Determination of Physicochemical Water Quality of the Ghis-Nekor Aquifer (Al Hoceima, Morocco) Using Hydrochemistry, Multiple Isotopic Tracers, and the Geographical Information System (GIS)

Nordine Nouayti 1,*, El Khalil Cherif 2,3,*©, Manuel Algarra 4©, Mª Luisa Pola 5, Sara Fernández 5, Abderrahim Nouayti 6©, Joaquim C. G. Esteves da Silva 3©, Khattach Driss 7©, Nouha Samlani 8©, Hilali Mohamed 9©, El Mustapha Azzirgue 10©, Dorota Anna Krawczyk 11© and Antonio Rodero 12,*©

Abstract: The chemical characterization of the Ghis-Nekor groundwater has become a concern of many researchers in Morocco. It is a crucial indicator for the environment situation and the socioeconomic development of this Moroccan region. Indeed, it helps decisionmakers carry out conscious and sustainable management. For this reason, 20 samples of the Ghis-Nekor aquifer were examined in terms of physicochemical parameters such as pH, temperature, electrical conductivity (EC), and total alkalinity (Alk), major cations–anions (Ca 2+, Na +, K +, HCO3 −, Cl −, SO4 2−, NO3 −, and TDS), isotopic elements (δ18O, δ2H, and δ13C), and concentrations of Br and Sr anions in 2020. Furthermore, spatial data analysis with a geographic information system (GIS) using the ArcGIS software (Redlands, California, USA). Indeed, static maps show significant water quality information that helps characterize the groundwater of the study area. The spatial analysis by the GIS indicates that except the EC (from 2630 to 6950 mS/cm), all the physical parameters showed standard concentration values in most of the samples. A significant concentration above the Moroccan norm of groundwater quality for sodium (Na +) from 264.3 to 1500 mg/L, chlorides (Cl −) concentrations from 408.3 to 1510 mg/L, SO4 2− from 313.1 to 999.2 mg/L, and bicarbonate (HCO3 −) from 283.7 to 679.8 mg/L was observed, while all the points exceeded the recommended standards norm for SO4 2−. Most of the points met the potability standards for potassium (K +). In terms of the isotopic elements, the concentration values of δ18O were from −3.92‰ to −5.60‰, while the δ2H concentration values varied between −28.67‰ and −39.99‰. The analysis revealed values of carbon isotope δ13C ranging between −3.15‰ and 3.15‰, thus suggesting that the origin of the carbon is mineral, mainly

1 Applied Sciences Laboratory, Water and Environment Management Team, National School of Applied Sciences, Abdelmalek Essaadi University, Al Hoceima 32002, Morocco
2 Institute for Systems and Robotics, Instituto Superior Técnico, University of Lisbon, 1649-004 Lisbon, Portugal
3 Chemistry Research Unit (CIQUP), DGAOT, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal; jcsilva@fc.up.pt
4 INAMAT2-Institute for Advanced Materials and Mathematics, Department of Science, Public University of Navarre, Campus de Arrosadia, 31006 Pamplona, Spain; manuel.algarra@unavarra.es
5 Central Service to Support Research Building (SCAI), University of Málaga, 29071 Malaga, Spain; mariapola@uma.es (M.L.P); sarafpc@uma.es (S.F.)
6 Geophysics and Natural Hazards Laboratory, Geophysics, Natural Patrimony and Green Chemistry Research Center “GEOPAC”, Mohammed-V University, Rabat 10000, Morocco; nouayti.sv68@gmail.com
7 Applied Geosciences Laboratory, Faculty of Sciences, University Mohammed Premier, Oujda 60000, Morocco; drisskhattach@gmail.com
8 Department of Hydro Sciences, Faculty of Environmental Sciences, Technische Universität Dresden, 01069 Dresden, Germany; nouha.samlani.1997@gmail.com
9 Applied Geology Laboratory, Faculty of Science Meknes, Moulay Ismail University, Meknes 50003, Morocco; hilali2@hotmail.com
10 Laboratory of Chemistry, Unit (LPMSE), University of Abdelmalek Essaadi, Tangier 90000, Morocco; elmustapha.azzirgue@gmail.com
11 Faculty of Civil Engineering and Environmental Sciences, Białystok University of Technology, 15-351 Białystok, Poland; dr.krawczyk@pb.edu.pl
12 School of Engineering Sciences of Belmez, University of Cordoba, 14071 Córdoba, Spain
* Correspondence: nnouayti@uae.ac.ma (N.N.); c.elkhalil@uae.ac.ma (E.K.C.); a.rodero@uco.es (A.R.)

Citation: Nouayti, N.; Cherif, E.K.; Algarra, M.; Pola, M.L.; Fernández, S.; Nouayti, A.; Esteses da Silva, J.C.G.; Driss, K.; Samlani, N.; Mohamed, H.; et al. Determination of Physicochemical Water Quality of the Ghis-Nekor Aquifer (Al Hoceima, Morocco) Using Hydrochemistry, Multiple Isotopic Tracers, and the Geographical Information System (GIS). Water 2022, 14, 606. https://doi.org/10.3390/w14040606

Academic Editor: Dimitrios E. Alexakis

Received: 19 December 2021
Accepted: 4 February 2022
Published: 16 February 2022

Publisher’s Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).
deriving from calcite dissolution. The analysis of the bromide and strontium contents made it possible to discriminate the origin of the salinity anomalies. The Cl/Br, Br/Cl, and Sr/Ca molar ratios distinguished the areas of influence of geological setting (saliferous facies outcrops) or anthropogenic effect (wastewater). The results of the analysis shed light on factors of contamination, which are as follows: urban zones (Imzourene, Ait Youssef, and Souani) and agricultural activities. Therefore, the use of these waters could pose a risk to the health of humans and animals. Similarly, the GIS is a practical and effective tool for the Ghis-Nekor groundwater quality diagnostics and could help decisionmakers establish solutions.

**Keywords:** isotopic tracers; hydrochemistry; chemical facies; water resources; water recharge; Ghis-Nekor aquifer

1. Introduction

In Morocco and other dry countries, water is a limited resource that needs optimal strategies of management and protection against all types of pollution [1]. The Ghis-Nekor alluvial aquifer is one of the most important aquifers in the northeast of the Loukkos hydrological basin, in the north of Morocco. It therefore plays a strategic role in the drinking water supply of the surrounding major cities and urban centers, and in the irrigation supply as well. Its importance triggered a huge body of research that investigated the aquifer in many aspects. Salhi [2] studied the Ghis-Nekor aquifer extensively and provided a reference for the following studies.

Moreover, the study area has been the subject of several mainly geophysical studies such as electrical geophysics studies [3,4] for qualitative purposes, remote sensing, GIS for mapping potential groundwater zones [5], and isotopic techniques for characterizing groundwater composition [6]. More recently, El Asri et al. [7] simulated the climate change impact following different projections on groundwater recharge in the region.

Aside from overexploitation, the aquifer suffers from a problem of high pollution [8], and its vulnerability to marine intrusion has been studied extensively [9–11]. This aquifer is characterized by naturally high ionic concentrations due to the geochemical composition of the crossed ground and the mineralized inputs of the returns of irrigation water [12]. The mismanagement of the aquifer and the increase in the anthropogenic activities are, hence, accentuating the situation. Consequently, for better management of the Ghis-Nekor aquifer resources, studies have been conducted concerning sustainability [13] and elaboration of participatory management action known as the aquifer contract [12].

The use and efficiency of isotopic techniques in water resources management studies are well-established. Since its introduction to hydrology applications in the 1960s, mainly to help identify the origin and the fate of water in the watershed, isotope studies have become essential in hydrological and hydrogeological investigations [14]. In studies of surface water, isotope techniques are used to estimate water or snow runoff [15–17], determine nutrients’ composition [18–22], identify evaporation effects [23], and estimate leakages from dams and reservoirs [24–27].

For groundwater studies, isotopic techniques using both stable (18O, 2H, 13C, 15N, 34S, 87Sr/86Sr, 11B) and radioactive (3H, 14C, 36Cl) isotopes have become indispensable, especially because they help to reach investigation results out of the scope of other means, such as geophysics. Indeed, isotope tracers enable determination of the groundwater recharge and drainage rate [28–33], the age of fossil groundwaters [34,35], the link between surface water and groundwater [36–41], groundwater vulnerability to pollution [42,43], sources of salinity and water pollution [44–47], and the impact of climate change on groundwater [48,49].

