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# Hydrogeochemical studies on Pazhayar river of Kanyakumari District in Southern Tamilnadu, India

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## ABSTRACT

Recently, the water contamination has been taking place by municipal, domestic, medical, agricultural and industrial waste stuff that alters the Hydrogeochemical parameters. River water is extraordinarily essential for drinking and using for all developmental activities. So, the water quality parameters of surface water management have been underestimated. In this work, we examined the physico–chemical properties of the river Pazhayar at nine stations *viz.,* Kovalam ($S_1$), Dwarakapathi ($S_2$), Naraiyanvilai ($S_3$), Kovilvilai ($S_4$), Manakudi ($S_5$), Ambalapathi ($S_6$), Sothavilai ($S_7$), Puthenthurai ($S_8$) and Kesavanputhanthurai ($S_9$) of Kanyakumari District in Southern Tamil Nadu. Furthermore, the water samples of each station were collected from Puthen dam to the tail end at Manakudy during the period of three years (July 2011–July 2014). The *in–situ* water quality and physico–chemical parameters of the samples were analyzed and compared with the standard WHO reports. The obtained results were confirmed by Piper's and Chadha's plot. Water Quality Indices for all sampling stations, indicate that the water quality rating for $\mathbf{S_7}$ is excellent**,** $\mathbf{S_1}$–$\mathbf{S_5}$ are good and $\mathbf{S_6}$**,** $\mathbf{S_8}$–$\mathbf{S_9}$ are moderately Polluted. The results indicate that level of contamination is below the WHO permissible limits. From the observed values of various physico–

chemical parameters in the study area it has been concluded that the water in Pazhayar river is moderately contaminated.

**Key word:** Pazhayar River water, Hydrogeochemical, Physico–chemical, Piper's and Chadha's plot, Water quality parameters.

## INTRODUCTION

In general, water is one of the natural sources for both drinking and growth of living organisms in the ecosystem [1] and said that "*Life on Earth would not exist without water"*. At present, the principal challenge is to preserve the fresh water resources from hazardous contaminants and also to curtail the current water demands due to fast emerging industrialization, human population, urbanization and developmental activities [2] in the world. Pathogenic microorganisms, heavy metals, waste disposal from agricultural and chemical industries *etc*., are the major toxic pollutants that rigorously limit the valuable use of water from domestic and other applications [3]. A number of studies on water quality have been assessed with respect to drinking and irrigation points [4,5]. Also, the river water is highly valued because of its unique properties which are not possessed by some other water sources [6]. Generally, the ground water contains huge amount of various ions, salts, toxic heavy metals *etc.*, and is not suitable for drinking and other human developmental activities because it leads to create various effects like water–borne diseases, diarrhea *etc*. Now, the removal of such contaminants from obtainable water resources is very expensive so, the significance and intractability of these problems have been shown the way of resource managers to pursue a prevention of water policy [7]. Heavy metals such as Cd, Hg, Pb, As, etc., are significant toxic pollutants that severely limit the beneficial use of water for domestic and industrial applications [8].

The present study bears the collection of water sample at nine ($S_1$ to $S_9$) stations which were taken from the river Pazhayar from Puthen dam to the tail end at Manakudy of Kanyakumari district in southern Tamil Nadu, India. We have presented the characterization of the various physico–chemical properties of profile during the study era of three years (July 2011–July 2014) and the reports were compared with the standard WHO values.

## STUDY AREA

The Southernmost tip of peninsular India holds one of the most significant divine situates for Hindus is named as Kanyakumari (in British – Cape Comorin), it is the place where three oceans namely Indian, Arabian and Bay of Bengal congregate and which is the head quarters of the District in Tamil Nadu also referred to as the feet of Bharata Mata. Kanyakumari is one of the *108 Sakthi Peeths* and it also spells as Kannyakumari since it is named behind the admired virgin deity, "Kannyakumari Amman" who is one of the incarnations of Goddess Parvati as Devi Kanniya (Bhagavathi). The prominence of the temple is that Devi Kanniya wears a precious diamond nose ring and carries a diamond necklace in her right hand.

Kannyakumari is an imperative pilgrim centre with serene atmosphere and famous for its seashore and the impressive sunrises & sunsets, especially on full moon days. The district is also known as “The District of Ponds” or “The Lands’ End”. Kanyakumari district (longitude: $77^o15'$ – $77^o36'$ E, latitude: $8^o03'$ – $8^o35'$ N) is situated in the Southernmost tip of the peninsular India. Regarding the boundary, on north-east is bounded by Tirunelveli; north-west is Thiruvananthapuram districts; south-eastern is Gulf of Mannar (Bay of Bengal); south and west is Indian Ocean and Arabian Sea respectively. It covers an area of about 1,675 square Km and it is a thickly populated district of south Tamil Nadu in India. It is administratively divided into 4 Taluks, 9 blocks and 88 villages. There are many historic memorials for the Tamil saint poet Thiruvalluvar, the great Indian philosopher Swami Vivekananda, the Father of Nation Mahatma Gandhiji, *etc.*

The river Pazhayar is of medium size and mentioned in Sangam classics as it is an extent of Pahruli in Kanyakumari District and it gains through both South–West and north–east monsoons. It begins at the southern slopes of the Mahendragiri hills which is a part of southern tip of the Western Ghats [9]. At Chrulakode (Shorlacode or Surulacode) is a place about 18 Km North-West of Nagercoil, here a number of tiny streams or odai (like Nachukal & Eassakkuthottam) confluences and form the origin of the river Pazhayar southwardly *via*. Thovalai, Ananthanar and Nanchinad Puthanar Channel. The tail end of this river empties into the Arabian Sea at Keezha Manakudy Estuary, 12 Km South of Nagercoil. This river Pazhayar contains a number of principal tributaries like Tharuvayar, Ulakkaruviar, Alathuraiar, Koyu odai, Poigaiar, *etc*. This river feeds water from Petchiparai and Perunchani dams through channels and many ponds in Kanyakumari district. Also the geomorphic and land use patterns (**Table 1**) existing in the study area are beach sand, pediments, sand dunes, beach terraces, mudflats, saline tracts and water bodies.

