NATURAL AND ANTHROPOGENIC CONTAMINANTS IN DUG WELLS ALONG PAMPA RIVER BANK

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ABSTRACT

Seasonal distribution of groundwater and river water quality along a 40 km Chengannur-Maramon stretch of Pampa river,central Kerala was studied. Natural and anthropogenicinfluence in water quality was studied during 2015-2017 period. After detailed observation in selected areas with particular reference to physiography, subsurface lithologic characteristics, three wells and a corresponding riverine spot were selected each in four locations such as Edanad, Arattupuzha, Thottappuzhassery and Maramon for water sample collection. Samples were collected during seasonally and analysed for pH, conductivity, Total dissolved solids (TDS), bicarbonate (HCO_3), dissolved CO_2 (dCO_2), Na, K, nitrate, sulphate, phosphate and total Iron following standard methods (APHA, 1998).

Results showed that the groundwater in the study area is characterized by acidic pH, moderate conductivity and TDS concentration. Factors affecting the fate of contaminants include climate, land and water usage, soil and contaminant properties and the prevailing geology and hydrogeology. Natural processes leading to changes in water quality include weathering of rocks, evapotranspiration, depositions due to wind, leaching from soil, run-off due to hydrological factors, andbiological processes in the aquatic environment. These natural processes cause changes in the pH and alkalinity of the water, and also phosphorus loading and high concentrations of sulphates. Values of Na, K, SO_4 and HCO_3 in the study area showed that the major source of contamination is through non-point sources. It is also observed that the river water quality during the non-monsoon season almost resembles with the groundwater quality of the adjoining aquifer. However, during NE monsoon/post SW monsoon period a considerable variation was found between groundwater and surface water quality which can be attributed to the movement of fertilizers and agricultural ashes with monsoon flows reaching the stream along with overland flow.

Key words: Groundwater quality, aquifer system, lateritic soil, surface run off, Pampa river

Introduction

There is a growing concern about the toxicity, persistence and bioavailability of a wide range of contaminants in groundwater. Once contaminated, it is difficult to restore the quality of ground water. Hence there is a need and concern for the protection and management of ground water quality. No straight forward reasons can be attributedto the deterioration of water quality, as it is dependent on several parameters. Sources of groundwater contamination can be naturally occurring or anthropogenic. Factors affecting the fate of contaminants include climate, land and water usage, soil and contaminant properties and the prevailing geology and hydrogeology. Pollution attributable to sources such as runoff from roadways, parking lots and other development on riparian areas, coupled with the removal of streamside vegetation, reduces the natural ability of self –purification of water resources. Runoff results from nonpoint source pollution may not be noticeable, but added together, they can have a significant impact on water quality. Anthropogenic factors affecting water quality of a river cause elevated concentrations of nutrient loads in the adjacent ground water also. To deal with point source and non-point source pollution in ground water, a comprehensive scale of analysis and management is required.

Under this context the present studyfocuses on to understand the natural and anthropogenic contamination in dug wells along the Pampa river between Chengannur and Maramon stretch.

Objectives of the study

1. To identify natural and anthropogenic contamination of dug wells along Pampa river bank.
2. To examine the influence of seasons on natural and anthropogenic contamination of dug well waters along Pampa river bank.

