

Mineralization process of spring in carbonate coastal aquifer in the massif Bokkoya (Central Rif, Morocco)

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Abstract

The study focuses on the monitoring of physico-chemical parameters and major chemistry elements in water from six springs and sinks during two seasons, rainy and dry. Samples taken in the coastal karst aquifer massif Bokkoya Al-Hoceima, were analyzed for their chemical quality and to quantify their state of anthropogenic and / or natural contamination, scientific and practical interest, because local population used to supply drinking water. The waters of the internal Rif region are highly mineralized and marked by a chloride-sodium or sodium-sulfated facies to connect mainly to a process of marine intrusion and dissolution of evaporitic minerals included in the on-site rocks. This mineralization of marine origin is partly due to the intensive exploitation of groundwater but also to landslides, that are known in the area, and which accelerate the phenomenon of saltwater intrusion in the coastal karstic aquifer. The salinity of this water presents levels of salinization C3 and C4 as classified by Wilcox log and water of the Bokkoya massif were qualified as very hard. The comparison of hydrochemical results to the quality standards for drinking water set by the World Health Organization shows that the majority of the water withdrawal is not suitable for consumption, especially because of the high levels of EC, TDS and Cl^- related to marine intrusion, together with the urban pollution factor which increases the content of NO_3^- in waters.

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1. Introduction:

In developing countries, much of the population suffers from health problems due to water shortage or contamination [1]. Approximately 2 billion people worldwide consume non-potable water [2], and waterborne diseases are the second leading cause of death in children [3]. The problem has rather worsened with the population growth more of a consideration than the actions carried by the authorities for effective management of water quality [4]. Coastal areas are defined as land areas whose environment, climate and economy are strongly influenced by their proximity to the sea. They attract people, both for their temperate climate and their quality of life for economic development. Over 60% of the world population lives in these coastal areas [5]. However, these areas are at risk of water shortages, due to saltwater intrusion into groundwater reservoirs often a result of a strong exploitation of the underground resource. Most locals of the Al Hoceima region prefer to consume water from springs and wells, which do not have the taste of chlorine used for treatment of tap water. However, the population ignores the quality of spring water with its potential deterioration by chemical and microbiological pollutants. The water spring and wells are easily subject to natural or anthropogenic contamination especially in karst areas where traffic speeds and infiltration are high. The intrusion of saltwater into aquifers is a phenomenon studied around the world and especially in recent years with the over-exploitation of coastal aquifers. In particular, the process of intrusion in coastal karst aquifers is better investigated in recent years by tracking changes in water quality. Many countries around the Mediterranean basin are affected by this risk including Italy, Greece, Turkey, Croatia, and Spain among others. This phenomenon is the result of over-exploitation of water springs and socio-economic development [6], and is characterized by the migration of saltwater into freshwater aquifers [7]. Its importance and its extension are variable and based on the nature of the underground reservoirs constituent materials and can be amplified by pumping and with the elevation of t marine level following climate warming. [8]. The area of the central Rif is characterized by frequent landslides [9-10]. Especially in 1994 and 2004, the region experienced two major earthquakes which resulted for the spring and water points, a marked increase in their flow. The presence of faults caused by ground movements may also increase the salinity intrusion process. Earthquakes also damage groundwater reservoirs whose quality can be altered by an increase of pression in confined aquifer that may result in reducing environment, causing the mobilization of some ions which are harmful to health. The limestone mountain chains play an important role in the water cycle of the Rif area. Their relatively large size, their position between low permeability series, the important local precipitations, their altitude, their karstification are all favorable to the large amounts of water storage which are available on the surface only with some delay. This conditions favor perennial streams, scarce in the Rif, and allows better the water supply of rivers that cross the limestone in summer, and corresponding alluvial groundwater [11]. Coastal heterogeneous aquifers, and in particular coastal karst limestone aquifers are schematically divided into a porous matrix or finely cracked cut by open fractures or karst conduits set up by the brittle tectonic and carbonates dissolution [12]. The hydrodynamic system operation is double, in conduits and in the host matrix. The concept of a representative volume element used in the modeling of porous media is no longer applicable. The water ideally flows in ducts, at high speed, is usually not Darcian, turbulent and occasionally exits into the air or as an underwater spring [13]. This duality of flow influence saline intrusion which is disturbed by the flow in the conduits and can have a very heterogeneous spatial distribution [12]. This work aims to characterize the geochemistry of localized springs in the Massif Bokkoya (Al-Hoceima) by analysis of major elements to evaluate the origin of the residual salinity.

1.1 Environmental data:

The study area is located in the massif Bokkoya, located in the eastern part of the rif, in northeast Morocco (between latitudes 35.15 ° and 35.25 ° N and between longitudes -3.85 ° and -4 ° E). The limestone mountain chain of the Rif is

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a major limestone chain of Morocco, characterized by cracks porosity developing important karstification. It covers an area of about 1100 km², from the region of "Sebta" in the north to the "Al-Hoceima" in the East. It is divided into three main units: the Haouz of Tetouan, Dorsal and limestone chain of [14]. The region is characterized by a semi-arid climate (Figure 1a, b) marked by an alternating dry season (June to September) and a wet season (October to May) [15]. Evaporation varies between 1200 mm and 1900 mm. It is lower in January while the maximum is reached in July and August. These two months account for nearly 30% of the total annual FTE. The Bokkoya massif receives an average pluviometry of 300 mm / year. Recharge by infiltration of rainwater is evaluated at approximately 15 M.m³ on the chain of Bokkoya [14].