In this study area, there are more than a dozen of dyeing industries without proper drainage facilities. This effluent and all the sewage from Nagercoil Town is dumped into Pazhayar. This polluted water affects the ecological system [10]. In the present study, the water quality of Pazhayar river has been surveyed because a very little water quality management studies so far. Hence the present study was carried out to cover a detailed impact made by the domestic sewage and industrial effluents on the physico–chemical properties of the Pazhayar river for the period of July 2011 to July 2014 at different stations mentioned as stations along the different localities on the Pazhayar. The Hydrogeochemical facies were found out using Piper and Chadha’s plots. Moreover, identification of the river standards for pollution control and quality management were carried out by the arithmetic calculation for the Water Quality Index values ($WQI$) made on the basis of observed $(V_n)$ and permissible values $(S_n)$ of about fifteen parameters.

## MATERIALS & METHODS

Pazhayar river from Puthen Dam to Keezha Manakudy for physico–chemical analysis and handling were adopted based on the standard methods (Indian standard Methods of Sampling, 1999–12). The distance between two sampling stations was kept more than 300 – 500 m. The temperature of the samples was measured in the field itself at the time of sample collection as per standard method [11,12]. After collection of the samples, the bottles were tightly sealed, suitably labeled, preserved and immediately kept in dark boxes. The samples were kept in refrigerator maintained at 4 $^{o}$C and analyzed for various parameters at their earliest. Collected water samples were analyzed by both classical and automated instrumental methods prescribed by the standard methods and the mean value of analytical data parameters among the nine stations ($S_1$ to $S_9$) were compared and tabulated. The panoramic location of sampling stations at Pazhayar river in India is shown in **Fig. S1 (Supplementary File).**

## RESULTS & DISCUSSION

Nine stations (**Fig. S1**) of Kanyakumari district were selected for the observation from July 2010–July 2013 and the results were compared with the World Health Organization [13]. Kanyakumari District has a unique advantage of rainfall during both the South-West and North–East monsoons, monthly rainfall varies from 44.0 mm (minimum–February) to 220.0 mm (maximum – October) and the mean annual rainfall will be 185.54 mm for the period of our study. Fortunately, there was a little rainfall in the month of February. The mean monthly temperature varies with a maximum of 35 $^{o}$C in the month of May to a minimum of 25.6 $^{o}$C in December. Some of the important physico–chemical parameters were found and compared with the WHO permissible values (**Table 2)**. The majorities of surface water bodies are slightly basic in nature, due to the presence of bicarbonate and carbonate ions. The maximum and minimum pH values were recorded for all the stations and the values (6.39–7.41) are within the permissible limit (6.50–8.50) [14]. Alkalinity of water was observed beyond Manakudy site before the river reaches near Arabian Sea. Electrical conductivity (EC) values are higher than the permissible limit.

High EC values were observed in Ambalapathi Station ($S_6$), indicating the presence of high amount of dissolved inorganic substances in ionized form. The amount of salinity found under the studied stations is within the range 10.33–33.28 ppt. All the sampling stations show high amount of dissolved oxygen (DO) during the month of September to November due to heavy rainfall and fresh water mixing. The desirable limit of total hardness (TH) according to Indian standard is 300 mg/L and WHO is 500 mg/L but in the study area, the TH values are within the acceptable limit. All the sampling stations show the sulphate levels are within the limit of the WHO. In our present study area, the chloride amount exceeds the WHO value and also the concentration of chloride and salinity is maximum in summer and minimum in monsoon season for all the stations. The concentrations of Na, K and Ca values were somewhat found higher than the WHO permissible limit because of high consumption of salts, particularly NaCl causes hypertension and increases the risk for stroke [15] left ventricular hypertrophy osteoporosis, renal stones and asthma [16]. High potassium values may cause nervous and digestive disorders [17]. The parameters such as TSS, TS and turbidity of the Pazhayar river exceeded the limit values which affect the aquatic life in Kanyakumari district.

Alkalinity of river water is caused mainly due to $OH^-$, $CO_3^{2-}$ and $HCO_3^-$ ions. Minimum alkalinity value is observed in $S_1$ & $S_8$ stations and maximum in all other stations (**Fig. 1**). At these stations, the water quality of river Pazhayar is poor for drinking purpose and it may be due to low water table and lower temperature which bringing down the rate of decomposition of salts to a minimum there by increasing the alkalinity. The high nitrate content value in Kesavanputhanthurai ($S_9$) may be due to the maximum domestic waste water load and human interference **Fig. 2**. The nitrate content was higher in the pre monsoon and post monsoon seasons due to the influence of rain water [18]. TS, TDS, TH and Cl average values of sampling stations are shown in **Fig. 3.**

To identify the river standards for pollution control and quality management, the arithmetic calculation for the Water Quality Index ($WQI : W_n.log$) values made on the basis of observed $(V_n)$ and permissible values $(S_n)$ of about fifteen parameters which are tabulated (**Table S1: Supplementary File**) for all sampling stations, indicates that the water quality rating for $\mathbf{S_7}$ is excellent**,** $\mathbf{S_1}$–$\mathbf{S_5}$ are good and $\mathbf{S_6}$**,** $\mathbf{S_8}$–$\mathbf{S_9}$ are moderately Polluted [19].

Hydrogeochemical facies interpretation is a useful tool for determining the flow pattern and origin of water masses. In the piper diagram the triangular fields are plotted separately with epm values of alkali earth cations ($Ca^{2+}$, $Mg^{2+}$), alkali cations ($Na^+$, $K^+$), weak acid ($HCO_3^-$) and strong acid ($SO_4^{2-}$ and $Cl^-$). Samples of the Kovalam coastal region (**Fig. 4**) show a complex facies environment dominantly representing NaCl type and CaCl type. It clearly indicates that the first mentioned facies is represented by the sea water intrusion. It is understood that there are two other minor facies $NaHCO_3$ and $CaHCO_3$. The variation of facies from $CaHCO_3$ to CaCl and NaCl to CaCl may be due to different pollution sources.

