

THE CHARACTERISTICS AND DISTRIBUTION OF DEEP GROUNDWATER IN DJIBOUTI

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ABSTRACT: Djibouti is one of the most arid areas in the world and rivers are not formed regularly in this region. So, groundwater has been used as the main water resource for humans and livestock. Therefore, necessary to understand the state of groundwater in terms of utilizing of sustainable water resources in this country. In this study, we measured ion contents (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_2^- , Br^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , HCO_3^-) in groundwater using ion chromatography, and analyzed characteristics groundwater quality using by multivariate analysis based upon groundwater quality with stable isotope ratio of hydrogen and oxygen and tritium concentrations, with reference to their locations and examined the distribution analysis using GIS data of watershed maps. As a result of groundwater quality measurements, the most of groundwater samples in this study mixed with seawater or hot spring water and fossil seawater. And the concentration of NO_3^- in groundwater was over 50 mgL^{-1} at 4 sites. In addition, as a result of the hierarchical cluster analysis, groundwater in this study showed different chemical characteristics even in the same watershed. As results of this study, although some important data of groundwater quality in Djibouti has been obtained, it is considered necessary to study in groundwater dating and water stable isotope ratios more wide area in order to understand its complex groundwater distribution and water quality characteristics.

Keywords: Ion chromatography, Arid area, Water resources, GIS, Stable isotope ratio

1. INTRODUCTION

Djibouti is located at the northeastern end of the African continent, called the "Horn of Africa", where the climate is extremely arid belonging to the Hot Desert or Semi-arid Climate of BWh in the Köppen classification. The climate of this region shows two seasons, a cold (winter) season from October to April and a warm season (summer) from May to September. Winters are relatively cool ($20\text{--}30^\circ\text{C}$) due to the northeast trade winds blowing from the Gulf of Aden, while in summer, the equatorial westerly winds blow over the mountains from Ethiopia and Somalia, which further enhances the hot and dry climate ($35\text{--}45^\circ\text{C}$) due to the foehn phenomenon [1]. As a result, precipitation is extremely low (c.a. $150 \text{ mm}^{\text{yr}^{-1}}$), in this region and only occurs irregularly short- time localized rainfall. Hence, rivers are not formed regularly in this region, and groundwater has been used as the main water resource for humans and livestock [2].

In recent years, however, as the lifestyle of nomads as most of the population living in the suburbs has shifted from pastoralism to a combined agro-pastoralism [3][4], the increased demand for groundwater resources, mainly for irrigation, and the pollution of groundwater quality due to rapid social development have become problems [2][5]. Previous study using nitrogen stable isotope ratio and oxygen stable isotope ratio of nitrate in groundwater at Djibouti indicated that the high

concentrations of nitrate in groundwater may have originated from livestock manure used mainly as organic fertilizer in agricultural activities [6]. Thus, groundwater is a very important resource in arid regions [7][8], but more extensive groundwater quality data updates are awaited to understand the state of groundwater quality resources, which change significantly with social development.

With this background, groundwater studies in Djibouti have been intensified in recent years with respect to groundwater quality, age, and flow systems. In Tadjoura area, the northern part of the country, previous study using stable isotope and radioisotope analyses to estimate groundwater recharge systems and ages [2]. The results indicate that the groundwater in the area is mixed with different geological formations, such as rhyolite, basalt, and alluvium, indicating that the area may have a complex hydrogeological system. In Alta area, the southern part of this country, groundwater in this region could be classified into three groups according to groundwater quality and indicated that it may be extensively influenced by seawater mixing [5].

However, there is still a lack of data to understand the state and distribution of groundwater quality in Djibouti, which varies according to anthropogenic or natural factors [9] In press [10] [11]. Therefore, from the perspective of sustainable use of limited water resources in this country with extremely low precipitation, it is necessary to

further accumulate a basic database on the quality and distribution of groundwater in Djibouti, which flows through a complex geological structure, and to understand the latest groundwater conditions.

