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# Radiocarbon Dating and Stable Isotopes Content in the Assessment of Groundwater Recharge at Santiago Island, Republic of Cape Verde

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Abstract: The over-exploitation of coastal aquifers has led to seawater intrusion issues in many parts of the globe; this problem, which is associated with water recharge deficit and anthropogenic pollution, represents the main source of groundwater degradation in Santiago Island in the Republic of Cape Verde's archipelago. Brackish groundwater for agriculture and human consumption is being provided to several areas on Santiago Island as the only type of available water. Chemical and isotopic data obtained in three main groundwater systems were used in the characterization of the groundwater resources and in the identification of the main source responsible for their degradation. The obtained results indicate water-rock interaction as the major process responsible for the groundwater quality reflecting its lithological composition. Carbonatite dissolution can be partially responsible for the calcium increase along the groundwater flow path. Isotopic data  $(\delta^2 H, \delta^{18} O; {}^{3}H \text{ and } {}^{14}C)$  combined with the water chemistry provided a wide characterization of the groundwater recharge and identification of salinization processes (like seawater intrusion and marine aerosols dissolution in different sectors of the island). In the eastern part of Santiago Island, a different isotopic pattern (<sup>2</sup>H-<sup>18</sup>O) was observed in the groundwater samples, which was likely ascribed to different climate conditions. Carbon-14 determinations indicate apparent groundwater ages between 3.5 and 5.1 ka BP.

**Keywords:** stable isotopes; groundwater salinization; radiocarbon dating; semi-arid climate; Santiago Island; Republic of Cape Verde

## 1. Introduction

Environmental isotope tracer methodologies have proved to be powerful tools in different hydrogeological investigations, thus allowing for a better characterization of groundwater systems as shown in different hydrogeological studies, namely in terms of the:

- (i) Identification of the origin of dissolved constituents in groundwaters related to seawater intrusion problems vs. salt dissolution—evaporitic minerals [1–7];
- (ii) Quantification of mixing between different water types characterized by distinct isotope signatures like groundwater age and age distribution [2,3,8];



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- (iii) Identification of groundwater recharge under different climatic conditions (paleowaters) [8,9];
- (iv) Quantification of groundwater vulnerability to pollution [10,11], and
- (v) Identification of the preferential elevation of recharge areas [12,13].

Additionally, the combined measurements of chemical parameters, jointly with stable ( $\delta^2$ H and  $\delta^{18}$ O) and radioactive (<sup>3</sup>H and <sup>14</sup>C) isotopes, provided a powerful approach in numerous studies of the groundwater evolution along the flow path, as well as recharge/discharge relationships [2,3,6,14–17].

Water resource systems have an essential place in the economic and social development of any region in the globe, particularly in arid and semi-arid regions. The high socioeconomic and ecological importance of groundwater systems and their significance as a strategic resource is recognized as vitally important in many African countries, like in the case of the Republic of Cape Verde. However, the available data and interpretation on groundwater systems in African countries are sparse, and the current state of knowledge is low, with serious limitations to the sustainable development of groundwater resources [18]. In addition, in coastal regions, groundwater exploitation is often vulnerable to seawater intrusion issues, leading to processes of salinization that threaten the exploitation of additional water resources [5,19]. Salinization can be the result of connected processes related to both seawater intrusion and water-rock interaction processes. Among them, the adsorption of sodium by the aquifer matrix, with the release of calcium, is a process that is activated when seawater intrusion occurs [12,20–22]. The incursion of seawater towards coastal terrains is a widespread water resources problem all over the world, especially under the threat of surface temperature increase and decrease in precipitation in the Mediterranean regions, Middle East and North African countries.

The water quality issues have been described by different authors in different geographic and hydrogeological environments, reported from the European continent dealing with brackish water such as in Portugal, Italy, Spain, France, Greece and Cyprus [2,16,23–29], but also identified from Australia to Asia, South America and Africa [1,3,6,7,19,30–32]. Additional issues can arise in karstic regions, as mentioned by Alexakis and Tasakisis [26,27] in their investigations at Almyros karstic spring (Crete). According to these authors, karstic springs in coastal areas present a different hydrological behavior, i.e., in karstic aquifers, the populations are dealing with brackish water all year, with only a few days of good quality water. Contributing to the increase in the water demand, the expansion of agricultural areas and the excessive use of fertilizers represent an additional source of groundwater resources salinization, where freshwater for the human supply becomes a scarce resource [6,31,33,34]. The relation between human activities and the increase of salinization of groundwater resources is well noticed in the reuse of fresh water in agricultural activities [35–37].

The Republic of Cape Verde is composed of 10 volcanic islands (Figure 1a) and is located about 500 km west of Senegal, Africa. Due to its proximity to the equator (15–17° N), the air temperature varies seasonally by 5 °C throughout the year [38,39]. At Santiago Island (Republic of Cape Verde), like in most African countries, the population is dependent on groundwater for domestic and agricultural uses; this water is pumped from boreholes or collected directly from springs and, in some areas, represents the only available water source. Surface water resources on Santiago Island are almost nonexistent, and only offer a few small dams and perennial streams [39]. According to data obtained in 2021 (last survey) performed by the Cape Verde National Institute of Statistics (CENSO 2021, Instituto Nacional de Estatística), the country has 505,044 inhabitants, of which about 266,161 live on Santiago Island [40].



**Figure 1.** (a) Republic of Cape Verde archipelago location the start stands for the (adapted from [38]) (b) Location of the sampling points at Santiago Island.

At Santiago Island, the population lives in rural areas and derives its livelihood from rain-fed agriculture. However, over the last two decades, farming activities have been changing in the valley areas near the coastal line, places where banana and papaya fields can be found. As a result of the intensification in agriculture, the monitoring of the fresh–saltwater interface and the rate of exploration is being carried out by the Republic of Cape Verde National Water Authority to avoid saltwater pumping. One of the actions implemented by the local water authority is that no new boreholes are allowed to be drilled near the coast, and the public boreholes are only allowed to work 2 to 3 h per day (for agriculture and to supply the population). The increasing salinity and vulnerability to pollution at Santiago Island aquifers encouraged the local government to seek external assistance in the framework of bilateral cooperation between the Republic of Cape Verde and Portugal. The groundwater salinity, its origin, and prevention are important components for groundwater resource protection and management, especially in the context of deterioration from pollution or overexploitation.

In this research, the two major challenges were: (i) to distinguish the main source of mineralization of the groundwater systems (seawater intrusion vs. marine aerosols dissolution); (ii) to estimate the mean groundwater residence time based on the radiocarbon content and the tritium data. From this research, groundwater dating information allowed Santiago Island groundwater to recharge in a different climatic scenario. With these goals, sampling campaigns were carried out at Santiago Island, and groundwater was collected to determine the chemical (major ions) and isotopic composition ( $\delta^2$ H,  $\delta^{18}$ O, <sup>3</sup>H, and <sup>14</sup>C) of the selected water samples.

#### 2. Climatology, Geological and Hydrogeological Setting

## 2.1. Climatology

Santiago Island is located in the southeastern part of the Republic of Cape Verde archipelago and presents climatic features similar to the Sahel regions, with seasonal changes related to the Inter-Tropical Front (ITF). The rain distribution is irregular and mainly observed from July to October [38,39,41–43]. The precipitation distribution is heterogeneous, varying from 50 mm/year along the coastal areas to 400–1000 mm/year at the highest mountains, respectively (Serra da Malagueta and Pico da Antónia, Figure 1b).

An important part of the precipitation is lost by evapotranspiration and runoff to the sea, mainly linked to the topographical gradient and to the thin soil thickness. During the year, the air temperature shows small fluctuations, around 5  $^\circ$ C between the mean winter season (minimum value around 22 °C in February) and the mean summer season (maximum value about 27 °C in September). The wind is rather constant all year, with north–northeast being the predominant direction. The regular winds that cross the island play an important role in the diffusion and transport of marine aerosols observed, particularly in the coastline areas. Marine aerosols represent one possible source of salts for the increase of groundwater systems mineralization. The wind regime throughout the year plays a more important role in Cape Verde climate, more important than the Intertropical Convergence Zone (ITCZ). As previously mentioned, the rainfall over Cape Verde, Santiago Island is concentrated over three to four months and is responsible for more than 75% of the total precipitation on the island, although the Intercontinental Convergence Zone plays an important role in the atmospheric dynamics of the tropics and in the rainfall over West Africa [43]. According to these authors, the rainfall is mostly related to the transient convective disturbances associated with the frontal systems that cross the Atlantic and not with the Intercontinental Convergence Zone or from squall lines from North Africa.

## 2.2. Geology and Hydrogeology

Santiago Island has a volcanic origin, being mainly composed of a volcano-stratigraphic sequence first reported by Serralheiro in 1974 [44] and later improved by Matos Alves and coauthors [45]. Three main geological units with hydrogeological interest were identified on the island, namely:

- (i) Pico da Antónia (PA) and (A) eruptive complex;
- (ii) Monte das Vacas formation (MV), and
- (iii) Sedimentary quaternary formations (a).

From the hydrogeological point of view, the most important reservoir of fresh water is the eruptive complex of Pico da Antónia with terrestrial and submarine facies (pillow-lavas) (Figure 2).



Figure 2. Santiago Island geological map. Adapted from [39].