But the Facies change from $CaHCO_3$ to $NaHCO_3$ is mainly due to ion exchange process. Hence the figure indicates a complex geochemical process in the Kesavanputhanthurai ($\mathbf{S_9}$). The water chemistry represented by the samples falling in **Fig. 4,** shows that most of the Kesavanputhanthurai ($\mathbf{S_9}$) samples are NaCl type. The Piper diagram shows the dominance of sodium and chloride distributed throughout the different parts of the study area due to sea water intrusion. They are also represented in $NaHCO_3$ type and followed by $CaHCO_3$ type.

The obtained hydro–chemical facies was further confirmed by Chadha's plot (**Fig. S2: Supplementary File**) The plot of Sothavilai ($\mathbf{S_7}$)shows that majority of the samples of study area fall in **Field–5** (Recharge type) with good representation in **Field–7** indicating sea water intrusion, few representation in **Field 6 & 8** indicating reverse ion exchange and base exchange respectively.

In Puthenthurai Station ($\mathbf{S_8}$), the nature of the sample scatter shows complex nature with very good representations in **Field 5 & 7** in the plot. This shows that Ca–$HCO_3$ type recharging waters in **Field 5** and $Na^+ + K^+$ is predominant than $Ca^{2+} + Mg^{2+}$ in **Field 7** along with predominance of $Cl^-$ indicating salt water intrusion. The **Field 6** shows the predominance of $Ca^{2+} + Mg^{2+}$ than $Na^+ + K^+$ along with high $Cl^-$ indicating reverse ion exchange or pollution. There are also very few representations in **Field 8** depicting ion exchange and recharge respectively. Water samples possibly represent Base Exchange reactions or an evolutionary path of groundwater from Ca–$HCO_3$ type fresh water to Na–Cl mixed sea water, where $Na^+$–$HCO_3^-$ is produced by ion exchange processes.

Discharge of industrial wastes and domestic sewage add to the concentration of sulphate. The highest level of sulphate content is observed in all the Stations and it may be due to the leaching of minerals by rain water and subsequent percolation into the earth surface. The concentration of inorganic phosphate values is low in pre and post monsoon season due to the decreased land drainage, sewage and fertilizer disposal from the surface run off. Minimum level of phosphate is recorded during June and maximum value is recorded during October (20).

In Pazhayar, there was no visible floating in the water sample indicating the absence of oil and grease. Due to various factors such as trace metal contents of the soil and crops, geographical location, fertilizers and fungicides applied in the area, environmental pollutions due to automobile emissions, industrial effluents, weathering of rocks and other agricultural activities, the Pazhayar river is being polluted (21).

## CONCLUSION

In the present study, we summarize the various physico–chemical parameters in nine stations of Pazhayar river, Kanyakumari district during the study period of July 2010–July 2013. The pH values of the water samples in the stations studied varies from 6.39 to 7.41, the pH values are also within the permissible limit. High electrical conductance values were observed Kesavanputhanthurai Station (**$S_9$**). The chloride concentration also influences the salinity which is maximum during summer and minimum during monsoon season. Also the TS, DO, TDS, TSS, TH, $Cl^-$, $Na^+$, $K^+$ and TN (Total Nitrogen) value contents of Pazhayar river were found within the WHO permissible limit. The concentration of nitrate and sulphate were higher in the monsoon and post monsoon seasons in all the Stations. The concentration of inorganic phosphate value goes beyond the peak value during the monsoon and gets decrease in its concentration during the post monsoon season. From the observed values of various physico–chemical parameters in the study area it has been concluded that the water in Pazhayar river is moderately contaminated and not safe for drinking but safe for domestic and irrigation purposes. Water Quality Indices for all sampling stations, indicate that the water quality rating for **$S_7$** is excellent**, $S_1$–$S_5$** are good and **$S_6$, $S_8$–$S_9$** are moderately Polluted.

## RECOMMENDATIONS

Even though groundwater resources at Kanyakumari district is currently plenty, conventional methods for water management practices like rainwater harvesting may be necessary in order to restrict any surprising water demand as a result of industrialization or population increase.

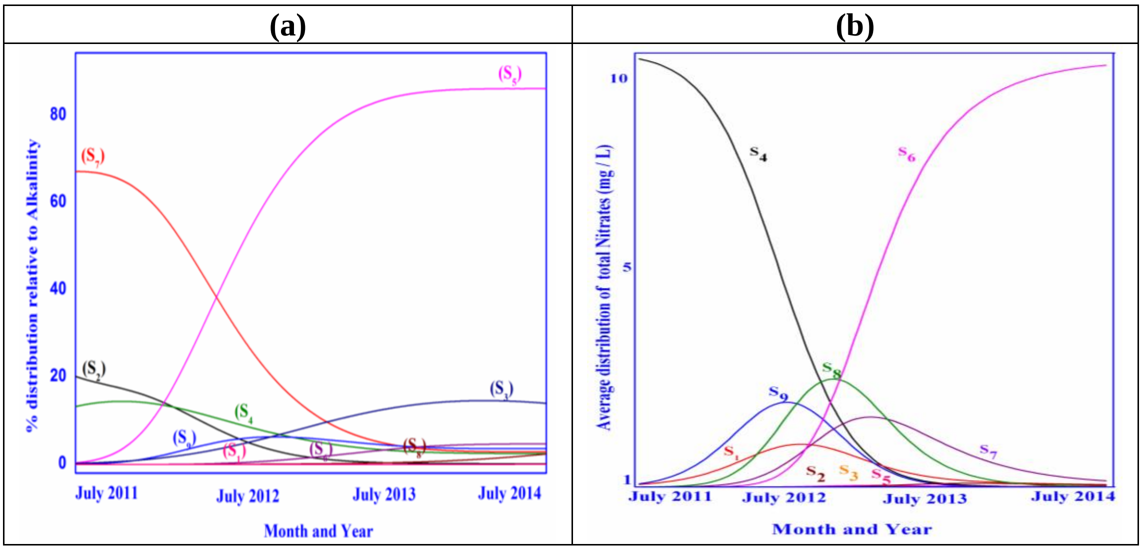



**Fig. 1. (a)** % distribution of alkalinity; **(b)** Average distribution of total nitrate content for sampling stations ($S_1$–$S_9$) during July 2011–July 2014.

