Geochemical Analysis of the Groundwater Quality along the Vrishabhavathi River Basin

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Authors' contributions

This work was carried out in collaboration between authors GNM and MHR. Author GNM performed the field work and chemical analysis in the laboratory, wrote the protocol and the first draft of the manuscript. Authors GNM and MHR designed the study and author MHR supervised the chemical analysis in the laboratory. Author DJ helped in the statistical study. All the three authors read and approved the final manuscript.

Article Information

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ABSTRACT

Aim: The current study aims at assessing the groundwater quality along the Vrishabhavathi river basin for various water quality variables.
Study Design: Conventional Titrimetric and Spectrophotometric methods were employed to estimate the different water quality variables which are briefly explained in the methodology.
Place and Duration of Study: During the monsoon, June 2015 the groundwater along the Vrishabhavathi river basin, Bengaluru, Karnataka, India were sampled for the present investigation.
Methodology: Water quality variables such as Temperature, pH, Electrical Conductivity and Total dissolved solids were estimated in the field using portable apparatus. Total Hardness, Cl^-, HCO_3^-, Ca^{++} and Mg^{++} were estimated by titremetry. Na^+ and K^+ were estimated using Flame photometry. SO_4^{2-} and F^- were estimated using Turbidimetry and SPADNS method [Spectrophotometry]. Pb and Cr were estimated using Atomic Absorption Spectrophotometry. The standard guidelines of APHA [1998] were used for the entire analysis. Descriptive statistics and Correlation study has been done using SPSS 22 and Minitab 14.

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Results: The detailed study of all the water quality variables is discussed in the paper. LSI calculation indicates that majorly 53% of the water samples are classified under the class 'D' [Slightly scale forming and corrosive] and 40% of the water samples fall under the group 'E' [Scale forming but non-corrosive]. Piper trilinear plot reveals that majorly Ca^{++} and Mg^{++} are the dominant cations and HCO_3^- and Cl^- are the dominant anions. Statistical measures such as Mean, SD, SE of sample means, coefficients of Skewness and Kurtosis have been computed using the statistical package to assess the characteristics of the selected water quality variables. Further, 95% confidence intervals have been obtained for the true means of these variables and water quality variables crossing the permissible limits of WHO [1993] have been identified using these confidence limits. Correlation study has been done to estimate the significance of the linear relationship between the pairs of variables at a given level of significance and thereby the set of water quality variables which are interlinked have been identified.
Conclusion: The water quality variables which have/have the tendency to cross the permissible limits set by WHO [1993] have been identified using the confidence intervals.
Through the Piper plot and LSI calculation, we can conclude that the groundwater samples are alkaline in nature and are not suitable for consumption.

1. INTRODUCTION

Bengaluru has acquired a lot of prominence over the years due to the establishment of number of MNCs, IT Companies, Industries, and premier research Institutes. This has resulted in the influx of large population from outside, which has paved way for the rise in overall population of the city. The Metropolis has no perennial source of fresh water as such. The city's fresh water requirements were taken care of by the river Cauvery and the reservoirs at Hesaraghatta and Thippagondanahalli. Due to the increase in population, these sources alone were insufficient to quench the elevated demands of the public, consequently the groundwater was targeted as an alternative source. The rate of drilling bore wells increased extensively throughout the city. Today there are approximately more than 3.12 lakhs tube wells in Bengaluru. Here about 7000 bore wells are owned by the BWSSB [Bangalore Water Supply and Sewage Board], More than 2 lakh private bore wells are drilled to meet the domestic and also industrial necessities [1]. A Large number of tube wells are drilled by private agencies to supply water through tankers in the city and suburbs [2]. As a consequence, the groundwater table of the city is declining with time. The rapid urbanization and demographic change have resulted in the drying up of many tanks and lakes who were an effective aquifer recharge zones in the past. The remaining few have been dumped with solid and liquid wastes, thereby making it unfit for utilization [3]. The current study focuses on a similar case, where the *River Vrishabhavathi*, an erstwhile source of fresh water, now carries only the waste, toxic materials and heavy metals as a Dead River due to its extensive contamination [4], which in turn is polluting the nearby groundwater sources [5] As per the literature the River has got two origins – One originating from the Peenya industrial suburbs and the other from Gavipuram in Guttahalli. Both the streams join together near Nayandahalli, flows as a single unit from there and ultimately joins the River Arkavathi which is a tributary of River Cauvery. The length of the river course being 52 km, it flows in the south-western part of Bengaluru parallel to the Bangalore – Mysore state highway and enters Kengeri [location containing the sampling stations]. There are about 21 major and 58 small scale industries which directly discharge their effluents into the river. Only 18% of them are found to possess effective effluent treatment plants [6]. Along the Mysore road there are numerous textile industries, factories manufacturing industrial components and carbonated drinks etc. discharge their untreated waste and effluents directly into the river via their drainage systems. The residents along the bank directly dump all the domestic wastes into the stream *[observed during sampling]*. These factors are instrumental in the effective pollution of the river. There are also a number of plantations and agricultural fields along the basin where the same toxic water is utilized for irrigation. Now, this is a potential health threat as the plants take up components like heavy metals, which ultimately enters the human body through consumption causing the respective metal poisoning [7]. So it is high time, the authorities

Photo 1. River Vrishabhavathi photographed during sampling

ought to understand the gravity of the situation and think is the direction of an appropriate solution which is the need of the hour.

2. PHYSIOGRAPHY

Bengaluru is the fastest growing city in Asia and the fifth biggest city in India which has recently attained the fame as 'Silicon City', due to its progressive trend in Information technology. The city, which was formerly known as the 'Garden City', is losing its foliage due to swift urbanization and multifaceted industrial development. Bengaluru is positioned in the south-eastern part of Karnataka state, at an average height of 920 m [3,018 ft.] above the Mean Sea Level [MSL]. The city is situated at 12.970° N, 77.56° E and shelters an area of about 850 sq. kms. It is the major administrative, industrial, commercial, educational and cultural capital of Karnataka state and is positioned in the South- Western part of India. The hottest month is April with an average high temperature of 33.6°C and the coolest month being January with an average low temperature of 15.1°C. The sampling stations are located along the bank of river Vrishabhavathi in Kengeri area which lies on the western corridor of Bengaluru Metropolis, Karnataka state. The stations are mentioned in Table 1 in detail.