The stable isotopes 18O and 2H are well-established environmental tracers because they are part of the water molecule. They allow us to understand the origin, pathways, and
chemical evolution of groundwater. In addition, dissolved inorganic carbon (DIC) isotopes, such as $^{13}$C, are used to indicate the biogeochemical evolution of groundwaters.

The first isotopic studies carried out in Morocco date back to the 1970s [50,51]. Since the 1990s, and thanks to the technical support of the International Atomic Energy Agency (IAEA), the integration of isotopic techniques has greatly expanded and become necessary to the hydrogeological understanding of aquifers.

The essential isotope hydrology studies conducted in Morocco concerned the recharge of the important aquifers [52]. The General Directorate of Hydraulics (GDH) (the national authority responsible for water resources management) manifested its interest after the first results. GDH solicited the support of the IAEA to start new endeavors, for instance, the studies that concerned the basins of Fès-Meknès, Errachidia, and the site of Kheng El Hamam, in the framework of the MOR8/004 project [53], or the basin of Maidere in the south of Morocco [54]. Other academic studies concerned essentially the basins of Tadla [55,56], Errachidia [57], and the coastal aquifers of the Chaouia region to identify the origins of water salinization [58].

Chafouq et al. [6] conducted a hydrochemical and isotopic characterization of the Ghis-Nekor groundwater, where they found a high concentration of nitrates (between 7 and 133 mg/L) and sulfates (between 292 and 2179 mg/L), the values of electrical conductivity varying between 2419 and 10,575 mS/cm and the total salinity varying between 1.60 and 7.50 g/L. Thus, the present paper aimed in the first place to actualize hydrochemical and isotopic data for the year 2020 and consequently update the qualitative situation of the groundwater resource. Secondly, it sheds light on the recharge area altitudes, the carbon origin in the groundwater (by the estimation of the Sr/Ca and Br/Cl ratios). Finally, GIS techniques were explored to give a visualization of the groundwater quality and thus help decisionmakers in this study area.

2. Study Area

The Ghis-Nekor watershed is located at the eastern end of the Rif arches, about a dozen kilometers southeast of the city of Al Hoceima. It is delimited by the Mediterranean Sea in the north and by the mountainous reliefs of the Rif in the south (Figure 1). It is surrounded by small towns and douars (the small town of Ajdir and the douars of Aït Youssef or Ali and Imrabtene to the west; the douars of Bouayach to the southwest, the Tessaaft douars to the south, the douar of Béni Akki and the douar Trougout to the southeast and south, respectively). It extends over an area of 100 km$^2$ with an average slope of 1% from south to north.

2.1. Climate and Hydrology

The Ghis-Nekor basin is subject to a Mediterranean climate characterized by hot dry summers and temperate winters. The temperature averages show generally strong variations owing to remarkable seasonal variations, with an extremely cold winter and an extremely hot summer. The average annual temperature exceeds 30 °C.

As shown for the year 2020 in Figure 2, the wet season in the Ghis-Nekor basin occurs generally from September to May with an average monthly rainfall of 30 mm and a maximum value around 43 m, while the rest of the year is characterized by little to no rain. Monthly rainfall is characterized by a very variable pattern from one year to another. This basin receives a low annual amount of rainfall with an average of 300 mm [13] and a rainfall deficit that can reach 90%, leading to a rapid drying-up of water resources.
Figure 1. Simplified map of the geological subdomains and units of the Rif domain in the north of Morocco. The study area, the zone covered by the sampling points, is located in the Ghis-Nekor plain.

Concerning temperature, two seasons can be distinguished: a hot season centered on the months of July and August and a cold season centered on the month of January. The temperatures, which can reach 35 °C in August, gradually decrease, sometimes registering lows of 3 °C in January. The annual average of monthly values is estimated at 18.4 °C [5]. This climatic variability is reflected in the variable flow rate regimes of the rivers of the region: Oued Nekor and Oued Ghis.

Hydrologically, the Ghis-Nekor plain is crossed by two perennial wadis: wadi Rhis and wadi Nekor (Figures 1 and 3). The wadi Nekor receives in its upstream half two tributaries—the Wadi Ameekrane and the Wadi Tifarouine—with the seasonal flow limited to periods of the flood (Figure 1). It is characterized by a watershed with an area of 911 km² and an average altitude of 1008 m (Figure 3). The length of the mainstream is 69 km, and its average slope is 2.4% [3,12,52].
Figure 3. Piezometric map of the unconfined alluvial coastal aquifer of Ghis-Nekor. The flow is generally from south to north. The red points from B1 to B17 are the geological boreholes for the lithological/geological information on the aquifer issued by ABHL [59] and used for the 3D geological model of the aquifer (see Figure 4).

Figure 4. Simplified 3D geological model of the Ghis-Nekor. The cross-sections were generated by interpolating data from geological boreholes using the Groundwater Modeling System 6.0 (GMS 6.0) software (Aquaveo L.L.C., Provo, UT, USA).
2.2. Geology and Hydrogeology

The study area is part of the Rif domain (Figure 1) that corresponds to the mountainous region in the Mediterranean part of Morocco where the predominant facies are schistous and pelitic [2]. Being one of the most important plains in the domain, the Ghis-Nekor plain is the result of a substratum depression that occurred following the tectonic collapse phase [12]. The depression is filled with heterogeneous alluvial sediments such as sands, gravels, and conglomerates from the Pliocene until the Quaternary [2].

The unconfined aquifer of the plain consists of a sandy gravel alluvium unit of the Quaternary age (blue in Figure 4). The thickness of this unit varies between 64 m in the south of the basin and increases towards the north to reach 125 m. The maximum thickness is found in the center of the basin where it can exceed 400 m. This alluvium unit is heterogeneous as it contains some silty and clayey–marly lenses. The base of the aquifer is a relatively thin aquiclude consisting of the marly clay layer that surmounts the Cretaceous schistous bedrock. This latter contains lenses or sandstone–quartzite beds of the Albo–Aptian age (Lower Cretaceous) [52].

The general flow is from south to north (Figure 3). The aquifer is characterized by a wide transmissivity range from \(6.7 \times 10^{-5}\) to \(6.4 \times 10^{-2}\) \(\text{m}^2/\text{s}\) with an average value around \(2.0 \times 10^{-2}\) \(\text{m}^2/\text{s}\) (1.73 \(\text{m}^2/\text{day}\)) which implies a high aquifer potential, a storage coefficient between \(6.5 \times 10^{-2}\) to \(5.3 \times 10^{-2}\) and an estimated productivity exceeding \(100 \text{ L/s}\) [3,12,52].

The aquifer is overexploited as the output terms exceed the natural recharge. The recharge of the aquifer is controlled by, in order of importance, lateral inputs from adjacent aquifers, infiltration of rainwater, inputs from the rivers (Ghis and Nekor), and the return of irrigation water. The pressure on the aquifer corresponds to natural factors, such as direct evaporation in the littoral zone and the outflow to the sea, and to anthropogenic factors, mainly water withdrawals either for drinking or agriculture [60].

3. Materials and Methods

With the aim of evaluating the physical and chemical quality of the Ghis-Nekor aquifer, a total of 20 wells representatively distributed to cover the entire aquifer of Ghis-Nekor were selected for the sampling campaign of January 2020 (Figure 1). From every well, two samples, one liter each, were collected in polyethylene bottles.

While physicochemical parameters such as pH, temperature, electrical conductivity (EC), and total alkalinity (Alk) were measured in situ using a multiparameter probe, analysis of the major cations, anions, isotopic elements (\(\delta^{18}\text{O}, \delta^{2}\text{H}, \text{and}\ \delta^{13}\text{C}\)), Br, and Sr were performed in the laboratory. The isotopic analysis, mainly executed to investigate the altitude of recharge zones, concerned only eight samples among the total 20 selected sites. These eight points are representative of the downstream conditions.