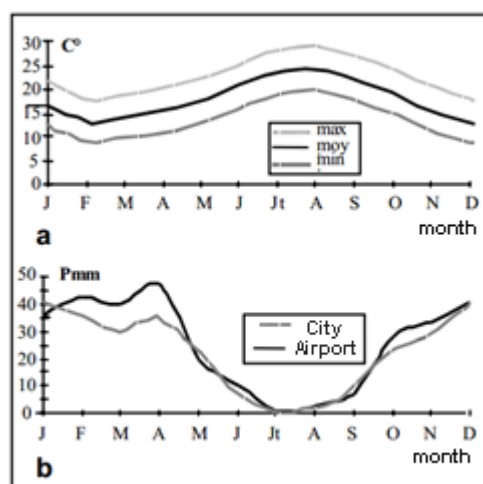


Figure 1: a) Average monthly temperatures in Al Hoceima city (1960-1990); b) Monthly average precipitation at Al Hoceima and its airport (20 km south of the city) [15].

Localization of the sampling points of water spring studied is given in Table 1, E1 and E5 spring are located near a watercourse.

Table 1: Geographical coordinates of samples.

| | Sidi Mansore | Tanoute | Thara Youssef | Thanote Nthrossi | Ghiss | Timachdine |
|------|--------------|------------|---------------|------------------|------------|------------|
| Code | E1 | E2 | E3 | E4 | E5 | E6 |
| Lat. | 35.234530° | 35.248126° | 35.232677° | 35.227798° | 35.178722° | 35.251417° |
| Long | -3.948208° | -3.929816° | -3.975497° | -3.981068° | -3.879167° | -3.949611° |
| Alt | 160 | 48 | 202 | 273 | 20 | 17 |

1.1 Geological Setting

The Massif of Bokkoya is a unit of the internal domain which outcrops in the north central part of the chain of the Rif (Figures 2 and 3). It consists of tectonic units forming the crystalline basement and covers Paleozoic and Meso-Cenozoic [16-17]. It is represented mainly by an internal limestone ridge and external limestone ridge that supports the form of tectonic klippe of Paleozoic land belonging to Sébtides and Ghomarides units [18]. The limestone ridge borders the West and South slopes of Ghomarides of the northern Rif. It is a set of "chips" to the massif Triassic-Liassic carbonate platform framework [19]. This series overcomes other series of condensed Jurassic-Cretaceous, capped with a tertiary detrital material [20]. In front of Bokkoya there is a narrow groove, filling in sub-equatorial orientation with plio-quaternary sediment framed by major accidents with synsedimentary vertical replays [4]. As in

all the southern Mediterranean rim, the Pliocene-Quaternary contains evaporite levels that consist mainly of gypsum. The Sèbtides units are all metamorphic and ultrabasic rocks, corresponding to poly-metamorphic units from Carboniferous to Triassic [21], and Paleozoic and Triassic coverage [22]. The Ghomarides contain a set of thrust sheets consisting of slightly metamorphic Paleozoic grounds, which are the epi-metamorphic strata of the Silurian to Carboniferous age [23], topped with a thin and discontinuous non metamorphic Meso-Cenozoic coverage [24-25]. They consist of three "chips" of Silurian-Devonian highly deformed material [26-27], a carboniferous with discordant facies, a Permo-Triassic red sandstone and dolomites and in a condensed secondary and tertiary coverage [28]. The translation of the limestone-dolomite Triassic series of hedging Ghomarides over the Triassic dolomites of the dorsal external limestone is facilitated by the presence of red clay rocks gypsiferous Triassic [18]. These structural units consist of several tectonic slices of varying importance, stacked on each other. Their structure, characterized by essentially brittle deformation within the upper structural level, results from the superposition of several compressional and extensional phases that have followed from the Eocene to the present [18, 29]. Shales and evaporites (mainly gypsum) from Trias are intermingled with higher Cretaceous marl. These deposits are referred to locally as "gypsum marl". Locally these sediments have a breach character, also comprising blocks of metamorphic and plutonic rocks, referred as "polygenic breccia gypsum matrix."

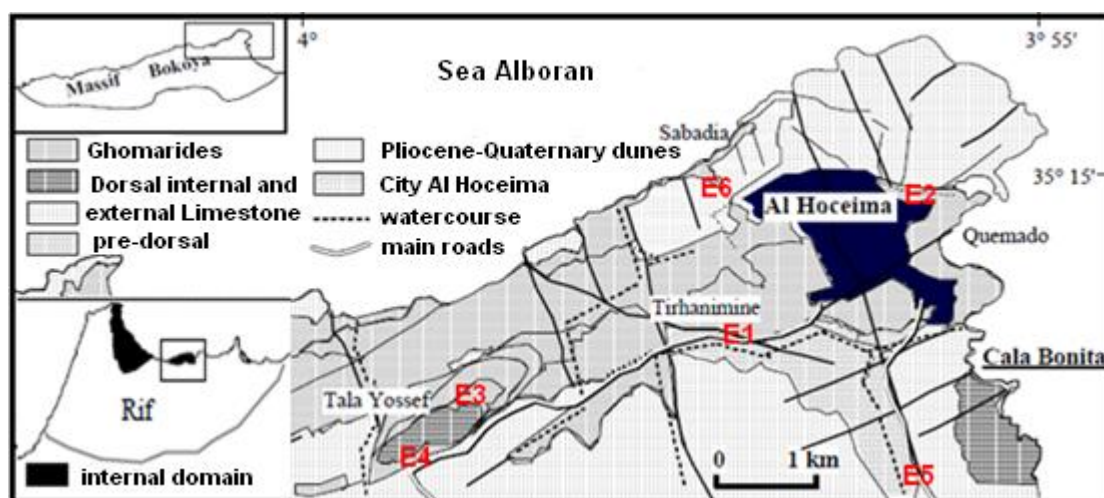


Figure 2: Diagram of structural Massif Bokkoya with the location of spring. [4]

E1: Watercourse, Dorsal limestone-Ghomarides, E2: City, Land Paleozoic Ghomarides-Dunes Pliocene-Quaternary, E3: Dorsal limestone E4: Dorsal limestone-Ghomarides, E5: River, coastal Pebble loam Dunes Pliocene-quaternary, E6: Lands Paleozoic Ghomarides

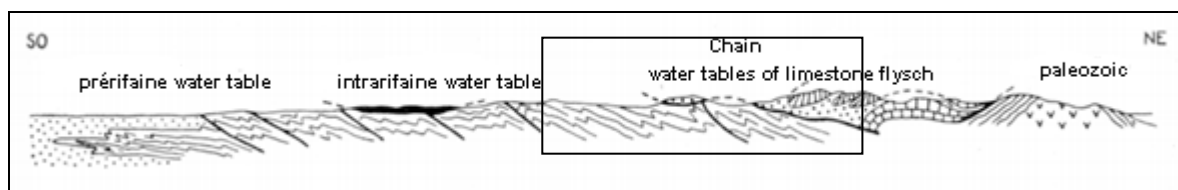


Figure 3: Schematic geological section of the Rif [30].