3. MATERIALS AND METHODS

Groundwater samples were collected from the identified tube wells in 15 locations along the Vrishabhavathi river basin [Kengeri] in the month of June 2015 [depth of the bore wells lied between 270 ft. [sample No.3] and 560 ft. [sample No. 7]. Polythene containers of 2 L capacity were pre-cleaned with detergents and rinsed with doubly distilled water before sampling. The groundwater on the spot was made to run out for about 7 minutes, the container was rinsed twice with the same, and the water was collected. Water quality variables such as Temperature, pH, EC, and TDS were measured in situ, using the portable water analyzer [Systronics – 371]. The samples were immediately carried to the laboratory of Atria Institute of Technology for further chemical analysis. Chemical parameters such as Total Alkalinity, Total Hardness, Chloride, Calcium, and Magnesium were estimated using titrimetry, Sulphate and Fluoride were estimated through Turbidimetry and SPADNS method using the Spectrophotometer [ELICO – SL 171]. Sodium and Potassium were estimated using the Flame photometer [Systronics FM 128] at the laboratory of Atria Institute of Technology. Lead and Chromium were estimated using Atomic Absorption Spectrophotometer at the Department of Mines and Geology, Bengaluru. All the samples were analysed as per the prescribed standard methods of APHA [1998].

4. HYDROGEOLOGICAL DATA

The river Vrishabhavathi is a tributary of the river Arkavathi. In terms of hydrogeology, most of the Arkavathi sub- basin is underlain by hard-rock that consists of gneisses and granites. The shallow aquifer consists of the highly-weathered zone extending to about 20 m BGL. The fractured zone, extending from 20–50 m, contains joints and cracks, some of which are well-connected to each other and can function as conduits. Yields drop off greatly beyond 60 m. At deeper levels, there are a few joints and fractures that have been enlarged by dissolution and can extend to considerable depths. The Geological Society of India estimates that 96% of the yield comes from the top 60 m.

Table 1. Showing the sampling locations

Sample no	Location
1	No. 303, Lilly block, Mahaveer lake apartments, Uttarahalli road
2	No.78, C.V. Raman Road, 5th cross, Meenakshi road, Kodipalya
3	No. 69, 1st main, 5th cross, Meenakshi road, Kodipalya
4	No.12, 5th cross. 1st main, Annapoorneshwari Homes, Kodipalya
5	Construction site, near Uttarahalli main road, Sultanpalya
6	6th cross, Vinayaka layout, near Anjaneya temple
7	No. 87, 13th cross, Satyanagara, Vidyapeeta road
8	No.94, near Bangalore-Mysore state highway, Vidyapeeta road
9	Construction site, 9th block, 7th main ,Garga, near nice road,
10	Chettupalya entrance, Ward No. 198
11	No.5 Vidyapeeta road, Kengeri
12	Construction site, 11th cross, Vidyapeeta road
13	Sri. Kalabhairaveshwara nilaya, NO. 12/2, 1[st]cross, Minugu layout
14	No. 30, 10th cross, Vinayaka layout, Kodipalya
15	Sri Lakshmi Venkateshwara Bricks, 1st cross, Good Earth road.

5. RESULTS AND DISCUSSION

5.1 Temperature

The temperature values of all the groundwater samples lie within 23.1° C and 28.5°C with a mean value of 26.35°C. The elevation or decrease in the temperature values influences the electrical conductivity of water. Even in the monsoon season, the samples Nos. 4 and 10 have shown elevated temperature values as shown in Table-2

5.2 pH

pH values of groundwater were ranged between 6.9 and 7.6, with a mean of 7.15 indicating very slight basic nature of the water samples. The required range of pH in water prescribed for potability by ISI [8] and WHO [1993] [9] is 6.5 – 8.5. All the sample of groundwater fall within the permissible limits of ISI and WHO [1993] as indicated in Tables 2 and 3. Here, during the investigation, there was no considerable variation of the pH values among the groundwater samples, which made way for the prediction that all the water samples were from a single aquifer.

5.3 Electrical Conductivity

Electrical conductivity measurement is a swift method to obtain an idea regarding the concentration of ionizable substances in water [10], it is also a measure of salinity, which greatly affects the taste and has a noteworthy impact on the user's acceptance of the potability of water [11]. The EC values varied from 570 to 1690 μS/cm with an average of 997.93 μS/cm as indicated in Tables 2 and 3. It is observable that elevated concentration of Sodium and Calcium ions in the water samples were responsible for the increase in Ionic Conductivity. According to US Salinity Laboratory's classification of water [1954], water samples 6,9,13, and 14 fall under 'GOOD' category and water samples 1,2,3,4,5,7,8, 10,11,12, and 15 are under the category of 'FAIR' [12].

5.4 Total Dissolved Solids

TDS in groundwater depends on the movement of water through rocks containing soluble mineral matter, concentration by evaporation, influx, and contamination of industrial and municipal waste water disposal [13]. TDS values fluctuated from 285 ppm to 864 ppm with a mean value of 499 ppm as indicated in Tables 2 and 3. As per the specification of WHO [1993] TDS upto to 1000 ppm is the maximum permissible limit. Here, in the current study, all the groundwater samples have the TDS values lying below the permissible limit of WHO [1993]. Based on the TDS, the groundwater can be classified as follows [Wilcox 1955]. Groundwater of TDS level upto 500 ppm as desirable for drinking and TDS level upto 1000 ppm as permissible for drinking, and finally TDS level upto 3000 ppm as useful for irrigation. Based on this classification, it was observed that water samples 1,2,3,6,9,10,12,13,14 are desirable for drinking and water samples 4, 5,7,8,11,15 are permissible for drinking [14]. Consumption of water having TDS values 1500 ppm and above results in the gastrointestinal irritation [15].

