

# The impact of hydrogeological settings on geochemical evolution of groundwater in karstified limestone aquifer basin in northwest Sri Lanka

Asanka Thilakerathne · Christoph Schüth · Rohana Chandrajith

Received: 25 April 2014 / Accepted: 11 December 2014 / Published online: 25 December 2014  
© Springer-Verlag Berlin Heidelberg 2014

**Abstract** The geochemical and isotope analysis of groundwaters from the Murunkan basin in north western Sri Lanka was carried out to examine their evolution and recharge sources in order to shed light to enhance the current knowledge of the hydro-geochemical processes in a karst geological setting. A total of 40 water samples from ground and surface water bodies were collected from the Miocene limestone terrain, nearby metamorphic and from unconsolidated Quaternary terrains for major anions, cations and environmental isotopes ratios ( $\delta^{18}\text{O}_{\text{VSMOW}}$  and  $\delta^2\text{H}_{\text{VSMOW}}$ ). Distinct geochemical differences were noted between waters from limestone terrain and nearby metamorphic terrain indicating the modification of groundwater flow paths. Bicarbonate-chloride rich water is dominated in the limestone terrain in which water flows through a less mineralized aquifer system and is modified by the sea water intrusion. Groundwater in the metamorphic terrain is modified by dissolving of Ca–Mg rich mineral phases and subsequent ion exchange processes. The environmental isotopes of groundwater from both limestone and metamorphic terrains vary from  $-0.38$  to  $-6.68$  ‰ and  $-2.41$  to  $-42.3$  ‰ for  $\delta^{18}\text{O}_{\text{VSMOW}}$  and  $\delta^2\text{H}_{\text{VSMOW}}$ , respectively. However, slightly enriched isotope signatures and low

d-excess values from limestone terrain indicate an excessive evaporation compared to that of the metamorphic terrain where rapid infiltration occurs through the overlying highly permeable grumusols soil layers.

**Keywords** Limestone aquifer · High grade metamorphic terrain · Ionic ratios · Stable environmental isotopes · Groundwater recharge · Seawater intrusion

## Introduction

Groundwater resources are of vital importance in all parts of the world under any climatic condition as nearly 30 % of fresh water on the earth occurs as groundwater (Gleick 2000). It has been already identified that climate change and global population growth cause a substantial impact on the global water resources (Vörösmarty et al. 2000). Simultaneously, intensive exploration of groundwater resources is evident in most of the arid and semi-arid regions of the world for agricultural and domestic needs. From among these groundwater resources, coastal aquifers provide water to more than one billion people who live near the coastal zone around the World (Post 2005; Small and Nicholls 2003). In these regions groundwater resources are depleting drastically due to both lack of recharge and saline water intrusion (Chandrajith et al. 2013). Rising sea level due to predicted global climatic changes could also create an additional burden on these coastal aquifer systems (Loaiciga et al. 2012). Therefore, adequate assessment, protection and management of coastal aquifer systems require better understanding of its behaviors and hydrogeochemical characteristics. In recent years, multi-tracer investigations coupled with stable isotope analyses are commonly used to understand groundwater movement, mixing patterns

---

A. Thilakerathne  
Groundwater section, National Water Supply and Drainage Board, Thelawala Road, Rathmalana, Sri Lanka

A. Thilakerathne · C. Schüth  
Institut für Angewandte Geowissenschaften,  
Technische Universität Darmstadt, Schnittspahnstraße 9,  
64287 Darmstadt, Germany

R. Chandrajith (✉)  
Department of Geology, Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka  
e-mail: rohanac@pdn.ac.lk

between different groundwater sources, salinity origin and recharge periods (Gammons et al. 2013; Khaska et al. 2013; Pu et al. 2013; Siebert et al. 2012; Wang and Yakir 2000; Chandrajith et al. 2012, 2013). Such information is essential to improve groundwater resource management, particularly in tropical equatorial regions. Applications of stable environmental isotopes in hydrological investigations has also evolved rapidly in the past few decades as conventional hydrogeochemical studies alone are not sufficient to investigate source areas of recharge water and hydrodynamics.

Sri Lanka is a tropical island, with an area of 65,630 km<sup>2</sup>, located in the Indian Ocean with a 1,340 km long coastal belt. It also has well demarcated climatic zones, known as wet zone and dry zone. As a vital resource, groundwater is gaining increasing importance in the supply of water to rural communities, particularly in the drier regions of Sri Lanka where surface waters are very scarce or compromised by poor quality. Particularly in the coastal belt of Sri Lanka, groundwater resource management is crucial due to rapid urbanization and consequent over exploitation (Chandrajith et al. 2013). Although over 90 % of the island is dominated by aquifers developed on Precambrian metamorphic rocks, the narrow coastal belt along the north and northwest of the island is characterized with karstified sedimentary limestone aquifers. These coastal sedimentary aquifers have been considered as highly productive, but extremely vulnerable to pollution. During the last few years, extensive development activities including resettlements and agricultural development have been initiated in the northern region of Sri Lanka that leads to overexploitation of groundwater resources from karstified coastal sedimentary aquifers. In the north and northwestern coastal region few well-known karstified aquifer basins are located (Fig. 1) (Basnayake 1988; Davis and Herbert 1988).

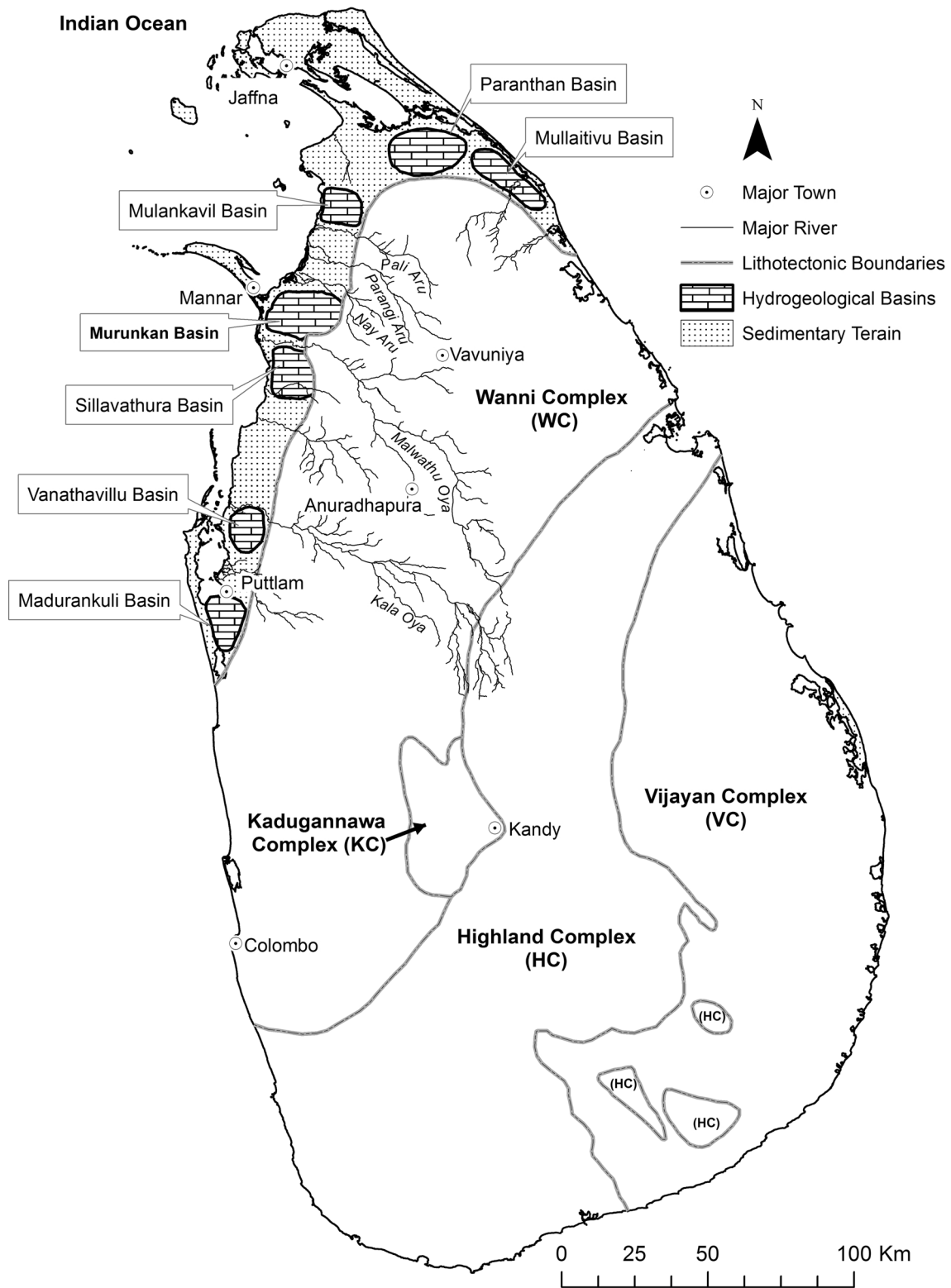
Therefore, an attempt is made to characterize one such karstified sedimentary aquifer basin in Sri Lanka located in the northwestern coastal belt using geochemical and isotope characters. Knowing the hydrodynamic characteristics of aquifer systems will lead to determine the predominant geochemical processes taking place along the inferred horizontal groundwater flow paths. Finally, knowledge on the groundwater behavior and its chemical quality will allow the water managers to properly govern the aquifers, fully utilize the system and provide good potable water to communities. Although the selected region is hydrogeologically important, extremely limited studies and investigations have been carried out to date.