It should be noted that the layer of flysch in the Rif is equivalent to the Guadalquivir allochthonous origin formation which presents an accretionary wedge [31].

1.3 Hydrogeology

As seen previously, the rainfall over the massif of Bokkoya is low (300 mm / year). It seeps into the limestone formation or is quickly discharged at sea by torrential superficial flow.

Earthquakes throughout this region including the important and most recent events of 1994, 2005, 2016 have resulted in an abnormal flow of rivers in the Massif of Bokkoya. The spring and water points have been marked by a sharp increase in their momentary flow. Locally carbonated, lapiazed materials are become highly fractured, increasing permeability then water infiltration and therefore outflow. These may well be true groundwater perched above impermeable clay layers that line the shallow dip of contacts at the base of the different plies. The abundant fracturing in vertical and horizontal limestone Dorsal induces a rapid recharge on the surface and deep circulation materialized by many seeps [4].

2. Materials and methods

Two sampling campaigns were carried out over a year (wet and dry). E1 water points, E2, E3, E5 and E6 are managed spring and E4 is a covered well with a depth of 15m. Temperature, electrical conductivity, pH and dissolved oxygen were measured in the field using a laptop bag brand multi-parameter DZB-718. Ions (HCO_3^-), (Cl^-), (Ca^{2+}) and (Mg^{2+}) were determined by the volumetric method using the techniques described by Rodier [32]. Nitrates (NO_3^-) and sulphates (SO_4^{2-}) were determined by colorimetric assay using a spectrophotometer (UV / Vis) [32]. Measurement of Potassium, Sodium and Lithium was performed by flame photometer Model 420. Measurement of Potassium, Sodium and Lithium was performed by flame photometer Model 420.

3. Results and discussions

3.1 Results

The ion balance is less than 7% for 8 samples and between 7 and 10% for the last 3, which is reasonable as a measure quality. The values of electrical conductivity are high ($> 1800\mu\text{S} / \text{cm}$) for samples E2, E3, E5 and E6. Although we can see that the conductivity varies between the wet and dry season, certainly in tune with the flow, there is a highest variation for the E3 source (about 50%). The pH remains relatively constant between 7.1 and 7.9. Temperatures are mild for both rain and dry seasons but are marked by seasonality. TDS measured show generally highly mineralized waters with the exception of E4. Geochemical analysis shows mainly predominance (mg / l) of sodium and chloride ions except for E4 whose bicarbonates for anion are higher. The sulphate ions show an equal abundance with chlorides in the E2 and E5 water in dry season. The nitrate concentration is relatively high in the samples E3 and E6. The elevation of the nitrate concentration is related to the location of water E3 and E6 points. Indeed, the position of the source E3, is located in an urban area, which does not have a sewage system. Local people pour their wastewater into individual septic tanks and contamination probably originated in the diffusion of elements from septic tanks into groundwater. As for the location of the source E6, it is crossed by the canal that drains wastewater from the city of Al Hoceima to STEP commissioned in 1996 and renovated in 2011. The leaks that knew the sewage canal probably causes significant levels of nitrates recorded at this region. The waters are usually highly mineralized and only the sample E4 agrees in terms of physical and chemical quality with the water potability standard in Morocco [33] (Table 2).

Table 2: Results of physicochemical analysis of spring water Massif of Bokkoya.

| Sample | E1 | | E2 | | E3 | | E4 | | E5 | | E6 | | NM [33] |
|--------------------------------------|-------|-------|-------|-------|--------|--------|-------|-------|-------|-------|-------|----|---------|
| Season | Wet | Dried | Wet | Dried | Wet | Dried | Wet | Dried | Wet | Dried | Dried | -- | |
| pH | 7.53 | 7.15 | 7.58 | 7.34 | 7.4 | 7.28 | 7.85 | 7.58 | 7.44 | 7.24 | 7.34 | -- | |
| T (°C) | 18.0 | 21.0 | 18.0 | 21.5 | 18.0 | 28.5 | 18.0 | 28.5 | 18.0 | 28.5 | 28.0 | -- | |
| E.C (µs/cm) | 1366 | 1187 | 2430 | 2130 | 2230 | 2690 | 594 | 602 | 1802 | 1993 | 2110 | -- | |
| TDS (mg/l) | 1288 | 989 | 2231 | 2104 | 2528 | 3110 | 444 | 531 | 1828 | 1958 | 1878 | -- | |
| Cl ⁻ (mg/l) | 468.5 | 355.0 | 507.6 | 454.4 | 1075.7 | 1008.2 | 131.4 | 113.6 | 411.8 | 390.6 | 820.7 | -- | |
| HCO ₃ ⁻ (mg/l) | 280.6 | 183.0 | 320.3 | 280.6 | 231.8 | 256.2 | 183.0 | 219.6 | 335.5 | 366.0 | 248.4 | -- | |
| SO ₄ ²⁻ (mg/l) | 112.3 | 127.2 | 680.4 | 622.1 | 377.2 | 416.3 | 69.0 | 57.5 | 618.2 | 604.7 | 268.2 | -- | |
| NO ₃ ⁻ (mg/l) | 21.3 | 22.5 | 35.2 | 40.2 | 63.4 | 71.4 | 24.1 | 26.3 | 9.2 | 10.0 | 55.6 | 50 | |
| Ca ²⁺ (mg/l) | 72.1 | 67.3 | 216.3 | 190.6 | 240.3 | 213.1 | 43.3 | 41.7 | 195.4 | 190.6 | 68.9 | -- | |
| Mg ²⁺ (mg/l) | 36.6 | 30.7 | 102.8 | 88.2 | 102.5 | 93.0 | 16.3 | 14.4 | 102.1 | 133.3 | 75.8 | -- | |
| Na ⁺ (mg/l) | 273.6 | 227.2 | 348.0 | 358.0 | 576.0 | 564.0 | 128.0 | 124.8 | 273.6 | 266.4 | 460.0 | | |
| K ⁺ (mg/l) | 6.1 | 5.2 | 12.5 | 13.8 | 12.7 | 16.1 | 0.9 | 0.8 | 3.9 | 3.8 | 30.0 | -- | |