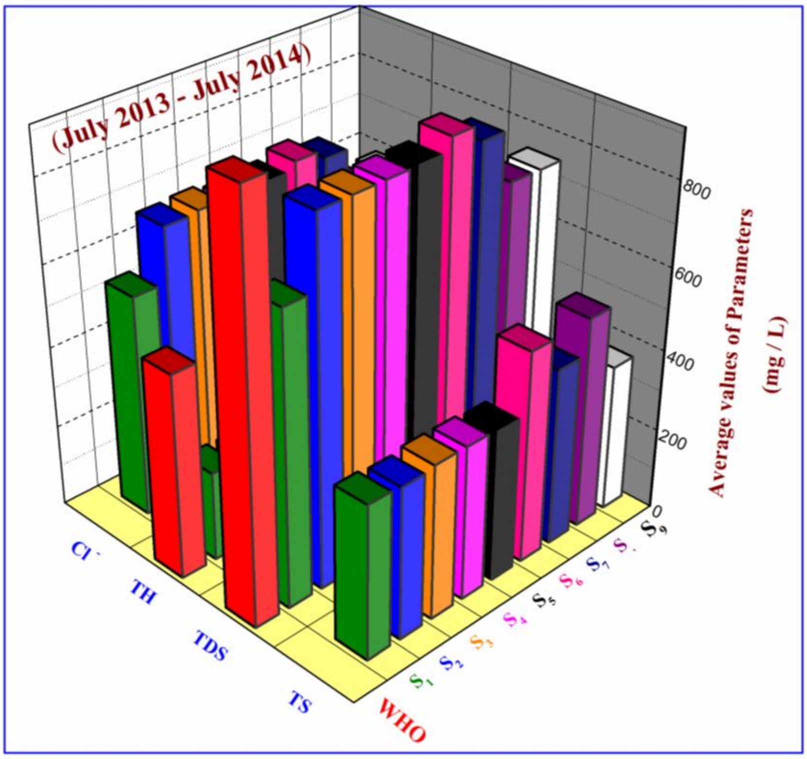



**Fig. 2.** TS, TDS, TH and Cl average values of sampling stations ($S_1$–$S_9$) during July 2013–July 2014.

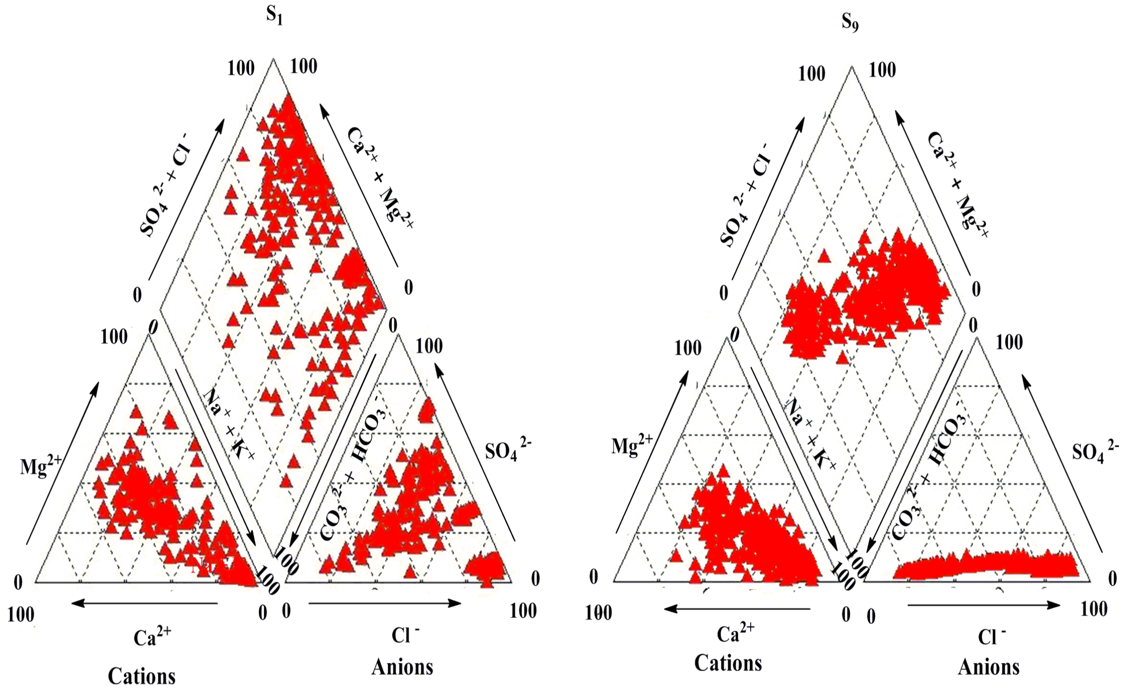
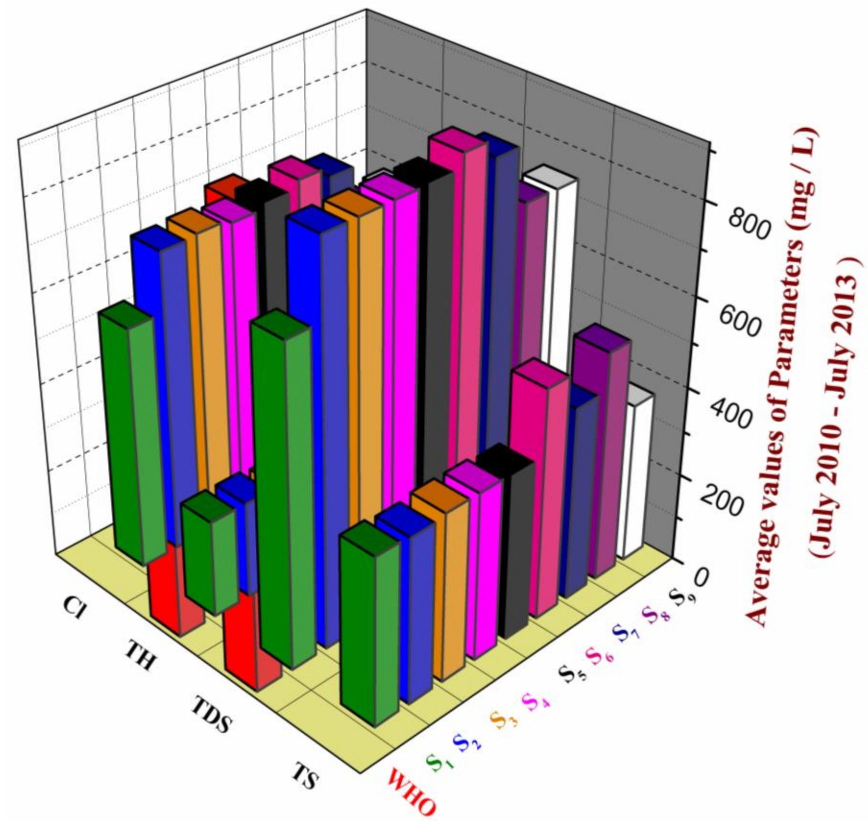



