

Article

Hydrochemistry and Evolution of Water Quality in a Context of Aridity and Increasing Agriculture in Three River Sub-Basins of Santiago Island (Cape Verde)

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Abstract: In regions under development and facing recurrent droughts, increasing the area of irrigated agriculture may create additional disruption in water resources management. The present study was focused on three river sub-basins with the highest agricultural intensity (S. Miguel, Ribeira Seca and S. Domingos) in Santiago Island (Cape Verde). Sets of wells were selected to evaluate the influence of salinization and agriculture practices on the hydrochemistry. This assessment was performed by using data from the bibliography (2003) and a recent campaign (2016). The water chemistry indicates lower mineralization in the S. Miguel sub-basin. Nitrates and nitrites, typically associated with diffuse pollution, are present in all sub-basins, but with varying patterns. Additionally, sodium chloride waters occur in all the three sub-basins, especially those closest to the coastline. In turn, a bicarbonate-magnesium facies was identified in S. Domingos, at the furthest point from the coast, indicating a geological control. The comparison between the two periods suggests a decrease in water quality. The rising extension of the irrigation area associated with aridity should intensify the already observed soil salinization. Thus, the present review highlights the strategic importance of water monitoring at the basin level as a management tool for resources preservation in insular arid and developing regions.

Keywords: river basin; agriculture pressure; hydrochemistry; water quality; salinization risk

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1. Introduction

The sustainable use of natural resources, especially water, has assumed an increasing relevance in unfavorable contexts, such as arid and semi-arid climates. The challenges to adequate resource management are even greater in territories subject to anthropogenic pressures associated with population growth and unregulated economic activities, as is the case in many developing countries.

Current scenarios of climate disruption, characterized by increasingly frequent and persistent droughts, make the preservation and sustainable management of the territory and its resources even more pressing in regions such as the west coast of Africa.

Water, a fundamental component of life and essential to a wide variety of economic activities, is one of the most abundant natural resources on the planet, but also one of the most susceptible to degradation. The need for its use for human consumption (e.g., drinking and cooking), and also for the development of activities such as agriculture, transport, industry and recreation, highlights the critical nature of this resource. It is, however, a limited and limiting resource, as shown by the recurrent water scarcity problems in many parts of the world, sometimes with tragic consequences [1].

The Cape Verde Archipelago, together with the archipelagos of the Canary Islands, the Azores and Madeira, constitutes the region of Macaronesia, known for its biogeographical specificities, including the floristic and faunistic richness [2]. The state of

the art focused on this territorial context also suggests similar problems related to water resources management. For example, the authors of [3–6] presented literature reviews and discussed problems associated with water quality, with reference to the main threats to supply in the Canary Islands. There are also several works focusing on hydrogeochemical controls and salinization of water in several islands from the Azores Archipelago [7–10]. The present study follows these approaches by reviewing the water quality situation in Santiago Island (Cape Verde), a developing and semi-arid territory located on the west coast of Africa, subject to water scarcity and anthropogenic activities, especially agriculture.

Cape Verde is a small country with ten islands (Figure 1). The focus of this article is Santiago Island, which is the most populated island, since about 55% of the Cape Verde population lives there [11]. The capital of the country is Praia City.