### Geological and hydrological settings

The sedimentary limestone beds of Miocene age occupies nearly one tenth of the land area of the island of Sri Lanka.

Groundwaters in these sedimentary beds are confined to a number of isolated basins (Fig. 1). Fault zones in limestone sequences form hydrogeological barriers segregating aquifers into a series of isolated blocks (Basnayake 1988). The Miocene limestone belt forms the largest sedimentary aquifer system in the north and north-western coastal zone of Sri Lanka covering an area of about 5,000 km<sup>2</sup>. In this stretch, seven isolated hydrogeological basins were identified, named as Madurankuli, Vanathavillu, Silavathurai, Murunkan, Mulankavil, Paranthan-Killinochchi and Muthathivu basins (Davis and Herbert 1988). These aquifer systems show a high degree of heterogeneity and anisotropy, which makes them behave differently from the metamorphic crystalline rock aquifers which are found elsewhere in the country.

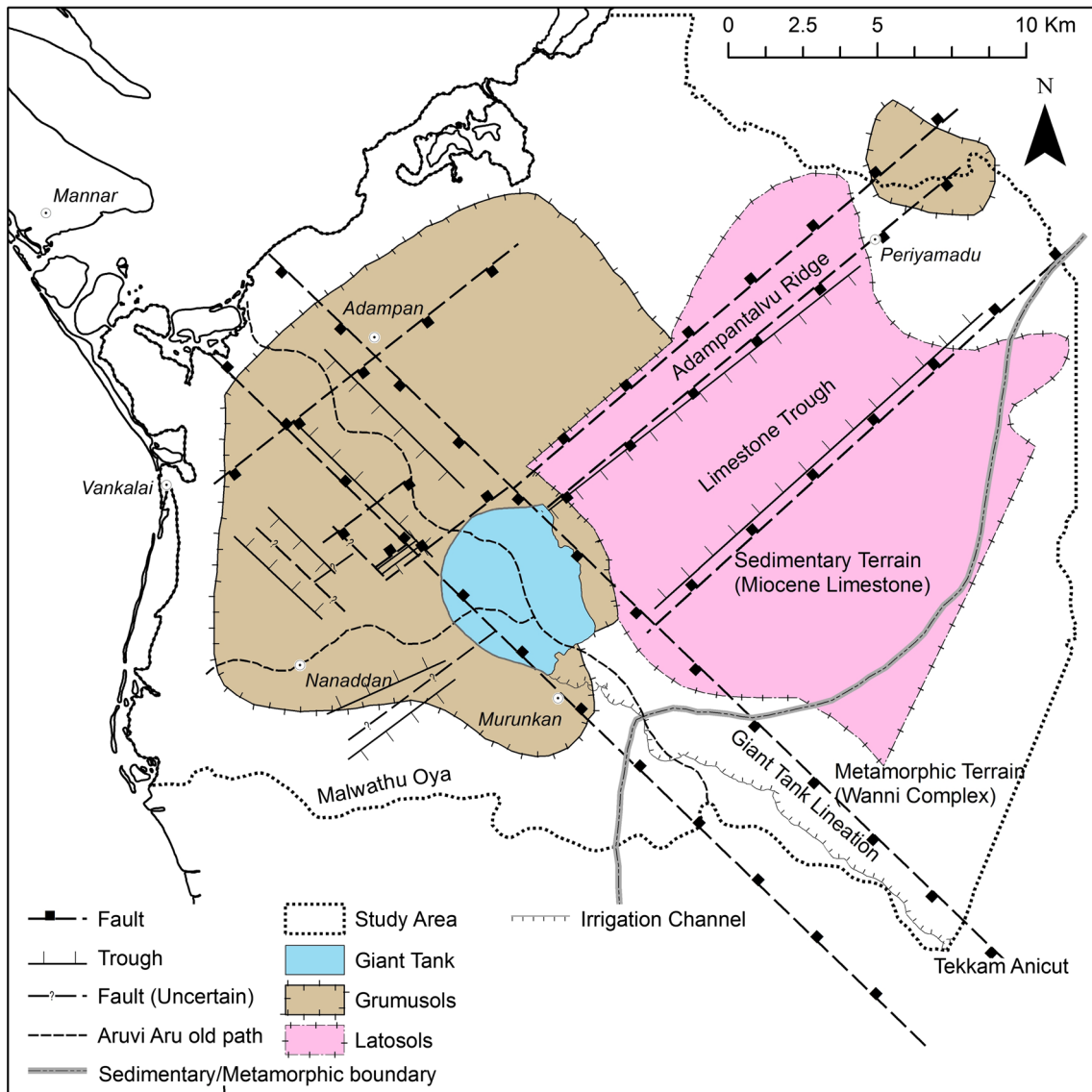
This study mainly earmarked the Murunkan hydrogeological basin which is located 212 km north to the capital Colombo in the Mannar district. The basin is bound by the Malwatu Oya River to the South, the Indian Ocean to the West, the Nayaru River to the north and Madhu-Mannar road to the east covering an area of 686 km<sup>2</sup> (Fig. 2). The basin is one of the most utilized aquifer systems in the northern region that supplies water to the Mannar Island. There are many high yielding wells constructed to extract groundwater from the Murunkan basin. A recent well drilled in the Murunkan basin yielded over 7,000 L/min of good quality water (Wickramaratne and Davies 2011). Some karstified features can be observed in the limestone stratigraphy that was created by sea level fluctuations in the post Miocene age (Davis and Herbert 1988). Within this region, the Precambrian metamorphic basement rocks are unconformably overlain by a sandstone stratum possibly belonging to the Jurassic period. Borehole data indicated that these rocks are not continuous (Basnayake 1988). Up in the sequence, sandstone layers gradually change from cream to yellow colour, hard siliceous to soft fossiliferous limestone. Alluvial sediments were then deposited on westerly dipping limestone sequences. Further up on the sedimentary sequences in the Murunkan region, non-marine Quaternary deposit of grumusols and latosols can also be observed (Basnayake 1988) in which Latosols are deposited unconformably on limestone (Fig. 3). The basin is characterized with large scale block faulting system. A down faulted limestone trough occurs in the northeast and southwest direction across the giant tank (reservoir); the main surface water body in the region is fed by monsoonal rain and used mainly for paddy cultivations; a dominant lineation trend can be observed across the giant tank in the northwest to a southeast direction. Malwatu Oya River may have flow through this lineation in the geological past (Davies and Selvarathnam 1982). Two main soil types are predominant in the study area. The