Study area

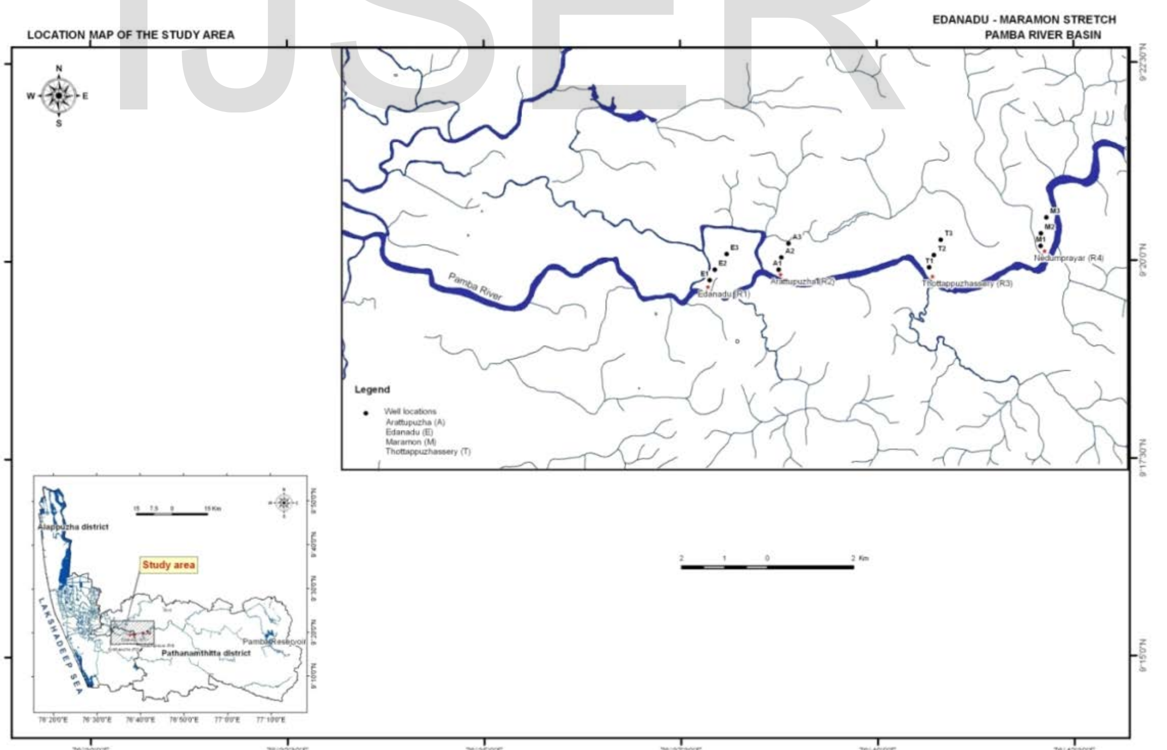


Fig. 1. Location map showing sampling points

Methodology

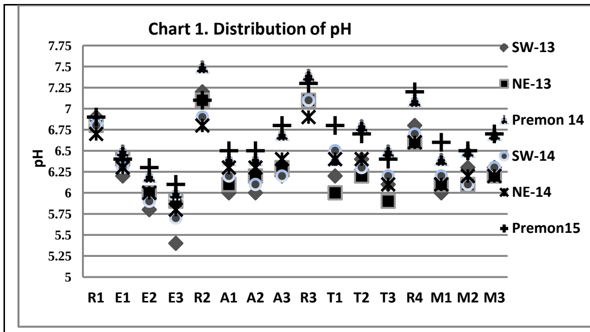
The study was confined to 40 km stretch of Pampa river bank which is made up dominantly of Quaternary sediments of highly diverse lithological characteristics. A detailed observation in selected areas with particular reference to physiography, subsurface lithologic characteristics based on dug well sections and direct observations on available drainage channels was made. Three wells were selected each in four locationssuch as Edanad, Arattupuzha, Thottappuzhassery and Maramon for water sample collection and a corresponding riverine spot is identified in the river channel closest to each of the four locations. Samples were collected during South West (SW) monsoon {June-September}, North East (NE) monsoon {October – December} and premonsoon {January – May}seasons of 2015-2017 period. Analysis was carried out for pH, conductivity, Total dissolved solids (TDS), bicarbonate (HCO_3), dissolved CO_2 (dCO_2), Na, K, nitrate, sulphate, phosphate and total Iron following standard methods (APHA, 1998).

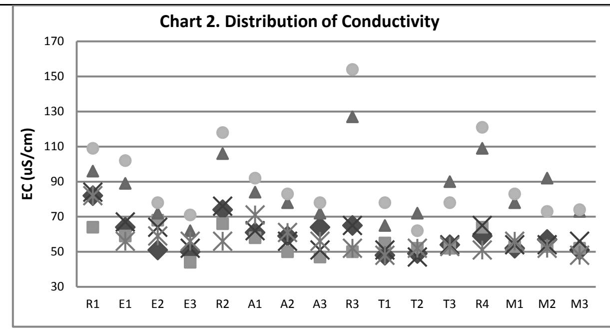
Particulars of dugwell stations

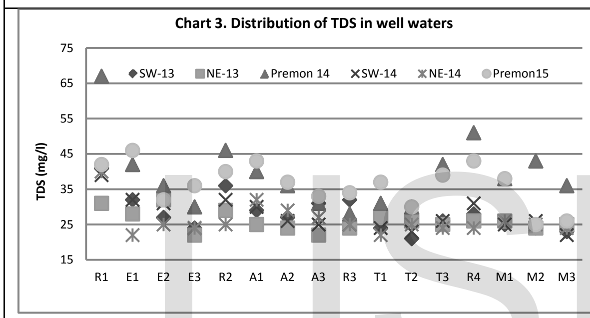
S. No.	Location Name	Total depth (m)	Distance from river (m)
1	Eadnad (E1)	6.6	1000
2	-do- (E2)	6.57	700
3	-do- (E3)	9.26	120
4	Arattupuzha (A1)	8.49	50
5	-do- (A2)	7.2	80
6	-do-(A3)	5.7	50
7	Thottappuzhasseri (T1)	8.49	100
8	-do- (T2)	7.2	75
9	-do- (T3)	8.0	250
10	Maramon (M1)	7.05	150
11	-do- (M2)	6.55	150
12	-do- (M3)	8.55	150

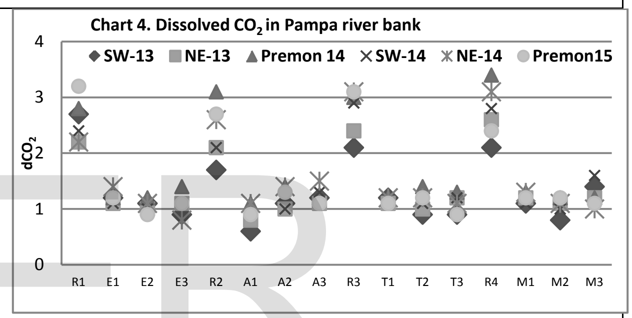
Results and discussion of the study

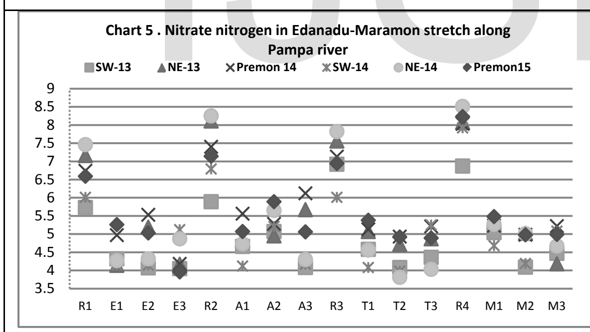
Distribution of pH in well and river waters along Pampa river bank: pH values broadly fluctuated from 5.3 at well no.3 at Edanad in SW monsoon 2015 to 7.5 from river water at Arattupuzha during premonsoon 2016. Mean pH was generally higher during premonsoon and post monsoon and lower during monsoon seasons. Impact of monsoon on pH value of river water was visible in all stations except Edanad. Though the values of all river samples were within the prescribed limits (BIS, 1991), well waters showed pH <6.5. This can be attributed to the acidic lateritic soil found in midlands of Kerala and to the influence of fertilizers like ammonium sulphate and super phosphate used in agriculture (Raghunath et al 2001). pH values @ 6.1 to 6.9 was recorded earlier from Pampa by Koshy (2001). Jalal and Kumar (2013) attributed slightly alkaline pH in river water at Chengannur to the presence of industrial effluents. The impact of rainfall at the sampling stations might have influenced the marginal changes with respect to carbonate and bicarbonate ions as reported by Sivasankar and Ramachandramoorthy (2009)in Ramanathapuram District of Tamilnadu.

