Deep Groundwater Recharge Mechanism in the Sedimentary and Crystalline Terrains of Sri Lanka: A Study Based on Environmental Isotopic and Chemical Signatures of Spring Water

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Abstract

In many instances, dynamic, potential status and geochemical characteristics of groundwater discharging through natural springs are not well known. Present study has assessed the deep groundwater in the form of thermal and non-thermal spring in artesian condition in the selected zones in Sri Lanka, using isotope and geochemical characteristics. The results revealed that evaporation-fractional crystallization and cation-exchange in the sedimentary aquifers while rock-water interaction in crystalline deep aquifers, are the significant mechanism that control the groundwater chemistry. All the deep groundwater recharged from meteoric water at different elevations and further influenced by either evaporation or rock-water interaction during the subsurface flow. Artesian aquifers in the sedimentary terrain in the north-western coastal zones showed the recharging elevation as from 100 to 200 m amsl. They are not mixed with sea water and slightly impacted by the locally evaporated surface waters. Almost all these waters are comparatively old; indicating slow movement along the regional flow paths. Considering the recharge and discharge conditions of artesian non-thermal waters in the Southern lowlands of crystalline terrain can be classified as non-mixed, non-evaporated and young groundwater with higher elevation recharge. The artesian non-thermal waters in the East North Central lowlands, have shown the same characteristics but with evaporated conditions. All artesian thermal waters are tritium free, hence they are older and deep percolated. Intensive rock-water interaction and higher altitude origin were observed in some thermal springs. Some spring clusters in the weathered overburden have shown significant mixing with recent local rains. Non-mixed, non-evaporated and less rock-water interacted nature is a significant in two thermal springs that emerges through (chemically inert) quartzite bed rock. Both thermal and non-thermal water with artesian condition have clearly indicated that they are

originated from a common recharge source but with different flow paths in different penetration depths and travel distances, resulting different chemical characteristics. Fresh water springs are mostly young and recharged from local rains followed with shallow percolation.

KEY WORDS:
deep groundwater, sedimentary formation, crystalline terrain, tritium free, old water, meteoric origin

1. INTRODUCTION

Deep groundwater occurs in the deep consolidated sedimentary formations stretching along the North-Western coast whereas deep fractured aquifers at 30 to 40 m depth in the hard metamorphic rock terrain of Sri Lanka. These waters are discharged at surface either through deep wells or naturally as springs and at a few locations as geothermal springs (Chandrajith et al., 2013; Jayasena and Dissanayake, 1988). Investigation of these water resources have taken place in 1960's for understanding aquifer depth, quality and yield using conventional methods (Panabokke, 2007). Since then, a series of many qualitative and quantitative studies have been conducted to identify the potable and agricultural water sources throughout the country. A groundwater potential of 7800 Million Cubic meters is estimated and more than 80% of the rural population particularly in the Dry Zone depend on the groundwater from deep aquifers (Niyangoda, 2008; Panabokke, 2007,).

Information on recharge, mobility, residence time, aquifer hydraulic connections, geothermal and geochemical evolution are still barely known though such knowledge is prerequisite to sustainable groundwater resource management especially in the water scares regions of the country.

The isotopic techniques combined with geochemistry are reliable and widely used in qualitative and quantitative assessment of groundwater worldwide. The natural isotopes Oxygen-18 and deuterium (^{18}O and ^{2}H) which are an intrinsic component of the water molecule (Clark, 2015) have been used to identify the source and pathways of groundwater recharge (Abbott et al., 2000; Ettify et al., 2012; Yousef et al., 2009), to determine the effects of condensation and evaporation (Araguas et al., 2000), to estimate advection/diffusion rates in unsaturated/saturated zones & to examine aquifer inter-connections (Jeelani et al.,2010; Mudd 2000), to assess the anthropogenic and sources of natural contaminant and salinization of coastal aquifers (Datta et al.,1996). On the other hand, measurements of stable water isotopes were used to genetic classification of geothermal waters (Bajjali et al., 1997; Kumara and Dharmagunawardhane, 2014). Radiogenic isotope (^{3}H) concentrations are used to calculate the age of recently recharged groundwater and it is a powerful tracer to discriminate groundwater older than 50 years from recent meteoric waters (Peng et al., 2012).

Investigation of water resources using stable isotopes is becoming popular in Sri Lanka. Several studies have been conducted so far in Sri Lanka to identify groundwater recharge conditions in Jaffna peninsula and Kalaoya basin (Edirisinghe et al., 2013; Edirisingheet al., 2014; Edirisinghe et al., 2015), to characterize geothermal springs (Chandrajith et al., 2013; Kumara and Dharmagunawardhane, 2014), to assess quality deterioration in sedimentary aquifers in Noth-Western coastal area (Edirisinghe et al., 2014) and to examine the spatial and temporal variation of stable isotopes in precipitation (Edirisinghe et al., 2017; Jayasena et al., 2008).

However, groundwater circulation mechanics as well as geochemical characteristics of deep groundwater aquifers in different flow regimes are yet to be understood. The present study therefore, is aimed to reveal possible recharge zones, aquifer interconnections, residence time and geochemistry of groundwater which are emerged through the artesian thermal and non-thermal wells and non-thermal springs, using chemical and isotopic methods. This work is the first detail study which interprets the groundwater dynamics with the mean residence time of deep aquifers in both sedimentary and high-grade metamorphic terrains of Sri Lanka.

1.1 Geology and Hydrology

Geologically nine-tenth of Sri Lanka is made up of highly crystalline amphibolite to granulite grade metamorphic rocks of Precambrian age (Chandrajith et al., 2013; Cooray, 1994). The rest of the Island, mainly the North-Western portion is covered by sedimentary sequences that belong to Jurassic, Miocene and Holocene periods (Figure1) (Cooray, 1994). The crystalline crust is further sub divided into three major lithological units based on geochronology, petrology and geochemistry named Highland Complex (HC), the Vijayan Complex (VC) and the Wanni Complex (WC) (Cooray, 1994). The HC mostly consists with granulite grade rocks with granitoid composition while the VC and WC with amphibolite grade rocks (Kroner et al., 1991). The boundary between the HC and the VC is well defined and it is considered to be a mineralized belt (Dissanayake, 1985) or a thrust zone (Kroner et al., 1991).

