Journal of Environmental Management 327 (2023) 116877

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Fluorescence characteristics and source analysis of DOM in groundwater during the wet season in the CKDu zone of North Central Province, Sri Lanka

Dazhou Hu[a,b,c,1], Suresh Indika[a,b,c], Hui Zhong[a,b], Sujithra K. Weragoda[d], K.B.S.N. Jinadasa[e], Rohan Weerasooriya[f], Yuansong Wei[a,b,c,f,2,**]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
[b] Laboratory of Water Pollution Control Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
[c] University of Chinese Academy of Sciences, Beijing, 100049, China
[d] National Water Supply and Drainage Board, Katugastota, 20800, Sri Lanka
[e] Department of Civil Engineering, Faculty of Engineering, University of Peradeniya, Peradeniya, 20400, Sri Lanka
[f] National Institute of Fundamental Studies, Hantana Rd, Kandy, 20000, Sri Lanka)

ARTICLE INFO

Keywords:
CKDu
DOM
Aquifers
Exogenous input
Drinking water

ABSTRACT

The dissolved organic matter (DOM) should be purified for safe drinking water due to disinfection by-products (DBPs) produced by disinfectants reaction with DOM. Current research on groundwater in the chronic kidney disease with unknown etiology (CKDu) zone of the North Central Province (NCP) in Sri Lanka has focused mainly on aquatic chemistry, with limited attention paid to the spatial distribution, compositional sources and factors of DOM. Therefore, the structure, composition, source and spatial distribution of the DOM of two kinds of groundwater samples collected from dug well and tube well in the NCP during the wet season were determined, compared and analyzed by analytical tools such as parallel factor analysis (PARAFAC). Results show that the average concentrations of TOC in these two groundwater samples are generally higher than 5.0 mg/L, and the concentration of TOC in the groundwater of the shallow weathered aquifer is higher than that of the deep hard rock aquifer, while its distribution of the two aquifers are on contrary. The DOM in the dug well has three types and four components, including humus-like component C1 (33.36%) and C2 (38.60%), protein-like component C3 (13.09%) and heterogeneous organic component C4 (14.95%). In the tube well, two types and two components of the DOM are determined, including humus-like component CI (69.80%) widely existing in natural water and soluble microbial by-product CII (30.20%) produced by microbial community activities. In the dug well, DOM is mainly exogenous input, the higher ion concentration in water affected the fluorescence intensity of humus and protein components. And in the tube well, DOM has obvious endogenous characteristics, and higher pH value may inhibit the production of protein like fluorescent substances to a certain extent.

1. Introduction

Groundwater is as one of the planet's most abundant freshwater resources, and approximately 1.5 billion people worldwide rely on groundwater as their primary source of water (Haddad et al., 2018). It is often considered as the most cost-effective way to provide safe water supply in rural area (United Nations, 2022). In 2018, approximately 33% of the population in South-Asia used self-supplied water as their

** Corresponding author. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, No. 18 Shuangqing Road, Haidian District, Beijing, 100085, China.

E-mail addresses: dzhu_st@rcees.ac.cn, dzhu_st@rcees.ac.cn (D. Hu), e11189suresh@yahoo.com (S. Indika), zhonghui1977@163.com (H. Zhong), skwera7@gmail.com (S.K. Weragoda), shamj@pdn.ac.lk (K.B.S.N. Jinadasa), rohan.we@nifs.ac.lk (R. Weerasooriya), yswei@rcees.ac.cn (Y. Wei).

[1] Research Interest: Membrane technology for drinking water treatment.

[2] Research Interest: water treatment; wastewater treatment and reclamation; river restoration; control of antibiotic resistance in biological treatment of sewage sludge/animal manure.

https://doi.org/10.1016/j.jenvman.2022.116877
Received 15 September 2022; Received in revised form 23 November 2022; Accepted 23 November 2022
Available online 30 November 2022
0301-4797/

primary source of drinking water with tube wells/boreholes, i.e., around 18% of the urban population and 34% of the rural population rely on self-supplied water (groundwater) in Sri Lanka (Foster et al., 2021), but this percentage exceeds 80% in rural areas of the North Central Province (NCP) (Balasubramanya et al., 2020). The groundwater from the shallow weathered aquifer of the dug well and the deep hard rock aquifer of the tube well, respectively, are important sources of drinking water for rural people (Sood et al., 2015; Young et al., 2011). The population covered with protected dug well and tube well in Sri Lanka remained stable at 36.6% and 3.2% in 2013 and 36.4% and 3.2% in 2019, respectively, but the population access to the pipe-born drinking water was increased to 51.8% in 2019 from 43.7% in 2013 (National water supply and drainage board, 2013, National water supply and drainage board, 2019). Recently high concentrations of hardness (Wasana et al., 2016; Kulathunga et al., 2019), fluoride (Chandrajith et al., 2011; Ranasinghe et al., 2018) and dissolved organic matter (DOM) (Cooray et al., 2019; Makehelwala et al., 2019) were reported as the main characteristics of groundwater in these areas of Sri Lanka, including dug well and tube well. According to the Clean Water and Sanitation of the United Nations Sustainable Development Goals (SDGs) by 2030, the Government of Sri Lanka plans to provide safe and affordable drinking water for all the people, and is implementing Water Safety Plans (WSPs) with the WHO recommendations to ensure all households with clean drinking water (National water supply and drainage board, 2020). In rural areas, the costs of pipe-born water supply is out of budget due to the scattered villages and low population density, making it more difficult to ensure safe drinking water. To address this issue, the National Water Supply and Drainage Board (NWSDB) is promoting reverse osmosis (RO) plants in rural areas especially for people lving in the areas affected with CKDu through community facilitation projects, more than 2000 RO stations have been already established in these regions of Sri Lanka to mitigate the drinking water quality issues (Indika et al., 2021, 2022).

Studies have shown that the rate of membrane contamination increases rapidly when the TOC of the RO feed water exceeds 4 mg/L, resulting in the decline of membrane flux and the deterioration of operation performance (Wu et al., 2020). In addition, the health risks associated with the presence of TOC in groundwater are increasingly paid attention. Researchers have conducted a large number of epidemiological study on effects of TOC in drinking water, and showed stated that disinfectants react with natural organic substances (NOMs) to produce disinfection by-products (DBPs) in the process of drinking water disinfection, which pose a potential threat to human health (Dong et al., 2019; Mian et al., 2018), i.e., increased risk of diseases such as bladder cancer (Li and Mitch, 2018), colorectal cancer and birth defects (Richardson et al., 2007). According to European Union Council directive (98/83/EC) (COE, 1998) and Standard for Drinking Water (GB5749-2006), the maximum oxidisability and COD_{Mn} concentrations in drinking water are at 5.0 mgO_2/L and 3.0 mg/L, respectively, and thus DOM in groundwater should be purified for providing safe groundwater-based drinking water.

