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Aquaculture International
Journal of the European Aquaculture Society

ISSN 0967-6120
Volume 21
Number 5

Aquacult Int (2013) 21:1137-1153
DOI 10.1007/s10499-012-9618-1

Springer

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Received: 20 March 2012 / Accepted: 7 December 2012 / Published online: 8 January 2013

Abstract Brackishwater aquaculture is basically farming in coastal region, and it utilizes the saline water from either sea or estuary or creek. Assessment of hydrogeochemisty of groundwater resources in shrimp farming areas is very much required not only for monitoring the shrimp farming impacts, but also to suggest better management strategies for the long-term sustainability of shrimp farming and integrated water resources management in coastal regions. Watershed-based assessment is ideal as watershed is a geohydrological unit, and it will give the realistic and cumulative effects more precisely. With this background, the present investigation was carried out to evaluate the geochemical process regulating groundwater quality in shrimp farming areas of coastal miniwatersheds of Vellar and Coleroon river, Cuddalore district, Tamil Nadu, along the east coast of India. Representative groundwater (29) samples from shallow aquifer (hand pump and open well) were collected periodically (June 2008, January 2009, April 2009 and July 2009) using the simple random sampling method and analyzed for various water quality parameters viz. pH, TDS, total hardness, alkalinity, cations (Ca^+, Mg^+, Na^+) and anions (Cl^-, $SO_4{}^-$, $NO_3{}^-$, $HCO_3{}^-$). The groundwater data indicated that the HCO_3 was the dominant ion in the study area with sodium ($Na > Ca > Mg$) and bicarbonate ($HCO_3 > Cl > SO_4$) as the predominant cation and anion, respectively. The large variations in mean and standard deviation of ionic concentration suggest that the water chemistry in the study region was not homogenous and may be influenced by complex sources for the hydrogeochemical processes. The piper trilinear diagram depicts the status of the groundwater quality and also suggests that the cation exchange and mineral dissolution was responsible for this elevated ionic composition at some locations in the study area. The multivariate statistical analysis viz., principal component analysis and cluster analysis clearly elucidated that the groundwater quality in the area is mainly due to natural process and the shrimp farming is not an influencing factor.

Keywords Hydrogeochemistry · Groundwater quality · Shrimp farming · Coastal watershed

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Introduction

Aquaculture is one of the fastest growing food-producing sectors and currently contributes over 45 % of world fish supplies for human consumption (FAO 2010). The rapid and worldwide expansion of aquaculture poses concerns with respect to its environmental impact and long-term ecological and economic sustainability. Shrimp farming has been attributed for a number of environmental impacts including salinization of drinking water and aquifers (Briggs 1993; Hein 2000). If the environmental concerns are scientifically addressed, the benefits of the aquaculture could be multiplied and more area could be brought under aqua farming in a sustainable manner which would definitely help the coastal population.

Brackishwater aquaculture is being practiced in coastal areas and it utilizes the saline water from either sea or estuary or creek. The coastal area is an interface between land and water and also an important zone of biogeochemical activities. The hydrological cycle in the coastal area is forced by both upstream and seaward phenomena. In this juncture, it is imperative to ascertain whether aquaculture activities had influenced the hydrology and hydrochemistry of both superficial water bodies and groundwater aquifers significantly or not along with other coastal activities. The quality of groundwater at any point below the surface reflects the combined effects of many processes along the groundwater flow path. Hydrogeochemical analysis is a useful tool to identify these processes that are responsible for groundwater chemistry. Generally, groundwater quality depends on the quality of recharged water, atmospheric precipitation, inland surface water and subsurface geochemical processes (Twarakavi and Kaluarachchi 2006). The chemical composition of the groundwater is controlled by mixing of seawater, ion-exchange reactions, dissolution processes and anthropogenic inputs (Jeevanandam et al. 2007). Seawater intrusion triggered by excessive groundwater pumping has been the focus of various researchers (Jones et al. 1999; Park et al. 2005; Bennetts et al. 2006; Petalas and Lambrakis 2006). Hydrogeochemical processes that control the groundwater chemistry of coastal watershed have not been studied adequately in shrimp farming areas, and the present investigation is an attempt in this direction so that site-specific best management practices can be evolved for sustainable shrimp farming.

Assessment of hydrogeochemistry of groundwater resources in shrimp farming areas is very much required not only for monitoring the shrimp farming impacts, but also to suggest better management strategies and integrated water resources management and watershed planning in coastal regions. Watershed is a geohydrological unit, and it will give the realistic and cumulative effects more precisely, thus making watershed-based assessment the most ideal. The watershed approach is a system-based approach that facilitates the holistic development of land- and water-based activity viz. agriculture, forestry and allied activities (Tideman 2000). Thus, the main objective of the present study is to understand the hydrogeochemical processes involved in groundwater chemistry to draw a bigger picture of watershed-based management for sustainable shrimp farming.

Materials and methods

Study area

The shrimp farming area studied covered three adjacent miniwatersheds, two in Lower Vellar subwatershed (4C1A1c4a4 and 4C1A1c3b1) and one in Colleroon watershed

(4B1A5a1b1e) in Cuddalore district, Tamil Nadu, along the east coast of India. The watershed boundary has been delineated in GIS environment using ARC GIS 10 (Fig. 1) and the river, tanks, Ist and IInd order streams in the selected study area were digitized. The total extent of the study area is about 213.438 km^2 in which the water spread area of shrimp farms is approximately 4 km^2.

