.33	393.01	0.579
Sodium	(mg/l)	240	17.30	38.00	25.56	24.75	5.80	0.227
Potassium	(mg/l)	240	0.13	0.27	0.20	0.19	0.04	0.189
Carbonate	(mg/l)	240	0.00	0.10	0.00	0.00	0.02	5.292
Bicarbonate	(mg/l)	240	135.80	380.70	231.89	212.00	81.14	0.350
Total Alkalinity	(mg/l)	240	135.80	380.70	231.89	212.00	81.14	0.350
Total Hardness	(mg/l)	240	243.69	875.98	494.44	423.73	222.09	0.449
Calcium	(mg/l)	240	55.00	183.00	102.55	89.05	42.65	0.416
Magnesium	(mg/l)	240	25.10	111.00	57.89	49.08	28.51	0.493
Chloride	(mg/l)	240	63.00	243.80	140.54	128.20	62.27	0.443
Sulphate	(mg/l)	240	20.67	165.00	77.57	61.50	44.76	0.577
Fluoride	(mg/l)	240	2.09	3.46	2.84	2.86	0.48	0.169
Nitrate	(mg/l)	240	0.05	0.46	0.19	0.15	0.13	0.687
Phosphate	(mg/l)	240	0.02	0.08	0.05	0.04	0.02	0.435
SAR	(mg/l)	240	0.35	0.89	0.53	0.50	0.13	0.254

[a] N – No. of samples [(20 sampling stations × 12 months) = 240], SD – Standard Deviation, CV – Co-efficient of variation, SAR-Sodium Adsorption Ratio

Table 5. Summary statistics of Physico-chemical characteristics of groundwater samples collected in the Profile C

Parameters	Unit	N [a]	Min.	Max.	Mean	Median	SD	CV
pH	-	240	7.1	7.8	7.5	7.6	0.18	0.024
Electrical Conductivity	(dS/m)	240	0.45	2.20	1.16	1.08	0.56	0.240
TDS	(mg/l)	240	286.00	1408.00	744.29	690.38	355.84	0.478
Sodium	(mg/l)	240	17.00	40.00	27.99	26.72	6.16	0.220
Potassium	(mg/l)	240	0.12	0.25	0.19	0.20	0.04	0.185
Carbonate	(mg/l)	240	0.00	0.00	0.00	0.00	0	0.00
Bicarbonate	(mg/l)	240	124.00	398.90	248.60	246.68	86.69	0.349
Total Alkalinity	(mg/l)	240	124.00	398.90	248.60	246.68	86.69	0.349
Total Hardness	(mg/l)	240	279.09	918.22	532.72	466.50	234.35	0.440
Calcium	(mg/l)	240	55.70	199.33	112.92	95.75	48.80	0.432
Magnesium	(mg/l)	240	31.10	111.00	60.89	55.23	28.31	0.465
Chloride	(mg/l)	240	65.33	276.80	151.49	138.28	67.69	0.447
Sulphate	(mg/l)	240	31.25	143.00	85.01	72.75	33.77	0.397
Fluoride	(mg/l)	240	1.79	4.00	2.91	2.97	0.67	0.230
Nitrate	(mg/l)	240	0.05	0.35	0.15	0.11	0.10	0.681
Phosphate	(mg/l)	240	0.02	0.10	0.05	0.05	0.03	0.505
SAR	(mg/l)	240	0.36	0.95	0.56	0.50	0.16	0.281

[a] N – No. of samples [(20 sampling stations × 12 months) = 240], SD – Standard Deviation, CV – Co-efficient of variation, SAR-Sodium Adsorption Ratio

presence of the total concentration of cation and anion gives us the TDS value. High TDS content in water increases its osmoregulatory behaviour which in turn decreases the solubility of oxygen in the water and minimizes the water quality for drinking purposes [7]. Based on the presence of TDS quantity, most of the samples analyzed in this study exceeded the desirable level (500 mg/l) of drinking water quality limit but were within the upper limit (1500 mg/l). Total Dissolved Solids in drinking water make it unfit, and not advisable for consumption if the consumer is suffering from kidney-related and heart issues.