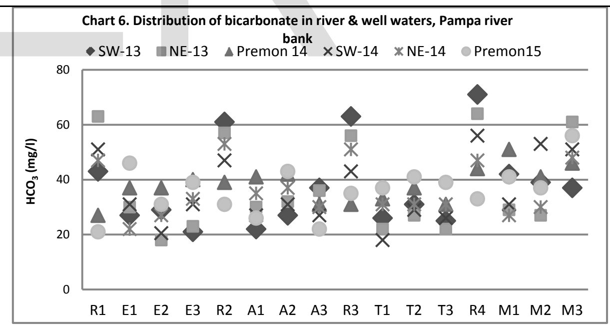


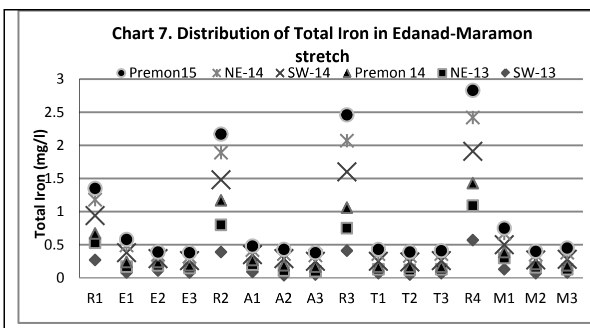


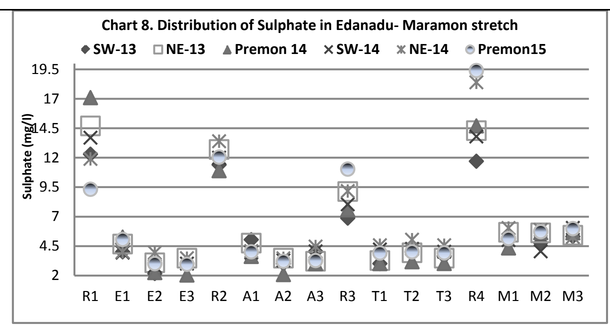


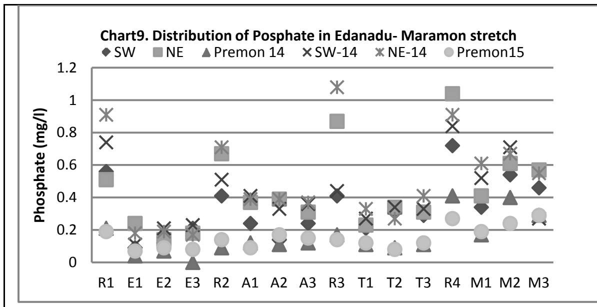


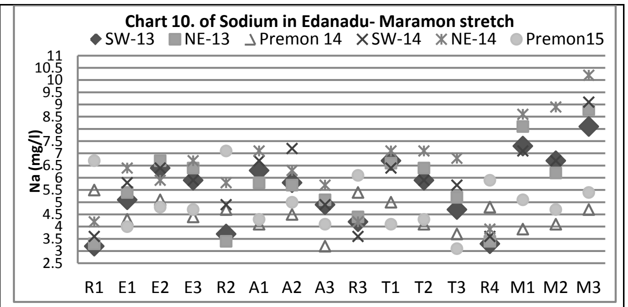












Conductivity in river and well waters along Pampa River bank: Conductivity values fluctuated between 44µmhos/cm in Edanad during NE monsoon 2016 to 127µmhos/cm in river station at Thottappuzhasseri during premonsoon 2016 (fig. 2). In general, the study indicates that both surface and ground water in the study area have conductivity below the recommended standards. Comparatively higher values noticed in pre and post-monsoon periods may be due to stagnation of water due to sand mining, decreasedwater volume and minerals coming through drainage and paddy fields. Conductivity values that vary from 70 - 1437 µmhos/cm meeting the criteria limit for drinking as well as irrigation purposes are reported by Central Pollution Control Board (MINARS-2010) from rivers of Kerala. The present conductivity values ofwell water are similar to that reported by CGWB (2014) and CPGB (MINARS-2010) from Alappuzhadistrict. Generally higher EC values noticed during pre-monsoon corroborate with observations of Sharma and Panda (1998).

Total Dissolved Solids (TDS) in river and well waters: TDS values broadly ranged between 21mg/l in Thottappuzhasseri(well no.2) in SW monsoon 2015 to 67mg/l in river station at Edanad during premonsoon 2016. In drinking water, the TDS may be due to dissolved inorganic salts, organic matter and dissolved gas. The solidsare composed mainly of carbonates, bicarbonates, chlorides, phosphates and nitrates of calcium, magnesium, sodium, potassium and manganese, organic matter, salt and other particles (Mahananda, 2010) contributed by anthropogenic contamination and local lithology. It is observed that the TDS variations are mainly controlled by Sodium (r=0.89), Potassium (r = 0.69) and Sulphate (r = 0.92) and TDS (r = 0.96) concentration. Significant interrelated values of TDS with K (r = 0.85), NO_3 (r = 0.97), SO_4 (r = 0.85) was also reported by Mufid al-hadithi (2012).Allthe ground water samples of the study area are registered with 100% belonging to fresh type (TDS<1000 mg/L) in both pre-monsoon and post-monsoon seasons as per TDS classification given by Fetter (1990).