3.2 Statistic study

3.2.1. Descriptive statistics

The table 3 shows the descriptive statistical summary of Chemical data. It is noted (Figure 4b) that the concentrations of K⁺, Cl⁻, Na⁺ are in the same plane as the E3 and E6 waters. The origin of the three ions in the two springs can't be due only to the geochemical equilibrium with the aquifer. A marine contribution is probably important in these two springs.

The graphical representation in space of statistical units of factorial F1-F2 (Figure 4.a) highlights two main groups of water points and three distinct groups (Figure 4b).

Table 3: Results of descriptive statistical analysis of chemical elements.

| Variable | Min. | Max. | Average | Std-Dev |
|-------------------------------|-------|--------|---------|---------|
| pH | 7.15 | 7.85 | 7.43 | 0.19 |
| E.C | 594.0 | 3110.0 | 1777.6 | 773.8 |
| TDS | 444.0 | 2690.0 | 1679.0 | 764.2 |
| Na ⁺ | 124.8 | 576.0 | 327.2 | 154 |
| K ⁺ | 0.8 | 30.0 | 9.6 | 8.6 |
| Mg ²⁺ | 14.4 | 133.3 | 72.3 | 40.8 |
| Ca ²⁺ | 41.6 | 240.3 | 139.9 | 79.6 |
| Cl ⁻ | 113.6 | 1075.6 | 521.6 | 318.8 |
| SO ₄ ²⁻ | 57.5 | 680.4 | 359.4 | 245.2 |
| HCO ₃ ⁻ | 183.0 | 366.0 | 264.1 | 59.7 |
| NO ₃ ⁻ | 9.2 | 71.3 | 34.4 | 201 |

Cl⁻ < 250mg/L, Na⁺ < 200mg/L, SO₄²⁻ < 250mg/L, NO₃⁻ < 50mg/L.

Table 4: Percentages and own values and variability defined by the principal axes.

| | F1 | F2 |
|-----------------|---------|---------|
| Own value | 6.8149 | 2.5203 |
| Variability (%) | 61.9537 | 22.9117 |
| % Accrued | 61.9537 | 84.8654 |

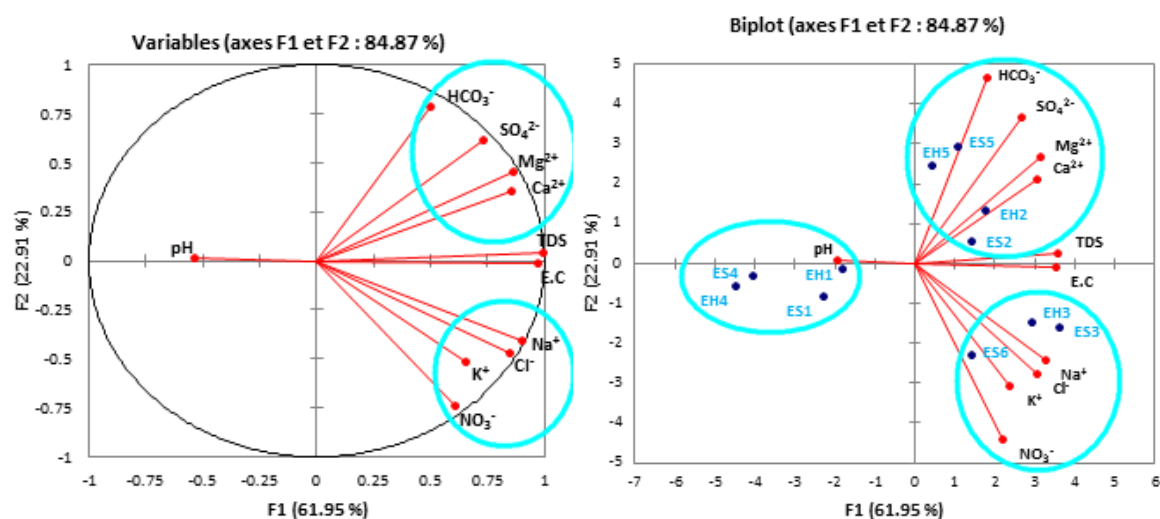


Figure 4: Principal components analysis standardized (variables a) (variables and observations; b) the waters of the factorial F1 - F2.

3.3 Classifications of water spring

To interpret the results of physicochemical analyzes and evaluate the quality of different spring studied, we applied different classifications according to the guidelines of the European Water Framework [34] [35].

3.4 Hydrochemical Facies of water

The representation of the samples in the Piper diagram (Figure 5) shows that the dominant chemical profile corresponds to a chloride-sodium. The sulfated-sodium and sodium carbonate facies occur for E2 and E5 linked to mineralogy of Pliocene-Quaternary dunes (Table 5).

