

Identification of Recharge Processes in Groundwater in Hard Rock Aquifers of Madurai District Using Stable Isotopes

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Abstract Stable isotopes of H and O are the integral parts of water molecule and serve as ideal tracers to understand the recharge processes in groundwater. Hence, a study has been conducted in hard rock aquifers of Madurai District of Tamilnadu to identify the recharge processes using stable isotopes. A total of 54 groundwater samples were collected representing the entire district from various lithounits during post monsoon. Samples were analysed for pH, EC, Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, HCO₃⁻, SO₄²⁻, PO₄³⁻, H₄SiO₄, F⁻, δ¹⁸O and δD. Cl⁻ and HCO₃⁻ were the dominant ions in groundwater samples. Average values of Cl⁻ and HCO₃⁻ ranged from 247 and 244 mg/L in fissile hornblende biotite gneiss, 262 and 268 mg/L in Charnockite, 75 and 185 mg/L in quartzite, 323 and 305 mg/L in granite, 524 and 253 mg/L in floodplain alluvium rock types. Geochemical signatures of groundwater were used to identify the chemical processes that control hydrogeochemistry. Interpretation of δ¹⁸O and δD indicates recharge from the meteoric water in charnockite, quartzite, granite and some samples of fissile hornblende biotite gneiss. It is also inferred that recharge take place from evaporated water in floodplain alluvium and fissile hornblende biotite gneiss.

Keywords Stable isotope · Groundwater recharge · Hard rock aquifers

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1 Introduction

In groundwater hydrology, stable isotopes provide an idea about movement and distribution processes within aquifers. A large number of studies for the past few decades have identified that stable oxygen and hydrogen isotope ratios provide useful tools for hydrological investigations (Clark and Fritz 1997; Mazor 1991; Fontes 1981; Bhattacharya et al. 1985; Yousif et al. 2015). In groundwater studies they are used to: estimate recharges (Gupta 1983); identify the effects of evaporation on groundwater systems (Hendry and Schwartz 1988; Krishnamurthy and Bhattacharya 1991); and also estimate advection/diffusion rates in unsaturated/saturated zones (Gupta 1983). The International Atomic Energy Agency (IAEA) has measured isotopes in precipitation worldwide (Gat 1981). Unfortunately only limited data of $\delta^{18}\text{O}$ and δD in precipitation is available from a few Indian stations. These isotopic compositions are sensitive tracers and they are widely applied to study the natural water circulation and groundwater movement (Krabbenhoft et al. 1990; Herczeg et al. 1992; Turner et al. 1992). The meteoric processes alter the isotopic composition of water in such a way that precipitation in a particular environment has a similar characteristic as that of stable isotope. This isotopic signature then serves as a natural tracer for identifying the groundwater recharge sources. The isotopic and geochemical analysis of various groundwaters of the Ranga Reddy district with undulating topography, fractured hard rock outcrops and basement, varying thickness of weathered zone with low primary porosity and dominant secondary porosity, identified various recharge processes operative in the study area (Sukhija et al. 1998).

Recharge process of groundwater is mainly replenished by precipitation. In the absence of this process, the groundwater would be completely depleted. Therefore, recharge processes play an important role in groundwater reserve assessment and its determination. They can be studied through various techniques using hydrogeochemical parameters, climatological studies (Jaiswal et al. 2015), and groundwater modeling such as statistical techniques (Viswanath et al. 2015). They are also helpful for the sustainable management and protection. These processes become more important in hard rock aquifers because the available quantity of groundwater is generally lesser. Madurai District is one such region with hard rock aquifers. There have been limited groundwater studies conducted in this region (e.g., Thivya et al. 2013, 2014a, 2014b, 2014c, 2014d, 2014e, 2015a, 2015b, 2015c; Navaraj and Krishnammal 2012; Dharmaraj et al. 2012; Balamurugan and Dheenadayalan 2013; Sivasankar et al. 2013; Padmanaban et al. 2013). The earlier studies have not attempted to investigate the recharge process. Hence, the present study has focused on identifying the recharge processes in hard rock aquifers using stable isotopes of oxygen and hydrogen.

2 Study Area

The study area is situated in the southern part of Tamil Nadu State covering an area of about 3741 km² (Fig. 1), which occupies 2.09 % of the total geographical area of the State. It lies in the north Latitude of 9°33'3.6" to 10°19'8.4" and East Longitude of 77°27'7.2" to 78°28'58.8". The district is characterized by Red soil, Black clayey soil and alluvial soil. Geological formations of the study area range from Archean to recent. The lithology of the study area comprises fissile homblende biotite gneiss, charnockite, granitic intrusions, quartzite and floodplain alluvium. The archean formations comprise khondalite, charnockite, garnitiferous granulite, biotite gniesses and fissile homblende biotite gniessic group of rocks. Quartzite

occurs as ridges and as low lying mounts in the study area (GSI 1995; Thivya et al. 2013). The recent alluvium comprises of clay, sand, gravel and silt along the Vaigai river course. The district is traversed by the Vaigai River along the Northwest – Southeast orientation, dividing the city of Madurai into two parts. The river is the lifeline of the district and its catchment is 1524 m above mean sea level (amsl) in the Western Ghats.