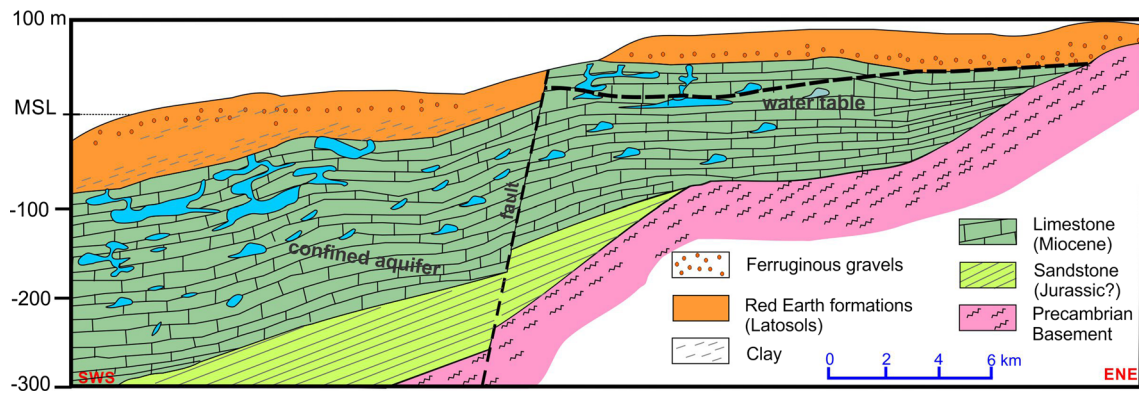
**Fig. 1** Generalized geology and sedimentary aquifer basins in Sri Lanka

eastern part of the Giant tank is composed of highly permeable red–yellow Latosols or red earth formations. The average thickness of the soil layer is about 2.5 m

while the occurrence of ferruginous gravel layers can be observed in certain locations. The western part of the region is composed mainly of grey colored grumusols



**Fig. 2** Site map of the Murunkan basin showing geological boundary and soil types



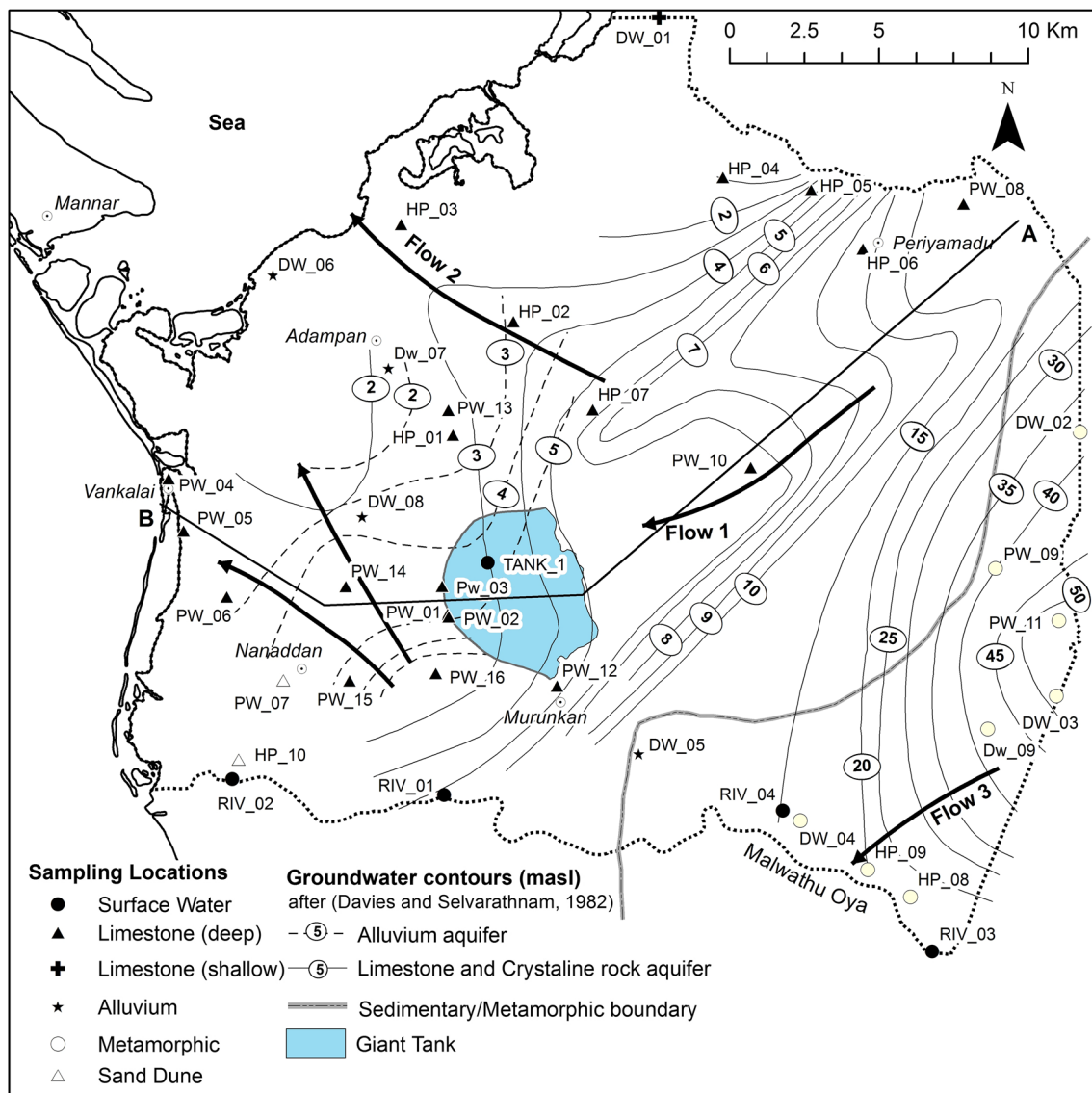
**Fig. 3** East–West geological cross-section through the study area showing hydrogeological connections and geological structure (Davies and Selvarathnam 1982)

derived from alluvial deposits washed into the flat area along river channels that are highly utilized for paddy cultivation because of their impermeable nature. In this part, a wide range of transmissivity values that vary from 650 to 2,000 m<sup>2</sup>/day were observed (Basnayake 1988). Towards the coast, quaternary deposits such as dune sands and alluvial deposits can be observed. In spite of its small land area of Sri Lanka, the distribution of average rain fall varies remarkably from 1,000 mm in the drier parts to over 5,500 mm in the wettest part. However, the study region is characterized by a semi-arid climate in which the annual rain fall is less than 800 mm per annum from which over 90 % will fall in November and December through the winter monsoon. Karstic carbonate rock outcrops slope gently towards the west favors higher

infiltration of rain water recharging the groundwater basins. Perennial rivers, Malwatu Oya and Nayaruru control the drainage network of the study area. From a hydrogeological point of view, three major water-bearing systems can be distinguished in and around the region as (1) limestone aquifer system, (2) water bearing zones in the metamorphic terrain and (3) aquifers developed on alluvial or lacustrine sedimentary formations.

**Materials and methods**

Water samples were collected mainly from production deep and shallow wells that extract water from aquifer systems in and around the Murunkan basin (Fig. 4). Depth



**Fig. 4** Murunkan basin showing the sampling location, generalized geology, hydrogeological regions and groundwater flow paths



of deep wells in the selected area varies from 20 to 30 m while shallow wells are 5–12 m deep. A total of 40 samples were collected from production deep wells ( $n = 16$ ), hand pump deep wells ( $n = 10$ ), shallow wells ( $n = 9$ ), nearby Malwatu Oya River ( $n = 4$ ) and Giant tank ( $n = 1$ ) during a single sampling event carried out in summer 2013. An effort was made to obtain a uniform distribution of sampling locations throughout the area as much as possible; however, due to the uneven distribution of population in the study area, this exercise proved to be difficult in some cases. In production wells with installed pumps, water was pumped out for several minutes before collecting the sample. Hand pumps were also operated for about 10 min before the sampling. A battery driven submersible sampling pump that was placed several meters below the water surface was used to collect samples from dug wells and also from some production wells. Geographic locations of all sampling points were recoded using a hand held GPS device. Depth to the water table and other important geological parameters were also recorded in every sampling location.