**Fig. 3.** Trilinear Piper diagram for Kovalam ($S_1$) Station and Kesavanputhanthurai ($S_9$) Station.

## Graphical abstract

In this work, we examined the physico–chemical properties of the river Pazhayar at nine stations *viz.*, Kovalam ($S_1$), Dwarakapathi ($S_2$), Naraiyanvilai ($S_3$), Kovilvilai ($S_4$), Manakudi ($S_5$), Ambalapathi ($S_6$), Sothavilai ($S_7$), Puthenthurai ($S_8$) and Kesavanputhanthurai ($S_9$) of Kanyakumari District in Southern Tamil Nadu. Furthermore, the water samples of each station were collected from Puthen dam to the tail end at Manakudy during the period of three years (July 2010–July 2013). The *in–situ* water quality and physico–chemical parameters of the samples were analyzed and compared with the standard WHO reports. The obtained results were confirmed by Piper's and Chadha's plot. The results indicate that level of contamination is below the WHO permissible limits.




**Highlights**

- Hydrogeochemical parameters of river Pazhayar at nine stations were carried out.
- *In–situ* water quality parameters were compared with the standard WHO reports.
- The obtained results were confirmed by Piper's and Chadha's plot.
- Arithmetic calculation for the Water Quality Index indicates the river standards
- The results indicate that level of contamination is below the WHO permissible limits.
- The results show that Pazhayar river is being polluted.

**Supplementary Files**

**Table S1**. Water Quality Index Rating *(WQI)* for nine stations ($S_1$–$S_9$) of Pazhayar river during the period of July 2011–July 2014.