5.5 Total Hardness

Hardness of water is normally defined as the soap-consuming capacity of water. It is caused due to the dissolution of salts present in the geological formations underneath the upper soil. The term *'Total Hardness'* specifically refers to the concentration of chlorides, bicarbonates and sulphates of Calcium and Magnesium ions, even the Manganese, Strontium, Aluminium, Zinc and Iron cations also cause hardness but in negligible amounts [16]. The solution of carbon dioxide released from bacterial action also causes hardness in the percolating water. The permissible limit of hardness prescribed by WHO [1993] is 500 ppm. Generally consuming water having hardness concentration more than 300 ppm causes Kidney and Heart disorders [17,18]. Normally the presence of Calcium and Magnesium salts uplifts the boiling point of water which would not be suitable for cooking purpose. In the present study, the Total hardness values varied from 280 ppm to 780 ppm with a mean value of 485.3 ppm as indicated in Tables 2 and 3. Authors found that 60% [9 out of 15] of the samples were above the permissible limit. Classification of water based on Hardness was done according to Sawyer [19] as depicted in the Table 9.

The values indicated in the above Table 2 infers that all the water samples fall into the category of 'Hard' [19].

5.6 Chloride

The permissible limit of Chloride in groundwater according to WHO [1993] is 200 ppm. The presence of chloride in excess amounts imparts a salty taste to water and people who are not adapted to this are prone to Laxative effects [20]. Elevated levels of chloride increase the rate of corrosion of metals in pipes, which in turn can lead to the increase in the metal concentration in the supply [21]. In the present investigation, the chloride values in the groundwater samples varied from 46.6 ppm to 233.8 ppm with an average value of 150.8 ppm as indicated in Tables 2 and 3. As per the study 27% of the samples have chloride values crossing the permissible limits, while the rest remain within the range. Water samples have been categorized into different groups based on the chloride values: [22], as shown in Table 8.

In the table-8 'µ' indicates the number of samples. As shown, 40% of the samples fall into the 'Fresh' category and the remaining 60% of the water samples fall into the 'Fresh-Brackish' category.

5.7 Bicarbonate

In natural water, bicarbonate is one of the key factors contributing to the total alkalinity [which is the acid neutralizing capacity of water]. The source of bicarbonate is credited to the natural process of the dissolution of carbonate minerals in presence of soil CO_2.

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^{\ominus}$$

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^{\ominus}$$
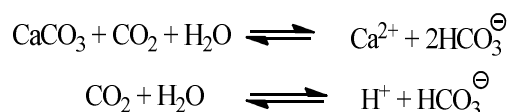
Other constituents contributing to water alkalinity include OH^-, CO_3^{2-}, $H_2BO_3^-$ and NH_3. In the current study, the bicarbonate values fluctuated between a lower value of 290 ppm and a higher value of 630 ppm with a mean of 433 ppm as indicated in Tables 2 and 3. In the current investigation 27% of the water samples have the bicarbonate values crossing the permissible limits of WHO [1993] i.e. 500 ppm. Similar observations were made by [23].

5.8 Calcium

Calcium gets into the groundwater due to its easy solubility and the contact of many calcium-bearing minerals such as limestone, gypsum, dolomite etc., in the aquifers [24]. It is one of the major bivalent cation causing hardness in water, and it generally forms scales in the pipes where water is supplied by anthropogenic utility. The permissibility limit of Calcium in water according to WHO [1993] is 75 ppm. The Ca^{2+} level in the body is regulated by the Vitamin D and the parathyroid hormones. Failure of the regulatory mechanism leads to the calcification of tissues. Excess of Ca – salts leads to the formation of stones in the Kidney and gall – bladder, and cataract in the eyes. [25] In the present research, the calcium concentration in the groundwater samples varied from 52 ppm to 136 ppm with a mean value of 88.6 ppm as indicated in Tables 2 and 3. Here 27% [4 out of 15] samples are within the permissible limits, and all the samples are within the excessive limits prescribed by BIS [1998] [26] and WHO [1993]. The majority of the samples here contained calcium in elevated concentrations indicating an increase in the hardness concentration as well.

5.9 Magnesium

Magnesium is another principle divalent cation along with calcium which is instrumental in initiating hardness in water. Magnesium is a significant component of basic igneous rocks such as Dunites, Pyroxenites and Amphiboles, Volcanic rocks and metamorphic rocks such as Talc and Tremolite – schists and sedimentary rocks such as dolomite, Olivine, augitebiotite, hornblende and serpentine. High concentration of magnesium may cause laxative effects [27]. Magnesium toxicity in higher doses greater than 400 mg/L results in Muscular weakness, Nausea, and paralysis in the mammals [Garg et al. 2004]. In the current investigation, the Magnesium values ranged from 55.63 ppm to 157.14 ppm with an average value of 96.80 ppm as shown in Tables 2 and 3. Here all the samples have the magnesium values above the permissible limit prescribed by WHO [1993] i.e. 50 ppm. The sampled area is composed only of the 'Gneissic Granites' of the 'Precambrian' age [28] which is not a chief source of Magnesium, but the values indicate high Magnesium concentration which may be due to the anthropogenic activities.

5.10 Sodium

Sodium is a vital element for the organisms, it is present in many minerals, and the 'Rock Salt' is its major source. Sodium doesn't occur in its free state in nature due to its high reactivity. It is widely distributed in the combined state and occurs in 2.6% of the Earth's crust. Sodium enters into the groundwater through the minerals namely Albite and others members of plagioclase feldspars, Nephelene and Sodalite [29]. The permissible limit prescribed for Sodium concentration in groundwater is 200 ppm according to WHO [1993]. In the current study, the Sodium concentration in the groundwater samples varied from 41.13 ppm to 348.5 ppm with a mean value of 95.05 ppm as indicated in Tables 2 and 3. Only one sample [No.5] has an elevated concentration of Sodium [348 ppm], while the remaining 14 groundwater samples lie within the permissible limit of WHO [1993]. Similar observation was made by [30] where only a single sample had crossed the permissible limits of WHO [1993].

5.11 Potassium

Potassium is important in irrigation water. Potassium is found as abundant as sodium in igneous rocks and metamorphic rocks, its concentration in groundwater various between on tenth and one hundredth when compared to that of sodium. The most common sources of potassium are the silicate mineral orthoclare, nepehline, leucite and bio line. In the present pursuit, the potassium values varied from 3.05 ppm to 22.1 ppm with a mean value of 10.56 ppm as found in Tables 2 and 3.

