Identification of the geochemical processes in coastal groundwater using hydrogeochemical and isotopic data: A Case study of the Gadilam river basin in southern India

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The Gadilam river basin in Tamilnadu is characterized by different geological formation viz. Archaean, Cretaceous, Tertiary to Recent Alluvium and groundwater serves as the major source for domestic, agriculture and other water-related activities. Forty four groundwater samples were collected during summer and post monsoon. Twenty three samples were analysed for stable isotopes ($\delta^{18}O$ and $\delta^D$). Geochemical signatures of groundwater were used to identify the chemical processes that control hydrogeochemistry. Chemical parameters of groundwater such as pH, EC, TDS, Na$^+$, K$^+$, Ca$^+$, Mg$^+$, HCO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$ and H$_4$SiO$_4$ were determined. Interpretation of hydrogeochemical data ascribes that secondary leaching, saline water intrusion and anthropogenic impact in this regime. Interpretation of $\delta^{18}O$ and $\delta^D$ indicates recharge from the meteoric water in Tertiary aquifer and from evaporated water in Alluvium aquifer.

Keywords: Hydrogeochemistry, Groundwater quality, Sea water intrusion, Stable isotopes, Gadilam river basin.

Introduction

The groundwater quality in an area depends on the physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities. There are many studies regarding the excessive extraction of groundwater and resulting in sea water intrusion contaminating coastal aquifers$^{3-5}$. Increased usage of groundwater has depleted the source of groundwater. The excess concentration of certain ions has made the water unfit for use. The discharges from the industries and land resource have led to serious problems in the water quality. Public health and agriculture were adversely impaired due to consumption of contaminated water and depleted ground water source. In the present study an attempt has been made to understand the complexity of hydrogeochemical characters and groundwater quality in the study area.

Study area

Lower sub basin of Gadilam river comes under Cuddalore district of Tamilnadu, south India. The area is bounded between $11^o40'N$ and $11^o50'N$ latitudes and $79^o30'E$ and $79^o45'E$ longitudes (Fig 1). The total length of the river Gadilam is 112 km. In the study area, the length of the lower Gadilam river is only 73 km. Gadilam river basin covers different litho units and forms a complex hydrogeochemical environment. The Tertiary formation is found in the midstream and the recent Alluvium in the downstream of the Gadilam river basin. The area of this Gadilam sub basin is more or less a plain terrain with small elevated tertiary upland hills and laterite hillocks occur in the cuddalore sandstone formations. The Neyveli open cast mines and Veeranam lake are the hot spots for maximum groundwater extraction for lignite excavation and domestic supplies respectively.

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Fig. 1—Location map of the study area.
fall in the study area. An industrial estate SIPCOT (small industries Promotion Corporation of Tamilnadu) with groups of industries located near the coast, which discharge multi facet chemicals and raw materials are distributed along the down stream of the river Gadilam.

Materials and methods

Groundwater samples were collected during summer (March 2005) and post monsoon (January 2006) seasons. A total of 44 samples (22 in summer and 22 in post monsoon) were collected from 22 stations from the study area (Fig 2). The samples collected were analyzed for major cations like, Ca and Mg by Titrimetry, Na and K by Flame photometer (CL 378); anions, Cl and HCO$_3$ by Titrimetry, SO$_4$, PO$_4$, and H$_2$SiO$_4$ by Spectrophotometer (SL 171 minispec). EC and pH were determined in the field using electrode (Eutech). The analyses were done by adopting standard procedures$^5$. 23 groundwater samples (9 in summer and 14 in post monsoon) were subjected to analysis of $\delta^{18}$O and $\delta$D by IRMS (Isotope ratio Mass Spectrometry).

Result and discussion
Water chemistry

The analysis of different chemical parameters (Appendix 1 and 2) shows that there are significant variations of ionic concentrations with season. Maximum, minimum, average and standard deviation values of the chemical composition for groundwater are presented in the Table 1. Bicarbonate represents the major sum of alkalinity. Alkalinity in water is the measure of its capacity of neutralization. It is formed mainly due to the action of atmospheric CO$_2$ and CO$_2$ released from organic decomposition. Sulfate is found in water due to its lesser breaking down of organic substances from weathered soil/water and due to the influence of saline waters$^{17}$. Silica is the second most abundant element in the earth crust and essential component of almost all minerals. In Alluvium formation, Chloride is the dominant anion followed by HCO$_3$ > SO$_4$ > PO$_4$ in both the seasons. In Tertiary

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formation, bicarbonate is the dominant anion followed by Cl > SO₄ > PO₄ during summer season and Chloride is the dominant anion followed by HCO₃ > SO₄ > PO₄ in post monsoon season.