Climatically, Sri Lanka is a sub tropical Island with three well distinguished climatic zones namely, Wet Zone, Dry Zone and Intermediate Zone. The Wet Zone covers South Western sector of the Island including the Central Highlands and receives annual rainfall from 2280 to 5100 mm while Intermediate Zone receives annual average of 1700 mm. The Dry Zone occupies Northern, Eastern and South Eastern part of the Island and receives annual average of 1000 mm rainfall that comes with monsoon and convectional rains in 2nd inter-monsoon (Edirisinghe et al., 2017; Jayasena et al., 2008).

Selected study area in the current study covers the lower part of the sedimentary formation in North Western region as well as North-Eastern to Southern low lying crystalline basement of Sri Lanka.

1.1.1 Confined and semi-confined aquifers in sedimentary terrain

Miocene and Quaternary sedimentary formations, which extend from Puttalam to Jaffna Peninsula and then towards Mulativu in the North East is the largest and least utilized aquifer system in the country compared to its proven potential (Panabokke, 2007). The area lies within a Dry Zone and receives rain from October and February (Edirisinghe et al., 2014; Panabokke, 2007). Average annual evaporation is 1700- 1900 mm and it exceeds the average annual rainfall resulting a soil moisture deficit during the dry period from June to September (Karunarathne et al., 2011; Panabokke and Perera, 2005).

Highly fractured, highly faulted and separated seven groundwater basins occur along this sedimentary formation and all these are low-lying and have a subdued relief (Kodithuwakku, 2009; Panabokke, 2007). Out of these seven, four basins are considered as semi-confined and among them Vanathavillu limestone and Mannar sandstone formations are the most productive aquifers with 600,000 acre feet of groundwater in their storage (Panabokke, 2007).

Artesian conditions exist along the coastal belt of the sedimentary formation where the limestone lies at the depth and is covered by Quaternary clay deposits. Majority of artesian wells in Karaitivu, Madurankuliya, Vanathavillu, Serakkuliya, Kalpitiya, Pulinduwal and Sewanthivu belongs to the Palavi and Vanathavillu groundwater basins (Figure1) (Panabokke, 2007).

Palavi Basin is situated at the southern end of the sedimentary terrain and it laterally covers approximately 96 km^2. This basin is bounded by the Mi Oya to the North, coast to the West, Deduru Oya to the South and basement outcrop to the East (Figure1) (Panabokke, 2007). Palavi aquifer system is inter-bedded with thin cavernous limestone, clay, sand and sandy clay (Balendran, 1970) and eastern boundary of the limestone belt lies 30-40 m below the surface along a strike of North–South direction. Artesian aquifer occurs at a depth of 60 m in the middle of basin whereas 25 m in the Eastern end (Cooray, 1967; Edirisinghe et al., 2014). Piezometric heads of artesian aquifers is about 0.5 to 2m and groundwater discharge is ranging from <10 to 20 l/min (Field Information, 2017).

Vanathavillu Basin covers 80 km^{2}of the area and is bounded by the kala Oya to the North, Puttalam lagoon to the West, geological faults along the Moongil Aru stream to the South and basement outcrop to the East (Figure 01) (WRB/ODA, 1981).

Westerly and North-Westerly dipping Precambrian basement is overlaying by the calcareous sandstone in the Eastern part and it gradationally contact with the overlaying Vanathavillu Miocene limestone (ML) within the basin. On the top, low permeable, thick (40m in the E and >150m in the W) sequence of Quaternary sand, silt and clay are found and this geological setup is named as Mongil Aru Formation. The ML formation has been uplifted along a major geological fault through Aruwakkaru rising about 67 meters near the coast.

Groundwater flows in the direction of NNE-SSW (Lawrence and Dharmagunawardhane, 1983) and extensive leakage occurs at the middle of the basin through Mongil Aru Formation to the underlying limestone formation (WRB/ODA, 1981). The Miocene aquifer is the main aquifer with a depth of more than 100 m (Cooray, 1984). Flowing artesian condition occurs with the piezometric head of up to 6 m above ground level in the extreme North and in the Western parts (Lawrence and Dharmagunawardhane, 1983; Panabokke, 2007) and yield excess of 20 l/s. Transmissivities are 20 to 40 m^2/day at the margins of the basins whereas 500 to 3000 m^2/day in the narrow belt of central of the basin which, increases towards the North. Vertical permeability of the leaky aquifer is 0.003 to 0.07 m/day while the horizontal permeability is 5 to 10 times greater than it (Lawrence and Dharmagunawardhane, 1983). The estimated annual recharge of the aquifer is 7.3 million m^3 and 4 million m^3 is available for the safe extraction (WRB/ODA, 1981).

1.1.2 Deep fracture zone aquifer in the crystalline terrain

The unweathered crystalline rock is relatively non-porous, impervious and water circulation is mainly along the joint, fissures and the planes of foliation. There are separate pockets of groundwater with distinct water table. Some productive wells occur in deep fracture zone aquifers in the rocks which are connected to regional lineaments with heavy fracturing and jointing at depth beyond 30 up to 100 m (Cooray, 1967; Panabokke, 2007). Yielding capacity of deep wells is ranging from 0.1 to 2.0 l/s with the high concentration of iron and fluoride in many areas. However, groundwater potential is limited in the hard rock aquifers due to the low storage capacity and low transmissivity (Panabokke, 2007).