5.12 Fluoride

Fluoride in potable water can be either helpful or harmful to human health depending on its concentration. The concentration of fluoride occurring in groundwater is a function of the ambient climate, host rock composition, Hydrogeology and increased residence time [31]. For instance, if the groundwater is rich in HCO_3^-, the following type of reaction occurs during the water-mineral [fluorite] interaction.

$$CaF_2 + 2NaHCO_3 \longrightarrow CaCO_3 + 2Na + 2\overset{\ominus}{F} + H_2O + CO_2$$

In the above reaction, the $NaHCO_3$ rich water in a weathered rock formation accelerates the dissolution of CaF_2 to release fluoride into groundwater with time [32]. The very first case of endemic fluorosis was reported in India as early as 1937 in Prakasam District, Andra Pradesh, India [33], later other important states namely Rajasthan, Andhra Pradesh, Karnataka, and Maharashtra have also reported severe problems due to abnormal levels of fluoride in the groundwater [34]. In the Indian subcontinent, elevated amounts of fluoride in groundwater is associated with Metamorphic and Igneous rocks [35,36,37]. The permissible limit of fluoride in water as prescribed by the WHO [1993] is 1.5 ppm. Low fluoride content [< 0.6 ppm] causes 'dental caries' resulting in the decay of teeth, while elevated concentration [>1.5 ppm] causes dental and skeletal fluorosis which results in the bone and joint deformations. [38,39,40]. Both these types of fluorosis are irreversible and no treatment as such exists till date. In the current investigation, fluoride concentration in groundwater varied between 0.22 to 0.78 ppm and the average value of 0.46 ppm indicating all the water samples are well within the permissible limits as indicated in Tables 2 and 3.But similar studies were carried out by others [41,42] and [43] where the fluoride values reported in the groundwater lie just below and above the permissible limits i.e. 1.47 ppm, 1.6 ppm and 1.8 ppm respectively.

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5.13 Sulphate

Sulphur gets into groundwater when it passes through minerals such as Epsom salt [$MgSO_4$], Glauber's salt [Na_2SO_4], and Gypsum [$CaSO_4.2H_2O$] beneath the soil [44]. Sulphide minerals upon oxidation give rise to soluble sulphates in water. Sulphate salts contribute to the water hardness, potable water containing sulphate above 500 ppm has a bitter taste and above 1000 ppm may cause intestinal problems. In the current research, the sulphate values varied from 45 ppm to 800 ppm with a mean value of 175.3 ppm as depicted in Tables 2 and 3. Here 67 % of the samples have the sulphate values exceeding the permissible limit of WHO [1993] i.e. 200 ppm.

5.14 Lead

Lead is a heavy metal which causes 'Lead Poisoning' in the human body. Lead has been used as a constituent of gasoline [as antiknocking agent], paint, glassware, metal pipes, and food containers, all of which have contained varying amounts of lead. Most of the normal individual's everyday lead exposure occurs from the food and water that he/she consumes. Lead in food can result from leaching of lead from lead-soldered cans or from lead-tainted dust deposited on the food. Lead enters the water as a result of industrial activity. But lead is much more likely to enter the water as it passes through household plumbing. Through corrosion, lead is dissolved from leaded solder and lead pipes in plumbing systems. Lead may originate from the corrosion of brass fittings on certain types of submersible pumps used in groundwater wells. Lead poisoning [also called 'Saturnism' or 'Plumbism'] in a condition wherein large amount of metal Lead gets accumulated in the human body. Lead poisoning basically causes 'Anaemia'. Pb^{2+} can interfere with Ca^{2+} and consequently, bones are also affected in Pb – poisoning. Excess of Lead can injure brain cells, cause reproductive problems, and damage the Mitochondria of the Kidney allowing the loss of Glucose, amino acids, and phosphates through Urine. It can also damage the liver and gastrointestinal tract [45]. The clinical symptoms of Lead toxicity are muscle pain, Joint pain, Depression, Chronic Nephritis, Farconi syndrome etc. At initial stages of Lead poisoning, lead is stored in bones in relatively inert forms without causing any ill effects. But when the body requires vital elements like Calcium, Phosphorous etc, lead starts to leach out from the bone, and in the due course lead becomes available to manifest the ill effects. Lead poisoning is more common in children as they are more prone to chewing toys painted with the lead based paints. In the present pursuit, all the water samples have shown the lead content below the detectable level [bdl], as in Table 2.
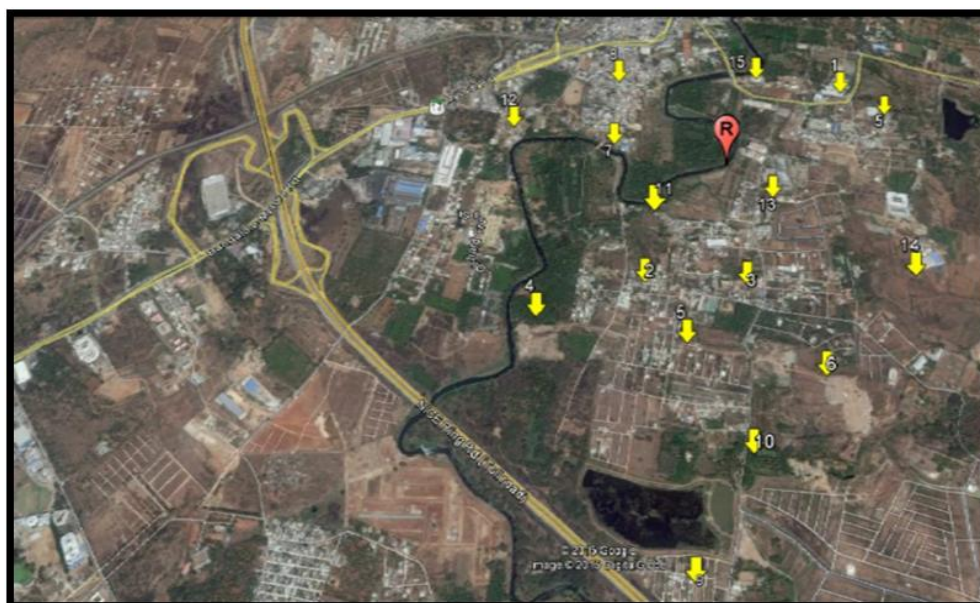
Map 1. Map showing the River Vrishabhavathi and the sampling stations