The study area consists of sedimentary formations, which include sandstone, clay, alluvium and small patches of laterite soils of quaternary age. The area is characterized with extensive built-up of alluvium consisting of mixtures of sand, silt and clay in the delta portions in and around watershed and the thickness varies from 10 to 15 m. The quaternary formations consist of sediments of fluvial, fluvio-marine and marine facies, which include various types of soils, fine to coarse-grained sands, silts, clays, laterite and lateritic gravels. In the coastal tract, except at the confluence point of river, wind-blown sands of 1.5–3 km width occur commonly in the form of low and flat-topped sand dunes. The groundwater occurs in both unconfined and confined conditions in alluvial and sandstone formations, respectively. Generally, the hydrogeological cross sections in the study area indicate the presence of alluvial sand and sandstones up to a depth of 50 m below ground level.

Sampling and analysis

Representative groundwater (29) samples from shallow aquifer (hand pump and open well) were collected periodically (January 2009, April 2009 and July 2009) after a preliminary pre survey during June 2008 using the simple random sampling method. The location of sampling units and their distance from the aqua farm, from the creek and from the seas could be seen as shown in Fig. 1. Water samples were collected from the shallow aquifer (6–12 m) and were analyzed for chemical constituents, such as sodium, sulfate, chloride, calcium, magnesium, bicarbonate, pH, electrical conductivity and total dissolved solids (TDS) in the laboratory using the standard methods as suggested by the American Public Health Association (APHA 2005).

Hydrogeochemical analysis

The hydrogeochemical analysis will be helpful for ascertaining various factors on which the chemical characteristics of water depends. The geochemical evolution of groundwater can be understood by plotting the concentration of major cations and anions which is assigned in percent (%) meq/l in the Piper (1953) trilinear diagram. The chief function of the Piper diagram is to identify the facies of groundwater, and it also helps us to understand the several geochemical processes along the flow path of the groundwater. Aquachem Software was used for the purpose.

Multivariate statistical analysis

Groundwater monitoring deals with large data sets and to identify the dominant mechanisms and factors controlling the groundwater chemistry, multivariate statistical analysis such as factor and cluster analysis proved to be helpful and have been applied by various researchers earlier. (Al-Rawi and Shihab 2005; Al-Tamir and Mus'ab 2008; Kim et al. 2005; Sarwade et al. 2007; Senthilkumar et al. 2008; Yaouti et al. 2009). Statistical Package of Social Studies (SPSS) version 16.0 was used for the purpose.

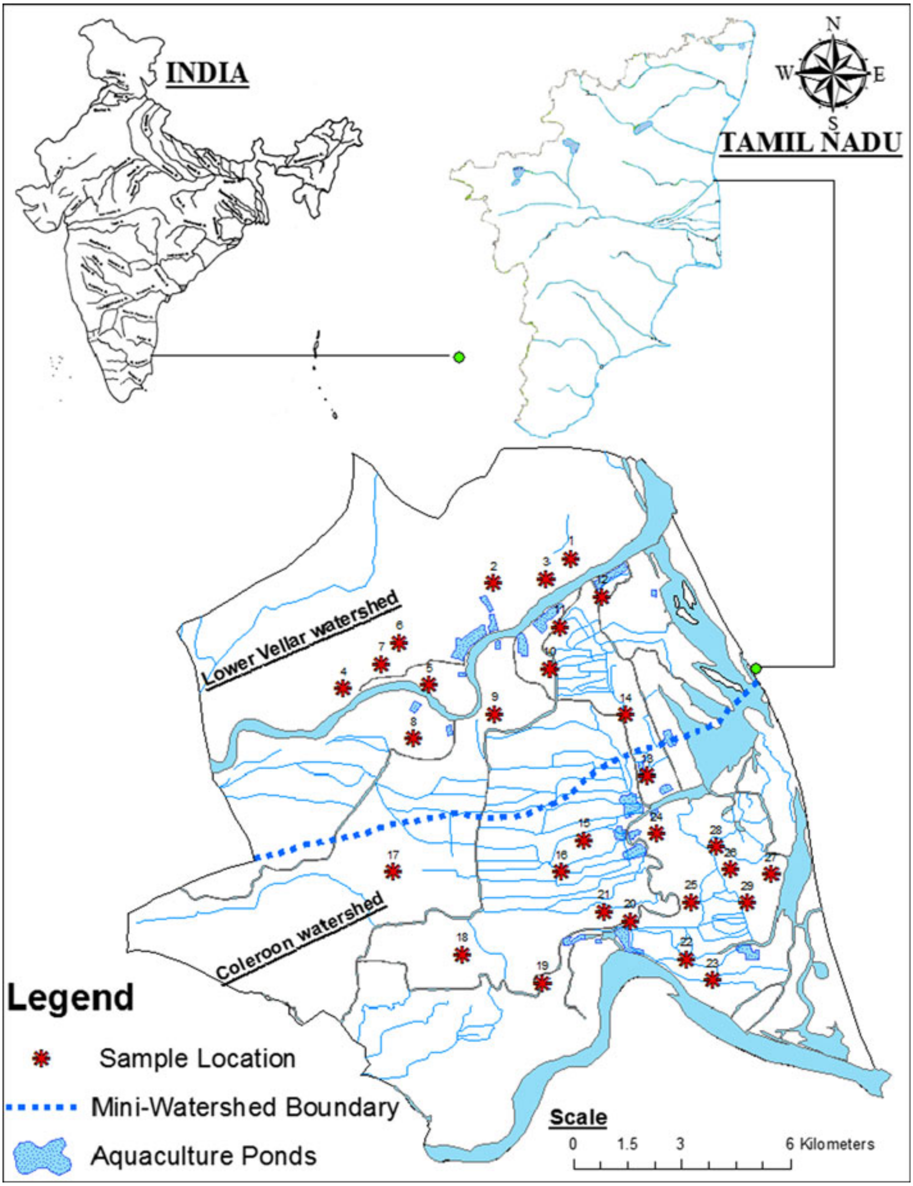

Fig. 1 Sampling location in the study area

Principal components analysis (PCA)