In the previous studies, inorganic ions in groundwater in the NCP of Sri Lanka were often reported such as hardness, fluoride and heavy metals (Botheju et al., 2021; Imbulana and Oguma, 2021; Liyanage et al., 2022), and only a few researches reported DOM of groundwater in the CKDu affected areas (Cooray et al., 2019; Makehelwala et al., 2019; Zeng et al., 2022). Humus like and protein like substances are the main components of DOM in natural water, its chemical diversity varies with the concentration of organic matter, water quality, location and season, and the composition of DOM is different in different periods and regions (Kellerman et al., 2014; Ma et al., 2021). It is the first time to report distribution and characteristics of DOM in groundwater of the different risk zones of the CKDu affected areas in Anuradhapura District, NCP of Sri Lanka in wet season and wet season, respectively (Cooray et al., 2019; Makehelwala et al., 2019). For example, TOC concentrations of groundwater were significantly higher in the wet season than in the dry season and DOM was mainly fulvic acid-like substances in CKDu areas (Cooray et al., 2019). TOC concentrations only in the CKDu low risk (LR) (Makehelwala et al., 2019) were the same as those in Cooray study, but TOC concentrations and in the CKDu high risk (HR) and no risk area (NR) were higher in the dry season than in the wet season. In addition, the COD_{Mn}/TOC ratio was essentially lower in the wet season than in the dry season, but the fluorescence index (FI) of DOM was all higher in the wet season than in the dry season (Makehelwala et al., 2019), which implies that organic matters infiltrated into groundwater along with runoff in the wet season. A recent study showed that groundwater from the CKDu risk area has more humic materials in its DOM composition and has a higher molecular weight (MW) and stronger exogenous signature than those groundwater from CKDu no risk areas (Zeng et al., 2022). The groundwater in tube well is relatively deep, DOM in the water is easy to be exposed to the surface of rocks and minerals, and its composition and influencing factors are different from that in dug well (Lawson et al., 2016; Pathak et al., 2022). In a word, these studies showed very useful knowledge about DOM characteristics in shallow groundwater of CKDu affected areas in Anuradhapura District, but more researches are needed to further understand characteristics and source of DOM in groundwater from deep hard rock aquifers. A comprehensive and in-depth understanding of the structure, composition, sources and spatial distribution of DOM in groundwater from different aquifers in the NCP during the wet season is of great significance for the identification of safety risks of groundwater as a water source and the safety of drinking water. More specifically, the objectives of this study are to firstly determine the spatial distribution and composition of DOM in groundwater from two aquifers during the wet season, to then analyze the key factors affecting the composition of DOM in groundwater, and to finally analyze the sources of DOM components in both types of groundwater.

2. Materials and methods

2.1. Study area and sampling sites

As is shown in Fig. 1, the study area includes one shallow weathered aquifer and one hard rock fracture aquifer in the NCP, Sri Lanka. The NCP covers an area of 10,714.0 km^2 and has a population of 1.26 million, and it is mainly composed of the holy cities of Anuradhapura and Polonnaruwa. The terrain is high in the south and low in the north, which is located in a tropical monsoon climate zone. Field sampling campaigns were conducted in Anuradhapura and Polonnaruwa in 1–29 December 2019, and samples from 311 dug wells at depth of 5–15 m and 21 tube wells at depth of 40–60 m were collected, respectively. Other detailed information of the study area is listed in the supplementary material.

2.2. Main ions

The pH, electrical conductivity (EC), and total dissolved solids (TDS) were determined on site by a water quality analyzer(WTW, MultiLine Multi 3530, Welheim, Germany). Alkalinity was measured using a Hach© (TNTplus Vials, Loveland CO, USA). Concentrations of K^+, Na^+, Ca^{2+} and Mg^{2+} ions were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 8300, Perking Elmer, Houston, USA), and other cations were determined by an inductively coupled plasma-mass spectrometry (ICP-MS) (NexION 300X Perking Elmer, Houston, USA). The anions were analyzed using an ion chromatography (ICS 1000, Dionex, Sunnyvale, CA, USA). The TOC concentration of the water samples was determined by a TOC analyzer (Elementra, Langenselbold, Germany). Other detailed information of the main ions is listed in the supplementary material.

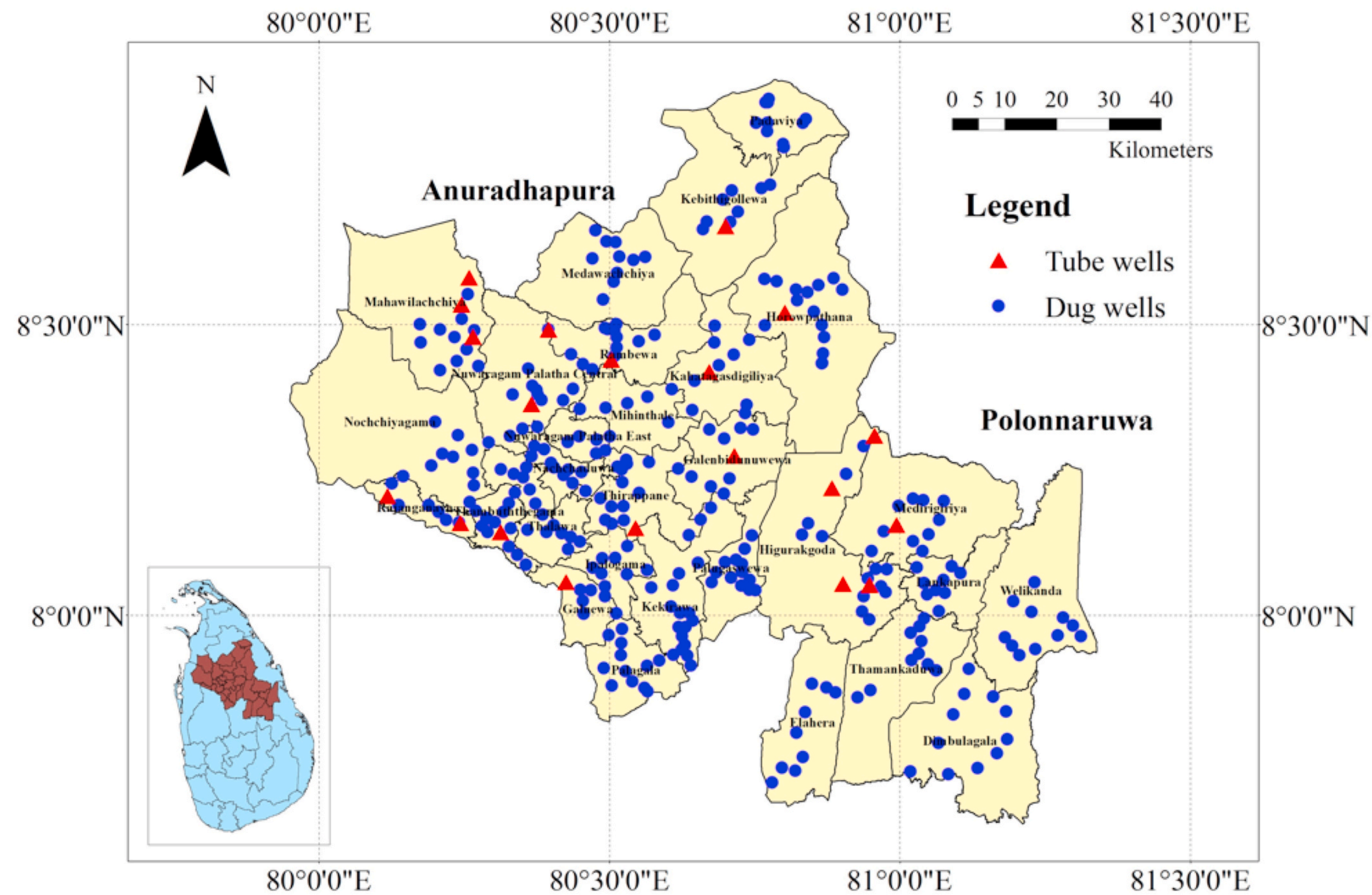

Fig. 1. Study area in the NCP, Sri Lanka (Sampling sites of dug well shown as blue dots; Sampling sites of tube well shown as red triangles). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

2.3. Analysis of DOM fluorescence and molecular weight

The fluorescence properties of DOM using a three-dimensional excitation matrices (3D-EEM) was investigated by a fluorescence spectrophotometer (F-7000, Hitachi, Tokyo, Japan), in which the excitation wavelength is 200–400 nm, the emission wavelength is 220–550 nm, and the excitation and emission slit width is set to 5 nm.

Size exclusion chromatography analysis was performed to identify molecular weight (MW) of TOC molecules with a high performance liquid chromatography (HPLC) system equipped with dual absorbance detector (Waters 2487) and binary HPLC pump (Waters1525, USA). Other detailed information of the fluorescence and molecular weight analysis is listed in the supplementary material.