In this study, we analyzed characteristics of groundwater quality using multivariate analysis and hierarchical cluster analysis based upon ion structure (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_2^- , Br^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , HCO_3^-) with stable isotope ratio of hydrogen and oxygen (δD and $\delta^{18}\text{O}$), and tritium contents, and distribution analysis by watershed mapping using GIS data to understand the characteristics and distribution of groundwater quality over a wide area in Djibouti.

2. RESEARCH SIGNIFICANCE

This study provides very important data on the distribution of groundwater quality in Djibouti, a country with very little precipitation and limited water resources, by analyzing and classifying groundwater quality over a wide area. Based on the results of this study, the accumulation of data on groundwater quality in this country will greatly contribute to the sustainable management and use of groundwater resources in the context of rapid economic development.

3. MATERIALS & METHODS

3.1 Sites Description

We selected 16 deep wells from 4 areas in Djibouti: Djibouti city area, Arta, Ali-Sabieh, and Dikihil. Djibouti city facing the Gulf of Tadjoura is the most urbanized area in Djibouti. More than 60% of the nation is concentrated in this area. Arta area has one of the largest wadis in the country called Ambouli Wadi, and most of the 250 wells are drilled along the wadi. Ali-Sabieh area is close to Somalia and has over 300 wells drilled. Dikihil area is close to Ethiopia and has the second largest population in Djibouti. Most of the about 270 wells are concentrated in densely populated areas, and some wells are in suburban areas.

3.2 Collection of Groundwater Samples

We collected groundwater samples from 16 deep wells (100-200m depth) in Feb. 2020 (Table 1). All groundwater samples were filtered using a $0.22 \mu\text{m}$ syringe filter and put into a 100 mL plastic bottle. All the bottle samples were refrigerated until analysis in Japan.