Dissolved CO_2 in river and well waters along Pampa river bank: Dissolved CO_2 concentration fluctuated between 0.6mg/l from well one at Arattupuzhaduring SW monsoon 2015 to 3.4mg/l in premonsoon 2016 at river station in Maramon during premonsoon 2017 (fig. 4). The amount of carbon dioxide determines the pH of water. Dissolved carbon dioxide, which forms carbonic acid in water, is an important control on the pH of natural waters and thus an important component of the buffer system (Hem, 1985). Current values corroborate with that of Shyamsunder (1988) who reported a mean value of 3.2 and 3.6mg/l in a stretch of Jhelum river. However, an earlier study in Pampa (Koshy, 2001) reported CO_2 in the range of 4.5-14.4mg/l and more recently a mean value of 0.81± 0.2 in monsoon, 1.11±0.0 in premonsoon, 1.11±

0.033mg/l in premonsoon and 1.11±0.02mg/l in summer was reported by Jalal and Kumar (2013). High free CO_2 noticed during summer in almost all stations was similar tothe results reported from Kalpathypuzha in Palakkad, Kerala (Divya and Manonmani, 2013).

Nitrate nitrogen in river and well water along Pampa river bank: Nitrate nitrogen concentration varied broadly from 3.81mg/l in NE monsoon 2015 in well 2 at Thottappuzhasseri to 8.51mg/l in NE monsoon 2016 at river station in Maramon during NE monsoon 2016 (fig. 5). Values are moderate both in ground water and river water though the monsoon elevates nitrate in the river water possibly due to surface runoff. The observed decrease in nitrate under rising water table conditions is due to dilution by rainwater, and in contradiction, the exceptional increase during monsoon in few wells may have caused by the contribution of NO_3 from the clayey soil. Also, under aerobic conditions, nitrate can percolate in relatively large quantities into the aquifer when there is no growing plant material to take up the nitrate and when the net movement of soil water is downward to the aquifer. The processes of sorption, retention and slow denitrification in clay are probably responsible for the contribution of nitrate to the groundwater in the SW monsoon season and post monsoon season. The current values are much higher than that of an earlier study by CPCB from Pampa river at Chengannur region which reported nitrate concentration @ 0.98-2.4mg/l (MINARS-2010). The presence of high or low water tables, the amount of rainwater, the presence of organic material and certain physicochemical properties are important determinants on the fate of nitrate in soil (Fewtrell, 2004).

Using the threshold of 3.0mg/l, the distribution of nitrate in the current study should be viewed with evidence of anthropogenic contamination. Risk to underlying groundwater emanates from the anthropogenic activities which are generally determined by land use and the associated management practices. High concentration in river water observed after the onset of rains may be due to runoff from the land drainage during monsoon and the sewage discharge in to the river. Thomas Mathews (2001) also made similar observation in his study on Pampa. Generally low concentration of nitrates was reported from major Indian rivers like Cauvery (Somasekhar, 1988)and Nandira (Tripathy and Adhikari, 1990). Nitrate content in Kuttanand region in the range of 5 to 17 ppm (mean: 11 ppm) was reported by CGWB (2014).
Sewage infiltration can also contribute to nitrate contamination in ground water. Rao et al (2013) in their geochemical studies in Mulbagal town, Karnataka State, showed leachate infiltration imposed nitrate concentrations ranging from 4 to 388mg/L in the groundwater samples.As per Madison and Brunett's (1984) concentration criteria, nitrate levels of less than 0.2 mg/L are considered to represent natural levels, from 0.21 to 3.0 mg/L are considered transitional which may or may not represent human influences and concentrations between 3.1 and 10 mg/L may represent elevated concentrations due to anthropogenic activities.

Distribution of bicarbonate in river and well waters along Pampa river bank: Bicarbonate values broadly fluctuated between 18.0mg/l during NE monsoon 2013 and SW monsoon during 2014 in well 2 at Edanad and to 71mg/l in 2013 at river station in Maramon during SW monsoon 2013 (fig. 6). Bicarbonates are formed in considerable amount from the action of carbon dioxide upon basic materials in soil and other salts of weak acids (APHA, 1998). The primary source of carbonate and bicarbonate ions in groundwater may be the dissolution of carbonate minerals in the study area. The decay of organic matter present in the soil releases CO_2. Water charged with CO_2 dissolves carbonate minerals, as it passes through soils and rocks to give bicarbonates. Bicarbonates dominate the anions in groundwater and the observation corroborates with the findings of Priju et al (2014) from the ground waters of the eastern part of the Kochi. Water in a Quaternary aquifer in USA predominately calcium-bicarbonate-type water with median dissolved-solids concentration of 439 mg/l was reported by Mashburn et al (2003).

The values observed in the present study are similar to the lower ranges reported from Bharathappuzha(Kannan and Joseph, 2009).Bicarbonate at slightly higher levels in the post-monsoon period indicates that some contribution might have come from the carbonate weathering process due to heavy downpour in the catchment as reported by Khound et al (2012) from JiaBharali river basin. This indicates that bicarbonate content is largely determined by CO_2 – water equilibrium followed by generation of carbonic acid, H_2CO_3 that interacts with the primary minerals increasing the bicarbonate concentration.

Total Iron in river and well water in Pampa river bank: Total Iron concentration broadly fluctuated from 0.04mg/l during premonsoon 2016 in well 3 at Edanad, SW monsoon 2015 in well 2 at Arattupuzha and premonsoon 2016 in well 1 and3 at Maramon to 0.54mg/l in SW monsoon 2017 at river water in Maramon. Although iron is an essential mineral helping in the transportation of oxygen in the blood, its presence in ground water above a certain level makes water unusable. Rainwater as it infiltrates the soil and underlying geologic formations dissolves iron, causing it to seep into aquifers that serve as sources of ground water. Water containing ferrous iron is clear and colourless due to its soluble nature. On exposure to air the ferrous iron is converted to ferric iron and turns water reddish brown appearance which then precipitates into sediment. The rates of oxidation are not rapid and this reduced form can persist for some time in aerated water at pH below 6. In addition, iron can form stable complexes with humic and tannic substances in water that can be even more resistant to oxidation than the inorganic species alone (Sawyer, 2003). The presence of iron in ground water is a direct result of its natural existence in underground rock formations and precipitation water that infiltrates through these formations. As the water moves through the rocks some of the iron dissolves and accumulates in aquifers which serve as a source for ground water.