For isotopic analyses, a Delta V Advantage mass spectrometer (Bremen, Germany, Thermo Fisher Scientific) coupled to a ConFlo IV interface and connected to a GasBench II with an autosampler (CTC Analytics AG, Zwingen, Switzerland) was employed.

An aliquot of the water sample was injected into a 12 mL borosilicate vial (Labco, High Wycombe, UK), capped with a Labco butyl rubber septum. The sample vials were loaded into a temperature-controlled rack.

To determine the dissolved inorganic carbon (DIC), the exetainers were flushed for 300 s at a flow rate of 100 mL/min. The samples were reacted with 5–8 droplets of 104% orthophosphoric acid (\(\text{H}_3\text{PO}_4\)) to \(\text{CO}_2\) gas, which was then sampled with a sampling loop of 100 \(\mu\text{L}\) and transported in a helium stream of 2 mL/min to the mass spectrometer. The acid–water reaction began immediately upon injection.

For hydrogen and oxygen isotopic analyses, the vials were filled automatically with the hydrogen/oxygen equilibration gas from a gas cylinder. The vials were left to equilibrate. A platinum-based hydrophobic catalyst made of platinum-coated polymer beads trapped inside a stainless-steel coil was used to reach isotopic equilibrium between liquid water and gaseous hydrogen. The helium stream transported the gas to the mass spectrometer.
All the samples were run against a working dioxide carbon or hydrogen reference gas that were calibrated against primary standards.

For δ\(^{13}\)C calibration, sodium bicarbonate and calcium carbonate solutions were used as internal laboratory standards (W-lab_1: \(δ^{13}C = -2.35 \pm 0.09\)‰ and W-Lab_2: \(δ^{13}C = -20.35 \pm 0.07\)‰). These were calibrated versus international standards NBS-19 (\(δ^{13}C = 1.95\)‰, \(δ^{18}O = 2.22\)‰) and LSVEC (\(δ^{13}C = 46.6 \pm 0.2\)‰, \(δ^{18}O = 26.7 \pm 0.2\)‰) distributed by IAEA (International Atomic Energy Agency). All the \(δ\) values were reported relative to the international standard reference “Vienna Pee Dee Belemnite” (VPDB) in this report. The standard deviation of repeated measurements of the \(δ^{13}C\) values of the standards was finer than \(±0.08\)‰.

The \(δ^2H\) and \(δ^{18}O\) compositions were analyzed using a liquid water isotope laser analyzer (Picarro L2120-i, Picarro, Inc., Santa Clara, CA, USA) in the same laboratory. Calibration was conducted directly against IAEA-certified water standards (VSMOW2, GISP and SLAP2) run during the same sequence for normalization. The isotopic data were expressed in the standard delta notation (\(δ\)) as per mil (±) relative to the Vienna Standard Mean Ocean Water (VSMOW, 0‰), and the measurement precision was ±0.5‰ and ±0.1‰ for \(δ^2H\) and \(δ^{18}O\), respectively. The minor elements were measured by inductively coupled plasma mass spectrometry (ICP-MS NexION300D, PerkinElmer, Inc., Shelton, CT, USA) at the Beijing Research Institute of Uranium Geology, and the analytical precision was ±3‰ of the concentration based on the reproducibility of samples and standards [61–63].

The external analytical precision was ±0.3‰ for \(δ^{18}O\) and ±1‰ for \(δ^2H\). This precision was determined on the basis of repeated measurements of sample replicates. All the samples were analyzed in triplicates. To monitor the reproducibility of analytical results, repetitive analyses of the secondary laboratory standards, carbonates and water, were analyzed routinely with the samples. These secondary laboratory standards were calibrated with IAEA-certified reference materials. The reproducibility was satisfactory, with a standard deviation (SD) of 0.09‰ for \(δ^{13}C\), 0.20‰ for \(δ^{18}O\), and 0.80‰ for \(δ^2H\).

A NexION 2000 (Perkin-Elmer SCIEX Instruments, Waltham, MA, USA) inductively coupled plasma mass spectrometer (ICP-MS) directly connected to Flexar HPLC was used for the Br and Sr analyses, both controlled by the Empower 3 v.1.0.0 software (PerkinElmer SCIEX Instruments, Waltham, MA, USA). ICP-MS uses standard nickel cones for sampling. The nebulizer gas flow rate was adjusted so that the Ce++ (70)/Ce (140) and CeO (156)/Ce (140) ratios were less than or equal to 0.03 and 0.025, respectively.

4. Results and Discussion

\(T, pH, EC, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, Alk, TDS,\) and isotopic elements (\(δ^{18}O, δ^2H,\) and \(δ^{13}C\)) were tested in 20 water samples. In the following sections, the hydrochemistry of the groundwater is characterized using static maps elaborated by the GIS geostatistics module. On the other hand, the results of the isotopic analysis were used to determine recharge altitudes and carbon origin.

4.1. Hydrochemical Analysis

The analysis of the results revealed that groundwater samples have temperatures between 18.78 °C (P19) and 23.07 °C (P9), with an average of 21.6 °C (Table 1). The temperature of groundwater samples was similar to the air temperature in the study area due to the shallowness of the sampled aquifer. These values are typical for cold hypothermal water, reflecting the seasonal increase in temperature. Furthermore, pH was close to neutrality at all the water points, with a value between 7.25 at the samples P1 and P13 and 7.65 at the sample P18 (Table 1), indicating a neutral or slightly alkaline nature of groundwater in the Ghis-Nekor aquifer. In addition, the registered EC values were between 2630 and 6950 mS/cm (Table 1) and characterized by an increase from south to north of our study area (Figure 5). The important values resulted from the leaching of the aquifer material and the influence of marine intrusion. The results revealed that groundwater samples have Alk between 283.7 (P13) and 679.8 (P12) (Table 1).
Table 1. Results of hydrochemistry measurements (pH, T, EC, Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\), HCO\(_3^{-}\), Cl\(^{-}\), SO\(_4^{2-}\), NO\(_3^{-}\), Alk, and TDS) at the 20 sample points of the Ghis-Nekor aquifer.

