ORIGINAL CONTRIBUTION

Environmental Isotopes of Water as Potential Tool to Distinguish the Sources of Groundwater Recharge in a Semi-arid Region: A Case Study Around Veeranam Tank, Tamil Nadu, India

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Abstract Stable isotope ratios of hydrogen and oxygen (δ^{18}O and δD) were analysed for different water sources around Veeranam Tank in Cuddalore District of Tamil Nadu, India, to understand the groundwater recharge sources in the region. Water samples were collected from the tank, open wells, deep bore wells and the feeding stream (Vadavar River) in the vicinity of the Veeranam Tank for stable isotope measurements. δ^{18}O of the water from open wells ranges from –5.07 to 1.25‰ and δD ranges from $-$32.93 to 3.01‰ with the mean concentrations of δ^{18}O and δD of $-$1.84‰ and $-$15.30‰, respectively. The δ^{18}O and δD values of the deep bore wells range from $-$5.23 to $-$3.28‰ and $-$37.21 to $-$23.09‰, respectively. The mean concentrations of δ^{18}O and δD in the deep bore well water are $-$4.52‰ and $-$31.25‰, respectively. In the tank water, δ^{18}O ranges from 1.10 to 1.45‰ and δD ranges from 1.65‰ to 4.14‰ with the mean concentrations of δ^{18}O and δD of 1.22‰ and 3.26‰, respectively. δ^{18}O versus δD plot and d-excess value were interpreted to distinguish the predominant sources of recharge of wells in the location. The study identified the wells that are recharged predominantly by rain water and also by the tank.

Keywords Isotopic signatures of water · d-excess · Surface water and groundwater interaction · Sources of water · Veeranam Tank

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Introduction

Groundwater and surface water are natural important sources of water for people's livelihood in terms of drinking, domestic and agricultural purposes [21]. In the last few decades, there is an increase in demand for water resources due to rapid population growth and extensive agricultural activities. This demand results in the uncontrolled use of available freshwater resources which in turn affects not only the quantity of water, but also its quality due to natural and anthropogenic interferences [3]. Thus, conservation and protection of the available freshwater resources are of prime importance. It is needless to reiterate that groundwater from shallow and deep wells is the major groundwater withdrawal structure for freshwater requirement in India. In this context, better understanding of the recharge characteristics of groundwater in relation to interconnection between surface and groundwater is imperative. The interaction between surface water and groundwater is governed by geological conditions, aquifer lithology, physiographic processes and also anthropogenic activities [38, 43]. The surface water also governs the groundwater level and vice versa [20]. Integrated hydrological study of surface water and groundwater is necessary for effective management of water resources [44]. Many conventional investigations are available for the study of interrelation between two water bodies. The groundwater recharge estimation using conventional methods such as

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water budget method, geophysical investigation and Darcy's techniques is a complex process. The water isotopic composition changes provide better understanding of groundwater recharge [36]. Thus, stable isotopes of oxygen-18 (δ^{18}O) and deuterium (δD) in water which are inert and conservative are widely used in hydrological studies in the recent past [42]. Isotopic signatures of precipitation and many water bodies vary significantly due to differences in their sources and forming mechanism [47]. Isotopic signatures of water are influenced by atmospheric processes, geographical variations, aquifer lithology and geological conditions [2, 18]. The variation in the isotopic composition of different water bodies is studied with reference to the global meteoric water line (GMWL), the relation developed by Craig [9]. Numerous hydrological and hydrogeological studies are carried out across the world using stable isotopes δ^{18}O and δD of water [5, 8, 15, 37, 39]. The water isotope signature is also useful to study lake dynamics [6, 46] to determine the interconnection between aquifers [27, 28], to identify and quantify the groundwater recharge [17, 36, 48], to estimate groundwater residence time [33, 54], to determine the source and mechanism of groundwater pollution [13] and to demarcate groundwater salinization [1, 26]. Besides, isotopic signature of groundwater is used to identify the source, movement and distribution of groundwater within the aquifer [40]. Integrated isotopic and hydrochemical studies help understand the hydrochemical processes such as isotopic exchange [25] and rock–water interaction [53]. Isotopic signatures are also used widely in various lake studies [10, 11, 47, 49, 51] to identify the mixing zone and the interaction between surface and groundwater [4, 52]. The present study is carried out around the Veeranam Tank which lies in the sedimentary region. Intensive groundwater extraction is also carried out around the tank for agricultural activities. Moreover, Veeranam Tank supplies 180 million litres per day of drinking water to Chennai residents. This study aims to identify the sources of groundwater recharge and to assess the interconnection between surface water and groundwater with the aid of stable isotope techniques.