The objectives of PCA in this study were data reduction and data interpretation. PCA reduces the large data matrix into two smaller matrices called principal component (PC) loadings and PC scores, which are obtained through the process of eigen analysis. Because PCA is simply the generation of pairs of eigenvalues and eigenvectors, the data do not need to be normally distributed (Johnson and Wichern 2002). Eigenvalues describe the amount of variation within the original data set explained by each principal component. Often the population variability for large data sets, such as those with large numbers of samples and variables, can be attributed to the number of principal components obtained in the analysis (Johnson and Wichern 2002). PC loadings, the elements of the eigenvectors, indicate the relative contribution of each element to the PC score (Stetzenbach et al. 1999). A loading value of zero would indicate no relationship between the PC and the original variable. PC scores are linear combinations of the standardized data and the loadings and therefore combine information on all of the hydrogeochemical measurements for a given sample into a single number.

Cluster analysis

Cluster analysis (Q mode) helps to group the samples in terms of similar water quality (Davis 2002; Tabachnick and Fidell 2006). In this study, hierarchical cluster analysis was used to group similar wells into separate clusters based on similar hydrogeochemical compositions. Although there are a number of hierarchical clustering techniques, all of which are regularly applied to the earth sciences, especially groundwater quality studies, the most widely used measure of ordering is Ward's criterion, which uses an analysis of variance approach that minimizes the sum of squares within the clusters and maximizes the variance between separate clusters (Ward 1963). The results are represented via a dendrogram and are separated into different clusters. The sample locations are grouped on the vertical axis, and the linkage distances, representing the relative differences between clusters, are shown on the horizontal axis.

Results

Major ion distribution

The descriptive statistics of the major ion concentration of the groundwater of shrimp farming area is given in Table 1. The groundwater data indicates that the abundance of the major ions is in the order $HCO_3 > Cl > Na > Ca > SO_4 > Mg > NO_3$, with sodium ($Na > Ca > Mg$) and bicarbonate ($HCO_3 > Cl > SO_4$) as the predominant cation and anion, respectively. The watershed wise major ion concentration was also observed to be in the same sequences of the abundance in both Vellar and Colleron miniwatersheds, indicating that the HCO_3 is the dominant ion in the shrimp farming area. The surface water quality in the area viz., the two rivers Vellar and Colleroon, and the pond water quality has been given in Table 2.

Hydrochemical facies

The interpretation of distinct facies from 0–10 to 90–100 % domains on the diamond shaped cation to anion graph is more helpful than using 25 % increments. The plot (Fig. 2a) shows that 38 % of the samples ($n = 11$) of the study area were of mixed Ca–Mg–Cl type followed by 31 % ($n = 9$) of samples were of in Na–Cl type, the remaining 17 % ($n = 5$) were of Mixed Ca–Na–HCO_3 type and 13 % ($n = 4$) were of Ca-HCO_3 type. From the plot, it is also shown that alkali (Na) exceeds the alkaline earths (Ca and Mg) and strong acid (Cl) exceeds the weak acids (HCO_3 and SO_4). The piper-tri-linear

Table 1 Descriptive statistics of the groundwater samples

S.·No.	Concentration of ions in the groundwater samples													WHO (1993)		ISI (1983)	
	Parameters	Total study area				Lower vellar watershed					Coleroon watershed			Maximum accept limit (mg/l)	Maximum allowable limit (mg/l)	Highest desired limit (mg/l)	Maximum permissible limit (mg/l)
		Min	Max	Avg	Std	Min	Max	Avg	Std	Min	Max	Avg	Std				
1	Ca (mg/l)	38.8	285.0	99.5	56.2	43.1	233.3	105.7	54.3	38.8	285.0	94.4	58.9	75	200	75	200
2	Mg (mg/l)	10.0	103.5	34.8	20.8	10.0	103.5	40.0	26.3	14.8	72.5	30.5	14.5	50	150	30	100
3	Na (mg/l)	75.3	359.0	176.7	79.8	89.3	359.0	176.5	82.9	75.3	354.0	176.9	80.0	–	200	–	–
4	Cl (mg/l)	61.1	1094	295.4	271.3	65.0	970.3	309.3	289.8	61.1	1,094	284.1	264.3	200	600	250	1,000
5	SO_4 (mg/l)	15.3	207.0	72.4	49.6	17.6	207.0	79.2	51.4	15.3	188.5	66.9	49.1	200	400	–	–
6	NO_3 (mg/l)	0.3	31.3	9.7	8.9	0.8	21.3	8.4	6.7	0.3	31.3	10.8	10.4	45	–	–	–
7	HCO_3 (mg/l)	146.7	457.3	318.7	82.2	193.3	457.3	353.5	71.0	146.7	416.0	290.5	81.7	–	–	–	–
8	pH	7.1	8.1	7.5	0.3	7.1	7.8	7.4	0.3	7.1	8.1	7.5	0.3	6.5	8.5	6.5–8.5	6.5–9.5
9	EC (µs/cm)	533.0	3713	1587	806.8	533.0	3330.	1587	822.5	662.0	3,713	1587	821	–	–	–	–
10	TDS (mg/l)	368.7	2865	1145.	603.3	368.7	2363.	1,145	602.1	489.0	2865	1,145	624.	500	1,500	500	2,000
11	Alkalinity (mg/l) Total	106.8	839.5	343.0	163.2	106.8	839.5	368.1	207.5	181.4	696.0	322.6	119.3	–	–	–	–
12	Hardness (mg/l)	152.0	747.5	367.0	149.9	152.0	710.0	382.7	154.9	184.8	747.5	354.2	149.5	–	–	–	–