| Stations | Water Quality Parameter | Table 3 Physico-chemical Parameters | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | EC µS/cm | TALK mg/L | TH mg/L | TDS mg/L | $Ca^{2+}$ mg/L | $Mg^{2+}$ mg/L | $Na^+$ mg/L | $K^+$ mg/L | $Cl^-$ mg/L | $NO_3^-$ mg/L | DO mg/L | $SO_4^{2-}$ mg/L | $NH_3$ mg/L | BOD mg/L |
| | $S_n$ [a] | 7–9 | 500–$10^3$ | 600 | 500 | 500–2000 | 75–200 | 30–150 | 50–200 | 10–12 | 250 | 45 | 6 | 200–600 | 5 | 5 |
| | $V_n$ [a] | 7.2 | 607 | 73 | 218.7 | 710.9 | 159 | 183 | 151.2 | 6.59 | 545 | 2.11 | 7.5 | 77 | 0.77 | 6.8 |
| | $W_n$ [a] | 0.13 | 0.002 | 0.002 | 0.002 | 0.0008 | 0.0072 | 0.011 | 0.008 | 0.09 | 0.004 | 0.022 | 0.166 | 0.0025 | 0.2 | 0.2 |
| **$S_1$** | $Q_n$ [a] | 95.6 | 121.4 | 12.17 | 43.74 | 56.872 | 115.6 | 203.3 | 120.96 | 59.9 | 218 | 4.688 | 125 | 19.25 | 15.4 | 136 |
| | $W_n$ log | 0.26 | 0.004 | 0.002 | 0.0032 | 0.00140 | 0.015 | 0.025 | 0.016 | 0.161 | 0.009 | 0.014 | 0.349 | 0.003 | 0.237 | 0.427 |
| | $\Sigma W_n . l$ $Q_n$ | 1.534 | | | | | | | | | | | | | | |
| | *WQI* | **42.7** (Good) | | | | | | | | | | | | | | |
| | $V_n$ [a] | 6.39 | 590 | 69 | 217 | 880 | 147 | 174 | 145 | 5.97 | 675 | 2.04 | 6.72 | 74 | 0.71 | 6.2 |
| | $W_n$ [a] | 0.13 | 0.002 | 0.002 | 0.002 | 0.0008 | 0.0072 | 0.0111 | 0.008 | 0.090 | 0.004 | 0.022 | 0.166 | 0.0025 | 0.2 | 0.2 |
| **$S_2$** | $Q_n$ [a] | 85.2 | 118 | 11.5 | 43.42 | 70.4 | 106.9 | 193.3 | 115.8 | 54.27 | 270. | 4.533 | 112 | 18.5 | 14.2 | 124 |
| | $W_n$ log | 0.26 | 0.0041 | 0.002 | 0.0032 | 0.0014 | 0.0148 | 0.0254 | 0.0165 | 0.158 | 0.009 | 0.015 | 0.342 | 0.0031 | 0.230 | 0.419 |
| | $\Sigma W_n . l$ $Q_n$ | 1.5 | | | | | | | | | | | | | | |
| | *WQI* | **40.5** (Good) | | | | | | | | | | | | | | |
| | $V_n$ [a] | 6.39 | 630 | 73 | 211.8 | 880 | 154 | 182 | 145.7 | 5.97 | 680 | 2.15 | 6.91 | 80 | 0.94 | 6.7 |
| | $W_n$ [a] | 0.13 | 0.002 | 0.002 | 0.002 | 0.0008 | 0.0072 | 0.0111 | 0.008 | 0.091 | 0.004 | 0.022 | 0.167 | 0.0025 | 0.2 | 0.2 |
| **$S_3$** | $Q_n$ [a] | 85.2 | 126 | 12.2 | 42.36 | 70.4 | 112 | 202.22 | 116.6 | 54.27 | 272 | 4.77 | 115.2 | 20 | 18.8 | 134 |
| | $W_n$ log | 0.26 | 0.0042 | 0.002 | 0.003 | 0.0014 | 0.0149 | 0.025 | 0.0165 | 0.157 | 0.009 | 0.015 | 0.343 | 0.0032 | 0.254 | 0.425 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Sigma W_n.l$ $Q_n$ | 1.535 | | | | | | | | | | | | | | |
| | $WQI$ [a] | **42.8** (Good) | | | | | | | | | | | | | | |
| **$S_4$** | $V_n$ [a] | 6.47 | 680 | 78 | 211.6 | 880 | 160 | 187 | 145.77 | 5.97 | 670.2 | 2.2 | 7.5 | 89 | 1.2 | 7.2 |
| | $W_n$ [a] | 0.133 | 0.002 | 0.002 | 0.002 | 0.0008 | 0.0072 | 0.011 | 0.008 | 0.909 | 0.004 | 0.022 | 0.166 | 0.0025 | 0.2 | 0.2 |
| | $Q_n$ [a] | 86.2 | 136 | 13 | 42.32 | 70.4 | 116.36 | 207.7 | 116.6 | 54.27 | 268.1 | 4.88 | 125 | 22.25 | 24 | 144 |
| | $W_n$ log | 0.25 | 0.004 | 0.002 | 0.003 | 0.0014 | 0.015 | 0.025 | 0.016 | 0.157 | 0.009 | 0.015 | 0.349 | 0.0033 | 0.276 | 0.431 |
| | $\Sigma W_n.l$ $Q_n$ | 1.57 | | | | | | | | | | | | | | |
| | $WQI$ [a] | **45.07** (Good) | | | | | | | | | | | | | | |
| **$S_5$** | $V_n$ [a] | 6.59 | 715 | 85 | 210.9 | 880 | 169 | 192 | 145.77 | 5.97 | 680 | 2.6 | 8.2 | 94 | 1.7 | 7.8 |
