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Article

Synergic Origin and Evolution of TDS, Mg and Fluoride in Groundwater as Relative to Chronic Kidney Disease of Unknown Etiology (CKDu) in Sri Lanka

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Abstract: The rural population in the Dry Zone of Sri Lanka is largely affected by Chronic Kidney Disease of Unknown etiology (CKDu). According to the multidisciplinary research carried out so far, quality of groundwater is considered one of the possible causative factors for CKDu. Therefore, the assessment of the quality of shallow groundwater that is being used for drinking and its evolution mechanism is the key to identifying the relationship between CKDu and the drinking water. The current study aimed to perform a detailed investigation on shallow groundwater sources using isotopic, chemical and hydrogeological methods in the CKDu-endemic, non-endemic and control areas selected for a systematic comparison. Our investigation shows that, elevated levels of TDS, magnesium and fluoride at the same time in the shallow groundwater, affected by climatic, geochemical and hydrogeological processes may contribute to the CKDu in the Dry Zone of Sri Lanka. All of the groundwater samples analyzed have exceeded the moderate hardness threshold. However, prominent Mg hardness proportion together with excess F⁻ in the CKDu endemic area may produce nephrotoxic MgF₂ complexes that may trigger renal damage. In contrast, produced NaF complexes in the CKDu control area leads to reduction of F⁻ toxicity in the human body. Although TDS, hardness, Mg²⁺, Na⁺ and F⁻ are the main parameters that cause water quality deterioration, their formation mechanism in the three selected areas are very different. The excess concentrations of F⁻ and Mg²⁺ in the CKDu endemic area, low F⁻ and high Mg²⁺ in the CKDu non-endemic sedimentary formation, and either combinations of low F⁻ and low Mg²⁺, high F⁻ and low Mg²⁺ or low F⁻ with high Mg²⁺ in the control area are the distinct features. The primary processes that regulate the evolution of groundwater types and contents in the CKDu endemic and control areas is the weathering of silicates. Similarly, in the CKDu endemic area, carbonate dissolution and reverse ion exchange are quite strong. Cation exchange and evaporite dissolution are more pronounced in the control area. Shallow groundwaters are evapo-concentrated hence it further deteriorates quality in the CKDu endemic area. Dilution decreases the ion content in the CKDu endemic area while evaporite dissolution further increases it in the control area after the rainy season. Evaporation, and seawater mixing affected the quality of groundwater in the non-endemic sedimentary formation. A statistically significant difference of F⁻ ionic ratio with Na⁺, Mg²⁺, Ca²⁺ in the endemic and control areas. Intensive rock weathering, combined with the desorption, has added excess F⁻ to the groundwater in the CKDu endemic area, while cation exchange and fluorite dissolution is a contributing factor in the CKDu control area.

Keywords: CKDu endemic; control; fluoride; water quality; evapo-concentration

1. Introduction

Chronic Kidney Disease (CKD) is a serious, non-communicable health problem predominantly affecting tropical countries (Levine et al., 2015; Nanayakkara et al., 2020) with the global prevalence rate of 8 to 16% (M Pry et al., 2021a; S et al., 2017). Because the cause of this disease diverges from the commonly known risk factor of CKD, it is referred to as Chronic Kidney Disease of unknown etiology or “CKDu” (T. Cooray et al., 2019; S. Imbulana & Oguma, 2021).

CKDu is an unusual form of renal disease reported only in the tropical countries such as India, Central America, Nicaragua, El Salvador, Costa Rica, Mexico, Egypt, and Sri Lanka (Faleel & Jayawardena, 2020; Torres et al., 2010; Wimalawansa, 2015). Low to middle-income countries have seen an alarming rise over the past 20 years. Prevalence of CKDu has now overtaken that in many high-income countries (Gifford et al., 2017). There have been several global epidemics of unexplained kidney disease, from that Uddanam Endemic Nephropathy in Andhra Pradesh of India, CKDu in Sri Lanka shows similarities such as the disease being progressive and asymptomatic until end stage, male predominance and clustered distribution among rural middle-aged communities (Faleel & Jayawardena, 2020; S. Imbulana & Oguma, 2021; McDonough et al., 2020).

CKDu in Sri Lanka was first reported in the mid-1990s and high prevalence was observed in the dry zone of Sri Lanka particularly in the North Central Province (NCP) and North Western Province (NWP). Currently it is spreading over other dry zone areas and some intermediate zone areas of Central, Eastern, and Southern Provinces (Cooray et al., 2019; Faleel & Jayawardena, 2020; Wickramarathna et al., 2017; Wimalawansa, 2015) (Figure 1). The majority of people in the affected areas are male, with the age group of 30 to 60 years (Edirisinghe et al., 2017; Imbulana & Oguma, 2021; Wickramarathna et al., 2017). More than 400,000 people are affected by this disease with the recent prevalence rate of 15-23% (Jayatilake et al., 2013; Rajapakse et al., 2016) while around 22, 000 deaths over the past 20 years (Faleel & Jayawardena, 2020).

Over past few decades multidisciplinary research studies were carried out focusing on environmental (Kulathunga et al., 2019; M Pry et al., 2021a), genetic (Friedman & Luyckx, 2019), occupational and socio-economic (M Pry et al., 2021b; Nanayakkara et al., 2020; Premadasa et al., 2020) disciplines to discover the possible risk factor of CKDu. Unfortunately, none of the risk factor alone could logically explain the coexistence of the disease. Later, it was suggested that the cause may be multifactorial in origin ((S. Imbulana & Oguma, 2021; Sandanayake et al., 2023), it needs to be established by unveiling the main possible component of the risk factors.

Since CKDu is linked with tubulointerstitial damage, and disease prevalent pattern coexist with the areas where groundwater is the main drinking water source, it is generally suspected that groundwater is an important risk factor for CKDu (Balasooriya et al., 2021; Vlahos et al., 2019).

The dry zone comprises all geographic hotspots of CKDu (Figure 1) and it suffers prolonged dry periods and limited rainfall (S. Imbulana & Oguma, 2021). Available water resources in these areas started stressing because of the increasing population and agricultural activities. Thus, to fulfil the requirement, exploitation of groundwater began in the 1980s (Panabokke & Perera, 2005). Over the last four decades, more than 98% of the population in the CKDu endemic areas solely adapted to the use of groundwater to fulfill their potable water requirement. The problem of CKDu began a few years after the adaptation to the groundwater (Edirisinghe et al., 2017; Pathmarajah, 2007). Interestingly, very low (1.5%) or zero prevalence of CKDu was reported in the people who consumed water from natural springs, rain water, surface water and treated water within the endemic area, (HM et al., 2016; JM et al., 2013; S et al., 2017) sedimentary limestone formation and the wet zone of Sri Lanka (Edirisinghe et al., 2017; Wimalawansa, 2015; Chandrajith & Nanayakkara, 2011). All these evidences implied that the close association of CKDu with the consumption of untreated groundwater (Imbulana & Oguma, 2021). Therefore, groundwater quality-based risk factors are important to hypothesize.

This paper aims to differentiate the water quality parameters which are in excess amount present in the CKDu endemic, non-endemic and control areas, to identify their evolution mechanism and coupled effects that trigger the nephrotoxicity to damage the kidney of the people in the CKDu endemic area.

2. Climatological, Geological, and Hydrological Setting of Sri Lanka

Climatically, Sri Lanka is a sub-tropical humid Island with three well-distinguished climatic zones namely, Wet Zone, Dry Zone, and Intermediate Zone (Figure 1). The Wet Zone receives annual rainfall from 2280 to 5100 mm while Intermediate Zone receives an annual average of 1700 mm. The Dry Zone occupies the Northern, Eastern, and South Eastern parts of the Island and receives an annual average of 1000 mm rainfall that comes with Northeast monsoon and convectional rains in 2nd inter-monsoon (Edirisinghe et al., 2017; Jayasena et al., 2008). The lowest precipitation, around 900 mm per annum is recorded on Mannar Island (Xu et al., 2021).

Geologically nine-tenth of Sri Lanka is made up of highly crystalline amphibolite to granulite grade metamorphic rocks of Precambrian age. The rest of the Island, mainly the North-Western coastal zone is covered by sedimentary sequences that belong to the Jurassic, Miocene, and Holocene periods (Figure 1). 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 Wannai Complex (WC) (P. G. Cooray, 1994).

Surface water resources in Sri Lanka are highly influenced by topographical characteristics and regional climatic patterns. The island with 103 river basins and enjoyed more than 30,000 freshwater reservoirs to regulate seasonal runoff (*Water Scarcity Variations Within a Country: A Case Study of Sri Lanka - Upali Ananda Amarasinghe, Lal Mutuwatta, R. Sakthivadivel - Google Books, n.d.*).

Annual run-off generation is estimated to be about five million ha m with a runoff ratio of 0.4 and it is estimated that 65% of the runoff escapes into the sea as stream runoff. Groundwater replenishment and evapotranspiration from the runoff are estimated to be 20% and 40% respectively (Gangadhara & Jayasena, 1999).

The Island comprises six types of groundwater aquifers and their position and distribution depend on the geomorphology of the country. Deep confined aquifers in the North-Western sedimentary formations, which extend from Puttalam to Jaffna Peninsula are the largest and least utilized aquifer system in the country compared to its proven potential (Panabokke, 2007). Average annual evaporation exceeds the average annual rainfall resulting in a soil moisture deficit during the dry period in this coastal zone (Panabokke & Perera, 2005). Highly fractured, highly faulted, and separated seven groundwater basins occur and out of these seven, four basins are considered as semi-confined (Panabokke, 2007; Priyadarshane et al., 2022).