Table 2 Surface water quality

S. No.	Concentration of ions in the surface water samples			
	Parameters	Vellar river	Colleroon river	Aquaculture ponds
1	Ca (mg/l)	249	216	234
2	Mg (mg/l)	621	626	574
3	Na (mg/l)	–	–	–
4	Cl (mg/l)	11,609	11,360	17,732
5	SO_4 (mg/l)	–	–	–
6	NO_3 (mg/l)	1	2	–
7	HCO_3 (mg/l)	150	177	–
8	pH	8	8	8
9	EC (μs/cm)	25,600	25,000	16,450
10	TDS (mg/l)	16,690	16,260	10,360
11	Alkalinity (mg/l) Total	150	163	221
12	Hardness (mg/l)	5,736	5,696	2,977

diagram for the Vellar and Coleroon watershed has been depicted in Fig. 2b, c, respectively. The dominant cations and anions present in water are generally reflected in the water type. The plot shows that the prominent chemical facies of the Lower Vellar miniwatershed is of mixed Ca–Mg–Cl type with 43 % ($n = 6$) of samples falling under this category, followed by 29 % ($n = 4$) of samples were of Na–Cl type, the remaining samples were equally distributed as ($n = 2$) were of Mixed Ca–Na–HCO_3 and ($n = 2$) Ca–HCO_3 type. Here, also the strong acid exceeds weak acid. In case of Coleroon miniwatershed, the water type is of mixed Ca–Mg–Cl type with 40 % ($n = 6$) of samples falling under this category, followed by 33 % ($n = 5$) of samples were of Na–Cl type, the remaining samples were equally distributed as ($n = 2$) were of Mixed Ca–Na–HCO_3 and ($n = 2$) Ca–HCO_3 type. In both watersheds, strong acid type is dominant. The percentage of the sample in mixed type is 58 % in Lower Vellar watershed and 53 % in Coleroon watershed. Alkaline earth (Ca + Mg) in lower Vellar is 57 %, and Coleroon watershed is 53 %. Alkalies (Na + K) have 43 % in Vellar watershed and 47 % in Colleroon watershed. The percentage of sodium chloride in Vellar is 29 and 33 % in Coleroon watershed. Weak acid have 29 % in Vellar and 27 % in Coleroon watershed. Magnesium bicarbonate present in Vellar watershed 14 % and in Coleroon watershed is 13 %. Almost all the samples fall in the mixed type followed by Na and K type in cation category and in anion category chloride type followed by bicarbonate type with few representations in mixed type.

Multivariate statistical analysis

The interelemental correlation matrix for the total study area has been presented in Table 3a. From the table, it could be seen that high correlation exists between TDS and all the major ions Ca, Mg, Na, Cl and SO_4. The EC was also showing high correlation with all these ions. It could also be seen that the high correlation among all the ions excepting HCO_3 and NO_3. The groundwater in Lower Vellar (Table 3b) and Coleroon watershed (Table 3c) also showed similar trend with high correlation between TDS and all the major ions Ca, Mg, Na, Cl, SO_4 and EC.