Table 2. Showing the values of all the water quality variables

Samples	pH	Temp	EC	TDS	TH	Cl$^-$	HCO$_3^-$	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	F$^-$	SO$_4^{2-}$	Pb	Cr
1	7.5	24.7	936	461	510	117.18	370	108	98.08	87.98	11.28	0.22	232.5	bdl	bdl
2	6.9	27	961	482	520	167.85	410	112	99.55	68.19	15.1	0.27	253	bdl	bdl
3	6.9	26.4	887	444	440	167.85	310	104	81.98	62.01	8.57	0.38	180	bdl	bdl
4	7.3	28.4	1127	561	550	186.5	430	100	109.8	84.24	12.84	0.4	337.5	bdl	bdl
5	7.3	25.8	1252	626	350	187	490	72	67.83	348.5	6.69	0.54	353	bdl	bdl
6	7	26.9	570	285	280	46.63	290	52	55.63	47.96	10.32	0.57	97.5	bdl	bdl
7	7.2	26.5	1690	864	780	233.13	630	136	157.14	111.12	7.58	0.58	800	bdl	bdl
8	7.2	27.9	1300	640	620	205.15	560	96	127.86	95.02	22.1	0.44	400	bdl	bdl
9	6.9	28.5	654	327	300	74.6	360	64	57.58	74.07	3.05	0.46	92.5	bdl	bdl
10	7.1	27.5	838	420	330	102.58	440	80	61	106.79	3.41	0.67	157.5	bdl	bdl
11	7.3	24.8	1420	711	720	233.8	630	76	157.14	84.94	20.29	0.23	345	bdl	bdl
12	6.9	25.8	877	440	500	167.85	380	88	100.53	76.29	7.86	0.5	355	bdl	bdl
13	7.2	26.4	703	351	390	93.25	320	81	75.4	49.41	16.8	0.52	195	bdl	bdl
14	7	25.5	571	285	350	74.6	330	64	69.78	41.13	5.91	0.78	45	bdl	bdl
15	7.6	23.1	1183	591	640	205.15	540	96	132.74	88.22	6.6	0.36	285.5	bdl	bdl

In the above table, the Temperature is measured is '°C'. EC is estimated is 'μS/cm', and the rest are measured in 'ppm'
'bdl ' refers to 'below detectable level'.

Table 3. Descriptive statistics of water quality variables

Variable	Min	Max	Mean	SD	SE (Mean)	Skewness	Kurtosis	Permissible limit [WHO 1993]	Excessive limit [WHO 1993]
pH	6.9	7.6	7.1533	0.2232	0.0576	0.51	-0.53	7 – 8.5	6.5 – 9.2
Temp	23.1	28.5	26.347	1.472	0.38	-0.49	0.26	-	-
EC	570	1690	997.9	326.5	84.3	0.54	-0.24		-
TDS [ppm]	285	864	499.2	165.6	42.8	0.63	0.04	500	1500
TH	280	780	485.3	155.5	40.2	0.44	-0.8	300 [BIS 1998]	600 [BIS 1998]
Cl^-	46.6	233.8	150.9	61.1	15.8	-0.29	-1.27	200	600
HCO_3^-	290	630	432.7	113.4	29.3	0.61	-0.85	500	-
Ca^{++}	52	136	88.6	21.98	5.68	0.36	0.09	75	200
Mg^{++}	55.63	157.14	96.8	34.32	8.86	0.58	-0.8	50	150
Na^+	41.1	348.5	95.1	73.1	18.9	3.35	12.2	-	200
K^+	3.05	22.1	10.56	5.81	1.5	0.73	-0.35	-	12
F^-	0.22	0.78	0.4613	0.1585	0.0409	0.2	-0.22	1.5	-
SO_4^{2-}	45	800	275.3	181.6	46.9	1.66	4.45	-	-
Pb	bdl	bdl	0	0	0	0	0	0.5	1.5
Cr	bdl	bdl	0	0	0	0	0	200	400

1. Here Sample size* n = 15. Here 'SD' – Standard Deviation, 'SE' – Standard Error
2. * - As per the familiar terminology used in Chemistry, a 'sample' refers to a container of the material collected in a study at a given time. According to the Stastical terminology, a sample refers to the set of all containers collected during the entire course of the study at a specified time
3. Since the maximum and minimum quantity of Lead and Chromium in the sample of size-15 are below the detectable level, all the remaining statistical measures are taken to be zero

Table 4. Confidence Interval values of different water quality variables

Parameters	95% Confidence interval	Parameters	95% Confidence interval
pH	[7.02974, 7.27693]	Mg^{++}	[77.7957, 115.8096]
Temp	[25.5317, 27.1616]	Na^+	[54.6621, 135.5873]
EC	[817.139, 1178.728]	K^+	[7.3408, 13.7792]
TDS	[407.480, 590.920]	Pb	[0.000000, 0.000000]
TH	[399.214, 571.453]	Cr	[0.000000, 0.000000]
Cl^-	[117.039, 184.710]	F^-	[0.373576, 0.549090]
HCO_3^-	[369.857, 495.476]	SO_4^{2-}	[174.680, 375.853]
Ca^{++}	[76.4280, 100.7720]		