The unweathered crystalline formation is relatively non-porous and impervious, and water circulation is mainly along the joint, fissures, and the planes of foliation. There are separate pockets of groundwater with distinct water tables. Some productive wells occur in deep fracture zone aquifers in the rocks which are connected to regional lineaments with heavy fracturing and jointing at depths beyond 30 up to 100 m. However, groundwater potential is limited in hard rock aquifers due to the low storage capacity and low transmissivity (Harris, 1991; Panabokke, 2007).

3. Materials and Methods

3.1. Study Area

Two main drainage basins namely, Malwathu Oya (Aruvi Aru) and Malala Oya Basins (Figure 01) in Sri Lanka were selected for the present study. Within the Malwathu Oya basin there have CKDu endemic and non-endemic area with different geological conditions. Malala oya basin area is considered as control area. The purpose of selecting the particular three areas are because the Magnitude of the prevalence of CKDu shows a distinct difference while they possess some different geological, hydrological and climatological conditions. Thus, the two basins provide a platform to compare and contrast these conditions and there with the prevalence and non-prevalence of CKDu, giving due consideration to the quality of potable water in the two basins.

Malwathu Oya is the second largest river in Sri Lanka with a total length of 164 km and a watershed area of 3246 km². It started from the North Central Province and merges into the sea at Mannar Bay on the Northwest coast. Geologically upper part of the basin is covered with metamorphic crystalline rocks with granitic gneiss, charnockitic gneiss, and garnet biotite gneiss (P.

G. Cooray, 1994). The soil thickness is 5-12 m, which is mainly the red-brown soil covered on the weathering crust of the rock. In addition, Miocene limestone, alluvial/lagoon sediment clay, silt, beach sand, and dunes are distributed in the sedimentary formation of the lower basin, and saline-alkaline soil is also distributed along the lower bank of the Malwathu Oya watershed. The aquifer system in the hard rock area comprises shallow regolith aquifers underlain by deep fracture zone aquifers, while sedimentary formation with the confined and semi-confined deep aquifers (Panabokke, 2007). The upper catchment area and the lower catchment area receive an average annual rainfall of 1750 mm and 900 mm respectively (Xu et al., 2021). Rainfall is restricted to a few months and a mostly dry and humid climate prevails throughout the year (Liyanage et al., 2022). The average temperature of the basin area is ranging from 30 to 33°C. Chronic Kidney Disease of unknown etiology (CKDu) is spreading in the middle part of the basin relative to the upstream and downstream.

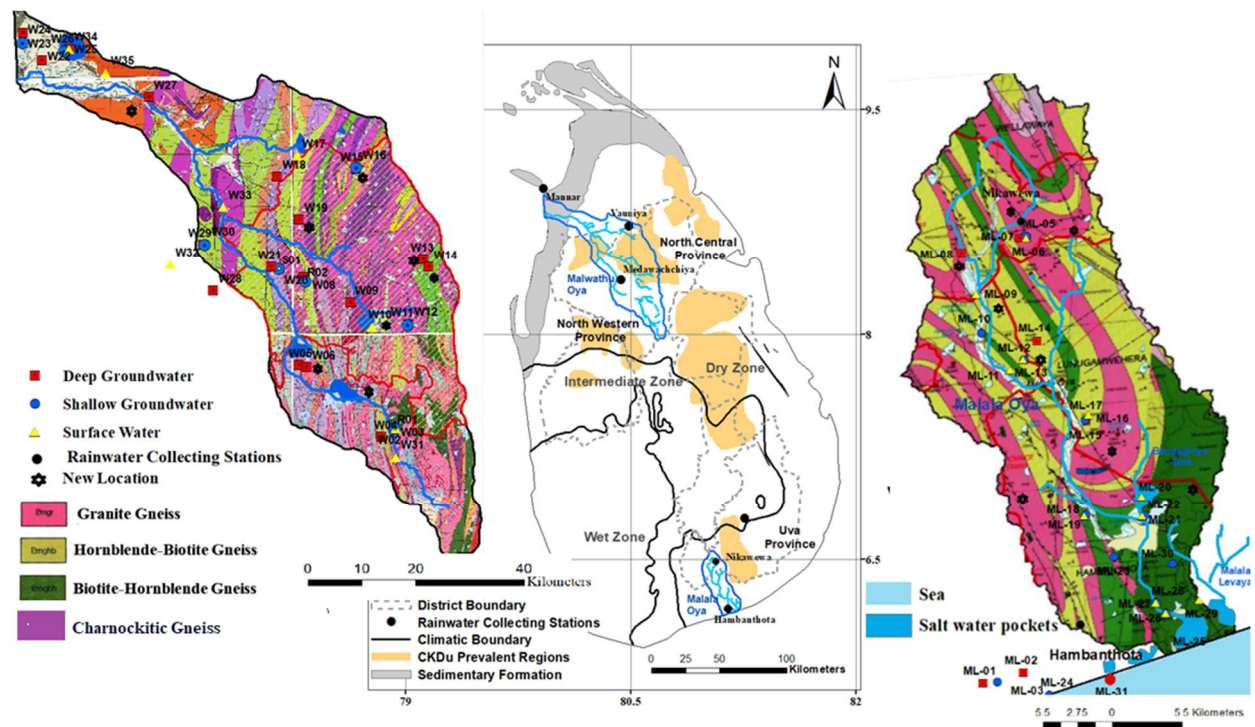


Figure 1. Maps showing sampling locations in the CKDu endemic, non-endemic and the control area.

Malala Oya river basin flows through the Southern Dry Zone and the basin extends up to 405 km². The entire river flows in a high-grade metamorphic basement complex that mainly comprises granitic gneisses, biotite-hornblende gneisses, and scattered bands of charnockitic gneisses (P. G. Cooray, 1994). This area is characterized by a nine-month-long dry period, followed by heavy precipitation during the year (November to February) and annual groundwater recharge is estimated as 41 MCM from the total precipitation (Senarathne et al., 2019). Low precipitation and higher evaporation have resulted a limited surface water availability. And it has led to the utilization of a significant amount of groundwater as the main source particularly for the industrialized zone in the area.

However, the annual extraction of groundwater from this basin is 0.13 MCM which is 3.42% of the total demand (K. A. U. S. Imbulana et al., 2002).

The principal groundwater reservoir is the weathered overburden (regolith) within which all domestic water supply wells have been constructed. Due to the variable thickness of the regolith and undulating terrain conditions groundwater does not occur as a continuous body but as several independent and semi-connected cells (P. G. Cooray, 1994; Panabokke, 2007). The depth to the groundwater table too is highly variable spatially and fluctuates from a depth of a couple of meters

in the rainy season to about more than 10m below ground during droughts. A considerable number of wells even become dry. Groundwater recharge takes place mainly from infiltration of rainwater within the basin and possibly to a lesser degree through the limited number of tectonically developed fracture/fault zones in the bedrock. A considerable number of water supply boreholes, often fitted with hand pumps are also present in both basins. These boreholes, which are about 40m deep on average penetrate the regolith and the underlying crystalline rock and often tap water from such fracture zones. Groundwater in these fracture zones too has a hydraulic connection with the water in the regolith at a distance or right at the well location.

On the contrary to the Malala Oya basin, there are thousands of small surface water reservoirs, to irrigate rice fields, are situated in the Malwathu Oya basin. These widespread small surface water bodies while providing surface water to rice fields also make a good contribution to the groundwater recharge in the basin. This condition does not prevail in the Malala Oya basin where only less than 20 such small reservoirs are present.

This situation can lead to two significant differences in the groundwater surface water interactions, mobilization of ionic species in groundwater. In addition, evaporation and concentration of salts in water in small tanks during prolonged droughts can infiltrate and enrich groundwater locally making complex and heterogeneous hydrochemical environments.

Further, the compositional differences in the rocks and soils of the two basins can lead to distinct differences in rock, soil-water interactions, and resulting chemical quality of the groundwater.

3.2. Sample Collection and Analysis

A total of Thirty-three water samples including 8 surface water (SW), 9 shallow groundwater (SGW: well depth <10m), and 16 deep groundwater (DGW: well depth 10-200m) from Malwathu Oya Basin and 30 water samples including 11 surface water, 12 shallow groundwater, and 7 deep groundwater from Malala Oya were collected to represent samples in CKDu endemic, non-endemic and control areas respectively (Figure 1). Two sessions of sampling were completed in each basin representing the dry and wet seasons.

Field data including coordinate, altitude, sample type, well depth, well diameter, static water level, piezo metric head, and geology were recorded. pH, electrical conductivity (EC), salinity, total dissolved solids (TDS), dissolved oxygen (DO), and temperature (T) were measured onsite with the standard deviations of ± 0.1 , $\pm 0.5\%$, $\pm 1\%$, $\pm 0.5\%$, ± 0.1 mg/L and ± 0.3 °C respectively using calibrated HACH HQ 40d multi PHC 30101 instrument connected with CDC 40101 and LDO 101 probes. Also, nitrate nitrite (NO_2^-) and ammonium (NH_4^+) were measured on-site using the HACH HQ 40d multi-parameter instrument. Total alkalinity was measured using the potentiometric titration method: APHA 2320B on-site (*Standard Methods for the Examination of Water and Wastewater- 22nd Edition*. APHA - Google Search, n.d.)