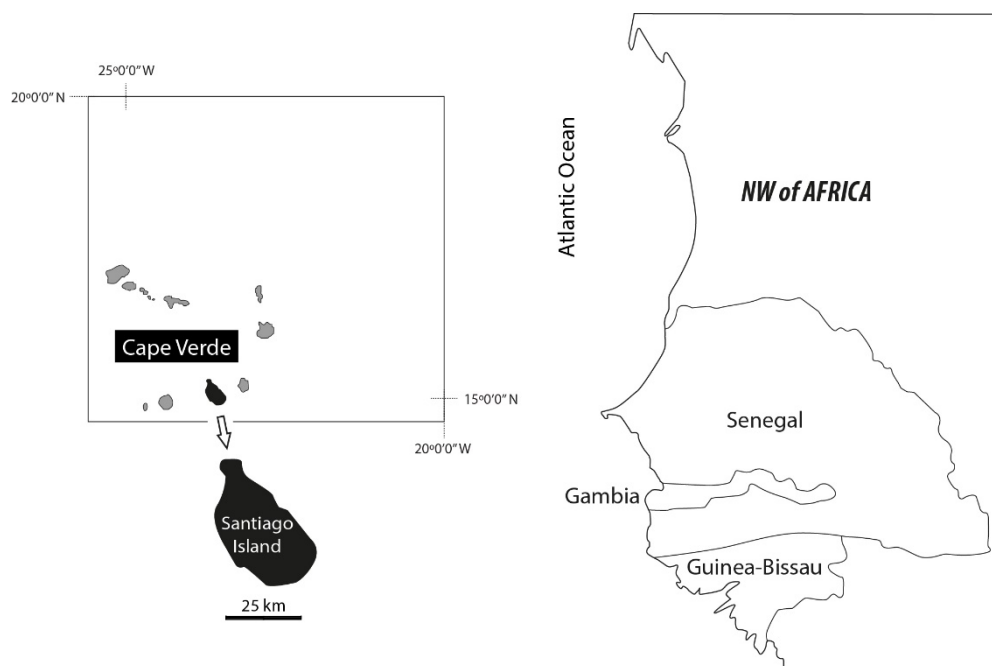


Figure 1. Geographic location of Cape Verde and Santiago Island (west coast of Africa).

Several technical and/or scientific studies can be cited (e.g., [12,13]). The first hydrogeological survey of the archipelago was carried out by [14], having also contributed to the discussion of the problem of the water supply, with the objective of advocating immediate solutions. Additionally, the project CVI 75/001, financed by the United Nations Development Programme (UNDP), is the source of the greatest hydrogeological knowledge of the island. The reports prepared by [15,16] should also be mentioned.

As a result of these projects, an extensive list of studies on the hydrogeological behavior in volcanic terrains can be cited, including [17–34].

In a more or less direct way, these works put forward in evidence the primordial strategic need for protecting the water, due to its scarcity and fragility. Indeed, groundwaters are one of the main sources of water in regions with surface water deficit or in territories without a centralized supply system. However, in many cases, the population consumes groundwater in a disorganized way and without quality control, with consequent risks to public health.

In general, the literature review indicates a reduction in water quality, often linked to salinization in coastal areas, as a direct result of overexploitation of aquifers (e.g., [35]) and sand extraction on beaches that destroy natural barriers against saline intrusion (Figure 2).



Figure 2. Images illustrating the exploitation of resources on Santiago Island: (A,B) extraction of sand on the beaches; (C) exploitation on the river channel; (D) extraction of pebbles on the beach.

Santiago Island has five river basins and numerous seasonal streams dependent on the rainy season. Close to the Atlantic Ocean, the valleys are filled with Quaternary sediments of alluvium and these are the best for agriculture. Nevertheless, most of these valleys are intensively cultivated throughout the year, since irrigation water is mostly from groundwater extraction. Although there are several degradation activities in these basins, such as the mentioned exploitation of sand and gravel, agriculture is the most important economic activity on the island. Therefore, it has the strongest impact in some of the basins. This justifies the approach of focusing the study on the sub-basins with a greater agricultural intensity (located on the east side of the island): S. Miguel, Ribeira Seca and S. Domingos.

The present work pursues the main following objectives: (i) general characterization of the river basins considering the state of the art; (ii) analysis of the hydrochemistry and evolution trends in one of the most cultivated basins; (iii) evaluation of the influence of agriculture and other control factors on the water quality.

This review and the obtained results intend to contribute with knowledge that could be applied in similar territories, for helping decision making on water resources management in arid insular contexts.

2. General Characterization of Santiago Island

2.1. Geomorphology and Geology

The archipelago of Cape Verde presents, in general, complex morphologies, characterized by high altitudes, large terrain slopes, accentuated orography and extensive highlands (“Achadas”). Santiago Island thus presents a great diversity of relief forms (Figure 3), from the steepest peaks and slopes with rocky outcrops, often separated by deep valleys (young relief forms), to flat surfaces, which mainly develop on the outskirts of the island [36]. It has an average altitude of 278.5 m, with a maximum altitude of 1392 m. The island has two asymmetrical mountainous areas (Figure 3), the Pico da Antónia (1392 m), to the south, and Malagueta mountain (1063 m), to the north, separated by a plateau area at an average altitude of 550 m, built from cones and other reliefs in various states of erosion [37].

Faults (NE–SW, WNW–ESE and NW–SE) are responsible for the insertion of the main valleys, namely, the S. Miguel, Ribeira Seca and S. Domingos valleys that have NE–SW directions.

The authors of [37,38] considered seven geomorphological units (Figure 3): Southern “Achadas” (I); Pico da Antónia Mountain Ridge (II); Santa Catarina Plateau (III); Eastern Flank (IV); Malagueta Mountain Ridge (V); Tarrafal (VI); Western Flank (VII).