Groundwater occurs under phreatic conditions in weathered and interconnected shallow fractures and under semi-confined to confined conditions in deeper fractures (CGWB 2010). In Usilampatty and Sedapatty union, the groundwater level is deeper than in other regions. The depth to water level in the district varies from 3.13 to 7.66 m below ground level (bgl) during premonsoon (May 2006) and 1.86 to 5.74 m bgl during post monsoon (CGWB 2010). The variations in the yield of bore wells are very high in the district. Potential fractures with high discharge have been established along Valandur – Usilampatti – Timmarasanayakanur - Thirali - Peraiyur tract and Palkalainagar - Nilayur tract in the district. The higher levels of groundwater are noted in the southern and the northern/northeastern part of the study area, which indicates that the groundwater moves towards the eastern part of the study area. The normal rainfall was 548 mm in year 2012 (Sholavandan Rain Gauge Station) (IMD 2014).

3 Methodology

A total of 54 groundwater samples were collected using drinking water handpumps in post-monsoon (POM) season in January 2012, irrespective of lithology, representing the entire district. 21 samples from fissile hornblende biotite gneiss (FHBG) and charnockite (Char), 3 from quartzite (Qtz), 4 from granite (Grt) and the rest of the samples from floodplain alluvium (FPA). pH and electrical conductivity (EC) were determined in the field using a field analysis kit (Eutech Handheld Instruments). 500 mL of groundwater samples were collected in polyethylene bottles and they were analyzed for major cations and anions using standard procedures (APHA 1995). Calcium, magnesium, bicarbonate and chloride were determined by titrimetric method. Sodium and potassium were analyzed through flame photometry (ELICO CL). The detection limit of flame photometry is 1–100 ppm with an accuracy of ± 1 digit. Silica, phosphate, and sulfate were determined by spectrophotometry (ELICO SL 171 minispec). The detection limit of spectrophotometry is 340–1000 ppm with an accuracy of

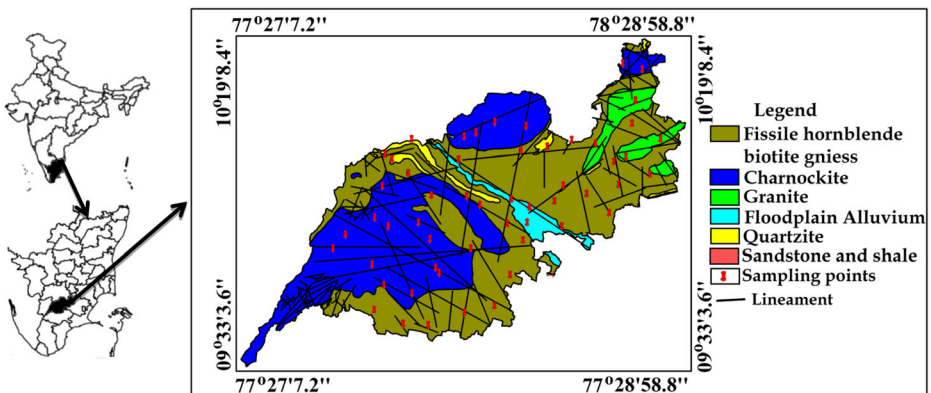


Fig. 1 Lithology and location map of the study area (after Thivya et al. 2013)

± 2.5 nm. The reliability of the results was determined by the ionic balance of groundwater samples and a 5–10 % of percentage error was noted.

The groundwater samples were collected in 60 mL capacity polyethylene bottles for stable isotope analysis. The sample bottles were filled completely and preserved air tight in order to avoid evaporation and they were measured for $\delta^{18}\text{O}$ and δD by mass spectrometer (Finnigan Deltaplus Xp, Thermo Electron Corporation, Bermen, Germany) using gas equilibration method with a precision of 0.5 ‰ and 0.1 ‰ (2σ criterion) accuracy, respectively. Stable isotope results were expressed with respect to Vienna Standard Mean Ocean water (SMOW) in units δ (Permil- ‰), as follows:

$$\delta = (R_{\text{sample}} - R_{\text{SMOW}} / R_{\text{SMOW}}) 10^3$$

where, $R = \text{D/H}$ or $^{18}\text{O}/^{16}\text{O}$.

Partial pressure of carbon dioxide (pCO_2) values were calculated using the WATEQ4F code (Trudell and Jones 1973). It is the significant factor for enhancing the solubility in carbonate rocks by the dissolution of minerals, such as mainly plagioclase, which increases the pH, resulting in the formation of bicarbonate, thus accumulates more cations in the remaining water (Chidambaram et al. 2011).

4 Results and Discussion

4.1 Hydrogeochemical Processes

The maximum, minimum and average values of stable isotopes are given in Table 1. The average concentrations of major ions are given in Fig. 2 and chemical composition of groundwater is given in Table 2. Cl^- is the dominant ion in the region which is observed along the floodplain alluvium in Vaigai river course (Ranjana et al. 2011; Thivya et al. 2013, 2014a). HCO_3^- is the next dominant ion, which is observed in granitic terrains, and is mainly due to the weathering process. The higher concentration of Na^+ and Ca^{2+} is observed in floodplain alluvium, which may be due to minerals like calcite, plagioclase and hornblende, as they are the primary sources for calcium in groundwater, and sodium bearing minerals like albite and other members of weathered plagioclase feldspars, nepheline and sodalite, releasing the primary soluble sodium.