2.4. Statistical analysis

Statistical analysis was performed using an Origin (2018, Originlab, U.S.A) software. The measured three-dimensional fluorescence data was input into a MATLAB (R2018a, MathWorks, U.S.A) software, to establish an EEM-PARAFAC model to obtain the fluorescence characteristics of different components.

3. Results and discussion

3.1. Groundwater quality

As shown in Table A1, the main chemical parameters of groundwater in the NCP were evaluated according to the Sri Lankan Drinking Water Standard (SLS 614–2013) and WHO Drinking Water Guide (4th). The results show that concentrations of hardness ions and fluoride in two kinds of groundwater exceed the standard, and is consistent with previous research results of Rohana, Rubasinghe and Kulathunga (Kulathunga et al., 2019; Rubasinghe et al., 2015). The average concentrations of hardness, fluoride and TOC of dug well are 277.37 ± 138.27, 0.83 ± 0.77 and 5.67 ± 3.55 mg/L, respectively, and those of tube well are 312.82 ± 133.20, 0.69 ± 0.48 and 5.31 ± 2.40 mg/L, which are higher than Sri Lanka Drinking Water Standard (SLS 614–2013; F^- as 1.0 mg/L and Hardness as 250 mg/L), WHO Drinking Water Guide (4th; F^- as 1.5 mg/L and Hardness as 500 mg/L) and Chinese Standard for Drinking Water Quality (GB 5749–2006, TOC as 5 mg/L). However, the concentrations of TDS, K^+, F^-, NO_3^- and TOC in the groundwater from dug wells are higher than those from tube wells, and others are lower than tube wells.

The studies think that the higher concentrations of hydrochemistry ions such as Ca^{2+}, Mg^{2+}, HCO_3^-, F^- and SO_4^{2-} ions in the groundwater in the NCP are due to the influence of rock weathering and evaporation (Rubasinghe et al., 2015; Wickramarathna et al., 2017). Marble, silicate, granite gneiss and quartzite and other fluorinated minerals are widely present in underground aquifers in the NCP (Gupta et al., 2018), and the ions concentrations in groundwater increase with the long-term rock-water and evaporation action. The average concentrations of NO_3^- and TOC in dug well are higher than in tube well, this may be the semi-open dug wells susceptible to human activities due to the shallow buried well groundwater and serious surface runoff during the wet season, leading to increased NO_3^- and TOC concentrations and poor water quality.

3.2. Distribution map of TOC in groundwater

The concentration of TOC in natural or unpolluted groundwater is usually lower than 4 mg/L (Regan et al., 2017). When the TOC concentration is higher than this limit, it indicated that there is pollution and poses a risk to the safety of the drinking water supply. The groundwater of TOC concentration in the dug well in the NCP ranges from 0.20 to 31.6 mg/L, with an average value of 5.67 mg/L; and TOC concentration in the tube well ranges from 1.70 to 10.7 mg/L, with an average value of 5.31 mg/L. These results indicated that the groundwater of the two aquifers is polluted to different degrees in wet season.

The map of TOC distribution in groundwater from different aquifers were drawn as shown in Fig. 2. The TOC concentration of dug well is higher than that in tube well in Anuradhapura area, while the opposite situation occurs in Polonnaruwa area. The TOC concentration in the groundwater of the two aquifers is generally between 5.0 and 8.0 mg/L, accounting for most of the NCP. Among them, the areas at over 5.0 mg/L of TOC concentration in dug well are mainly in the north of Anuradhapura and Polonnaruwa. In the tube well, the TOC concentrations is higher than 5.0 mg/L in almost all Polonnaruwa area and the eastern

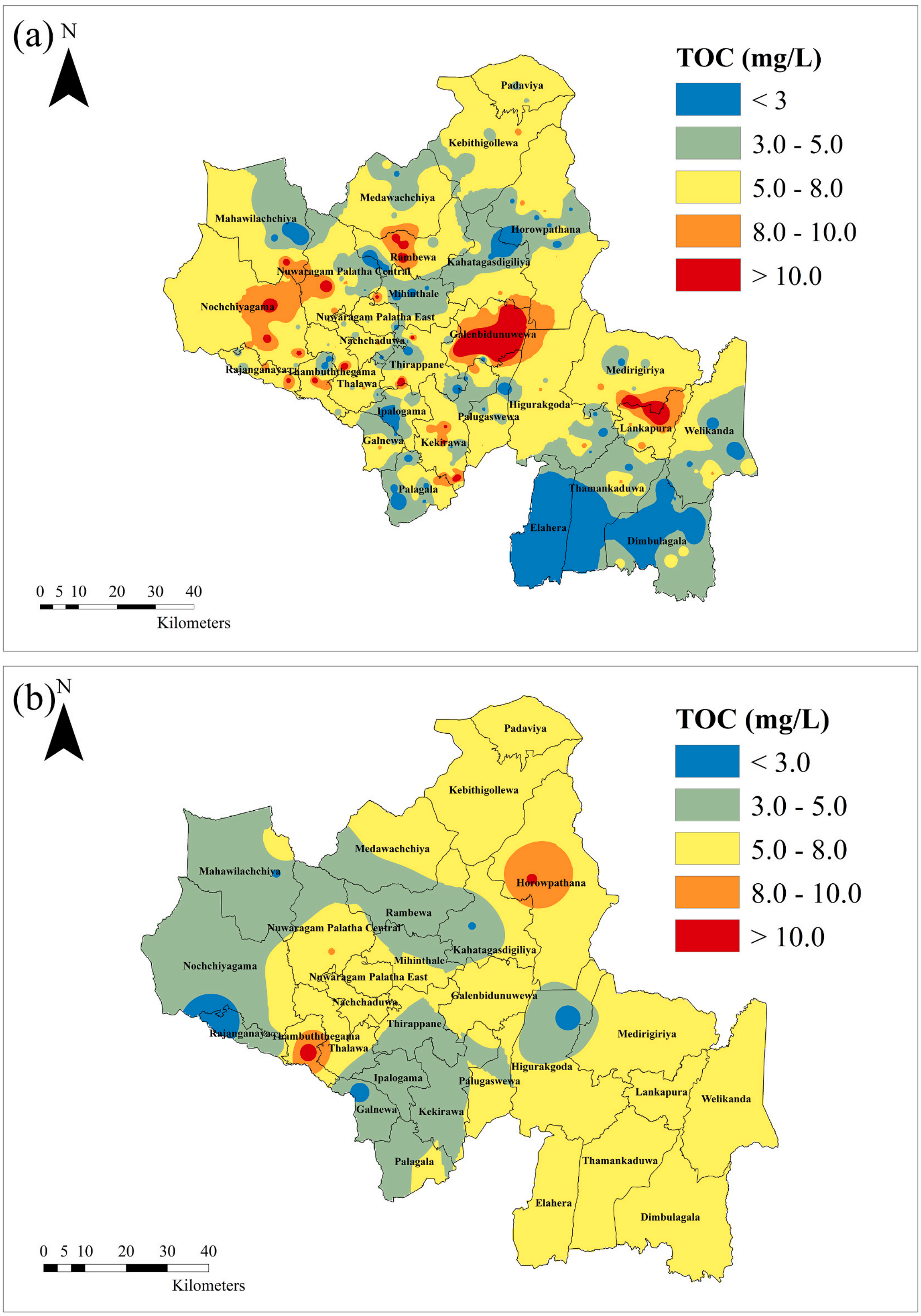

Fig. 2. TOC distribution of groundwater in different aquifers in the NCP.

area of Anuradhapura. In the shallow weathered aquifer groundwater areas where the TOC concentration is greater than 10 mg/L, except for the concentrated area in Galenbidunuwewa. The areas at less than 3.0 mg/L of TOC are mainly located in Elahera, Thamankaduwa and Dimbulagala. While in the tube well, TOC concentrations greater than 10.0 mg/L were only observed in Horowpathana and Thambuththegama areas. The concentration of TOC in some areas of Rajanganaya and Higurakgoda was less than 3.0 mg/L. It is noted that the area with a TOC concentration of 3.0–5.0 mg/L shown in Fig. 2a is mainly located at the boundary of each partition with a small population distribution area, which shows that human activities have a certain impact on the source of DOM in groundwater. The study by Imbulana et al. reported that the average concentration of TOC in the groundwater in the Medawachchiya, Galnewa, and Nuwaragampalatha Central areas of the NCP were 2.36 mg/L, 5.31 mg/L and 5.49 mg/L, respectively (Imbulana and Oguma, 2021), similar to the results of this study.