Table 5. Correlation matrix of different water quality variables

	pH	EC [μS/cm]	TDS	TH	Cl⁻	HCO3⁻	Ca⁺⁺	Mg⁺⁺	Na⁺	K⁺	F⁻	SO₄²⁻
pH	1.00											
EC [μS/cm]	0.497	1.000										
TDS	0.483	**0.999**	1.00									
TH	0.460	**0.857**	**0.856**	1.00								
Cl⁻	0.396	**0.923**	0.919	0.864	1.00							
HCO3⁻	0.505	**0.924**	**0.922**	**0.806**	**0.829**	1.000						
Ca⁺⁺	0.233	**0.626**	**0.631**	**0.714**	**0.632**	0.411	1.00					
Mg⁺⁺	0.473	**0.850**	**0.848**	**0.994**	**0.856**	**0.827**	**0.633**	1.00				
Na⁺	0.295	0.413	0.409	-0.064	0.327	0.346	-0.042	-0.064	1.00			
K⁺	0.189	0.317	0.299	0.461	0.367	0.291	0.165	0.483	-0.182	1.00		
F⁻	-0.343	-0.325	-0.309	-0.475	-0.445	-0.226	-0.386	-0.465	0.073	-0.504	1.00	
SO₄²⁻	0.303	**0.896**	**0.905**	**0.794**	**0.788**	**0.762**	**0.713**	**0.767**	0.302	0.205	-0.128	1.00

5.15 Chromium

Chromium exists both in the trivalent and hexavalent state in nature. The chromium [III] is a vital nutrient for humans required in the amounts of 0.05 ppm to 0.20 ppm per day. Chromium existing in the trivalent state which is less toxic than hexavalent chromium. Chromium [VI] is a carcinogen to both animals and humans. The Bronchial cancer is mainly caused due to the consumption of hexavalent chromium through various sources. The Table 2 shows, all the water samples have the Chromium levels below the detectable level [bdl].

5.16 Langelier-Saturation Index

The corrosive nature or the scale forming tendency of water is determined by employing Langelier – Saturation Index [LSI] where pH is used as the main variable in combination with the Total alkalinity [mg/L as $CaCO_3$], calcium hardness [mg/L Ca^{2+} as $CaCO_3$], total dissolved solids [mg/L TDS] and the temperature [^oC] [46]. Here LSI indicates the degree of saturation of water with respect to Calcium Carbonate as in Tables 6 and 7.

LSI = pH – pHs

Here, 'pH' is the actual estimated value and 'pHs' is the theoretical value calculated using the formula

pHs = [9.3 + α+ β] – [δ + σ](47).

Where:

σ = [Log_{10} [TDS] – 1] / 10

β = -13.12 x Log_{10} [^oC + 273] + 34.55

δ= log_{10} [Ca^{2+} as $CaCO_3$] – 0.4

σ = log_{10} [alkalinity as $CaCO_3$]

The LSI values generally lie between -3 and +3. LSI value of zero indicates that the water is chemically balanced. The positive and negative LSI values indicate the deposition [Scaling] or dissolution [corrosion] of $CaCO_3$ [48]. LSI was modified by carrier [1965], he has categorized water based on the LSI values as follows.

Here as per the Tables 6 and 7, 53% of the water samples fall into the category 'D' and 40% of the water samples fall into the category 'E'. Only one sample [No 6] revealed a slight corrosive nature by falling into the category 'B'.

Table 6. Different categories of LSI values

LSI [carrier]	Inference	Category
-2.0 < LSI < 0.5	Serious corrosion	A
-0.5 < LSI < 0	Slightly corrosive but non scale forming	B
LSI = 0.0	Balanced	C
0.0 < LSI < 0.5	Slightly scale forming and corrosive	D
0.5 < LSI < 1.2	Scale forming but non corrosive	E

5.17 Piper Trilinear Plot

The Piper – Hill Diagram [49] in used in the interpretation of geochemical data. It comprises an Anionic as well as a Cationic field where the relative abundances of the respective ions are grouped into different Hydrochemical facies and are plotted in terms of the % meq/L. The two-data plotted on both the triangles [anionic and cationic] are then combined into the quadrilateral field that shows the overall chemical property of the water samples [50]. The Piper diagram not only graphical depicts the nature of the given water sample, but in turn, also correlates the association amongst each other. Here the water samples are classified into different types are designated according to the zones in which these points fall on the quadrilateral and triangular plot, each point represents one water type [51]. In the Piper plot (Fig. 1), in the cationic field triangle the water samples fall under the categories Mg^{2+}-type and non-dominant type. In the anionic field triangle the water samples are classified into HCO_3^--type and non-dominant type. As observed in the Quadrilateral field, the samples belong majorly to two classes namely Ca^{2+} - HCO_3^- type and the Mixed Ca^{2+}- Mg^{2+}-Cl^- type. Sample No.5 fall into the class of Na^+-Cl^- type.
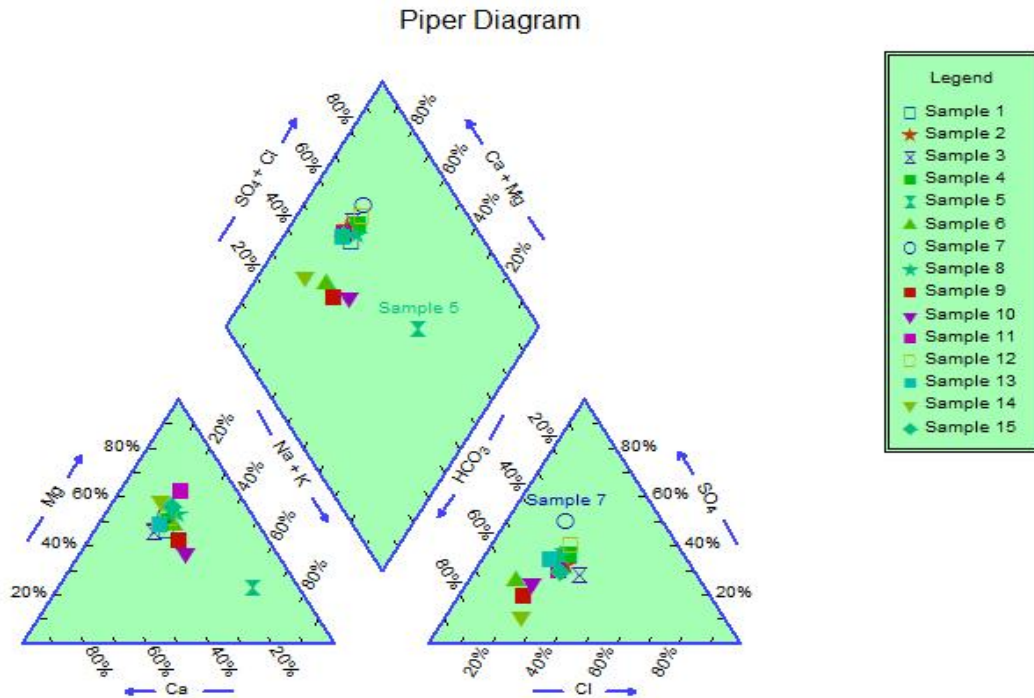
Fig. 1. Piper trilinear plot