Table 1 Maximum, minimum and average values of δD and $\delta^{18}\text{O}$ for different lithological unit (all values are in ‰)

Statistics		FHBG ($n = 21$)	Char ($n = 21$)	Qtz ($n = 3$)	Grt ($n = 4$)	FPA ($n = 5$)
$\delta\text{D}(\text{‰})$	Maximum	-13.00	-25.65	-29.86	-22.98	-10.99
	Minimum	-45.10	-37.61	-33.40	-29.98	-31.89
	Average	-28.79	-32.06	-32.17	-26.72	-21.55
$\delta^{18}\text{O}(\text{‰})$	Maximum	-1.37	-3.61	-4.61	-3.30	-0.98
	Minimum	-6.44	-5.50	-5.00	-4.33	-4.80
	Average	-4.11	-4.69	-4.83	-3.83	-3.16

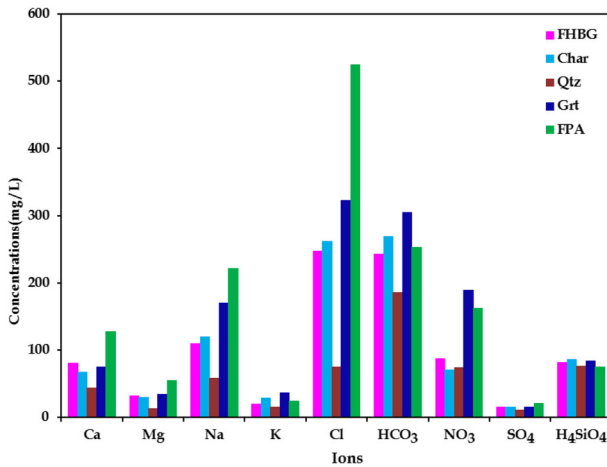
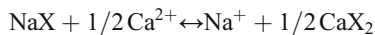


Fig. 2 Average concentration of ions for various lithologic units

The trilinear plot developed by Piper (1944) is used to delineate variability and trends in water quality to understand groundwater flow and geochemistry (Dalton and Upchurch 1978; Wu et al. 2014). The Piper diagram was made in such a way that the milliequivalent percentages of the major cations and anions were plotted in separate triangles. These plotted points in the triangular fields are projected further into the central diamond field, which provides the overall character of the water. The triangular fields are plotted separately with epm values of cations alkali earths (Ca^{2+} , Mg^{2+}), alkali (Na^+ , K^+), weak acid (HCO_3^-), and strong acid (SO_4^{2-} and Cl^-). The samples fall in Ca^{2+} - Na^+ - HCO_3^- and Ca^{2+} - Cl^- type. Most of the samples reflect the mixing type of cations and anions, which may be due to the additional leachate after monsoon (Chidambaram et al. 2012). During this season, ion exchange process/ weathering exists and the mixed type of Ca^{2+} - Na^+ - HCO_3^- - Cl^- type dominates, and this type may be due to the influence of monsoons (Fig. 3). Some of the samples of FHBG, Qtz and FPA fall in recharge zones with Ca - HCO_3 type. Overall, the mixed type of all monsoon and non-monsoon characteristics are reflected in the groundwater samples. The concentrations of Ca^{2+} in groundwater may decrease while the concentration of Na^+ increases during groundwater mixing, due to the ion exchange with the aquifer matrix. The Ca^{2+} ions are substituted by the Na^+ ions on the solid surface, as demonstrated in the equation below:



X is considered to be a soil exchanger, and the groundwater comes into contact with Na^+ , which originated from seawater or halite minerals (NaCl) or from plagioclase feldspar that precipitated on the aquifer matrix. The Na^+ ion pushes away the Ca^{2+} ion, and thus, it becomes dominant in the groundwater through the process of cation exchange.

4.2 Stable Isotopes (δD & $\delta^{18}\text{O}$)

The general meteoric relationship between the oxygen and hydrogen isotopes has been described by the global meteoric water line (GMWL) with a definite equation.

Table 2 Chemical constituents of groundwater samples (All values are in mg/l except EC ($\mu\text{S/cm}$) and pH). [FHBG- Fissile hornblende biotite gneiss; Char- Charnockite; Qz- Quartzite; Grt- Granite; FPA- Flood Plain alluvium]