3.3. Fluorescence characteristics of DOM in different aquifers

The coefficients of variation (CV) of TOC concentration in groundwater of dug well and tube well are 0.63 and 0.45, respectively, indicating that many factors cause TOC in the two types of groundwater. The groundwater of two aquifers in the NCP was analyzed on the basis of the PARAFAC model, as shown in Fig. 3. There are three types and four components (a-d) of DOM in the dug well, and two types and two components (e-f) of DOM in the tube well. DOM in dug wells were mainly influenced by inputs from terrestrial sources, while tube wells were dominated by authigenic sources.

In the dug well, the component C1 (Ex 250 nm, Em 465 nm) ascribed to fulvic acids in the ultraviolet region, is a common fluorescent component in natural water and a typical terrestrial organic matter (McKnight et al., 2001). The component C2 (Ex 250/315 nm, Em 400 nm) is mainly related to stable macromolecular humus, which generally is used to indicate exogenous input (Stedmon et al., 2003). The component C3 (Ex 275 nm, Em 350 nm) can be classified as protein-like fluorescent substance (Li et al., 2014), its peak is associated with tryptophan component of microbial origin. Some researches have shown that tryptophan fluorescence related to activities of microbial communities is a soluble microbial metabolite in the degradation process of microorganisms and bacteria, it is often used to indicate endogenous input (Cammack et al., 2004). The peak value of component C4 (Ex255nm, Em295nm) is less reported in previous researches and is mainly derived from heterogeneous organic substances such as pharmaceuticals and pesticides (Baker and Curry, 2004).

The NCP agriculture in the study area is mainly rice planting. In most cases, the dosage of chemical fertilizers and pesticides used in agricultural production exceeds the local regulatory limit (Jayasumana et al., 2015a, 2015b). In the wet season, water mixed with organic matter and pesticide residues enter the groundwater with surface runoff, resulting in groundwater detected heterogeneous organic matter and terrestrial humus substances (Gunarathna et al., 2018; Rubasinghe et al., 2015). In previous research, Makehelwala detected a certain amount of pentachlorophenol in the shallow groundwater of the high CKDu prevalence (HR) in the NCP (Makehelwala et al., 2019). In tube well, the

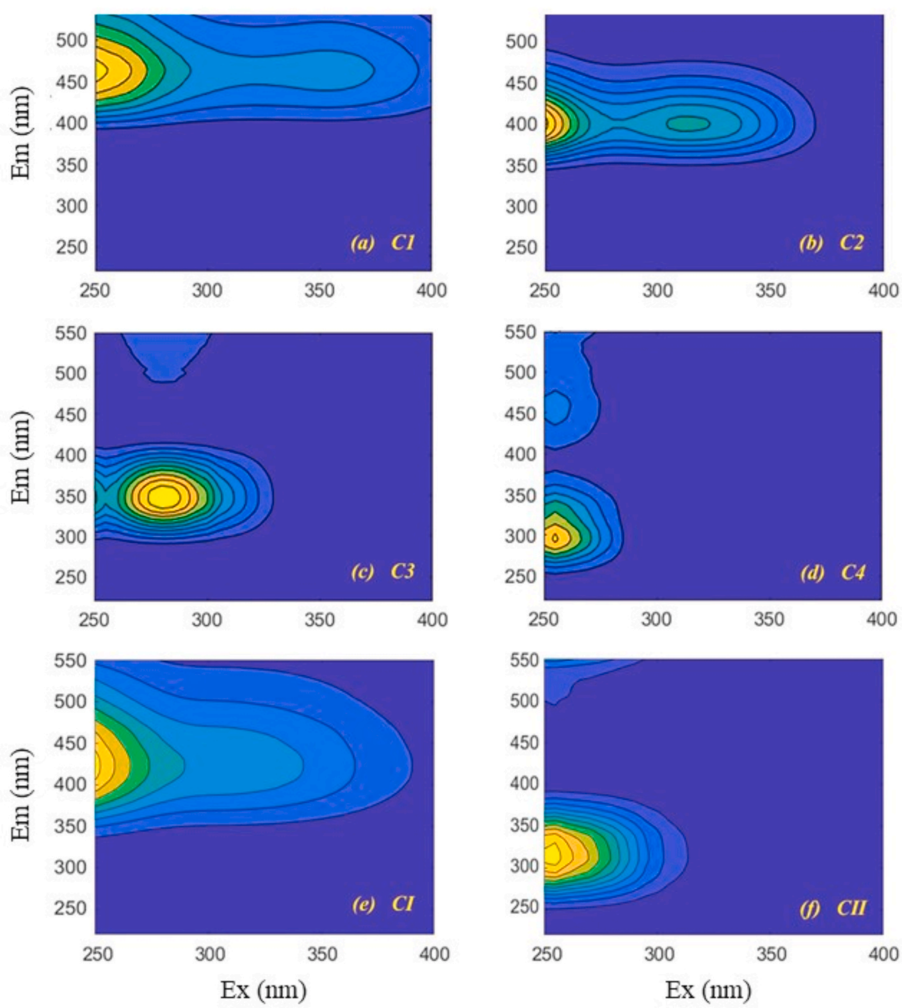

Fig. 3. Fluorescence spectra of different components identified by PARAFAC.

fluorescence characteristics of component CⅠ (Ex 250 nm, Em 430 nm) are the same as the component C1 from the dug well. The component CII (Ex 255 nm, Em 315 nm) has the same fluorescence characteristics as the component C3, which is ascribed to protein-like fluorescent substance. During field investigation and sampling, we found that compared with the dug well, the tube well is usually far away from the farmland, so the external input has less impact on its water quality.

The relative content of each component is calculated based on the amount of fluorescence intensity of the analytical components in the total fluorescence intensity, as shown in Fig. 4. The DOM in dug well groundwater, are mainly terrestrial humus component C1 and C2, accounting for 71.96%, while the component C2 as external input accounts for the main part, accounting for 38.60%, which indicated anthropogenic activities and exogenous surface runoff in the wet season. The component C4 as the heterogeneous organic substances, accounts for 14.95%, while the component C3 as the protein fluorescent substance, accounts for the smallest proportion at 13.09%. In the DOM of tube well groundwater, the content of humus-like component CⅠ is as high as 69.80%, and the protein-like substance component CII accounts for 30.20%.