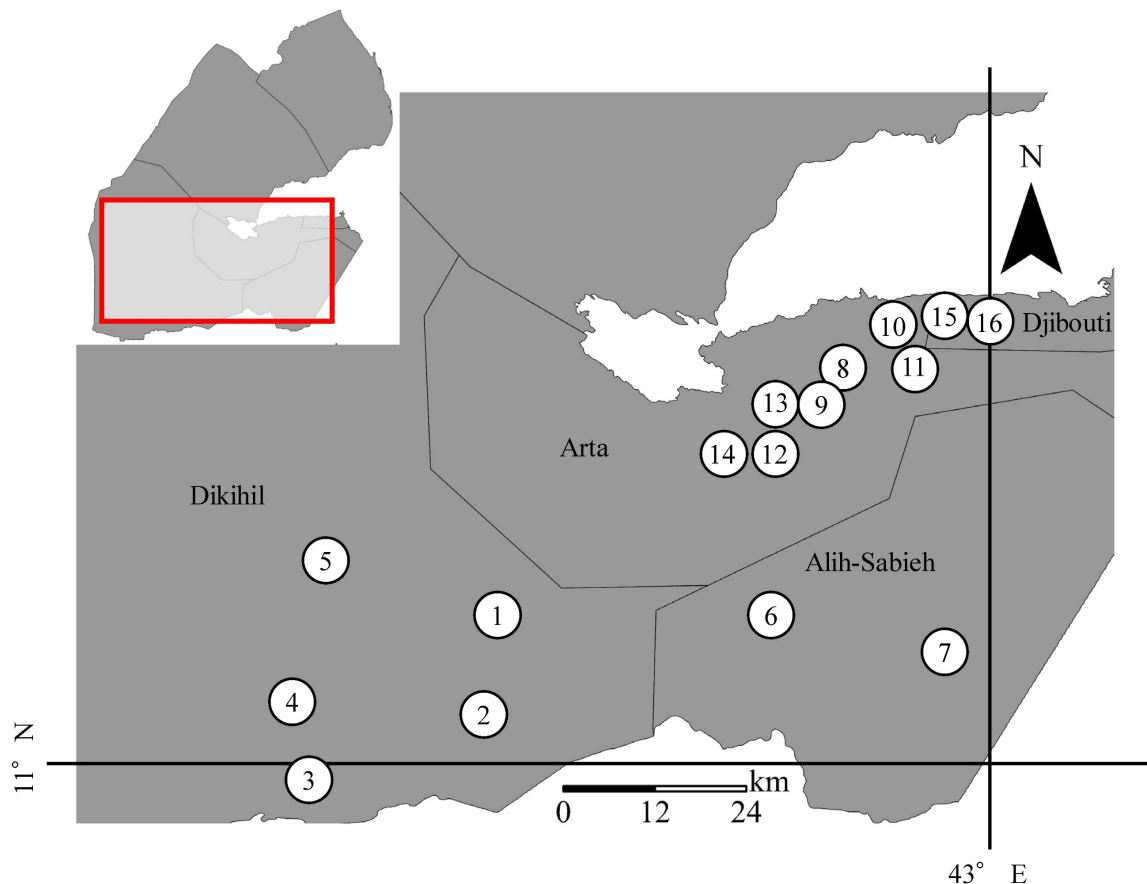


Fig. 1 Location of sampling points of the groundwater samples in Djibouti.

Table 1. Details of collection points of the groundwater samples.

No.	District	Latitude	Longitude
1	Dikhil	N11°12'23.8"	E42°25'54.6"
2		N11°05'10.6"	E42°24'25.9"
3		N11°16'09.1"	E42°13'45.5"
4		N11°06'04.68"	E42°10'49.43"
5		N11°00'13.32"	E42°12'27.35"
6	Alih-Sabieh	N11°12'42.6"	E42°45'19.0"
7		N11°09'40.2"	E42°57'49.6"
8	Arta	N11°26'23.6"	E42°48'12.6"
9		N11°29'16.4"	E42°50'19.0"
10		N11°31'22.1"	E42°54'45.0"
11		N11°31'22.1"	E42°54'45.0"
12		N11°26'15.79"	E42°47'1.11"
13		N11°26'14.86"	E42°46'57.16"
14		N11°25'24.24"	E42°45'37.59"
15	Djibouti	N11°33'9.95"	E42°57'47.24"
16		N11°32'42.35"	E42°43'00.72"

3.3 Ion Structures of Groundwater Quality

Ion concentrations of groundwater were measured by ion chromatography (Shimadzu; HIC-SP) for 6 cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and 7 anions (F^- , Cl^- , NO_2^- , Br^- , SO_4^{2-} , NO_3^- , PO_4^{3-}). HCO_3^- concentrations were measured at pH 4.8 and by the alkalinity titration method. Water temperature (WT), pH, electric conductivity (EC), oxidation-reduction potential (ORP), and dissolved oxygen (DO) in groundwater samples were measured at study sites using portable instruments (MM-42DP; TOADKK) at study points. The characteristics of ion structure in the groundwater samples were classified by piper [12] and hexa-diagrams using equivalent concentrations of ion components measured by ion chromatography.

3.4 Chemical Characteristics of Groundwater

The chemical characteristics of groundwater were classified by hierarchical cluster analysis (Ward's method). These analyses were based upon equivalent concentrations of 14 major ion components (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- ,

NO_2^- , Br^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , HCO_3^-), EC, hydrogen, and oxygen stable isotope ratio (δD and $\delta^{18}\text{O}$) and tritium concentrations [9]. Principal component analysis (PCA) using the values of EC, DO, ORP, pH, water temperature (WT), Na^+ , Ca^{2+} , Cl^- , Mg^{2+} , SO_4^{2-} .

3.5 Watershed Map with Study Points

Watershed map of Djibouti was sourced from database of Ministry of Agriculture, Water, Fishery and Livestock in Charge of Marine Resources of Djibouti. All study points were plotted on this map using Arc GIS and indicated by classification using hierarchical cluster analysis.