The iron concentration observed in ground water in the study area is expected in lateritic soil. Mean iron concentration during different seasons showed significant difference. Lower concentration was observed during summer and premonsoon, whereas, monsoon and post monsoon concentrations were higher with the highest value during post monsoon. The increase in concentration of iron observed in some wells during rainy season could be due to leaching of iron naturally present in lateritic soil. The unlined nature of wells facilitated its entry, increasing iron content after rain. However, iron concentration in the groundwaters in the present study falls below the permissible WHO standard (0.3mg/l) irrespective of space and time (WHO, 1993). The river water crossed this threshold particularly in rainy season (fig. 7). However, all values in the study area fall within the standard (1.0mg/l) prescribed by BIS (1991). Kerala is counted among the top five states in terms of the presence of iron and nitrates in groundwater and Pathanamthitta district was also included in the parts of districts in Kerala state having iron >1.0 mg/litre by CGWB (2010). Iron observed indug wells are <1.0mg/l that can be removed by precipitation by aeration and filtration through activated charcoal if needed.

Sulphate in river and well waters in Pampa river bank: Sulphate concentration broadly fluctuated between 2.04mg/l in well 3 at Edanad during premonsoon 2016 and 19.4mg/l in premonsoon during 2017 in river station at Maramon (fig. 8). The acceptable limit of sulphates in drinking water is 200mg/l. Sulphate concentrations observed in the present study are below the desirable limit and indicate that the origin of sulphate is mainly from natural sources. The sulphateranging from 0.325 to 15.75 mg/l during monsoon season and from 2.5 mg/l to 12 mg/l during summer was reported by Paul et al (2014) from ground waters of NellikkuzhiPanchayat in Kerala. Sulphate values @ 2-16mg/l reported by Athira and Jaya (2014) from Anjarakandy river in Kannur, Kerala corroborate with the values observed in the present study. In most of the dug wells in the current study, the sulphate content is more in the wet season possibly due to action of leaching and anthropogenic activities in a metamorphic environment. The occasional higher values observed in the river water during pre and post monsoon season can be attributed to anthropogenic contribution.

Phosphate in river and well waters: Phosphate concentration broadly fluctuated between nil in well 3 at Edanad during premonsoon 2015 and 1.08mg/l in NE monsoon during 2017 in river station at Maramon. Anthropogenic sources of phosphate in groundwater include domestic sewage, animal wastes, agricultural effluents with fertilizers and industrial effluents. There are no drinking water guidelines for phosphorus, however the Australian Water Quality for Fresh and Marine Waters (ANZECC, 1992) suggest that total phosphorus concentrations at or above the range of 0.01 to 0.1 mg/l may cause undesirable algal growth in inland surface waters. Phosphate in natural water mostly ranges between 0.005 and 0.020 mg/l (Chapman and Kimstach, 1992). For this range, values of all samples in the study area are comparatively higherduring all seasons. Its quantity in the present investigation ranges from below detectable levels to 0.71mg/L during monsoon season in Maramon (fig. 9). The valuesare highly fluctuating and reaches peak during post SW monsoon. Spatial and temporal variation was negligible except the high occurrence at Maramon, a highly urbanised point among the study stations. High values noticed during premonsoon can be attributed to reduced water flow and detergents used during washing and bathing while high values in monsoon can be attributed to surface runoff and sewage discharge. Use of phosphate as fertilizer perhaps contributed to its presence in surface water as the basin is predominantly agricultural and in Kerala, application of fertilizers is a common practice as reported by Chattopadhyay et al (2005) from Chalakkudy river basin in Kerala. This together with the surface water runoff might have elevated phosphate level in the river water. The enrichment of phosphate in monsoon period reveals that leaching through soil has a strong bearing on the nutrient levels in groundwater (Babu*et al*., 2007).

Sodium in river and well water along Pampa river bank: Sodium concentration broadly fluctuated between 3.1mg/l in well 3 at Thottappuzhasseri during premonsoon 2017 and 10.2mg/l in NE monsoon during 2017 in well 3 at Maramon. All groundwater contains traces of sodium because most rocks and soils contain sodium compounds from which sodium is easily dissolved. For aesthetic reason the guideline value given by WHO is 200mg/L. *The ranges of sodium concentration in the aquifer samples show higher values in the wet season than that in the dry season.* However all the aquifers show Na content well below the WHO (1993) recommended value of 200 mg/L and the BIS (1991) permissible limit of 60 - 120 mg/l. It is confirmed that all the dug wells were characterized by low amount of sodium (>200 mg/l) indicating no influence of saline water incursion (fig.10). ~~Majority of the surface water samples show higher values of sodium in dry season than in the wet season~~. Being entrapped water bodies, the surface waters are likely to accumulate Na from domestic effluents and runoff. Value as high as 388mg/l is reported from areas of Palakkad (Kumar *et al*., 2014) which are covered mainly by hornblende-biotitegneiss and are migmatised.

Pottassium in river and well watersalong Pampa river bank: Potassium concentration broadly fluctuated between 0.91 in well two during premonsoon 2017 at Edanad and 7.1mg/l in NE monsoon during 2016 in well three at Maramon (fig.11). Though potassium is extensively found in some of igneous rocks such as feldspars, mica and sedimentary rocks as well as silicate and clay minerals, its concentration in natural waters is usually quite low. This is due to the fact that potassium minerals offer resistance to weathering and dissolution. K contamination in groundwater can result from the application of inorganic fertilizer at greater than agronomic rates (WHO, 1993). Neither BIS nor USEPA lay down any limits for potassium content in drinking water except the prescribed the guideline level of 10 mg/l in drinking water by the European Economic Community (EEC). Though, most of the source rocks contain approximately equal amounts of Na and K, and both are released during weathering, a part of the K goes into clay structure and thereby its concentration gets reduced in water.
Meena and Bhargava (2012) demonstrated that the seasons' effect does change the concentration of various ions including K^+.Higher values appear in post-monsoon period. Potassium content in ground water was in the range of 0.5-47.5mg/l and 0.6-8.2mg/l respectively in pre and post monsoon season. Raju and Puttaiah (2012) reported 0.1 – 21 mg/l from ground waters along the Vrushabhavathi River stream in Karnataka. Values varying from 2.6 to 22.7 mg/l in wet season and 2.0 – 16.7 mg/l in dry season were reported by Khound et al (2012) from Jia – Bharali river basin, Assam. Values in the range of 32 to 60mg/l were reported by Farid et al (2012) from Pakistan. Adegbola et al (2015) attributed high values of K in groundwater to the presence of clay, a rich source of potassium. As in the case of Na, majority of the surface water samples showed more potassium content in the dry season than in the wet season.