Artesian condition is found in the low-lying crystalline terrain due to the hydrostatic pressure of water column which originates mainly from Highlands. Lithologically these areas composed of undifferentiated metasedimentary and metaigneous rocks with banded quartzite and marble, hornblende biotite gneiss, granites and granitic gneisses (Cooray, 1984; Cooray 1994). All these artesian non-thermal wells are lies within the Dry and Intermediate Climatic Zones with the annual rainfall ranging from 1000 to 1700 mm. Some outlets are highly mineralized, but wells in Southern part (foothill of the Rakwana mountain range) have water good in quality and these sources are directly connected to the regional drinking water supply schemes (Field Information, 2017).

Thermal artesian condition is found around or close to the boundary between HC and VC (Chandrajith et al., 2013; Dissanayake and Jayasena, 1988) with the basement rocks of meta-granites, granitic gneisses, quartzite and scattered bodies of dolerite dykes (Chandrajith et al., 2013; Samaranayake et al., 2015). Sri Lanka is away from the recent volcanic/tectonic activities, therefore, low-enthalpy (34-62 ^{0}C) geothermal springs describes their origin from deep percolation of meteoric water through weak structural discontinuities under heterogeneous geothermal gradients (Adikaram and Dharmagunawardhane, 2013; Chandrajith et al., 2013; Kumara and Dharmagunawardhane, 2014). These ductile and brittle fractures, faults and joint planes provide an interconnected network to groundwater circulation for several kilometres in some instances before emerges to the surface as geothermal springs (Chandrajith et al., 2013). However, interconnections between thermal water with dolerite dykes through the deep fractures have been identified in Marangala, Nelumwewa and Kapurella (Kumara and Dharmagunawardhane, 2014; Samaranayake et al., 2015). Geothermal waters from springs in Kanniyai and Rankihiriya are flowing through some carbonate and chemically inert quartzite formation before emergence to the surface (Panabokke, 2007).

All the thermal artesian spring clusters are located in the Dry and Intermediate Zones of the Island with <100 m altitudes except at Marangala (Wahawa) with altitude about 100 m above mean sea level (amsl) (Chandrajith et al., 2013; Senarathne and Chandima, 2011). One of the thermal well in Wahawa spring cluster shows artesian condition with piezometric head of 3 m above the surface level (Chandrajith et al., 2013). All these thermal springs have variable flow rates and surface and reservoir temperature are ranged from 35 to 62^{0}C and ~150^{0}C respectively (Chandrajith et al., 2013; Kumara and Dharmagunawardhane, 2017).

pH varies from 5.7 to 8.4 and low electrical conductivity (998 to 1403 μS/cm) value suggested that the low mineralization of thermal water in all the places except Mahapellessa (Chandrajith et al., 2013, Panabokke, 2007).

2. MATERIALS AND METHODOLOGY

In the current study, water samples from 22 artesian non-thermal wells in both sedimentary and crystalline terrain, as well as seven outlets of the Mahaoya and Kanniyai thermal springs, five outlets from the Nelumwewa thermal spring clusters, four different springs in Wahawa and single outlet of Mahapelessa and Rankihiriya and adjacent non-thermal springs (Figure1) were collected during the period from March to June 2017.

[Insert Figure 1]

Field data including longitude, latitude, altitude, sample type, well depth, static water level, piezometric head, geology and discharging rate were recorded. pH, electrical conductivity (EC), salinity, total dissolved solids (TDS), dissolved oxygen (DO) and temperature (T) were measured on-site using calibrated HACH HQ 40d multiPHC 30101 instrument connected with CDC 40101 and LDO 101 probes.

Unfiltered and unpreserved water samples were collected into 500 ml double capped HDPE bottles for major ion analysis as well as for tritium analysis separately. Unfiltered 30 ml of water samples were collected into double capped polyethylene bottles for oxygen and hydrogen isotope analysis. All these samples were properly labelled and transported to the Isotope Hydrology Laboratory (IHL) at the Sri Lanka Atomic Energy Board (SLAEB).

The concentrations of CO_3^{2-} and HCO_3^- were calculated from phenolphthalein and total alkalinity using potentiometric titration method: APHA 2320B (APHA, 2012). EDTA titrimetric method: APHA 2340B was used to calculate total hardness in water (APHA, 2012). Major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, Br^-, NO_3^- and SO_4^{2-}) were determined using non-suppressor dual flow Shimadzu prominence IC system with a conductivity detector. Nitrate and fluoride content were double checked/measured using HACH DR/2400 portable spectrometer with reference to the Cadmium Reduction method 8171 (measurement range: 0.1 to 10.0 mg/L NO_3^-) at 430 nm and SPADNS method 8029 (measurement range: 0.02 to 2.00 mg/L F^-) at 580 nm (HACH, 2004) respectively. The analytical precision for the cation and anion measurements is indicated by the ionic balance error within the standard limit of ± 5%.

Stable isotopic composition ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) of groundwater samples were measured using Liquid Water Isotope Analyzer (LWIA) LGR-V2 100 model no: 908-0008-200 with off-axis integrated cavity spectroscopy (off-axis ICOS) method at IHL, SLAEB (IAEA, 2009). Isotope results are reported in the delta notation (δ) versus Vienna Standard Mean Ocean Water - 2 (VSMOW- 2) standards and expressed in per-mill (‰). Samples were analysed in duplicate and precision of the measurement was within ± 0.2 ‰ for $\delta^{18}O$ and ± 1.0‰ for $\delta^{2}H$.

Water samples were electrolytically enriched from Electrolytic Enrichment Setup and tritium concentration was measured using Liquid Scintillation Analyzer TRI-CARB 3170TR/SL at SLAEB (IAEA, 2005). Its concentration is expressed as Tritium Unit (TU) with the minimum detection limits of 0.4 TU. Age/ residence time of the water samples were calculated using Tritium half-life calculation method with the $T_{1/2} = 12.32$ years.

The ambient meteoric isotope data in few locations of Sri Lanka were obtained from the Isotope Hydrology Information System (ISOHIS) database of the International Atomic Energy Agency/ World Meteorological Organization (IAEA/WMO, 2006) and they were used to interpret the stable isotope results as reference to specific area.