In situ determination of pH, electrical conductivity (EC)/total dissolved solids (TDS), water temperature and salinity were carried out using field devices. The alkalinity was determined titrimetrically using Hach<sup>®</sup> Field titration kit with 0.16 N sulfuric acid cartridges. Samples collected for anion (chloride, sulfate, fluoride, phosphate and nitrate) and cation (Na, K, Ca, Mg, Fe and Mn) analyses were filtered through 0.45  $\mu\text{m}$  disposable membrane syringe filters in situ in which the samples collected for cation analysis were acidified with ultrapure nitric acid. For oxygen and hydrogen isotope ratio analyses, 15 mL of water was collected from each location into screw capped high density polyethylene tubes that were wrapped using parafilm to avoid any possible evaporation. All samples were kept in the dark and at 4 °C until the analyses were performed. Hardness and chloride in collected water samples were measured by the titration method while the other anionic parameters were determined using a Hach<sup>®</sup> DR2700 spectrophotometer. All cations were measured using a Varian 240FS Atomic Absorption Spectrophotometer (AAS). Bicarbonate and Carbonate contents were calculated using pH and alkalinity values. The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of water samples were determined with Picarro L2130i wavelength-scanned cavity ring-down infrared spectroscopy instrument at the Isotope Laboratory of Technical University of Darmstadt, Germany. The results are expressed in  $\delta$  per-mille ( $\delta\text{‰}$ ) (Clark and Fritz 1997), reported as relative differences ( $\delta$  values) with respect to Vienna Standard Mean Ocean Water (V-SMOW) where  $\delta = (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}$  in which  $R$  is the ratio of  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$ . Analytical precision of the stable isotope analyses is in the order of 0.037 ‰ for  $\delta^{18}\text{O}$  and 0.100 ‰ for  $\delta^2\text{H}$ .

## Results and discussion

### Physical and chemical characteristics of groundwater

During this study, water samples were obtained from wells located in the limestone aquifer terrain (21), metamorphic aquifer terrain (8), alluvial aquifers (4) and sand dune (2) while five surface water samples were obtained from the reservoir and the river. Table 1 gives the main geochemical characteristics of sampled waters. All groundwater in the area is neutral to slightly alkaline with pH ranging from 6.52 to 7.93, while slightly higher pH was observed from water samples from the alluvial aquifer (pH 7.53–7.93). Slightly lower pH levels are predominant in the north-eastern recharge areas, while it increases along groundwater flow paths towards the coast. Surface water samples that were obtained from Malwatu Oya River and Giant tank have also given higher pH values compared to that of the groundwater. Wider variations of TDS values were noted in different aquifers in the study area where TDS in limestone aquifers were between 109 and 2,120 mg/L (Table 1). As expected, high TDS values were obtained in samples collected closer to the sea, indicating possible intrusion of saltwater into the aquifer systems. Considerably low TDS values were observed in samples obtained from the metamorphic terrain (76–710 mg/L) and the alluvial aquifers (647–771 mg/L) suggesting a low level of mineralization. Surface water samples in the region are dominated by relatively lower TDS values ranging from 381 to 674 mg/L. Usually TDS less than 1,000 mg/L are considered as potable water (WHO 1996).

In decreasing order, bicarbonates, chloride and sulfates are the dominant anions in groundwater examined in which the metamorphic aquifer showed slightly lower  $\text{HCO}_3^-$  and  $\text{Cl}^-$  contents compared to the limestone terrain. The mean chloride content of groundwater samples is 353 mg/L. Although no health-based guideline values have been given for chloride in drinking water, chloride contents above 250 mg/L can induce a taste in water (WHO 2008). Heavy use of high chloride water can cause soil salinization as these wells are being used extensively for agricultural purposes. Among other water quality parameters, fluoride and nitrate in drinking water are more important due to their public health concerns. The fluoride concentrations of all groundwater samples ranged from 0.02 to 0.90 mg/L with the mean value of 0.53 mg/L. However, the fluoride in the metamorphic terrain is slightly lower (mean 0.41 mg/L) compared to that of the limestone terrain. However, most of these values are below the WHO recommended limit of 0.6 mg/L for tropical countries (WHO 2008). Although the dry zone of Sri Lanka is characterized with high fluoride groundwater and associated dental diseases, in the study regions, however, most

**Table 1** Summary of hydrogeochemical and isotope data; grouped according to underlying lithology

Terrain	pH	EC $\mu\text{S/cm}$	TDS	Alk	HD	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup> :N	PO <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	$\delta^{18}\text{O}$ ‰ VSMOW	$\delta\text{D}$ ‰ VSMOW	
<b>Limestone (n = 21)</b>																			
Mean	6.92	1,575	803	368	344	736	23	449	0.55	60	0.8	0.43	210	7.09	64	29.58	-3.244	-21.38	
Min.	6.52	570	109	252	104	504	6.0	36.3	0.02	3	0.3	0.13	16.1	0.70	25.28	2.540	-6.667	-42.29	
Median	6.88	1,481	766	345	348	690	15	391	0.58	42	0.7	0.42	171	4.89	59.96	27.40	-2.485	-17.13	
Max.	7.31	3,680	2,120	684	584	1,366	56	1510	0.84	180	1.6	0.72	510	24.4	137.7	68.41	-1.867	-12.58	
<b>Metamorphic (n = 8)</b>																			
Mean	7.2	837	458	272	325	543	32	175	0.41	26	0.9	0.45	84.3	4.38	48.65	29.94	-4.525	-28.55	
Min.	6.67	143	76	57	58	114	2.0	26.0	0.02	3	0.5	0.22	9.7	2.04	16.03	2.600	-6.207	-39.33	
Median	7.22	834	454	253	340	505	28	183	0.41	22	0.8	0.36	81.7	2.86	50.95	21.83	-4.795	-30.33	
Max.	7.65	1,289	710	496	652	990	63	314	0.72	55	1.8	1.1	140	16.0	71.62	77.37	-0.879	-10.51	
<b>Alluvial (n = 4)</b>																			
Mean	7.7	1,274	702	424	328	842	145	230	0.60	77	0.9	0.69	173	18.2	46.23	32.43	-3.396	-21.06	
Min.	7.57	1,177	647	304	161	605	93	155	0.26	34	0.6	0.25	129	2.69	21.66	17.74	-4.907	-29.06	
Median	7.64	1,262	695	428	369	852	102	220	0.71	52	0.7	0.51	172	6.82	53.67	33.89	-3.37	-21.23	
Max.	7.93	1,395	771	534	412	1,059	282	324	0.74	170	1.7	1.5	218	56.5	55.91	44.20	-1.938	-12.72	
<b>Metamorphic (n = 8)</b>																			
Mean	7.2	837	458	272	325	543	32	175	0.41	26	0.9	0.45	84.3	4.38	48.65	29.94	-4.525	-28.55	
Min.	6.67	143	76	57	58	114	2.0	26.0	0.02	3	0.5	0.22	9.7	2.04	16.03	2.600	-6.207	-39.33	
Median	7.22	834	454	253	340	505	28	183	0.41	22	0.8	0.36	81.7	2.86	50.95	21.83	-4.795	-30.33	
Max.	7.65	1,289	710	496	652	990	63	314	0.72	55	1.8	1.1	140	16.0	71.62	77.37	-0.879	-10.51	
<b>Surface water (n = 4)</b>																			
Mean	7.8	990	542	266	341	532	113	250	0.97	20	0.9	0.42	109	6.42	37.34	40.48	-1.508	-11.08	
Min.	7.53	703	381	207	204	411	54	167	0.79	15	0.8	0.13	77.1	5.00	23.02	30.34	-2.539	-17.42	
Median	7.89	1,015	556	261	330	520	118	249	0.95	20	0.8	0.46	113	6.60	36.06	37.63	-1.541	-12.16	
Max.	7.9	1,225	674	340	500	675	164	335	1.18	27	1.1	0.65	132	7.47	54.24	56.32	-0.411	-2.55	

All the ions were measured in mg/L, unless otherwise mentioned  
 TDS total dissolved solids, Alk alkalinity as CaCO<sub>3</sub>, HD hardness as CaCO<sub>3</sub>, n number of samples

groundwaters are well within the WHO recommended levels. The nitrate-N and ortho-phosphate ( $\text{PO}_4^{3-}$ ) contents in most of the groundwater collected from three types of aquifers vary from 0.3 to 1.8 mg/L and 0.13 to 1.5 mg/L, respectively, in which DW06 samples showed the highest values for both parameters, possibly an indication of anthropogenic pollution.