3.4. Index analysis of DOM in two aquifers

The Fluorescence Index (FI) of DOM, the Biological Index (BIX) and the Humification Index (HIX) are used to describe characteristics of DOM in the water and the fluorescence intensity of DOM from different sources. As FI is > 1.9, it has a greater metabolic relationship with the microbial community in the groundwater, and when FI < 1.4, non-biological sources account for the main contribution, and DOM has a greater relationship with external input such as surface runoff (Lavonen et al., 2015). When BIX$<$0.8, it indicates that the sample is not affected by microbial activities, and the self-generating characteristics of the water are not obvious. When BIX$>$0.8, the characteristics of the natural source of bacteria and microbial activities are more significant (Huguet et al., 2009). When HIX$>$4, the degree of humification is higher, When HIX$<$4, it means that DOM is mainly affected by various biological activities, and the degree of humification is weak (Huguet et al., 2009). As shown in Table 1, the groundwater FI values of dug well and tube well are 1.52–2.37 and 1.78–2.37, with their average values of 1.89 and 1.97, respectively, indicating that the organic matter in the groundwater of the two different aquifers comes from both terrestrial sources and microbial activities. These results are similar to the FI values (1.8–2.55) of DOM in dug wells in wet season (Makehelwala et al., 2019). The BIX

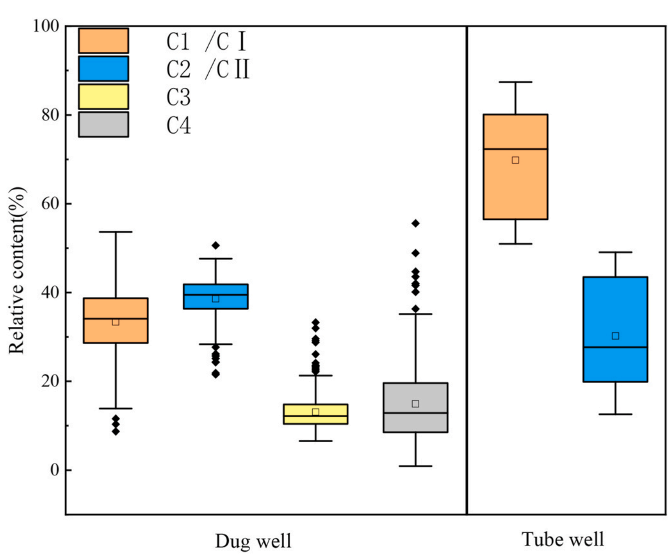

Fig. 4. Comparison of DOM components of Dug well and Tube well in the NCP.

values of groundwater in the dug well and tube well are between 0.55 and 1.84, 0.69–1.23 with their average values of 0.91 and 1.00, respectively, indicating that there are bacterial and microbial community activities in both groundwaters. The HIX of groundwater in the dug well and tube well are between 0.34-0.93 and 0.49–0.89 with average values of 0.76 and 0.70, respectively, indicating that the degree of humification of groundwater in the two aquifers is relatively low. Usually, the organic matter from land sources has a higher HIX value, while the self-produced HIX value of water bodies is relatively low. Therefore, the HIX in the two types of groundwater mainly comes from self-produced. Fn280 and Fn355 represent relative concentrations of protein-like substances and humus-like components, respectively. These two indicators can be used to characterize the contribution of authigenic and terrestrial sources to DOM components in water (Zhang et al., 2009). Among them, the average values of Fn280 is 475.70 and 376.20 respectively in the dug well and tube well, while Fn355 is 508.59 and 342.88, respectively. It is obvious that the Fn280 values of the tube well are much higher than Fn355, showing strong self-generating characteristics. Therefore, the DOM of tube well is mainly affected by endogenous input.

Some researches have shown that DOM in groundwater can not only come from the external input of soil organic matter after the surface runoff, but also from the microbial metabolism of aquatic animals and plants, microorganisms or algae (Lipczynska-Kochany, 2018). Results of this study show that DOM as manily humus-like components in the dug well groundwater is mainly controlled by external input, which has a greater impact on the composition of the water. The DOM of groundwater in tube well is affected by endogenous input and dominated by protein-based fluorophores, indicating that autogenous input is dominant. The results of fluorescence index (FI, HIX, BIX) further prove that most of the dug well samples fall within the exogenous input range, while the tube well samples fall in the range of endogenous input. Therefore, in addition to natural components of DOM, external input and microbial community activities caused a further increase of in the DOM fluorescence intensity in the dug well, while the mainly soluble microbial metabolites, endogenous input, cause a further increase of the DOM fluorescence intensity in the tube well.

Further analysis of the molecular weight distribution of DOM in both groundwaters revealed that the overall absorbance of DOM molecular weight in dug well groundwater was higher than that in tube well groundwater, indicating that the concentration and composition of DOM in dug well groundwater is higher and more complex (Fig. 5). At the same time, the absorption peaks of DOM in the lower molecular region of the two groundwaters are essentially the same, indicating that the small molecular weight substances are of the same type, which is consistent with the results of the PARAFAC (Fig. 3). Specifically, there are significant absorption peaks at 500, 700 and 800 Da for groundwater from dug wells and at 900 Da for groundwater from tube wells. Previous studies show that the DOM less than 4000 Da is mainly low molecular weight microbial metabolites and small molecular proteins (Komatsu et al., 2020), among which 1000–1800 Da are mainly fulvic acids and metabolites that are difficult to be bioavailable, and above 1800 Da are mainly polysaccharides or hydrophobic organic substances such as large molecules of humic substances (Kent et al., 2014; Tang et al., 2016). In summary, the small molecular weight organic matter in both types of groundwater is mainly fulvic acid-like substances with a molecular weight of 500–1000 Da, while the large molecular weight material (e.g. humic and heterogeneous organic matter) is mainly greater than 2000 Da.

3.5. Principal component analysis (PCA)

As shown in Fig. 6, principal component analysis using DOM variables from two aquifers including TOC concentration and fluorescent component, FI, BIX and HIX was carried out to understand their relationship.

In the dug well, the PC1 and PC2 obtained could explain 48.86% and

Table 1
Fluorescence spectra parameters of groundwater in the NCP.

Parameters	FI		BIX		HIX		Fn280		Fn355	
Well	Dug well	Tube well	Dug well	Tube well	Dug well	Tube well	Dug well	Tube well	Dug well	Tube well
Min	1.52	1.78	0.55	0.69	0.34	0.49	130.10	191.20	84.21	101.30
Max	2.37	2.37	1.84	1.23	0.93	0.89	29,510	943.10	3554.00	1291.00
Average	1.89	1.97	0.91	1.00	0.76	0.70	475.70	376.20	508.59	342.88

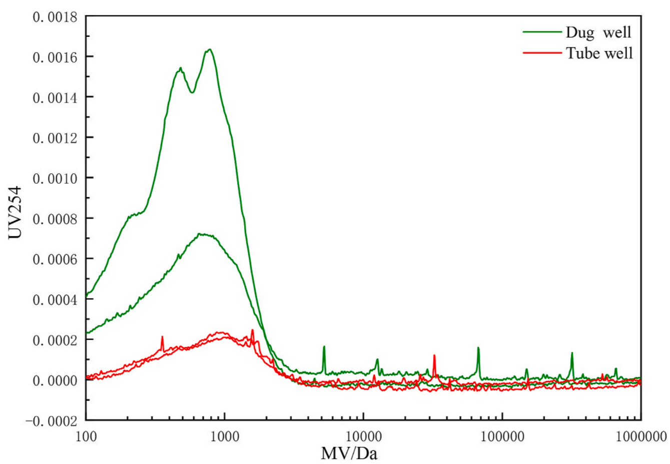

Fig. 5. Molecular weight distribution of groundwater.

20.75% of the variances, respectively, and the PC1 and PC2 variance contribution rates of groundwater in the tube well are 42.41% and 29.55%, respectively. A significant correlation was found between the C1, C2, C3 and TOC concentration; the fluorescence intensity of humic-like material C1 and C2 is negatively correlated with FI and BIX; the fluorescence intensity of component C4 shows a negative correlation with HIX, this indicated that external input (surface runoff) caused the increase of DOM components in groundwater, the fluorescence intensity of DOM in groundwater was mainly caused by humus-like substances and protein material, and the presence of heterogeneous organic matter inhibited the putrefaction. In the groundwater of deep hard rock aquifer, a significant correlation was found between the concentration of TOC and fluorescence intensity of CII, and the fluorescence intensity of component CII is negatively correlated with HIX. This result might indicate that the DOM fluorescence intensity is mainly caused by the protein-like substances produced by the activities of the microbial community, which were consistent with the result in Fig. 4. Therefore, the DOM in tube well groundwater mainly comes from microbial community activities.