The geology of Santiago is mainly composed of volcanic and volcanoclastic materials, outcropping predominantly basalts and pyroclastic products ($\approx 91\%$), limburgites ($\approx 5\%$) and phonolites ($\approx 2\%$). Although to a lesser extent, basanites and tephrites, leucitites and nefelinites and associations of sedimentary rocks grouped in two facies (marine and terrestrial) can also be found. The magmatic rocks are distributed by different ages and various geological formations. The oldest formations are mostly located in eroded sectors (e.g., river beds). Metamorphic rocks are almost non-existent, and their presence is limited to a small amount of evidence of contact metamorphism phenomena.

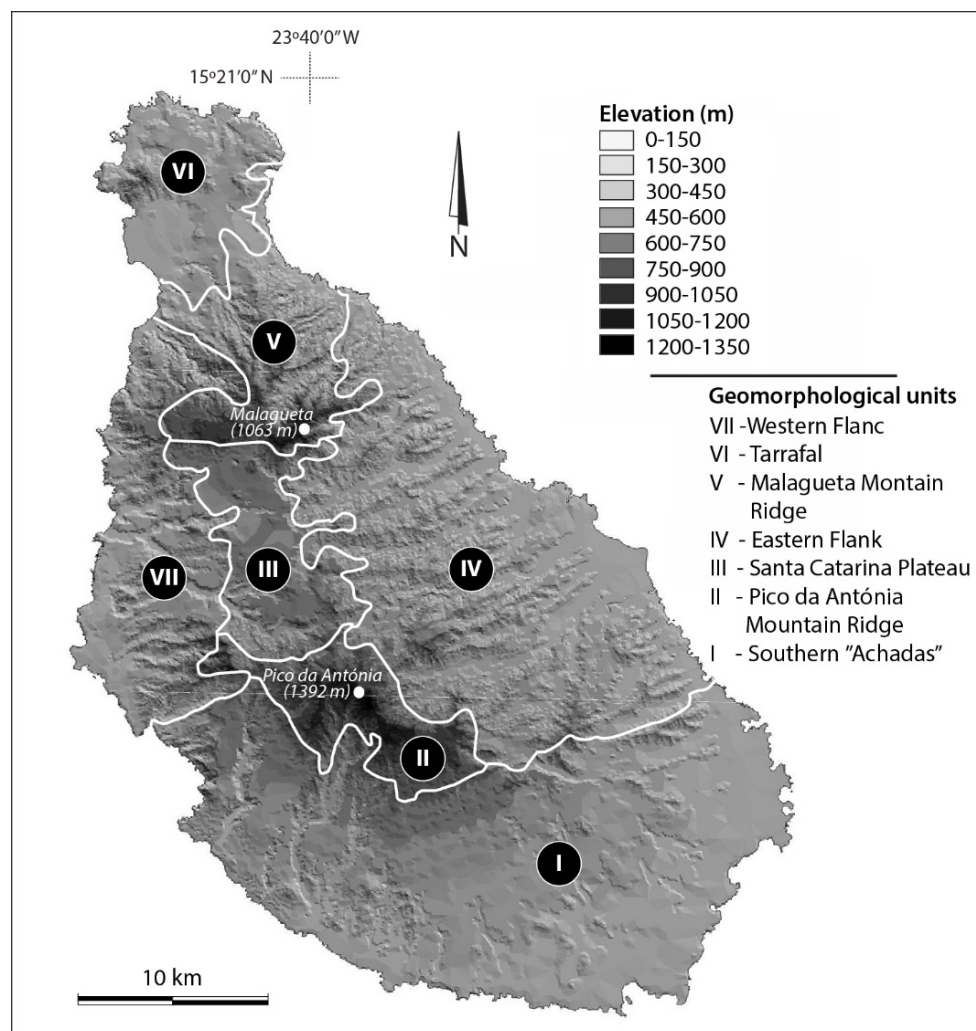


Figure 3. Santiago Island geomorphological units (adapted from [37,38]). GIS 2D terrain digital map (after [39]).

The hydrogeological map of Santiago Island is schematized in Figure 4 where the main units are reported. The three main geological units with hydrogeological importance are the Pico da Antónia Eruptive Complex (PA), Monte das Vacas Formation (MV) and Recent Sedimentary Quaternary Formations (a) ([40]). Based on data from the

National Institute of Water Resources of Cape Verde, and as evidenced by [40], the pillow lavas of the Pico da Antónia Eruptive Complex (PA) represent the most hydrogeological productive level.