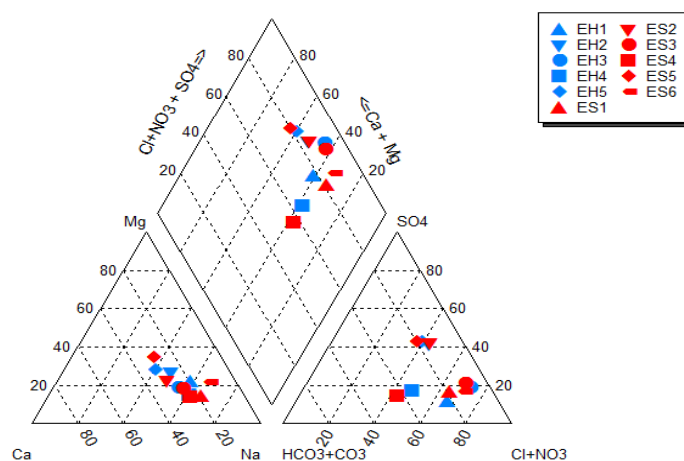


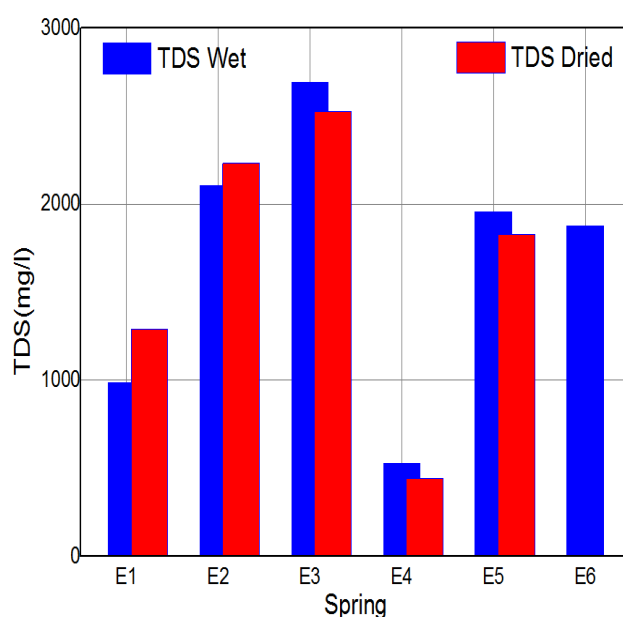
Figure 5: Piper Diagram of the massive source of water Bokkoya.

Table 5: Hydrochemical Facies of spring water and temporal evolution.

| Sample | Season | Type of water |
|--------|--------|------------------------------|
| E1 | Wet | Na-Cl |
| | Dry | Na-Cl |
| E2 | Wet | Na-Ca-Cl-SO ₄ |
| | Dry | Na-SO ₄ -Cl |
| E3 | Wet | Na-Cl |
| | Dry | Na-Cl |
| E4 | Wet | Na-Cl-HCO ₃ |
| | Dry | Na-HCO ₃ -Cl |
| E5 | Wet | Na-Ca-Mg-SO ₄ -Cl |
| | Dry | Na-Mg-Ca-SO ₄ -Cl |
| E6 | Dry | Na-Cl |

3.5 Mineralization water

Water classification according to mineralization depends on the content of the solid residue after evaporation of the water at 105°C (Figure 6). We note that the mineralization is low E4 ($E4 < 500$ mg / l), moderate for E1 ($1000 < E1 < 1500$ mg / l) and higher for E2, E3 and E5 (> 1500 mg / l). TDS values for most samples exceed the recommended value by the WHO (TDS 1000 mg / l) [1]. The low mineralization observed in the well E4 is probably due to its shallow depth (15 m) from where the vertical transfer is faster, recharging taking place by direct infiltration. However, the transit time is still short and the salt content is lower than the other points. Comparison of TDS for two seasons shows a variation in general to an increase in the dry season. The difference is greater for low mineral spring E1 and E4 ($\approx 20\%$) and lower for more mineralized waters E2, E3 and E5 ($\approx 5\%$). The correlation between the calculated and measured TDS is good (Figure 7) with a coefficient of 1.03 director ($TDS_{mes} = 1.03 * TDS_{calc}$) and $R = 99.5\%$.

**Figure 6:** Content (mg / l) of the total solid residue in source waters after evaporation at 105 ° C.

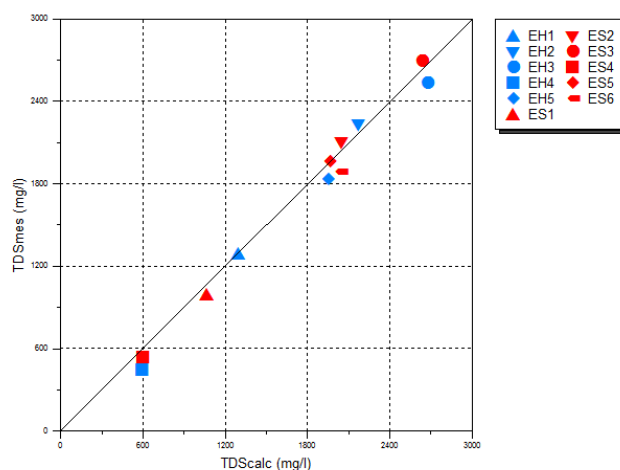


Figure 7: Correlation between the calculated and measured TDS, spring waters of Bokkoya .