3.4. Chemical characteristics of groundwater resources

3.4.1. Sodium and Potassium -

The values of sodium are given in Fig.6 as a percentage frequency histogram, which revealed that all the analyzed samples were not exceeding the desirable level of sodium (<200 mg/l).

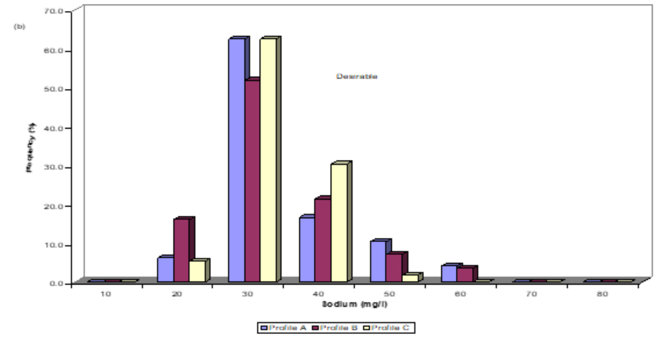

Figure 6. Percentage frequency histogram of sodium values in the groundwater samples collected from the study area

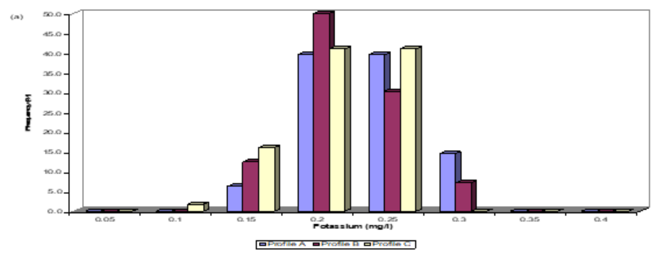

Figure 7. Percentage frequency histogram of potassium

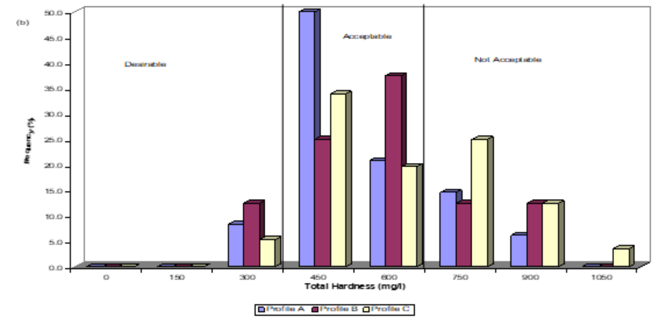

Figure 8. Percentage frequency histogram of total hardness values in the groundwater samples collected from the study area

The presence of salt makes the water saline. Salts such as sodium and potassium are naturally available in groundwater. Besides, wastes from industries also supportive for the presence of higher levels of these salt in groundwater. The consumption of water with high EC, sodium and chloride may not cause any health-related problems, but can impair the potability of water and can give an unacceptable taste to the consumers [8]. From the results of the hydro-chemical investigation in the study area, the sodium content levels of all samples were within the desirable level drinking limit of sodium (<200 mg/l). Therefore all the collected samples are good for drinking according to sodium content. The highest sodium concentration 40 mg/l (S-20) was found in profile C during rainy seasons and this may be due to heavy rain.

The element potassium is considered a minor element in groundwater. It varied from 0.12 to 0.27 mg/l in profile A, 0.13 to 0.27 mg/l in profile B and it fluctuated from 0.12 and 0.25 mg/l in profile C. No guideline value for potassium was proposed for drinking purposes. The frequency percentage histogram of the potassium profile was given in Fig.7. The highest potassium concentration was found in profile B of sample numbers S-9 (0.27 mg/l) and the lowest recorded in the sample collected from the sampling station S-6 & S-17 (0.12 mg/l). Higher potassium is likely due to silicate minerals and agricultural activities. Here the study area is covered from a large number of agricultural lands.