4 RESULTS

4.1 Ion Structures of Groundwater

The characteristics of the groundwater quality composition were classified by piper and hexa-diagrams based upon the value of ionic constituents in the groundwater. According to the piper diagram (Fig.2), the groundwater in this study was classified into two main types. All groundwater of Djibouti City and Ali-Sabieh area were classified as Na-Cl type, while most of groundwater of Dikhil and 3 points of Arta were classified as Na- HCO_3 type.

However, Point 1 in Dikhil and Point 9, 10, 12 and 11 in Arta were classified as Na-Cl type. According to the hexa-diagram (Fig. 3), the groundwater in this study was classified into two

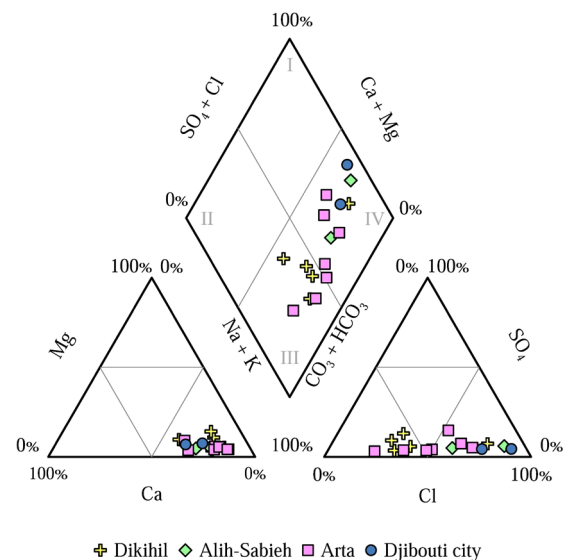


Fig. 2 A piper diagram of groundwater samples in Djibouti. Greek numeral shows type of groundwater quality. I: Ca- SO_4 II: Ca- HCO_3 III: Na- HCO_3 IV: Na-Cl.