Study Area

Study Area Description

Veeranam Tank, located in Cuddalore district, is one of the largest freshwater tanks in Tamil Nadu state, India. The study location covers an area of 422 km^2 around the Veeranam Tank. Location and drainage map of the study area is shown in Fig. 1. Geographically, it is located in between 11°11′38.4″ and 11°28′14.8″ N and 79°27′39.6″ and 79°48′7.2″ E. During monsoon season, Veeranam Tank receives water from its catchment area of 25 km^2 and Vadavar River as the main feeding stream to Veeranam Tank throughout the year [29]. The mean annual temperature is 32 °C [30]. The south-west monsoon (June–September) and north-east monsoon (October–December) contribute 29.5% and 56.5% of the rainfall, respectively [31]. The remaining rainfall occurs during the hot weather (March–May) and winter periods (January and February).

Fig. 1 Location and drainage map of the study area
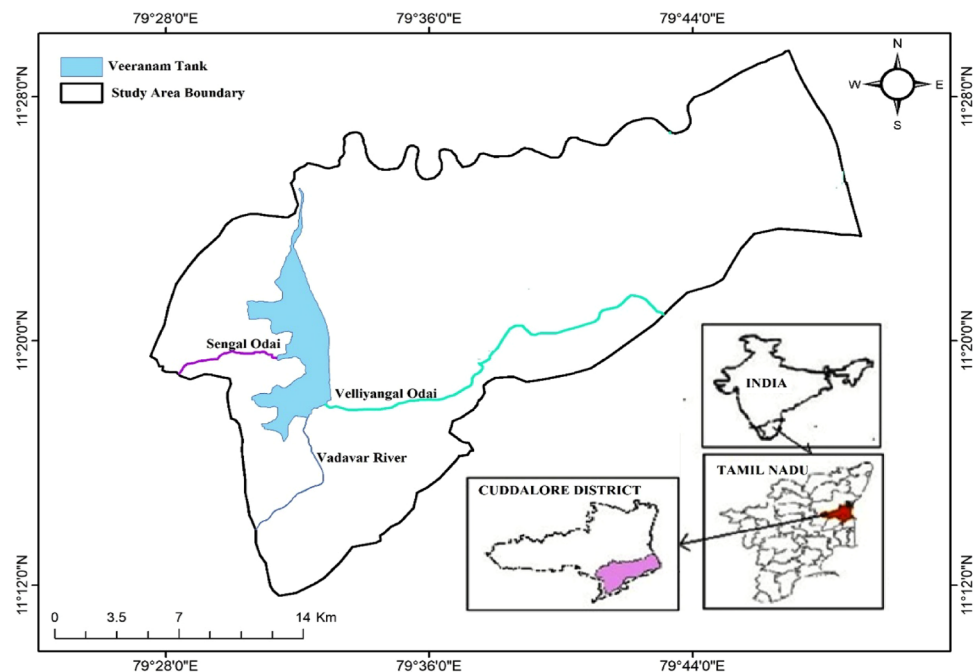
Geology and Geomorphology