3.4.2. Total hardness, calcium and magnesium –

Hardness is the property of water which does not produce lather with soap. Cations like calcium and magnesium and anions like carbonate, bicarbonate, chloride and sulphate ions are responsible for hardness. According to the presence of hardness causing ions, hard water is generally categorized into soft (<75 mg/l), moderately hard (75 – 150 mg/l), hard (150 – 300 mg/l) and very hard (> 300 mg/l) [9]. A perusal of hardness values depicted in the percentage frequency histogram (Fig. 8), shows that all the groundwater samples are hard. i.e moderately hard to very hard in nature. From Fig. 8, it is clear that about 37.5% of samples from profile A, 25% of samples from profile B and 32.1% of samples from profile C exhibited higher hardness values (>600 mg/l), not acceptable for consumption.

A higher concentration of hardness was recorded in the present work. A higher concentration of hardness affects the groundwater and it is also harmful to human beings. Direct release of waste from small scale industries into land, agricultural waste and large- scale human used wastes [10] may be the reason for higher values of hardness.

Fig. 9 depicted the calcium ion of the study area as a percentage frequency histogram which denoted that about 25% of water samples from profile A, 39.3% of water samples from profile B and 32.1% of samples from profile C were in the desirable range (<75 mg/l) of calcium. Then, 75% of samples from profile A, 60.7% of samples from profile B and 67.9% of samples from profile C were in the acceptable range (75-200 mg/l). Magnesium ion concentration fluctuated from 27 to 110.33 mg/l with a median of 59.38 mg/l in the profile A, 25 to 111 mg/l with a median of 49.08 mg/l in the profile B and the values extended between 31.10 and 111 mg/l with a median value of 55.23 mg/l in the groundwater samples of the profile C. The profile of magnesium values was presented in Fig. 10, as a percentage frequency histogram which denoted that 8.3% of the samples from the profile A and 10.7% of samples from profile B and none of the water samples from the profile C exhibited in the desirable range of magnesium (<30 mg/l). Then, 79.2% of water samples from profile A, 78.6% of samples from profile B and 82.1% of samples from profile C were in the acceptable range (30-100 mg/l). This could be used as drinking water when alternate water was not availble. Besides, 12.5% of samples from profile A, 10.7% of samples from profile B and 17.9% of samples from profile C went beyond the allowable range.

Bedrock minerals with magnesium salts are responsible for the concentration of magnesium ions in groundwater, higher

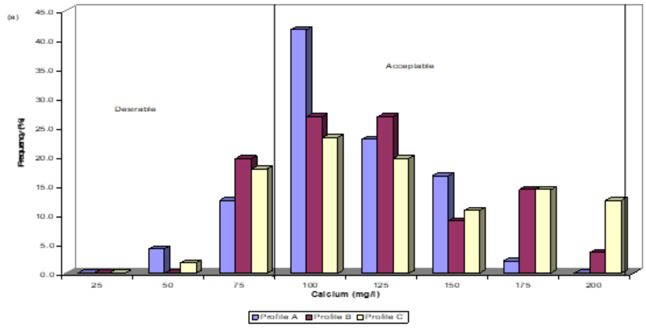

Figure 9. Percentage frequency histogram of Calcium

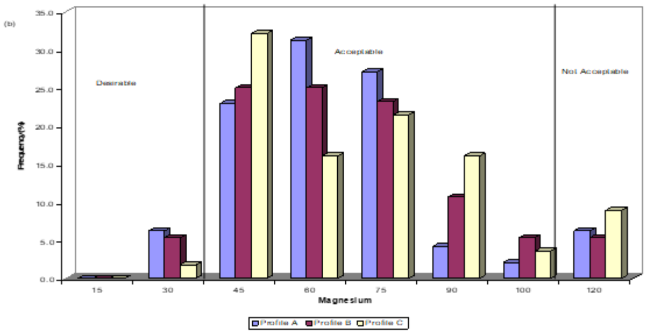

Figure 10. Percentage frequency histogram of magnesium values in the groundwater samples collected from the study area