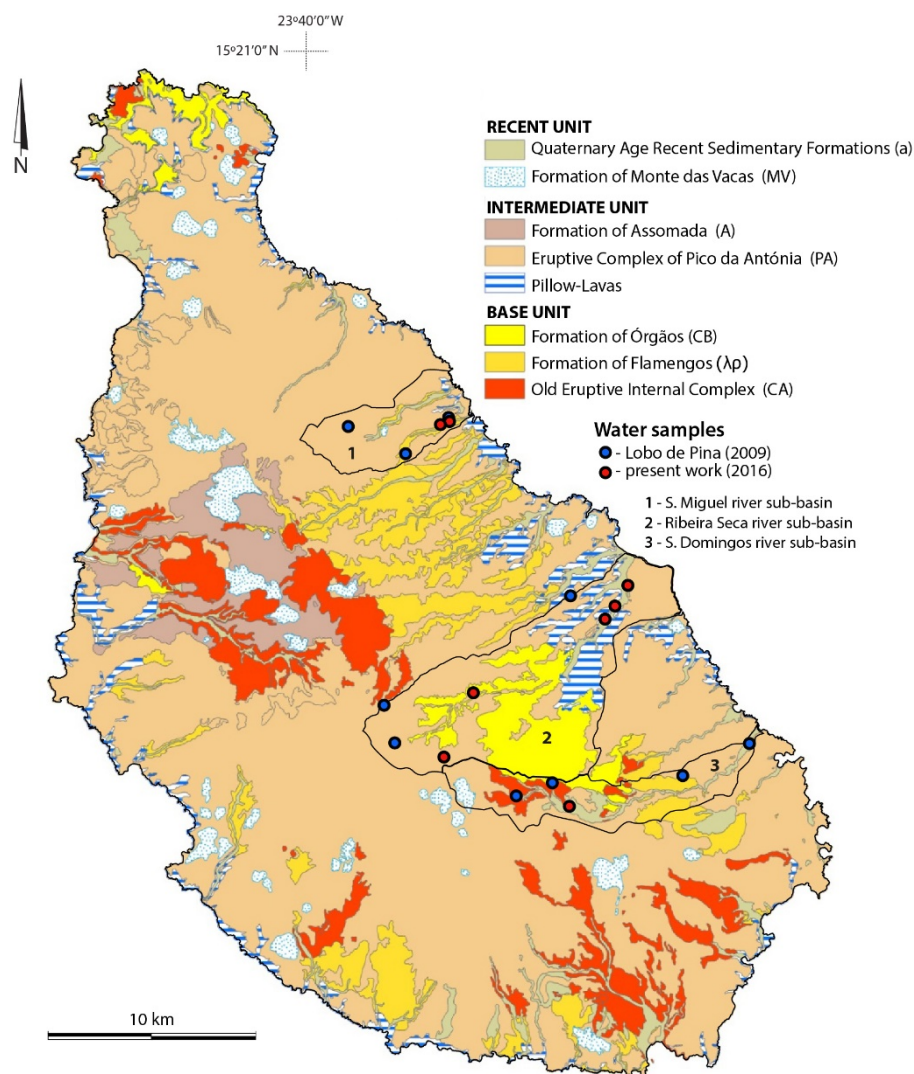


Figure 4. Map of hydrogeological units (adapted from Cape Verde geological map to the scale 1:25,000 [29,41,42]). The circles represent the location of the water samples in the river sub-basins: 1—S. Miguel, 2—Ribeira Seca and 3—S. Domingos.

2.2. Climate

Cape Verde is located between the subtropical Atlantic North high-pressure area (Azores anticyclone) and the West Africa Intertropical Convergence Zone (ITCZ). The orientation and position of these systems have a great impact on the archipelago [37]. When the later is shifted to the south, precipitation drops dramatically as the archipelago stays exposed to the northeast dry winds from the Sahara Desert.

The study area is characterized by a tropical climate with two distinct seasons: dry season (December to June), where the influence of the eastern sector of the Azores anticyclone is felt, often interrupted by episodes of precipitation of low intensity due to invasions of polar air; wet season (August to October), where more than 90% of annual precipitation occurs. The months of June and November are considered the transition months [37]. The meteorological characteristics, in addition to the geographical conditions, are also strongly conditioned by local factors, such as altitude, relief and distance to the sea, and the insular structure. The altitude is one of the geomorphological

characteristics that most influences the temperature and precipitation regime. Irregular rainfall is a typical climate feature, and there may be years or successive years of extreme dry seasons.