Hydrogeological studies carried out on Santiago Island show that the storage coefficient of the Pico da Antónia and Eruptive Complex is relatively high when compared to the other hydrogeological formations on the island [30,31,36]. The mean transmissivity values presented by these authors range between  $10^{-1}$  to  $2 \times 10^{-2}$  m<sup>2</sup>/s; the permeability of these

layers avoids a rapid discharge of groundwater from these high-transmissivity aquifers, which is compensated for by rapid recharge. The Pico da Antónia eruptive complex covers an impermeable formation known as the Base Unit (CA/ $\lambda \rho$ /CB), which is composed of the Ancient Internal Eruptive Complex (AIEC). The Ancient Complex Formation (CA) is the oldest geological formation identified at Santiago Island (Upper Jurassic) and is mainly represented by aphanitic rocks, mostly by basic dykes and phono-trachyte, sometimes with intrusions of silicate granular rocks. This formation is visible in different parts of the island, particularly in the great plateau depression between Pico da Antónia and Serra Malagueta. This formation is made up of vertical or subvertical veins, representing a dense network of basaltic veins, gabbroic granular rocks, syenites and sometimes carbonatites rocks [39]. The Flamengo and the Conglomerate-Breccia formation represent the two components of the AIEC, which is characterized by a generalized degree of weathering and a high rate of compactness and low permeability (Figure 2). According to Lobo de Pina [39], this formation is in unconformity over the CA, consisting of the mantle, breccias, and basic pyroclastics of great uniformity and is an extension of submarine nature. Locally pillow lavas were identified. The outcrops of Flamengo formation occur mainly in valleys and along streams.

The Pico da Antónia unit (PA) is responsible for the higher altitude reliefs found on the island, but also for their main structural platforms. The PA unit is composed of products of explosive and effusive subaerial and submarine activities that occurred at different time periods [44]. According to this author, it is possible to identify sedimentary events interspersed with magmatic episodes, but these are difficult to reconstruct. According to Serralheiro [44], the terrestrial volcanic events are composed of pyroclastic and intercalated flows, tuff breach, phonolites and trachytes. It should be mentioned that the Pico da Antónia formation is well marked by lava and tuffs of high porosity representing the best aquifers systems on the island [39]. The eruptive Complex Unit, also called "Formação da Assomada" (A), has exclusively subaerial volcanic activity, such as lava flows with basaltic facies and the scarce presence of pyroclasts [45]. The Monte das Vacas Unit (MV) is the most recent volcanic record that can be found at Santiago Island. This unit is characterized by a reduced-thickness MV formation and is made of very porous materials, such as basaltic pyroclastic (tuffs, bombs, and slag) and small lava flows scattered throughout the island [39]. At Santiago Island, terrestrial and marine Quaternary formations abound, including alluvium deposits, terraces, slope deposits, dune sands and marine beaches. These formations were identified at different altitudes [44,46], playing an important hydrogeological role, particularly in large valleys, such as Ribeira Seca and Picos, due to their thicknesses greater than 40 m [39].

The Santiago Island stratigraphy was established by Serralheiro and Matos Alves [44,45] and comprised six units, including the old Eruptive Complex date > 20 Ma, Flamengos Formation (45 to 5.5 Ma), Pico da Antónia formations with ages of 2.3–3.3 Ma; the Assomada formations and Monte das Vacas dated from 2.3–2.6 Ma and 1.1 to 0.7 Ma, respectively [47], and the Quaternary alluvial deposits.

The National Institute of Water Resources and Management (INGRH) of the Republic of Cape Verde performed pumping tests and some drilling throughout Santiago Island. The results indicate that the pillow lava layers with their fissures and holes constitute the hydrogeological formation, with the highest productivity (approximately 40 m<sup>3</sup>/h) being the stabilization reached in the first minutes [48]. Additionally, the study performed at Monte das Vacas formation (MV), composed mainly of pyroclastic material cones, suggests a good vertical flow component and a high degree of permeability and porosity. In the Tarrafal area (Figure 2), a mean value of 10% of porosity was obtained [48–50]. The Monte das Vacas formation outcrops mainly at Santiago Island peaks (Pico da Antónia and Serra Malagueta), which are the areas with the highest recorded precipitation. Due to its permeability, infiltration is favored. The infiltrated water is rapidly drained to lower levels of Monte das Vacas formation, reaching the AIEC, with low permeability and a high rate of compactness.

Water balance studies performed at Santiago Island indicate that 18% of precipitation is converted into runoff and directly discharged to the sea—only 13% infiltrates the soil, and the remaining water is lost to evapotranspiration [46].

Geophysical investigations using electromagnetic surveys were carried out on Santiago Island [48–50] to characterize the quality of water resources in the coastal areas. Geophysical surveys identified two main zones, according to the water depth and mineralization: an intermediate and a deep zone. As stated by Gonçalves and co-authors [49], the intermediate zone represents the groundwater mostly used for irrigation purposes, while the deep zone (groundwater more mineralized) is related to seawater intrusion and/or to leaching of ancient salt deposits associated with the depositions of marine aerosols. In this work, the authors mentioned the delicate balance between the freshwater with "marine aero-salt deposits" in the Tarrafal region (N part of the island) and in Ribeira Grande valley (SW part of Santiago), where overexploitation conditions were observed. Based on resistivity data, a cross-section along Ribeira Grande valley suggests that the fresh–saltwater interface rises from -60 m a.s.l. to -20 m a.s.l. [39,46]. A similar situation was also reported by those authors at São Domingos Valley, pointing to the occurrence of seawater intrusion.

### 3. Sampling and Analytical Approach

Groundwater sampling campaigns were performed at Santiago Island in November 2005, February 2006 and November 2006. In total, 115 selected points were sampled, and groundwater was collected from boreholes and springs for chemical (major ions and cations) analysis and isotopic ( $\delta^2$ H,  $\delta^{18}$ O and <sup>3</sup>H) determinations. Radiocarbon and <sup>13</sup>C determinations were performed in six selected points located in the eastern part of the island. Before the sampling, electrical conductivity ( $\mu$ S/cm), pH and temperature (°C) were measured in situ.

Water chemical analyses were performed in the INIDA Laboratory at São Jorge dos Orgãos-Santiago Island, the Republic of Cape Verde, for major ion content (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2</sup>) and silica content [39]. The analytical methods used were flame photometry (Na and K), titration with EDTA (Ca and Mg), potentiometric titration to predefined pH (HCO<sub>3</sub>), atomic and molecular adsorption spectrophotometry (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and SiO<sub>2</sub>), and precipitation volumetry according to the Mohr method for the Cl [39]. In the Supplementary Materials, the analytical values and the estimated mass balance error are presented. All the chemical determinations had charge balance errors <  $\pm 10\%$  and 32% of the analyses an error <  $\pm 5\%$ .

Tritium content and stable isotopic determinations were performed at Centro de Ciências e Tecnologias Nucleares (C<sup>2</sup>TN) of IST (Instituto Superior Técnico—University of Lisbon, Portugal), formerly designated by Instituto Tecnológico e Nuclear, ITN—Chemistry Department, Sacavém, Portugal. The <sup>2</sup>H and <sup>18</sup>O results are reported in  $\delta$  notation and were measured with the accuracy (1 $\sigma$ ) of 1‰ for  $\delta^{2}$ H and 0.1‰ for  $\delta^{18}$ O.  $\delta^{2}$ H and  $\delta^{18}$ O were determined three times for each sample to increase the precision analysis. These determinations were conducted by mass spectrometer SIRA 10 VG-ISOGAS using the methodology proposed by Friedman in 1953 [51] and modified by Tanweer and coauthors [52,53] for deuterium. For the oxygen-18 measurements, the methodology proposed by Epstein and Mayeda in 1953 was applied [54]. The tritium content was determined using the electrolytic enrichment and liquid scintillation counting method (PACKARD TRI-CARB 2000 CA/LL). The error associated with the <sup>3</sup>H measurements (around 0.6 TU, 1 $\sigma$ ) varies with the <sup>3</sup>H concentration in the water sample [55]. The tritium data is expressed in Tritium Units (TU), where 1 TU represents a ratio of <sup>3</sup>H/<sup>1</sup>H = 10<sup>-18</sup>.

The isotopic determinations (in the Total Dissolved Inorganic Carbon—TDIC) were performed at Geochron Laboratories, USA. The  $\delta^{13}$ C was measured by mass spectrometry and the values are reported in ‰ vs. V-PDB, with an accuracy (1 $\sigma$ ) of  $\pm 0.1$  ‰. The <sup>14</sup>C content (measured by AMS) is given in pMC (percentage of Modern Carbon).

## 4. Results and Discussion

## 4.1. Hydrogeochemical Characterization

In order to characterize the different aquifer units, the groundwater samples were grouped into three different units according to the geological formations: the Base Unit composed of the eruptive complex of Pico da Antonia (PA) and (A); the Middle Unit represented by Monte das Vacas' formation (MV), and the Recent Unit constituted by sedimentary Quaternary formations (a).

No trend was identified between the temperature of the groundwater and the different units. The electrical conductivity values of the sampled waters at Santiago Island ranged from 128  $\mu$ S/cm (FT-81), with a borehole situated in the southeastern region of the island and around 15 km from the coastline, to 9400  $\mu$ S/cm in FT-23, located at Pico da Antónia mountain, approximately 25 km from the coastline. Both of the extreme values were obtained in the Middle Unit formation, and from one instance of fieldwork to another, a fluctuation of the groundwater mineralization was observed. Such a wide spread of mineralization values can be derived from different mechanisms from water–rock interaction processes and salt dissolution to fresh water–seawater mixing mechanisms. However, due to the constant windy conditions, one should also consider the deposition of marine aerosols as NaCl salts on land, which during the precipitation. All over the island, a wider range of groundwater mineralization content is observed.

The pH ranged between 6.6 and 8.0 for most samples. To evaluate and discriminate the different groundwater facies in the three-aquifer units, the chemical composition of the water samples was represented in a Piper diagram to assess some of the chemical evolution along the flow paths (Figure 3). In analyzing the Piper diagram, no clear distinction between the base and middle groups was observed; no correlation between the geochemical evolutions with a specific geological formation or type of sampling point (spring or borehole) was recognized. However, a trend line evolution towards seawater intrusion processes seems to be present, decoded by the relation between the Cl<sup>-</sup> and Na<sup>+</sup>. Based on the sample distribution in the Piper diagram, it seems that the main process controlling the groundwater unit distribution can be seawater intrusion of salt dissolution. As previously mentioned, the hypothesis of marine aerosols dissolution cannot be excluded in different parts of the island, not only in coastal areas, as these salts can present similar chemical composition as seawater composition (halite dissolution, for example).