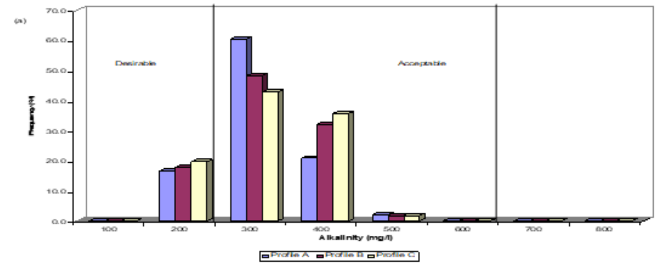

Figure 11. Percentage frequency histogram of alkalinity

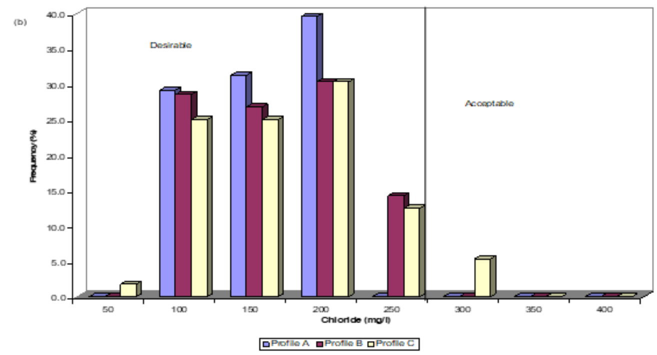

Figure 12. Percentage frequency histogram of chloride values in the groundwater samples collected from the study area

value of magnesium ions in water may alter the taste of water.

The sampling stations S-19 (918 mg/l) and S-20 (199 mg/l) in profile C recorded the highest value of total hardness and calcium during the summer season respectively. But the sampling station S-5 (110 mg/l) in profile A recorded the highest value of magnesium during the summer season. A higher concentration of hardness related parameters (TH, calcium and magnesium) during the summer season may be due to the large scale human use, regular addition of large quantities of waste from industry and agricultural activity. The high concentration of hardness related parameters can impair the potability of water [11]. The presence of a large amount of calcium and magnesium may be due to the presence of limestone in the bedrock.

3.4.3. Total Alkalinity –

The presence of hydroxide, carbonate and bicarbonate ions makes the water neutral to alkaline nature. Here bicarbonate alkalinity is reported for all samples but carbonate alkalinity is below the detectable limit.

The measured alkalinity of this study is presented in Fig. 11, as a percentage frequency histogram. From the observation, 25% of the groundwater samples from profile A, 35.7% of the samples from profile B and 35.7% of the samples from profile C fell within the desirable range (<200 mg/l), the remaining samples from all the three profiles were in the acceptable limit (200-600 mg/l) of guideline value for drinking water quality. According to Tables 3-5, groundwater samples collected from profile A exhibited higher alkalinity with the obtained median value of 257.98mg/l when compared with profiles B and C.

During biodegradation of natural material carbon dioxide is released into the soil, mixed with water and converting the water into carbonate-rich.

In this study, many samples crossed the desirable limit of alkalinity but were within the acceptable limit. High alkaline nature can impair the potability of water. Groundwater samples collected from the sampling station S-5 in profile A recorded the highest value of total alkalinity (400.8 mg/l). This high value in S-5 may be due to the percolation of water from sewage water and industrial waste in the land [12].

3.4.4. Chloride –

The chloride values of this study is given in Fig. 12, as percentage frequency histogram. According to the Fig. 12, all of the groundwater samples from profiles A, B and 89.3 % of the collected samples from profile C were less than (<250 mg/l), which is the desirable limit for chloride. The remaining samples from profile C were within the unacceptable limit (250-1000 mg/l).