3. RESULTS AND DISCUSSION

Geographical locations with measured physical and chemical parameters, stable isotope ($\delta^{18}O$ and $\delta^{2}H$) values and Tritium concentration of non-thermal artesian wells, non-thermal springs and most representative outlet of each artesian thermal cluster are listed in table1.

Thermal spring clusters have several outlets next to each other, indicating that they are from the same source at depth. Variations of temperature and water quality of these spring outlets would be due to different flow rates and near surface obstacles. The outlet with highest yield and mostly with highest temperature is taken as the most representative spring outlet of a particular cluster/location.

3.1 Groundwater Chemistry

Chemical composition of recharge water, water-rock interactions, evaporation and relative mobility of ions are the major factors influencing the geochemistry of groundwater (Yousef et al., 2009). The results indicate wide variations of chemical concentrations even in the artesian thermal and non-thermal waters within the same formation.

pH of the water samples in the sedimentary terrain varied from 6.67 to 7.83 with the median of 6.99 and EC from 2720 to 5760 µS/cm in the Palavi, but from 1647 to 2390 µS/cm in the Vanathavillu basins. One location (Art-15) in Palavi basin shows exceptionally higher EC value (20480 µS/cm) with elevated cations and anions probably due to mixing of lagoon water. The other locations with relatively low values imply that the hydraulic connection between deep water and salinized or evaporated surface water is insignificant. In the crystalline terrain, pH ranged from 6.37 to 8.41 with a median value of 7.11. EC of the crystalline non-thermal artesian waters are comparatively lower and was ranging from 483 to 733 µS/cm, is possibly due to less ion dissolution during the flow through the fractures of the crystalline rock (Panabokke, 2007). However artesian thermal spring cluster at Wahawa (Marangala) shows a relatively high value (1408 µS/cm). Na^{+} is the dominant cation with an order of abundance of Na > Ca > Mg > K while the same of anions showed Cl > HCO_3 > SO_4 > F = NO_3 in the sedimentary artesian waters. Ca^{2+} and HCO_3^{-} are the dominant ions with an order of abundance of Ca > Mg >Na > K and HCO_3 > Cl > SO_4 > F = NO_3 in crystalline non-thermal artesian waters at; Sudugala, Middeniya and Hingurakgoda. However, Na^{+} and $SO_4^{2-}$are dominant in Wahawa thermal artesian well with the opposite order of abundance when they are compared with other non-thermal artesian waters in the crystalline terrain.

The maximum temperature of discharging artesian thermal water is varied from 37.9 ^{0}C to 61.2^{0}C. EC and DO are ranged from 309 to 7810 µS/cm and 0.48 to 6.33 mg/L in thermal waters respectively and the same is from 418 to 7680 µS/cm and 0.2 to 3.73 mg/L in non-thermal spring waters respectively. Both artesian thermal and non-thermal spring waters except Mahapellessa (MP) indicate comparatively low mineralization.

[Insert Table 2]

The chemical results revealed that the Na^{+} is the dominant cation while Cl^{-} and SO_4^{2-} are the dominant anions in Mahapelessa (MP), Wahawa (WH), Mahaoya (MO) and Nelumwewa (NW) thermal spring fields. However, Kanniyai (KN) and Rankihiriya (RK) thermal springs as well as all other non-thermal springs except MP have relatively high concentrations of Ca^{2+} and HCO_3^{-} ions. Enrichment of F^{-} up to 5.1 mg/L was observed in the artesian thermal water and non-thermal spring water along HC-VC boundary with possible course of desorption from mineral phases (Sexana and Ahmed, 2001) in alkaline environment such as micas and amphiboles in high-grade metamorphic regions (Dissanayake and Weerasooriya, 1986). However negligible amount of F^{-} was observed in the deep waters from North-Eastern part of the country. All the other samples show concentration of F^{-} < 1.5 mg/L. NO_3^{-} concentrations of all the water samples are less than 2.3 mg/L indicating all these waters are relatively old and are have insignificant affect of anthropogenic sources during their subsurface flow. However PO_4^{3-} and Br^- were not detected in any of the deep groundwater samples. Mechanisms controlling the groundwater chemistry is depends on the climatic condition and mineralogy of the underground aquifer. Gibbs diagram (Gibbs, 1970) illustrates the ratio of $Na^+/(Na^+ + Ca^{2+})$ or $Cl^-/(Cl^- + HCO_3^-)$ as a function of TDS and it is an effective tool to assess the natural mechanisms controlling water chemistry and also represents three distinct fields such as evaporation dominance, rock weathering dominance and precipitation dominance (Figure 2 (a) & (b)).

Evaporation dominant waters are generally occur in arid (high temperature) zones (Clark I. , 2015). This is due to evaporation-fractional crystallization process causing-rich, intermediate salinity to Na-rich, high salinity waters (Gibbs, 1970; Kumar and Logeshkumaran, 2015). Sedimentary terrain's artesian water in both Palavi and Vanathavillu basins and both artesian thermal and non-thermal spring waters in Mahapellessa fall in to this category indicating the evaporation affecting their water chemistry. Crystalline non-thermal artesian water, non-thermal spring water and thermal waters in Kanniyai and Rankihiriya fall into the category of water-rock interaction. Chemically rock dominant field is characterized by the abundance of calcium and carbonate from the shallow zone of active flushing (Clark, 2015) and this characteristic is dependent on the relief, climate and composition of geological material which are contact with their flow (Clark, 2015; Kumar and Logeshkumaran, 2015). Thermal springs in Nelumwewa, Mahaoya and Wahawa fall into the transition zone of evaporation and rock dominance field indicating water chemistry of these systems are dependent on both evaporation -fractional crystallization process and rock-water interaction.

[Insert Figure 2]

The piper diagram is a method of graphical representation of major ionic composition of groundwater and hence it is used to classify groundwater (Piper, 1944).