Geographic and climatic conditions are responsible for the constant wind regime crossing Cape Verde islands, inducing the deposition of marine aerosols inland, in which presence/dissolution cannot be excluded as a potential source of groundwater mineralization. The dissolution of the marine salts inland can be responsible for an increase in the water mineralization, which supports the dispersion of the EC values found all over the island [39,49]. From the chemical point of view, this dissolution of marine aerosols will be similar to the chemical evolution content during freshwater–seawater mixing processes, highlighted by the strong correlation between sodium and chloride, or even by the Ca<sup>2+</sup>-SO<sub>4</sub><sup>2+</sup> relation, which trends previously reported by other authors [2,6,10,11,56–59]. Such assumptions seem to be feasible for Na<sup>+</sup>-Cl<sup>-</sup>. The strong correlation observed between these two "parameters" is well noticed in the Middle Unit formation (r = 0.91 considering FT-109 or r = 0.81 without FT-109), which can be ascribed to water–rock interaction processes (dissolution of salts) or to seawater mixing process. However, in the case of Ca<sup>2+</sup>-SO<sub>4</sub><sup>2+</sup>, the correlation will change largely if the FT-109 water sample is considered (r = 0.67) or not (r = 0.23).



**Figure 3.** Piper diagram for Santiago Island groundwater samples. The symbols stand for: (●) base unit formation; (●) middle unit formation; (●) recent unit formation.

Plotting the chemical composition of the water samples, orthogonal diagrams (Figure 4), in all plots, the outlier FT-109 stands out. In Figure 4a, this borehole (located in Praia Baixa coastal region, about 19 m a.s.l.) stands far from the halite dissolution line and from the seawater- fresh water mixing line, indicating an additional source of  $Cl^-$  and  $Na^+$ , such as the dissolution of marine aerosols. The additional  $Cl^-$  and  $Na^+$  origins are also visible in most of the samples when FT-109 is not considered (Figure 4b), thus enhancing an additional source of sodium that can be ascribed to cation exchange processes. This hypothesis is supported by the sample's distribution above the two lines (seawater–freshwater mixing line or halite dissolution line).

Geological studies (including mineralogical and petrological approaches) carried out at Santiago Island identified the presence of carbonatites layers in different places on the island [47,60]. Carbonatites are magmatic rocks containing more than 50% of carbonate minerals, like calcite, dolomite and/or ankerite. The carbonatites are generally characterized by the presence of accessory minerals such as pyroxenes and amphiboles. To identify the calcium origin ascribed to carbonatites dissolution, the groundwater samples were plotted in a  $Ca^{2+}$  vs.  $HCO_3^-$  diagram (Figure 4c). Almost all water samples are plotted below the carbonates dissolution line. Like in the previous diagrams, the water sample FT-109 is an outlier (Figure 4c). The groundwater from borehole FT-109 presents a  $Ca^{2+}$  content high above the mean concentrations (Figure 4c). Not considering this sample (FT-109), it is possible to identify two-trend lines away from the carbonate dissolution line, which are likely ascribed to different calcium sources (Figure 4d).

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**Figure 4.** (a) Na<sup>+</sup> vs. Cl<sup>-</sup> content; (b) Na<sup>+</sup> vs. Cl<sup>-</sup> content without FT-109; (c) Ca<sup>2+</sup> vs. HCO<sub>3</sub><sup>-</sup> (d) Ca<sup>2+</sup> vs. HCO<sub>3</sub><sup>-</sup> without FT-109. The symbols stand for: ( $\bullet$ ) base unit formation; ( $\bullet$ ) middle unit formation; ( $\bullet$ ) recent unit formation.

Studies carried out in carbonatite formations in a semi-arid region of India (Western Gujara) mention the variability of the calcium content in the groundwater during the post and pre-monsoon periods [61], which were not detected in the Santiago Island samples. These authors [62] also call attention to the importance of fluoride in the water system in the health risk assessment, mentioning that the  $F^-$  in water is defined by lithology and by the water–rock interaction mechanisms, where acidic and alkaline igneous rocks can release high concentrations of fluoride into groundwater. At Santiago Island,  $F^-$  determination was performed in 27 groundwater samples (see Supplementary Material). The  $F^-$  concentrations varied from below the detection limit (n = 21) to 2.96 mg/L (sample 49–16), while in the remaining samples, it ranged between 0.07 to 0.08 mg/L. According to [62], fluoride content in water between 0.6 and 1.2 mg/L is considered safe; however, lower values can also lead to health problems.

Within the scope of seawater intrusion processes, the high Na<sup>+</sup>/Cl<sup>-</sup> ratio (surplus of sodium) points to the seawater intrusion mechanism. Nevertheless, in coastal areas, the dissolution of carbonate minerals is often noticed, leading to an increase in the calcium and bicarbonate content in the groundwater [56]. The increase of Ca<sup>2+</sup> in the groundwater is a function not only of the geological formations but also of the presence of atmospheric CO<sub>2</sub> involved in the carbonate dissolution reaction, i.e., closed (1) or open (2) system to CO<sub>2</sub>:

$$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^-$$
(1)

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^{-}$$
<sup>(2)</sup>

In Figure 4c,d, two dissolution carbonate lines are plotted. The equivalence ratio (1:1) stands for an open CO<sub>2</sub> system (Equation (2)); the equilibrium concentration adds Ca<sup>2+</sup> to the solution [56]. In terms of equivalence ratio, the relation between Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> should be represented by a straight line with a slope equal to 1. In a close system to the CO<sub>2</sub>, the equivalent ratio of 2:1 (Equation (1)) indicates that the Ca<sup>2+</sup> content is lower than the dissolution of carbonate minerals.

To assess if the addition of marine salts by dissolution occurred, the ratios of  $Na^+/Cl^$ and  $Cl^-/SO_4^{2-}$  ratios versus  $Cl^-$  were plotted, together with the seawater ratio line (Figure 5). As mentioned, the line plotted in the diagram  $Na^+/Cl^-$  versus  $Cl^-$  (Figure 5a,b) represents the seawater ratio (0.56 [63]); most of the groundwater samples are projected



above the ratio line, pointing to an additional source of sodium to the groundwater systems. One possible hypothesis to explain the sodium increase is the ion exchange mechanisms.

**Figure 5.** (a) Na<sup>+</sup>/Cl<sup>-</sup> vs. Cl<sup>-</sup> content; (b) Na<sup>+</sup>/Cl<sup>-</sup> vs. Cl<sup>-</sup> content without FT-109; (c) Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> vs. Cl<sup>-</sup> content (d) Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> vs. Cl<sup>-</sup> without FT-109. The symbols stand for: ( $\bullet$ ) base unit formation; ( $\bullet$ ) middle unit formation; ( $\bullet$ ) recent unit formation.

Slightly different behavior is noticed when the  $Cl^-/SO_4^{2-}$  ratio is plotted versus  $Cl^-$  content (Figure 5c,d); in these two diagrams, the plotted line (7.16 [64]) stands for the  $Cl^-/SO_4^{2-}$  seawater ratio. Most of the groundwater samples are projected below the ratio line; only 32 samples (about 22% of the samples) have a  $Cl^-/SO_4^{2-}$  ratio higher than the sea, which is likely related to the dissolution of marine aerosols dispersed along the island.

With the aim of identifying seawater intrusion processes from salts dissolution (marine aerosols), the chemical composition (Na<sup>+</sup>/Cl<sup>-</sup> and Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ratios) of the springs sampled from different places on Santiago Island were projected versus the Cl<sup>-</sup> content (Figure 6). In the plot titled Na<sup>+</sup>/Cl<sup>-</sup> versus Cl<sup>-</sup>, most of the springs are projected above the value of the seawater ratio (0.56 [63]), suggesting that the salt origin should be ascribed to marine aerosols dissolution. However, a different pattern is noticed when the spring samples are projected in the Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> versus Cl<sup>-</sup> diagram (Figure 6b). In this case, the majority are plotted below the seawater ratio line (7.16 [64]), supporting the previous hypothesis of marine salts dissolution.

Cation exchange processes between the clay matrix and the groundwater can play an important role in the chemical evolution of the water systems, particularly in sedimentary basins [2,6,11,65]. This process can be present in different proportions and is able to modify the ion concentration in the aqueous systems. The enrichment in sodium (Figures 4b and 5b) observed in most of the groundwater samples could indicate water–rock interaction, mixing with seawater, or even dissolution of marine aerosols. However, the hypothesis of cation exchange becomes stronger when the ( $Ca^{2+} + Mg^{2+}$ ) and ( $Na^+ + K^+$ ) are plotted in the diagram (Figure 7).



**Figure 6.** (a) Na<sup>+</sup>/Cl<sup>-</sup> vs. Cl<sup>-</sup> content; (b) Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> vs. Cl<sup>-</sup> the content of the springs sampled on Santiago Island. The symbols stand for: ( $\bullet$ ) base unit formation; ( $\bullet$ ) middle unit formation.



**Figure 7.** (a)  $[(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})]$  vs.  $[(Na^+ + K^+) - Cl^-]$ ; (b)  $[(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^2)]$  vs.  $[(Na^+ + K^+) - Cl^-]$  without the water sample FT-109. The symbols stand for: (•) base unit formation; (•) middle unit formation; (•) recent unit formation.

Two ion exchange processes can be identified in the studied water samples:

(i) Sodium fixation and release of calcium: cation exchange process strongly observed in FT-109 water sample; this process is frequently observed in sedimentary basins [2,3,11] and often reported when seawater intrusion processes occur;

(ii) Cation exchange is represented by the fixation of calcium and release of sodium trapped in the clay minerals [56,65].

In summary, the physicochemical data of groundwater samples from Santiago Island allow us to enhance:

- (i) The existence no correlation between the aquifer formation and the high water salinity;
- (ii) The increases in salinity should be ascribed to the dissolution of marine aerosols or to the seawater intrusion mechanism;
- (iii) Ion exchange processes play an important role in the chemical evolution of the studied groundwaters.