All the water samples were collected into pre-cleaned, double-capped high-density polyethylene (HDPE) bottles. Unfiltered 30 ml and 1000 ml samples were collected for stable water isotope ($\delta^{18}\text{O}$, $\delta^2\text{H}$) analysis, tritium (^3H) analysis, and DIC14-C analysis respectively. Filtered, non-acidified 200 ml of sample were collected for cation and anion analysis. Filtered and ultrapure HNO_3 (1% v/v) added 200 ml samples were collected for trace element analysis. All water sample bottles were sealed with parafilm to prevent them from evaporation and leakage. During the sample collection, pumping was carried out for 10 min by deep tube wells while shallow dug well samples were obtained from 1 m below the standing water level using a horizontal depth water sampler.

EDTA titrimetric method: APHA 2340B was used to calculate total hardness (*Standard Methods for the Examination of Water and Wastewater- 22nd Edition*. APHA - Google Search, n.d.). The HCO_3^- concentration was calculated based on the equation of $[\text{HCO}_3^-] = 1.22 \times (\text{Total Alkalinity/mg/L})$ (Indika et al., 2023). The anions (Cl^- , F^- , Br^- , NO_3^- and SO_4^{2-}) were analyzed at the Beijing Research Institute of Uranium Geology (BRIUG) by the Ion Chromatograph (Dionex DX-500, Poway, CA, USA) with a detection limit of 0.05 mg/L. Major cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and trace elements were determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS NexION300D, PerkinElmer, Inc., Shelton, CT, USA) at the same laboratory with an analytical precision of 0.5%.

Stable Isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of the water samples were analyzed using a liquid water isotope laser analyzer (Picarro L2130-i, Picarro, Inc., Santa Clara, CA, USA) in the BRIUG and (LGR DLT-100,

USA) in the Isotope Hydrology Section, Sri Lanka Atomic Energy Board (IHS-SLAEB). Water isotope results are reported in the delta notation (δ) versus Vienna Standard Mean Ocean Water - 2 (VSMOW-2) standards and expressed in per-mill (‰) notation. Samples were analyzed in duplicate and the precision of the measurement was within $\pm 0.1\text{‰}$ for $\delta^2\text{H}$ and $\pm 0.025\text{‰}$ for $\delta^{18}\text{O}$ in the Picarro L2130-i and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for $\delta^2\text{H}$ in the LGR DLT-100. The local meteoric water line and evaporation lines established for the North Central dry zone and Hambanthota of Sri Lanka (E. A. N. V. Edirisinghe, Pitawala, et al., 2017; Senarathne et al., 2019) were used to interpret the isotope results of Malwathu Oya and Malala Oya basin areas.

The mixing proportion of surface water into the groundwater system of these two basins was calculated using the mass balance equation defined with non-reactive geochemical tracers of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ (Barth & Veizer, 2004).

$$X = (\delta_{\text{GW}} - \delta_{\text{RW}}) / (\delta_{\text{SW}} - \delta_{\text{RW}}) * 100$$

where X = proportion of percolated surface water; δ_{GW} = isotope composition of the groundwater sample; δ_{RW} = average isotopic composition of rainwater in the recharge area; δ_{SW} = average isotopic composition of the surface water in the relevant basin. This equation was tested for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and yielded the same results within a range of $\pm 5\%$.

Water samples collected from the CKDu endemic area were electrolytically enriched and Tritium concentration was measured using Liquid Scintillation Analyzer (Packard; TRI-CARB 3170TR/SL, Shelton, CT, USA) at SLAEB. Its concentration is expressed as a Tritium Unit (TU) with a minimum detection limit of 0.3 TU. Radiocarbon dating of the seven selected deep groundwater samples was analyzed using Atomic Mass Spectrometer (AMS) at the Beta Analytic Testing Laboratory, Miami, USA relative to NIST SRM-4990C. Carbon isotopes ($\delta^{13}\text{C}$) of the same samples were measured using gas-bench IRMS relative to VPDB.

4. Results and Discussion

The water samples collected during this study include surface water (mainly from tanks and rivers), shallow groundwater, and deep groundwater. Surface water sources, both tanks and rivers become dry during the dry season and some stagnated water pockets can be seen along the river and even in the larger tanks. However, water levels become full supply levels or flooding during the wet season. Shallow groundwater is buried in a depth of around 10m and is mainly stored in the weathered overburden. The depth of shallow dug wells in the study area are generally 3 to 10m and the water level fluctuation is around 1 to 4m during the dry and wet seasons. Deep groundwater in the study area is mainly through the 30 to 60 m deep fractures and fishers of the basement rock in the metamorphic region while 20 to 200m deep confined to semi-confined limestone aquifers in the sedimentary terrain.

4.1. Groundwater Chemistry

Summary of the hydrogeochemical data of CKDu endemic and non-endemic areas of Malwathu (MO) and CKDu control Malala Oya (ML) basins are shown in table 1.

The pH of the water in both shallow and deep groundwaters in the CKDu endemic, non-endemic and control areas during the wet and dry seasons are within the WHO and SLS maximum permissible limit of 6.5 to 8.5. Slightly alkaline condition is prominent in the groundwater in the surface waters of CKDu endemic area.

The TDS in groundwater is a direct indicator of to identify the rock-water interaction, mineral dissolution, and evaporation effect in the groundwater system (Indika et al., 2023). The average TDS content of all waters except for surface waters during both seasons exceeded the SLS desirable level of 500 mg/L. The surface water with very low TDS suggests that these waters may regularly mix with surface runoff or infiltrated rainwater (Balasooriya et al., 2021). Shallow groundwater has comparatively higher TDS than deep groundwater and sedimentary rock area than metamorphic rock area. According to the TDS classification, groundwater in the crystalline formation are of poor quality (900 to 1200 mg/L), and the sedimentary formation with unfavorable condition (Chabuk et al., 2021). Shallow groundwater with a high content of TDS may be due to the high rate of evaporation and/or mineral dissolution from the unsaturated zone. However, shallow and deep-water wells close

to the coastal area with high TDS ($>1000\text{mg/L}$) may be due to the mixing of a small amount of saline water, sea spray, or dissolution of buried alluvial material in this area.

The hardness of water is caused mainly due to the presence of alkaline earth elements calcium (Ca) and magnesium (Mg) together with carbonate, bicarbonate, sulfate, and chloride anions (Dissanayake & Weerasooriya, 1986) and it is the most important factors suggested for the etiology of CKDu. The total hardness of groundwater collected in both seasons in the CKDu endemic area is higher than in the CKDu non-endemic and control area. Also, total hardness in the dry season is comparatively higher than in the wet season. Based on the WHO guidelines, water can be classified into four categories according to their hardness level as follows: soft water at CaCO_3 hardness $< 60\text{ mg/L}$, moderately hard water at $60\text{--}120\text{ mg/L}$, hard water at $120\text{--}180\text{ mg/L}$, and very hard water at $> 180\text{ mg/L}$. Almost all the collected water from the dry season with the hardness exceeded the WHO desirable level of 300 mg/L . However, the hardness of all surface and groundwater samples is below the value of 300 mg/L in the wet season with few exceptions. Shallow groundwater is always subjected to a higher rate of evaporation and intensified rock weathering under the tropical climatic conditions, added excess amount of Ca^{2+} and Mg^{2+} into the groundwater system which leads the higher total hardness in the CKDu endemic area. Deep groundwater with more or less similar hardness and TDS values in both seasons indicate that these waters are not affected by immediate recharge and it controlled only by the dissolution of the aquifer matrix.

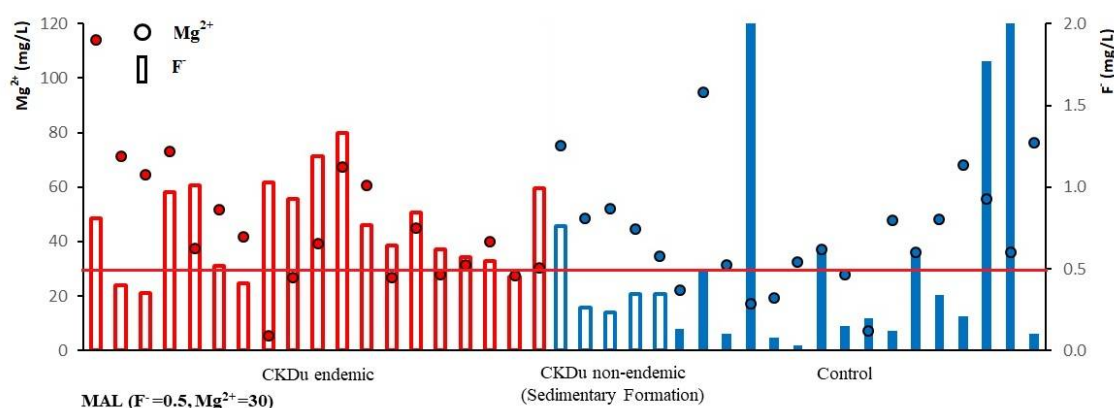


Figure 2. The plot showing the F^- and Mg^{2+} variation of groundwater during the dry season .

Among the studied geochemical parameters, fluoride is one of the major geogenic constituents in drinking water and excessive intake can cause serious health issues (Dissanayake & Chandrajith, 2017). Nearly 60% of absorbed total fluoride per day is filtered and excreted via urine, hence kidneys are one of the target organs for fluoride accumulation. Long-term fluoride exposure can enhance renal damage and it has been suggested as a possible causative factor for the etiology of CKDu (Balasooriya et al., 2021). Rocks are the main source of groundwater fluoride and it leached from common rock-forming minerals such as apatite, mica, sphene, fluorite, hornblende, amphibole, and pyroxene with high F⁻ content (Ranasinghe et al., 2019; R et al., 2011). F^- concentration of deep groundwater taken in both CKDu endemic and control areas are from underlying metamorphic rocks such as biotite gneiss, granites, and charnockitic gneiss. However, carbonate rocks produce less amount of fluoride and its concentration is quite low in the sedimentary formation ($< 0.5\text{ mg/L}$).