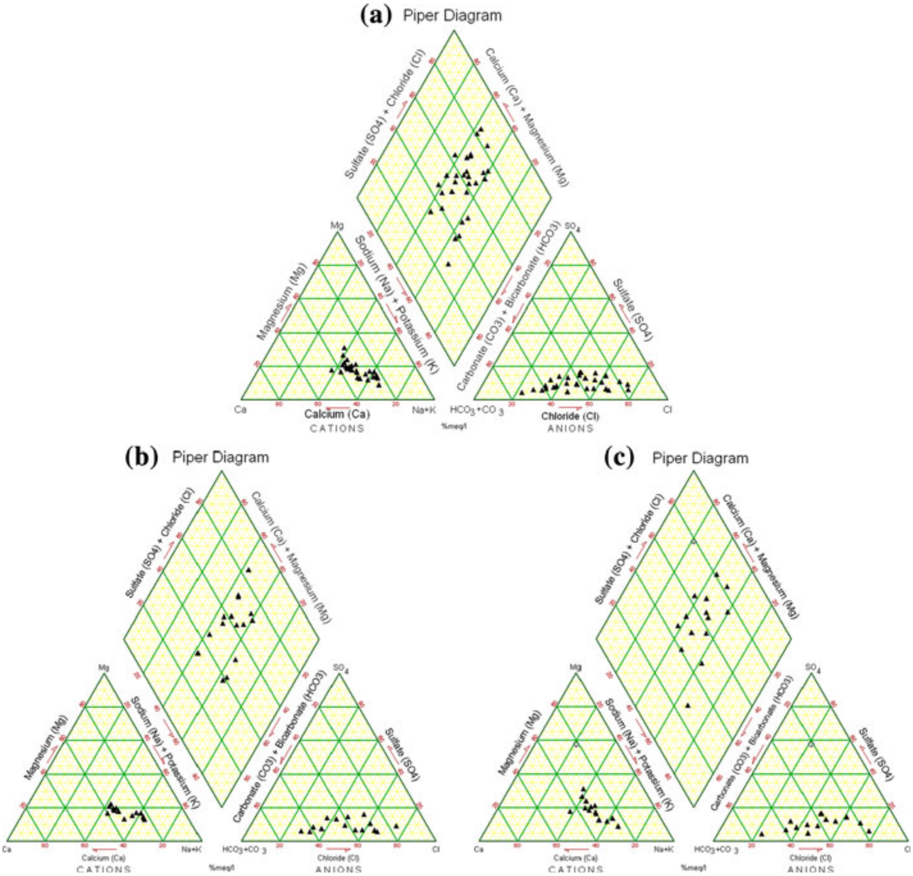

Fig. 2 **a** Piper diagram of study area. **b** Piper diagram of Lower vellar. **c** Piper diagram of Colleroon

Principal components analysis (PCA)

Principal components analysis (PCA) extracted two factors with eigenvalues greater than 1 that accounts 79 % of the total variance of water quality in the total study area. The 12 variables were concentrated into two principal components. Eigenvalues, their loadings after rotation, percentage of variances and communalities are showed in Table 4. Communalities provide an index to the efficiency of degree of contribution of each variable in the selected two components. The pH has the lower communality (0.239). For component loadings, the values which are greater than the radius of the equilibrium circle of contribution radius = (no. of extracted components/no. of variables) $^{0.5} = (2/12)^{0.5} = 0.408$, so the loadings greater than 0.408 are considered significant (Table 3). The Varimax rotation matrix for Lower Vellar shows that two factors have been extracted for Lower Vellar explaining the 80 % of total variability. The first factor is dominated by all the major ions except for HCO_3 NO_3 and pH, indicating the multiple source and second is dominated by HCO_3 with natural weathering. In case of Colleroon watershed, three factors were extracted and 90 % of total variability could be explained. The first factor with 67 % was represented by all the major ions indicating the multiple sources, the second factor with pH and the third factor was dominated by HCO_3.

Table 3 Interelemental correlation of groundwater

	Ca	Mg	Na	Cl	SO_4	NO_3	HCO_3	pH	EC	TDS	Alk	TH
(a) Study area												
Ca	1.0											
Mg	0.9	1.0										
Na	0.7	0.6	1.0									
Cl	0.9	0.8	0.9	1.0								
SO_4	0.9	0.8	0.7	0.8	1.0							
NO_3	0.4	0.3	0.5	0.3	0.4	1.0						
HCO_3	0.4	0.4	0.4	0.4	0.5	−0.1	1.0					
pH	−0.3	−0.3	−0.2	−0.3	−0.4	−0.1	−0.3	1.0				
EC	0.9	0.8	0.9	1.0	0.8	0.3	0.4	−0.3	1.0			
TDS	0.9	0.8	0.9	1.0	0.8	0.4	0.4	−0.3	1.0	1.0		
Alkalinity	0.8	0.9	0.6	0.8	0.8	0.2	0.5	−0.2	0.8	0.8	1.0	
TH	0.9	0.9	0.7	0.8	0.9	0.4	0.4	−0.3	0.8	0.9	0.8	1.0
(b) Lower Vellar												
Ca	1.0											
Mg	0.9	1.0										
Na	0.7	0.6	1.0									
Cl	1.0	0.8	0.8	1.0								
SO_4	0.9	0.9	0.5	0.8	1.0							
NO_3	0.1	0.2	0.5	0.2	0.2	1.0						
HCO_3	0.4	0.5	0.2	0.3	0.4	−0.2	1.0					
pH	−0.4	−0.3	−0.2	−0.5	−0.3	0.1	−0.4	1.0				
EC	0.9	0.9	0.7	0.9	0.8	0.2	0.3	−0.5	1.0			
TDS	1.0	0.9	0.7	1.0	0.8	0.2	0.3	−0.5	1.0	1.0		
Alkalinity	0.9	1.0	0.6	0.8	0.9	0.1	0.4	−0.2	0.8	0.8	1.0	
TH	0.9	0.9	0.5	0.7	1.0	0.1	0.4	−0.4	0.8	0.8	0.9	1.0
(c) Coleroon												
Ca	1.0											
Mg	0.9	1.0										
Na	0.8	0.8	1.0									
Cl	0.9	0.9	0.9	1.0								
SO_4	0.8	0.7	0.9	0.8	1.0							
NO_3	0.6	0.6	0.5	0.4	0.6	1.0						
HCO_3	0.4	0.3	0.5	0.6	0.5	0.0	1.0					
pH	−0.2	−0.1	−0.2	−0.1	−0.4	−0.3	−0.2	1.0				
EC	0.9	0.9	1.0	1.0	0.8	0.4	0.5	−0.2	1.0			
TDS	0.9	0.9	1.0	1.0	0.8	0.5	0.5	−0.2	1.0	1.0		
Alkalinity	0.9	0.8	0.7	0.8	0.6	0.3	0.5	−0.1	0.8	0.8	1.0	
TH	1.0	0.9	0.8	0.8	0.8	0.7	0.3	−0.3	0.9	0.9	0.8	1.0