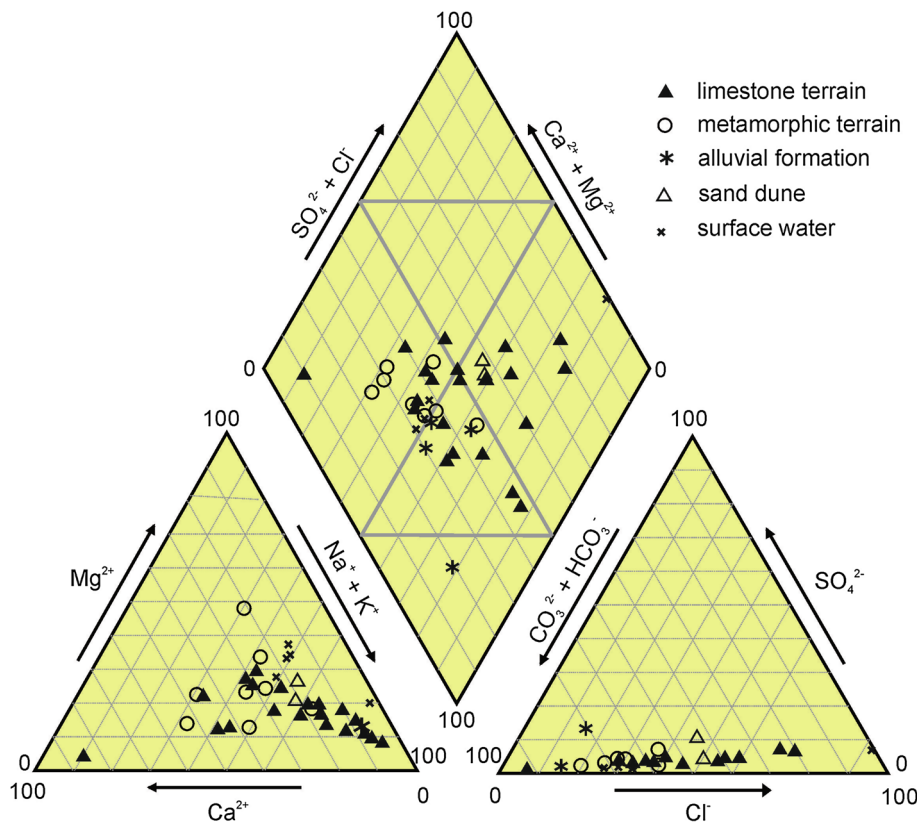
The dominant cation in study aquifers is  $\text{Na}^+$  followed by  $\text{Ca}^{2+}$  in the limestone aquifer but  $\text{Mg}^{2+}$  in the metamorphic aquifer. In all groundwater samples ( $\text{Na}^+ + \text{K}^+$ ) exceeds ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ). Based on the Piper trilinear plot, a majority of the groundwater samples collected from the limestone terrain are plotted in the mixed zone and in the Na-sulfate–chloride region (Fig. 5); however, only a few samples fall in the Ca–Mg–bicarbonate zone. Waters that circulate through the carbonate aquifer indicate possible intrusions of sea water or leaching of residues of saline soils into the groundwater. High evaporation under semi-arid condition that prevails in the region can considerably increase the soil salinity. The  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions most likely are due to weathering and dissolving of minerals such as calcite, dolomite and gypsum in the limestone aquifer. Groundwater from the metamorphic terrain is predominantly of Ca–Mg– $\text{HCO}_3^-$  type, but some samples lie in the mixed zone. The excess alkaline earth elements

are possibly leached from weathering of silicate minerals, such as calcic-feldspar, pyroxenes and amphiboles, that are dominant in high-grade rocks of Sri Lanka.

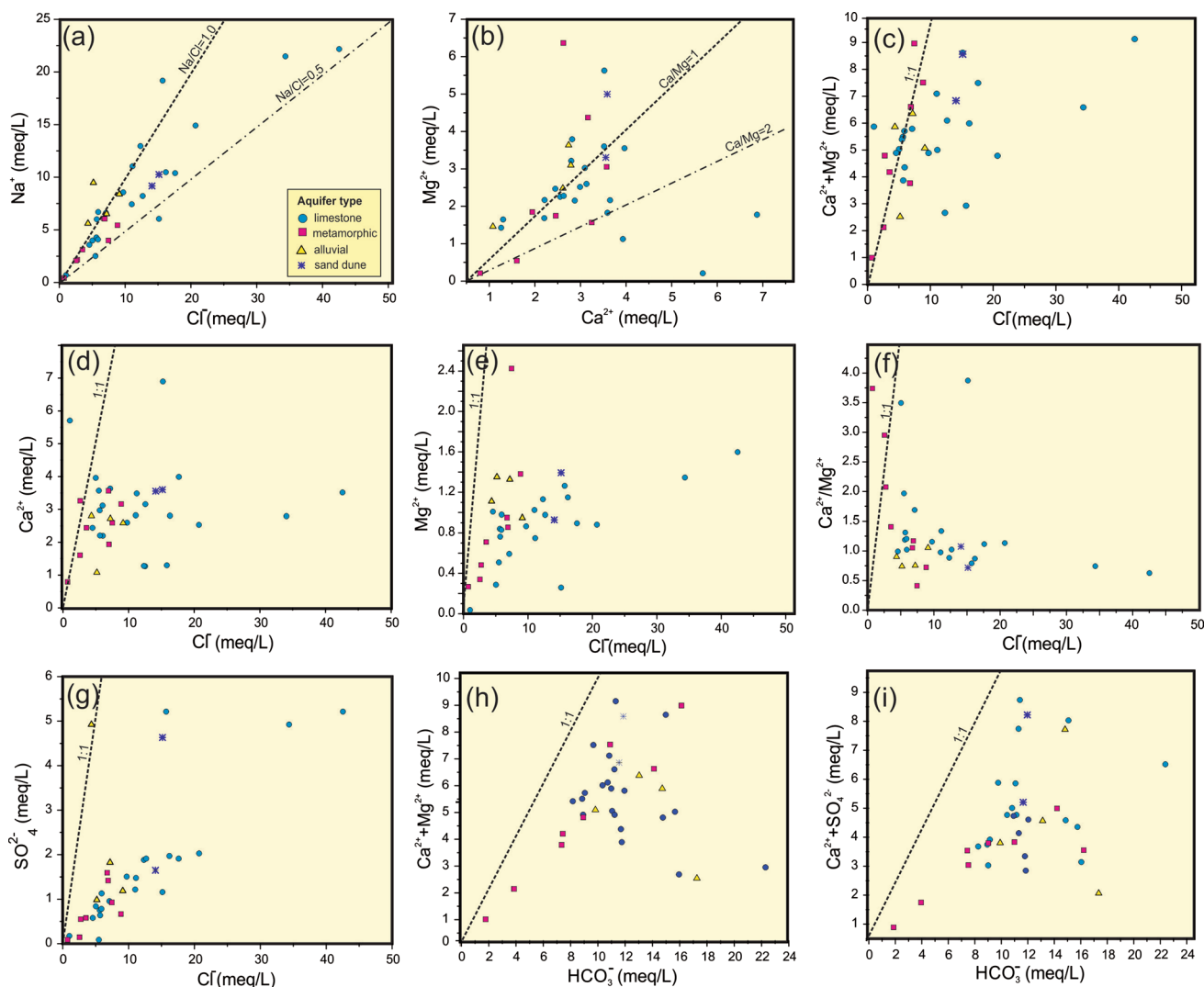
#### Geochemical evolution of groundwater