Results of the present study show that fluoride content of the shallow and deep groundwater in the CKDu endemic area varied from 0.3 to 1.6 mg/L and 0.4 to 1.3 mg/L in the dry season and 0.3 to 2.2 mg/L and 0.2 to 2.7 mg/L in the wet season respectively. The fluoride content of the shallow and deep groundwater of the control area varied from < 0.2 to 2.1 mg/L and < 0.2 to 5.9 mg/L in the dry season and 0.2 to 5.8 mg/L and 1.5 to 7.8 mg/L in the wet season respectively. More than 80% of the samples collected during both seasons of the CKDu endemic area exceeded the maximum permissible limit ($> 0.5\text{ mg/L}$) established by WHO. Interestingly, 20% and more than 75% of the water samples collected in the control areas exceeded that limit during the dry and wet seasons respectively.

The results imply that the CKDu endemic area with higher groundwater fluoride than the non-endemic and control area and the wet season shows elevated levels than in the dry seasons. This difference in the F⁻ concentration of groundwater may be due to the presence of various mineral components in the aquifer rocks and their F⁻ dissolution capability. In addition to that, long residence time leaves deep groundwater to interact with F⁻-bearing minerals and lead to the accumulation of dissolved F⁻.

Furthermore, evaporation under dry climatic conditions causes the enrichment of groundwater F⁻ (Balasooriya et al., 2021; Chandrajith et al., 2020; R et al., 2011). Usually, the components in shallow groundwater are likely to be diluted due to mixing with infiltrated rainwater in the wet season while concentrated due to the high evaporation in the dry season. However, F⁻ content in deep groundwater in the CKDu endemic area and both shallow and deep groundwater in the control area showed an opposite phenomenon. This implies the high fluoride concentration in the wet season may not controlled by the individual factor. According to (Saxena & Ahmed, 2001; Su et al., 2013), chemical properties of groundwater such as weakly alkaline pH condition (7.2 to 8.2), moderate TDS, and dominant ions of HCO₃⁻ and Na⁺ are the favorable conditions for the enhancement of groundwater F⁻. These may suggest that the geochemical cycling of F⁻ in groundwater could be highly influenced by the combined effect of the underground geology, hydrodynamic, and geochemical nature of the aquifer system. The fluoride geochemistry and its fate in groundwater in the CKDu endemic and control area are further discussed in section 3.5.

Many previous studies identified the presence of Calcium (Ca²⁺), magnesium (Mg²⁺), and sodium (Na⁺) in drinking water are important parameter, and the dominance of these ions in the water control the onset of CKDu (Balasooriya et al., 2021; Dharma-wardana, 2018; Liyanage et al., 2022). However, the Mg²⁺ concentration of the both shallow and deep groundwater in both CKDu endemic and non-endemic areas and deep groundwater in the control area exceeded the Maximum Allowable Limit (MAL) of Mg²⁺ (30 mg/L). None of the water samples collected during the dry season exceeded the limit of Ca²⁺ while two samples from the CKDu endemic area and one sample from the control area collected after the wet season exceeded the MAL of Ca²⁺ (100 mg/L).

Table 1. Summary of the hydro geochemical data of water samples in the Malwathu and Malala Oya basins.

Water Type	pH		TDS		TA		TH		Na ⁺		Ca ²⁺		Mg ²⁺		SO ₄ ²⁻		Cl ⁻		NO ₃ ⁻		F ⁻		
			(mg/L)		(mg/L as CaCO ₃)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		(mg/L)		
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	
Malwathu Oya Basin (CKDu endemic area)																							
Surface Water	Min	7.4	7.4	304	200	176	136	200	163	68	35.4	28.	15.5	26.5	9.7	2.5	0	94.5	29.7	<0.008	0.1	0.26	0.3
	Max	9.1	8.9	427	501	200	321	200	264	103	99	35	52.8	30.6	30.3	7.5	18	163	95.7	3.6	0.6	0.34	1.2
	Avg	8.3	8	366	338	188	209	200	209	85	63.4	31.7	28.6	28.6	18.5	5	7.4	129	57.3	1.8	0.3	0.30	0.7
Crystalline Terrain																							
Shallow GW	Min	7	6.8	366	215	160	189	208	154	36.4	29.6	45.9	38.5	37.6	7.7	11.8	2	43.4	23.9	<0.008	0.2	0.35	0.3
	Max	7.7	8.3	1032	1394	448	537	820	950	148	192	128	427	114	107	52.3	142	390	728	15.4	1.8	1.6	2.2
	Avg	7.4	7.7	744	792	301	414	553	453	87.5	88.9	68.4	135	72.6	50.4	29.9	57.3	217	226	4.5	0.9	0.8	0.9
Deep GW	Min	6.6	6.7	102	107	104	88.2	68	70.4	28.5	21.8	12.7	0.4	5.4	3.4	7.8	6	7.2	3.9	<0.008	<0.008	0.4	0.2
	Max	7.4	8.5	663	729	456	473	616	295	157	167	58	88.8	67	50.2	36.6	49	152	153	27.6	8.5	1.3	2.7
	Avg	7	7.5	423	425	266	322	305	201	79	72.6	45	35.8	36	21.4	21.3	25.8	77	60	5.5	1.8	0.8	0.9
Sedimentary Terrain (CKDu non-endemic area)																							
Shallow GW	Min	7.7	7.7	904	912	288	393	380	44	239	340	57.8	7.2	48.5	3.6	55	62	378	445	<0.008	0.6	0.3	0.5
	Max	8.1	8.6	2570	1289	520	453	420	290	987	590	71	94.4	75	23.6	220	136	1246	484	<0.008	1.5	0.8	1.7

	Avg	7.9	8.1	1737	1102	404	423	400	167	613	465	64.4	50.8	61.8	13.6	138	99	812	465	-	1.1	0.5	1.1
Deep GW	Min	7.3	7.6	531	530	232	305	204	89.2	117	114	52.9	49.6	34.4	15.6	25.9	29	171	129	<0.008	0.4	0.2	0.3
	Max	7.5	7.7	1290	1294	360	373	336	317	425	360	78.8	70.8	51.9	35.4	89.4	132	578	380	<0.008	1.1	0.3	0.6
	Avg	7.4	7.7	925	928	296	329	276	225	264	237	66	60.9	43.6	25.3	56.2	76.7	376	275	-	0.9	0.3	0.4
Malala Oya Basin (CKDu control area)																							
Surface Water	Min	7.2	6.95	177	130	74	3.36	112	52	25	24	1.0	18	0.4	10	<0.2	7	<0.2	16	<0.2	<0.2	<0.2	0.4
	Max	8.2	9.19	952	1810	195	1831	716	668	305	303	52.7	119	44.7	102	125.1	151	375	705	506.5	27.6	0.6	3.1
Water Avg		7.7	7.87	470	628	126	850	250	261	139	127	28.3	38	23.2	31	44.7	44	138	177	106.6	4.8	0.1	1.1
Shallow GW	Min	6.7	7.09	257	143	90	3.19	136	132	26	22	17.5	14	7.0	4	25.9	8	27.4	20	<0.2	<0.2	<0.2	0.2
	Max	7.8	8.38	2310	2530	527	1270	872	980	968	970	69.2	129	94.8	117	312.4	450	1008	992	6.3	26.4	2.1	5.8
	Avg	7.6	7.84	786	851	210	625	381	338	237	304	37.2	50	33.8	48	112.2	132	262.9	330	2.0	8.6	0.4	2.3
Deep GW	Min	6.8	7.14	655	493	187	435	268	220	100	149	12.1	10	35.9	29	34.1	41	137.2	32	<0.2	1.7	<0.2	1.5
	Max	7.9	7.64	1354	1166	357	1000	728	748	324	350	84.8	71	76.3	74	169	155	497	363	15.7	138.7	5.9	7.8
	Avg	7.3	7.39	901	863	252	620	443	513	187	260	48.0	36	53.4	50	101.6	83	230	205	5.9	18.4	1.5	3.7
Maximum Permissible Limits																							
SLS		6.5-8.5		500		200		250		200		100		30		250		250		50		1.0	
WHO		6.5-8.5		600		500		300		200		100		30		250		250		50		1.5	

4.2. TA, Total Alkalinity; TDS, Total Dissolved Solids; TH, Total Hardness

Na⁺ concentration of the groundwater collected from the CKDu control area exceeded the MAL of Na⁺ (200 mg/L) in both seasons. The ratio between Ca²⁺ and Mg²⁺ can be applied to identify their source as well as Na⁺/Ca²⁺ ratio can be used to compare their activities(Dissanayake & Chandrajith, 2017; Kumar & Singh, 2015; Liyanage et al., 2022). The calculated Na/Ca ratio of groundwater collected in the dry season varied from 0.5 to 3.1 in the CKDu endemic area and 0.4 to 44.1 in the control area. However, the similar ratio in the wet season varied from 0.4 to 5.9 in the CKDu endemic area while 0.5 to 59.2 in the control area.

Nitrate is one of the major constituents in freshwater and their concentration is mostly controlled by anthropogenic factors rather than natural factors (Vaheesar, n.d.). Almost all the water samples collected from the CKDu endemic area during both seasons had lower nitrate levels compared to the drinking water quality standards (50 mg/L) given by WHO. NO₃⁻ concentration of surface and groundwater ranged from 0.1 to 3.6 mg/L and 0.1 to 27.6 mg/L in the dry season while 0.1 to 0.6 mg/L and 0.2 to 8.5 mg/L in the wet season respectively. Undetectable amount of NO₃⁻ presence in the all water types of the CKDu non-endemic area. However, three surface water samples collected from the CKDu control area in both seasons with unacceptable levels of nitrate (up to 120 mg/L) may probably be due to its addition from intense agricultural activities.