S.No	Lithology	Ca	Mg	Na	K	F	Cl	HCO ₃	NO ₃	PO ₄	SO ₄	H ₂ SiO ₄	pH	EC
1	FHBG	49.00	18.00	56.37	30.10	0.26	64.99	277.53	1.70	0.16	6.52	96.50	7.10	792.00
2	FHBG	49.00	16.00	74.83	12.83	0.58	112.26	203.33	30.00	0.08	11.67	93.33	7.50	924.00
3	FHBG	56.00	16.00	91.00	23.00	0.12	152.67	244.33	127.50	0.11	9.23	64.67	7.10	1843.75
4	FHBG	39.00	13.00	77.33	17.47	0.22	107.72	183.00	2.00	0.30	10.60	74.50	7.40	1045.31
5	FHBG	165.00	74.00	108.30	4.50	1.58	555.65	187.07	97.50	0.11	31.17	107.00	7.40	2687.50
6	FHBG	98.00	32.00	93.37	41.93	0.16	267.37	279.93	130.00	0.19	23.83	83.50	7.30	1984.38
7	FHBG	49.00	21.00	205.47	26.43	0.39	292.78	256.20	22.50	0.19	12.13	76.17	7.50	1641.33
8	FHBG	78.00	20.00	103.73	42.20	0.15	196.80	284.67	56.25	0.19	15.10	86.67	7.60	1320.31
9	FHBG	32.00	20.00	41.53	12.23	0.22	59.08	170.80	0.85	0.11	12.60	85.67	7.60	651.56
10	FHBG	45.00	35.00	74.03	8.80	1.39	129.98	321.27	80.00	0.14	14.43	83.17	7.10	1282.81
11	FHBG	106.00	56.00	47.50	24.40	0.77	242.24	264.33	155.00	0.47	13.62	94.57	7.00	1339.06
12	FHBG	57.00	14.00	46.33	7.47	0.19	100.44	207.40	5.00	0.07	11.47	88.50	7.80	1198.44
13	FHBG	163.00	41.00	145.00	10.57	0.15	354.50	211.47	295.00	0.08	9.33	84.77	7.60	2175.00
14	FHBG	71.00	21.00	81.00	15.10	0.16	118.17	252.13	180.00	0.05	8.90	62.17	7.20	651.56
15	FHBG	59.00	21.00	170.33	34.67	0.62	299.65	333.13	4.50	0.05	13.37	89.00	7.70	1811.00
16	FHBG	84.00	15.00	79.57	7.13	0.15	135.89	264.33	80.00	0.48	23.67	111.67	7.30	1271.00
17	FHBG	32.00	24.00	122.90	5.60	0.90	171.34	276.53	0.95	0.50	16.97	75.50	7.50	954.00
18	FHBG	61.00	37.00	225.00	5.70	1.84	444.93	295.00	81.25	0.08	11.57	77.33	7.50	2447.00
19	FHBG	42.00	18.00	34.73	12.97	0.72	64.99	191.13	12.50	0.11	13.80	94.83	7.80	812.00
20	FHBG	294.00	131.00	255.00	5.53	0.12	1087.13	223.67	300.00	0.53	23.60	88.67	6.50	3593.75
21	FHBG	60.00	22.00	156.00	56.80	0.17	237.28	183.40	177.50	0.06	21.00	4.17	6.30	932.81
22	Char	68.00	22.00	96.70	7.03	0.27	214.89	215.53	0.90	0.22	15.63	77.00	7.50	789.06
23	Char	49.00	35.00	154.00	91.00	0.20	289.51	402.60	127.50	0.28	20.18	77.50	7.40	1587.50
24	Char	83.00	41.00	276.67	98.90	1.99	584.93	435.13	20.00	0.45	33.47	100.50	7.10	3359.38
25	Char	63.00	29.00	147.73	38.10	0.41	319.05	272.47	21.25	0.22	11.50	83.17	6.80	1968.75
26	Char	43.00	23.00	120.03	9.93	0.72	153.62	264.33	8.75	0.59	18.77	91.00	7.30	859.38
27	Char	39.00	19.00	39.03	6.27	0.35	100.44	146.40	12.20	0.21	11.57	91.33	6.60	670.31
28	Char	74.00	26.00	106.90	7.57	2.68	319.05	187.07	12.92	0.09	9.83	78.83	7.10	995.31

Table 2 (continued)

S.No	Lithology	Ca	Mg	Na	K	F	Cl	HCO ₃	NO ₃	PO ₄	SO ₄	H ₄ SiO ₄	pH	EC
29	Char	48.00	47.00	144.43	13.90	0.45	366.32	207.40	7.50	0.12	19.37	48.67	7.50	2609.38
30	Char	69.00	29.00	117.40	40.70	1.23	271.78	284.67	6.25	0.24	18.27	73.67	7.60	2484.38
31	Char	56.00	44.00	164.00	54.03	0.24	324.96	317.20	182.50	0.19	13.53	113.33	7.60	1942.19
32	Char	105.00	39.00	51.77	27.30	0.55	248.15	207.40	127.50	0.63	14.73	68.23	7.00	764.06
33	Char	61.00	27.00	106.67	13.37	0.96	189.07	264.33	137.50	0.12	12.53	81.67	7.20	1381.25
34	Char	120.00	45.00	132.00	10.47	0.16	384.04	260.27	142.50	0.11	12.20	88.83	6.60	1678.13
35	Char	53.00	12.00	58.85	9.23	0.21	112.26	140.30	80.00	0.55	11.75	97.50	7.10	645.31
36	Char	93.00	47.00	136.00	11.65	1.00	401.77	276.53	78.33	1.29	9.80	69.83	7.10	1628.13
37	Char	100.00	24.00	145.73	5.60	0.43	283.60	345.67	92.50	0.23	19.97	84.50	7.00	2359.38
38	Char	48.00	21.00	145.00	78.90	0.14	183.16	402.60	145.00	4.98	11.60	87.13	7.10	2468.75
39	Char	37.00	13.00	70.00	56.57	2.19	82.72	239.93	107.50	0.27	11.37	82.57	7.30	1053.13
40	Char	121.00	60.00	199.47	21.67	0.16	549.48	329.40	130.00	0.10	13.47	86.67	7.10	2781.25
41	Char	41.00	16.00	48.73	3.70	1.99	47.27	207.40	35.00	0.06	11.87	113.17	6.90	704.00
42	Char	39.00	19.00	53.33	6.40	0.68	70.90	227.73	1.00	0.03	10.70	107.17	6.80	706.00
43	Qtz	33.00	10.00	19.00	18.27	0.13	35.30	120.53	2.20	0.11	9.98	81.83	6.12	107.66
44	Qtz	40.00	14.00	67.00	21.00	0.50	59.08	174.87	135.00	0.21	11.53	70.00	7.50	518.75
45	Qtz	57.00	16.00	86.33	7.73	0.48	129.98	260.27	82.50	0.74	12.03	74.33	7.60	726.56
46	Grt	92.00	31.00	144.60	16.23	0.20	347.25	292.80	65.00	0.21	18.00	49.17	7.50	2503.00
47	Grt	52.00	22.00	132.00	53.73	1.12	165.43	235.87	280.00	0.27	21.03	63.33	7.40	700.00
48	Grt	85.00	32.00	182.00	54.00	0.24	295.42	361.93	322.50	0.08	12.53	112.33	7.30	2248.00
49	Grt	71.00	52.00	223.00	20.63	0.44	482.62	329.53	88.75	0.68	9.60	108.50	7.20	1845.00
50	FPA	99.00	52.00	87.17	14.10	0.18	339.82	195.20	122.50	0.03	10.57	87.67	7.40	2846.00
51	FPA	133.00	35.00	82.50	11.37	0.18	200.88	284.67	85.00	0.08	15.30	65.83	6.70	1657.81
52	FPA	57.00	31.00	121.00	11.77	0.33	212.70	288.73	137.50	0.28	13.27	74.50	6.90	1393.75
53	FPA	290.00	131.00	654.00	67.00	0.14	1637.71	248.07	310.00	0.08	38.07	90.90	6.80	5218.75
54	FPA	57.00	21.00	162.00	18.93	0.19	230.43	248.07	155.00	0.06	24.80	55.33	7.83	1396.00