## 4.2. Isotope Hydrology

## 4.2.1. Stable Isotopes ( $\delta^2$ H and $\delta^{18}$ O)

At Santiago Island, groundwater recharge results from direct infiltration of precipitation or by wasted water used in agriculture activities (recycled waters). The groundwater samples can reflect, in this situation, the mean isotopic composition of the regional precipitation and also an isotopic enrichment due to evaporation during agriculture irrigation (Figure 8).



**Figure 8.** Example of wastewater used in banana field agricultural activities at Santiago Island. The arrow indicates the wastewater in this banana plantation.

Occasionally, isotopic shifts are noticed among the mean groundwater isotopic composition and the mean isotopic composition of the regional precipitation. In these cases, different hypotheses to explain the deviations must be formulated: (i) evaporation before infiltration occurred, for example, infiltration of wastewater during agriculture procedures or by the use of recycled waters; (ii) recharge can be derived from different sources, either from direct infiltration of the regional precipitation, like mixing with surface water like rivers, lakes and/or dams; (iii) mixing with seawater and (iv) precipitation recharge under the different climatic regime (paleowaters).

As mentioned, 115 groundwater samples were collected from boreholes and springs for stable isotopic determinations ( $\delta^2$ H and  $\delta^{18}$ O). The isotopic content in the water samples was plotted in an orthogonal diagram  $\delta^{18}$ O vs.  $\delta^2$ H (Figure 9), ranging between -4.98% to -2.61% in oxygen-18 and from -44.6% to -14.9% in deuterium. From the observation of Figure 9, no clear "aquifer trend" is visible in the isotopic composition of the water samples, i.e., no strong relationship was found between the groundwater isotopic values and the type of aquifer, geological formation. The distribution of isotopic values seems to be controlled by the recharge altitude, according to the island topography, i.e., more depleted delta values at high altitudes. The mean isotopic content of the groundwater samples ( $\delta^2$ H mean value =  $-25.9 \pm 5.4\%$ , and  $\delta^{18}$ O  $-3.88 \pm 0.53\%$  vs. V-SMOW (*n* = 115)) is rather similar to the values found in the database of the I.A.E.A. [42]. Based on the deuterium excess data, the isotopic composition of the water samples suggests that no evaporation processes before infiltration are present, and no strong isotopic fractionation due to evaporation occurred (use of wastewater recycling in agriculture practices). Considering the groundwater distribution in the  $\delta^2$ H vs.  $\delta^{18}$ O plot of Figure 9, two trends can be identified, namely:

- A first group, composed of the water samples collected in the eastern part of the island, with a correlation coefficient of 0.92 and a trend line equation rather parallel to the G-MWL equation [66–69] and slightly parallel to the Local-MWL;
- A second group is composed of the other water samples located all over the island (east and west of the island) being, their isotopic composition mainly controlled by the geomorphology (recharge altitude). The local trend of the groundwater isotopic composition was calculated using the groundwater samples with minor mineralization (EC below 500  $\mu$ S/cm) to minimize the possible contribution of seawater to their composition. Although, the EC value chosen does not exclude a possibility of a slight contribution of seawater in the groundwater samples able to modify their initial isotopic composition. The obtained trend line equation is:  $\delta^2 H = 7.27 \ \delta^{18}O + 2.82$ (r = 0.64; *n* = 27). The designation of local trend instead of Local Meteoric Water Line is adopted since the water samples, even with low mineralization, can be subject to small mixing processes with seawater or even with recycling water subject to evaporation. All these processes can induce a deviation of the initial isotopic composition. In Figure 9, the mean seawater isotopic composition is also plotted, and it seemed that no relevant mixing occurred between the Eastern Group and seawater.



**Figure 9.** (a)  $\delta^{2}$ H vs.  $\delta^{18}$ O diagram for groundwater samples from Santiago Island. (b) The "rectangle" in the map points out the regional location on Santiago Island of the "Eastern Group". The symbols stand for: ( $\blacklozenge$ ) IAEA database Santiago Island groundwater isotopic composition [41]; ( $\blacklozenge$ ) Base Unit formation; ( $\blacklozenge$ ) Middle Unit formation; ( $\blacklozenge$ ) Recent Unit formation and ( $\bigcirc$ ) not labeled unit formation.

Both  $\delta^{18}$ O and  $\delta^{2}$ H values encoded in groundwater systems, if different from the isotopic composition of modern regional precipitation, can be used as a "tool" in climatic studies (groundwaters as archives of ancient climates), knowing that one of the main factors guiding the regional precipitation isotopic composition is temperature [67–69]. Besides the influence of temperature, the regional isotopic values of precipitation may also vary due to changes in the vapor source/sources, degree of rainout of water vapor air masses

and reflect the variation in the isotopic composition of the global ocean—global climatic variations [14,69].

At Santiago Island, one hypothesis that can be formulated to explain the isotopic deviation in the "eastern group" is that these samples can represent ancient precipitation, i.e., recharge under a different climatic regime. Studies performed in groundwater systems from the European continent show that during the Last Glacial Maximum (LGM), the continent remained under prevailing westerly circulation, a colder regime leading to an isotopic depletion in precipitation waters when compared to modern precipitation [67–69].

As mentioned previously, the major challenge of this work was to distinguish the main source of mineralization in the groundwater systems, i.e., be able to distinguish between seawater and marine aerosols dissolution, using chemical and isotopic data. With this aim, the <sup>18</sup>O content was plotted *versus* the electrical conductivity (EC) values. Like in the previous diagrams, no clear correlation between the geological formations with the water mineralization was identified. Although mixing with seawater intrusion seems to be present in some areas, the hypothesis of dissolution of marine aerosols cannot be excluded. The Cl<sup>-</sup> content was applied in the identification of the main source of salinity; Cl<sup>-</sup> enrichment is noticed by the groundwater samples, above the seawater—freshwater mixing line. Although, the number of water samples revealing a significant enrichment in<sup>18</sup>O is high, but not only explained by seawater intrusion mechanism. It is important to mention that when seawater intrusion is occurring or had occurred, the groundwater will be noticed an increase in both parameters (isotopic enrichment and mineralization increase). This single feature enables the identification of the main processes based on isotopic and geochemical data [2,70,71].

Simultaneously, based on the  $Mg^{2+}/Ca^{2+}$  ratios of the water samples, the hypothesis of extended water–rock interaction and cation exchange mechanisms can be partially responsible for a change in seawater chemical composition, such as a decrease in the  $Mg^{2+}/Ca^{2+}$  ratios [2,6,57,59].

Although is difficult to establish for Santiago Island the initial groundwater composition, due to the scarce information available concerning the precipitation isotopic content and, the precise knowledge of groundwater composition, i.e., free of evaporation or mixture processes, the percentage of seawater mixture was estimated using two parameters, namely the electrical conductivity and the <sup>18</sup>O content (Table 1). The values 52,000  $\mu$ S/cm and  $\delta^{18}$ O = 0‰, and 415.8  $\mu$ S/cm and -3.88‰ were selected for seawater and groundwater end-members composition, respectively. The groundwater composition stands for the average value using the data of the samples with mineralization lower than 500  $\mu$ S/cm.

In Table 1, the percentage of seawater in the groundwater is represented for the samples with a mineralization (EC values) higher than 2000  $\mu$ S/cm. Equation (3) was used to estimate the percentage of seawater in the mixture:

$$X = [[Cm - Co]/(Csea - Co)] \times 100$$
(3)

where X stands for the percentage of seawater in the mixture, Cm represents the composition in the mixture (groundwater sample), Co is the same parameter in the groundwater mean value, and Csea stands for the concentration in the sea.

In some cases, the absence of similarity between the value of percentage of mixing using EC or  $\delta^{18}$ O content is well noticed. The different percentage values can be ascribed to:

- The origin of the groundwater mineralization is mainly linked to the dissolution of marine aerosols, particularly observed in the samples FT-23, FT-59, FT-202 (2007), 58-1, 58-56, SST-55;
- 2— The high percentage of seawater just when using the <sup>18</sup>O content, i.e., in the samples SP-12; 49/18 and FT-202 (2006), is probably related to evaporation processes that induced an enrichment in the water isotopic composition;
- 3— The similar percentage of mixing is attributed to seawater mixing processes, well noticed in samples FT-153, 51-201, FT-81; and,

4— The dissimilarities due to the lack of precise information concerning the "correct value", i.e., the initial end-member composition of the groundwater, either isotopic or electrical conductivity.

**Table 1.** Percentage of seawater in the groundwater samples. The data represent the amount of seawater estimated in percentage using the different tracers A—Electrical Conductivity and B—<sup>18</sup>O content (data from 2005 and 2006 sampling campaigns).