| Well | PH | Temperature (°C) | EC (mS/cm) | Ca\(^{2+}\) | Mg\(^{2+}\) | Na\(^{+}\) | K\(^{+}\) | HCO\(_3^{-}\) | Cl\(^{-}\) | SO\(_4^{2-}\) | NO\(_3^{-}\) | Alk | TDS |
|------|----|------------------|-----------|-------------|-------------|-----------|----------|--------------|--------|----------|--------|------|-----|
| P1   | <7.25 | 21.90 | 3550 | 152.0 | 128.9 | 537.1 | 9.00 | 585.3 | 947.8 | 567.3 | 86.90 | 583.5 | 3040 |
| P2   | 7.26 | 23.07 | 6190 | 171.3 | 137.0 | 930.3 | 36.28 | 532.5 | 1320 | 891.3 | 27.25 | 532.5 | 4610 |
| P3   | 7.36 | 21.93 | 5770 | 142.1 | 170.0 | 537.4 | 4.16 | 460.2 | 1120 | 820.8 | 51.20 | 460.2 | 2840 |
| P4   | 7.36 | 21.93 | 5590 | 253.3 | 157.3 | 346.5 | 5.04 | 374.1 | 1090 | 900.0 | 12.03 | 374.1 | 2930 |
| P5   | 7.36 | 21.93 | 5660 | 253.3 | 167.7 | 474.4 | 3.04 | 376.2 | 956.0 | 720.0 | 13.65 | 376.2 | 2930 |
| P6   | 7.26 | 23.07 | 5190 | 253.0 | 180.0 | 480.0 | 1.39 | 340.0 | 1430 | 801.3 | 33.23 | 340.0 | 3170 |
| P7   | 7.37 | 22.63 | 6950 | 300.0 | 255.1 | 585.0 | 7.32 | 530.2 | 1510 | 999.2 | 41.36 | 530.2 | 4520 |
| P8   | 7.43 | 22.23 | 3890 | 192.4 | 162.4 | 279.0 | 10.1 | 447.1 | 860.0 | 735.6 | 48.70 | 447.1 | 2390 |
| P9   | 7.26 | 23.07 | 6540 | 329.4 | 295.0 | 762.2 | 4.02 | 537.0 | 1510 | 332.1 | 40.00 | 537.0 | 2930 |
| P10  | 7.37 | 22.63 | 5800 | 270.0 | 209.4 | 615.3 | 2.33 | 475.0 | 1430 | 321.5 | 48.39 | 475.0 | 3670 |
| P11  | 7.43 | 22.23 | 4100 | 271.9 | 221.0 | 630.2 | 2.88 | 476.0 | 1020 | 313.1 | 46.00 | 476.0 | 3670 |
| P12  | 7.36 | 21.93 | 5900 | 141.2 | 145.2 | 386.2 | 1.22 | 679.8 | 892.0 | 387.2 | 122.3 | 679.8 | 2630 |
| P13  | 7.25 | 21.90 | 4200 | 212.3 | 118.9 | 348.9 | 1.33 | 283.7 | 845.5 | 387.2 | 10.23 | 283.7 | 2100 |
| P14  | 7.40 | 21.52 | 3510 | 278.5 | 208.7 | 629.7 | 3.70 | 463.7 | 987.8 | 365.0 | 46.00 | 463.7 | 3690 |
| P15  | 7.35 | 21.03 | 3320 | 341.1 | 372.3 | 1500 | 9.01 | 390.0 | 947.8 | 338.2 | 122.3 | 390.0 | 1950 |
| P16  | 7.44 | 20.70 | 3030 | 211.3 | 143.4 | 377.7 | 5.06 | 423.8 | 515.3 | 399.1 | 12.00 | 423.8 | 2700 |
| P17  | 7.49 | 20.24 | 2820 | 182.0 | 115.7 | 333.0 | 2.60 | 434.6 | 480.0 | 391.4 | 8.20 | 434.6 | 2410 |
| P18  | 7.65 | 19.02 | 2790 | 189.0 | 115.0 | 264.3 | 1.03 | 352.7 | 465.0 | 386.0 | 17.50 | 352.7 | 1950 |
| P19  | 7.52 | 18.78 | 2630 | 168.2 | 120.6 | 264.3 | 1.56 | 372.0 | 408.3 | 390.3 | 23.00 | 372.0 | 2340 |
| P20  | 7.49 | 19.72 | 2890 | 323.5 | 160.7 | 619.5 | 1.20 | 370.4 | 456.0 | 398.1 | 41.48 | 370.4 | 3720 |

The Na\(^{+}\) values ranged from 264.3 mg/L at P18 to 1500 mg/L at P15 (Table 1, Figure 5h) and the Cl\(^{-}\) concentrations ranged from 408.3 mg/L at P19 to 1510 mg/L at P9 (Table 1, Figure 5c). The highest concentration of Na\(^{+}\) was registered at P15 (Figure 5h). Except the samples P2, P3, P4, P8, P12, P13, P16, P17, P18, and P19, all the points showed high concentration of Cl\(^{-}\) (Figure 5c). The high concentrations are most likely the result of either a natural cause such as the contact with evaporite formations of the Triassic gypsifer and marine intrusion or anthropogenic activity, mainly the infiltration of brackish irrigation returns. These levels do exceed the potability threshold set by the World Health Organization (WHO) at 200 and 750 mg/L for sodium and chlorides, respectively. According to the Moroccan standards for the quality of drinking water [64], the maximum recommended concentration of Cl\(^{-}\) is 300 mg/L, while the allowable threshold is set at 750 mg/L. SO\(_4^{2-}\) ranged from 313.1 mg/L at P11 to 999.2 mg/L at P7 (Table 1, Figure 5d). In addition, all the points exceeded the recommended standards (Figure 5d)—250 mg/L [2]. These concentrations result from the effect of the carbonate matrix and sulfate-bearing minerals present on the geological formations rich in gypsum and influence of Triassic saline soils [2].

The HCO\(_3^{-}\) concentrations values ranged from 283.7 mg/L at P13 to 679.8 mg/L at P12 (Table 1, Figure 5j). The high-grade points are located in the area where the water flows in the carbonate matrix lands [52]. NO\(_3^{-}\) values of the samples were between 8.20 mg/L and 122.3 mg/L (Table 1, Figure 5g). The highest values were recorded in the center of the basin at P15 (Figure 5g). This nitrate pollution is due essentially to human activity, in particular the nitrogenous fertilizing of agriculture fields, wastewater, and livestock waste [52]. Ca\(^{2+}\) values of the samples were between 141.2 mg/L (P12) to 341.1 mg/L (P15) (Table 1, Figure 5i). Except for the samples P1, P19, and P20, the points showed concentrations exceeding the recommended standard, 160 mg/L, which corresponds to
the standards of potability. High levels of Ca$^{2+}$ can be attributed to the dissolution of calcites and/or dolomites as well as other calcium minerals such as gypsum [52]. K$^+$ values of the samples were between 1.03 mg/L (P18) to a high of 36.28 mg/L (P2) (Table 1, Figure 5e). According to these grades, all the water points sampled excluding two do meet the potability standards recommended by the WHO in 2011.

Mg$^{2+}$ values of the samples ranged between 115.0 mg/L (P18) to 372.3 mg/L (P15) (Table 1, Figure 5f). All the samples recorded concentrations above 100 mg/L, which is the maximum limit of the Moroccan standard for potability. High levels in the upstream portion of the study area were due to the effect of dolomitic limestones and dolomites and the influence of Triassic saline soils. The total dissolved solids showed high concentration values at P18, P15, and P13 while registering weak values going towards P9, P2, P7, P20, P14, and P11 (Table 1, Figure 5b). The hydrochemical results were analyzed using a Piper diagram. The Piper plot consisted of two triangular diagrams representing the anions and cations concentrations and one diamond that summarized information of both triangles (Figure 6) [65]. According to the position of the samples in this diagram, the hydrochemical facies or types could be identified. In this paper, the most abundant dissolved cations (Na$^+$, Ca$^{2+}$, and Mg$^{2+}$) and anions (HCO$_3^-$, SO$_4^{2-}$, and Cl$^-$) were considered.

Figure 5. Cont.
Figure 5. Spatial distribution of the major elements: (a) electrical conductivity, (b) total dissolved solids, (c) chlorides, (d) sulfates, (e) potassium, (f) magnesium, (g) nitrates, (h) sodium, (i) calcium, and (j) bicarbonates of the Ghis-Nekor groundwater.
The Piper diagram shows that strong acids (SO$_4^{2-}$ + Cl$^-$) largely exceeded the weak bicarbonate acid (HCO$_3^-$) and that sodium (Na$^+$) was the most abundant alkali metal in the studied aquifer. The water types and their proportions are shown in Figure 6. This representation reveals that all the wells included in the campaign are influenced by evaporites. In particular, P1, P2, P3, and P15, with the NaCl type water, are the most affected wells. This may suggest that the evaporitic Triassic salt-rich water/rock interaction is accentuated in the northeast of the study area. The resulting mixture of water/rock rich in evaporitic Triassic salts is responsible for water type transition from NaCl to NaSO$_4$.

Another method of visualizing the chemistry of water samples is the Schoeller–Berkaloff diagram. In this diagram, the concentration of each element is represented with vertical lines with a logarithmic scale, and the points obtained are connected by line segments in order to identify the similarities and differences between the samples [66]. In Figure 7, water chemistry appears to be consistent in most of the wells sampled. However, there were some remarkable discrepancies relative to nitrate, chloride, potassium, calcium, and sodium concentrations, especially in the points P2, P6, P7, and P15 (Figure 7).

Particularly, water points P2 and P15 showed high concentrations of chlorides, potassium, and sodium (Figure 7). These important concentrations are due to saliferous sediments being leached, especially the Triassic gypsum (Ketama and Tizirene Unit), marine intrusion that causes the presence of salt levels in the aquifer, and the return of irrigation water. The results are in the same range as in the previous studies [6,12,67-69].
Figure 7. Schoeller–Berkaloff diagram of the groundwater of the Ghis-Nekor aquifer for sample points 1–20.