PCA results and correlation analysis show (Table A2and Table A3) that in dug well, significant correlation was found between the ions and TOC concentration, C1, C2, C3 (***p* < *0.01***), indicating that TOC of both the concentration and fluorescence characteristics are affected by the chemical composition of groundwater, and high concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-} could promote the formation of protein-like and humic-like components. Inorganic ions and organic matter enter the groundwater along with surface runoff during the wet season, causing the increase of total dissolved solids, meanwhile, the DOM can provide substrates for microorganism. In tube well, the above characteristics are not obvious. TOC only has a significant positive correlation with hardness, Na^{+} and HCO_3^{-} (***p* < *0.05***), and pH has a significant negative correlation with component CII (***p* < *0.05***), indicating that higher pH inhibits the activity of microorganism. Some researches has shown that DOM in the aquatic environment is rich in carboxyl alicyclic molecules, except the presence of a large number of benzene rings, humic acids also contain a large number of carboxyl groups, alcohol groups and phenyl groups, while fulvic acids contain a large amount of oxygen functional group and have better hydrophilicity (McDonough et al., 2020). These functional groups can ionize in water and produce chemical effects, and humus can form complexes with metal ions. In groundwater from dug well, a significant correlation was found between metal ions and humus-like components C1 and C2 in DOM (***p* < *0.01***). Humic acids usually have a negative charge, and metal ions in the groundwater can combine with its carboxyl and hydroxyl groups to form a new complex, or between two carboxyl groups, and can also form a complex with a carboxyl group, which increase the complexity of DOM in the water and thus affect the migration and transformation of DOM (Specht et al., 2000). However, the significant negative correlation between pH and component CII in the tube well groundwater indicated that higher pH value may inhibit the production of protein like fluorescent substances to a certain extent. Hemingway

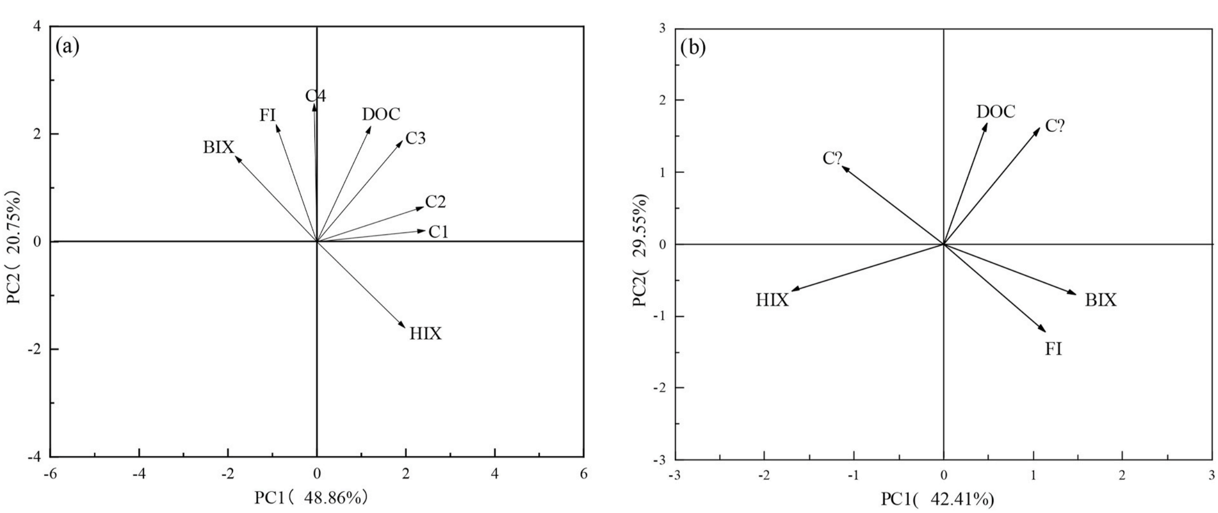

Fig. 6. PCA of samples using Fluorescence component, FI, BIX, HIX and TOC concentration (a: shallow weathered aquifer, dug well; b: hard rock fracture aquifers, tube well).

et al. proposed that the selective preservation mechanism will lead to the decrease of DOM diversity determined by the distribution of C bond strength, and the mineralization interaction caused by microorganisms will increase the DOM diversity (Hemingway et al., 2019). When the fluorescent substances are weak acid or weak alkali, the change of pH in groundwater has a great impact on the fluorescence intensity.

4. Conclusions

This study comprehensively analyses the spatial distribution, composition and characteristics of DOM in groundwater of two aquifers in the NCP during the wet season, and major conclusions are drawn as following:

1. The mean concentrations of hardness and fluoride were 277.37 ± 138.27 and 0.83 ± 0.77 mg/L for dug well water and 312.82 ± 133.20 and 0.69 ± 0.48 mg/L for tube well water respectively, and both exceeded limits of the Sri Lankan Drinking Water Standard (SLS 614–2013; F^- as 1.0 mg/L and Hardness as 250 mg/L) and WHO Guidelines for Drinking Water Quality (4th; F^- as 1.5 mg/L and Hardness as 500 mg/L).
2. The average concentration of TOC in the groundwater of both aquifers is higher than 5.0 mg/L, and in the dug well is higher than that in the tube well.
3. Exogenous inputs such as human activities and rainfall runoff significantly affect the composition of DOM in the dug well. The DOM in the groundwater of the shallow weathered aquifer contains four fluorescent fractions, including terrestrial humic-like substances C1 and C2 of 71.96%, exogenous inputs causing fluorescence peaks (C2) accounting for 38.60%, followed by protein fluorescent substance fractions C3 and heterogeneous organic matter fractions C4, 13.09% and 14.95% respectively.
4. The DOM in the groundwater of the deep hard rock aquifer contains two fractions, with humic-like substances of 69.80%, andprotein-like substances of 30.20%. Endogenous inputs are present in the groundwater of both aquifers, but the autogenous source characteristics of the tube well water are higher than those of the dug well water.
5. The fluorescence intensity of DOM fractions in two groundwater correlates differently with fluorescence indices and ions. In dug well groundwater, DOM fluorescence intensity is mainly caused by humus-like and protein-like substances, whereas in tube well groundwater, DOM fluorescence intensity is mainly caused by protein-like substances produced by microbial community activity.

Future recommendations

These areas should regularly monitor and assess groundwater quality in order to develop management plans to prevent groundwater from contamination and provide safe drinking water.

Credit author statement

Dazhou Hu: Field investigation, Sampling, Experiment, Writing original & revised draft, Formal analysis and curation, **Suresh Inkdika**: Field investigation, Sampling, Formal analysis and curation, **Hui Zhong**: Coordination of field investigation and sampling, **Sujithra K. Weragoda** & **K. B. S. N. Jinadasa** & **Rohan Weerasooriya**: Coordination of field investigation and sampling, **Yuansong Wei**: Conceptualization, Supervision, Funding acquisition, Review, Note: **Dazhou Hu** and **Suresh Indika** contribute to this work equally.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgements

The Joint Research Programme of the National Natural Science Foundation of China (NSFC) and National Science Foundation of Sri Lanka (NSFC-NSF SL) (21861142020); Alliance of International Science Organizations Collaborative Research Program (ANSO-CR-KP-2020-05); Program of China-Sri Lanka Joint Center for Water Technology Research and Demonstration by the Chinese Academy of Sciences (CAS); China-Sri Lanka Joint Center for Education and Research by the CAS.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2022.116877.

References

Baker, A., Curry, M., 2004. Fluorescence of leachates from three contrasting landfills. Water Res. 38, 2605–2613. https://doi.org/10.1016/j.watres.2004.02.027.

Balasubramanya, S., Stifel, D., Horbulyk, T., Kafle, K., 2020. Chronic kidney disease and household behaviors in Sri Lanka: historical choices of drinking water and agrochemical use. Econ. Hum. Biol. 37, 100862 https://doi.org/10.1016/j.ehb.2020.100862.