Reference	Electrical Conductivity (μS/cm)	A Seawater Percentage (%)	δ <sup>18</sup> Ο (‰)	B Seawater Percentage (%)	
PT-29	2130	3.3	-3.85	0.8	
SP-12	2510	4.1	-2.61	32.7	
FBE-194	2320	3.7	-3.5	9.8	
49/18	2650	4.3	-2.96	23.7	
FT-47	2160	3.4	-3.61	6.9	
FT-84	3560	6.1	-3.43	11.6	
FT-153	8800	16.3	-3.28	15.4	
SST-55	3340	5.7	-4.27	-	
51-201	3005	5.0	-3.55	8.5	
FT-81	2460	3.9	-3.64	6.2	
FT-23	9400	17.4	-3.94	-	
FT-59	3870	6.7	-4.48	-	
58-1	3800	6.6	-4.07	-	
58-56	2160	3.4	-3.99	-	
FT-202 (2006)	2610	4.3	-3.22	17	
FT-202 (2007)	8840	16.3	-4.05	-	
Seawater	52,000		0		
Groundwater	415.8		-3.88		

4.2.2. Radioactive Isotopes (<sup>3</sup>H and <sup>14</sup>C)

Tritium determinations were carried out only in 70 water samples distributed all over Santiago Island. The <sup>3</sup>H content varies between <0.6 TU and 2.9  $\pm$  0.6 TU (Figure 10). The tritium content indicates the presence of young water—and thus an active recharge of the systems. The <sup>3</sup>H half-life of about 12.32 years [72] makes tritium an ideal tracer in the identification of active recharge of the aquifers systems. Being part of the water molecule, the geochemical reactions with soil gases and biogeochemical reactions will not affect its abundance, making <sup>3</sup>H ideal for tracing recent recharge events [73]. According to Heilweil and coauthors [38], between 1975–1979, the tritium content in the atmosphere (precipitation samples) extended from 15.6 to 67.0 TU at Bamako, Mali (IAEA nearest station to the Republic of Cape Verde archipelago); decreasing this content during the 1980ss to values around 5 TU. From the five precipitation samples collected at Santiago Island during 1984, the <sup>3</sup>H concentrations range from  $2.3 \pm 0.1$  to  $4.4 \pm 0.2$  TU [74]. For the mean residence time calculation, it was assumed that the initial tritium content in the atmosphere in this region was 3 TU. Most of the samples analyzed, show no tritium in their composition, indicating a mean residence time higher than 30 to 40 years (assuming <sup>3</sup>TU as initial atmospheric content). The mean residence time higher than 30-40 years agrees with the values presented by Akiti [74]. According to this author, in Achada Baleia (the eastern part of the island), the shallow boreholes show active recharge, while the deep boreholes are being recharged slowly through joints and fractures. No correlation was found either with the altitude of the sampling sites, with the electrical conductivity, or even with the geology (Figure 11).



Figure 10. Schematic map of Santiago Island, with the tritium content in TU, adapted from [57].

Carbon-14 measurements were performed only in six groundwater samples from the Middle Unit. The <sup>14</sup>C content in groundwater allows dating "old" water systems. The <sup>14</sup>C content present in the Total Dissolved Inorganic Carbon (TDIC) may be used to estimate the mean residence time in the range of 2000 to 30,000 years [68,73]. However, groundwater dating with <sup>14</sup>C is complex due to different carbon origins and processes that could be present, being this contribution rather random. Some of the different C sources, for example, dissolution of carbonate minerals, oxidation of old organic matter, dissolution of volcanic gases, etc., are carbon-14 free, inducing an aging signal to the water. Different mathematical models try to minimize the contribution of old carbon; nevertheless, it is not straightforward to determine the contribution of old carbon that might be present. According to Cartwright and coauthors [73], groundwater dating with <sup>14</sup>C is very useful in semi-arid and arid climates where low recharge rates will lead to finding old groundwater at shallow depths, which are also suitable in the identification of mixing of different aquifer systems where old waters can be mixed with modern recharge.



**Figure 11.** (a) Plot of tritium versus electrical conductivity; (b) Tritium content versus  $\delta^{18}$ O. The symbols stand for: (•) Base Unit formation; (•) Middle Unit formation; (•) Recent Unit formation and (•) not labeled unit formation.

The easiest approach for carbon-14 groundwater dating is to assume that the <sup>14</sup>C "travel" with the water along the flow path, where the main process able to modify the <sup>14</sup>C content in the TDIC is by "pure" radioactive decay. With this assumption, knowing the <sup>14</sup>C half-life (5730 years) and the initial carbon content, the age of the inorganic carbon (TDIC) can be calculated. The main constraint is the initial <sup>14</sup>C content that may have been modified [73,75] by different carbon sources. Nonetheless, Han and coauthors [76] proposed a graphical method to help in the identification of the main geochemical reactions able to modify the radiocarbon content in the groundwater system.

The graphical <sup>14</sup>C method was applied to the 6 samples from Santiago Island to assess the predominant geochemical processes occurring during the groundwater flow. This graphical approach provides links to distinguishing the major geochemical reactions needed for the interpretation of <sup>14</sup>C groundwater apparent ages (Figure 12). This approach is useful for a simultaneous comparison of the isotopic composition of different water samples (<sup>14</sup>C content and  $\delta^{13}$ C values and Dissolved Inorganic Carbon—DIC). The graphic method considers the most important and most common geochemical processes and isotopic effects, which can occur from infiltration and along the flow, and, for example, accounts for the dissolution of soil CO<sub>2</sub>, dissolution of carbonate minerals, incorporation of organic matter (young and old) and carbonates precipitation.



**Figure 12.** Graphical method to evaluate predominant geochemical processes occurring in groundwater samples from Santiago Island (Middle Unit) for radiocarbon dating (**a**)  $\delta^{13}$ C vs. 1/DIC; (**b**) <sup>14</sup>C vs. 1/DIC; (**c**) <sup>14</sup>C vs.  $\delta^{13}$ C.

Although all water samples are plotted near to each other, they fall in different areas of the diagrams indicating that different geochemical processes are present, being able to modify the initial carbon of the water samples. Sample FT-78 position (Figure 12a) indicates an open system to  $CO_2$ , while the samples FT-39, FT-40, and FT-44, their isotopic content, indicate mixing with additional carbon more depleted in <sup>13</sup>C. This carbon can be ascribed to mixing with old organic matter or even weathering silicates. According to Han and coauthors [77], the location of the FBE-201 and 59-24 samples represents an evolution from line *Z*, which stands for the mixing of two carbon reservoirs in a closed system. On the other hand, the "new" additional carbon (FT-78) is more depleted at <sup>13</sup>C than the current soil  $CO_2$ . The authors call attention to the samples plotted in this graph region, which may also indicate weathering of silicates by additional carbonic acid (an increase of DIC and decrease of  $\delta^{13}$ C and <sup>14</sup>C). This hypothesis should be considered since most of the geological formations of the island have a volcanic origin (Figure 12a).

In Figure 12b,c FT-78 sample continuous to "fall" in a different region of the diagram, suggesting a different evolution/story of the geochemical processes involved. Its location points to an open system to CO<sub>2</sub>, inducing younger radiocarbon ages. Nonetheless, the other samples fall in the field of additional carbon, which can be from an organic origin or the water samples reflect methanogenesis processes involving organic matter containing <sup>14</sup>C (e.g., landfill). Although the hypothesis of fermentation of organic matter (FBE-201 and 59-24 samples) cannot be excluded (Figure 12c), the hypothesis of methanogenesis processes involving organic matter is reliable.

Different geochemical processes (methanogenesis, open system to CO<sub>2</sub>—soil contribution by plants respiration, weathering of silicates) seems to be present and able to modify the initial carbon-14 content in the groundwater samples; the apparent carbon-14 age was calculated using Equations (1) and (2) [57,78]:

$$t = 8267 \ln (C_0/C)$$
 (4)

$$C_{\rm o} = [100 (\delta_{\rm TDIC} - \delta_{\rm R}) (1 + (2.3\varepsilon_{13})/1000)] / [(\delta_{\rm S} - \delta_{\rm R} + \varepsilon_{13})]$$
(5)

where:

 $\delta_{\text{TDIC}}$  stands for the measured <sup>13</sup>C in the samples;

 $\delta_R$  is the <sup>13</sup>C concentration of carbonates fraction in the reservoir rock matrix;

 $\delta_S$  represents the <sup>13</sup>C concentration of soil CO<sub>2</sub> (varying with the type of vegetation), and  $\epsilon$  is the <sup>13</sup>C enrichment factor associated with the dissolution of soil CO<sub>2</sub> by the infiltrating water [78].

One of the problematic issues when dating groundwater with <sup>14</sup>C is to define which are the predominant plants in the region since nowadays, changes in agriculture "practices" are reported. C4 plants ( $\delta^{13}C = -15 \%$ ) probably represented the initial vegetation of the island, but part of these C4 plants was replaced by other types of vegetation (C3 plants,  $\delta^{13}C = -23 \%$ ) associated with changes in agriculture practices.

From the two above equations (Equations (4) and (5)), the unique initial parameter that will be changed during the calculations of the apparent carbon-14 groundwater age (as the initial condition) will be the isotopic composition of the soil  $CO_2$ , since this isotopic content is directly linked to the soil occupation.

According to the literature, most  $\delta^{13}$ C variation observed in the biosphere is a consequence of the isotopic fractionation of carbon during the photosynthesis cycle. The terrestrial plants can be divided into three photosynthesis pathways (C<sub>3</sub>, C<sub>4</sub>, and CAM plant types) due to CO<sub>2</sub> fixing enzymes and the limitation of CO<sub>2</sub> diffusion into the leaves [68]. Each photosynthesis pathway presents a different  $\delta^{13}$ C range, namely from -33 to -24%, -16 to -10%, and -20 to -10%, respectively [68]. Furthermore, the isotopic composition of soil organic matter reflects the photosynthetic pathway type of the dominant species in the plant community.

Although no isotopic data concerning this subject is available for Santiago Island, isotopic determinations were carried out in terrestrial samples (goat bones) from São Vicente Island, Cape Verde Archipelago, in the oldest remains of human origin found on this island from Cape Verde Archipelago, indicate carbon-13 values characteristic of C4 plants [79].

For <sup>14</sup>C, the enrichment factor ( $\varepsilon_{13}$ ) during CO<sub>2</sub> dissolution was assumed to be equal to 7.5 and the value of  $\delta_R = 0 \pm 1$  ‰ was adopted for soil and rock carbonates present in the system. Also, C<sub>o</sub> stands for the initial carbon-14 content in the atmosphere in the case of Cape Verde was assumed to be 100 pMC, and C is the carbon-14 content measured in the TDIC of the sample. As above-mentioned, for the C4 plants, the  $\delta$ s value will be equal to -15 ‰, and for the C3 plants,  $\delta$ s will be -23 ‰, (isotopic content used in Equation (4)). Applying these  $\delta^{13}$ C values of the soil, the apparent <sup>14</sup>C groundwater ages were calculated (Table 2) using as age correction both  $\delta^{13}$ C values for C3 and C4 plants. The apparent ages obtained are far different, varying from modern to 5000 years BP. When the  $\delta^{13}$ C of C3 plants is applied, all water samples are "modern"; yet when the probably original vegetation of the island (C4 plants) is used in the equation the apparent radiocarbon ages increase, varying from 3.51 to 5.07 ka BP.