Geologically, the study area is covered by sedimentary formations that belong to the tertiary group in the western region and the quaternary group in the eastern region. The geology map of the study area is shown in Fig. 2. Manaveli and fluvial formation covers the western and central parts of the study area, respectively. Marine lagoon and marine tidal deposits cover the eastern region of the study area. The lithological unit of Manaveli formation mainly consists of an alternate course of clay and sandstone. The downstream flood plain region of the tank is covered by the fluvial formation, and it consists of different lithological units in which clay is predominant. Marine tidal deposits consist of sand, clay and shell, whereas marine lagoon deposits mainly consist of black clay. The maximum elevation is 27.74 m AMSL (above mean sea level) in the west, and the minimum elevation is Bay of Bengal in the east. The geomorphology map of the study area is shown in Fig. 3. The study area is mainly occupied by pediplain in the western regions, alluvial plain in the middle regions and coastal plain in the eastern regions. The pediplain formation represents the end product of erosion which is found in Veeranam Tank and its upstream side. The pediplain comprises mostly clay and sandstone. Alluvial and flood plain forms due to the influence of the Coleroon River and Vellar River. The alluvial plain is mostly
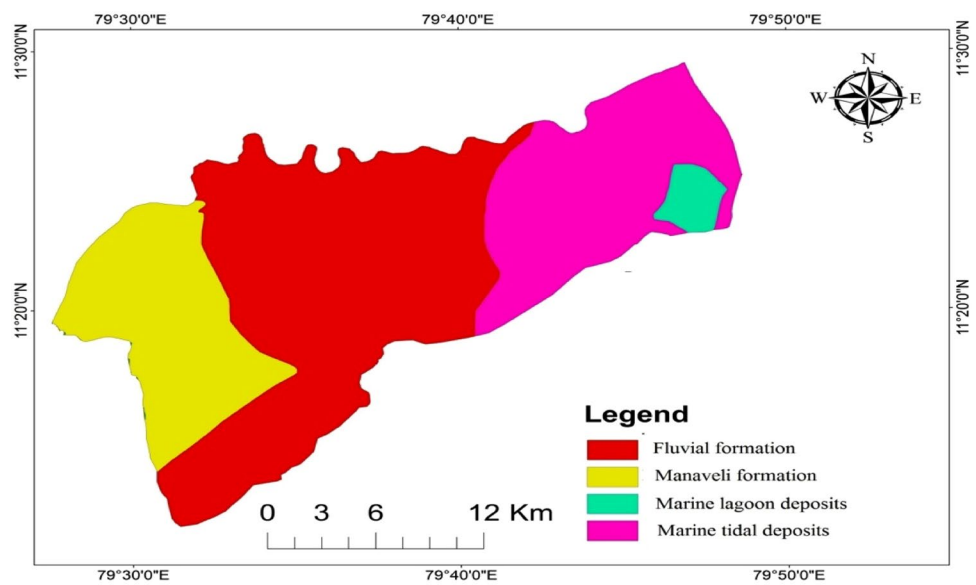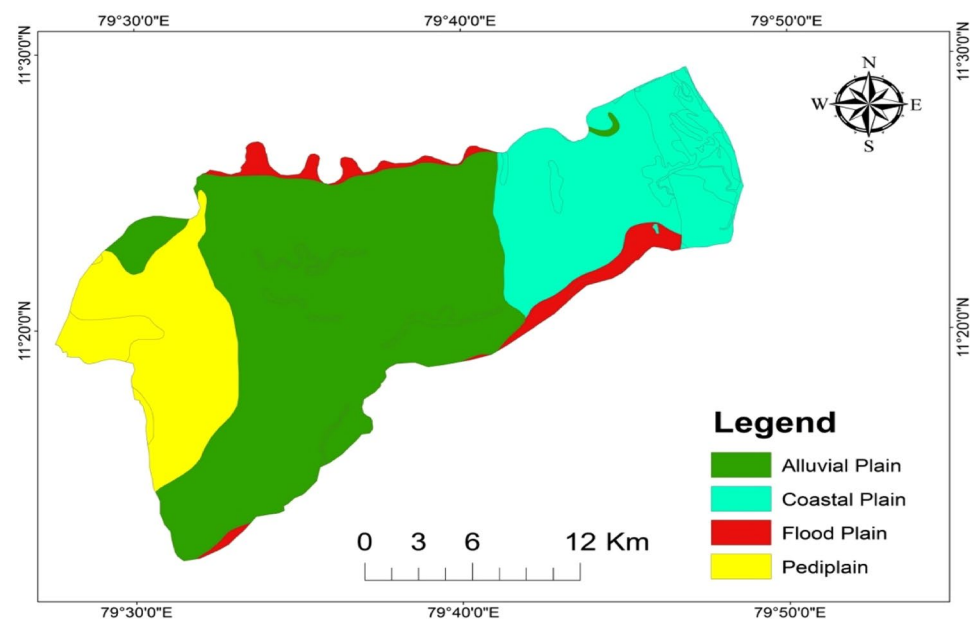

Fig. 2 Geology map of the study area

Fig. 3 Geomorphology map of the study area

bounded by clay formation. The coastal plain is found in eastern regions and consists of black clay formation [31].