The Na–Cl relationship has been widely used to identify groundwater evolution and mixing mechanisms particularly in arid and semi-arid regions (Vengosh and Rosenthal 1994; Dixon and Chiswell 1992; Hidalgo and Cruz-Sanjulián 2001). The Na/Cl molar ratio ranges from 0.86 to 1.0 in groundwater that flows through the active hydrological cycle (Hem 1985; Vengosh and Rosenthal 1994). The scatter plots of the variation of  $\text{Na}^+$  and  $\text{Cl}^-$  in the study region (Fig. 6a), shows good linear relationships in which most wells are plotted very close to or below the isolines. The Na/Cl molar ratio becomes approximately equal to one, if the mixing between sea water and fresh water occurred in the aquifer (Vengosh and Rosenthal 1994) or halite dissolution is responsible for Na (Meybeck 1987). However, the low  $\text{Na}^+$  and  $\text{Cl}^-$  values obtained from most groundwater indicate that these parameters are probably derived from water–rock interactions. In the limestone terrain, particularly the few deep wells located close to the coastline showed higher values of both  $\text{Na}^+$  and  $\text{Cl}^-$

**Fig. 5** Piper plot of chemical analysis of groundwater samples in the Murunkan basin



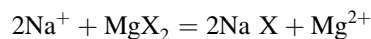




**Fig. 6** Major ion relationships for groundwater in the study area

possibly due to sea water intrusion. Weathering of Ca–Mg bearing silicates occurs in the metamorphic terrain while calcite dissolution can provide these ions from the limestone and subsequently modified by cation exchange processes. The dominance of  $\text{HCO}_3^-$  and high  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratio ( $>1.0$ ) (Fig. 6b) in most groundwater samples in the region provides further evidence for rock-water interactions that governs the hydrogeochemical composition. Katz et al. (1997) inferred that higher  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratio ( $>2$ ) indicates the dissolution of silicate minerals, while the ratio between 1 and 2 indicate the dissolution of calcite (Rajmohan and Elango 2004). The groundwater from the limestone aquifer shows the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratio between 0.63 and 3.87 (mean 1.37) except the sample HP-07. As illustrated in Fig. 6c, the  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  content increases with the increasing  $\text{Cl}^-$ ;

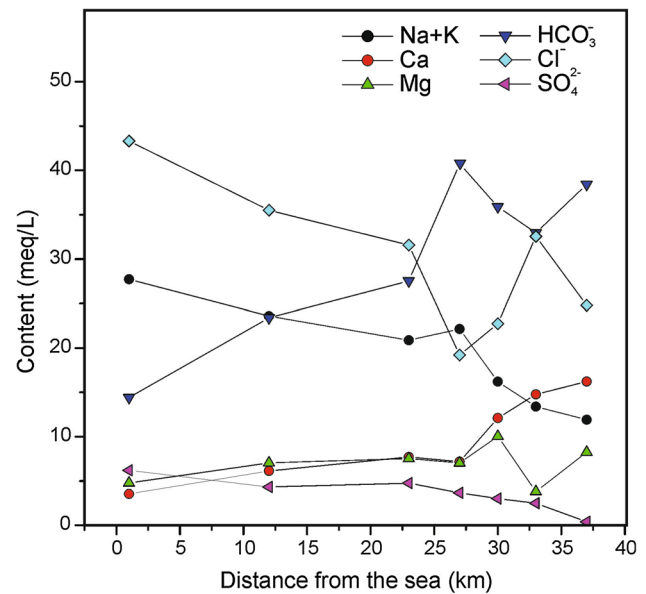
however, the relationship is more prominent and linear in the metamorphic terrain. This may be due to reverse ion exchange that occurs between clay minerals and the solution in which dissolved Na exchange for both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Rajmohan and Elango 2004). The linear relationships between  $\text{Cl}^-$  and  $\text{Mg}^{2+}$  (Fig. 6e) indicate the cation exchange process that takes place in coastal freshwater aquifers with the sea water intrusion as given by Appelo and Postma (2005);



where, X represents ion exchange sites in aquifer materials. The reverse reactions occur when fresh groundwater flushes out saline groundwater in the aquifer. Hence, high  $\text{Mg}^{2+}/\text{Cl}^-$  ratio is an indicator for the influence of saline water.

Except for a few wells in the limestone terrain, all other wells show a very good linear relationship between  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  indicating their common source (Fig. 6g). Most groundwater from all study aquifer systems showed a  $\text{Cl}^-/\text{SO}_4^{2-}$  molar ratio close to 7.5. All wells in the study terrain fall below the isoline 1:1 of  $(\text{Ca}^{2+} + \text{Mg}^{2+})$  versus  $\text{HCO}_3^-$  plot (Fig. 6h). A fairly similar scatter pattern is also obtained in  $(\text{Ca}^{2+} + \text{SO}_4^{2-})$  versus  $\text{HCO}_3^-$  plot (Fig. 6i). Very strong correlation between alkali earths and  $\text{HCO}_3^-$  ( $r = +0.963$ ;  $p = 0.0001$ ) can also be observed in water from the metamorphic aquifer. The lower  $\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-$  ratio in both limestone and hard rock terrain indicates a depletion of alkaline earths over  $\text{HCO}_3^-$ , which possibly occurs due to cation exchange processes. Particularly in the limestone aquifers, due to enrichment of Na, replacement of  $\text{Mg}^{2+}$  can occur through cation exchange process (Appelo and Postma 2005). Although the relative content of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  increases with dissolution of calcite, the evaporation process will decrease ions by precipitation of  $\text{CaCO}_3$  and returns to the sea water composition that is dominated by  $\text{Na}^+$  and  $\text{Cl}^-$  (Appelo and Postma 2005). The  $\text{Na}^+/\text{Cl}^-$  ratio would be unchanged if the evaporation process is dominant, assuming that no mineral species are precipitated, (Janowski and Acworth 1997).

Davies and Selvarathnam (1982) mapped the groundwater flow paths in the region using piezometers (Fig. 4) and indicated that the main groundwater flow is towards the limestone terrain from the direction of the crystalline metamorphic complex. This flow continues through the limestone terrain across the giant tank and finally flows towards the ocean (flow 1 in Fig. 4). However, some other minor flows were also observed in the north-west coast from Adampanthalvu ridge (flow 2 in Fig. 4) to the Malwatu Oya River from the metamorphic terrain (flow 3 in Fig. 4). Due to the gentle dipping of limestone beds towards the sea, a steep flow gradient is created from the center of the terrain. The geographic distribution of the major ionic geochemical parameters in the study area also indicates clearly that chloride is the dominating ion towards the coast while bicarbonate dominates in the upper part of the flow (Fig. 7).  $\text{Na}^+ + \text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  increases towards the coast in the flow path while  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are dominated in the upper part of the flow path. Therefore, the hydrogeochemical evolution in the Murunkan limestone basin takes place from less saline water that converts to saline water towards the coast with increasing contribution from  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  that contribute from sea water intrusions. Along the groundwater flow

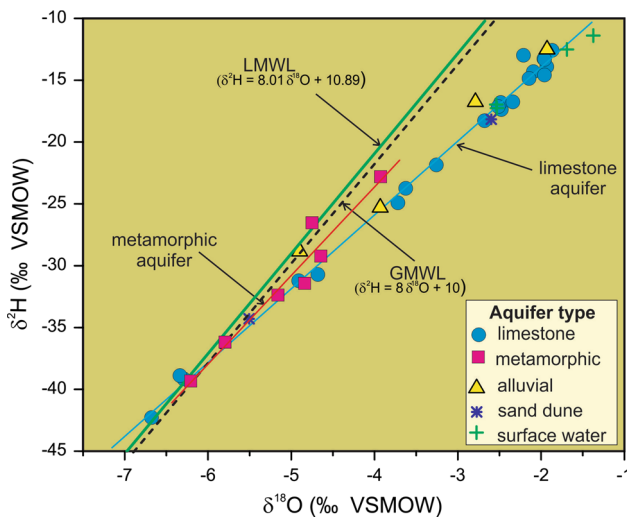


**Fig. 7** Geochemical variation of groundwater along the flow path 1 A-B (as show in Fig. 2)

path carbonate mineral dissolution, enrichment of Na due to sea water intrusion and consequent ion exchange produces the entire geochemical composition of the aquifer system. In the upper part of the flow paths and particularly in the hard rock formations, weathering of minerals and consequent leaching, ion exchange processes control the concentration of Ca, Mg and Na concentrations. In general, excessive evaporation under high ambient temperature conditions would cause an enrichment of all chemical species in groundwater.