Potential nephrotoxic effects of environmental exposure to heavy metals and metalloids, mainly As, Cd, Pb, and Cr have been identified as a causative factor for CKDu (Jayasumana et al., 2014; Kulathunga et al., 2019; Wimalawansa, 2015). These metals in groundwater may be derived from rock weathering or by the use of agrochemicals (Jayasumana et al., 2014; Xu et al., 2021). Measured heavy metal concentration except for As of the water from all three area well below the MALs. However, the average Arsenic (As) concentration of surface water, shallow and deep groundwater in the control area are exceeded the standard limits of 10 µg/L and reported as 42.7 mg/L, 28.7 mg/L, and 17.1 mg/L respectively. These high As, content may be derived from the heavily used chemical fertilizers of that area.

All measured surface water parameters in both CKDu endemic, non-endemic and control areas are well below their MALs.

Considering the combined ionic ratios, the excess F⁻ and Mg²⁺ ions are presence in the groundwater samples in the CKDu endemic area in the Malwathu Oya basin, but F⁻ is relatively low in the lower part of the basin where sedimentary formation with non-prevalence of CKDu. In the control area there are three different types of waters showing low F⁻ and low Mg²⁺, high F⁻ and low Mg²⁺ or low F⁻ with high Mg²⁺ (Figure 2). Chandrajith et al., 2017 explained either low F⁻ with high Mg²⁺ or high Mg²⁺ with low F⁻ has an inhibitory effect on CKDu. According to the generated results, combined effect of high F⁻ and high Mg²⁺ may be the possible causative factor for the CKDu.

To consider the spatiotemporal variation of measured water quality parameters exceeded the MAL in CKDu endemic, non-endemic and control areas TDS, and Na^+ concentrations are higher in the CKDu non-endemic and control areas while total hardness, F^- and Mg^{2+} concentrations are higher in the CKDu endemic area. The concentration of the water quality parameters in the CKDu endemic area is higher in the dry season than wet season while shallow groundwater is higher than deep groundwater. However, the same ion concentrations in the control area are higher in the wet season than dry season while deep groundwater than shallow groundwater. Ionic concentration of the shallow groundwater in the both basins are increases towards downstream. However, there is no significant spatial variation can be identified in the deep groundwater except for F^- in the control area. High F^- spot during the dry season probably from geogenic origin.

4.3. Hydrogeochemical Evolution of Groundwater

Distinct geological, hydrological and climatic conditions must play an important role in the geochemistry of CKDu causative factors (Chandrajith et al., 2020). Depending on the geological, hydrological, and climatological conditions, the groundwater type of the area may differ.

The Piper trilinear diagrams are widely used for the geochemical classification of groundwater (Figure 03). Groundwater in the CKDu endemic area mostly consists of Ca^{2+} , Mg^{2+} , and HCO_3^- ions, and the Ca-HCO_3 type is predominant. Chemical results revealed that Mg is dominant in the dry season while Ca is dominant in the wet season of the shallow groundwater. That may be due to the dissolution of carbonate and silicate minerals in the wet season and the reduction of Ca ions by the ion exchange process during the dry season.

In CKDu non-endemic and control region has predominantly Na-Cl , Ca-Mg-Cl , and Ca-Na-HCO_3 together with Na^+ , K^+ , and Ca^{2+} as dominant cation and HCO_3^- and Cl^- as dominant anions. Hydrochemical facies of Na-Cl may have a link to seawater mixing and/or cation exchange (Priyadarshane et al., 2022). Ca-Mg-Cl and Ca-Na-HCO_3 water types in the CKDu control area suggest a significant contribution to the weathering of mica, amphibolite, and pyroxene in the high-grade metamorphic rocks in the evolution of groundwater type in that basin area.

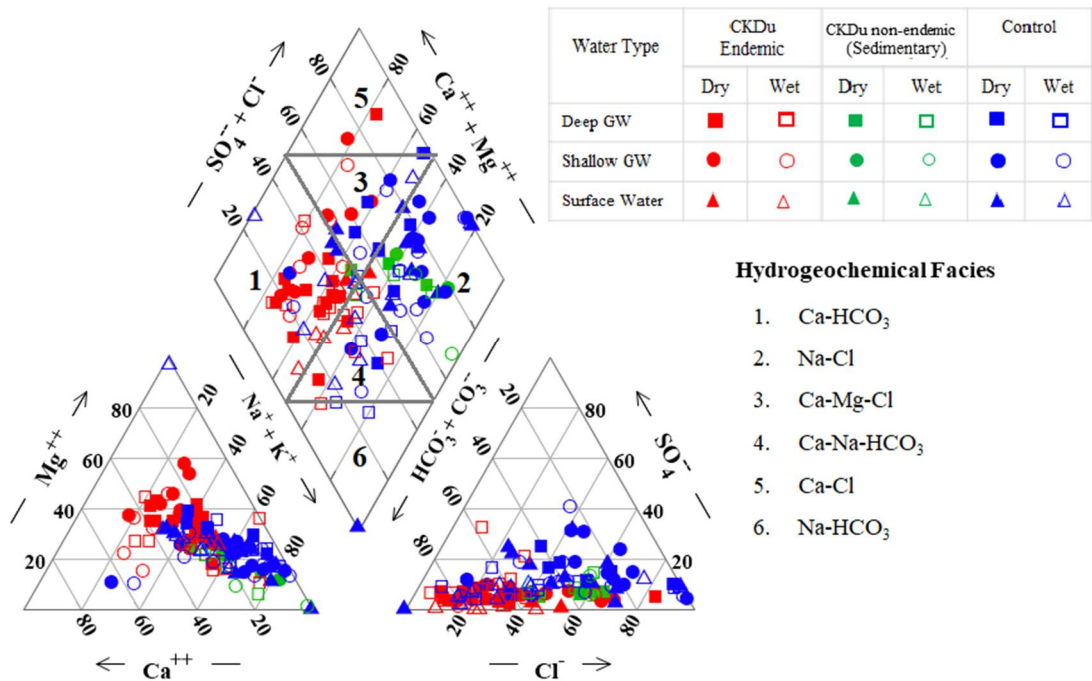


Figure 3. A piper trilinear plot illustrating the hydro-geochemical facies of groundwater during the wet and dry seasons.

Gibb's plot (Gibbs, 1970) is widely used to describe the source of dissolved chemical constituents in groundwater contributing from rock-weathering, evaporation-crystallization, and atmospheric precipitation. Evaporation-dominant waters generally occur in arid (high temperature) or coastal

zones and this is due to the evaporation-fractional crystallization process causing rich, intermediate salinity to Na-rich, high salinity waters (Gibbs, 1970; Krishna kumar et al., 2015). Groundwater collected in both seasons of the CKDu endemic, non-endemic as well as the control area fall in the transition zone of rock weathering dominance and evaporation concentration fields indicating the influence of different degree of water-rock interaction and evaporation concentration (Figure 04). However, the contribution rate of evaporation concentration to shallow groundwater is higher than that of deep groundwater in the CKDu endemic area. Rock-dominance component is higher in the deep groundwater samples and a lower $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio specifies the dominance of carbonate minerals in the CKDu endemic area whereas a higher value represents the dominance of silicate minerals/sea water mixing in the non-endemic and control area.

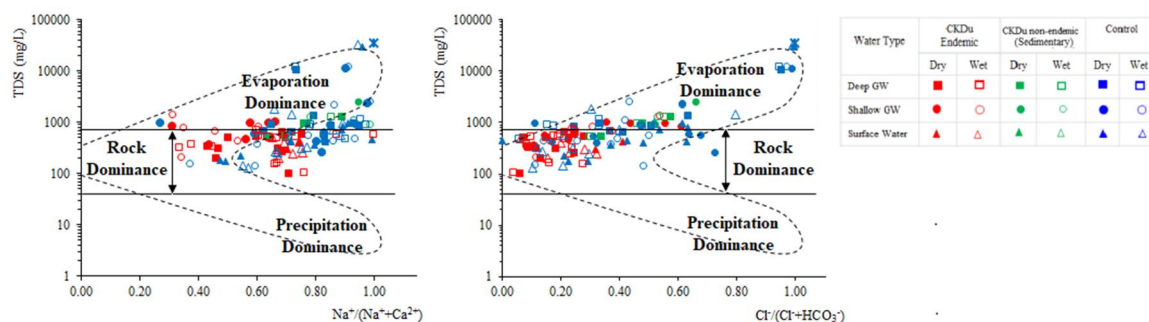


Figure 4. Gibb's plot illustrating the hydro-chemical facies of groundwater during the wet and dry season.

Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , and HCO_3^- are the major ions in the study area and are mainly influenced by rock weathering, evaporation crystallization and cation exchange. The relationships between major ions are generally used to identify the evolution of groundwater and its mixing mechanisms (Raja et al., 2021; Rubasinghe et al., 2015; Senarathne et al., 2019). Measured ion content shows that a significantly higher linear relationship among each other in the dry season because of the higher rock-water interaction in the dry season (Figure 5). On the other hand, the linearity of the relationship was scattered in the wet season because of the dilution effect. The molar ratio of $\text{Na}^+ / \text{Cl}^-$ is widely used to evaluate silicate weathering, seawater intrusion, halite dissolution, and ion exchange processes (Rubasinghe et al., 2015). Groundwater samples collected from the non-endemic sedimentary formation of the MO area and two samples collected in the control area near the coast were scattered along a 1:1 line of $\text{Na}^+ / \text{Cl}^-$ indicating that this groundwater chemistry is based on seawater mixing (Figure 5a). The $\text{Na}^+ / \text{Cl}^-$ ratio greater than 1 represents silicate mineral weathering (Senarathne et al., 2019) which is common in the CKDu control area. Similarly, this ratio greater than 1.5 indicates the additional source contributing to the dissolved Na^+ , which is potentially due to the weathering of Na-bearing silicates, a dissolution of Na-bearing evaporites, and cation exchange between Ca^{2+} and Mg^{2+} in groundwater with Na^+ on the aquifer matrix (Lyu et al., 2019). This phenomenon is common in the wet season of the control area.