Table 1 shows the maximum and minimum values of precipitation and temperature for a series of at least 25 years, registered in the different meteorological stations in Santiago Island. Figure 5 graphically represents the distribution of mean annual precipitation (1990 to 2016) and the distribution of the mean annual temperature in Santiago Island (1981 to 2016) for four stations. These meteorological stations (Figure 4), except Praia-Aeroporto, cover the river sub-basins under study: S. Miguel, Ribeira Seca and S. Domingos. The only meteorological station with a regular record of the temperature is Praia-Airport, indicating a variation between 24 and 26.5 °C.

Table 1. Meteorological stations of Santiago Island with the precipitation and temperature maximum (max) and minimum (min) values: precipitation is based on the temporal series 1990 to 2016; temperature is based on the series 1981 to 2016.

Meteorological Station	Annual Precipitation (mm)		Annual Temperature (°C)	
	Maximum	Minimum	Maximum	Minimum
Praia-Airport	410	17.8	26.3	24.2
S. Jorge dos Órgãos	1013	174	23.3	21.5
Chão Bom	664	51,3	26.5	23.8
S. Domingos	707	35.8	25.5	22.2

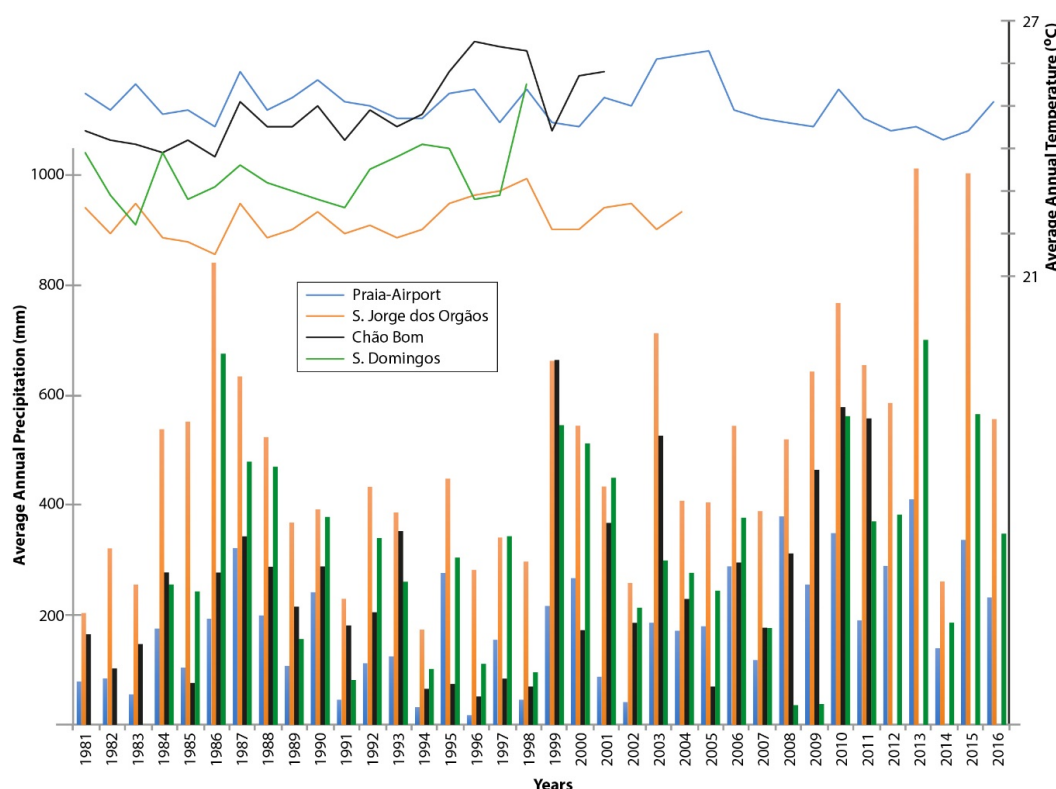


Figure 5. Distributions of average annual precipitation (1990 to 2016) and of average annual temperature (1981 to 2016) in Santiago Island (data provided by INMG—Instituto Nacional de Meteorologia e Geofísica de Cabo Verde).

The average annual precipitation has not exceeded 300 mm in about 65% of the territory, located at less than 400 m altitude, while in the areas located at more than 500 m altitude (Pico da Antónia and Malagueta), the total annual precipitation can reach more than 700 mm [43]. Precipitation, though scarce, can occur in a torrential manner, causing

floods. In addition, a marked irregularity during the year leads to long periods of drought, with almost no precipitation. The periods of heavy rains are usually accompanied by a large surface runoff along the slopes and rivers (dry most of the year because there are no restraints that prevent the flow of water into the sea).