Correlation between physicochemical parameters
In general, pH values positively correlated with conductivity, TDS, bicarbonate, dissolved CO_2, nitrate nitrogen, sulphate and total iron and negatively correlated with Na and K. Positive correlation was observed between conductivity and pH, TDS, dissolved CO_2, nitrate nitrogen, sulphate (0.01) and total iron (0.05) and negatively correlated with Na, K and phosphate. TDS expressed positive correlation with pH, conductivity, dissolved CO_2, nitrate nitrogen and sulphate and negatively correlation with Na, K and phosphate. Na showed positive correlation with K and negative correlation with pH, conductivity, TDS, bicarbonate, dissolved CO_2, nitrate, sulphate and total Iron while K showed positive correlation with Na (0.01 level) and pH(0.05) and negative correlation with pH, conductivity, TDS (0.01 level), dissolved CO_2 and phosphate (0.05 level). Positive correlation was seen between bicarbonate Vs pH, dCO_2, dissolved CO_2, nitrate, phosphate, sulphate and total Iron and negative correlation with Na. Dissolved CO_2 indicated positive correlation Vs pH, conductivity, TDS, bicarbonate, nitrate, phosphate, sulphate and Total iron and negative correlation Vs Na and K. Nitrate values revealed positive correlation with pH, conductivity, TDS, bicarbonate, dCO_2, phosphate, sulphate and Total iron and negative correlation with Na while phosphate showed positive correlation with bicarbonate, dCO_2, nitrate, sulphate (0.01 level) and K (0.05) and negative correlation Vs conductivity and TDS. Correlation of sulphateVs pH, conductivity, TDS, bicarbonate, dCO_2, nitrate, phosphate and Total iron was positive while that Vs Na was negative. Total Iron showed positive correlation with pH,

bicarbonate, dCO_2, nitrate, phosphate, sulphate (0.01 level), conductivity (0.05 level) and negative correlation with Na.

There exists strong correlations among different parameters and a combined effect of their inter-relatedness indicates the water quality (Jothivenkatachalam*et al*., 2010). During SW monsoon 2015, correlation was very conspicuous between pH and EC, TDS, bicarbonate, CO_2, NO_3, PO_4 and Fe, Na^+, K^+ and SO_4^{2-}. Similar positive correlation between TDS and conductivity was reported by Joshi and Sati (2011). Both in ground and surface waters, there exists significant correlation of pH with EC and TDS. Significant correlation of EC with TDS and CO_2, TDS with CO_2 was also reported by Jagadeeshappa and Vijayakumara (2013). Heydari et al (2013) also recorded positive correlation between nitrate and pH, TDS and sulphate, EC and sulphate, Na^+ and sulphate and Na^+ and K^+. Conductivity showing significant correlation with pH, free CO_2, TDS, phosphate and sulphate concentration of water was also reported by Kumar (2010). The TDS showed significant and positive correlation with EC, Nitrate, Phosphate and Magnesium and the pH showed significant negative correlation with TDS, EC, and Nitrate for Ganga river water (Khatoon*et al*., 2013) and in ground water by Sharma and Chippa (2013). Strong correlation between TDS and NO_3 (r=0.654) was also observed by Charkhabi and Sakizadeh (2006) in ground waters. TDS showing high positive correlation indicate that electrical conductivity increases as the concentration of all dissolved constituents/ions increases. It is observed that the TDS variations are mainly controlled by calcium (r = 0.9), Sodium (r=0.89), Potassium (r = 0.69), Nitrite (0.85) andSulphate (r = 0.92) concentration (Mufid al-hadithi, 2012).Na^+ with K^+, SO_4^{2-} also shows good to very good correlation (0.470-0.825). Sodium showed significantly positive correlation (r = 0.77) with potassium and results are in accordance with the findings of Jain et al (2005). From the above observations, it can be postulated that the concurrent increase/decrease in the composition of ions in these waters is predominantly due to the result of dissolution/precipitation reaction and concentration effects.