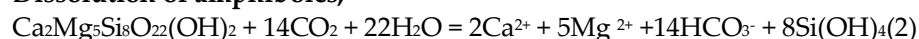
On the other hand, as shown in Figure 5b & c water samples collected from the CKDu endemic and non-endemic areas are located on the 1:1 line of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs HCO_3^- (meq/L) and $\text{Ca}^{2+} / \text{Mg}^{2+}$ ratio between 1 and 2 indicates the calcite dissolution process (Indika et al., 2023; Senarathne et al., 2019). Evaluation of the groundwater chemistry from the carbonate dissolution and silicate mineral weathering process can also be reconfirmed by the end-member diagrams (Figure 5d & e). However, Ca^{2+} , Mg^{2+} , and HCO_3^- in the control area is mainly affected by silicate weathering and evaporite dissolution.

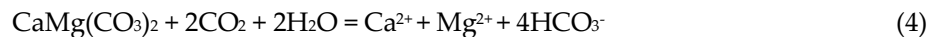
Evolution process of Ca^{2+} , Mg^{2+} , and HCO_3^- in the CKDu endemic and the control are as shown below;

Dissolution of pyroxenes:



Dissolution of amphiboles:



Dissolution of calcite and dolomites:

Cation exchange mainly occurs at the interface of groundwater and aquifer matrix, during which Ca^{2+} and Mg^{2+} in groundwater are adsorbed into aquifer material and Na^+ and K^+ are desorbed into groundwater. Groundwater containing HCO_3^- and SO_4^{2-} are from carbonate mineral dissolution and silicate weathering process, hence cation exchange is calculated by subtracting the equivalent concentration of HCO_3^- and SO_4^{2-} from Ca^{2+} and Mg^{2+} ($(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$). Na^+ and K^+ come from the desorption and it can be calculated by subtracting an equivalent concentration of Cl^- from $\text{Na}^+ + \text{K}^+$ ($(\text{Na}^+ + \text{K}^+) - \text{Cl}^-$) (Wei et al., 2016). Almost all groundwater samples collected from both seasons were plotted near the line with a slope of -1, indicating the presence of alternating cation adsorption in both CKDu endemic and control areas (Figure f). Water samples collected in the CKDu endemic area during both seasons were plotted around a 1:1 line in the fourth quadrant of the coordinates, suggesting that alternate cation adsorption exists, mainly in the form of Ca^{2+} release and Na^+ adsorption (Hu et al., 2023). However, the regression line between $((\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-}))$ and $((\text{Na}^+ + \text{K}^+) - \text{Cl}^-)$ in samples collected during the dry season had a slope of -1.1 which is slightly different from the wet season with the value of -0.8. In addition, the median value of $((\text{Na}^+ + \text{K}^+) - \text{Cl}^-)$ in samples collected from the dry season (1.05) is slightly higher than that of the wet season (1.02), meaning that the Ca^{2+} release into the groundwater during the wet season is higher than the dry season of CKDu endemic area (Area A: reverse ion exchange).



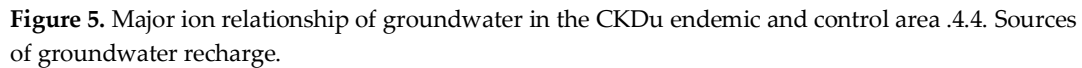
During this process, clay minerals absorb Na^+ from the water, and releasing Ca^{2+} or Mg^{2+} into the water may cause to increase in the hardness and Ca^{2+} or Mg^{2+} in water.

In contrast, samples collected from the wet season of the CKDu non-endemic and control areas are moving towards the first quadrant of the coordinates (median value changing from dry to wet season are 1.90 to 5.21 respectively), suggesting that the ion exchange happening in this groundwater system below (Area B).



During this process, the absorption of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in clay water and release of Na^+ into the groundwater happens and it causes to decrease of Mg^{2+} and/or Ca^{2+} in the water body.

All the findings mean that cation exchange in the CKDu control area is more evident than in the CKDu endemic area.



Minimum and maximum $\delta^{18}\text{O}$, $\delta^2\text{H}$, and d-excess values of collected water sources of the MO and ML in both wet and dry seasons are presented in Table 2. The relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is graphically illustrated in Figure 6 a, b & d, e. Also, the relationship of deuterium excess and TDS are represented in Figure 6 c & f.

Water Type	$\delta^{18}\text{O}$ (‰)				$\delta^2\text{H}$ (‰)				D-excess			
	Minimum		Maximum		Minimum		Maximum		Minimum		Maximum	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Malwathu Oya												
Surface Water	1.0	-3.3	2.5	-1.8	3.2	-25.0	12.2	-16.4	-14.8	-2.4	-5.1	1.8
Metamorphic Granite Area (CKDu endemic)												
Shallow Groundwater	-5.6	-5.6	-3.2	-2.7	-34.5	-35.2	-21.5	-19.1	2.1	1.0	9.9	9.8
Deep Groundwater	-5.9	-6.3	-4.6	-4.6	-36.8	-38.8	-29.6	29.0	6.0	8.9	10.7	11.9
Sedimentary Limestone Area (CKDu non-endemic)												

Shallow Groundwater	-2.2	-2.4	-2.0	-1.9	-15.8	-17.5	-14.4	-13.0	1.9	1.5	2.0	1.8
Deep Groundwater	-2.8	-2.4	-1.9	-2.0	-19.2	-17.3	-13.5	-13.7	1.3	1.8	2.9	2.2
Malala Oya (CKDu control)												
Surface Water	-1.0	-5.0	5.8	-1.0	-7.7	-30.2	19.8	-9.6	-26.8	-2.6	0.5	11.0
Shallow Groundwater	-3.9	-5.6	0.6	0.1	-29.2	-32.3	1.8	-7.1	-7.2	-8.1	6.9	12.4
Deep Groundwater	-5.0	-6.0	-2.3	-2.1	-34.8	-36.3	-14.7	-17.0	1.4	0.0	7.6	12.2

(a) Recharge source of Malwathu Oya (MO)

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope value of surface water, shallow, and deep groundwater in the MO shows significant differences (Figure 6(a)). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of surface water of the dry season in the MO are enriched than the isotopic values of seawater indicating strong evaporation. However, surface waters and shallow groundwater after the wet season (Figure 6(a) &(d)) shows similar depleted isotopic signature implying that the groundwater in the regolith area may interconnected with adjacent surface water bodies and fully saturated due to the heavy rainfall. In contrast, deep groundwater has no immediate recharge effect after the rainy season.

Almost all the water samples collected during the dry season lie on the evaporation lines of North-Central Dry Zone [Figure 6(a)], but deep groundwater close to LMWL indicating that these waters are mainly recharged from monsoon rain and slightly mixed with evaporated water. The basin area receives rainfall from the North East monsoon and 2nd Inter monsoon, and the long-term average rain index of the basin with $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of -6.7‰ and -40.7‰ (E. A. N. V. Edirisinghe, Pitawala, et al., 2017). The $\delta^{18}\text{O}$ confluence point (EM 2) of LMWL and evaporation line is -7.7 ‰ showing a more depleted isotopic signature than the rain index of the MO basin area would probably be due to higher elevation recharge condition.

The identified $\delta^{18}\text{O}$ depletion in the rain per 100 m elevation is $0.6\pm0.2\text{‰}$ (E. A. N. V. Edirisinghe, Pitawala, et al., 2017), considering the isotopic values and altitude effect, it is suggested that the deep groundwater in this basin is recharged from an altitude of 100 to 200 m amsl (Priyadarshanee et al., 2022).

Both shallow and deep groundwater in the sedimentary limestone area (CKDu non-endemic) have enriched isotopic signatures than the CKDu endemic area. These water samples are aligned in between the LMWL and evaporation line as well as pointing to the seawater indicating that these waters are not only affected by evaporation but also mixing with seawater.

The slope of the evaporation line varies with the evaporation condition and is usually less than 8 in the groundwater that are originating from atmospheric precipitation and affected by the evaporation. It is 4 to 6 in open water bodies and can reach 2 to 3 during soil evaporation. The slope of the evaporation line in CKDu endemic area is 5.7 and it indicates that the groundwater in this study area may be recharged by the already evaporated surface water or shallow groundwater may be directly affected by evaporation. Hence, the isotopic composition of recharged groundwater in the 100 m (EM-2: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are -7.7‰ and -47.5‰) and average isotopic signature of the surface water (EM-1: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are 1.7‰ and 8.0‰) were considered as the end-members to calculate the mixed surface water proportion during the dry season of the study area.

It implies that the evaporated surface water proportion of the deep and shallow groundwaters are between 19 to 33% and 23 to 48% respectively. Also, the proportion of mixed sea water in the CKDu non-endemic sedimentary formation was calculated using the confluence point of the groundwater regression line into the evaporation line (EM-3: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are -2.8‰ and -19.2‰) and isotopic signature of seawater (EM-4: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are -0.4‰ and 2.1‰). The calculated mixed seawater proportion varies between 23 to 39%.