Hydrogeology

Groundwater occurrence in the study area can be categorized into semiconsolidated and unconsolidated formations. The semiconsolidated formation mainly comprises sandstone in which groundwater occurs in the form of semi-confined to confined conditions. This formation thickness ranges from 50 to 450 m (Sahebrao [35]). In this formation, permeability is moderate and the infiltration rate is good. Thus, semiconsolidated formation is the most productive aquifer zone. The unconsolidated formation consists of alluvial and coastal plains in which the groundwater occurs in the water table and semi-confined conditions. The infiltration rate is very high in this formation, and groundwater potential is also very good. Along the coastal plain, the quality of groundwater in this region is polluted due to seawater intrusion [7]. The yield of well is greater in semiconsolidated formation than in unconsolidated formation. The well yield of the former is 500–2000 lpm (litres per minute), and the well yield of the later is 50–1500 lpm (Sahebrao [35]. The specific capacity and permeability of semiconsolidated formation are 78 lpm/m and 16–33 m/d, respectively. The specific capacity and permeability of the unconsolidated formation are 208 lpm/m and 19.7 m/d, respectively [31].

Methodology

Water samples were collected from five locations within the Veeranam Tank (T1–T5), two locations from the Vadavar River, the main feeding stream to the tank (R1 and R2), 12 water samples from the open wells (OW1–OW12) and four samples from the deep bore wells (DBW1–DBW4) located around the tank during August 2015 (south-west monsoon). Map showing the sampling locations is presented in Fig. 4. Tank and river water samples were collected at a mid-depth from the water surface level to minimize the effect of evaporation. Water samples were collected in the airtight 60-ml polyethylene bottles without entrapping any air bubbles and its geographical coordinates were determined by hand-held GPS. The water samples were then transported to the Centre for Water Resources Development and Management (CWRDM) Laboratory, Kozhikode, Kerala, for the analyses of isotopic composition. The $\delta^{18}O$ and δD of water samples were determined by isotope ratio mass spectrophotometer (IRMS), model Finnigan Delta PluxXP, made by Electron Corporation, Bremen, Germany. $\delta^{18}O$ isotope ratio was analysed by the CO_2–H_2O equilibration method [39]. About 200μL of each sample was equilibrated with laboratory standard CO_2 gas at 32 °C. The δD isotope ratio was analysed by the H_2–H_2O equilibration method using platinum catalyst supported on hydrophobic material. The equilibrated gas reflects the isotope ratio of water samples, and the data acquisition system directly provides the isotopic composition of water samples. The isotopic values are reported in terms of per mil (‰) deviation of the isotope ratio from the international standard V-SMOW (Vienna-Standard Mean Ocean Water) by the following relation [16]:

$$\delta(‰) = \left(\frac{R_{Sample} - R_{VSMOW}}{R_{VSMOW}} \right) X 10^3$$

Fig. 4 Map showing the sampling sites in the study area
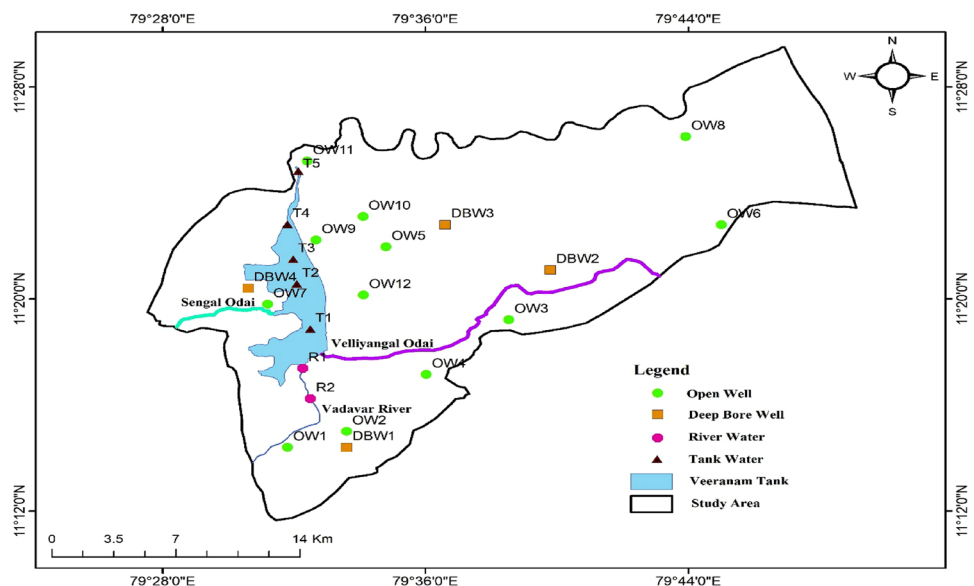
where R denotes abundance ratio of heavier to lighter isotopes ($R = \frac{^{18}O}{^{16}O}; \frac{^{2}H}{^{1}H}$).