3.6 Distribution of ions

The Different waters show variables concentrations of major ions (Cl^- , SO_4^{2-} , Na^+ , HCO_3^- , Ca^{2+} , Mg^{2+} , K^+ , NO_3^-). The distribution of ions in each water mass concentrations is represented in Figure 8 (Figure 8: left the wet season, to right the dry season). The heterogeneity and anisotropy characterizing the karst aquifers are highlighted in Figures 7 and 8 resulting to the strong geochemical variability of water. For the well E4, which presents a shallow water level (15m) and a significant altitude (273m), it is recharged by direct infiltration, the transit time is still short and the salt content lower than other points. The geochemical repartition of the six water were drawn in the Schoeller diagram [36] to better understand the lateral distribution of selected ions. The equivalent molar concentration is between 1 and 10 meq / l (Figure 9). Concentrations of Na^+ and Cl^- are greater than 10 meq / l for most of the samples except for the E4 well. The shape of the sample curves E2, E5 and E6, located at low altitude, is in good agreement with seawater distribution, would seem to imply the presence of sea water in these springs, but remains low in volume.

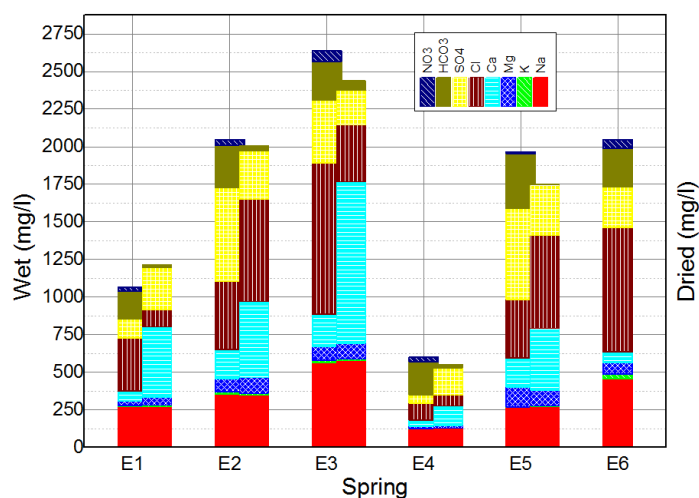


Figure 8: Respective chemical concentration in the 6 points and for wet and dry season

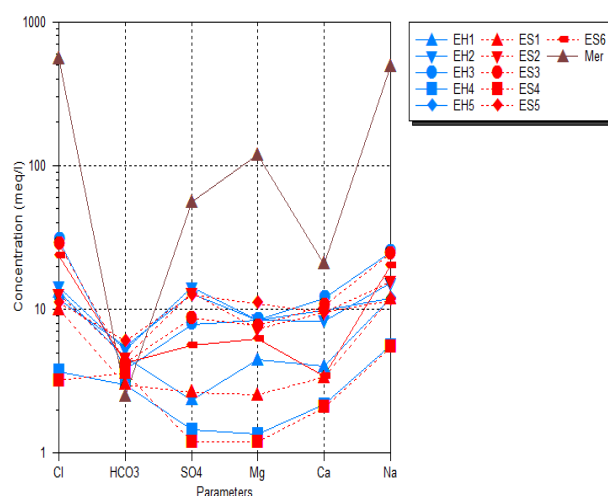


Figure 9: Schoeller diagram.

3.7 Water Hardness

The total water hardness or total hardness TH expressed in mg of CaCO_3 , is the sum of calcium and magnesium concentrations. The classification source of water of the Massif of Bokkoya depending on the hardness is reported in Figure 10.

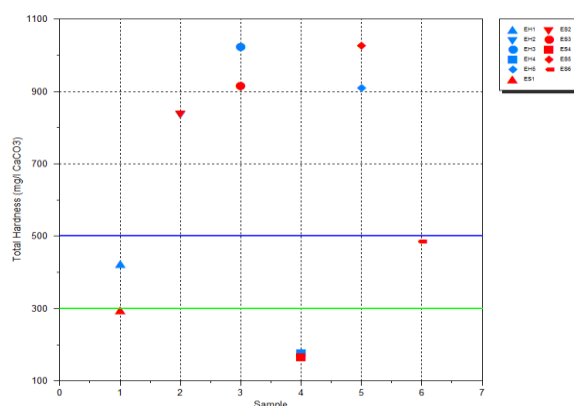


Figure 10: Water Hardness.

The majority of water in the Massif of Bokkoya (E1, E2, E3, E5 and E6) is classified as very hard ($> 300 \text{ mg / l CaCO}_3$). WHO recommends a maximum hardness of $500 \text{ mg / l CaCO}_3$ [1]. The representation of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ versus $(\text{HCO}_3^- + \text{SO}_4^{2-})$ (Figure 11) of different samples, shows that most of the points are more or less aligned on the line $(\text{Ca}^{2+} + \text{Mg}^{2+} / \text{HCO}_3^- + \text{SO}_4^{2-} = 1)$, suggesting the levels of Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} ions mainly come from the dissolution of calcite and gypsum, related to the lithology of formations in the region. [37]

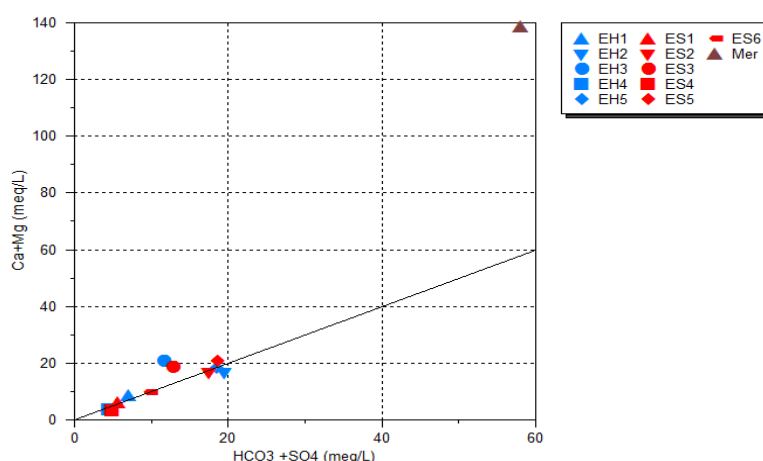


Figure 11: Graph $(\text{Ca}^{2+} + \text{Mg}^{2+}) = f(\text{SO}_4^{2-} + \text{HCO}_3^-)$.