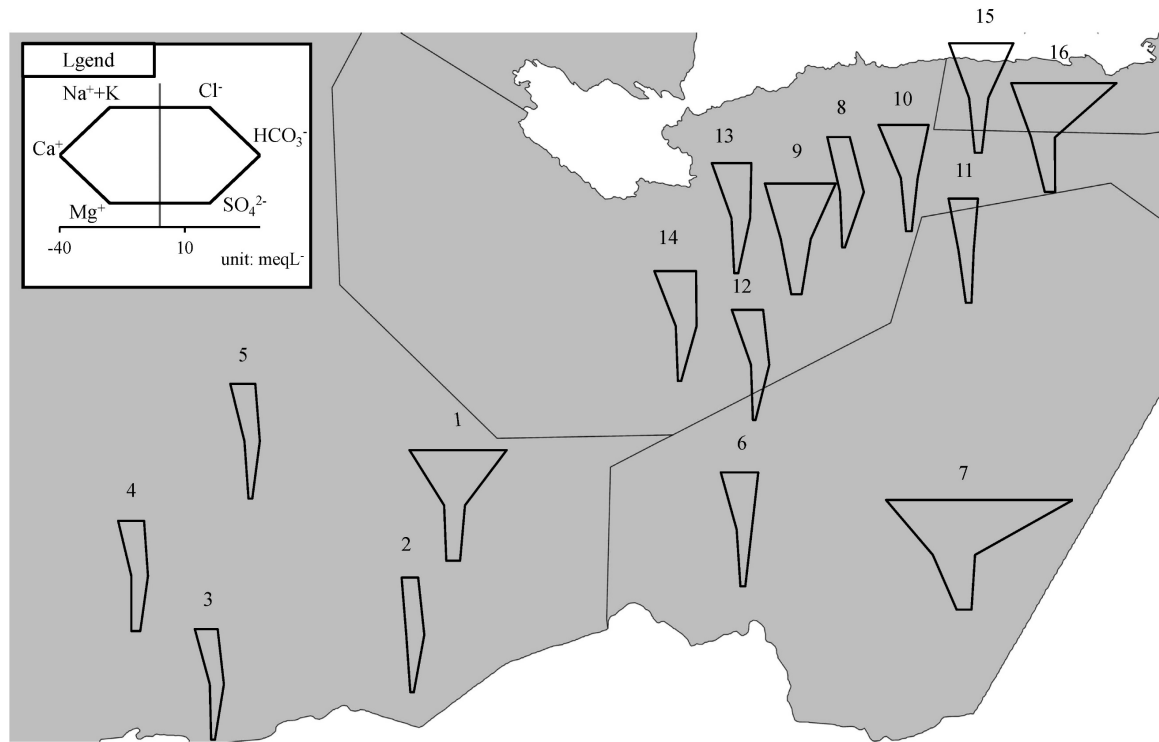


Fig.3 Hexa-diagram of groundwater samples on study sites map in Djibouti.

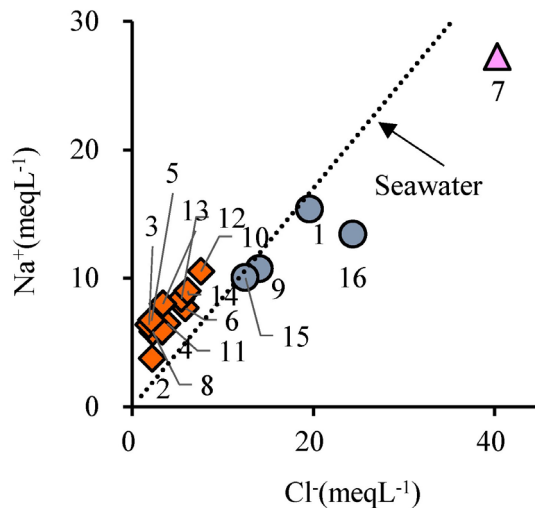


Fig. 4 Relationship between concentrations of Cl^- and Na^+ in groundwater samples. The black dot line shows Cl^- and Na^+ ratio in seawater. Each symbol shows cluster based on clustering analysis as Fig. 6. Dimond symbols are cluster1, circle symbols are cluster 2, and triangle symbol is cluster 3.

main types of water quality composition. In Djibouti area, located on the coast, and in Ali-Sabieh area, Na-Cl type was predominant. On the other hand, in Dikihil area, located furthest from the

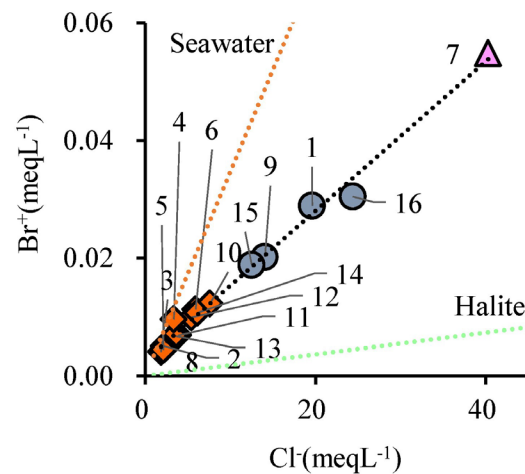


Fig. 5 Relationship between concentrations of Cl^- and Br^- in groundwater samples. The black dot line shows Cl^- and Br^- ratio in seawater and halite. Each symbol shows cluster based on clustering analysis as Fig. 6. Dimond symbols are cluster1, circle symbols are cluster 2, and triangle symbol is cluster 3.

sea, and in Arta area, Na- HCO_3 type was predominant. The equivalent concentration ratio of Cl^- to Na^+ in groundwater was richer than in seawater ($\text{Cl}^- : \text{Na}^+ = 1 : 0.85$) at most of the study sites (Fig. 4). The equivalent concentration ratio of Cl^- to Br^- in all groundwater samples was plotted on seawater between halite (Fig. 5).