Due to high attraction of chloride towards sodium, chloride ion is abundantly present in water. Next the high temperature and low rainfall also enhances its presence in ground water. Besides porous nature of soil also increases its presence in water [13]. Based on the low results obtained for chloride, the study area samples can be used for drinking purpose.

3.4.5. Sulphate –

The data on sulphate values are given in (Tables 3 - 5).The sulphate values in the groundwater samples of profile A fluctuated between 22.33 and 139.80 mg/l with a median value of

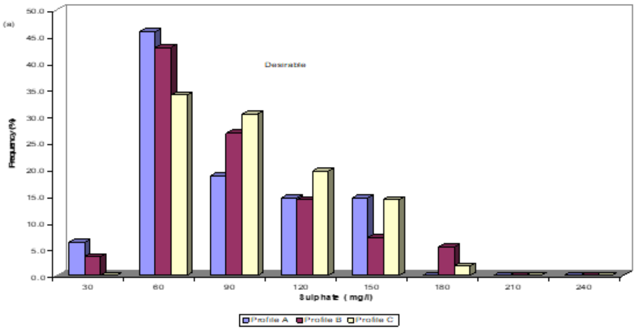

Figure 13. Percentage frequency histogram of sulphate

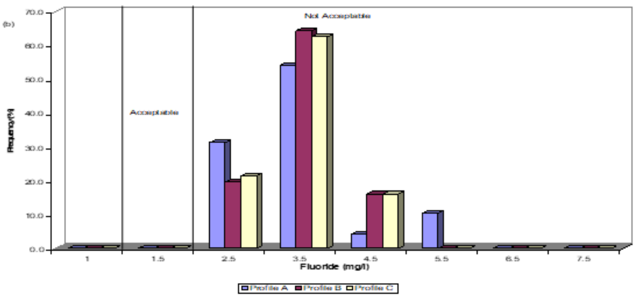

Figure 14. Percentage frequency histogram of fluoride values in the groundwater samples collected from the study area

68.63mg/l, profile B ranged between 20.67 to 165 mg/l with a median value of 61.5 mg/l while in the profile C, it changed from 31.25 to 143 mg/l with a median value of 72.75 mg/l. The sulphate values of this study area were given in Fig. 13 as frequency percentage histogram.

Based on the type of bedrock present sulphates are present in different forms in soil. Its quantity varied from minor to major. But higher sulphate concentration along with the presence of magnesium ion i.e. exceeding 1000mg/l may cause laxative effect on human beings [14-15]. But in this study, from Fig. 13 it was observed that all the analyzed samples were below the desirable level (<200 mg/l) of sulphate. Therefore, the water of this study area can be used for drinking purpose. The obtained data reveal that the groundwater samples collected from the sampling station S-13 in profile B recorded the highest value of sulphate (165 mg/l) during summer. This highest level of sulphate may be due to the waste received from municipality and sewage water.

3.4.6. Fluoride –

Fluoride concentrations in the profile A varied between 1.96 to 5.13 mg/l, 2.09 to 3.46 mg/l in the profile B whereas in the profile C region, it ranged from 1.79 to 4.00 mg/l. Fluoride values were presented in Fig.14. From the diagram it is clear that all the analyzed samples exceeded the desirable limit of fluoride (>1.0mg/l). Besides all the analyzed samples were crossed the maximum acceptable limit (>1.5mg/l), which is recommended for drinking water quality.