| | $W_n$ [a] | 0.13 | 0.002 | 0.002 | 0.002 | 0.0008 | 0.0072 | 0.011 | 0.008 | 0.909 | 0.004 | 0.022 | 0.166 | 0.0025 | 0.2 | 0.2 |
| | $Q_n$ [a] | 87.7 | 143 | 14.16 | 42.18 | 70.4 | 122.90 | 213.3 | 116.61 | 54.27 | 272 | 5.77 | 136.6 | 23.5 | 34 | 156 |
| | $W_n$ log | 0.259 | 0.004 | 0.002 | 0.003 | 0.0014 | 0.015 | 0.025 | 0.016 | 0.157 | 0.009 | 0.016 | 0.355 | 0.0034 | 0.30 | 0.43 |
| | $\Sigma W_n.l$ $Q_n$ | 1.61 | | | | | | | | | | | | | | |
| | $WQI$ [a] | **47.99** (Good) | | | | | | | | | | | | | | |
| **$S_6$** | $V_n$ [a] | 7.41 | 745 | 92 | 240.6 | 910.9 | 177 | 201 | 187.9 | 12.81 | 699.7 | 3.1 | 9.5 | 9.7 | 2.4 | 8.3 |
| | $W_n$ [a] | 0.13 | 0.002 | 0.0016 | 0.002 | 0.0008 | 0.0072 | 0.011 | 0.008 | 0.909 | 0.004 | 0.022 | 0.166 | 0.0025 | 0.2 | 0.2 |
| | $Q_n$ [a] | 98.8 | 149 | 15.33 | 48.12 | 72.872 | 128.72 | 223.3 | 150.32 | 116.45 | 279.88 | 6.88 | 158.33 | 24.25 | 48 | 166 |
| | $W_n$ log | 0.265 | 0.004 | 0.0019 | 0.0033 | 0.0014 | 0.015 | 0.026 | 0.0174 | 0.187 | 0.097 | 0.018 | 0.366 | 0.0034 | 0.336 | 0.44 |
| | $\Sigma W_n.l$ $Q_n$ | 1.70 | | | | | | | | | | | | | | |
| | $WQI$ [a] | **53.18** (Moderately Polluted) | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$S_7$** | $V_n$ [a] | 7.37 | 757 | 97 | 223.6 | 870.5 | 182 | 207 | 171.4 | 9.61 | 675.1 | 3.7 | 10.7 | 110 | 3.2 | 8.7 |
| | $W_n$ [a] | 0.13 | 0.002 | 0.0016 | 0.002 | 0.0008 | 0.0072 | 0.011 | 0.008 | 0.909 | 0.004 | 0.022 | 0.166 | 0.0025 | 0.2 | 0.2 |
| | $Q_n$ [a] | 98.2 | 151.4 | 16.16 | 44.72 | 69.64 | 132.36 | 230 | 137.12 | 87.36 | 270.4 | 8.22 | 178.3 | 27.5 | 64 | 174 |
| | $W_n$ log | 0.265 | 0.004 | 0.002 | 0.003 | 0.0014 | 0.015 | 0.026 | 0.0171 | 0.176 | 0.009 | 0.020 | 0.375 | 0.0036 | 0.361 | 0.455 |
| | $\Sigma W_n.l$ $Q_n$ | 1.28 | | | | | | | | | | | | | | |
| | $WQI$ [a] | **24.84** (Excellent) | | | | | | | | | | | | | | |
| **$S_8$** | $V_n$ [a] | 7.5 | 500 | 600 | 500 | 1250 | 137.5 | 90 | 125 | 11 | 250 | 4.5 | 6 | 400 | 5 | 5 |
| | $W_n$ [a] | 7.29 | 765 | 110 | 223.8 | 747.17 | 191 | 213 | 173.4 | 8.28 | 571.6 | 4.6 | 11.2 | 120 | 3.7 | 9.5 |
| | $Q_n$ [a] | 97.2 | 153 | 18.3 | 44.76 | 59.77 | 138.9 | 236.66 | 138.72 | 75.27 | 228.6 | 10.22 | 186.7 | 30 | 74 | 190 |
| | $W_n$ log | 0.265 | 0.004 | 0.002 | 0.003 | 0.0014 | 0.0156 | 0.026 | 0.0171 | 0.171 | 0.009 | 0.022 | 0.378 | 0.003 | 0.373 | 0.455 |
| | $\Sigma W_n.l$ $Q_n$ | 1.75 | | | | | | | | | | | | | | |
| | $WQI$ [a] | **55.97** (Moderately Polluted) | | | | | | | | | | | | | | |
| **$S_9$** | $V_n$ [a] | 7.9 | 782 | 110 | 210.6 | 744.67 | 206 | 221 | 173.5 | 8.26 | 581 | 5.1 | 12.1 | 129 | 4.7 | 11.2 |
| | $W_n$ [a] | 0.133 | 0.002 | 0.001 | 0.002 | 0.0008 | 0.0072 | 0.011 | 0.008 | 0.09 | 0.004 | 0.022 | 0.167 | 0.0025 | 0.2 | 0.2 |
| | $Q_n$ [a] | 105.33 | 156.4 | 18.33 | 42.12 | 59.5736 | 149.81 | 245.55 | 138.8 | 75.09 | 232.4 | 11.33 | 201.6 | 32.25 | 94 | 224 |
| | $W_n$ log | 0.264 | 0.0041 | 0.0018 | 0.0032 | 0.0014 | 0.015 | 0.025 | 0.0166 | 0.161 | 0.009 | 0.014 | 0.349 | 0.0032 | 0.238 | 0.427 |
| | $\Sigma W_n.l$ $Q_n$ | 1.53 | | | | | | | | | | | | | | |
| | $WQI$ [a] | **58.56** (Moderately Polluted) | | | | | | | | | | | | | | |