4.1.1. \( \text{Sr}^{2+} / \text{Ca}^{2+} \) Ratio

Strontium is an element linked to evaporites. It is very weakly integrated into the carbonate network and is poorly adsorbed by clays. The high levels of \( \text{Sr}^{2+} \) in water can only be explained by the dissolution of the celestite \((\text{SrSO}_4)\) mineral associated with gypsum. It thus is a good marker of the presence of evaporites [70]. Strontium thus makes it possible to distinguish the sulfates resulting from the oxidation of sulfides (low contents) from those resulting from the dissolution of evaporites (high contents).

The determination of strontium in the waters of the northern region (Figures 8a,b and 9a and Table 2) showed that most of the controlled points have a \( \text{Sr}/\text{Ca} \) ratio which varies between \( 2.24 \times 10^{-3} \) (P8) to \( 8.37 \times 10^{-3} \) (P7), with values of sulfates oscillating between 567.3 mg/L (P1) and 999.2 mg/L (P7) (Figures 8a,b and 9a and Table 2). The values of the \( \text{Sr}/\text{Ca} \) ratio and sulfates rank the water from this source in the same category as the water in contact with Triassic evaporites. These high ratio values are another proof of the sedimentary effect on the chemistry of the water studied, added to the large concentrations of sulfates, chlorides, and sodium.
Table 2. Results of the measurements of $\delta^{18}$O, $\delta^2$H, $\delta^{13}$C, Br, and Sr in the eight selected wells of the Ghis-Nekor aquifer.

| Well | $\delta^{18}$O $(\%$ VSMOW) | $\delta^2$H $(\%$ VSMOW) | $\delta^{13}$C $(\%$ VPDB) | Sr (mg/L) | Br (mg/L) |
|------|--------------------------|--------------------------|--------------------------|----------|----------|
| P1   | $\sim30.48$              | $\sim8.18$              | $\sim8.18$              | $1.66$   | $2.84$   |
| P2   | $\sim31.40$              | $\sim7.42$              | $\sim7.42$              | $2.72$   | $8.80$   |
| P3   | $\sim35.20$              | $\sim5.91$              | $\sim5.91$              | $2.36$   | $2.50$   |
| P4   | $\sim31.01$              | $\sim4.28$              | $\sim4.28$              | $2.70$   | $3.00$   |
| P5   | $\sim36.01$              | $\sim5.56$              | $\sim5.56$              | $3.17$   | $0.95$   |
| P6   | $\sim37.02$              | $\sim3.70$              | $\sim3.77$              | $3.53$   | $0.80$   |
| P7   | $\sim37.02$              | $\sim8.61$              | $\sim8.61$              | $5.49$   | $13.81$  |
| P8   | $\sim39.03$              | $\sim3.15$              | $\sim3.15$              | $0.94$   | $2.76$   |

Figure 8. Dependence of the Sr/Ca ratio on $\text{SO}_4^{2-}$ (a) and $\text{Ca}^{2+}$ (b) in the water in the study areas (eight water points analyzed).

Figure 9. Spatial distribution of the (a) Sr/Ca ratio and (b) the Cl/Br and Br/Cl ratios in the Ghis-Nekor groundwater.

4.1.2. Contribution of the Cl$^-$/Br$^-$ Ratio

The monovalent anions chlorides and bromides are present in all natural waters in the aqueous form. Chlorides are present in higher concentrations compared to bromides, with
values higher by up to 8000 times. In the sea, the highest water, the Cl/Br ratio does not variate in a wide range but is rather stable at around $655 \pm 4$ [71,72] (Figure 10). The Cl/Br ratio value varies for every different source of chlorine and bromide ions (atmosphere, evaporates, leaching, sea water intrusion) [71]. Therefore, this Cl/Br ratio is used as a tracer to determine the origin and behavior of groundwater and it is an interesting tool for hydrogeological studies [72].

![Figure 10. Plot of the Cl/Br ratio versus chloride concentration for six types of salinity described in 24 selected aquifers of Spain and Portugal [71] (used under CC BY 3.0/desaturated from original).]

The analysis of the bromide contents made it possible to discriminate the origin of the salinity anomalies in an unconfined aquifer. The Cl/Br molar ratio distinguished the areas of evaporitic (saliferous facies outcrops) or anthropogenic (wastewater) influence. Figures 9b, 11 and 12 show the Cl/Br ratios of water from the wells sampled in the north of the region, with the values varying between 246.5 (P7) and 4010 (P6).

On the other hand, Figure 12 presents the values of the Cl/Br ratio together with the corresponding Cl/Na ratio. Most of the studied wells have ratios higher than the seawater value of 655. This is typical for coastal areas. The generation of seawater droplets in the surface of waves and the transportation of these doplets, poor in Br, towards the coast, where it is deposited, results in a high Cl/Br ratio in these areas.

Exceptions to this general behavior were the P2 and P7 wells. They presented the Cl/Br ratios of 338.3 and 246.5 for Cl$^-$ concentrations of 1320 mg/L and 1510 mg/L, respectively. This could be due to the agricultural activity in the zone (Figures 5 and 12).

Conversely, the wells P5 and P6 had much higher Cl/Br ratios than seawater, 2254.51 with 956.0 mg/L of Cl$^-$ and 4010 with 1430 mg/L of Cl$^-$, respectively. These anomalous values could be due to anthropogenic activity, leaching of garbage and solid waste, or leaching of industrial halite (Figures 5 and 12). The same Cl$^-$ enrichment is evident in Figure 5, associated with an increase in NO$_3^-$, which confirms this anthropogenic origin.
Figures 11, 9b, and 12 show the Cl/Br ratios of water from the wells sampled in the north of the region, with the values varying between 246.5 (P7) and 4010 (P6).

Figure 11. Dependence of the Cl/Br ratio on Cl⁻ concentration in water in the study area (eight water points analyzed).

Figure 12. Cl/Na ratio with respect to the Cl/Br ratio compared to seawater values (Cl/Br = 655; Cl/Na = 1.2).

Exceptions to this general behavior were the P2 and P7 wells. They presented the Cl/Br ratios of 338.3 and 246.5 for Cl⁻ concentrations of 1320 mg/L and 1510 mg/L, respectively. This could be due to the agricultural activity in the zone (Figures 5 and 12).

Conversely, the wells P5 and P6 had much higher Cl/Br ratios than seawater, 2254.51 with 956.0 mg/L of Cl⁻ and 4010 with 1430 mg/L of Cl⁻, respectively. The same anomalous values could be due to anthropogenic activity, leaching of garbage and solid waste, or leaching of industrial halite (Figures 5 and 12). The same Cl⁻ enrichment is evident in Figure 5, associated with an increase in NO₃⁻, which confirms this anthropogenic origin.

4.2. Isotopic Analysis

Deuterium is one of the two stable isotopes of hydrogen. It accounts for approximately 0.0156% (0.0312% by mass) of all the naturally occurring hydrogen in the oceans [67,73,74]. Measurements of small variations in the natural abundances of deuterium, along with those of the stable heavy oxygen isotopes ¹⁷O and ¹⁸O (oxygen-¹⁸ is a natural, stable isotope of oxygen and one of the environmental isotopes), are of importance in hydrology to trace the geographic origin of Earth’s waters.

The heavy isotopes of hydrogen and oxygen in rainwater (so-called meteoric water) are enriched as a function of the environmental temperature of the region in which the precipitation falls (and thus enrichment is related to mean latitude). The relative enrichment of the heavy isotopes in rainwater (as referenced to mean ocean water), when plotted against temperature, falls predictably along a line called the global meteoric water line (GMWL). This result allows us to determine precipitation water origin and its climate condition [67,74,75].

Evaporative and other processes in water bodies, including groundwater, also differentially alter the ratios of heavy hydrogen and oxygen isotopes and make clear the difference between the fresh and saline waters. The ratios of the concentrations of stable isotopes ²H and ¹⁸O to their corresponding more abundant isotopes ¹H and ¹⁶O, respectively, are usually indicated with a delta, δ ²H.
4.2. Isotopic Analysis

Deuterium is one of the two stable isotopes of hydrogen. It accounts for approximately 0.0156% (0.0312% by mass) of all the naturally occurring hydrogen in the oceans [67,73,74]. Measurements of small variations in the natural abundances of deuterium, along with those of the stable heavy oxygen isotopes \(^{17}O\) and \(^{18}O\) (oxygen-18 is a natural, stable isotope of oxygen and one of the environmental isotopes), are of importance in hydrology to trace the geographic origin of Earth’s waters.