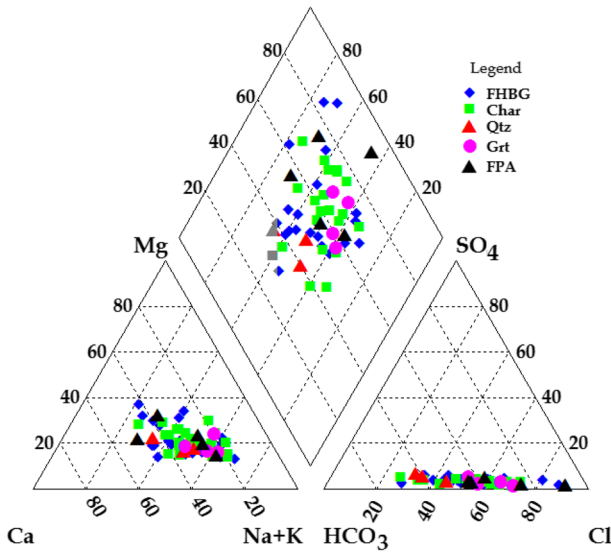


Fig. 3 Piper plot of the various samples to decipher the hydrogeochemical processes

Unfortunately, isotopic data on precipitation are not available for all samples, but it is available only in certain regions of the study area. The plot of $\delta^{18}\text{O}$ and δD of the rainwater samples of the Tamilnadu, derived for south west monsoon (SWM) precipitation (after Chidambaram et al. 2009), was used for the local meteoric water line (LMWL). A regression of 0.992 was noted for the various samples collected. The LMWL showed an equation of $\delta\text{D} = 7.89 \delta^{18}\text{O} + 10.38$, against the GMWL ($\delta\text{D} = 8 \delta^{18}\text{O} + 10$) of Craig (1961) and Rozanski et al. (1993). The slope of the LMWL is close to that of the GMWL (Fig. 4). The isotope results obtained were given in terms of δ units (per mil deviation of the isotope ratio from the international standard SMOW); the maximum, minimum and average values are presented in Table 1.

The δD and $\delta^{18}\text{O}$ data gives an idea about the secondary processes in the water as it moves into the subsurface. The slight deviation of LMWL from GMWL may be due to the effect of climatic factors such as air, temperature, secondary evaporation, seasonality of precipitation

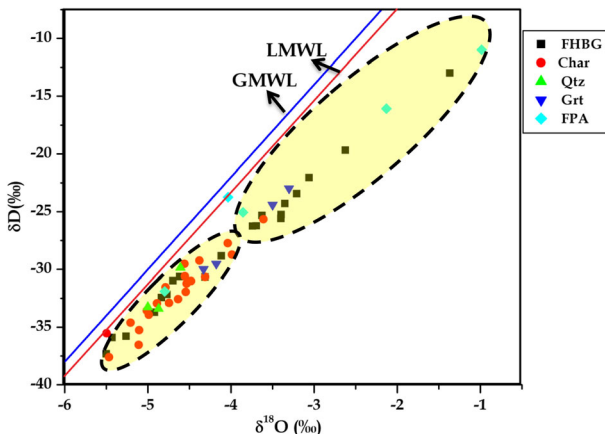


Fig. 4 Plot of δD versus $\delta^{18}\text{O}$ of groundwater samples compared with of the LMWL and GMWL