#### Isotope characteristics

The isotope signature of the groundwater collected from different hydrogeological domains in the Murunkan region is discussed with the regional precipitation. The isotope composition of atmospheric precipitation was obtained from the database at Global Network of Isotopes in Precipitation of the framework of the global network of isotopes in precipitation (IAEA/WMO 2004) at International Atomic Energy Authority (IAEA) since no other isotope data sources are available for precipitation of Sri Lanka. Average monthly isotope values ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) recorded in meteorological stations at Mannar, Puttalam and Anuradahapura for the period of 1983–1994 were used to obtain the local meteoric water line (LMWL). All the monthly weighted rainwater data fits a least-squares regression line of the following equation:



**Fig. 8** Variation of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in groundwater from the Murunkan aquifer systems with respect to the Global Meteoric Water Line (GMWL) and Local Meteoric Water Line (LMWL)

$$\delta D = 8.01\delta^{18}\text{O} + 10.89 \quad (1)$$

The LMWL obtained for the northwestern part of the dry zone of Sri Lanka is almost similar to that of the Global meteoric water line (GMWL);  $\delta^2\text{H} = 8.01\delta^{18}\text{O} + 10$ , derived by Craig (1961). Isotope composition of different water samples collected from the study terrain is plotted in Fig. 8 with the GMWL and LMWL. The mean  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  signatures of water samples from metamorphic aquifer are  $-5.05$  and  $-31.13$  ‰, respectively, whereas for the limestone aquifer, the values are  $-3.24$  and  $-21.4$  ‰, respectively. One sample collected from the metamorphic aquifer (PW\_11) showed enriched isotope signatures possibly due to excessive evaporation. The same sample showed the highest Mg content from among other samples. Compared to the groundwater from limestone terrain, metamorphic aquifers show more depleted isotope signatures. The mean  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values are  $-3.40$  and  $-21.06$  ‰, respectively, for the samples from the alluvial aquifer. In the limestone terrain, both PW\_04 and HP\_03 that are located close to the sea (<2 km) show enriched isotope signatures. Both wells also showed enriched chloride contents, indicating the admixing of sea water with groundwater. Some samples (e.g., PW\_14, PW\_01 and PW\_02) that are located in the alluvial terrain indicates the possible mixing of aquifer water with river water. Groundwater flow direction of the alluvial aquifer also provides evidence for this mixing. Majority of the data obtained from Murunkan regions plotted below both global and local meteoric water lines, indicating partial evaporation

during the precipitation or during the infiltration with the influence of high ambient temperature conditions. For the limestone terrain the regression line obtained was  $\delta^2\text{H} = 5.97\delta^{18}\text{O} - 2.00$  ( $R^2 = 0.997$ ) while it is  $\delta^2\text{H} = 7.17\delta^{18}\text{O} + 5.05$  ( $R^2 = 0.971$ ) for the metamorphic terrain.

In the metamorphic terrain the slope of the regression line (7.17) is somewhat closer to the slope of the GMWL as described by Craig (1961), but the intercept (5.05) is considerably lower. Dansgaard (1964) described this intercept as the deuterium-excess (*d*-excess), defined by  $d = \delta^2\text{H} - 8 \delta^{18}\text{O}$ , which is a very useful indicator for explaining secondary processes influencing groundwater. High *d*-excess values indicate more evaporated moisture that has been added to the atmosphere while low values are associated with the fractionation caused by evaporation (Gat and Matsui 1991). The calculated *d*-excess values for the groundwater in the limestone terrain range from 1.1 to 11.8 ‰ with an average of 4.57 ‰. Except for three samples (HP\_04, 07 and PW\_10), all samples showed less than 10 ‰ of *d*-excess with an average of 3.44 ‰. On the other hand, samples from metamorphic terrain indicate higher *d*-excess values that ranged from 7.29 to 11.5 ‰ with the mean of 9.24 ‰. This sharp deviation of *d*-excess values between two main aquifer systems in the Murunkan region is possibly due to different infiltration rates that governs the groundwater.

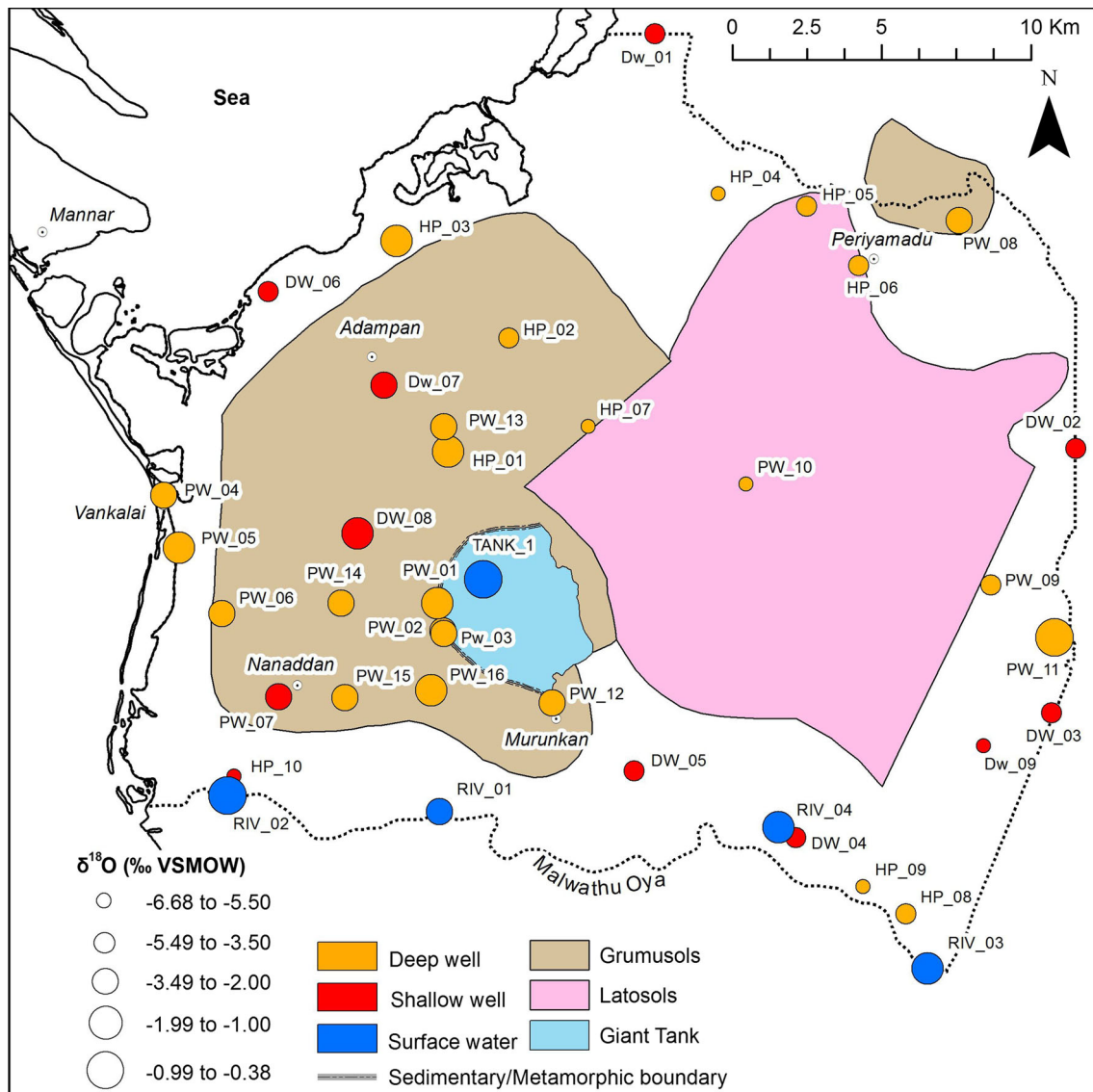
It is important to note that the isotope compositions significantly vary in wells built in latosols and grumusols soil regions (Fig. 9). Particularly the north-east recharge area of the study region comprises latosols, which show relatively high permeability compared to that of grumusols (Davies and Selvarathnam 1982) that which occupies mainly in the western part of the study area. The grumusols are rich with clay and infiltration is relatively low. Therefore, this part of the land gets flooded even with moderate rainfall. It is likely that in the metamorphic terrain, rain water infiltrates vigorously without any modifications. The evaporation affects under restricted infiltration conditions, however, makes significant changes in the isotope signatures in groundwater from the limestone terrain as shown by lower *d*-excess and more enriched  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values.