Table 4 Varimax rotated matrix in groundwater system

Variable	Total study area			Lower Vellar watershed			Coleroon watershed			
	Component		Communality	Component		Communality	Component			Communality
	1	2		1	2		1	2	3	
Ca	0.9	0.2	0.9	1.0	0.2	1.0	1.0	0.2	0.0	0.9
Mg	0.9	0.3	0.8	0.9	0.2	0.9	1.0	0.1	−0.1	0.9
Na	0.9	0.1	0.8	0.9	−0.1	0.8	0.9	0.2	0.2	0.9
Cl	0.9	0.2	0.9	0.9	0.1	0.9	0.9	0.0	0.3	1.0
SO_4	0.9	0.2	0.8	0.9	0.1	0.8	0.8	0.5	0.2	0.9
NO_3	0.6	−0.6	0.7	0.3	−0.7	0.6	0.6	0.4	−0.5	0.8
HCO_3	0.3	0.8	0.7	0.3	0.8	0.7	0.4	0.2	0.8	0.8
pH	−0.3	−0.4	0.2	−0.4	−0.5	0.4	0.0	−1.0	−0.1	0.9
EC	0.9	0.2	0.9	1.0	0.1	0.9	0.9	0.1	0.3	1.0
TDS	0.9	0.2	0.9	1.0	0.1	0.9	1.0	0.1	0.2	1.0
Alkalinity	0.8	0.4	0.8	0.9	0.2	0.8	0.9	−0.1	0.3	0.8
TH	0.9	0.2	0.9	0.9	0.3	0.8	0.9	0.3	−0.1	1.0
Eigenvalue	7.8	1.6		8.1	1.6		8.0	1.5	1.3	
Percent Var	65.2	13.4		67.5	12.9		66.9	12.4	11.0	
Cummulative %	65.2	78.7		67.5	80.4		66.9	79.3	90.3	

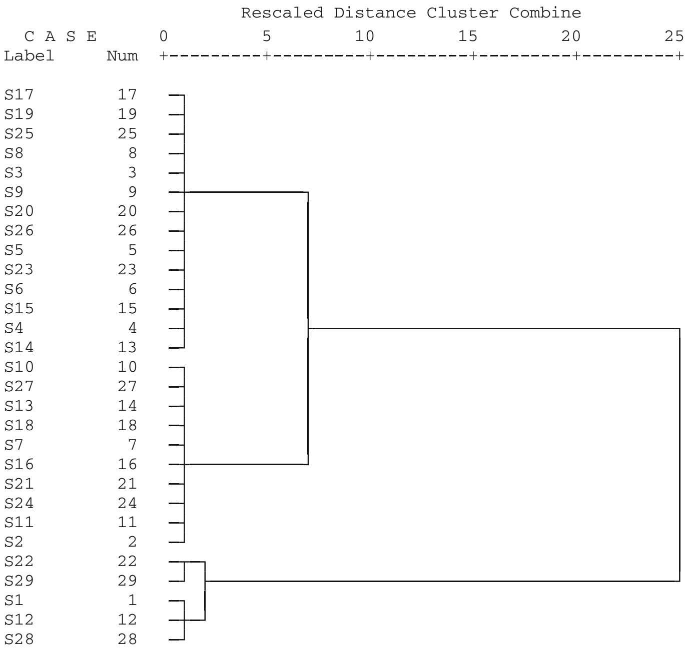

Fig. 3 Q-mode cluster analysis for 29 samples in total study area

Cluster analysis

Resulting dendrogram based on agglomerative hierarchical clustering (Wards) for the total study area has been presented in Fig. 3, which suggests that two major clusters exist in the study area with two subclusters in each cluster. The second cluster was represented by only five wells (S22, S29, S1, S12 and S28), and it occupies 17 % of the water samples and the mean value of TDS is 2248.5 mg/l. The sampling locations of this second cluster were not located together but it is very evident that all were in proximity to the coast and there is no aquaculture activity except in sample location S12. In the first cluster, two subclusters exist and it describes that groundwater is relatively fresh with a mean TDS of 696.29 mg/l, which is the characteristic of less saline water and it is composed of the wells 14 sampling locations (S17, S19, S25, S8, S3, S9, S20, S26, S5, S23, S6, S15, S4 and S14) and concerns 48 % of the water samples. The other subcluster includes 10 sample wells (S10, S27, S18, S13, S7, S16, S21, S24, S11 and S2,) and concerns 35 % of the water samples, and it shows a mean TDS of 1221.69 mg/l values which are well within the permissible limit.

Discussion

The chemical composition of the water is decided by the concentration of major ions and the study of major ion chemistry gains more significance in the overall geochemistry of groundwater. The large variations between the minimum and maximum values and the high standard deviation of the major ion concentration suggest that the groundwater chemistry in the study region is not homogenous and influenced by complex sources for the hydrogeochemical processes. Similar observation has been made earlier by Chidambarm et al. (2009) on his study with the coastal aquifer. The coastal aquifer is usually influenced by many sources as it is a transgenic zone between land and sea.