Botheju, W.S.M., Liyanage, J.A., Kannangara, S.D.P., 2021. The groundwater geochemistry and the human health risk assessment of drinking water in an area with a high prevalence of chronic kidney disease of unknown etiology (CKDu), Sri Lanka. J. Chem. 2021 https://doi.org/10.1155/2021/1755140.

Cammack, W.K.L., Kalff, J., Prairie, Y.T., Smith, E.M., 2004. Fluorescent dissolved organic matter in lakes: relationships with heterotrophic metabolism. Limnol. Oceanogr. 49, 2034–2045. https://doi.org/10.4319/lo.2004.49.6.2034.

Chandrajith, R., Dissanayake, C.B., Ariyarathna, T., Herath, H.M.J.M., Padmasiri, J.P., 2011. Dose-dependent Na and Ca in fluoride-rich drinking water —another major cause of chronic renal failure in tropical arid regions. Sci. Total Environ. 409, 671–675. https://doi.org/10.1016/j.scitotenv.2010.10.046.

Cooray, T., Wei, Y., Zhong, H., Zheng, L., Weragoda, S.K., Weerasooriya, R., 2019. Assessment of groundwater quality in CKDu affected areas of Sri Lanka: implications for drinking water treatment. Int. J. Environ. Res. Publ. Health 16. https://doi.org/10.3390/ijerph16101698.

Dong, H., Qjang, Z., Richardson, S.D., 2019. formation of iodinated disinfection byproducts (I-DBPs) in drinking water: emerging concerns and current issues. Acc. Chem. Res. 52, 896–905. https://doi.org/10.1021/acs.accounts.8b00641.

European Commission, 1998. SCHER Opinion: Derogation on the Drinking Water Directive 98/83/EC. https://health.ec.europa.eu/latest-updates/scher-opinion-derogation-drinking-water-directive-9883ec-2010-04-19_en/. (Accessed 20 November 2022). accessed on.

Foster, T., Priadi, C., Kotra, K.K., Odagiri, M., Rand, E.C., Willetts, J., 2021. Self-supplied drinking water in low- and middle-income countries in the Asia-Pacific. NPJ Clean Water 4, 1–10. https://doi.org/10.1038/s41545-021-00121-6.

Gunarathna, S., Gunawardana, B., Jayaweera, M., Manatunge, J., Zoysa, K., 2018. Glyphosate and AMPA of agricultural soil, surface water, groundwater and sediments in areas prevalent with chronic kidney disease of unknown etiology, Sri Lanka. J. Environ. Sci. Heal. Part. B, Pestic. food Contam. Agric. wastes 53, 729–737. https://doi.org/10.1080/03601234.2018.1480157.

Gupta, S.D., Mukherjee, A., Bhattacharya, J., 2018. Groundwater of South Asia. Springer Hydrogeol, pp. 247–255.

Haddad, M., Ohkame, T., Bérubé, P.R., Barbeau, B., 2018. Performance of thin-film composite hollow fiber nanofiltration for the removal of dissolved Mn, Fe and NOM from domestic groundwater supplies. Water Res. 145, 408–417. https://doi.org/10.1016/j.watres.2018.08.032.

Hemingway, J.D., Rothman, D.H., Grant, K.E., Rosengard, S.Z., Eglinton, T.I., Derry, L.A., Galy, V.V., 2019. Mineral protection regulates long-term global preservation of natural organic carbon. Nature 570, 228–231. https://doi.org/10.1038/s41586-019-1280-6.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J.M., Parlanti, E., 2009. Properties of fluorescent dissolved organic matter in the Gironde Estuary. Org. Geochem. 40, 706–719. https://doi.org/10.1016/j.orggeochem.2009.03.002.

Imbulana, S., Oguma, K., 2021. Groundwater as a potential cause of Chronic Kidney Disease of unknown etiology (CKDu) in Sri Lanka: a review. J. Water Health 19, 393–410. https://doi.org/10.2166/wh.2021.079.

Indika, S., Wei, Y., Hu, D., Ketharani, J., Ritigala, T., Cooray, T., Hansima, M.A.C.K., Makehelwala, M., Jinadasa, K.B.S.N., Weragoda, S.K., Weerasooriya, R., 2021. Evaluation of performance of existing RO drinking water stations in the North