and moisture source (Clark and Fritz 1997; Rozanski et al. 1993; Deshpande and Gupta 2012). The groundwater samples fall right on the LMWL, indicating that these samples have undergone some evaporation prior to infiltration (Baskaran et al. 2009). It also indicates that precipitation is not significantly modified by secondary evaporation. Some groundwater samples of floodplain alluvium, granite and charnockite show enriched values indicating evaporation trend. Some samples of fissile hornblende biotite gneiss are recharged by precipitation, and most of the samples are recharged by evaporating water bodies. It is also evident that the study area has more open ponds in addition to agricultural activities (Thivya et al. 2015c), which contribute significant moisture to the atmosphere. There is a clear representation of samples close to the LMWL and the enrichment is due to the strong evaporation (Datta et al. 1991; Mukherjee and Chandrasekharan 1993). Under low or average flow condition or with long residence time, groundwater tends to be isotopically enriched which is a very prominent condition in the hard rock aquifers of the study area. The samples of other lithology are clustered close to LMWL indicating that they are recharged by direct precipitation.

The samples that are recharged by evaporation are compared with Land use and lineament maps (Figs. 5 and 6). It is observed that the isotope signatures of samples from floodplain alluvium and fissile hornblende biotite gneiss vary according to water level, and they are influenced by surface water bodies, like open ponds and rivers (Thivya et al. 2015a). They also spatially fall along the lesser lineament density region because of the higher residence.

4.3 Deuterium Excess

The deuterium excess (d-excess) is generally used to identify the source of vapor source of precipitation (Kondoh and Shimada 1997; Deshpande et al. 2013). Lower d-excess indicates evaporated rainfall and high d-excess is considered as a footprint of recycled moisture (Machavaram and Krishnamurthy 1995). It also helps in identification of the origin of air masses from which precipitation is formed (Rozanski et al. 1993).

If the d-excess values ranges between 8 and 10, it is expected that it may be due to primary precipitation. Lower d-excess values (< 10) imply evaporation of rain water leaving the impact on residual groundwater with d-excess values, while d-excess > 10 values indicate that

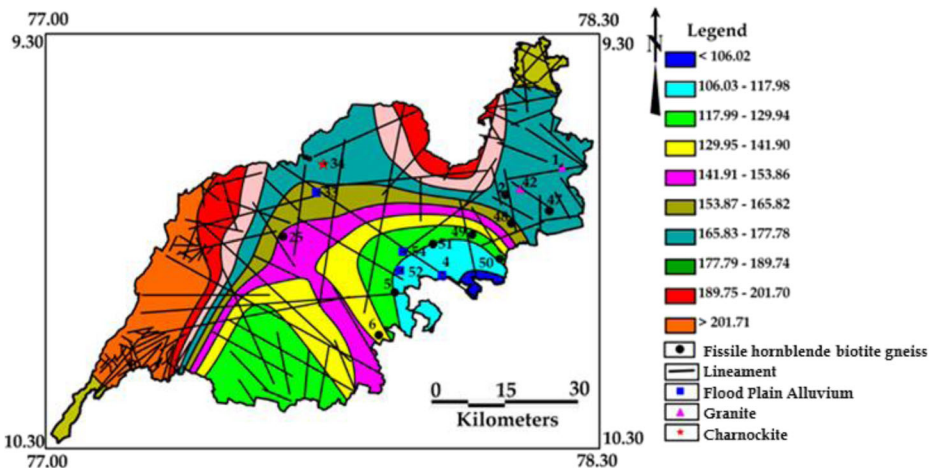


Fig. 5 Comparison of lineament, water level (amsl) with enriched isotopes in groundwater samples

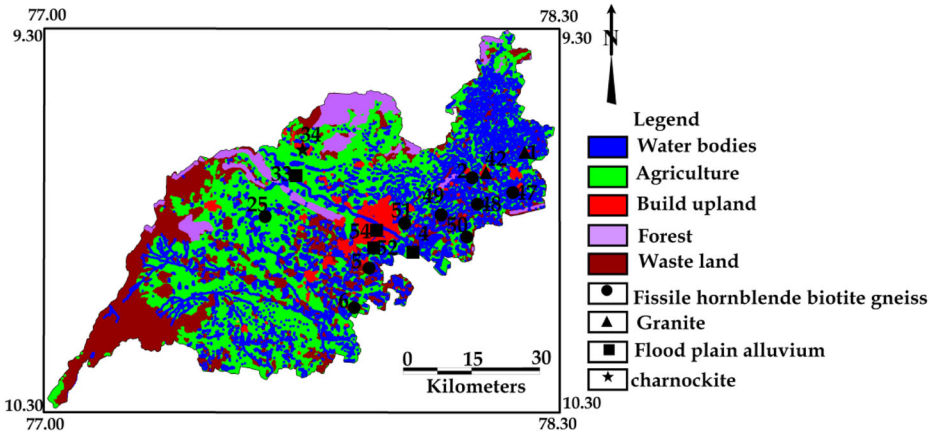


Fig. 6 Comparison of landuse with enriched isotopes in groundwater samples

evaporation in the source region takes place under lower humidity (Gat 1981). Samples show d-excess values ranging from -4 to 10 ‰ which could be attributed to contribution from evaporation of surface water bodies like open ponds and rivers (Fig. 7). The value less than 3 per mil reveals the source as evaporative enrichment with certainty (Harvey 2005). An inverse relation is observed between d-excess and $\delta^{18}\text{O}$ which shows the kinetic evaporation of water before recharging groundwater (Tirumalesh et al. 2007), intent the precipitation dominance. It is observed from the plot that floodplain alluvium and fissile hornblende biotite gneiss samples fall on the enriched part with relatively low d-excess, which again reflect the contribution of evaporated waters, like open ponds or agricultural return flow. It may also be due to the fact that long residence in FHBG may result in enrichment of stable isotopes. The deep fractures