3.8 Water salinity

The value of absorbable sodium (SAR) shows information on the exchange of calcium ions base by sodium ions. This parameter is of particular significance for water irrigation. Higher SAR values higher the hardness of the soil, reducing its permeability. [38] From Wilcox log diagram (Figure 12a), connecting the electrical conductivity and sodium levels, we can identify the following information:

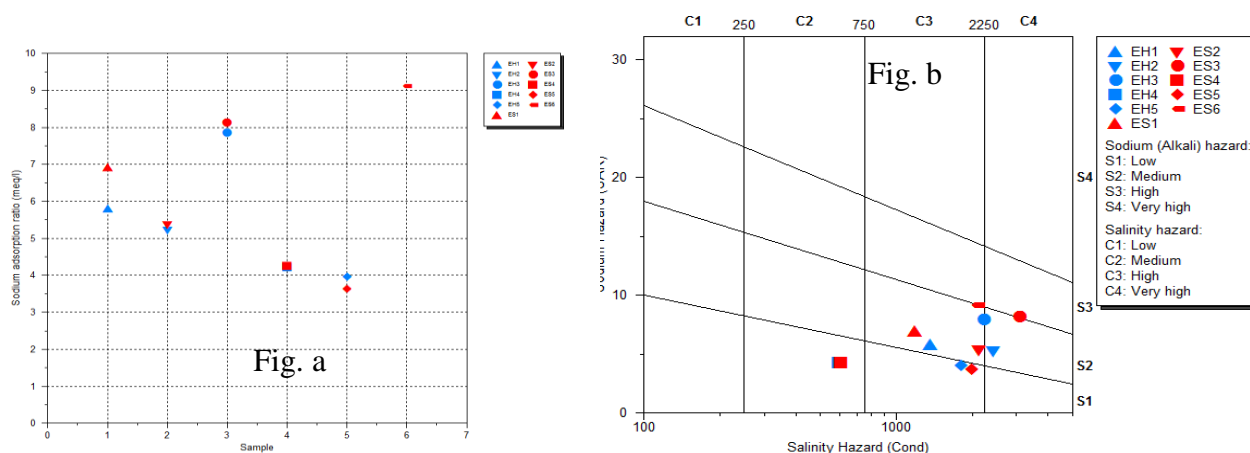


Figure 12: (a) Diagram of Wilcox log and (b) SAR function samples.

- E4 water belongs to C2S1 class: having a very low salinity and a low risk of alkalizing. This means that water quality is consistently good with low mineral content.
- E1 and E5 waters belongs to C3S1 and C3S2 classes, they are poor quality water with medium to high salinity and risk alkalizing low to medium.
- E3 and E2 water belongs to C3S2 and C4S2 classes are with poor quality and highly mineralized water, characterized by a salinity ranging from high to very high, and an alkalizing medium risk.
- The difference in salinity between dry and wet season is low (Figure 12b), except for E3 spring, the most mineralized springs which show a high variability depending on seawater part in the karst conduit depending on the season, the rains enhancing the flow of fresh water. This is consistent with other studies of coastal brackish spring in karst during floods and have identified three processes: the drain conduit karst, the dilution with fresh water and the regulation of intrusion sea water into the pipe via the increase or decrease of load [39].

3.9 Correlation between measured chemical parameters

3.9.1. Correlation between Na^+ and Cl^-

All Bokkoya samples are marked by more or less strong concentrations of sodium and chloride. Sodium levels in the water E1, E2, E3, E5 exceed 200 mg / L (Table 2). Sodium concentrations in drinking water are typically less than 20 mg / L. The human body needs about 120 mg / day of sodium chloride [40]. A higher concentration of sodium in drinking water is suspected to act adversely on blood pressure which may be elevated out of the norm [5, 41].

High levels of chlorides are common in coastal aquifers,; they can be the marker of seawater intrusion [7]. The chloride concentrations measured in the samples are very high; they reach in E3 spring a value of 1075.6 mg / l.

A comparative interpretation of our data and sea water in a diagram (Na^+) = f (Cl^-) show E3 and E6 with proportionally more chlorides, as against other waters are enriched in sodium (Figure 13). Positioning the various points of water samples relative to the seawater line highlights the saltwater intrusion process, is more pronounced for E3 and E6 spring. For other water springs, excess sodium may be associated with a greater contribution of Na^+ linked to dissolution of sodium minerals (feldspar) present in geological formations or the base exchange process with sodium argillaceous sediments. The molar ratios $[\text{Na}^+] / [\text{Cl}^-]$ measured in the springs are given in Table 6.

The molar ratio $[\text{Na}^+] / [\text{Cl}^-]$ in the case of saltwater intrusion is generally lower than the ratio of sea water (0.879), and present values less than 0.86 in aquifers subject to saltwater intrusion [42]. Thus the low ratios $[\text{Na}^+] / [\text{Cl}^-]$, combined with other geochemical parameters, can be an indicator of saltwater intrusion, even at relatively low

concentrations of chlorides in the early stages of salinization. [43] The loss of sodium in seawater intrusion into the aquifer is mainly attributed to the cation exchange process by the balance carbonates. Elevated concentrations of Ca^{2+} and the reduction of Na^+ levels were explained by the retention of Na^+ by exchange with Ca^{2+} and Mg^{2+} [44]. The $[\text{Na}^+] / [\text{Cl}^-]$ ratios of E3 and E6 spring are less than 0.88 thus indicating a salinity mainly due to the intake of seawater. The values found for the spring E1, E2, E4 and E5 are superior to 0.88. This difference can be interpreted by the coupling of sea intrusion and exchange reactions with clay minerals where the Na^+ ions are released into the water against the setting of Ca^{2+} and Mg^{2+} [45].