The heavy isotopes of hydrogen and oxygen in rainwater (so-called meteoric water) are enriched as a function of the environmental temperature of the region in which the precipitation falls (and thus enrichment is related to mean latitude). The relative enrichment of the heavy isotopes in rainwater (as referenced to mean ocean water), when plotted against temperature, falls predictably along a line called the global meteoric water line (GMWL). This result allows us to determine precipitation water origin and its climate condition [67,74,75].

Evaporative and other processes in water bodies, including groundwater, also differentially alter the ratios of heavy hydrogen and oxygen isotopes and make clear the difference between the fresh and salt waters.

The ratios of the concentrations of stable isotopes \(^{2}H\) and \(^{18}O\) to their corresponding more abundant isotopes \(^{1}H\) and \(^{16}O\), respectively, are usually indicated with a delta, \(\delta^{2}H\) and \(\delta^{18}O\). Figure 13 plots the dependence between these parameters for the measured samples.

\[
\delta^{18}O = \frac{\text{sample} - \text{standard}}{\text{standard}} \times 1000
\]

\(\delta^{18}O\) varies between the maximum value of \(-3.92\text{%}\) according to the Vienna Standard Mean Ocean Water (VSMOW) (found in well P1) to the minimum value of \(-5.60\text{%}\) VSMOW (found in well P6) with the mean value around \(-4.60\text{%}\) VSMOW. For deuterium (\(\delta^{2}H\)), variations are from \(-28.67\text{ to } -39.99\text{%}\) VSMOW (wells P1 and P6, respectively), with the mean value around \(-34.70\text{%}\) VSMOW (Figure 13 and Table 2).

Although the eight water samples presented varying isotopic concentrations, they all plotted near and below the Global Meteoric Water Line (GMWL) defined by the equation \(\delta^{2}H = 8 \delta^{18}O + 10\) [61,62], (Figure 13 and Table 2). The regression line of the sampled points corresponded to \(\delta^{2}H = 5.79 \delta^{18}O - 6.30\) (Figure 13 and Table 2) with a high correlation coefficient (\(R^2 = 0.855\)). This proves that water resulting from rain events had undergone evaporation or been mixed with evaporated water before infiltrating the aquifer. In the study by Chafouq et al. [6], the sample points followed the line \(\delta^{2}H = 4.42 \delta^{18}O - 13.35\). Comparing our isotopic values in \(\delta^{2}H\) and \(\delta^{18}O\) with those in the water of the western Mediterranean Sea (...
Mediterranean Sea ($\delta^{18}$O $\frac{1}{4} = 0.97\%o$ and $\delta^2$H $\frac{1}{4} = 2.50\%o$) [76] shows that the Ghis-Nekor waters are depleted in heavy isotopes.

Our results agree with the results obtained by Elgettafi et al. [77]. The analysis of spring water in the Kert aquifer (NE Morocco) shows variations in $\delta^{18}$O, ranging from $-3.92\%o$ to $-5.60\%o$ with an average of around $-4.56\%o$ and variations in deuterium from $-34.10\%o$ to $-40.80\%o$ with an average of around $-32.15\%o$. They found that all the samples with a slope less than 8 do not fall on the meteoric water line and indicate light evaporation.

Moreover, the results obtained from the analysis of spring water from the limestone ridge of the Rif, south and north of Tetouan [77], show variations in $\delta^{18}$O ranging from $-3.92\%o$ to $-5.60\%o$ with an average of around $-4.6\%o$ and variations in deuterium from $-28.40\%o$ to $-41.70\%o$ with an average of around $-32.15\%o$. The report of these results in the $\delta^2$H–$\delta^{18}$O diagram shows that all the representative points of the sources are aligned between the two meteoric lines of Craig and of the western Mediterranean, with a regression line of equation $\delta^2$H = 5.79, $\delta^{18}$O = 6.30 ($R^2 = 0.855$). A slope value of 5.8 (less than 8) indicates a tendency for evaporation [77].

### 4.2.1. Altitudes of Recharge Areas

The isotopic composition of precipitation water changes with altitude. A systematic decrease in $^{18}$O and $^2$H isotopes is observed as the elevation increases. This phenomenon is called “altitude effect” and makes possible one of the most useful applications in isotope hydrology which is the identification of groundwater recharge areas. The altitude effect results from the cooling of air masses while ascending and the consequent condensation of the moisture excess.

For $\delta^{18}$O, the isotope depletion varies from $-0.15$ to $-0.50\;\delta^{18}$O‰/100 m with the global average of $-2.70\%o/100$ m [78]. This variation corresponds to a deuterium depletion from $-1$ to $-4\;\delta^2$H‰/100 m [78].

The isotopy of water depends on temperature and, therefore, on altitude. In mountainous areas, we can determine the relationship between the altitude and the isotope content when we have records of rainfall according to the altitude of the area. When there are no rainfall records, staged sources whose impluvium is known can be used to determine this relationship.

The global average depletion of the heavy isotopes of oxygen and hydrogen with altitude due to lower temperatures occurring at higher altitudes is from $\delta$ 0.15 to $\delta$ 0.50‰ for $\delta^{18}$O and from $\delta$ 1 to $\delta$ 4‰ for $\delta^2$H for every 100 m of altitude [74].

In Morocco, the regional isotopic altitude gradient at the city of Fez was found to be $\delta$ 0.27‰ per 100 m elevation [75]. For the Rif, this gradient was $\delta$ 0.25‰ per 100 m [79]. In another study, Bouchaou et al. [73] found a gradient of $-0.27\;\%o/100$ m and the average altitude of the estimated recharge area between 450 and 1770 m for the karstic sources of the Atlas of Beni Mellal.

In other Mediterranean countries, the isotopic gradient found in the Betic Cordillera (Spain) was $\delta$ 0.28‰ per 100 m altitude [80].

Recharge areas of the studied points following the regional isotopic altitude gradients of rainfall can be inferred from projecting $\delta^{18}$O concentrations for the analyzed sources [79,81]. By adopting the isotopic altitude gradient calculated in [79] and [81] ($-0.27\;\delta^{18}$O‰/100 m), the altitude of the studied area was estimated (Figures 14 and 15).

All the studied points showed an altitude of infiltration higher (isotope concentration lower) than the local altitude and lower than 775 m (Figure 15). The recharge areas of the points P4, P3, and P6 are located in the highest altitudes (between 560 and 715 m), corresponding to an infiltration in the mountains upstream of the basin, with altitudes varying between 900 m and 1000 m (Figure 15).
Figure 14. $\delta^{18}O$ concentrations (‰ VSMOW) as a function of sampling altitude (m) for the studied wells.

Figure 15. Altitude recharge map of the sampled wells.

On the other hand, the recharge areas of the points P1, P2, P5, P7, and P8 are at lower altitudes (around 190–440 m) (Figure 15). These results agree with the observations of the reliefs of the Ghis-Nekor basin. Towards the west of the basin, the altitude increases from 144 m at the level of wadi Nekor towards 786 m at Jbel Taourda and 803 m at Jbel Mahajar. Towards the east, the altitude oscillates between 484 m at Jbel Ait Karal up to 510 m at Jbel Zaouit Si Aissa. Upstream of the basin, the altitude varies between 1000 m at Jbel Ait...
Messoud and 1071 m at Jbel Bni Bouayache (Figure 15). Our results are in agreement with the work of Bouissa et al. [81] just at the boundary between our basin (Ghis-Nekor) and the Bokoya massif (central Rif, northern Morocco). These authors found that the stable isotope contents varied from $\delta^13$C 6.69 to $\delta^13$C 4.84‰ for $\delta^{18}$O and $\delta^{30}$H for $\delta^{2}$H, indicating an altitude of recharge for most of the springs between 350 m and 750 m and exceptions by recharging from the flysch of Tizirene at altitudes higher than 1000 m.