In Santiago Island, the atmospheric temperature is also determined by a combination of factors, such as the exposure of the reliefs relative to the dominant winds (N to NE), the altitude and the distance to the sea.

2.3. Land Use

The authors of [44] presented the situation of agricultural production in the archipelago, highlighting the importance of this activity in Santiago Island, which occupies more than 50% of its surface area. More than 90% of the arable surface in Santiago is used for rain-fed agriculture, particularly staple crops (maize and beans), and about 5% is used for irrigated crops (sugarcane, fruits, vegetables, cassava and sweet potato) [45].

According to the General Census of Agriculture [46], the land use types in Santiago Island have been classified into five classes (Figure 6), each one corresponding to a specific behavior towards soil erosion.

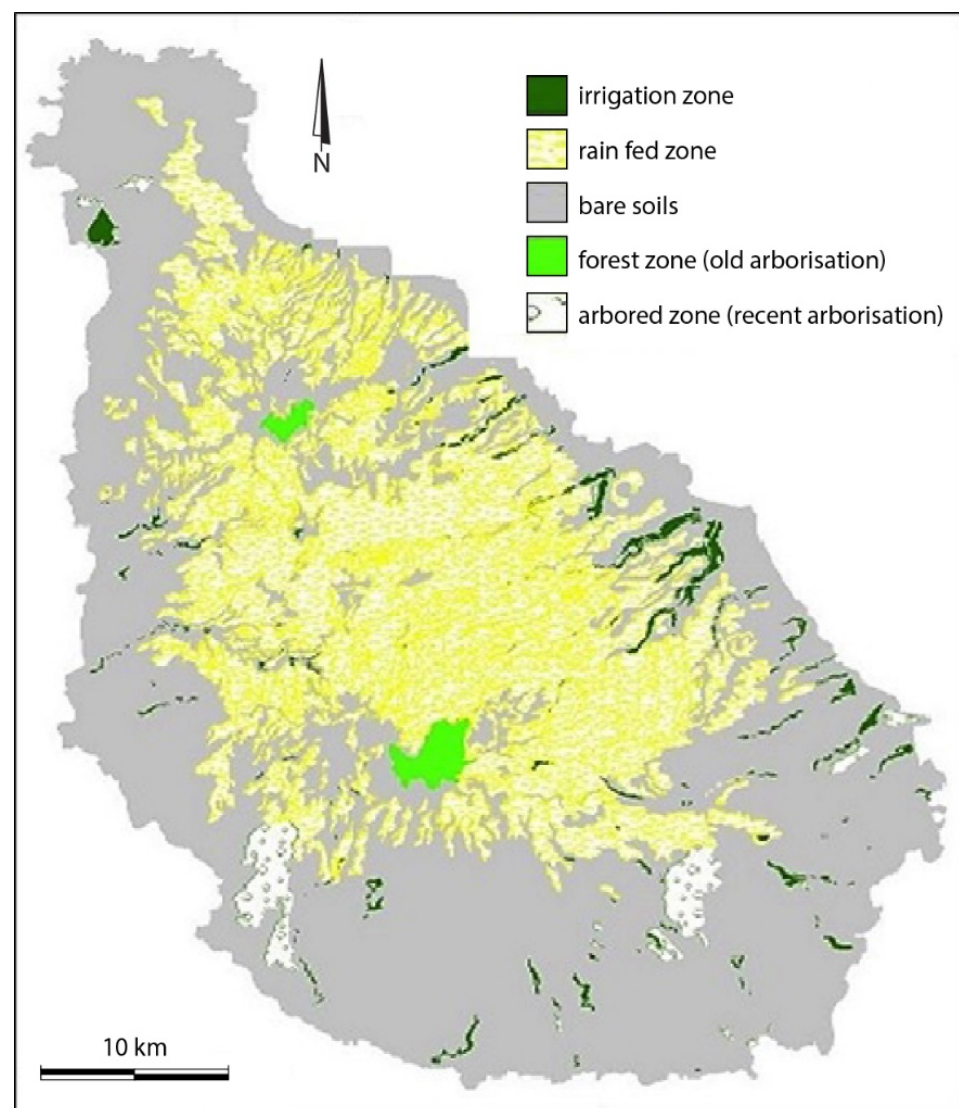


Figure 6. Land use of Santiago Island (adapted [47,48]).