Natural and anthropogenic influence and seasonal impact on water quality

Low pH observed in the dug well waters can be attributed to the acidic lateritic soil found in midlands of Kerala and to the influence of fertilizers like ammonium sulphate and super phosphate used in agriculture. Comparatively higher conductivity values noticed in pre and post-monsoon periods may be due to stagnation of water due to sand mining, decreased water volume and minerals coming through drainage and paddy fields. All the ground water samples of the study area are registered with 100% belonging to fresh type (TDS<1000 mg/L) in both pre-monsoon and post-monsoon seasons as per TDS classification. High free CO_2 noticed during summer in almost all stations. Nitrate nitrogen values are moderate both in ground water and river water though the monsoon elevates nitrate in the river water possibly due to surface runoff. Using the threshold of 3.0mg/l, the distribution of nitrate in the current study should be viewed with evidence of anthropogenic contamination from sewage discharge and surface run off during monsoon. The primary source of carbonate and bicarbonate ions in groundwater may be the dissolution of carbonate minerals in the study area. The decay of organic matter present in the soil releases CO_2. Bicarbonate at slightly higher levels in the post-monsoon period indicates that some contribution might have come from the carbonate weathering process due to heavy downpour in the catchment. The presence of iron in ground water is a direct result of its natural existence in underground rock formations and precipitation water that infiltrates through these formations. In most of the dug wells in the current study, the sulphate content is more in the wet season possibly due to action of leaching and anthropogenic activities in a metamorphic environment. Sulphate concentrations below the desirable limit indicate that their origin is mainly from natural sources. In most of the dug wells, the sulphate content is more in the wet season possibly due to action of leaching and anthropogenic activities in a metamorphic environment. High phosphate values noticed during premonsoon can be attributed to reduced water flow and detergents used in washing and bathing while high values in monsoon can be attributed to surface runoff and sewage discharge. Use of phosphate as fertilizer perhaps contributed to its presence in surface water as the basin is predominantly agricultural land. This together with the surface water runoff might have elevated phosphate level in the river water. The enrichment of phosphate in monsoon period reveals that leaching through soil has a strong bearing on the nutrient levels in groundwater. The ranges of sodium concentration in the aquifer samples show higher values in the wet season than that in the dry season. However, majority of the surface water samples show higher values of sodium in dry season than in the wet season. High values of K in groundwater may be due to the presence of clay, a rich source of potassium. As in the case of Na, majority of the surface water samples showed more potassium content in the dry season than in the wet season.

Conclusion

Groundwater in the study area is characterized by acidic pH. Under-saturation of the groundwater samples with calcite can be attributed to increased dissolution of the mineral in the acidic environment of the groundwater as suggested by Rao et al (2013). Factors affecting the fate of contaminants include climate, land and water usage, soil and contaminant properties and the prevailing geology and hydrogeology. Natural processes leading to changes in water quality include weathering of rocks, evapotranspiration, depositions due to wind, leaching from soil, run-off due to hydrological factors, andbiological processes in the aquatic environment. These natural processes cause changes in the pH and alkalinity of the water, and also phosphorus loading and high concentrations of sulphates. Values of Na, K, $SO_4$and HCO_3in the study area showed that the major source of contamination is through non-point sources. It is also observed that the river water quality during the non-monsoon season almost resembles with the groundwater quality of the adjoining aquifer. However, during NE monsoon/post SW monsoon period a considerable variation was found between groundwater and surface water quality which can be attributed to the movement of fertilizers and agricultural ashes with monsoon flows reaching the stream along with overland flow.

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Reference

Adegbola, A., Oluwatosin, A., Akeem, J., Adewale, A and Opeyemi, A (2015). Physico-Chemical Evaluation of Groundwater Quality in Lawyer Hammed Street, Stadium Area, Ogbomoso, Nigeria. *International Journal of Management, Information Technology and Engineering*, **3**(3):17-26.

ANZECC (Australian and New Zealand Environment and Conservation Council). (1992). Australian water quality guidelines for fresh and marine waters. National Water Quality Management Strategy, Canberra, Australia.

APHA, (1998). Standard Methods for the Examination of Water and Wastewater, 20th Ed. Washington, D.C.

Athira, N and D.S. Jaya (2014). Assessment of water quality status of Anjarakandy river in Kannur district of Kerala, *Asian Journal of Environmental Science*, **9**(2): 68-74.

Babu, K.N., Padmalal, D., Maya, K., Sreeja, R. and Arun, P.R., (2007). Quality of Surface and Ground Water around Tile and Brick Clay Mines in the Chalakudy River Basin, SWern India. *Jour. Geol. Soc. India*, **69**: 279-284.

BIS (Bureau of Indian Standards) (1991). Indian Standards for drinking water specification (BIS 10500: 1991).

CGWB (2010). Central Ground Water Board, Ministry of Water Resources, Government of India. *Ground Water Quality in Shallow Aquifers of India*. Faridabad. February

CGWB (2014). Report on status of ground water quality in coastal aquifers of India (2014). Government of India, Ministry of Water Resources, *Central Ground Water Board*, Faridabad, February 2014.

Chapman, D. and Kimstach, V. (1992). Selection of water quality variables. In: Chapman, D. (Ed.), *Water Quality Assessment UNESCO, WHO and UNEP*, pp. 59–126.

Charkhabi, A. H. and Sakizadeh, M. (2006). Assessment of Spatial Variation of Water QualityParameters in the Most Polluted Branch of the Anzali Wetland, Northern Iran. M. Sakizadeh, *Polish J. of Environ. Stud.*,**15**(3): 395-403.

Chattopadhyay, S., Asa Rani, L. and. Sangeetha, P.V., 2005. Water quality variations as linked to landuse pattern: A case study in Chalakudy river basin, Kerala. *Curr. Sci.*, **89** (12): 2167p.

Divya, K. R. and K. Manonmani (2013). Assessment of water quality of river Kalpathypuzha, Palakkad district, Kerala. *IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)*, **4**(4): 59-62.

Farid, S., Baloch, B. M and Ahmad, A. S. (2012). Water pollution: Major issue in urban areas, *International Journal of Water Resources and Environmental Engineering*. **4**(3): 55-65.

Fetter, C. W. (1990). TDS classification, *Applied hydrology*, New Delhi, CBS, 1990.

Fewtrell, L (2004) Drinking-water nitrate, methaemoglobinaemia, and global burden of disease: a discussion. *Environmental Health Perspectives*, **112**(14):1371–1374.

Hem, J. D. (1985). Study and interpretation of the chemical characteristics of natural water (3d ed.): *U.S. Geological Survey, Water Supply Paper*, 2254.

Heydari, M. M., Abasi, A., Rohani, M. S. and Ali, M. S. (2013). Correlation Study and Regression Analysis of Drinking Water Quality in Kashan City, Iran, *Middle-East Journal of Scientific Research*, **13** (9): 1238-1244.

Jagadeeshappa, K. C. and Vijayakumara (2013). Physico-chemical characteristics of water Invignasanthe wetland, Tikpur, *Nature Environment and Pollution Technology*, **12** (1):115-119.