central Province, Sri Lanka. Membranes 11. https://doi.org/10.3390/membranes11060383.
Indika, S., Wei, Y., Hu, D., Ketharani, J., Ritigala, T., Cooray, T., Hansima, M.A.C.K., Makehelwala, M., Jinadasa, K.B.S.N., Weragoda, S.K., Weerasooriya, R., 2022. Groundwater-based drinking water supply in Sri Lanka: status and perspectives. Water 1–24. https://doi.org/10.3390/w14091428.
Jayasumana, C., Fonseka, S., Fernando, A., Jayalath, K., Amarasinghe, M., Siribaddana, S., Gunatilake, S., Paranagama, P., 2015a. Phosphate fertilizer is a main source of arsenic in areas affected with chronic kidney disease of unknown etiology in Sri Lanka. SpringerPlus 4. https://doi.org/10.1186/s40064-015-0868-z.
Jayasumana, C., Paranagama, P., Agampodi, S., Wijewardane, C., Gunatilake, S., Siribaddana, S., 2015b. Drinking well water and occupational exposure to herbicides is associated with chronic kidney disease. In: Padavi-Sripura, Sri Lanka. Environ. Heal, p. 14. https://doi.org/10.1186/1476-069X-14-6.
Kellerman, A.M., Dittmar, T., Kothawala, D.N., Tranvik, L.J., 2014. Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. Nat. Commun. 5, 1–8. https://doi.org/10.1038/ncomms4804.
Kent, F.C., Montreuil, K.R., Stoddart, A.K., Reed, V.A., Gagnon, G.A., 2014. Combined use of resin fractionation and high performance size exclusion chromatography for characterization of natural organic matter. J. Environ. Sci. Health - Part A Toxic/Hazard. Subst. Environ. Eng. 49, 1615–1622. https://doi.org/10.1080/10934529.2014.950926.
Komatsu, K., Onodera, T., Kohzu, A., Syutsubo, K., Imai, A., 2020. Characterization of dissolved organic matter in wastewater during aerobic, anaerobic, and anoxic treatment processes by molecular size and fluorescence analyses. Water Res. 171 https://doi.org/10.1016/j.watres.2019.115459.
Kulathunga, M.R.D.L., Ayanka Wijayawardena, M.A., Naidu, R., Wijeratne, A.W., 2019. Chronic kidney disease of unknown aetiology in Sri Lanka and the exposure to environmental chemicals: a review of literature. Environ. Geochem. Health 41, 2329–2338. https://doi.org/10.1007/s10653-019-00264-z.
Lavonen, E.E., Kothawala, D.N., Tranvik, L.J., Gonsior, M., Schmitt-Kopplin, P., Köhler, S.J., 2015. Tracking changes in the optical properties and molecular composition of dissolved organic matter during drinking water production. Water Res. 85, 286–294. https://doi.org/10.1016/j.watres.2015.08.024.
Lawson, M., Polya, D.A., Boyce, A.J., Bryant, C., Ballentine, C.J., 2016. Tracing organic matter composition and distribution and its role on arsenic release in shallow Cambodian groundwaters. Geochem. Cosmochim. Acta 178, 160–177. https://doi.org/10.1016/j.gca.2016.01.010.
Li, X.-F., Mitch, W.A., 2018. Drinking water disinfection byproducts (DBPs) and human health effects: multidisciplinary challenges and opportunities. Environ. Sci. Technol. 52, 1681–1689. https://doi.org/10.1021/acs.est.7b05440.
Li, W.-T., Chen, S.-Y., Xu, Z.-X., Li, Y., Shuang, C.-D., Li, A.-M., 2014. Characterization of dissolved organic matter in municipal wastewater using fluorescence PARAFAC analysis and chromatography multi-excitation/emission scan: a comparative study. Environ. Sci. Technol. 48, 2603–2609. https://doi.org/10.1021/es404624q.
Lipczynska-Kochany, E., 2018. Effect of climate change on humic substances and associated impacts on the quality of surface water and groundwater: a review. Sci. Total Environ. 640–641, 1548–1565. https://doi.org/10.1016/j.scitotenv.2018.05.376.
Liyanage, D.N.D., Diyabalanage, S., Dunuweera, S.P., Rajapakse, S., Rajapakse, R.M.G., Chandrajith, R., 2022. Significance of Mg-hardness and fluoride in drinking water on chronic kidney disease of unknown etiology in Monaragala, Sri Lanka. Environ. Res. 203 https://doi.org/10.1016/j.envres.2021.111779.
Ma, Y., Mao, R., Li, S., 2021. Hydrological seasonality largely contributes to riverine dissolved organic matter chemical composition: insights from EEM-PARAFAC and optical indicators. J. Hydrol. 595 https://doi.org/10.1016/j.jhydrol.2021.125993.
Makehelwala, M., Wei, Y., Weragoda, S.K., Weerasooriya, R., Zheng, L., 2019. Characterization of dissolved organic carbon in shallow groundwater of chronic kidney disease affected regions in Sri Lanka. Sci. Total Environ. 660, 865–875. https://doi.org/10.1016/j.scitotenv.2018.12.435.
McDonough, L.K., Rutlidge, H., O'Carroll, D.M., Andersen, M.S., Meredith, K., Behnke, M.I., Spencer, R.G.M., McKenna, A.M., Marjo, C.E., Oudone, P., Baker, A., 2020. Characterisation of shallow groundwater dissolved organic matter in aeolian, alluvial and fractured rock aquifers. Geochem. Cosmochim. Acta 273, 163–176. https://doi.org/10.1016/j.gca.2020.01.022.
McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46, 38–48. https://doi.org/10.4319/lo.2001.46.1.0038.
Mian, H.R., Hu, G., Hewage, K., Rodriguez, M.J., Sadiq, R., 2018. Prioritization of unregulated disinfection by-products in drinking water distribution systems for human health risk mitigation: a critical review. Water Res. 147, 112–131. https://doi.org/10.1016/j.watres.2018.09.054.
National water supply and drainage board, 2013. Piped Water Supply Connected Coverage as at End of Year - 2018 District. http://www.waterboard.lk/web/index.php?option=com_content&view=article&id=78&Itemid=425&lang=en. (Accessed 20 November 2022). accessed on.
National water supply and drainage board, 2019. Progress Status on Key Result Areas (KRAs) of the Corporate Action Plan as at End 1 St Quarter 2019 Goal 1 - Increase the Water Supply and Sanitation Coverage Goal 2 - Improve Business Efficiency Progress Status on Key Result Areas (KRAs) of the Corpo, Groundwater Development and Management: Issues and Challenges in South Asia. https://doi.org/10.1007/978-3-319-75115-3.
National water supply and drainage board, 2020. Progress Status on Key Result Areas (KRAs) of the Corporate Action Plan as at End 1 St Quarter 2019 Goal 1 - Increase the Water Supply and Sanitation Coverage Goal 2 - Improve Business Efficiency Progress Status on Key Result Areas (KRAs) of the Corpo. http://www.waterboard.lk/web/index.php?option=com_content&view=article&id=78&Itemid=425&lang=en. (Accessed 20 November 2022). accessed on.
Pathak, P., Ghosh, P., Banerjee, S., Chatterjee, R.S., Muzakkira, N., Sikdar, P.K., Ghosal, U., Liang, M.-C., Meeran, K., 2022. Relic surface water (clay-pore water) input triggers arsenic release into the shallow groundwater of Bengal aquifers. J. Earth Syst. Sci. 131 https://doi.org/10.1007/s12040-022-01819-y.
Ranasinghe, N., Kruger, E., Chandrajith, R., Tennant, M., 2018. Groundwater fluoride in Sri Lanka: opportunities to mitigate the risk at maximum contaminant level. Ceylon Med. J. 63, 174–179. https://doi.org/10.4038/cmj.v63i4.8768.
Regan, S., Hynds, P., Flynn, R., 2017. An overview of dissolved organic carbon in groundwater and implications for drinking water safety. Hydrogeol. J. 25, 959–967. https://doi.org/10.1007/s10040-017-1583-3.
Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. Mutat. Res. Mutat. Res. 636, 178–242. https://doi.org/10.1016/j.mrrev.2007.09.001.
Rubasinghe, R., Gunatilake, S.K., Chandrajith, R., 2015. Geochemical characteristics of groundwater in different climatic zones of Sri Lanka. Environ. Earth Sci. 74, 3067–3076. https://doi.org/10.1007/s12665-015-4339-1.
Sood, A., Manthrithilake, H., Siddiqui, S., Rajah, A., Pathmarajah, S., 2015. Managing shallow aquifers in the dry zone of Sri Lanka. Environ. Monit. Assess. 187 https://doi.org/10.1007/s10661-015-4584-5.
Specht, C.H., Kumke, M.U., Frimmel, F.H., 2000. Characterization of NOM adsorption to clay minerals by size exclusion chromatography. Water Res. 34, 4063–4069. https://doi.org/10.1016/S0043-1354(00)00148-2.
Stedmon, C.A., Markager, S., Bro, R., 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Mar. Chem. 82, 239–254. https://doi.org/10.1016/S0304-4203(03)00072-0.
Tang, F., Hu, H.-Y., Sun, L.-J., Sun, Y.-X., Shi, N., Crittenden, J.C., 2016. Fouling characteristics of reverse osmosis membranes at different positions of a full-scale plant for municipal wastewater reclamation. Water Res. 90, 329–336. https://doi.org/10.1016/j.watres.2015.12.028.
United Nations, 2022. The United Nations World Water Development Report 2022: Groundwater: Making the Invisible Visible. https://www.undp.org/publications/united-nations-world-water-development-report-2022-groundwater-making-invisible-visible/. (Accessed 20 November 2022). accessed on.
Wasana, H.M.S., Aluthpatabendi, D., Kularatne, W.M.T.D., Wijekoon, P., Weerasooriya, R., Bandara, J., 2016. Drinking water quality and chronic kidney disease of unknown etiology (CKDu): synergic effects of fluoride, cadmium and hardness of water. Environ. Geochem. Health 38, 157–168. https://doi.org/10.1007/s10653-015-9699-7.
Wickramarathna, S., Balasooriya, S., Diyabalanage, S., Chandrajith, R., 2017. Tracing environmental aetiological factors of chronic kidney diseases in the dry zone of Sri Lanka—a hydrogeochemical and isotope approach. J. Trace Elem. Med. Biol. 44, 298–306. https://doi.org/10.1016/j.jtemb.2017.08.013.
Wu, Y., Wang, Q., Tong, X., et al., 2020. The Evaluation methods and index system of reverse osmosis membrane fouling potential of the influent in wastewater reclamation process: a review. Environ. Eng. 38 (3), 51–57. https://doi.org/10.13205/j.hjgc.202003009, 109.
Young, S.M., Pitawala, A., Ishiga, H., 2011. Factors controlling fluoride contents of groundwater in north-central and northwestern Sri Lanka. Environ. Earth Sci. 63, 1333–1342. https://doi.org/10.1007/s12665-010-0804-z.
Zeng, X., He, W., Guo, H., Shi, Q., Zheng, Y., Vithanage, M., Hur, J., 2022. Recognizing the groundwater related to chronic kidney disease of unknown etiology by humic-like organic matter. NPJ Clean Water 5. https://doi.org/10.1038/s41545-022-00151-8.
Zhang, Y., Liu, M., Qin, B., Feng, S., 2009. Photochemical degradation of chromophoric-dissolved organic matter exposed to simulated UV-B and natural solar radiation. Hydrobiologia 627, 159–168. https://doi.org/10.1007/s10750-009-9722-z.