Fluoride ion is the required ion for human beings but if it exceeds it creates dangerous effects on humans [16]. For proper functioning of teeth and bone, the presence fluoride ion is the important one. Human health and fluoride ion present in the environment are interrelated to each other [17, 37]. Deficiency of fluoride ion may be harmful to teeth. It creates dental carries on human teeth. Excess quantities of fluoride ion consumption make it unfit for human health because it creates the disease fluorosis on humans [18]. Drinking water with high levels of fluoride ion triggers the disease skeletal fluorosis, which deforms the bone structure on humans [19-21]. Hence, usage of water with allowable limit of fluoride prescribed by various organizations namely the Bureau of Indian Standards (BIS) and World Health Organization (WHO) is the most important. 1.5 mg/l, is the acceptable limit for the ion fluoride in drinking water. But in water scarce areas this limit can be increased [36]. Drinking water limit for fluoride ion is 1.0 and 1.5 mg/l. But [22] has prescribed the limiting values on the basis of the climatic conditions and quantity of water consumed by individual.

In this study, the collected samples crossed the upper fluoride limit. Bedrock, temperature of the soil, amount of rainfall [23] may influence the presence of fluoride ion in water. Here the presence of fluoride supportive rock was responsible for high levels of fluoride ion in the samples [24-25].

Rocks with fluoride ion minerals may increase the fluoride ion concentration in surface and ground water [26-27]. The presence of fluoride in groundwater was also supported by the factors such as alkali enduring of silicate rocks, igneous rocks and sedimentary rocks. Except natural cause none is the cause for the presence of fluoride ion in water. High concentration of fluoride causes dental fluorosis [28-30]. Water with greater fluoride concentration in drinking water developed the symptoms of dental fluorosis and skeletal fluorosis in the residents of the study place.

3.4.7. Nitrate –

Fig. 15 represents the analyzed nitrate values of the study area as percentage frequency histogram. From the analyzed values, nitrate levels present in the samples were below the desirable limit (45 mg/l). This limit has been suggested by [4-5] for drinking water. From the (Tables 3 - 5), the nitrate values in the groundwater samples of profile A varied in the range of 0.06 - 0.61 mg/l with a median value of 0.22 mg/l, profile B varied in the range of 0.05 to 0.46 mg/l with a median of 0.15 mg/l while in the profile C, it oscillated between 0.05 and 0.35 mg/l with a median value of 0.11 mg/l.

Several sources are responsible for the presence of nitrate content in water. Prime factor is usage of fertilizers in the nearby agricultural field. Decay of died plants and animals are also the major cause for the presence of nitrogen in the water samples. The releasing nitrogen from decay process is converted into nitrate. Natural nitrate concentrations in groundwater span are from 0.1 to 10 mg/l [31]. The continuous use of water containing higher concentration of nitrate can cause blue baby syndrome, cancer in gastric system, birth deformations and hypertension in human system [15, 32, 41-42]. Here nitrate ion concentration in the analyzed samples were within the desirable and it was suitable for drinking.

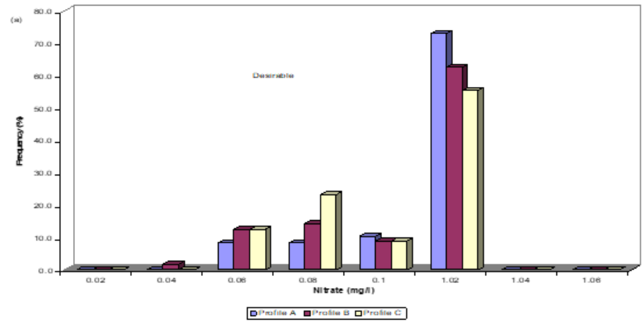

Figure 15. Percentage frequency histogram of nitrate

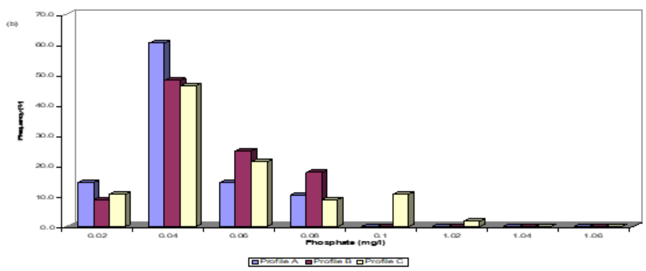

Figure 16. Percentage frequency histogram of phosphate values in the groundwater samples collected from the study area

From the obtained analytical results groundwater samples collected from the sampling station S-3 in profile C recorded the highest value of nitrate (0.61 mg/l) during monsoon season. This highest value of nitrate in sampling station-3 may be due to the filtration of nitrogen content from the nearby municipal waste dumping sites. Besides the surrounding agricultural field was also reason for the nitrogen content in water [12, 33, 39-40].