The five classes are described as follows [48]:

1. Irrigation zone—low erosion rate;
2. Rain-fed zone—rain-fed agricultural activities (essentially maize and beans);
3. Bare soils;
4. Forest zone (old trees)—low erosion rate except in cases of steep slopes. The vegetal cover generates organic matter and, also, a root mechanical action, which gives structure and cohesion to the soil;
5. Arbored zone (recent arborization).

3. River Basins

For the author of [49], the river basin can be defined as "the area drained by a given river or by a fluvial system, functioning as an open system", where each of the elements, materials and energies present in the system has its own function, and where these components are structured and intrinsically related to each other.

The hydrographic network, responsible for the drainage of a basin, has configurations or spatial arrangements that reflect the geological structure and morphogenetic composition of the basin area.

Regarding the conservation of natural resources, the concept has been extended, with a scope beyond hydrological aspects, involving knowledge of the biophysical structure of the river basin, as well as changes in land use patterns and their environmental implications. In this sense, they emphasize the importance of using the concept of a basin as analogous to that of an ecosystem, as a practical unit, both for study and for environmental management [50].

The hydrographic basins, due to the orographic conditions of Santiago Island and the limited rainfall, play a central role in the water supply and in the development of agricultural practices. The island's population is heavily dependent on agriculture for self-sustainability, and, therefore, as stated by [44], the sector plays a bacillary role in economic development.

The Santiago Island topography is characterized by a great density of deep valleys (Section 2.1), starting from the highest zones towards the ocean, facilitating the transport of the residues by erosion, which consequently causes difficulties in the development of the vegetal cover.

These structures are fed by the Pico da Antónia massif, which is the most important drainage area, with a dense network of valleys to the east. In the same way, numerous valleys cut Malagueta mountain; in its evolution, some of the headwaters of the drainage network approach the scarp morphology (Figure 3). The headwaters of the basins contiguous to Malagueta mountain are sectors of great rainfall; therefore, floods are frequent during the rainy season, since the beds of these basins are relatively flat, increasing their altitude very gently upstream.

Santiago Island has five main hydrographic basins with different total precipitation surfaces and volumes (Figure 7, Table 2).

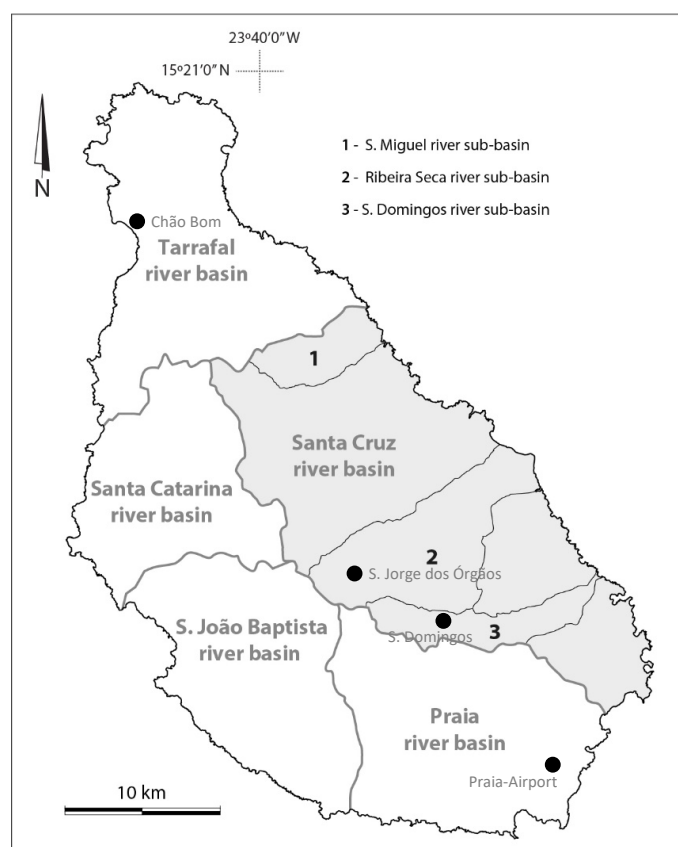


Figure 7. River basins and the most important sub-basins (main agricultural valleys) of Santiago Island (adapted from [24,29]). • Indicates the location of the meteorological stations with complete series in the island.

Table 2. The main river basins of Santiago Island total area and precipitation volumes (adapted from [29]).