The precision of measurement for $\delta^{18}O$ and δD was $\pm 0.18‰$ and $\pm 1.8‰$, respectively.

Results and Discussion

Isotopic Signatures of Groundwater

The $\delta^{18}O$ signature for the open wells ranges from -5.07 to $1.25‰$, and the δD varies from -32.93 to $3.01‰$. The mean values of $\delta^{18}O$ and δD in open wells are $-1.84‰$ and $-15.30‰$, respectively. $\delta^{18}O$ value in deep bore wells ranges from -5.23 to $-3.28‰$ with a mean of $-4.52‰$. δD value of deep bore wells ranges from -37.21 to $-23.09‰$, and its average level is $-31.25‰$. Stable isotope compositions of open wells and deep bore wells are presented in Tables 1 and 2, respectively. The shallow aquifer (open wells) shows enriched stable isotope values compared to the deeper aquifer showing depleted values. This implies that the sources of recharge may be from different origins. Wide variations in the groundwater isotopic signatures may also be due to the isotopic variations that occur along the groundwater flow path through physical and chemical reactions [50].

Isotopic Composition of River Water and Tank Water

The $\delta^{18}O$ values of the Vadavar River water at locations R1 and R2 are $-0.57‰$ and $-0.14‰$, respectively. The δD signature at R1 is $-8.7‰$ and at R2 is $-5.1‰$. $\delta^{18}O$ value of the tank water ranges from 1.10 to 1.45‰ with a mean concentration of 1.22‰, and that of δD ranges from 1.65 to 4.14 ‰ with a mean concentration of 3.26‰. Stable isotope compositions of tank water at different locations (T1, T2, T3, T4 and T5) are presented in Table 3. All tank water samples showed positive or near-positive isotopic signatures, indicating evaporative enrichment. The high solar radiation tends the tank water to evaporate, and thus, the $\delta^{18}O$ and δD values of tank water samples are enriched [19]. The Vadavar River isotopic signature is slightly depleted than tank water as the water is originating from high altitude with increased flow velocity and absence of residence time.

Relationship Between $\delta^{18}O$ and δD

The trendline showing the relationship between $\delta^{18}O$ and δD values developed by Craig [9] is referred to as the global meteoric water line (GMWL), and the GMWL equation is $\delta D = 8\delta^{18}O + 10$. Similarly, the local meteoric water line (LMWL) is constructed with respect to the area of the study which is controlled by locally prevailing climate and weather condition. For the present study, the relationship

Table 1 $\delta^{18}O$ and δD values of the open wells with location

Well ID	Latitude (N)	Longitude (E)	$\delta^{18}O$ (‰)	δD (‰)	d−excess (‰)	Total Depth of the Well (m) bgl	Depth to Water Level (m) bgl
OW1	11.24	79.53	−3.09	−23.73	0.99	8.0	2.5
OW2	11.25	79.56	−2.07	−14.24	2.32	9.1	1.7
OW3	11.31	79.63	−5.07	−32.93	7.63	6.0	3.0
OW4	11.30	79.60	−3.40	−23.87	3.33	9.0	5.1
OW5	11.37	79.58	−1.46	−15.67	−3.99	8.5	4.0
OW6	11.38	79.75	−3.96	−28.01	3.67	8.0	4.2
OW7	11.33	79.52	−0.92	−11.71	−4.35	7.5	0.6
OW8	11.44	79.72	−4.1	−29.27	3.53	7.0	3.4
OW9	11.36	79.54	−0.22	−5.34	−3.58	6.5	2.3
OW10	11.36	79.55	1.25	3.01	−6.99	7.0	1.2
OW11	11.42	79.54	0.76	−1.59	−7.67	8.0	4.1
OW12	11.33	79.55	0.19	−0.23	−1.75	9.5	5.0