Jain, P., Sharma, J. D., Sohu, D and Sharma, P. (2005). Chemical analysis of drinking water of villages of Sanganer Tehsil, Jaipur District. *Intnl. J. Environ. Science and Tech.*, **2**(4): 373- 379.

Jalal, N. F., and Kumar M.G.S. (2013). Water Quality Assessment of Pamba River of Kerala, India in Relation to Pilgrimage Season. *Int. J. Res. Chem. Environ.*, **3**(1): 341-347.

Joshi, N and Sati, V. (2011). Assessment of Water Quality of River Ganges at Haridwar during KumbhMela - 2010, *Report and Opinion*, **3**(7): 30-36. http://www.sciencepub.net/report

Jothivenkatachalam, K., Nithya, A and S. Chandra Mohan (2010). Drinking Water Quality In Coimbatore District. *Rasayan J. Chem*., **3**(4): 649-654. http://www.rasayanjournal.com. Accessed on 20th May 2015.

Kannan, N and Joseph, S (2009). Quality of Groundwater in the Shallow Aquifers of a Paddy Dominated Agricultural River Basin, Kerala, India, *World Academy of Science, Engineering and Technology*, **3**(4): 21-25.

Khatoon, N., Khan, H, A., Rehman, M.,andPathak, V. (2013). Correlation Study for The Assessment of Water Quality and its Parameters of Ganga River, Kanpur, Uttar Pradesh, India *IOSR Journal of Applied Chemistry (IOSR-JAC)*, **5**(3):80-90, www.iosrjournals.org

Khound, J. N., Phukon, P., and Bhattacharyya, G. K. (2012). A comparative study of ground water and surface water quality in the Jia – Bharali river basin, Assam, India with reference to physico -chemical characteristics, *Int. Journal of Applied Sciences and Engineering Research*, **1**(3).

Koshy, M (2001). Hydrochemical and biogeochemical studies on River Pamba in Kerala, India. PhD Thesis, University of Kerala.

Koshy, M and Nayar, T.V. (1999). Water quality aspects of River Pamba. *Poll. Res.***18**(4): 501-510.

Kumar, N (2010). An Approach to River Water Quality Management through Correlation Study among Various Water Quality Parameters, *Report and Opinion*, **2**(10): 58-63. http://www.sciencepub.net/report,

Madison, R. J., and Brunett, J. O. (1984). Overview of the occurrence of nitrate in ground water of the United States, in National Water Summary 1984: *U.S. Geological Survey*, Water Supply Paper 2275

Mahananda, M.R, (2010). Physico-Chemical analysis of surface water and ground water of Bargarh District, Orissa, India. *International Journal of Research and Review in Applied Sciences*, **2**(3):284-295.

Mashburn, L. S., Cope, C. C. and Abbott M. M. (2003). Aquifer Characteristics, Water Availability, and Water Quality of the Quaternary Aquifer, Osage County, North-eastern Oklahoma, 2001-2002, *Water-Resources Investigations Report 03–4235*, United States Government Printing Office: Oklahoma City 2003

Meena, B.S. and Bhargava, N. (2012). Seasonal Variations of Physicochemical Characteristics in Open-Well Water Quality in Bakani Tehsil of Jhalawar District, Rajasthan, India, *Ultra Chemistry*, **8**(3): 386-390.

MINARS (2010) Monitoring of Indian National Aquatic Resources Series: Status of water quality in India- 2010, *Mini.of Environ. & Forests*, Govt. of India

Mufid al-hadithi (2012). Application of water quality index to assess suitability of groundwater quality for drinking purposes in Ratmao–PathriRao watershed, Haridwar District, India. *Am. J. Sci. Ind. Res***.,** **3**(6): 395-402.

Paul, M. J., Arya V. S, Jesteena George, Reji K. J. and Sumitha, K. S. (2014). Assessmentof Ground Water Quality in NellikkuzhyPanchayat of Kerala State, India., *International Journal of Engineering Science Invention (ijesi).* **3**(4): 21-28.

Priju, C.P., Neerajamol, T.P., Ramisha, N., Madhavan, K. and N. B. N. Prasad, (2014).Groundwater quality in shallow coastal aquifers of central Kerala: natural and anthropogenic factors, Research Gate, http://www.researchgate.net/publication/ 275585104 accessed on 17/04/2014.

Raghunath, R., Sreedhara Murthy, T.R. and Raghavan, B.R., (2001). Spatial distribution of pH, EC and total dissolved solids of Nethravathi river basin, Karnataka state, India, *Poll. Res*. **20**(3): 413-418.

Raju, H. M. and E. T. Puttaiah (2012). Seasonal variation of physico-chemical properties of ground water along the Vrushabhavathi River stream, International *Journal of Innovative Research in Science, Engineering and Technology*, **1**(1): 94-99.

Rao, M. S., Asha, K. and S. Shivachidambaram (2013). Influence of anthropogenic contamination on ground water chemistry in Mulbagal town, Kolar district, India, *Geosciences Journal*, **17**(1): 97-106.

Sawyer, C. N. (2003). Chemistry for Environmental Engineering and Science, Fifth edition by *Tata McGraw – Hill*, 659-665

Sharma, S and R.C. Chippa (2013). Interpretation of groundwater quality parameters for selected area of Jaipur using regression and correlation analysis, *Journal of Scientific & Industrial Research*, **72**:781-783.

Shyamsunder, A. (1988). Monitoring of the water quality in a stretch of river Jhelum, Kashmir. In: Ecology and pollution of Indian rivers (Ed.R.K.Trivedi), pp.131-161. *Ashish Pub. House*, New Delhi.

Somasekhar, R.K. (1988). Ecological studies of the two major rivers of Karnataka. In: Ecology and Pollution of Indian Rivers (Ed. R.K. Trivedy), p.39-53. *Ashish Pub. House*, New Delhi.

Tripathy, P.K. and Adhikari, S.P. (1990). Preliminary studies on the water pollution of river Nadira. *Indian J. Environ.Hlth*., **32**(4): 363-368.