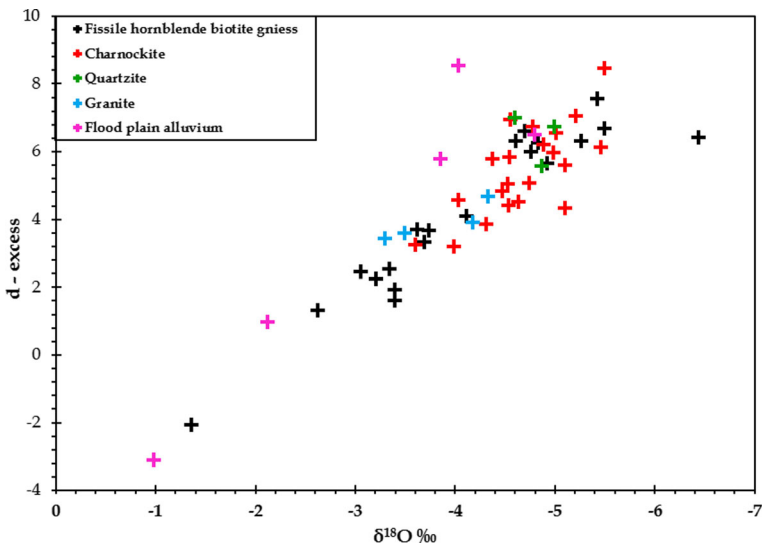


Fig. 7 Plot for d-excess versus $\delta^{18}\text{O}$ (per mil) data of groundwater samples

lineament with slightly elevated temperatures may also result in variation of stable isotope fractionation.

4.4 Stable Isotopes and Chloride

Chloride is naturally a conservative ion in groundwater which is not participating in geochemical reactions and remains in the system. It is observed that groundwater samples with high chloride contents are relatively enriched (Fig. 8a). The probable reasons may be congruent dissolution of dry chloride deposits in the soil zone or other anthropogenic factors like fertilizer, salts from septic tanks, etc. (Chidambaram et al. 2010).

The higher Cl^- is noted with enriched $\delta^{18}O$ and δD (Fig. 8b). This enrichment is observed in floodplain alluvium and higher Cl^- is noted along the Vaigai river bed

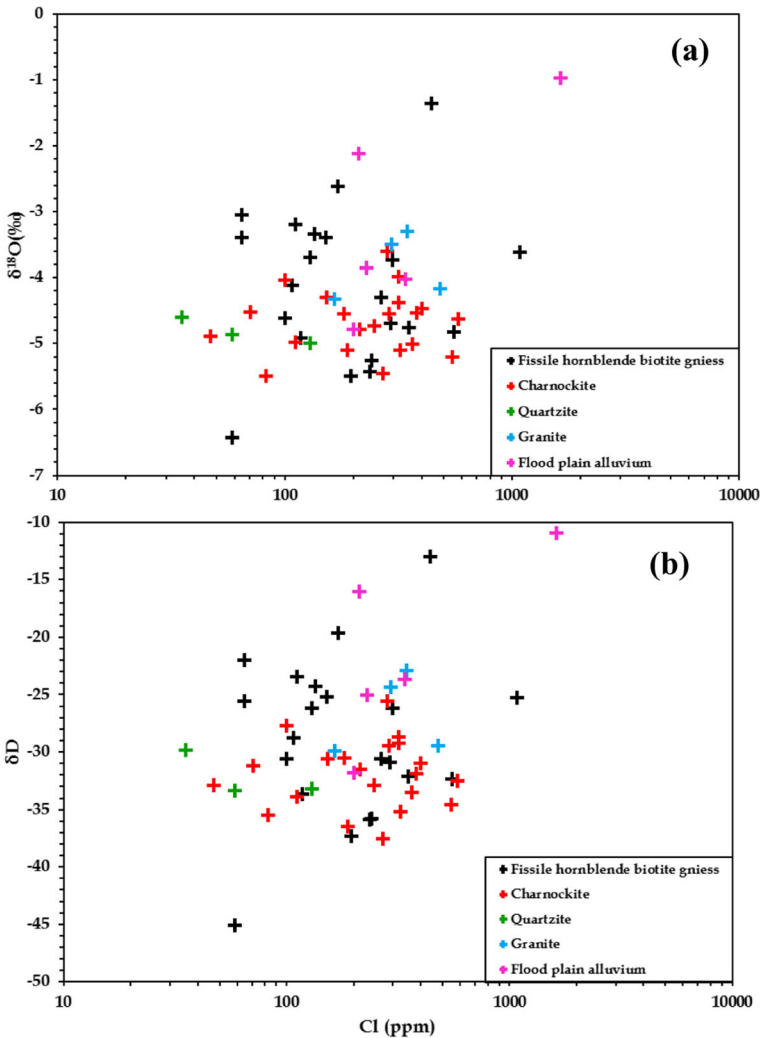


Fig. 8 Plot for (a) $\delta^{18}O$ versus Chloride and (b) δD versus Chloride for groundwater samples