Figure 3 show that all the sedimentary artesian waters belong to Na-Cl and Na-HCO_3-Cl type while non-thermal spring water, crystalline artesian non-thermal water and Kanniyai and Rankihiriya thermal waters belong to Ca-HCO_3 water type. However, thermal water from Mahapelessa is Na-Cl type and Wahawa, Mahaoya and Nelumwewa are Na-SO_4 and Na-Cl-SO_4 types.

[Insert Figure 3]

Na-Cl hydrochemical facies of sedimentary artesian waters might be related to the sea water mixing (Chandrajith et al., 2013), However, low EC and distance to salinity end of the mixing line (figure 4 (a)) does not support to prove this fact. Also, highly faulted and clay filled geological structures in this area can act as barriers to the sea water intrusions (Panabokke, 2007). However higher concentration of Na^+ may be from dissolution of Na-bearing minerals and cation exchange (Li et al., 2015) while elevated Cl^- is identified as salt leaching from slatterns through unconsolidated sediments (Edirisinghe et al., 2014).

Ca^{2+}/Mg^{2+} and HCO_3^- are the dominant ions in the Miocene Limestone aquifer but emergence water with dominant Na^+ and Cl^- indicates a trend towards maturity (Qin et al., 2005) and it confirms the cation exchange is also dominant process in these study areas.

Sedimentary artesian waters with relatively low concentration of Ca^{2+} and Mg^{2+} with high concentration of Na^+ are evolved from the Mongil Aru Formation (Lawrence and Dharmagunawardhane, 1983). Three artesian wells in northern part of the Vanathavillu basin (Art-23, SE and KT) shown such characteristics. It explains, source waters of these three wells are from leakage through central area of the Moongil Aru Formation and flowing northwards to only minimal mixing with the older, more saline confined groundwater.

Chloro-Alkaline Indexes (CAI 1 and CAI 2) are used to identify the possible ion exchange reactions occurring in the groundwater system (Li et al., 2015). In the current study, calculated CAI 1 ($[Cl^- - (Na^+ + K^+)]/Cl^-$) and CAI 2($[Cl^- - (Na^+ + K^+)]/(SO_4^{2-}+CO_3^{2-}+HCO_3^-+NO_3^-)$) both are positive in the sedimentary artesian water except three locations (Figure 5 (c)). It confirmed the possible ion exchange between dissolved Na^+ and K^+ in the flowing water and Ca^{2+} and Mg^{2+} in the limestone aquifer during the flowage. However, these indexes are negative in the locations of northern part of the Vanathavillu basin (Art-23, SE and KT) indicating the reverse ion exchange process in this system. Upper red latosol soil act as a source of Ca^{2+} and Mg^{2+}in percolated water and lower vertical permeability of Moongil Aru Formation promotes the exchange of Na^+ and K^+ from the thick clay beds during water infiltration.

In order to further explain the origin of sedimentary artesian waters, the relationship between Na^+ and Cl^- (Figure 4(b)) is used. This relationship is commonly used as a first order indicator of rock-water interaction (Lyu et al., 2019). None of the samples falls on the 1:1 regression line indicating the halite dissolution is not a factor in this groundwater system. However, sedimentary artesian waters of Art-23, SE and KT with the molar Na/Cl ratio above 1.5 further confirms that additional sources contribute to the dissolved Na^+ in the groundwater system because of cation exchange between Ca^{2+}/ Mg^{2+} in groundwater and Na^+ in the clay minerals (Cartwrite and Weaver, 2005; Foster, 1950). All the other sedimentary artesian water samples with Na/Cl ratio less than 1 (figure 4) show opposite order of cation exchange between the aquifer material and the groundwater system. Elemental composition of groundwater depends on the basement mineralogy and sub surface temperature (Jayawardana et al., 2016).

[Insert Figure 4]

Correlations between selected ions and ionic ratios with Cl^- (figure 5) were plotted to identify the possible rock-water interaction of deep groundwater in the crystalline terrain and the scatter distribution of ionic ratios of Ca/Cl, SO_4/Cl and HCO_3/Cl versus Cl (figure 5 (c-e)) are used separately to identify the source of Ca in the water, depth to water-rock equilibrium and nature of the flow paths respectively.

Higher Ca/Cl ratio of the groundwater indicates the weathering of plagioclase feldspar bearing granitic rocks and calcite and dolomite-bearing marble in the host rock (Jayawardana et al., 2016; Nur et al., 2012). Crystalline artesian non-thermal wells, non-thermal springs, thermal springs at Mahapelessa and most of them in Northern Sri Lanka (Rankihiriya and Kanniyai) with higher Ca/Cl ratio would be from probable sources of Ca in host rock. These minerals are unstable at low temperatures and therefore they release some Ca into water even in geothermal systems with low temperatures.

Elemental correlation of Cl with Na/K (figure 5 (a-b)) indicate decreasing dilution trend from thermal waters to non-thermal waters. This relationship signifies the rock-water interaction of thermal artesian water in eastern part of Sri Lanka (Nelumwewa, Mahaoya and Wahawa) with the Na/K and Cl rich minerals such as alkali feldspar, apatite, biotite, muscovite, and amphibole in the crystalline basement rocks (Cooray, 1994).These minerals are unstable under high temperatures; hence these minerals are dissolved in thermal waters (Jayawardana et al., 2016).

Thermal springs of Rankihiriya and Kanniyai shows comparatively high amount of $HCO_3^-$and intermediate HCO_3/Cl ratio indicating these groundwaters have long flow paths and higher travel times (Chandrajith et al., 2013; Jayawardana et al., 2016). Presence of SO_4 usually indicates the deep water-rock equilibria and higher SO_4/Cl ratio of Wahawa artesian thermal well represents more deep circulated water than the same in Mahaoya and Nelumwewa thermal springs. However, very low

SO_4/Cl and high to intermediate HCO_3/Cl ratios of non-thermal spring water represent non-deeper (shallow) water-rock equilibria and comparatively shorter flow paths with faster water cycles than the artesian thermal waters.