[a] $S_n$ = Permissible values; $V_n$ = Observed value; $W_n$ = Unit Weight; $Q_n$ = Quality rating; Water Quality Index Rating

$WQI = Anti\,log \sum W_n.log\,Q_n$ (0 – 25: Excellent; 26 – 50: Good; 51– 75: Moderately Polluted; 76 – 100: Very Poor; > 100: Unsuitable)

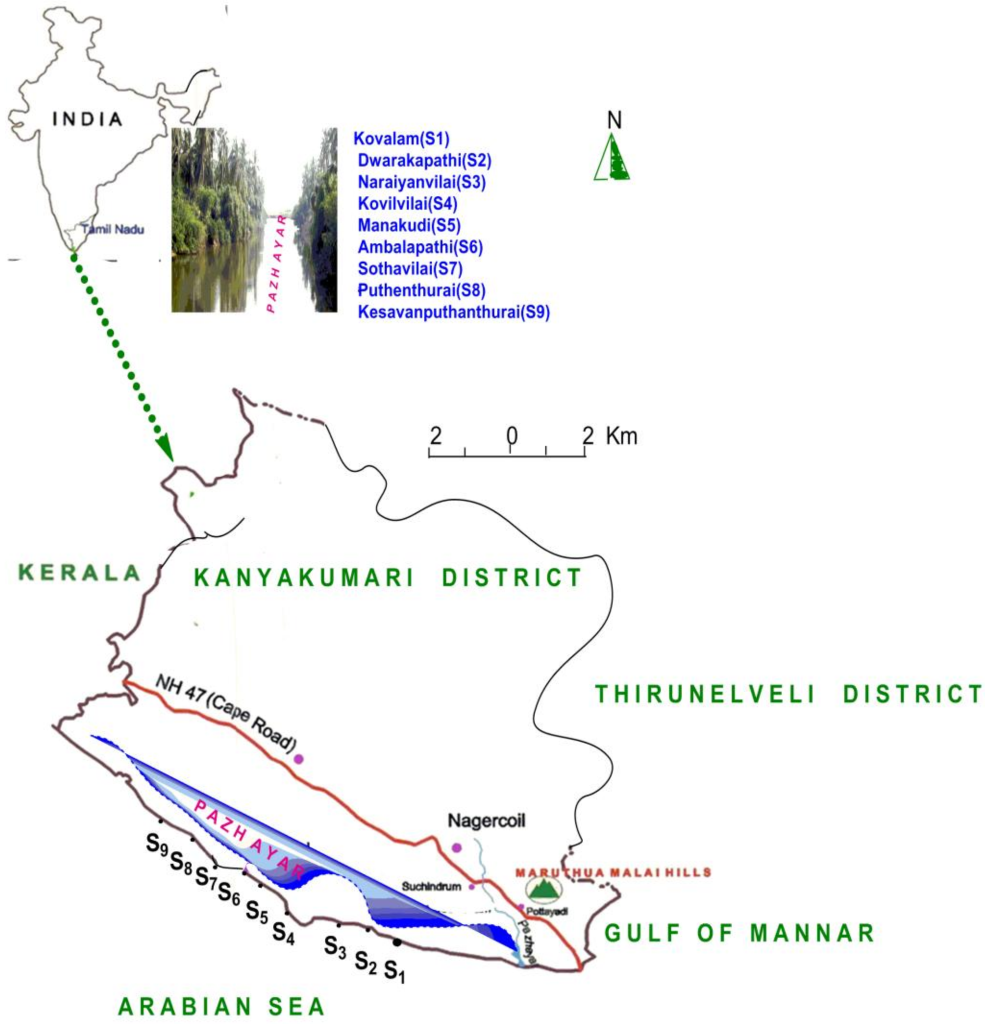



**Fig. S1.** Panoramic Location of sampling stations at Pazhayar river in India.

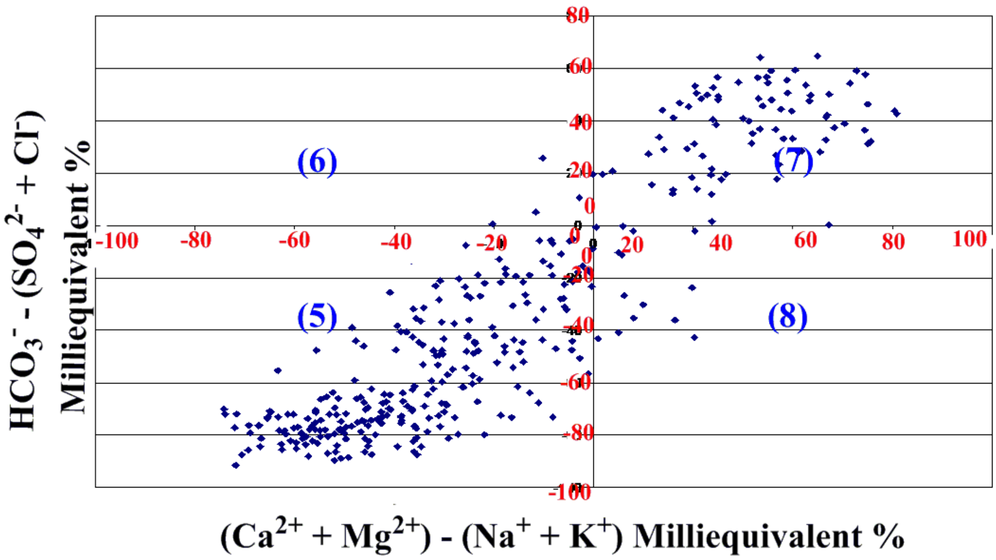



**Fig. S2.** Chadha's Plot for Sothavilai ($S_7$) Station

**Table 1.** Description of Land forms in the study area.

| Sl. No. | Geomorphic | Characteristics | Hydrogeology |
|---|---|---|---|
| 1. | Shallow buried pediment (Sothavilai) | Intermediate zone between pediment and deep buried pediment, appreciable weathering thickness | Moderate infiltration recharge influenced by hydrological features |
| 2. | Flood plain (Near Pazhayar river) | Gentle plain adjacent to river comprising of river alluvium | High infiltration provides good recharge, mainly from river and other hydrogeological features |
| 3. | Pediment (Manakudi area) | It forms outcrops with or without soil cover | Run off zone |
| 4. | Coastal plain (Coastal area) | Unstabilised and stabilized sand dunes and comprising of medium to fine sandy windblown particles | Recharge zone with good infiltration |
| 5. | Lineament (Kanyakumari area) | Linear feature may be a geological contact or fractured joined zone | Infiltration is good in fracture joined lines and geological contact |
| 6. | Deep buried pediment (In all parts of the other area) | Shallow depressed low relief area with good drainage networks. Weathering thickness is more. | Infiltration moderate to good-recharge by hydrological feature storage complemented by secondary fractures. |

**Table 2.** Average value of the physico–chemical parameters determined for sampling stations ($S_1$–$S_9$) of Pazhayar river from during July 2011–July 2014.

| Parameters | Units | WHO Values | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ | $S_9$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | | -- | 27.21 | 25.5 | 25.5 | 25.5 | 25.5 | 36.7 | 31.8 | 30.23 | 31.69 |
| pH | -- | 6.50–8.50 | 7.17 | 6.39 | 6.39 | 6.47 | 6.59 | 7.41 | 7.37 | 7.29 | 7.22 |
| EC | mmho/cm | -- | 1.09 | 1.37 | 1.38 | 1.36 | 1.38 | 1.42 | 1.37 | 1.16 | 1.18 |
| TS | mg / L | -- | 376.3 | 371.3 | 378.3 | 377.3 | 370.9 | 518.1 | 434.9 | 518.4 | 360.7 |
| TDS | mg / L | 1000 | 710.9 | 880 | 880 | 880 | 880 | 910.9 | 870.5 | 747.17 | 744.67 |
| TSS | mg / L | -- | 71.9 | 85.5 | 85.5 | 87.5 | 85.5 | 215.7 | 147.8 | 144.2 | 144.6 |
| DO | mg / L | -- | 3.65 | 3.54 | 3.55 | 3.57 | 3.54 | 4.35 | 4.06 | 4.04 | 4.33 |
| BOD | mg / L | 5.0 | 8.34 | 7.45 | 7.45 | 7.45 | 7.45 | 11.57 | 9.57 | 8.54 | 9.42 |
| COD | mg / L | 10.0 | 16.99 | 14.45 | 14.87 | 14.77 | 14.97 | 23.47 | 19.22 | 19.29 | 19.31 |
| TH | mg / L | 500 | 218.7 | 217.1 | 211.8 | 211.6 | 210.9 | 240.6 | 223.6 | 223.8 | 210.6 |
| Cl | mg / L | 250–600 | 545.23 | 675.1 | 680 | 670.2 | 680 | 699.7 | 675.1 | 571.6 | 581.0 |
| Na | mg / L | 200 | 151.2 | 144.7 | 145.77 | 145.77 | 145.77 | 187.9 | 171.4 | 173.4 | 173.5 |
| K | mg / L | -- | 6.59 | 5.97 | 5.97 | 5.97 | 5.97 | 12.81 | 9.61 | 8.28 | 8.26 |
| $PO_4^{2-}$ | mg / L | 0.1 | 0.091 | 0.018 | 0.017 | 0.012 | 0.015 | 0.127 | 0.104 | 0.104 | 0.45 |
| Total Nitrate | mg / L | -- | 2.11 | 1.04 | 1.02 | 1.00 | 1.00 | 9.22 | 3.64 | 5.67 | 4.49 |

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