3.4.8. Phosphate–

The phosphate concentrations in water were from 0.02 to 0.07 mg/l in the groundwater samples of profile A, 0.02 to 0.08 mg/l in profile B and 0.02 to 0.10 mg/l in profile C. Fig. 16 showed the percentage frequency histogram of the phosphate values in the study area. The observation from the percentage frequency histogram clearly revealed that the phosphate values for all the analyzed samples were lesser than 1 mg/l. According to phosphate values, groundwater samples collected from the sampling stations S-18, S-19 & S-20 recorded the utmost high value of phosphate i.e., 0.10 mg/l. The usage phosphatic fertilizers for agricultural activity, filtration of agricultural wastes into the soil and human bone excreta may cause this ion concentration in water. No guideline value was proposed for drinking water quality.

3.4.9. Sodium Adsorption Ratio (SAR) –

Sodium Adsorption Ratio measure the comparative amount of the ions such as sodium, magnesium and calcium which affects penetration power of water into the soil. The change is penetration power of water is also caused by electrical conductance property. SAR value of irrigation water is computed as per [34, 38]. [Eq. 1]

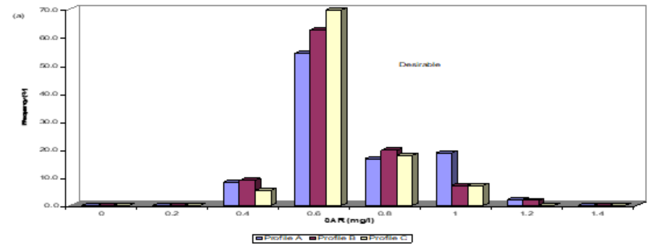

Figure 17. Percentage frequency histogram of SAR values in the groundwater samples collected from the study area

$$\mathrm{SAR} = \frac{Na^{+}}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \tag{1}$$

where the concentrations are reported in meq/l.

SAR indicates irrigation water quality which tends to go in for the reactions which are involving with cation-exchange in soil. Soil which is exchanging sodium ion with calcium and magnesium ions, damages the soil structure. Water with more salt content increases infiltration and vice versa. This dual phenomenon may function simultaneously. If the land is continuously irrigated with water with rich sodium ion lowers the soil [35-37].

The data on SAR values were given in Fig. 17 as percentage frequency histogram. From the Fig. 17, the SAR values for all the analyzed samples were within the low category (1-10). Thus all the collected samples which were analyzed were appropriate for irrigation.

4. Conclusion

Groundwater samples collected from the Mayiladuthurai district were generally characterized by fresh, moderately hard water to strongly hardness in nature. The samples were alkaline in nature. From the obtained results of hydrochemistry, it was noticed that a number of groundwater samples from all the three profiles exhibited higher levels of hardness and magnesium. These samples exceeded the desirable level for drinking water quality suggested by BIS (2003) and WHO (2006b). Besides, almost all the sites fluoride ion concentration went beyond the upper limit of its concentration value (>1.5 mg/l). Fluoride ion is a health wise important parameter. Its higher concentration greatly affects the quality of water, which in turn the quality of water for drinking purpose was greatly impaired. The present investigation of hydrochemistry concludes that drinking nature of the analyzed samples were very weak in quality wise and could not be used for drinking as such. Besides, fluoride ion related health problems raised in some packets of the study area. Although many parameters were within the allowable limit, but most of the health oriented parameters were crossed the permissible limit. Hence the present investigation confirmed that the quality of water was deteriorated and this may have severe impact on human beings and other organism in the study area.

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