Table 2 $\delta^{18}O$ and δD values of the deep bore wells with location

Well ID	Latitude (N)	Longitude (E)	$\delta^{18}O$ (‰)	δD (‰)	d-excess (‰)
DBW1	11.24	79.56	−4.41	−32.57	2.71
DBW2	11.34	79.65	−3.28	−23.09	3.15
DBW3	11.38	79.61	−5.23	−32.12	9.72
DBW4	11.34	79.51	−5.17	−37.21	4.15

Table 3 δ^{18}O and δD values surface water with location

Well ID	Water source	Latitude (N)	Longitude (E)	δ^{18}O (‰)	δD (‰)	d-excess (‰)
R1	Vadavar River	11.29	79.54	-0.57	-8.7	-4.14
R2	Vadavar River	11.27	79.54	-0.14	-5.1	-3.98
T1	Tank water	11.32	79.52	1.15	3.06	-6.14
T2	Tank water	11.35	79.54	1.10	1.65	-7.15
T3	Tank water	11.42	79.53	1.45	3.57	-8.03
T4	Tank water	11.36	79.54	1.25	3.87	-6.13
T5	Tank water	11.38	79.53	1.15	4.14	-5.06

developed by [22] for south India is considered as the local meteoric water line (LMWL) represented by the equation δD = 7.82δ^{18}O + 10.22 which is close to the GMWL. The slight deviation of slope between GMWL and LMWL is due to the variations in local factors such as meteorological and geographical features which include air, temperature, different sources of moisture and rainfall [34, 45].

The δ^{18}O versus δD plot drawn for the measured stable isotope concentration of open wells, deep bore wells and tank water with respect to the LMWL is shown in Fig. 5. The δ^{18}O versus δD of groundwater in the study area is close to LMWL denoting that rain water is one of the sources to groundwater in the region. The Veeranam Groundwater Line for open wells (VGWL1) and Veeranam Groundwater Line for deep bore wells (VGWL2) in the plot fall right of the local meteoric water line (LMWL) with a slope of 5.84. The lower slope values clearly indicate the evaporative enrichment with a slope between 4 and 6 generally observed in semi-arid region [8]. Further, the δ^{18}O and δD values of the tank water are enriched and fall on the on the upper right of the local meteoric water line (Fig. 5). As the tank water remains at the surface for a long time and is usually subjected to evaporation, the enriched data were observed.

Interconnection Between Water Bodies in the Study Area

Based on groundwater isotopic composition, groundwater sources in the study area are classified into two categories:
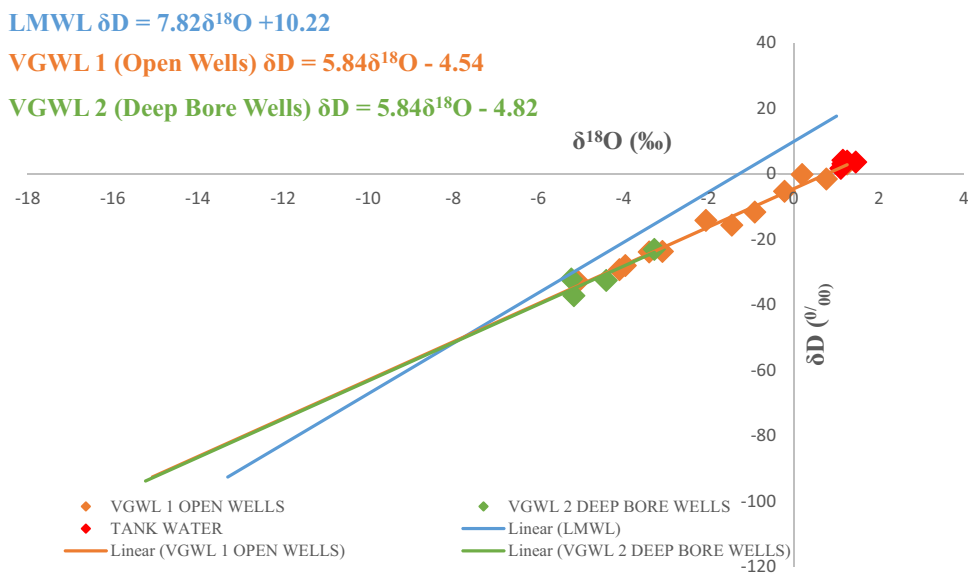
Groundwater Predominantly Recharged by the Tank Water (Group A)

The wells OW5, OW7, OW9, OW10, OW11 and OW12 around the Veeranam Tank (both upstream and downstream) fall under one group (Group A). The δ^{18}O value of these wells ranges from -1.46 to 1.25‰ with a mean of 0.07‰, whereas the δD value ranges from -15.67 to 3.01‰ with a mean of -5.26‰. Enriched isotopic composition values are observed in this group, which is due to the infiltration of evaporated tank water into these wells recently.