The well mixed, comparatively high mineralized nature of Mahapelessa springs is characterized by higher concentration of sodium and chloride ions as well as high EC content. These higher concentrations are not related to sea water intrusion because the spring is located about 40 km away from the sea. Chandrajith, 2013 explains shallow and deep water in the nearby terrain has high concentrations of dissolved solids with high saline character. The Na/Cl and Mg/Ca ratio are used in the current study to identify the mechanism of salinity and saline water intrusion in semi-arid regions. Na/Cl and Mg/Ca ratio are 0.43 and 0.005 while 0.43 and 0.009 in Mahapelessa thermal and non-thermal springs respectively and it suggests that these spring waters are altered by the saline water within the terrain during the subsurface flow.

Both artesian thermal water and non-thermal spring water in Mahapelessa and Rankihiriya show similar chemical and physical characteristics and they indicate a common recharge source and different level of lateral mixing during the deep circulation (figure 5).

[Insert Figure 5]

3.2 Stable Isotopic Characteristics

Stable isotopic compositions of meteoric waters are useful to interpret the origin of groundwater in tropical countries with minimal seasonal climate variation with constant atmospheric temperatures. Previous works by Jayasena et al (2008) and Edirisinghe et al (2014, 2017) discriminate the moisture origin of different monsoon patterns in Sri Lanka and they identified the correlations between rain isotopes in different geographical and environmental conditions. They have shown that the degree of isotopic depletion in rain water across the country depends on the altitude, distance from the coast and amount of precipitation (Edirisinghe et al., 2017, Jayasena et al., 2008).

The $\delta^{18}O$ and $\delta^{2}H$ values with d-excess of both sedimentary and crystalline deep groundwater are presented in Table 1. The relationship between $\delta^{18}O$ and $\delta^{2}H$ are graphically illustrated with the local meteoric water lines with evaporation lines in figure 6 and 7. The Meteoric Water Lines (MWL) previously identified (Edirisinghe et al., 2017), evaporation lines and LMWL constructed using the available data in IAEA ISOHIS database (IAEA/WMO, 2006) (Table 2) have provides the basis for interpretation of isotopic data of groundwater in different flow regimes of the country. However, rain isotopic signatures in the highland areas from South-West to South-East of Sri Lanka are not found in the literature. Thus, LMWL constructed using monthly average rainwater collected during the period from January to December 2016 in the Central Highlands of Sri Lanka is used as a representative of the isotopic signature of Central Highlands.

[Insert Table 2]

3.2.1 Sedimentary terrain

The $\delta^{18}O$ and δ^2H of artesian waters in Palavi basin vary from -6.09 to -4.97‰ and -36.4 to -29.0‰ respectively with the variation of d-excess from 9.3 to 14.5‰. However, the same in Vanathavillu basin is ranged from -6.51 to -5.19‰ and -39.9 to -30.2‰ with the d-excess from 9.2 to 12.2‰. D-excess values with their isotopic composition indicate the source of water for all artesian wells is from the North East monsoonal rain (Edirisinghe et al., 2017).

Almost all the artesian water samples have slight evaporation effect and lies between the evaporation lines of Puttalam and North-Central Dry Zone (figure 6) indicating that these waters have slight mixing component with evaporated surface waters in North-Western region. Relatively depleted $\delta^{18}O$ and δ^2H values of artesian water in Pulinduwal (Art-15) (-5.22‰ and -32.52‰) are suggested the absence of sea water intrusion as well as high ionic concentrations that would be due to dissolution of geological material in the area.

[Insert Figure 6]

The regression lines of artesian waters in Palavi basin is $\delta^2H=5.3\delta^{18}O-4.3$‰ whereas in Vanatrhavillu basin it is $\delta^2H=6.4\delta^{18}O +2.0$‰ indicate distinct evaporation effects and it is more in Palavi basin than in Vanathavillu basin. The $\delta^{18}O$ confluence point of LMWL and regression lines of Palavi basin and Vanathavillu basin are -6.56‰ and -7.21‰ respectively. Vanathavillu basin shows more depleted isotopic signature than the rain index of Puttalam that would probably be due to higher elevation recharge condition or due to amount effect (Mook, 2001). However this area is dry with low annual precipitation (Karunarathne et al., 2011), thus amount effect can be negligible and more depleted isotopic signatures are a result of higher elevation recharge. Considering the isotopic values and correlation of $\delta^{18}O$ with altitude (Edirisinghe et al., 2017), it is suggested that the deep groundwater in Vanathavillu basin is recharged from altitude of 100 to 200 m amsl and Palavi basin is recharged from around 100m amsl. Piezometric head of the artesian water in Palavi basin varies from o.5 to 2m while western and northern part of the Vanathavillu basin varies from 1.5 to 6m and this high discharge rates in Vanathavillu basin confirm that the its recharging elevation is higher than the same of Palavi Basin. These waters would be flowing through the fractures of crystalline rock from the East and enters into the groundwater basin of the sedimentary terrain. Hence evaporated isotopic signature of almost all the artesian water samples could be identified as mixing of locally evaporated surface water that percolates through the Mongil Aru Formation or already evaporated surface water and/or rain waters which are recharged from higher elevated areas.

3.2.2 Crystalline terrain

The $\delta^{18}O$ and $\delta^{2}H$ values of artesian non-thermal water in crystalline terrain range from -6.36‰ (Sudugala: SU-1) to -4.37‰ (Hingurakgoda: HG) and from -35.3‰ to -24.9‰ respectively. Also the same in artesian thermal springs range from -6.43 to -5.06‰ and -38.9 to -26.8‰ while non-thermal springs range from -6.19 to -5.00‰ and from -37.8 to -26.2‰ respectively for $\delta^{18}O$ and $\delta^{2}H$. D-excess of the all crystalline waters except the waters from four locations indicates that these waters are recharged from both NE and 2nd inter-monsoonal rains (Edirisinghe et al., 2017). However, larger d-excess values in Wahawa artesian thermal well (WH-A: 18.5‰) and Sudugala artesian non-thermal well (SU-2: 19.1‰) indicates that it may be due to the higher elevation recharge (~ 1400m) and/or long residence time. Nelumwewa (NW) thermal spring as well as non-thermal springs in Bibile (BB) shows lower d-excess value (9.9‰ and 6.2‰) that would be due to evaporation effect and/or rock-water interaction along their flow paths (Mook, 2000).