### Conclusions

The Murunkan basin is one of the most important aquifer systems in Sri Lanka that supplies drinking water to the nearby community and also to the Mannar Island. These hydrogeochemical and environmental isotope studies were

carried out to evaluate the recharging mechanism and potential geochemical processes involved in the recharge. The composition of groundwater is modified by mineral dissolution during the subsurface flow and enhanced by seawater intrusion in the coastal region. Stable isotope composition of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of groundwater closely follows the meteoric composition but is slightly modified by the evaporation processes. Enriched isotope signatures and lower  $d$ -excess values obtained from groundwaters of the limestone terrain suggest a high vapor flux through excessive evaporation under semi-arid condition and also

subjected to slow infiltration. However, in the metamorphic terrain only slight evaporation occurs at or near the soil surface before percolating into depth. Groundwater in the coastal belt, particularly in the limestone terrain where discharge areas are located, is vulnerable to salinization by sea water. Therefore, proper management of water resources in the Murunkan basin is highly recommended. Detailed investigations of this nature are warranted to understand important geochemical processes affecting water quality in other limestone aquifer basins in northern and northwestern Sri Lanka.



**Fig. 9**  $\delta^{18}\text{O}$  variation in the study area with respect to the overlaying soil types



**Acknowledgments** AT gratefully acknowledges a Grant from the Deutscher Akademischer Austausch Dienst (DAAD), Germany, for this work. The authors thank the valuable comments and suggestions of Professors C.B.Dissanayake and Rohan Weerasooriya.

## References

- Appelo CAJ, Postma D (2005) *Geochemistry, groundwater and pollution*. Taylor & Francis, Boca Raton
- Basnayake BMSB (1988) Groundwater potentials in the sedimentary rock of Sri Lanka. In: Fernando LJD (ed) *Felicitation volume*. Geological Society of Sri Lanka, Peradeniya, pp 71–77
- Chandrajith R, Barth JA, Subasinghe N, Merten D, Dissanayake C (2012) Geochemical and isotope characterization of geothermal spring waters in Sri Lanka: evidence for a steeper than expected geothermal gradients. *J Hydrol* 476:360–369
- Chandrajith R, Chaturangani D, Abeykoon S, Barth JAC, van Geldern R, Edirisinghe V, Dissanayake CB (2013) Quantification of groundwater-seawater- interaction in a coastal sandy aquifer system—a study from panama. *Sri Lanka Environ Earth Sci* 72(3):867–877
- Clark ID, Fritz P (1997) *Environmental isotopes in hydrogeology*. CRC Press/Lewis Publishers, Boca Raton
- Craig H (1961) Isotopic variations in meteoric waters. *Science* 133:1702–1703
- Dansgaard W (1964) Stable isotopes in precipitation. *Tellus* 16(4):436–468
- Davies J, Selvarathnam R (1982) The groundwater resources of the Murunkan area. North-West Land Water Resources Development Project Sri Lanka. Water Resources Board, Groundwater Division, Colombo
- Davis J, Herbert R (1988) Hydrogeology of the miocene sedimentary belt of Sri Lanka. *J Geol soc Sri Lanka* 1:45–63
- Dixon W, Chiswell B (1992) The use of hydrochemical sections to identify recharge areas and saline intrusions in alluvial aquifers, southeast Queensland. *Aust J Hydrol* 135(1):259–274
- Gammons CH, Pape BL, Parker SR, Poulson SR, Blank CE (2013) Geochemistry, water balance, and stable isotopes of a “clean” pit lake at an abandoned tungsten mine, Montana, USA. *Appl Geochem* 36:57–69
- Gat J, Matsui E (1991) Atmospheric water balance in the Amazon Basin: an isotopic evapotranspiration model. *J Geophys Res Atmos* 1984–2012 96(D7):13179–13188
- Gleick PH (2000) A look at twenty-first century water resources development. *Water Int* 25(1):127–138
- Global network of isotopes in precipitation—the GNIP database (2004). <http://isohis.iaea.org>. Accessed 10 Oct 2013
- Hem JD (1985) Study and interpretation of the chemical characteristics of natural water, vol 2254. Department of the Interior, US Geological Survey, Washington, D.C., pp 263
- Hidalgo MC, Cruz-Sanjulián J (2001) Groundwater composition, hydrochemical evolution and mass transfer in a regional detrital aquifer (Baza basin, southern Spain). *Appl Geochem* 16(7):745–758
- Jankowski J, Acworth RI (1997) Impact of Debris-flow deposits on hydrogeochemical processes and the development of dryland salinity in the Yass River Catchment, New South Wales. *Aust Hydrogeol J* 5(4):71–88
- Katz BG, Coplen TB, Bullen TD, Davis JH (1997) Use of chemical and isotopic tracers to characterize the interactions between ground water and surface water in mantled karst. *Ground Water* 35(6):1014–1028
- Khaska M, Le Gal La Salle C, Lancelot J, team A, Mohamad A, Verdoux P, Noret A, Simler R (2013) Origin of groundwater salinity (current seawater vs. saline deep water) in a coastal karst aquifer based on Sr and Cl isotopes. Case study of the La Clape massif (southern France). *Appl Geochem* 37:212–227
- Loáiciga HA, Pingel TJ, Garcia ES (2012) Sea water intrusion by sea-level rise: scenarios for the 21st century. *Ground Water* 50(1):37–47
- Meybeck M (1987) Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am J Sci* 287(5):401–428
- Post V (2005) Fresh and saline groundwater interaction in coastal aquifers: is our technology ready for the problems ahead? *Hydrogeol J* 13(1):120–123
- Pu T, He Y, Zhang T, Wu J, Zhu G, Chang L (2013) Isotopic and geochemical evolution of ground and river waters in a karst dominated geological setting: a case study from Lijiang basin, South-Asia monsoon region. *Appl Geochem* 33:199–212
- Rajmohan N, Elango L (2004) Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins. *South India. Environ Geol* 46(1):47–61
- Siebert C, Rosenthal E, Möller P, Rödiger T, Meiler M (2012) The hydrochemical identification of groundwater flowing to the Bet She’an-Harod multiaquifer system (Lower Jordan Valley) by rare earth elements, yttrium, stable isotopes (H, O) and Tritium. *Appl Geochem* 27(3):703–714
- Small C, Nicholls RJ (2003) A global analysis of human settlement in coastal zones. *J Coastal Res* 19(3):584–599
- Vengosh A, Rosenthal E (1994) Saline groundwater in Israel: its bearing on the water crisis in the country. *J Hydrol* 156(1):389–430
- Vörösmarty CJ, Green P, Salisbury J, Lammers RB (2000) Global water resources: vulnerability from climate change and population growth. *Science* 289(5477):284–288
- Wang XF, Yakir D (2000) Using stable isotopes of water in evapotranspiration studies. *Hydrol Process* 14(8):1407–1421
- WHO (1996) *Guidelines for drinking-water quality*, 2nd ed. Health criteria and other supporting information, vol 2. World Health Organization, Geneva
- WHO (2008) *Guidelines for drinking-water quality*, 3rd Edition, Recommendations, vol 1. World Health Organization, Geneva
- Wickramaratne U, Davies J (2011) Reconnaissance hydrogeology in Madu area for high-yielding groundwater aquifer. *J Geol Soc Sri Lanka* 14:55–63