Furthermore, our results are in agreement with the works of Qurtobi et al. [75], where the average altitude of the recharge area estimated for the sources was between 441 m and 1200 m, and Bouchaou et al. [73], where the estimated altitude of the recharge area was between 450 m and 1770 m for the karstic sources of the Atlas of Beni Mellal.

4.2.2. Origin of Carbon

The inorganic carbon dissolved in groundwater is a footprint of the transport history of this water and the processes originating that carbon. Total dissolved inorganic carbon (TDIC) is a measure of the total amount of CO$_2$, HCO$_3^-$, and CO$_3^{2-}$ in water. The origin of this carbon can be very complex and varied. The carbon isotopic composition provides insight into the carbon transfer between the water and the environment.

The TDIC in groundwater is a mix of carbon coming from different sources [82]:

- Decomposition of organic matter of aquifer sediments, with a typical isotopic composition $\delta^{13}$C (ratio between $^{13}$C and $^{12}$C) around $-28$‰;
- Dissolution of calcites or other carbonate minerals from the rock, with a $\delta^{13}$C value between $-14$‰ and $+1$‰;
- Diffusion of the atmospheric CO$_2$, with a $\delta^{13}$C from $-6$‰ to $-8$‰.

The waters from the Ghis-Nekor basin show concentrations of total dissolved inorganic carbon (TDIC) from 300 mg/L to 584 mg/L, with values of $\delta^{13}$C in the range of $-3.15$‰ and $-8.61$‰ (Figure 16).

![Figure 16. Composition of $^{13}$C of CO$_2$ in isotopic equilibrium with TDIC (in ‰ VPDB) as a function of TDIC content (total dissolved inorganic carbon, mg/L).](image-url)
The TDIC results are similar to those in the work of Winckel et al. [79] where waters from the Liassic limestone showed TDIC contents close to 500 mg/L. However, the range of δ¹³C of CO₂ in isotopic equilibrium with TDIC in this work was wider (between −20% and −3%). According to the authors, this range was representative of mixing between two end members: biogenic carbon and mineral carbon [75].

In the present study, the values of δ¹³C (ranging between −3.15‰ and −8.61‰) suggested that the origin of carbon is mainly mineral from the dissolution of calcites or other carbonate minerals, corresponding to a soil with poor biology activity.

Additionally, a linear relation was found between the TDIC and the isotopic δ¹³C (Figure 16). This is indicative that the increment of the TDIC in the samples was produced by an increase in carbon concentration coming from CO₂ dissolution.

This study presents the results of a joint application of hydrochemical analysis and several isotopic tools to reveal the origin of recharge water and the origin of carbon in groundwater resources of the Ghis-Nekor aquifer in northern Morocco. Figure 17 is a model that summarizes the main results found in this work, essentially the hydrogeological functioning and the associated phenomena (evaporation, recharge).

Figure 17. Summary of the determination of physicochemical water quality of the Ghis-Nekor aquifer (Al Hoceima, Morocco) using hydrochemistry and multiple isotopic tracers.

5. Conclusions

The analysis and interpretation of the results allow us to make the following conclusions:

– The aquifer is subject to a notable marine intrusion proved by a water type transition from NaCl to NaSO₄. This phenomenon is accentuated in the east. The projection of the analyzed sample results in the Piper diagram shows two distinct facies; the sodium chloride facies and chloride and calcium and magnesium sulfated facies. Chloride concentrations varied between 277 mg/L and 2976 mg/L. The relationship between Na⁺ and Cl⁻ shows that some coastal wells, located in the extreme NE
of the plain, are located on the NaCl correlation line, and their molar ratio Cl/Na does not differ very tangibly from that of seawater. This indicates the presence of freshwater–saltwater mixing process without ion exchange reactions.

- Cl/Na ratio was also studied and compared with the Cl/Br ratio to attest the possible presence of saltwater intrusion. Besides, NaCl is widely used in various human activities, and a high Cl/Br ratio is generally considered a good indicator of the impact for domestic water. They classified the waters of the plain of the Nekor into two classes, the vulnerable wells in the north affected by high salinity and characterized by Cl/Na and Cl/Br ratios close to sea water (Cl/Na = 1.2; Cl/Br = 650); the salinity of the samples described above is probably attributed to the intrusion of saline water; and the other class located upstream of the basin with lower salinity than in the first class, with the influence of geology, agriculture, and anthropogenic activities.

- The δ¹⁸O values varied between −3.92‰ and −5.60‰, while the δ²H values varied between −28.67‰ and −39.99‰. These ranges of values indicate that the recharge water undergoes evaporation before reaching the aquifer. This proves that resulting rain events result from evaporation or the elements are mixed with evaporated water before infiltrating the aquifer. The sample points followed the line δ²H = 5.79 δ¹⁸O −6.30. Comparing with the values of δ²H and δ¹⁸O in the western Mediterranean Sea, our isotopic values in the Ghis-Nekor waters are depleted in heavy isotopes.

- The results show that the recharge areas of the points of the study area are situated at altitudes between 190 m and 775 m.

- The calculated δ¹³C concentration is between −3.15‰ and −8.61‰, which indicates the carbon origin is mainly the dissolution of calcites or other carbonate minerals from the rock.

- The analysis of the bromide and strontium contents made it possible to discriminate the origin of salinity anomalies in the water table. The Br/Cl and Sr/Ca molar ratios distinguished the areas of evaporitic (saliferous facies outcrops) or anthropogenic (wastewater) influence.

Author Contributions: Conceptualization, N.N. and E.K.C.; formal analysis, N.N., E.K.C., M.A., M.L.P., S.F., J.C.G.e.d.S., H.M. and K.D.; resources, N.N., A.N. and E.K.C.; writing—original draft preparation, N.N. and E.K.C.; writing—review and editing, E.K.C., N.S., D.A.K., A.R. and E.M.A.; funding acquisition, D.A.K. and A.R.; supervision, A.R. and E.K.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research did not receive any specific grants from funding agencies in the public, commercial, or not-for-profit sectors.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors would like to thank all the researchers who worked hard to advance knowledge and improve outcomes of this paper. We would also like to thank the editor and the reviewers for their comments which helped us improve the paper. Dorota Anna Krawczyk and Antonio Rodero would like to acknowledge the financial support from funds of the BUT Inter Academic Partnerships (PPI/APM/2018/1/00033/DEC/1) NAWA project and WZ/WBiIS/9/2019 scientific research at Białystok University of Technology. El Khalil Cherif would like to mention the financial support by FCT with the LARSyS—FCT project UIDB/50009/2020 and FCT project VOAMAIS (PTDC/EEIAUT/31172/2017, 02/SAICT/2017/31172). Joaquim G.C. Esteves da Silva would like to acknowledge the financial support by FCT (project UIDB/00081/2020).

Conflicts of Interest: The authors declare no conflict of interest.
52. Kabbaj, A.; Zeryouhi, I.; Carlier, P.; Marco, A. Contribution Des Isotopes Du Milieu à l’étude de Grands Aquifères Du Maroc [Contribution of Environmental Isotopes to the Study of Large Aquifers of Morocco]. In Proceedings of the International Symposium on Isotope Hydrology, Vienna, Austria, 27 March–1 April 2011; Volume 2, pp. 491–523.

53. Michélot, J.L.; Sinan, M.; Krimissa, M.; Krimissa, M.; Bichara, S.; Louvat, D. Hydrologie Isotopique Des Systèmes Aquifères de Fès-Meknès, Er-Rachidia et Kheng El Hamaniy Rapp; AIEA MGR/008/4. Vienne, Austria, 1992.

54. Ouda, B.; Marah, H.; Mokadem, K.; Zine, N.; Filali, M.; Lahmouri, A.; Mudry, J. Geochemical and Isotopic Characterization of Groundwater Resources in Maidere Basin (Southern Part of Morocco). Adv. Isot. Hydrol. Its Role Sustain. Water Resour. Manag. IHS—2007. 2007, 21, 149.