**Table 2.** Apparent radiocarbon groundwater ages, using C4 and C3 plants (n.d. stands for not detected).

Ref	<sup>3</sup> H (TU)	δ <sup>13</sup> C <sub>TDIC</sub> (‰)	$^{14}$ C $\pm$ $\sigma$ (pMC)	<sup>14</sup> C Uncorrected Age (ka)	C3 Plants <sup>14</sup> C Apparent Age (ka)	C4 Plants <sup>14</sup> C Apparent Age (ka)
FT-39	n.d.	-13.1	$95.24 \pm 0.38$	FT-39		
FT-39	n.d.	-13.1	$95.24 \pm 0.38$	0.40	Modern	$4.36 \pm 1.42$
FT-40	n.d.	-11.9	$83.43\pm0.37$	1.50	Modern	$4.77 \pm 1.44$
FT-78	n.d.	-12.7	$95.72\pm0.38$	0.36	Modern	$4.10\pm1.42$
FBE-201		-9.0	$76.91 \pm 0.36$	2.17	Modern	$3.51 \pm 1.51$
FT-44	n.d.	-12.7	$85.12\pm0.39$	1.33	Modern	$5.07 \pm 1.42$
59-24	n.d.	-9.9	$73.20\pm0.35$	2.58	Modern	$4.56 \pm 1.48$

The isotopic composition  $\delta^{13}$ C, <sup>14</sup>C and  $\delta^{18}$ O was plotted as a function of the bicarbonate content and <sup>14</sup>C groundwater apparent age (using C4 plants). No robust correlation is observed between the alkalinity content and the  $\delta^{13}$ C values measured in the TDIC, possibly due to the different sources of carbon that can be present in the water system, as suggested by the graphical method (see Figures 12 and 13). On the other hand, from the observation of Figure 13d, a trend between the oxygen-18 content and the apparent carbon-14 groundwater age can be recognized, i.e., an isotopic <sup>18</sup>O enrichment with the age of water probably ascribed to changes in the climate during this period. Another hypothesis to be formulated is that this oxygen-18 enrichment could be due to a mixture with seawater, which would induce an enrichment in groundwater composition. However, if this last hypothesis can be used in the sample FT-78 (EC > 2900 µS/cm), although for the other points like FT-40 the mean value of the EC is 1397 µS/cm.



**Figure 13.** (a)  $HCO_3^-$  vs.  $\delta^{13}C$ ; (b)  $HCO_3^-$  vs. Apparent <sup>14</sup>C age; (c)  $\delta^{18}O$  vs. Carbon-14; (d)  $\delta^{18}O$  vs. Apparent <sup>14</sup>C age.

Projecting carbon-14 and carbon-13 values on the Santiago Island map, the previous hypothesis of seawater-freshwater mixing does not seem feasible, not only due to the salt content already mentioned but also due to the location of the boreholes, which are quite distant from the coastline. From the six carbon-14 determinations, three boreholes belonging to the "Easter Group" (Figure 9), namely FT-40, FT-44, and FT-78, corroborate the hypothesis that the isotopic shift (<sup>2</sup>H-<sup>18</sup>O) can be derived from the precipitation under a different climatic regime. Studies performed by [80] on climate change in Macaronesia (biogeographical region composed of the volcanic archipelagos of Azores, Madeira, the Canaries and Cape Verde (northeast Atlantic Ocean), mentioned an important climate change in the mid-Holocene, at the end of the African Humid Period, ca. 5.5 ka BP. These authors reported on the scarce palaeoecological and palaeoclimatic studies available for Cape Verde to support this information. The isotopic values (O-18 enrichment and apparent radiocarbon ages) support the assumption that the stable isotopic composition of the "eastern group samples" could be linked to a climatic pattern, e.g., groundwater recharge in a different climatic environment that differs from today's conditions (Figure 14).



Figure 14. Map of Santiago Island. Location of the groundwater samples with carbon-14 data.

## 5. Concluding Remarks

One of the major challenges in this research was to distinguish between the major processes responsible for groundwater salinization using different approaches, such as hydrogeochemical data, environmental isotopes and geophysical research. Although three major aquifer units have been identified at Santiago Island, no clear distinction within the groundwater samples issued from each hydrogeological unit was observed. No strong correlation between the geochemical evolution with a specific geological formation or type of sampling point (spring or borehole) was observed. From the geochemical representation in the Piper diagram, an evolution trend line towards seawater composition seems to be present. However, it was impossible to clarify the importance of marine aerosols dissolution in the water's chemical evolution. Even so, the results point out that the land's extent of seawater intrusion and the influence of marine aerosol appears to be moving inland, which is accelerated in the case of seawater mixing due to the intense exploitation of water for human consumption and agriculture uses.

The cation exchange processes between the aquifers clay matrix and groundwater play an important role in the water chemical evolution. The "exchange processes" are present in different proportions at Santiago Island and can modify the ion concentration in the aqueous system: (i) sodium fixation and release of calcium strongly presented at FT-109 water sample (often observed in seawater intrusion processes); (ii) fixation of calcium and release of sodium trapped in the clay minerals. Nonetheless, the presence of carbonatite formations on the island, can also contribute to the addition of calcium in the groundwater composition by dissolution along the flow path.

As before, with the chemical data, no clear "aquifer trend" between the geological unit and the delta values is recognized.

Two isotopic trends can be identified in the classical  $\delta^{18}$ O vs.  $\delta^2$ H diagram: (i) one group is composed of groundwater samples collected in the eastern part of the island, and (ii) a second group is composed of the other water samples located all over the island (east and west of the island). The isotopic composition of groundwaters from this second group is mainly controlled by the altitude of recharge. Concerning the "eastern group", the

hypothesis that these samples represent ancient precipitation, i.e., recharge under a different climatic regime, should be formulated. In this situation, the groundwaters are acting as a climate archive, which is reflected in their isotopic composition as a palaeoclimatic fingerprint.

Tritium content measured in the groundwater samples indicates an active recharge of the aquifers systems, although in some boreholes, no tritium was found. The apparent radiocarbon ages obtained corroborate the hypothesis formulated that the stable isotopic composition of the "eastern group samples" represents a climatic pattern. The apparent ages obtained, used as a correction of the isotopic composition of C4 plants, place these samples between 3500 to 5000 years BP (Figure 14). Regarding the increase of groundwater salinization, the stable isotopic composition suggests two main sources of mineralization: seawater intrusion and the dissolution of marine aerosols. In the coastal regions, seawater intrusion is a serious problem, and the adequate assessment and knowledge of the risks involved in the groundwater resources degradation make it of huge importance for proper water management. Santiago Island requires a future detailed assessment of available groundwater resources that focuses on the definition of potential areas where seawater intrusion is already occurring or where it will have a higher probability of occurring to avoid/control this situation while also considering that the Republic of Cape Verde archipelago is located in a semi-arid climate.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/w14152339/s1, Table S1—Representative physical and chemical data of groundwater samples from Santiago Island [39] collected in two field work campaigns in 2003. The aquifer units stands for Buf—Base Unit formation; MUF—Middle Unit Formation and RUf—Recent Unit formation. Sp stands for spring and B for borehole. The chemical parameters are in mg/L; b.d. stands for below the detection limits. EC stands for electrical conductivity and  $\Sigma$ cat stands for cations sum and  $\Sigma$ ani.stands for anions sum. The charge balance (Error in %) was estimated using Appleo & Postma equation [56].

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#### References

- 1. Cartwright, I.; Weaver, T.R.; Fulton, S.; Nichol, C.; Reid, M.; Cheng, X. Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. *Appl. Geochem.* **2004**, *19*, 1233–1254. [CrossRef]
- Carreira, P.M.; Marques, J.M.; Nunes, D. Source of groundwater salinity in coastline aquifers based on environmental isotopes (Portugal): Natural vs. human interference. A review and reinterpretation. *Appl. Geochem.* 2014, 41, 163–175. [CrossRef]