(Thivya et al. 2013), suggesting recharge by surface water; this higher Cl^- is mainly due to domestic sewage, as it is discharged into the Vaigai River of Madurai city. The majority of samples of FHBG formation show linear relationship between $\delta^{18}\text{O}$ enrichment and Cl^- , indicating the leaching of evaporative salts deposited in the pore spaces during the previous summer (Chidambaram 2000). Higher concentration of chloride with enriched $\delta^{18}\text{O}$ also indicates recharge from the evaporated water bodies or due to the evaporation taking place along the fractures or due to the diffusive recharge along the flow path. Consequently, low chloride and depleted $\delta^{18}\text{O}$ represent the areas recharged frequently by rainfall (Baskaran et al. 2009; Prasanna et al. 2010). $\delta^{18}\text{O}$ and Cl^- values gradually increase in other formations reflecting the higher residence time and enrichment of Cl ions.

4.5 Relationship between Log pCO₂ and $\delta^{18}\text{O}$

The Log pCO₂ (Raymahashay 1986) for each sample were determined to study its relation to recharge (Prasanna et al. 2007; Chidambaram et al. 2009). Log pCO₂ in the groundwater samples ranged between -0.99 to -2.49 irrespective of lithology and these values are higher than the Log pCO₂ of the atmosphere (-3.75) which specifies that CO₂ is incorporated from the soil during infiltration through the unsaturated zone (Raymahashay 1986) (Fig. 9). Lesser Log pCO₂ values and depleted $\delta^{18}\text{O}$ indicates recent recharge by the local precipitation. The samples with higher Log pCO₂ and enriched $\delta^{18}\text{O}$ values indicates long residence time which is observed in some samples of fissile hornblende biotite gneiss, floodplain alluvium. When depletion of $\delta^{18}\text{O}$ is noted, there is also a decrease of pCO₂ observed in the sample that varies according to lithology. This also suggests that the rainwater charged with atmospheric CO₂ has acquired additional CO₂ from the soils, and thereby, develops high pCO₂ water on its travel to deep unsaturated zone (Chidambaram et al. 2009).

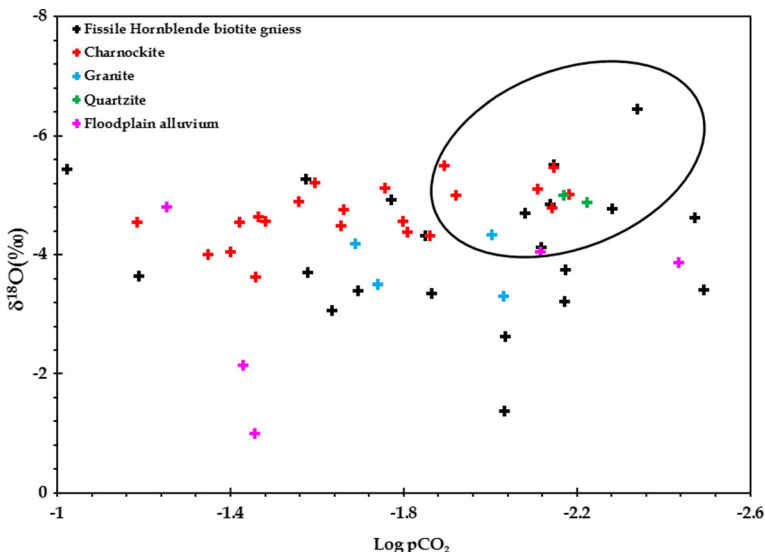


Fig. 9 Bivariate plot between log pCO₂ and $\delta^{18}\text{O}$ to decipher the relationship

5 Conclusions

The results indicate that the study area is dominated by ion exchange/weathering processes, and predominantly, by mixed type of Ca^{2+} - Na^+ - HCO_3^- - Cl^- type due to the influence of monsoons. It is inferred that under long residence time in the hard rock aquifers of the study area, under low/average flow condition, groundwater tends to be isotopically enriched. The samples from floodplain alluvium and few samples from fissile hornblende biotite gneiss show representation from evaporated surface waters, like open ponds or agricultural return flow. Samples collected from floodplain alluvium along the Vaigai river are enriched isotopes due to the recharge by surface water, and higher Cl^- is mainly due to domestic sewage. The majority of samples with linear relationship between $\delta^{18}\text{O}$ and Cl^- reflects the leaching of evaporative salts deposited in the pore spaces during the previous summer. Thus, they indicate recharge from evaporated water bodies, or evaporation taking place along fractures, or diffusive recharge along the flow path. In general, few samples from fissile hornblende biotite gneiss showed recharge by precipitation and most of the samples recharge by evaporating water bodies. The study also reflects that low Log pCO_2 values and depleted $\delta^{18}\text{O}$ indicate recent recharge by local precipitation. Hence, the study indicates that recharge of these aquifers takes place by two main processes namely precipitation and surface water sources. The study also shows the influence of the surface water bodies and its significance on the sustainable water resources management, and throws light for construction of artificial recharge structures in this region.

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