55. Bouchaou, L.; Michelot, J.L.; Qurtobi, M.; Zine, N.; Gaye, C.B.; Aggarwal, P.K.; Marah, H.; Zerouali, A.; Taleb, H.; Vengosh, A. Origin and Residence Time of Groundwater in the Tadla Basin (Morocco) Using Multiple Isotopic and Geochemical Tools. J. Hydrol. 2009, 379, 323–338. [CrossRef]

56. Hsiissou, Y.; Chauve, P.; Manja, J. The aquifer of Turonian limestones (Tadla Basin, Morocco). Local and remote groundwater recharge from the Atlas. J. Hydrol. 1996, 3–4, 433–443. [CrossRef]

57. El Ouali, A. Modalités d’alimentation et échanges Entre Aquifères de Piémont en Conditions Climatiques Arides. Cas des Systèmes Aquifères du Haut Atlas/Bassin Créétu d’Errachidia (Maroc); Université Mohamed-V & Ecole Mohammadia d’ingénieurs: Rabat, Morocco, 1999.

58. Marjoua, A.; Olive, P.; Jusserand, C. Apports des outils chinoques et isotopiques à l’identification des origines de la salinisation des eaux: Cas de la nappe de La Chaouia côté (Maroc). Rev. Sci. Eau J. Water Sci. 1997, 10, 489–505. [CrossRef]

59. ABHL. Lokous Hydraulic Basin Agency, Morocco. Available online: http://www.abhloukkos.ma/index.php/fr/ (accessed on 28 January 2022).

60. ABHL. Étude d’élaboration Du Schéma d’aménagement Des Ressources En Eau Du Bassin de Ghiss-Nekkor. Mission 1: Évaluation Des Ressources En Eau Sous-Mission 1.2: Évaluation Quantitative Des Ressources En Eau; ABHL: Rabat, Morocco, 2015.

61. Revézès, K.M.; Doctor, D.H. Automated Determination of the Stable Carbon Isotopic Composition (δ13C) of Total Dissolved Inorganic Carbon (DIC) and Total Nonpurgeable Dissolved Organic Carbon (DOC) in Aqueous Samples: RSIL. Lab Codes 1851 and 1852. Tech. Methods Book 2014, 10. [CrossRef]

62. Waldron, S.; Scott, E.M.; Viherrna, L.E.; Newton, J. Quantifying Precision and Accuracy of Measurements of Dissolved Inorganic Carbon Stable Isotopic Composition Using Continuous-Flow Isotope-Ratio Mass Spectrometry. Rapid Commun. Mass Spectrom. 2014, 28, 1117–1126. [CrossRef]

63. Torres, M.E.; Mix, A.C.; Rugh, W.D. Precise δ13C Analysis of Dissolved Inorganic Carbon in Natural Waters Using Automated Headspace Sampling and Continuous-Flow Mass Spectrometry. Limnol. Oceanogr. Methods 2005, 3, 349–360. [CrossRef]

64. Ministre de l’Équipement et du Transport du Ministre de la Santé, du Ministre de l’Aménagement du territoire, de l’Eau et de l’Environnement et du Ministre de l’Industrie, du Commerce et des Télécommunications. NM 03.7.001. Available online: https://pdfcoffee.com/nm-037001-norme-maroccaine-eau-alimentation-4-pdf-free.html (accessed on 15 July 2021).

65. Piper, A.M. A Graphical Procedure in the Geochemical Interpretation of Water-Analyses. Eos. Trans. Am. Geophys. Union 1944, 25, 914–928. [CrossRef]

66. Schoeller, H. Qualitative Evaluation of Groundwater Resources. In Methods and Techniques of Groundwater Investigations and Development; The United Nations Educational, Scientific and Cultural Organization: Paris, France, 1965; pp. 54–83.

67. Ghali, M.; Yousfi, E.B.; Zouhairi, M.; Gharibi, E.; Taupin, J.D. Hydrochemical Characterization of Groundwater in the Nekor Basin Located in the North-East of the Rif of Morocco. Moroc. J. Chem. 2017, 5, 272–284. [CrossRef]

68. Lamhamdi, A.; Ghali, M.; Gharibi, E.; Anafous, A.; Elyounsi, K.; Essaki, F.; Azzaoui, K.; Zarrouk, A. Physico-Chemical and Bacteriological Study of Water from a Few Sources in al Hoceima Region–Morocco. Pharm. Lett. 2015, 7, 195–202.

69. Petelas, C.P.; Diamantis, I.B. Origin and Distribution of Saline Groundwaters in the Upper Miocene Aquifer System, Coastal Rhodope Area, Northeastern Greece. Hydrogeol. J. 1999, 7, 305–316. [CrossRef]

70. Carre, J. Geochemistry of Strontium in Groundwater and Surface Water in the Paris Region. Ph.D. Thesis, University of Paris VI, Paris, France, 1975.

71. Naily, W. Cl/Br Ratio to Determine Groundwater Quality. In Proceedings of the IOP Conference Series: Earth and Environmental Science; IOP Publishing: Tokyo, Japan, 2018; Volume 314, p. 07006.

72. Alcalá, F.J.; Custodio, E. Using the Cl/Br Ratio as a Tracer to Identify the Origin of Salinity in Aquifers in Spain and Portugal. J. Hydrol. 2008, 359, 189–207. [CrossRef]

73. Bouchaou, L.; Michelot, J.-L.; Chauve, P.; Manja, J.; Mudry, J. Apports Des Isotopes Stables à l’étude Des Modalités d’alimentation Des Aquifères Du Tadla (Maroc) Sous Climat Semi-Aride. C. R. Académie Sci. Sér. 2 Sci. Terre Planètes 1995, 320, 95–101.

74. Aeschbach-Hertig, W.; El-Gamal, H.; Dahab, K.; Friedrich, R.; Kipfer, R.; Hajdase, I. Identifying and Dating the Origin of Groundwater Resources in Reclamation Areas of Egypt. In Proceedings of the Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management, International Atomic Energy Agency (IAEA), Vienna, Austria, 21–25 May 2007; pp. 395–403.

75. Qurtobi, M.; Marah, H.; El Mahboul, A.; Emblanch, C. Groundwater Tracing Using Stable Isotope in the Western Mediterranean (Case of Rif Chain in the North of Morocco). In Advances in Research in Karst Media; Springer: Berlin/Heidelberg, Germany, 2010; pp. 183–188.
76. Alia, A.C. Etude Hydrogéologique et Hydrochimique de La Plaine Côtière de Bou-Areg (Maroc Nord-Oriental). Ph.D. Thesis, University of Gent, Gent, Belgium, 2001.

77. Elgettafi, M.; Elmandour, A.; Himi, M.; Casas, A. The Use of Environmental Markers to Identify Groundwater Salinization Sources in a Neogene Basin, Kert Aquifer Case, NE Morocco. *Int. J. Environ. Sci. Technol.* 2013, 10, 719–728. [CrossRef]

78. Clark, I.D.; Fritz, P. *Environmental Isotopes in Hydrogeology*; Taylor & Francis Group: Boca Raton, FL, USA, 1997; 348p.

79. Winckel, A.; Marlin, C.; Dever, L.; Morel, J.-L.; Morabiti, K.; Makhlouf, M.B.; Chalouan, A. Apport Des Isotopes Stables Dans l’estimation Des Altitudes de Recharge de Sources Thermales Du Maroc. *C. R. Geosci.* 2002, 334, 469–474. [CrossRef]

80. Julián, J.J.C.S.; Benavente, J.; Garrido, J.C.M.; Moral, F.; Aragúas, L.; Vera, F.L. Deuterium And Oxygen-18 Content in Karstic Aquifers in the Sierras de Cazorla and Segura (Betic Cordillera, Spain). *Water Resour. Mt. Reg. Parriaux Ed Memoires IAH* 1990, 22, 424–433.

81. Bouaissa, M.; Gharibi, E.; Ghalit, M.; Taupin, J.D.; El Khattabi, J. Identifying the Origin of Groundwater Salinization in the Bokoya Massif (Central Rif, Northern Morocco) Using Hydrogeochemical and Isotopic Tools. *Groundw. Sustain. Dev.* 2021, 14, 100646. [CrossRef]

82. Porowska, D. Determination of the Origin of Dissolved Inorganic Carbon in Groundwater around a Reclaimed Landfill in Otwock Using Stable Carbon Isotopes. *Waste Manag.* 2015, 39, 216–225. [CrossRef] [PubMed]