- Carreira, P.M.; Bahir, M.; Ouhamdouch, S.; Galego Fernandes, P.; Nunes, D. Tracing salinization processes in coastal aquifers using an isotopic and geochemical approach: Comparative studies in western Morocco and southwest Portugal. *Hydrogeol. J.* 2018, 26, 2595–2615. [CrossRef]
- Ammar, S.B.; Taupin, J.-D.; Zouari, K.; Khouatmia, M. Identifying recharge and salinization sources of groundwater in the Oussja Ghar el Melah plain (northeast Tunisia) using geochemical tools and environmental isotopes. *Environ. Earth Sci.* 2016, 75, 606. [CrossRef]
- Mahlknecht, J.; Merchán, D.; Rosner, M.; Meixner, A.; Ledesma-Ruiz, R. Assessing seawater intrusion in an arid coastal aquifer under high anthropogenic influence using major constituents, Sr and B isotopes in groundwater. *Sci. Total Environ.* 2017, 587–588, 282–295. [CrossRef]
- Kammoun, S.; Re, V.; Trabelsi, R.; Zouari, K.; Daniele, S. Assessing seasonal variations and aquifer vulnerability in coastal aquifers of semi-arid regions using a multi-tracer isotopic approach: The case of Grombalia (Tunisia). *Hydrogeol. J.* 2018, 26, 2575–2594. [CrossRef]
- Bahir, M.; Ouhamdouch, S.; Carreira, P.M. Geochemical and isotopic approach to decrypt the groundwater salinization origin of coastal aquifers from semi-arid areas (Essaouira basin, Western Morocco). *Environ. Earth Sci.* 2018, 77, 485. [CrossRef]
- 8. Carreira, P.M. Paleoáguas de Aveiro [Aveiro palaeowaters]. Ph.D. Thesis, Universidade Aveiro, Aveiro, Portugal, 1999.
- 9. Galego Fernandes, P.; Carreira, P.M. Isotopic evidence of aquifer recharge during the last ice age in Portugal. *J. Hydrol.* **2008**, *361*, 291–308. [CrossRef]
- 10. Re, V.; Sacchi, E.; Martin-Bordes, J.L.; Aureli, A.; El Hamouti, N.; Bouchnan, R.; Zuppi, G.-M. Processes affecting groundwater quality in arid zones: The case of Bou-Areg Coastal aquifer (North Morocco). *Appl. Geochem.* **2013**, *34*, 181–198. [CrossRef]
- 11. Re, V.; Sacchi, E.; Mas-Pla, J.; Menció, A.; El Amrani, N. Identifying the effects of human pressure on groundwater quality to support water management strategies in coastal regions: A multi-tracer and statistical approach (Bou-Areg region, Morocco). *Sci. Total Environ.* **2014**, *500–501*, 211–213. [CrossRef]
- 12. Bouchaou, L.; Michelot, J.L.; Vengosh, A.; Hsissou, Y.; Qurtobi, M.; Gaye, C.B.; Bullen, T.D.; Zuppi, G.M. Application of multiple isotopic and geochemical tracers for investigation of recharge, salinization, and residence time of water in the Souss–Massa aquifer, southwest of Morocco. *J. Hydrol.* **2008**, *352*, 267–287. [CrossRef]
- 13. Marques, J.M.; Graça, H.; Eggenkamp, H.G.M.; Neves, O.; Carreira, P.M.; Matias, M.J.; Mayer, B.; Nunes, D.; Trancoso, V.N. Isotopic and hydrochemical data as indicators of recharge areas, flow paths and water-rock interaction in the Caldas da Rainha—Quinta das Janelas thermomineral carbonate rock aquifer (Central Portugal). *J. Hydrol.* **2013**, 476, 302–313. [CrossRef]
- 14. Edmunds, W.M. Contribution of isotopic and nuclear tracers to study of groundwaters. In *Isotopes in the Water Cycle. Past Present and Future of Developing Science*, 1st ed.; Pradeep, K.A., Gat, J.R., Froehlich, K.F.O., Eds.; Springer: Dordrecht, The Netherlands, 2005; pp. 171–192.
- 15. Gonfiantini, R.; Simonot, M. Isotopic Investigation of Groundwater in the Cul-de-Sac Plain, Haiti. Isotope Techniques in Water Resources Development; International Atomic Energy Agency: Vienna, Austria, 1987; pp. 483–504.
- 16. Grassi, S.; Cortecci, G.; Squarci, P. Groundwater resource degradation in coastal plains: The example of the Cecina area (Tuscany—Central Italy). *Appl. Geochem.* **2007**, *22*, 2273–2289. [CrossRef]
- Bahir, M.; Ouazar, D.; Goumih, A.; Ouhamdouch, S. Evolution of the chemical and isotopic composition of groundwater under a semi-arid climate; the case of the Cenomano–Turonian aquifer within the Essaouira basin (Morocco). *Environ. Earth Sci.* 2019, 78, 353. [CrossRef]
- Xu, Y.; Seward, P.; Gaye, C.; Lin, L.; Olago, D.O. Preface: Groundwater in Sub-Saharan Africa. *Hydrogeol. J.* 2019, 27, 815–822.
   [CrossRef]
- 19. Eissa, M.A.; Shawky, H.; Samy, A.; Khalil, M.M.H.; El Malky, M. Geochemical and isotopic evidence of groundwater salinization processes in El Dabaa area, Northwestern coast, Egypt. *Geosciences* **2018**, *8*, 392. [CrossRef]
- Mondal, N.C.; Singh, V.S.; Saxena, V.K.; Singh, V.P. Assessment of seawater impact using major hydrochemical ions: A case study from Sadras, Tamilnadu, India. *Environ. Monit. Assess.* 2011, 177, 315–335. [CrossRef] [PubMed]
- 21. Ben Hamouda, M.F.; Carreira, P.M.; Marques, J.M.; Eggenkamp, H.G.M. Geochemical and isotopic investigations to study the origin of mineralization of the coastal aquifer of Sousse, Tunisia. *Procedia Earth Planet. Sci.* 2013, 7, 61–64. [CrossRef]
- 22. Ben Hamouda, M.F.; Carreira, P.M.; Marques, J.M.; Eggenkamp, H.G.M. Multi-isotope approach to study the problem of salinity in the coastal aquifer of Oued Laya, Tunisia. In *Advances in Sustainable and Environmental Hydrology, Hydrogeology, Hydrochemistry and Water Resources. Advances in Science, Technology & Innovation (IEREK Interdisciplinary Series for Sustainable Development,* 1st ed.; Chaminé, H., Barbieri, M., Kisi, O., Chen, M., Merkel, B., Eds.; Springer: Cham, Switzerland, 2019; pp. 203–206.
- 23. Calvache, M.L.; Pulido-Bosch, A. Effects of geology and human activity on the dynamics of salt-water intrusion in three coastal aquifers in southern Spain. *Environ. Geol.* **1997**, *30*, 215–223. [CrossRef]
- 24. Kloppmann, W.; Bourhane, A.; Schomburgk, S. Groundwater Salinization in France. *Procedia Earth Planet. Sci.* 2013, 7, 440–443. [CrossRef]
- Petelet-Giraud, E.; Négrel, P.; Aunay, B.; Ladouche, B.; Bailly-Comte, V.; Guerrota, C.; Flehoc, C.; Pezard, P.; Lofi, J.; Dörfliger, N. Coastal groundwater salinization: Focus on the vertical variability in a multi-layered aquifer through a multi-isotope fingerprinting (Roussillon Basin, France). *Sci. Total Environ.* 2016, 566–567, 398–415. [CrossRef] [PubMed]
- 26. Tsakiris, G.; Alexakis, D. Karstic spring water quality: The effect of groundwater abstraction from the recharge area. *Desalination Water Treat*. **2014**, *52*, 2494–2501. [CrossRef]

- 27. Alexakis, D.; Tsakiris, G. Drought impacts on karstic spring annual water potential. Application on Almyros (Crete) brackish spring. *Desalination Water Treat.* 2010, *16*, 229–237. [CrossRef]
- 28. Milnes, E. Process-based groundwater salinisation risk assessment methodology: Application to the Akrotiri aquifer (Southern Cyprus). *J. Hydrol.* **2011**, 399, 29–47. [CrossRef]
- 29. Ergil, M.E. The salination problem of the Guzelyurt aquifer, Cyprus. Water Res. 2000, 34, 1201–1214. [CrossRef]
- Jalali, M. Salinization of groundwater in arid and semi-arid zones: An example from Tajarak, western Iran. *Environ. Geol.* 2007, 52, 1133–1149. [CrossRef]
- 31. Kim, Y.; Lee, K.; Koh, D.; Lee, D.; Lee, S.; Park, W. Hydrogeochemical and isotopic evidence of groundwater salinization in a coastal aquifer: A case study in Jeju volcanic island, Korea. *J. Hydrol.* **2003**, 270, 282–294. [CrossRef]
- 32. Carol, E.; Kruse, E.; Mas-Pla, J. Hydrochemical and isotopical evidence of ground water salinization processes on the coastal plain of Samborombón Bay, Argentina. *J. Hydrol.* **2007**, *365*, 335–345. [CrossRef]
- Pratheepa, V.; Ramesh, S.; Sukumaran, N.; Murugesan, A.G. Identification of sources of groundwater salinization in the coastal aquifers of Southern Tamil Nadu, India. *Environ. Earth Sci.* 2015, 74, 2819–2829. [CrossRef]
- 34. Sebei, A.; Slama, T.; Helali, M.A. Hydrochemical characterisation and geospatial analysis of groundwater Quality in Cap Bon region, northeastern Tunisia. *Environ. Earth Sci.* 2018, 77, 557. [CrossRef]
- 35. Alcalá, F.J.; Custódio, E. Using the Cl/Br ratio as tracer to identify the origin of salinity in aquifers in Spain and Portugal. *J. Hydrol.* **2008**, *359*, 189–207. [CrossRef]
- Stoecker, F.; Babel, M.S.; Gupta, A.D.; Rivas, A.A.; Evers, M.; Kazama, F.; Nakamura, T. Hydrogeochemical and isotopic characterisation of groundwater salinization in the Bangkok aquifer system, Thailand. *Environ. Earth Sci.* 2013, 68, 749–763. [CrossRef]
- 37. Gaye, C.B.; Tindimugaya, C. Review: Challenges and opportunities for sustainable groundwater management in Africa. *Hydrogeol. J.* **2019**, 27, 1099–1110. [CrossRef]
- Heilweil, V.M.; Solomon, D.K.; Gingerich, S.B.; Verstraeten, I.M. Oxygen, hydrogen, and helium isotopes for investigating groundwater systems of the Cape Verde Islands, West Africa. *Hydrogeol. J.* 2009, *17*, 1157–1174. [CrossRef]
- 39. Lobo de Pina, A.F. Hidroquímica e qualidade das águas subterrâneas da ilha de Santiago—Cabo Verde [Hydrochemistry and groundwater quality of the island of Santiago—Cape Verde]. Ph.D. Thesis, Universidade de Aveiro, Aveiro, Portugal, 2009.
- 40. Instituto Nacional de Estatística. Cabo Verde, Statistical Yearbook 2015; Instituto Nacional de Estatística: Praia, Cape Verde, 2015.
- 41. Lobo de Pina, A.F.; Mota Gomes, A.; Condesso de Melo, M.T.; Marques da Silva, M.A. Caracterização hidrogeoquímica das principais unidades aquíferas da ilha de Santiago, Cabo Verde. In Proceedings of the Actas da XIV Semana de Geoquímica e do VIII Congresso de Geoquímica dos Países de Língua Portuguesa, Aveiro, Portugal, 2005; Volume 1, pp. 379–382.
- 42. International Atomic Energy Agency. *Atlas of Isotope Hydrology–Africa*, 1st ed.; International Atomic Energy Agency: Vienna, Austria, 2007; pp. 15–16.
- Varela-Lopes, G.E.; Molion, L.C.B. Precipitation patterns in Cape Verde Islands: Santiago Island Case Study. *Atmos. Clim. Sci.* 2014, 4, 854–865. [CrossRef]
- Serralheiro, A. A geologia da Ilha de Santiago (Cabo Verde) [Santiago Island Geology (Cape Verde)]. Ph.D. Thesis, Universidade de Lisboa, Lisboa, Portugal, 1974.
- Matos Alves, C.A.; Macedo, J.R.; Celestino Silva, L.; Serralheiro, A.; Peixoto Faria, A.F. Geologic, petrological and vulcanological study of Santiago Island (Cape Verde). *Rev. Garcia Orta Série Geol.* 1979, 3, 70–81.
- 46. Mota Gomes, A. Hidrogeologia e recursos hídricos da ilha de Santiago—Cabo Verde [Hydrogeology and water resources of the Santiago Island—Cape Verde]. Ph.D. Thesis, Universidade de Aveiro, Aveiro, Portugal, 2007.
- Martins, S.; Mata, J.; Munhá, J.; Mendes, M.H.; Maerschalk, C.; Caldeira, R.; Mattielli, N. Chemical and mineralogical evidence of the occurrence of mantle metasomatism by carbonate-rich melts in an oceanic environment (Santiago Island, Cape Verde). *Miner. Petrol.* 2010, 99, 4365. [CrossRef]
- 48. Monteiro Santos, F.A.; Almeida, E.P.; Mota Gomes, A.; Lobo de Pina, A. Hydrogeological investigation in Santiago Island (Cabo Verde) using magnetotellurics and VLF methods. *J. Afr. Earth Sci.* **2006**, *45*, 421–430. [CrossRef]
- Gonçalves, R.; Farzamian, M.; Monteiro Santos, F.A.; Represas, P.; Mota Gomes, A.; Lobo de Pina, A.F.; Almeida, E.P. Application of time-domain electromagnetic method in investigating saltwater intrusion of Santiago Island (Cape Verde). *Pure Appl. Geophys.* 2017, 174, 4171–4182. [CrossRef]
- Gonçalves, R.; Monteiro Santos, F.A.; Farzamian, M.; Represas, P.; Mota Gomes, A.; Lobo de Pina, A.F.; Almeida, E.P. Water resources detection at Santiago Island, Cape Verde using electromagnetic methods. *First Break. Spec. Top. EM Potential Methods* 2018, 36, 53–59. [CrossRef]
- 51. Friedman, I. Deuterium content of natural waters and other substances. Geochim. Cosmochim. Acta 1953, 4, 89–103. [CrossRef]
- 52. Tanweer, A.; Hut, G.; Burgman, J.O. Optimal conditions for reduction of water to hydrogen by zinc for mass spectrometric analysis of the deuterium content. *Chem. Geol.* **1988**, *73*, 199–203. [CrossRef]
- 53. Tanweer, A. Importance of clean metallic zinc for hydrogen isotope analysis. Am. Chem. Soc. 1990, 62, 2158–2160. [CrossRef]
- 54. Epstein, S.; Mayeda, T. Variation of <sup>18</sup>O content of waters from natural sources. *Geochem. Cosmochim. Acta* **1953**, *4*, 213–224. [CrossRef]
- 55. International Atomic Energy Agency. *Procedure and Technique Critique for Tritium Enrichment by Electrolysis at IAEA Laboratory;* Technical Procedure 19; International Atomic Energy Agency: Vienna, Austria, 1976.