Isotope composition of three artesian non-thermal wells in Southern region; Kella Junction (KBU), Middeniya (MD-5) and one in-between Sudugala and Middeniya (SU-1) falls near the LMWL of Central Highlands (figure 7) and they indicate that all these wells are recharged by high elevated meteoric waters. Higher yielding capacity, elevated piezometric head with more depleted isotopic signatures of SU-1 indicate that this well is probably recharged from adjacent Rakwana Mountains. Artesian non-thermal well in Sudugala (SU-2) and Wahawa thermal artesian well showing horizontal negative shift (0.3‰) from local rain origin, may be due to the exchange of ^{18}O in water and CO_2 in carbonate bearing host rock (Pang et al., 2017) during their longer flow paths.

The non-thermal artesian well with higher discharge in Hingurakgoda shows more enriched and evaporated isotopic signature indicating possible mixing of deep groundwater with surface waters which are already evaporated. Piezometric head of the above well is about 1.5 m and discharge rate is more than 1000 litters/minutes. This confirms that these groundwater would be recharged from highlands. This well is located in different flow regime than other artesian wells and groundwater movement of this area is from South West (SW) to North East (NE) (Panabokke, 2007). The marble formation in the area is also trending towards the similar direction which indicates that the groundwater flows are probably along the rock bad with the possible Ca dissolution (Edirisinghe et al., 2017) from North-Eastern slopes of Central Highlands.

[Insert Figure 7]

Average $\delta^{18}O$ and $\delta^{2}H$ values of artesian thermal and non-thermal springs lie along or close to the LMWLs of Dry Zone - NE valley, Dry Zone – East Coast and Intermediate Zone. They indicate that all these springs are recharged from local meteoric waters of different climatic zones (figure 7). Both thermal and non-thermal waters from Mahapelessa (MP) springs are slightly enriched while artesian thermal waters of Mahaoya (MO), Nelumwewa (NW) and one non-thermal spring water in Middeniya (MD-2) show moderate enrichment. Waters from both thermal and non-thermal springs in Wahawa and Rankihiriya, thermal spring in Kanniyai as well as non-thermal springs in Bibile and Middeniya (MD-3) show more depleted isotope values.

Thermal waters are expected to have enriched isotopic signature due to the evaporation process in high temperature reservoirs (Clark and Fritz, 1997). Therefore slight enrichment of isotopes composition in artesian thermal waters of Mahapelessa (MP, MP-1), Mahaoya (MO) and Nelumwewa (NW) is possible. Isotopic values of both thermal and non-thermal springs in Wahawa (WH, WH-1) and Rankihiriya (RK, RK-1) and non-thermal spring named Bibile (BB) and Middeniya (MD-3 and MD-2) are well-matched with isotopic signature of Intermediate Zone indicating that these springs are recharged from rainfall of the Intermediate Zone. Location of thermal spring in Kanniyai is very close to the North-East coast. The weighted mean isotope value of precipitation in that area is -5.17‰ and -30.4‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively (Edirisinghe et al., 2017). However, more depleted isotopic signature of above spring evident that absence of local rain recharge and possible higher elevation rain inputs.

Changes in isotopic compositions in geothermal systems are temperature dependent, fast process associated with rock-water interaction, steam separation, dilution and mixing. Correlation between $\delta^{2}H$ vs $\delta^{18}O$ and T (^{0}C) vs $\delta^{18}O$ are more useful tool to identify the degree of isotopic fractionation (α), magnitude of oxygen isotope shift and evaporation process of the geothermal system (Mook, 2001).

Isotopic composition of different thermal spring outlets in Wahawa except thermal artesian well (WH-A) is aligned with the LMWLs which have rain indexes similar to the Intermediate Zone (figure 8 (a)). This shows that all these individual springs undergo similar recharge mechanism and are mixed with significant amount of local meteoric waters in the area. Constant $\delta^{18}O$ values with slightly varied temperatures (figure 8 (a)) suggest that the isotopic fractionation is comparable and largely unaffected by chemical and physical processes during the movement (Mook, 2001). However artesian thermal well shows more depleted isotopic signatures with negative horizontal shift probably due to exchange of ^{18}O in calcite rich minerals and water during the vertical migration (Clark and Fritz, 1997; Pang et al., 2017).

[Insert Figure 8]

Relationship of water isotopes in seven thermal water outlets of Mahaoya spring field shows the positive $\delta^{18}O$ shift along the horizontal axis with the trend line of $\delta^{2}H$=-0.1$\delta^{18}O$ - 31.4‰ (R^2=0.001). Shifting of $\delta^{18}O$ with constant $\delta^{2}H$ (figure 8 (b)) indicates that the system is attributed to water-rock interaction usually at high temperatures and constant $\delta^{2}H$ evident due to lack of hydrous mineral in the host rock (Mook, 2001; Pang et al., 2017). 1-2 ‰ of $\delta^{18}O$ shift is as an indication of the large amount of local meteoric water having passed through this thermal system (Mook, 2001). Comparatively small $\delta^{18}O$ shift with the fluid dominated system is generally associated with the shallow levels of igneous body (Mook, 2001; Suwar, 2009). It suggests that the dolerite dike in this area act as a possible heating source for the thermal water of Mahaoya spring field.