Table 2, DO, EC, ORP, water temperature, pH and concentrations of NO_3^- in groundwater samples.

No.	DO	EC	WT	pH	NO_3^-
	mgL^{-1}	mScm^{-1}	$^{\circ}\text{C}$		mgL^{-1}
1	6.08	2.78	31	7.87	50.9
2	5.68	0.84	37	7.98	24.4
3	6.40	0.91	32	8.28	20.1
4	5.47	1.20	36	8.12	94.2
5	6.43	1.00	32	8.52	10.0
6	6.90	1.26	32	8.35	47.2
7	5.90	4.42	32	7.34	39.1
8	6.50	0.91	38	7.84	14.5
9	6.85	2.15	34	7.39	63.3
10	6.16	1.48	30	7.99	37.3
11	2.61	1.16	31	7.86	34.5
12	5.32	1.28	39	7.64	22.4
13	6.07	1.08	37	8.14	16.1
14	6.08	1.29	36	8.30	16.3
15	3.71	1.93	52	7.45	38.3
16	5.87	2.83	48	7.77	61.1

Table 2 shows the values of EC, DO, ORP, pH, and water temperature of groundwater collected at study sites. The values of EC showed high at all sites (0.84 to 6.90 mScm^{-1}), there was no significant correlation with elevation or distance from the ocean. Water temperature was over 30°C at all sites, with a maximum of 52°C . There was a significant negative correlation between water temperature and elevation. pH was around 7.5 , maximum was 8.52 with no significant correlation with water temperature. DO ranged from 2.61 to 6.90 mgL^{-1} . The concentration of NO_3^- in groundwater was over 50 mgL^{-1} at 4 sites (Table2). The concentrations of HCO_3^- in groundwater were high at all study sites.

4.2 Chemical Characteristics of Groundwater

Hierarchical cluster analysis using values of 14 major dissolved ions and EC and DO, all groundwater collected at study sites were classified into three clusters at a height of 20. At Cluster 3,

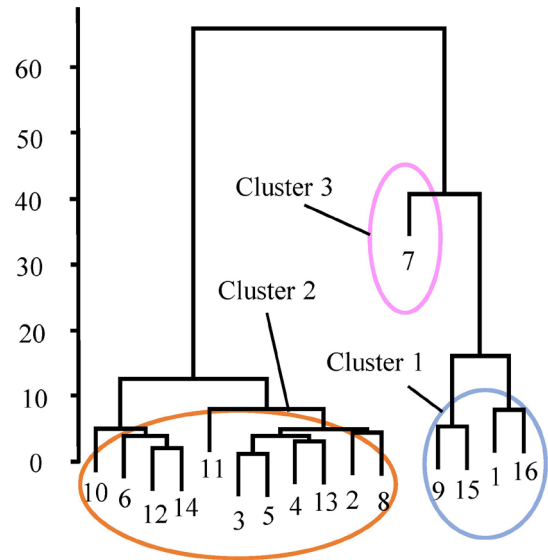


Fig. 6 Hierarchical cluster analysis of groundwater samples in Djibouti. The numeral of x axis shows sampling points.