The bicarbonate ion being the dominant anion in the study area emphasizes the fact that the groundwater quality could be due to the mineral dissolution and natural recharge. Surface water charged with atmospheric and biogenic CO_2 infiltrates into the subsurface and aggressively attack feldspar liberating Ca and Mg into the water and leaving residues of clay minerals. A consequence to this is incongruent dissolution and rise in pH and HCO_3 concentration of the water (Freeze and Cherry 1979). Similar scenario has been explained by Prasanna et al. (2010) based on earlier studies at Gadilam basin in Cuddalore district. Some of the HCO_3 must have been derived from soil $CO_{2.}$ In some places, it may be due to the geochemical evolution of the water from carbonate aquifer dissolution. If aquaculture impact could have been felt in the groundwater quality, then the simple indicator for salinization viz., chlorides should have been the dominant ion in the study area which is not the case. Moreover, the fact that needs to be highlighted here is shrimp ponds were more in Lower Vellar watershed (257 ha) when compared to Colleroon watershed (153 ha) but there is no appreciable difference in the ionic concentration between the watershed. This elucidated the missing link between the areal extent of shrimp ponds and the groundwater quality.

The second dominant ion in the study area is chloride, and it is a minor constituent of the earth's crust but a major dissolved constituent of most natural waters. By far, the most common chloride in natural water is sodium chloride and is also found in the form of calcium, magnesium and iron salts which are responsible for the non-carbonate hardness of water. Results showed that the chloride concentrations near the sea coast are high and near shrimp farming are not appreciably high. It could be observed that there were more first-order and second-order streams in both the watershed influencing the natural recharge and thereby quality of the groundwater. In the Vellar watershed, the shrimp ponds were concentrated on both sides of the Vellar river and extend up to 10.5 km from the mouth to inland, and in Colleron watershed, it extends up to 8 km inland. In these watersheds, there are ephemeral streams spreading out which are more influenced by the tidal influx with brackishwater streams. In the study area, in spite of these conditions, only bichorbonate is dominant and it elucidates that the natural geological process dominates. It is to be highlighted here that since the area is conducive for brackishwater aquaculture activities, shrimp farming is being carried out, and in these places, agriculture is otherwise not possible.

Other anions such as sulfate ion concentrations were probably derived from oxidative weathering of sulfide-bearing minerals like malcite which is abundant in these regions (Prasanna et al. 2009; Chidambarm et al. 2009 and gypsum-bearing sedimentary rocks (Elango et al. 2003; Jeevanandam et al. 2007). The pockets of higher nitrate concentration in the groundwater of the study area are related to the use of fertilizers in agricultural land and sewage effluents (Jeevanandam et al. 2007; Rekha et al. 2004, 2011). Since there is no lithology relationship between nitrate and the nitrate in groundwater, the latter is mainly due to the land use impact and could be attributed to the agriculture activity in the watershed. In the upstream area of the study area, agriculture and aquaculture co-exist, with definite surface barriers like roads or trenching in between them.

Among the cation, sodium is the dominant in the study area. Sodium is more mobile and dominates the natural solutions (Milliot 1970; Ramanathan et al. 1999). High sodium waters can be explained by the combination of dilution factors, ion exchange and sulfate reduction (Krothe and Oliver 1982). The base exchange process could be responsible for the elevated sodium content near the coast. The calcium content is high in the groundwater of the shrimp farming area when compared with magnesium. In general, freshwater is dominated by calcium and sea water by magnesium (Mondal et al. 2008).

The piper diagram classify the water types (Wen et al. 2005), which are generally distinct zones that cation and anion concentrations are described within the defined composition categories clearly indicating the ion-exchange process. There is no significant change in the hydrochemical facies noticed in the both watershed which indicates that the aquaculture ponds are not influencing the groundwater quality in the study area. Moreover, piper diagram depicts that strong acids and Cl, Ca and Na are more dominant in the study area explaining that chemical composition of the groundwater is controlled by ion-exchange reactions and dissolution processes.

The high correlation exists between TDS and all major ions indicating the TDS is due to the ionic concentration. The study revealed that there is no higher values of TDS in and around shrimp farms. But a small region in the east coast near the shore line shows high TDS value (2864 mg/l) where shrimp farming is not prevalent. The main factor for the increased amount of TDS in groundwater could be due to the sea water as it was supported by a high value of sodium (359 mg/l) and chloride (1093.75 mg/l) as well. Aiuppa et al. (2000) reported that the water with high concentration of sodium and chloride could be of sea water origin. A study conducted in the coastal aquifer at Visakhapatinam by Sarma and Krishnaiah (1976) states that seawater intrusion could be checked with presence of chlorides as dominant ion, a low calcium/magnesium ratio and an excess of Total Alkalinity over Total hardness. These three conditions could not be demonstrated significantly in the study area; hence, sea water intrusion could not be attributed solely. It could also be observed that the wells in the vicinity of shrimp farming activity have comparatively lower concentration. This is the clear elucidation that the groundwater quality is not dependent on shrimp farming activity. The results also shows that the average groundwater quality with respect to TDS concentration is within the permissible limit of 1500 mg/l, respectively, as per the standards of WHO (1993); ISI (1983). Jeevanandam et al. (2007) based on the earlier study in Lower Ponniar basin adjacent to Vellar basin have shown that geochemical process is responsible for the elevated ionic distribution.