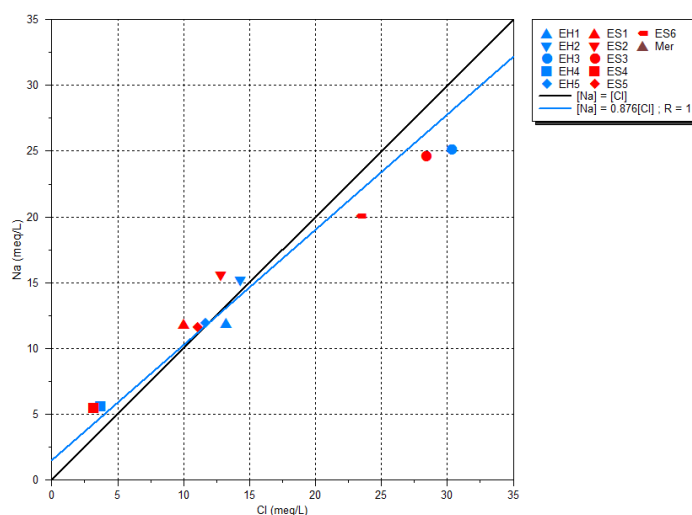


Figure 13: Graph $[\text{Na}^+] = f[\text{Cl}^-]$ of 6 samples (dry and wet season); sea water ratio is $[\text{Na}^+] / [\text{Cl}^-] = 0.879$.

Table 6: Molar ratio of $[\text{Na}^+] / [\text{Cl}^-]$ on spring and seawater.

| Saison | EH1 | ES1 | EH2 | ES2 | EH3 | ES3 | EH4 | ES4 | EH5 | ES5 | ES6 | Mer |
|-----------|-----|------|------|------|------|------|-----|------|------|------|------|------|
| Na/Cl (n) | 0,9 | 1,18 | 1,05 | 1,21 | 0,82 | 0,86 | 1,5 | 1,69 | 1,02 | 1,05 | 0,85 | 0,88 |

3.10 Correlation with the dry residue

To make assumptions about the mineralization origin of the waters from Bokkoya, a first approach is to present the relationships between key major elements related to saline intrusion (Na^+ , Cl^-) and total solid residue (TDS).

In general, the amount of NaCl in a coastal karstic aquifer does not exceed 2 g / l [16], in our case values are between 0.2 and 1,7 g / l with higher values for E3 and E6 (>1.2 g / l).

The weight contribution of Na^+ and Cl^- ions in TDS is between 40 and 70% (Figure 14). The highest value refers to E3 and E6 and lowest to E2 and E5. The importance of halite in TDS shows the salt contribution from marine origin in waters mineralization.

For E6 spring, located at low altitude (17 m) and close to the coast, the proximity of the sea induces high concentration of Na^+ and Cl^- through rainy loaded chlorides and sea spray marine [46]. Increase levels of NaCl can also be caused by overuse of aquifers; lowering the groundwater level and locally promoting mixture between fresh and sea water.

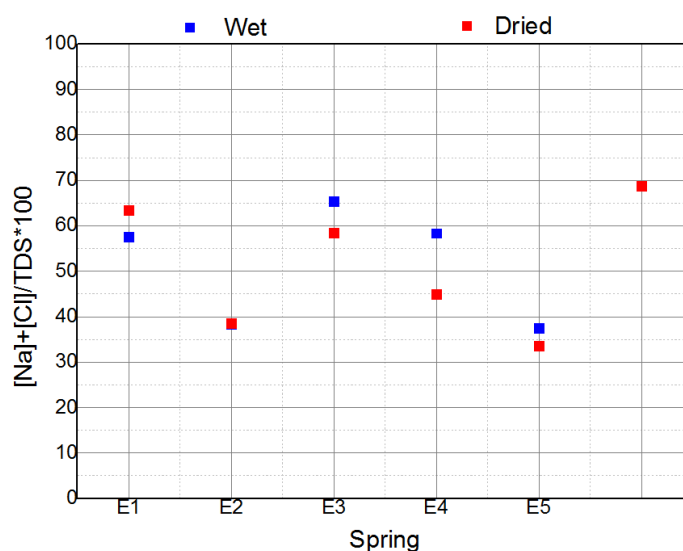


Figure 14: (Na+Cl) compared to the TDS according to the samples.

4. Conclusion

The hydrochemical study of coastal groundwater in the karst of Bokkoya heavily exploited area and its extension, showed the mineralization of water depends on several key factors: the dissolution of minerals from geological formations in place, the exchange ion in water-clay interaction and the contribution of sea water intrusion into the aquifer. The latter process can be accentuated by earthquakes to which the region is subject. The principal component analysis (PCA) was able to identify two important parameters that determine the contents of the measured quantities. The first factor is related to the lithology of the aquifer and the second factor is associated with the phenomenon of saltwater intrusion. The dominant hydrochemical facies is a chloride-sodium type related to the contribution, with marine waters and evaporite dissolution, to freshwater salinization. The different waters studied show a high hardness, a consequence of the dissolution of calcite and gypsum from geological formations defining the aquifer. For sample E3, high hardness is related primarily to saline intrusion. However, the salinity level in the study area is heterogeneous. It is important for E3 spring belongs to the dorsal internal limestone; it is lower for spring located next to watercourses (E1 and E5). The characteristic of the sample E3 is evidenced by the clear correlation between Cl^- and Na^+ . The molar ratio of $[\text{Na}^+] / [\text{Cl}^-]$ is lower than seawater for E3 and E6, but superior for the other waters. The constituent ions of halite in the solid dry residue TDS represents 40 to 70% of the total ions, showing the importance of the intake of sea salt in the water mineralization with variable mineralization depending on local conditions and the position of spring. There was also a significant anthropogenic contribution mark on the E5 and E6 water with higher nitrates concentration highlighting the vulnerability of this kind of karst geological karst formation at anthropogenic contamination from surface.

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