Sodium is the important and most abundant alkali metal which is highly mobile and soluble in groundwater. Potassium in groundwater is generally lesser due to its higher solubility. In Alluvium formation, Sodium is the dominant cation followed by Ca > Mg > K in both the seasons. In Tertiary formation, sodium is the dominant cation followed by Ca > K > Mg in both the seasons.

**Geochemical Classification**

The geochemical evolution of groundwater can be understood by plotting the concentrations of major cations and anions in the Piper trilinear diagram (Fig 3). The plot shows that majority of the samples in both the seasons fall in the field of Na-Cl type. Some samples are also representing mixed Ca-Na-HCO₃ and mixed Ca-Mg-Cl type. From the plot alkali (Na) exceeds the alkaline earths (Ca and Mg) and strong acid Cl exceeds the weak acids (HCO₃ and SO₄). It is noted in Alluvium irrespective of seasons samples fall in the Na-Cl region in the diamond field of Piper. Few samples of Tertiary show higher Bicarbonate.

Ionic strength is a measure of total concentration of ions which emphasizes increased contribution of species with charges greater than one to solution non-ideality.

\[ I = 0.5 \sum m_i z_i^2 \]  \hspace{1cm} \text{(1)}

Where \( m_i \) is the atomic/molecular weight and \( z_i \) is the valence of the respective ion. It was reported that ionic strength of fresh water is less than 0.005. In
summer season, higher ionic strength was noted in Alluvium formation indicating lesser inflow of fresh water into the system (Fig. 4). Low ionic strength was noted in Tertiary formation indicating higher inflow of fresh water into the system. Same trend was followed in post monsoon season (Fig 4) and some samples in Tertiary formation fall nearer to 0.005 line indicating recharge water i.e., fresh water.

**Variation of Log \( P_{CO_2} \)**

The trend of high \( P_{CO_2} \) in rivers are commonly out of equilibrium with atmosphere. Two possible explanations have been offered for this apparent paradox. (1) River waters particularly perennial rivers contains a significant fraction of high \( CO_2 \) groundwater (2) the rate of re-equilibration with the atmosphere by releasing the excess \( CO_2 \) is relatively slow\(^{10,11} \). The Log \( P_{CO_2} \) is calculated by the following equation\(^{12} \).

\[
\text{Log} \ P_{CO_2} = 7.9 + \text{Log} \ m \ HCO_3 - \text{pH} \quad \ldots \ (2)
\]

In summer season, lesser values of \( P_{CO_2} \) was noted in Tertiary formation followed by Alluvium formation indicating that the groundwater just entered into the system or the residence time in the aquifer matrix is considerably lesser or recently recharged waters\(^{13} \) (Fig 5). In Post monsoon season, majority of the samples in both the terrains (Alluvium and Tertiary) fall nearly to the atmospheric value (-3.5). It also evident that recharge is taking place in both terrains.

**Isotopic Signatures**

Two stable isotopes, deuterium (δD) and oxygen (δ\(^{18}\)O) were measured from 23 groundwater samples collected selectively for the purpose. It had been subjected to analysis of δD and δ\(^{18}\)O by IRMS (Isotope Ratio Mass Spectrometry) at CWRDM, Kozhikode.

Deuterium and oxygen isotopes are expressed as per mill difference of the isotope ratios of a sample (sp) and a standard (std), which is usually referred to as SMOW (Standard Mean Ocean Water). They are defined as follows,

\[
\delta^{18}\text{O}(\delta\text{D}) = \left( \frac{R_{sp} - R_{std}}{R_{std}} \right) \times 10^3 \quad \ldots \ (3)
\]
where \( R \) is the ratio of the heavy to the light isotope, that is, \( R = \left( \frac{^{18}O}{^{16}O} \right) \) (or D/H).