Both $\delta^{18}O$ vs $\delta^{2}H$ and T (^{0}C) plots (figure 8 (b)) indicate that the $\delta^{18}O$ is enriched when the temperature decreases. The $\delta^{18}O$ value is enriched due to progressive isotopic exchange when increasing the flow distance (Mook, 2001) and fluid temperature is decreased when flow distance is increased. This phenomenon explains the reason for low temperature thermal outlets having enriched $\delta^{18}O$ composition whereas high temperature thermal outlets are having depleted isotopic compositions in Mahaoya spring field.

Temperature of five different artesian thermal outlets in Nelumwewa is ranging from 31.6 to 61.2 ^{0}C and isotope composition of highest temperature outlet among these five, is aligned along LMWLs which indicates that this spring cluster has a meteoric origin (figure 8 (c)). Isotopic values of all other low temperature outlets show some degree of enrichment and evaporation effect. Evaporation line of this area was constructed using isotopic values of Nelumwewa reservoir and highest temperature spring outlet with the correlation of $\delta^{2}H$= 4.7$\delta^{18}O$-4.0‰. Isotopic values of spring outlets aligned in-between the evaporation line and line of geothermal exchange explain these thermal waters have possible mixing of evaporated non-thermal shallow water prior to discharge at the outlets. Degree of enrichment is increased when the temperatures is decreased in Nelumwewa spring field. The reason would be the increases of mixing proportion of evaporated non-thermal water from Nelumwewa reservoir with thermal spring water.

Temperatures of seven thermal outlets in Kanniyai are around 40 ^{0}C and isotopic values appeared as cluster explains that all springs have similar origin and similar circulation pattern. Isotope compositions of all spring waters are aligned along the LMWLs with more depleted isotopic signature (figure 8 (d)). It indicates that these springs are recharged from higher elevated meteoric waters. Slight variation of $\delta^{18}O$ with constant temperature indicates that these water are un-altered with host rock (Qin et al., 2005) and it confirms that these waters are flowing and emerged through the chemically inert quartzite formation.

3.3 Tritium

Tritium is a radioactive isotope of hydrogen and it is a reliable tracer to discriminating groundwater older than 50 years from recent meteoric waters (Clark and Fritz, 1997). Tritium concentration of water is expressed as Tritium Units (TU), and 1 TU = 0.11919 Bq/L with the Half-life of 12.32 years (4500 days).

Long term average tritium concentration of the country is ~1.5TU (Edirisingheet al., 2017) and this value is used as initial value for the age/residence time calculations using the half-life calculation method.

Tritium values of all the artesian waters except only two locations in the sedimentary terrain are below the detection limit of 0.4TU and hence are considered to be tritium free water (old waters) with long residence time. Two locations with the tritium value of 0.62 and 0.65TU indicate these waters having mean residence time (MRT) of ~ 15 years.

Three groups of tritium values are identified in the different flow regimes of the crystalline metamorphic terrain. Artesian non-thermal water except SU-2 (KBU, SU-1, MD-5) in southern part and all the non-thermal spring waters of the country are ranging from 0.40 to 0.56 TU with the mean values of 0.48TU indicating that these waters having MRT of ~17 to 23 years. However, artesian non-thermal water from Hingurakgoda spring shows tritium value of 0.76 TU with the MRT of 12 years. Groundwater age of all these locations confirm their shorter flow paths, shallow penetration depths and shorter residence time.

Thermal springs in Mahapelessa, Mahaoya, Kanniyai and Rankihiriya, non-thermal artesian well in Sudugala (SU-2) and artesian thermal well in Wahawa (WH-A) are having tritium concentration of <0.4 TU are classified as “old water” (more than 50 years). However 0.86TU value in Wahawa thermal springs explains a mixing of non-thermal surface waters in shallow levels. Meanwhile relatively high tritium (0.73 TU) value similar to Wahawa in Nelumwewa thermal spring water confirms the possible mixing of recently precipitated non-thermal waters from Nelumwewa reservoir with emerged thermal waters. All the artesian thermal waters in Sri Lanka are considered as “old waters” with low tritium concentrations confirming that this thermal water penetrates to the deeper levels prior to discharge.

All the generated findings of deep originated groundwaters in both sedimentary and crystalline terrains in Sri Lanka are summarized as Table 03 and Figure 09 & 10.

[Insert Table 3]

[Insert Figure 9]

3.4 Proposed Models

Following figures represent the proposed models depicting the hydrogeological conditioned associated with the studied aquifers.

`

[Insert Figure 10 (a)]

[Insert Figure 10 (b)]

[Insert Figure 10 (c)]

[Insert Figure 10 (d)]

4. CONCLUSIONS

Chemical and isotopic signatures of studied groundwater reveal that, there are different recharge mechanisms and distinct flow regimes specific to the sedimentary and crystalline terrains of Sri Lanka (Table 3).

Studied artesian aquifers in the sedimentary terrain are recharged by the higher elevated meteoric water and flowing along regional and longer flow paths through fractured basement rock and have a long residence time. There is no evidence for sea water mixing with these water through a sedimentary aquifers are situated bordering the West coast. Possibility of some percolation of locally evaporated surface water in to the sedimentary aquifers is evident probably where that aquifer is semi-confined.

Artesian but non-thermal groundwater in the crystalline terrain shows two different recharge and discharge mechanisms. (a). In the Southern lowlands, groundwater is non-mixed, non-evaporated, highlands originated fast replenished and 17 to 23 years old. (b) In the East North Central lowlands, groundwater is evaporated, lowlands originated, fast replenished and approximately 12 years of age. All geothermal spring waters are of meteoric origin, tritium free and hence older (>50 years) and deep percolated. Some thermal springs (Wahawa) show that water is high altitude originated and intensely rock-water interacted groundwater. Since some springs have several outlets in the weathered overburden, mixing with recently precipitated, non evaporated rainwater takes place resulting overall young ages (10-13 years) of the water. Non-mixed, non-evaporated and less water-rock interacted nature is a significant feature in two (Kanniyai and Rankihiriya) thermal springs that emerges through (chemically inert) quartzite bed rock.

All other fresh water springs have locally recharged, recently precipitated and shallow percolated waters.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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