When the concentrations of Ca and Mg ions increase, the total hardness (TH) generally increases. The significant amounts of alkalinity justify the contribution of carbonate dissolution in the area. The geology of the study area also implies this. The weathering of plagioclase feldspar by dissolved atmospheric carbon dioxide will release sodium and calcium which progressively increase the pH and alkalinity, and this kind of observation has been earlier reported by Njitchoua et al. (1997). It could be observed that total hardness is slightly greater than total alkalinity (TH 367 $>$ TA 343) in the study area and the watershed wise analysis reveals that the same trend is also observed in both watersheds. Water hardness in most groundwater is naturally occurring weathering of sedimentary rock and calcium-bearing minerals.

Principal components analysis revealed that two factors are responsible for the variation in the groundwater quality. Principal component I accounted for 65 % of the variance, and it has high loading of all the major ions, Ca, Cl, Mg, Na, SO_4, NO_3, TDS, and EC. This could be seen from the table that the two dominated variables are in the positive pole of the component which means that they are positively correlated with each other. The hardness and alkalinity also have high loading indicating that the water on the region is Ca and Mg hardness. The high levels of Na^+ and Cl^- ions in coastal groundwater may indicate a significant effect of seawater mixing, while considerable amounts of HCO_3 and Ca mainly reflect the contribution from water–rock interaction (Park et al. 2005). Since the chemical composition of groundwater is characterized by mostly all the major inorganic compounds Ca, Mg, Na, HCO_3, CI, SO_4, and NO_3, it is indicative of as multiple sources such as sea water mixing, chemical weathering and due to atmospheric and anthropogenic inputs (Chan 2001). Principal component II accounts 13 % of the percentage variance in water quality. It is dominated by HCO_3 on its positive pole and NO_3, and pH on its negative pole. The presence of HCO_3 reflects the signatures of natural water recharge and rock–water interaction. The NO_3 in the study area has no lithology sources, and it could be seen due to the agriculture activity as is the dominant land use along with settlement in the watershed. Further, the nitrate ion has no significant lithologic source in the area and it may be associated mainly with surface run-off of nitrate fertilizer as the aquifer surface is used for agricultural purposes. The Varimax rotation matrix for Lower Vellar and Colleroon watersheds has been presented in Table 3. It could be observed that two factors have been extracted for Lower Vellar explaining the 80 % of total variability. The first factor is dominated by all the major ions except for HCO_3 NO_3 and pH, indicating the multiple source, and second is dominated by HCO_3 with natural weathering. In case of Colleroon watershed, three factors were extracted and 90 % of total variability could be explained. The first factor with 67 % was represented by all the major ions indicating the multiple sources, the second factor with pH and the third factor dominated by HCO_3. Chidambarm et al. (2009) based on his earlier analysis reported that multiple sources such as dissolution and leaching of secondary salts along with ion-exchange process plays a dominant role in hydrogeochemistry in Cuddalore region. It thus confirms the multiple sources for the groundwater chemistry in the area.

Through the cluster analysis, it is evident that the elevated ionic concentration at only 17 % of the samples apparently have no relationship with geographical distribution and could be explained due to base exchange process in weathered zones. The degree of weathering as such may be responsible for the elevated ionic concentration in some wells in the study area. Having unable to attribute the cluster in some pocket, it simply implies localized weathering zones in the study area which has earlier reported by Prasanna et al. 2009 and the salinity in these can be attributed to many origins, such as marine contribution (Groen et al. 2000; Jorgensen et al. 2002; Kim et al. 2005), the dissolution of secondary minerals within the sedimentary formations (Howard and Lloyd 1983), rock–water interaction, return flow from irrigation water, anthropogenic contamination, or most often, the combination of some of these processes (Marimuthu et al. 2005; Park et al. 2005; Ghabayen et al. 2006; El Mandour et al. 2008). It is conclusively shown that the groundwater quality in the study area is independent of the aquaculture activities.

Conclusion

The purpose of the study is to identify and evaluate the main factors affecting the groundwater quality in shrimp farming areas. To accomplish this purpose, physico-chemical properties of groundwater, especially major ions and TDS concentrations have been examined. Also, hydrogeochemical analysis and multivariate statistical method have been used to classify and characterize the groundwater quality. The results showed that there were multiple sources influence the groundwater quality in the study area. The bicarbonate ion is the dominant ion indicating the natural recharge, mineral weathering and rock–water interaction. The ionic concentrations in both watersheds are more or less similar. The piper diagram elucidates that chemical composition of the groundwater is controlled by ion-exchange reactions and dissolution processes. Moreover, the percentage of strong acids is higher in Colleroon watershed when compared to Vellar watershed but shrimp ponds are more in Vellar watershed reflecting the missing link between aquaculture and groundwater quality. Principal components analysis explains two components as the main factors to contribute variation at different degree to such and they are mixed process and the rock–water interaction. The result of Q mode cluster analysis shows that there in no linear relationship between ionic concentration and distance from aqua farm as stumpy ionic concentration has been observed in shrimp farming area when compared to the other land use. Above methods explain conclusively that the changes in groundwater quality are at some localized well due to mineral weathering and not due to the aquaculture activity. The quality in the study area can be attributed to many origins, such as marine contribution, the dissolution of secondary minerals within the sedimentary formations, return flow from irrigation water, anthropogenic contamination, or most often, a combination of some of these processes. However, to identify the origin of salinization in the study area, isotopic analysis should be performed.

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