Groundwater Predominantly Recharged by Rainwater (Group B)

Water from the wells OW1, OW2, OW3, OW4, OW6, OW8, DBW1, DBW2, DBW3 and DBW4 fall under one group

Fig. 5 Relationship between δ^{18}O and δD of water from open dug wells, deep bore wells and the tank water with respect to LMWL

LMWL δD = 7.82δ^{18}O +10.22
VGWL 1 (Open Wells) δD = 5.84δ^{18}O - 4.54
VGWL 2 (Deep Bore Wells) δD = 5.84δ^{18}O - 4.82

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(Group B) showing depleted isotopic composition. The $\delta^{18}O$ ranges from -5.23 to $-2.07‰$ with a mean composition of $-3.98‰$. The δD ranges from -37.21 to $-14.24‰$ with a mean composition of $-27.70‰$. The groundwater recharged through rainwater possesses depleted isotopic signatures. Further, the isotopic signatures of these wells fall exactly on the LMWL, which also further confirms that these wells are predominantly recharged through rainwater. The presence of high permeable sandstone formation [23] tends the rainwater to be easily infiltrated and results in further depletion of isotopic signatures in groundwater due to the dissolution process. The deeper aquifer may also be recharged by shallow aquifer where the intervening clay layers are very thin [32]. The deeper aquifer which is connected to a shallow aquifer with depleted isotopic signatures exhibits no evaporation in the deeper aquifer as compared to the shallow aquifer [41].

Deuterium Excess

Deuterium excess (d-excess) is the second-order parameter, and it is based on non-equilibrium fractionation [24]. d-excess is used to identify the vapour source of water and the evaporation process [34]. If no other reaction occurs within the aquifer, then the groundwater d-excess should be equal to rainfall d-excess and it varies with groundwater residence time also [14]. The d-excess of different water sources in the study area was calculated based on the relation, d-excess $= \delta D - 8\delta^{18}O$, proposed by Dansgard [12].

The open well water d-excess ranges from -7.67 to 7.63. The d-excess for the water from deep bore wells ranges between 2.71 and 9.72, whereas the tank water d-excess ranges from -8.03 to -5.06. The deep bore wells possessing high d-excess than open wells are due to the high residence time of water in the aquifer. If water is subjected to evaporation, then $\delta^{18}O$ in water is enriched resulting in a decrease of d-excess [18]. Wells that possess negative d-excess are subjected to evaporation before or after percolation of water into the aquifer. All the tank water samples possessed negative d-excess, and this further confirms that surface water is subjected to the evaporation [49].

Conclusions

In this study, stable isotopic composition of water ($\delta^{18}O$ and δD) was used to understand the interconnection between Veeranam Tank (a surface water source) and groundwater sources (open dug wells and deep bore wells) in a semi-arid region in Tamil Nadu, India. Isotopic signatures of water from the tank and wells were measured and the observed variations were analysed to distinguish the groundwater recharge sources in the study area. Oxygen and hydrogen

isotopic data of the water samples from the wells OW5, OW7, OW9, OW10, OW11 and OW12 which are adjacent to the Veeranam Tank showed enriched values, indicating that these wells are predominantly recharged from the tank water. Further, the tank water samples possessed negative d-excess, indicating that tank water is strongly influenced by the evaporation process. Water samples from the wells OW1, OW2, OW3, OW4, OW6, OW8, DBW1, DBW2, DBW3, DBW4 and DBW5 showing depleted Isotopic composition and the points lying on the local meteoric water line in the $\delta^{18}O$ versus δD plot clearly revealed the precipitation as the main recharge source for these wells. This study has provided valid information that can be useful for groundwater resources management at regional as well as national scales. The study also suggests the construction of more artificial recharge structures in the zones groundwater recharged by rainwater on the basis of site suitability, so as to enhance the water availability for any beneficial uses. The study has opened new avenues for further investigations to quantify the percentage of contribution from different sources in the region for better water resources management.

Data Availability   The data that support the findings of this study are available on request from the corresponding author.

Declarations

Conflict of interest   The authors declare that there is no conflict of interest.

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