- 56. Appelo, C.A.J.; Postma, D. *Geochemistry, Groundwater and Pollution*; Appelo, C.A.J., Postma, D., Eds.; Balkema: Rotterdam, The Netherlands, 1994.
- Carreira, P.M.; Marques, J.M.; Pina, A.L.; Mota Gomes, A.; Galego Fernandes, P.; Monteiro Santos, F.A. Groundwater assessment at Santiago Island (Cabo Verde): A multidisciplinary approach to a recurring source of water supply. *Water Resour. Manag.* 2010, 24, 1139–1159. [CrossRef]
- 58. Carreira, P.M.; Lobo de Pina, A.; Mota Gomes, A.; Marques, J.M.; Monteiro Santos, F. Geochemical and isotopic marks for tracing groundwater salinization: Santiago Island, Republic of Cape Verde, case study. In Advances in Sustainable and Environmental Hydrology, Hydrogeology, Hydrochemistry and Water Resources. Advances in Science, Technology & Innovation (IEREK Interdisciplinary Series for Sustainable Development, 1st ed.; Chaminé, H., Barbieri, M., Kisi, O., Chen, M., Merkel, B., Eds.; Springer: Cham, Switzerland, 2019; pp. 161–164.
- 59. Re, V.; Sacchi, E. Tackling and salinity-pollution nexus in coastal aquifers from arid regions using nitrate and boron isotopes. *Environ. Sci. Pollut. Res.* **2017**, *24*, 13247–13261. [CrossRef]
- 60. Mata, J.; Moreira, M.; Doucelance, R.; Ader, M.; Silva, L.C. Noble gas and carbon isotopic signatures of Cape Verde oceanic carbonatites: Implications of carbon provenance. *Earth Planet Sci. Lett.* **2010**, *291*, 70–83. [CrossRef]
- 61. Shirke, K.D.; Kadam, A.K.; Pawar, N.J. Temporal variations in hydro-geochemistry and potential health risk assessment of groundwater from lithological diversity of semi-arid region, Western Gujarat, India. *Appl. Water Sci.* 2020, *10*, 156. [CrossRef]
- 62. Shirke, K.D.; Kadam, A.; Pawar, N.J. Health risk assessment and prevalence of fluoride in groundwater around the geological diversity of Ambadongar South Gujarat, India. *Hum. Ecol. Risk Assess. Int. J.* **2021**, 27, 1523–1542. [CrossRef]
- 63. Möller, D. The Na/Cl ratio in rainwater and the seasalt chloride cycle. Tellus 1990, 42, 254–262. [CrossRef]
- 64. Mukhopadhyay, A. Cl-SO4 mass ratio as an indicator of contamination of freshwater resources in Kuwait by seawater and oilfield brine. *J. Water Resour. Hydraul. Eng.* **2015**, *4*, 23–55. [CrossRef]
- 65. Pennisi, M.; Bianchini, G.; Muti, A.; Kloppmann, W.; Gonfiantini, R. Behaviour of boron and strontium isotopes in groundwateraquifer interactions in Cornia Plain (Tuscany, Italy). *Appl. Geochem.* **2006**, *21*, 1169–1183. [CrossRef]
- 66. Craig, H. Isotopic variations in meteoric waters. *Science* **1961**, *133*, 1702–1703. [CrossRef] [PubMed]
- 67. Rozanski, K.; Araguás-Aráguas, L.; Gonfiantini, R. Relation between long-term of oxygen-18 isotope composition of precipitation and climate. *Science* **1992**, *258*, 981–985. [CrossRef]
- 68. Mook, W.G. Environmental isotopes in hydrological cycle. In *Principles and Applications. IHP-V Technical Documents in Hydrology;* UNESCO and IAEA: Paris, France, 2000.
- Rozanski, K. Deuterium and oxygen-18 in European groundwaters: Links to atmospheric circulation in the past. *Chem. Geol.* 1985, 52, 349–363. [CrossRef]
- Araguás-Araguás, L.; Gonfiantini, R. Environmental Isotopes in Seawater Intrusion Studies; Internal Report; International Atomic Energy Agency: Vienna, Austria, 1989.
- 71. Edmunds, W.M.; Droubi, A. Groundwater salinity and environmental change. In *Isotope Techniques in the Study of Environmental Change*; International Atomic Energy Agency: Vienna, Austria, 1998; pp. 503–518.
- Lucas, L.L.; Unterweger, M.P. Comprehensive review and critical evaluation of the half-life of tritium. *J. Res. Natl. Inst. Technol.* 2000, 105, 541–549. [CrossRef] [PubMed]
- 73. Cartwright, I.; Cendón, D.; Currell, M.; Meredith, K. A review of radioactive isotopes and other residence time tracers in understanding groundwater recharge: Possibilities, changes and limitations. *J. Hydrol.* **2017**, *555*, 797–811. [CrossRef]
- 74. Akiti, T. Environmental Isotope Study of the Groundwaters of the Island of Santiago, Cape Verde. Report; International Atomic Energy Agency, Division of Research and Laboratories, Section of Isotope Hydrology: Vienna, Austria, 1985; p. 54.
- Carreira, P.M.; Marques, J.M.; Graça, R.C.; Aires-Barros, L. Radiocarbon application in dating "complex" hot and cold CO<sub>2</sub>-rich mineral water systems: A review of case studies ascribed to the northern Portugal. *Appl. Geochem.* 2008, 23, 2817–2828. [CrossRef]
- 76. Han, L.F.; Plummer, L.N. A review of single-sample-based models and other approaches for radiocarbon dating of dissolved inorganic carbon in groundwater. *Earth-Sci. Rev.* **2016**, *152*, 119–142. [CrossRef]
- 77. Han, L.F.; Plummer, L.N.; Aggarwal, P. A graphical method to evaluate predominant geochemical processes occurring in groundwater systems for radiocarbon dating. *Chem. Geol.* **2012**, *318–319*, 88–112. [CrossRef]
- 78. Gonfiantini, R.; Zuppi, J.-M. Carbon isotope exchange rate of DIC in karst groundwater. Chem. Geol. 2003, 197, 319–336. [CrossRef]
- 79. Monge Soares, A.M.; Martins, J.M.M.; Cardoso, J.L. Marine radiocarbon reservoir effect of coastal waters off Cape Verde. *Radiocarbon* **2011**, *50*, 289–296. [CrossRef]
- 80. Fernández-Palacios, J.; Nogué, S.; Criado, C.; Connors, S.; Góis-Marques, C.; Sequeira, M.; Nascimento, L. Climate change and human impact in Macaronesia. *Past Glob. Changes Mag.* **2016**, *24*, 68–69. [CrossRef]