5.18 Statistical Analysis

The Standard deviations indicate the spread of the sample values around the sample mean. The SDs of all the water quality variables except pH, Temperature, and Potassium, are quite high. Inspite of low SD of Temperature, the EC has shown a high degree of dispersion (shown in Table 3). This clearly indicates that the variation in EC cannot be attributed to the changes in Temperature alone-Table 3. It could be probably due to the geological conditions of sampled areas and many other contributing factors.

As per the relation TDS = *[0.56] EC* [52] even the SD of TDS values fall into this approximate relation i.e. *σ [TDS] = 0.56 × σ [EC].* Similar arguments can be given to the other water quality variables if any.

Skewness indicates the asymmetry of the given data around the mean. The coefficient of Skewness close to zero is an indication of symmetry. In the light of this, we can say, the variable Na^+ is exhibiting a high degree of asymmetry. The measure of skewness, in this case, is highly positive. Infact, too many water samples are having the Sodium concentration

below 100. [being the mid value of the permissible range].

Kurtosis indicates the peakedness in the data relative to Gaussian. The coefficient of Kurtosis is very high for the variable Na^+. It is observed that too many values of Sodium have concentrated at a value below 100 which indicates more density of Sodium values around the mean resulting in *Leptokurtosis*. On the contrary, the interpretation can also be given in the case of EC, where in, there is a high SD of 326.5 ppm resulting in *Platykurtosis.*

5.18.1 Confidance interval

100 [1- α] % confidence interval is an interval computed on the basis of sample observations in such a way that, in repeated selection of the samples of given size [n], we can expect 100 [1- α] % of the corresponding intervals to contain the true value of the parameter i.e., the true mean of the water quality variable.

The interval plots [shown in Fig. 2] are the graphical representations of the 95% confidence intervals of various water quality variables. The midpoints of the vertical lines are the point estimates of the true mean values of the respective water quality variables*.*
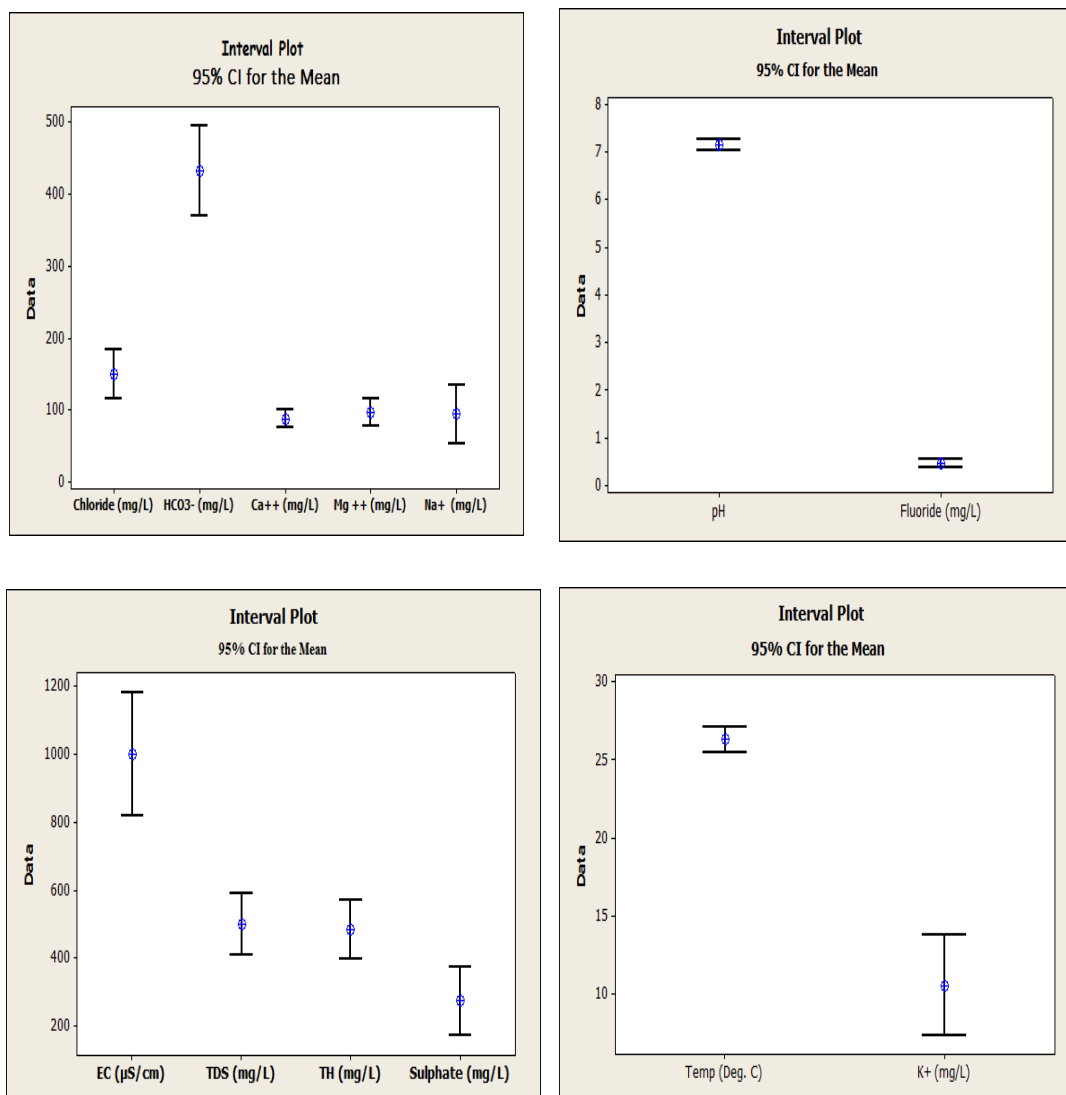
Fig. 2. Confidence interval plot