The relationship of D-excess with TDS (Figure 6 (c) & (f)) indicates that the mineral dissolution mostly contributes to the salinity of deep groundwater in the CKDu endemic area. However, surface water is affected by evapo-concentration and seawater mixing is prominent in the CKDu non-endemic area.

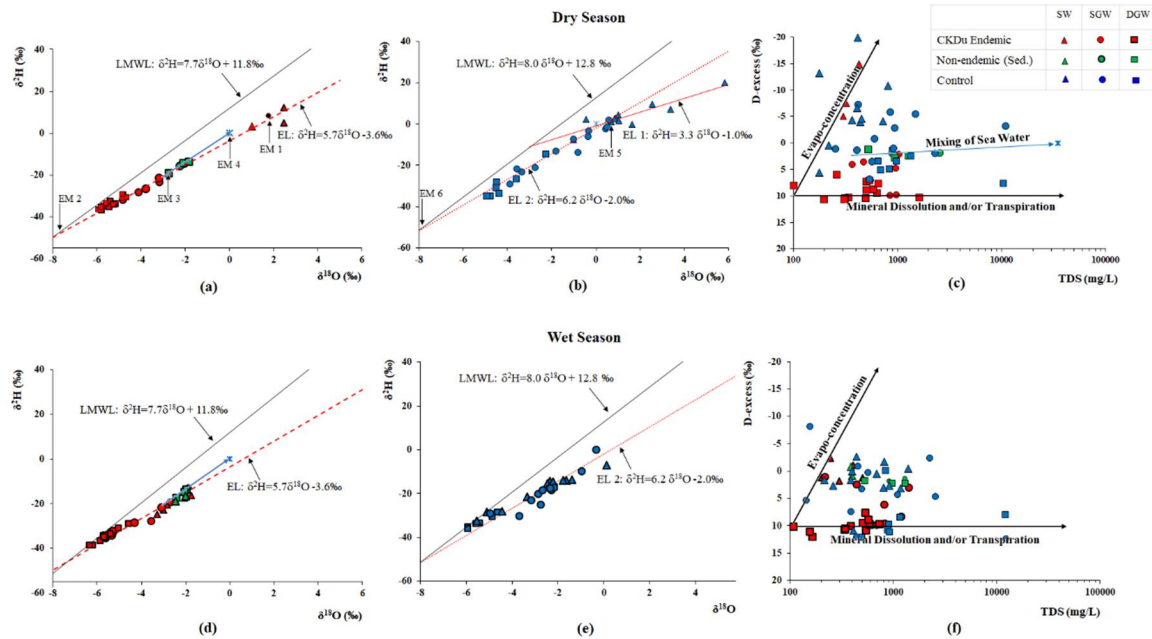


Figure 6. $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ relationship of groundwater in (a & d). CKDu endemic Malawthu Oya (b & e). CKDu control Malala Oya and (c & f). relationship of D-excess and TDS in both dry and wet seasons.

(b) Recharge source of Malala Oya (ML)

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope value of surface water, shallow and deep groundwater in the CKDu control area shows significant differences (Figure 6(b) & (e)) during both seasons. All the water in the CKDu control area are plotted away from the LMWL of Hambanthota implies that all these waters are affected by evaporation of varying degrees. Making of poorly interconnected surface water-groundwater network due to the depleted groundwater levels during the dry season may be the possible reason for this isotopic separation. After the wet season, similar isotopic signatures can be seen in the shallow groundwater and surface water because they may interconnect and saturated with heavy rainfall.

Groundwater collected during the dry period of the CKDu control area was plotted on the regression line (EL 2) denoted by $\delta^2\text{H}=6.2 \delta^{18}\text{O}-2.0\text{‰}$ ($r^2=0.96$) (Figure 6(b)). However, surface water appears to have a different origin and the isotopic composition of surface water represents the evaporation line (EL 1) of $\delta^2\text{H}=3.3 \delta^{18}\text{O}-1.0\text{‰}$. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value of the confluence point of EL 1 into the LMWL is -2.9‰ and -10.7‰ represents the rain index of Southwestern (SW) monsoon (E. A. N. V. Edirisinghe, Pitawala, et al., 2017) and it suggests that the surface waters are recharged only from SW monsoonal rain. However, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the confluence point of EL 2 into the LMWL (EM 6: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are -8.2‰ and -52.8‰) show a more depleted isotopic signature than the local rain index of the basin area. This can suggest that the shallow and deep groundwaters have recharge origin from the adjacent mountainous area. The enriched and evaporated isotopic composition of shallow and deep groundwater composition could have been attributed to mixing with already evaporated surface water.

Mixing the proportion of evaporated surface water into the groundwater system is calculated using end-members of EM-5 and EM-6. The mixing proportion of evaporated surface water in deep groundwater varies from 37 to 69% and in shallow groundwater from 53 to 100%. Three shallow groundwater wells in this basin area are fully recharged from the evaporated surface waters.

Deep groundwater collected after the rainy season aligned along the evaporation line but close to the LMWL indicating that these waters are mainly recharged from monsoon rain. The deviation of shallow groundwater and surface water from the LMWL indicates intensive evaporation under prevailing dry conditions even after the rainy season (Figure 6(e)). However, the evaporation effect is lesser compared to the dry season.

The relationship of D-excess with TDS (Figure 76c) & (f)) confirms that both mineral dissolution and evapo-concentration partially contribute to the salinity of groundwater during the dry season. However, surface water is only affected by the evapo-concentration, and mixing proportion is

different from each other. After the wet season, the salinity of the deep groundwater is controlled only by mineral dissolution.

4.4. Groundwater Age

Tritium is a radioactive isotope of hydrogen and it is a reliable tracer to discriminating groundwater older than 50 years from recent meteoric waters with a Half-life of 12.32 years (4500 days).

The measured long-term average tritium concentration in the precipitation in Sri Lanka is ~1.5TU (E. A. N. V. Edirisinghe, Manthirithilake, et al., 2017) and the minimum detection limit of the instrument is 0.4 TU.

Tritium concentration of the surface and shallow groundwater in the CKDu endemic area ranges from 0.64 to 1.07 TU and 0.4 to 0.67 TU shows that they are recently precipitated. Almost all the deep groundwater samples analyzed in CKDu endemic, non-endemic and the control areas are tritium-free (<0.4 TU) indicating their prolonged retention time with very low recharge rate along the aquifer (Priyadarshane et al., 2022; Senarathne et al., 2019)

Radiocarbon (^{14}C) is a widely used groundwater dating method (Lyu et al., 2019) that can be used to date groundwater up to thousands of years based on the measurement of ^{14}C of the DIC (dissolved inorganic carbon) in groundwater and the age is determined according to the following equation.

$$t = -\left(\frac{5730}{\ln 2}\right) \ln \left(\frac{^{14}\text{C}_{\text{DIC}}}{^{14}\text{C}_0}\right)$$

Where, t is the groundwater age; 5730 is the half-life of ^{14}C ; $^{14}\text{C}_{\text{DIC}}$ is the measured ^{14}C value of the DIC in the groundwater sample; and $^{14}\text{C}_0$ is the initial ^{14}C content of DIC.

The apparent radiocarbon age of the selected seven groundwater samples measured in the MO shows that their age is > 150a BP except for one location (W07). Also, an artesian well in the sedimentary formation with ~4500a BP. This further confirms that the deep groundwater in the Malwathu Oya basin is flowing along the regional flow paths with a longer mean residence time.

4.5. Correlation between Groundwater Fluoride, Hardness, TDS and Occurrence of CKDu

Spatiotemporal variation of water quality parameters exceeded the MALs of the CKDu endemic and control areas are described in section 3.1. However, their individual impact is cannot correlate with the CKDu even with the higher concentrations. Therefore, correlation coefficient matrix analysis was performed to identify the combined effect of water quality parameters with CKDu (Figure 7a, b, c, & d).

The TDS in the water collected from both seasons of the CKDu endemic area and the wet season of the control area shows a strong positive correlation with Mg^{2+} , Ca^{2+} , Na^+ , and Cl^- , SO_4^{2-} which indicate that TDS may derived from weathering and/or dissolution of aquifer material from the same source (Hu et al., 2023). The TDS and Ca^{2+} are non-correlated in the dry season with a strong positive correlation during the wet season which reflects that its mineralization was mainly caused by Ca^{2+} in the control area (Hu et al., 2023).

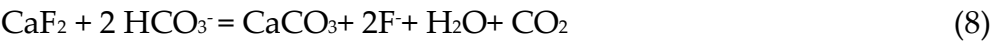
The correlation of Mg^{2+} and total hardness (TH) is higher than the correlation of other cations with TH implying that TH is more influenced by Mg^{2+} ions (Egbueri, 2019). Mg hardness is prominent in the dry season while Ca hardness is prominent in the wet season. In contrast, Ca hardness is prominent in the dry season of the control area. The more or less similar correlation coefficient of hardness with Ca and Mg (0.96) in the wet season indicates their equal contribution to the formation of total hardness in the control area.