There is a significant variation of isotopic characters with respect to Cl in both the formations. In general, the tertiary has lower \( \delta D \) and Cl values it gradually increases in alluvium irrespective of seasons. In summer (Fig 6), chloride-deuterium plot suggests that two types of groundwater occur in the study area namely: (i) groundwater samples from the Tertiary formations characterized by low chloride and depleted D representing areas that are recharged frequently by rainfall\(^{14}\) (ii) groundwater samples in the Alluvium formation with high chloride and enriched D, indicating rarely receive recharge from meteoric water and recharge of the evaporated waters from a different source nearby which has to be established. Same trend was followed in post monsoon.

In summer, \( \log P_{\text{CO}_2} - \delta^{18}O \) plot suggest that majority of groundwater samples in Tertiary formation characterized by low \( P_{\text{CO}_2} \) values and depleted \( \delta^{18}O \) indicating recent recharge by the local precipitation (Fig 7). Groundwater samples from the Alluvium formation with higher \( P_{\text{CO}_2} \) values and enriched \( \delta^{18}O \) indicates long residence time. This also suggest that the rainwater charged with atmospheric \( \text{CO}_2 \) has acquired additional \( \text{CO}_2 \) from the soils and thereby developing high \( P_{\text{CO}_2} \) water on their travel to deep unsaturated zone. In post monsoon (Fig 7), majority of the samples in both the terrains (Alluvium and Tertiary) fall nearly to the atmospheric value -3.5 atm indicates recently recharged waters in both the terrains.

**Water Quality**

Groundwater with Electrical conductivity (EC) below 2000 mg/l is portable\(^{15}\). The spatial distribution of EC indicates that the groundwater generally falls under EC value of less than 2000 \( \mu \text{s/cm} \), which is portable in both the seasons (Fig 8). The groundwater has EC value of more than 2000 \( \mu \text{s/cm} \) in Karaikadu, Veeraperumanallur and Kothavacheri locations. The spatial distribution of chloride indicates that higher values are noted in location Karaikadu in both the seasons (Fig 9). This may due to anthropogenic impacts from the nearby industry (SIPCOT). If the chloride vs. bicarbonate ratio is above 2, it indicates the water is highly saline. It may be due to sea water intrusion\(^{16}\). In most of the samples, the Cl/\( \text{HCO}_3 \) ratio falls below 2 in both the seasons (Fig 10). At a few locations along the coast, the Cl/\( \text{HCO}_3 \) ratio is more than 2. This may be due to saline water intrusion or over exploitation of groundwater in Neyveli open cast mine, which led to sea water encroachment or upcoming of saltwater- freshwater interface.
Conclusion

In the study area, groundwater shows that the alkalies (Na and K) exceed alkaline earths (Ca and Mg), strong acid (Cl, SO$\text{\textsubscript{4}}$) exceed weak acids (HCO$\text{\textsubscript{3}}$) indicates the salinity nature in the groundwater. The major ions concentration in groundwater increases during summer season in comparison to the post monsoon season. Lower ionic strength is noted in Tertiary formation. This indicates the higher inflow of fresh water into the system. Log P$_{CO_2}$ variation diagram shows that recharge takes place in post monsoon period. Groundwater samples in tertiary formations with lower $\delta^D$ and Cl values indicate that it is recharged frequently by rainfall. There is a notable increase of both in the Alluvium formation. This reveals that it rarely receive recharge from meteoric water. In summer, Log P$_{CO_2}$ – $\delta^{18}O$ plot suggest that majority of groundwater samples in Tertiary formation characterized by low P$_{CO_2}$ values and depleted $\delta^{18}O$ indicating recent recharge by the local precipitation. Groundwater samples from the Alluvium formation with higher P$_{CO_2}$ values and enriched $\delta^{18}O$ indicates long residence time. In post monsoon, samples in both the terrains fall nearly to the atmospheric value indicate recently recharged waters. It is also inferred that the effect of salt water intrusion in the alluvial aquifer has increased the ionic strength and enriched isotopic values with Na-Cl facies. From the higher EC, Cl and Cl/HCO$_3$ ratio using spatial distribution analysis, it is inferred that saline water intruded to the adjoining coastal area due to over exploitation of groundwater and anthropogenic impact nearby industry.

Acknowledgement

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Reference