The confidence intervals in Table-4 have been constructed under the assumption that sample of values with regard to an individual water quality variable has been drawn from the *Normal [Gaussian]* distribution. These intervals are given by-

$$[\ \bar{x} - t_{\alpha/2[n-1]}.\,S/\sqrt{n},\ \bar{x} + t_{\alpha/2[n-1]}.\,S/\sqrt{n}]$$

where $\bar{x}$ and S are sample mean and sample standard deviation with respect to 'n' observations obtained on the given water quality variable. The interval plots are depicted in Fig. 2. The following observations can be made on the basis of Table 4: with 95% confidence, we can say that the true mean values of pH, HCO_3^-,

Chloride and Sodium, are well within the permissible limits given by WHO [1993].With the same confidence coefficient, we can interpret that, TDS, Ca^{++}, Mg^{++}, F^- and SO_4^{2-} have started crossing the permissible limits. Bicarbonate is on the verge of crossing its permissible limit. This statement is made on the basis of a *relatively lower gap* between the upper limit of the confidence interval with respect to HCO_3^- and the permissible limit of WHO [1993].

These arguments hold good for the given geographical location, *provided* the environmental and geochemical conditions under which the sampling has been done remains the same.

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Table 7. Showing the LSI categories for different sampling locations

Sample No	pHs	LSI	Inference
1	6.7	0.77	Scale forming but non corrosive.
2	6.6	0.27	Slightly scale forming and corrosive
3	6.8	0.12	Slightly scale forming and corrosive
4	6.7	0.65	Scale forming but non corrosive.
5	6.8	0.49	Slightly scale forming and corrosive.
6	7.0	-0.044	Slightly corrosive but non-scale forming
7	6.5	0.74	Scale forming but non corrosive.
8	6.6	0.61	Scale forming but non corrosive
9	6.8	0.055	Slightly scale forming and corrosive
10	6.7	0.39	Slightly scale forming and corrosive.
11	6.7	0.59	Scale forming but non corrosive.
12	6.8	0.12	Slightly scale forming and corrosive.
13	6.8	0.35	Slightly scale forming and corrosive.
14	6.9	0.073	Slightly scale forming and corrosive.
15	6.7	0.91	Scale forming but non corrosive

Table 8. Showing the Stuyfz and classification of water samples

Chloride type	Chloride [ppm]	Sample nos
Very Oligohaline	< 5	
Oligohaline	5-30	
Fresh	30-150	[μ=6] 1,6,9,10, 13,14
Fresh-Brackish	150-300	[μ=9]2,3,4, 5,7,8,11,12,15
Brackish	300-1,000	
Brackish – Salt	1,000-10,000	
Salt	10,000-20,000	
Hypersaline	>20,000	

Table 9. Showing Sawyer classification of water samples

Hardness as CaCO$_3$	Water class	Water samples
0-75	Soft	-
75-100	Moderately hard	-
150-3000	Hard	1 to 15
>3000	Very hard	-

5.18.2 Pearson's correlation

The matrix in the Table-5 shows the sample correlation co-efficient [r] between all pairs of water quality variables. [In the present study 15C$_2$ pairs]. These sample values are the estimates of the true Pearson's correlation co-efficient between the respective pairs of variables. In the sample data used for our study, the true correlation between the variables will be insignificant at α=5% if -0.513912 < r <0.513912.This range has been fixed using the formula:

$$- [1+\frac{t^2 \alpha/2[n-2]}{[n-2]}]^{-1/2} < r < [1+\frac{t^2 \alpha/2[n-2]}{[n-2]}]^{-1/2}$$

The bold values in the matrix of Table 5 should be taken to be significant at α = 0.05.

Lead and Chromium are absent in the sample observations gathered in the study. Hence they been omitted from the correlation matrix. pH, Sodium, Potassium and Fluoride are not exhibiting any significant linear relationship with the other water quality variables. Sulphate is significantly correlated with all the water quality variables except pH, Sodium, Potassium and Fluoride. EC is linearly correlated with TDS, TH, Chloride, bicarbonate, Calcium and Magnesium except pH, Sodium, Potassium and Fluoride. TDS, TH and Chloride are correlated with pH, Sodium, Potassium and Fluoride, but insignificantly. Bicarbonate is also having the same relation with the above three water quality variables additionally with one more variable namely calcium.

6. CONCLUSION

As per the current study of the groundwater along the Vrishabhavathi river basin, the water quality variables viz., Magnesium, Sulphate, Calcium, Bicarbonate, Chloride, Total Hardness, Total Dissolved Solids, and EC are observed to be interlinked at 5% level of significance.

Excluding Lead and Chromium, with 95% confidence we can conclude that nearly 50% of the remaining 13 water Quality variables have started crossing the permissible limits of WHO [1993] provided the environmental and geochemical conditions remain unaltered. From the Piper plot, it is evident that the water samples are rich in Calcium, Magnesium, Bicarbonate, and Chloride which is also confirmed by the LSI calculation where all the samples majorly fall into category D [Slightly scale forming and corrosive] which shows the alkaline nature of the groundwater samples. The water may be used for the domestic consumption after simple methods of purification namely Reverse Osmosis through which, the quantity of ions present in excessive amounts can be controlled. The dense urbanization and industrialization on the banks of River Vrishabhavathi is the main reason for its pollution as it paves way for easy disposal of anthropogenic wastes [both domestic and industrial] directly or indirectly into the stream. It is high time that the concerned authorities at the state and national domain should focus on this problem and think it in the positive direction of solving the water contamination issue. Further, the residents along the river banks should be educated about the ill effects of waste disposal into the environment [also into the river]. Rejuvenating the river with fresh water may greatly solve the current water crisis undergoing by the study area in the Bengaluru Metropolis. It also sets a check to severe health problems caused by the [indirect] consumption of the polluted water. There is a dearth for a driving force to solve this major issue.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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