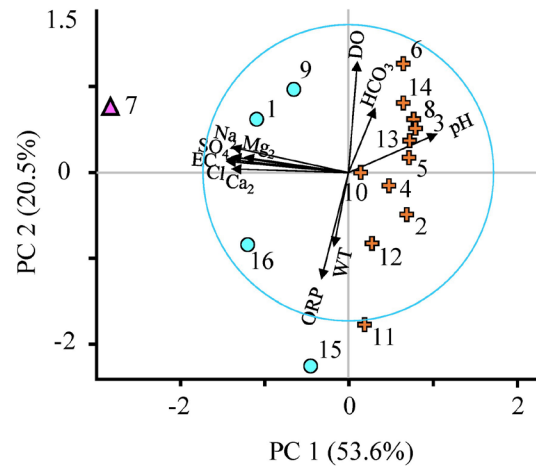


Fig. 7 Principal component analysis (PCA) using the values of EC, DO, ORP Water temperature (WT), pH, Na^+ , Ca^{2+} , Cl^- , Mg^{2+} , SO_4^{2-} . Circle symbols are cluster 1, cross-symbols are cluster 2, and triangle symbol is cluster 3.

only Point 7 was classified (Fig. 6). As a result of PCA, the factorial axis 1 represented 53.6 % of the variance and groundwater classified in Cluster 2 was characterized by positive factor in pH, DO and HCO_3^- . The factorial axis 2 represented 20.5 % of the variance and groundwater classified in Cluster 1 and 3 were characterized by positive factor in EC, Na^+ , Ca^{2+} , Cl^- , Mg^{2+} , SO_4^{2-} and negative factor in ORP, water temperature (Fig. 7).

4.3 Watershed Map with Study Points

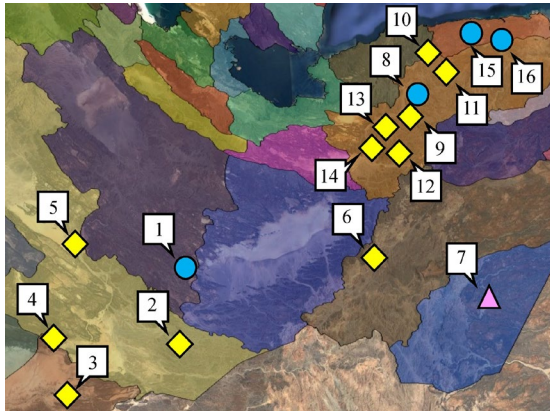


Fig. 8 Study site with watershed map of Djibouti. The area divided by color gradients shows watershed (source: Ministry of Agriculture, Water, Fishery and Livestock in Charge of Marine Resources of Djibouti). Diamond symbols are cluster 1, circle symbols are cluster 2, and triangle symbol is cluster 3.

Fig. 8 showed study points on watershed map of Djibouti. In the Dikihil area, study points were distributed in 3 watersheds. Points 3 and 4 were in the same watershed and were also classified in the same cluster, Points 2 and 5 were also in the same. Point 1 was classified in a different cluster from other four points, and its watershed was also different from the other four sites. Although all study points in Arta and Djibouti area were distributed in same watershed, these points classified two clusters. In Ali-Sabieh area, study points were distributed two watersheds.

5 DISCUSSIONS

5.1 Ion Structures of Groundwater Quality

According to Fig. 2 and Table 2, various factors such as mixing with seawater, weathering of bedrocks, and leaching of inorganic constituents from minerals may be influenced the differences in values of EC in groundwater (0.84 to 6.90 mScm^{-1}). In general, it has been reported that groundwater quality classified as Na-Cl type is likely affected by mixing with fossil seawater confined in the underground [13]. Therefore, the mixing of fossil seawater and groundwater was considered at the study sites classified as Na-Cl type groundwater. In this study, piper diagram classified groundwater quality into four types to estimate the origin of ions in groundwater. Ca-SO₄ type (I): This type contains hydrothermal water and fossil seawater. Ca-HCO₃ (II): This type is the commonly found in shallow groundwater. Na-HCO₃ (III): This type is commonly found in deep groundwater with very old age. Na-Cl type (IV): This type is commonly found in seawater and hot spring water. Therefore, in this

study, groundwater classified as Na-HCO₃ type may have been in deep stagnation for a long time, and groundwater classified as Na-Cl type may be mixed with seawater or hot spring water [14]. The relationship between the equivalent concentration ratios of Na⁺ and Cl⁻ suggests possibility that groundwater at most of study sites may be affected by sodium leaching from volcanic rocks and by mixing seawater and fossil seawater [4][15].