The correlation between F^- with other chemical components can be used to further understand the source of groundwater F⁻ (Liu et al., 2021; Narsimha Adimalla, 2020). There was a negative correlation between groundwater fluoride and Ca^{2+} in the CKDu endemic area during the both seasons and the control area during the dry season, with $r = -0.30$, $r = -0.09$, and $r = -0.50$ respectively. As groundwater Ca^{2+} increases from dry to wet season in the CKDu endemic area, the reaction shown in Eq.7 will proceed, thereby decreasing the content of F^- in groundwater due to the formation of CaF_2 .



pH is an important factor that affects the desorption of groundwater F^- (Saxena & Ahmed, 2001) and a high concentration of HCO_3^- will result in an alkaline groundwater environment (Liu et al.,

2021). There is a positive correlation between groundwater F⁻ with pH and HCO₃⁻ in the CKDu endemic area indicating that an alkaline environment is more conducive to fluoride enrichment. As HCO₃⁻ is the main groundwater anion in the CKDu endemic area (Chandrajith, Dissanayake, et al., 2011; T. Cooray et al., 2019; Hettithanthri et al., 2021), with alkaline groundwater may lead to desorption of F⁻ as in eq.8.



In contrast, F⁻ desorption is unfavorable in the CKDu control area because, there was a non-correlation between groundwater F⁻ with pH and a weak positive correlation between F⁻ with HCO₃⁻. However, F⁻ concentration in the control area is considerably high, especially during the wet season. Also, this study has shown there is a strong positive correlation between F⁻ with Na⁺ (r = 0.90). The main sources of Na⁺ are the weathering of sodium silicates, the dissolution of evaporites as well as cation exchange process.

However, the weathering of silicates and dissolution of evaporites are not directly related to groundwater fluoride (Liu et al., 2021), hence, the positive correlation between F⁻ and Na⁺ may be due to cation exchange and it encouraged the CaF₂ dissolution. Thus, the F⁻ concentration increases where Ca²⁺ ions have dropped.

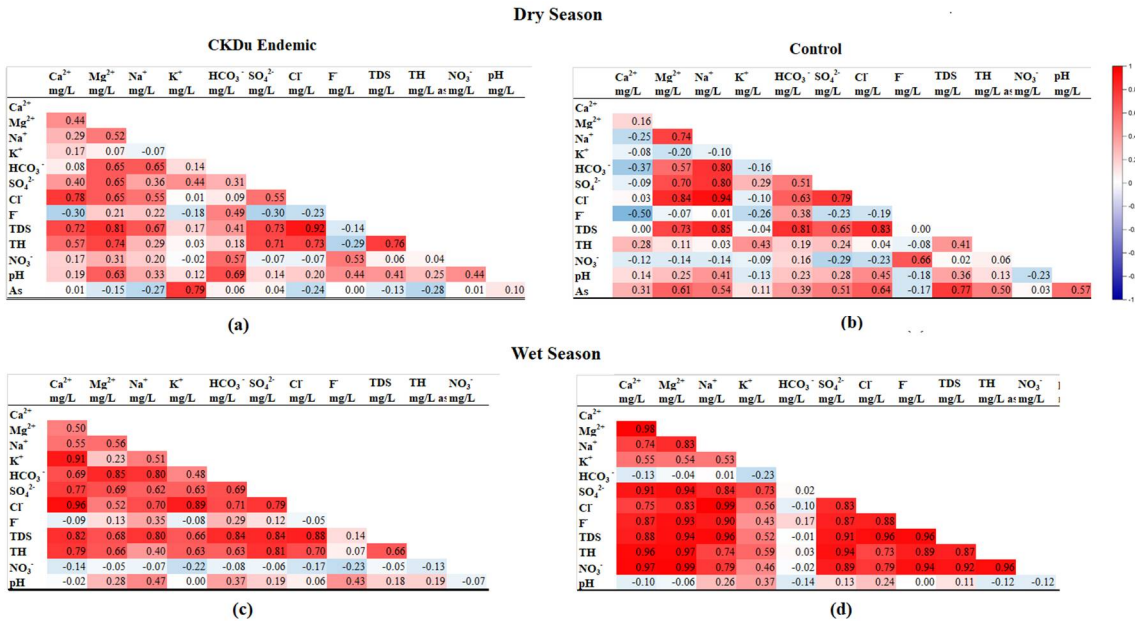


Figure 7. Pearson's correlation analysis among water quality parameters of groundwater in CKDu endemic (a & c) and control areas (b & d).

High concentrations of major ions present in the water contribute to the TDS and certain concentrations of these ions can activate the Hofmeister series effects leading to kidney damage in humans (Dharma-wardana, 2018; Hettithanthri et al., 2021). The results from the present study showed a direct correlation of TDS with other major ions of drinking water that can be used to identify their increasing and decreasing toxicity in the human body. Also, ionic ratios of F⁻ with Mg²⁺, Ca²⁺, and Na⁺ and their impact on the biological mechanism leading to the disease may provide evidence as to its actual cause (Dissanayake & Chandrajith, 2017). The present study identified a positive correlation between F⁻ with pH, Mg²⁺, and HCO₃⁻ in the CKDu endemic area while F⁻ with Na⁺ in the control area. In addition to that, the calculated Na/Ca ratio in the endemic and control area is different and it has been identified as a promising factor to indicate major geochemical dissimilarities. The Na/Ca ratio is strongly related to the F⁻ concentration and in the CKDu endemic area, the lower Na/Ca ratio could be due to either the lower Na⁺ activity or high Ca²⁺ activity. Ca²⁺ activity is more prominent compared to the Na⁺ activity in the CKDu region and F⁻ showed more affinity towards Ca²⁺ (Dissanayake & Chandrajith, 2017; Liyanage et al., 2022).

Several studies conducted by previous authors highlighted the relationship between F⁻ and TH with CKDu (Balasooriya et al., 2021; Wickramaratna et al., 2017). Even with the high TH in both

CKDu and the control area, this study showed the TH in the CKDu area induced by a higher content of Mg^{2+} ion and Mg hardness could be a causative factor for CKDu. Consideration of the Hofmeister-type action of anions (Dharma-wardana, 2018) showed that the pairing of F^- and Mg^{2+} in groundwater is expected to form more nephrotoxic MgF_2 complexes that lead to the etiology of CKDu.

In contrast, the formation of NaF by complexation of F^- with Na^+ leads to decreased F^- toxicity in the human body (Rajapakse et al., 2016). The control area with a higher Na/Ca ratio due to the increase of Na^+ concentration during the ion exchange process leads to a reduction of toxicity. Furthermore, high evaporation rates due to prevailing high temperatures in the control area may further concentrate ions in the groundwater system.

5. Conclusion

Geochemical and isotopic evidence of the present study was used to differentiate the variations of water quality, formation and evolution mechanism of water quality parameters, and their possible association with the emergence of CKDu in the endemic and non-endemic (sedimentary formation) areas in the Malwathu Oya basin and the control area in the Malala Oya basin of Sri Lanka.

Elevated and unacceptable levels of TDS, Mg^{2+} , Na^+ and F^- are the main parameters that cause water quality deterioration and their combined association in the groundwater is significantly different between the CKDu endemic, non-endemic and control areas. The excess F^- and Mg^{2+} ions are present in the groundwater samples in the CKDu endemic area in the Malwathu Oya basin, but F^- is relatively low in the lower part of the basin where sedimentary formation with non-prevalence of CKDu. In the control area there are three different types of waters showing low F^- and low Mg^{2+} , high F^- and low Mg^{2+} or low F^- with high Mg^{2+} . TDS is higher than the MALs in all these three regions but their derived mechanism is distinctly different.

In the CKDu endemic area, both silicate weathering and carbonate dissolution are the leading processes that control the geochemistry while a minor contribution of reverse ion exchange is present. Isotopic signature of shallow groundwater with the depth around 10 m which are mainly stored in the weathered overburden show the effects of intensive evaporation but deep groundwater with high elevation recharge (between 100 to 200 m altitude) does not show any evaporation effect. Surface water infiltrated through the widespread network of tanks in this area diluted the ionic concentration of shallow groundwater during the wet season. However, this effect is insignificant in the deep groundwater system because they are recharged only through the regional flow paths of the hard rock fracture system.

In contrast, silicate weathering, evaporite dissolution and ion exchange processes lead to control of the ionic content in the groundwater in the CKDu control area. Surface waters are strongly evaporated hence it provides a considerable proportion to recharge of shallow and deep groundwater during the dry season. A shallow regolith aquifer is saturated with heavy rainfall and a considerable amount of rainwater infiltrated and mixed with groundwater making a depleted isotopic signature during the wet season. Dissolution of geogenic elements in this region is prominent and the TDS of deep groundwater is controlled by the evaporite dissolution in the soil medium during the wet season.

Water quality of the CKDu non-endemic sedimentary formation in the MO basin is derived from rock weathering, evaporation concentration, and seawater mixing. Approximately 4500 BP radiocarbon apparent age in artesian water confirmed that the deep groundwater in this formation is recharged through the regional flow paths and have a long residence time.

Correlation of F^- with pH, HCO_3^- , Ca^{2+} , Na^+ , and Mg^{2+} of groundwater is significantly different between CKDu endemic and control area. Weathering of silicate rocks under tropical climatic conditions produces a considerable amount of F^- in the groundwater in both basin areas. In addition to that, desorption of F^- into groundwater in the CKDu endemic area is present while the ion exchange process in the control area produces an additional amount of F^- in the groundwater system. Ca-hardness, and Mg hardness is more important than TH when correlating disease patterns with geological parameters. Prominent Mg hardness and excess F^- in the CKDu area produce nephrotoxic MgF_2 complexes that trigger protein denaturation, thus the synergic effect may cause renal damage. In contrast, the control area with a higher Na/Ca ratio due to the increase of Na^+ concentration during the ion exchange process encourages CaF_2 dissolution. Complexation of Na^+ with F^- producing NaF complexes leads to a reduction of F^- toxicity in the human body.

In conclusion, increased levels of magnesium, fluoride and TDS in the shallow groundwater, along with geochemical, hydrogeological, and climatological factors, may contribute to the CKDu in the Dry Zone of Sri Lanka.

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