5.2 Origin of NO₃⁻ in Groundwater

According to Fig. 3, the concentration of NO₃⁻ in groundwater was over 50 mgL^{-1} at 4 sites. Generally, NO₃⁻ in groundwater may be derived from fertilizers, livestock manure, domestic wastewater, and soil organic matter. In particular, it has been reported that high concentrations of NO₃⁻ in groundwater in arid areas are likely to originate from natural soil sources [16] [6]. But most of the wells in study sites are also used by local nomads as drinking water for their livestock too, it is possible that NO₃⁻ in the groundwater was also originated from livestock manure.

5.3 Chemical Characteristics of Groundwater

The results of the hierarchical cluster analysis (Fig. 6) indicated that Point 7 in the Ali-Sabieh area has different characteristics compared to the other study points. The results of the principal component analysis also indicated the characteristics were positive factors in EC, Na⁺, Ca²⁺, Cl⁻, Mg²⁺, and SO₄²⁻. This suggest that inorganic constituents into the groundwater primarily cause to weathering of the basalts and seawater intrusion [17]. Groundwater at Points 1, 9, 15, and 16 were classified in the same Cluster 1 in the hierarchical cluster analysis, and the principal component analysis results also characterized groundwater at these Points by similar factors. But there was difference between groundwater at Points 1, 9 and Points 15, 16 based on water temperature and ORP. The water temperature of groundwater at Points 15 and 16 was approximately 50°C , and they were plotted as Type IV in piper diagram, suggesting that these groundwaters was influenced by the mixing of hot spring water and seawater [18]. Groundwater classified as Cluster 2 was characterized primarily by positive factors in pH and HCO₃⁻. The high concentrations of HCO₃⁻ detected in groundwater are reported to be supplied from soil [19]. Therefore, high concentrations of HCO₃⁻ means groundwater age is old. So, groundwater at these study points were likely to have been in residence for a long time. However, point 11 was plotted in a different direction than the groundwater in the same cluster 2. This was mainly due to positive water temperature and ORP factors, with a negative

direction for the HCO_3^- factor. This result suggests that the groundwater at this site is relatively young and may have been mixed with hot spring water [18].

5.4 Relationships between Cluster of Groundwater and Watersheds

According to Fig. 8, we found a variety of groundwater quality in same watershed. Distribution of watersheds of Djibouti are characterized by the Great Rift Valley that crosses the country. At Arta and Djibouti City area included more than half of the study points, they were plotted within the same watershed. Cluster analysis also showed that 6 of the 9 sites were classified in the same cluster, suggesting that groundwater quality in eastern Djibouti is characterized by inorganic component runoff due to weathering of basaltic rocks. However, the characteristics of groundwater quality was not unitary even in the same watershed, since there are groundwaters influenced by hot springs or geothermal waters, such as at Points 11 and 12. On the other hand, groundwater plotted in different watershed in Dikihil area was in the same cluster, suggesting that groundwater characterized by the same sediments or basalt were widely distributed.

6 CONCLUSION

As results of this study, although some important data of groundwater quality in Djibouti has been obtained, it is considered necessary to study in groundwater dating and water stable isotope ratios more wide area to understand its complex groundwater distribution and water quality characteristics. In addition, it is considered important to conduct long-term monitoring studies at a large number of study sites in order to consider anthropogenic influences on groundwater. In Djibouti, groundwater is the only freshwater resources of domestic water for local nomads. Although there have been no reports of groundwater being affected by nitrogen contamination due to human activities, it was considered important to estimate the origin of NO_3^- in groundwater using nitrogen stable isotope ratio in this study and to understand groundwater contamination in detail to propose appropriate management for sustainable and stable groundwater resources in Djibouti.

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