River Basin	Basin Area (km ²)	Precipitation Total Volume (hm ³)
Tarrafal	188	45
Santa Cruz	355	121
Santa Catarina	128	62
S. João Batista	155	47
Praia	179	33

Among these river basins, Santa Cruz is the one with the largest area (355 km²) and the largest total precipitation volume (121 hm³). It is known for its agricultural importance (e.g., [51–53]). Within this basin, due to its greater agricultural potential, the river sub-basins of S. Miguel, Ribeira Seca and S. Domingos were selected for a more detailed analysis (Figure 7; river sub-basins 1, 2 and 3).

3.1. General Description of the River Sub-Basins

The S. Miguel sub-basin (14.4 km²) is limited, both in the north and in the south, by slopes in the order of 20°. In the interior, the width of the valley varies between 500 m and 1.5 km, narrowing to the sea.

In this sub-basin, the Quaternary alluvium sediments are very shallow and thin, except for the downstream locations, that is, near the shoreline. Together with the common basalt structures (more or less fractured), there are also pillow lava and greenish tuff layers. Agriculture activities are restricted to the areas near the coastline. It is agriculture of a "high level of intuition and little technical apparatus" [54].

The sub-basin of Ribeira Seca—located on the east-central part of Santiago Island (Figures 2 and 7), 10 km north of the S. Domingos valley, near the village of Santa Cruz—is the largest sub-basin of the island and has the largest agricultural extension. According to [55], it has a drainage area of about 72 km² and represents four agro-climatic zones: semi-arid (49%), arid (20%), sub-humid (20%) and humid (11%), based on altitude, vegetation and relief. This sub-basin also has the highest rate of soil use, thus requiring more water for irrigation. However, the dominant land use is rain-fed agriculture, particularly the staple crops (maize and beans) and groundnut, occupying 83% of the area. The remaining area is used for: irrigated crops (banana, sugarcane, fruits, vegetables, cassava and sweet potato) at 5% (362 ha), and forest at 4% (251 ha). In addition, 1% of the area is rock outcrops, and 7% is built environments. Livestock is an important activity as most families depend on animals, such as cows, goats, pigs and chickens that often graze freely [45].

The soils, developed on a basaltic substrate, are mainly shallow and low in organic matter (OM), generally with low to medium fertility [56,57] and medium to coarse texture, and exhibit marked symptoms of degradation by erosion (i.e., rills and gullies). Deeper soils with a higher OM content can be found on the plateaus of less steep slopes (“Achadas”). In the valley bottoms, alluvial soils are predominant and used for irrigated agriculture.

The S. Domingos stream valley is the southernmost of the surveyed sub-basins. The surface area is 44.3 km² including part of the Southern “Achadas” plateau, and it has an extension of 16 km. In this sub-basin, the rainfall has a value close to the annual average of Santiago Island, about 360 mm. This region depends on agricultural practices, although green vegetable production is in decline, especially in the sector closest to the shoreline. The work found in [58] indicated a cultivated area of 694 ha (dry: 594 ha; irrigated: 100 ha), values that would not have changed significantly in the last decade [46].

3.2. Hydrochemistry and Water Quality

The author of [29] pointed out the compositional variability of the groundwater in Santiago Island that is dependent on the geological characteristics and residence time. Besides geological control, it should be noted that other factors may influence the chemistry of water, particularly anthropic activity that manifests, for example, in overexploitation of water and soil.

The scarcity and lack of a controlled public supply force populations to use water from boreholes and dug wells without monitoring. Often, water points known for their lack of quality are used for irrigation. These aspects justify the approach presented in this section on the hydrochemical characteristics of wells located in the three sub-basins subjected to higher anthropic pressure.

3.2.1. Methodological Approach

The hydrochemical evolution and possible changes in water quality over time are reviewed and discussed by comparing data from the bibliography, specifically the works by [29,40], with a recent campaign conducted for the present study. Therefore, this analysis comprehends two periods: summer of 2003 [29] and summer of 2016. For the recent campaign, the pH, electrical conductivity (EC) and temperature (T) were measured in situ with a portable meter, Thermo Scientific Orion. Dissolved major metals were obtained by inductively coupled plasma optical spectroscopy (ICP-OES) after filtration with 0.45 µm syringe filters and acidified until pH < 2 to assure the preservation of the samples. Anions were determined by ionic chromatography with suppressed conductivity, while alkalinity was analyzed by potentiometric titration. Samples were kept refrigerated (<4 °C) until the laboratory analysis.

Figure 8 illustrates the distribution of the water points analyzed in the three sub-basins evaluated in the Santa Cruz basin. The blue circles represent points from the work of [29], while the red circles are for the summer of 2016.

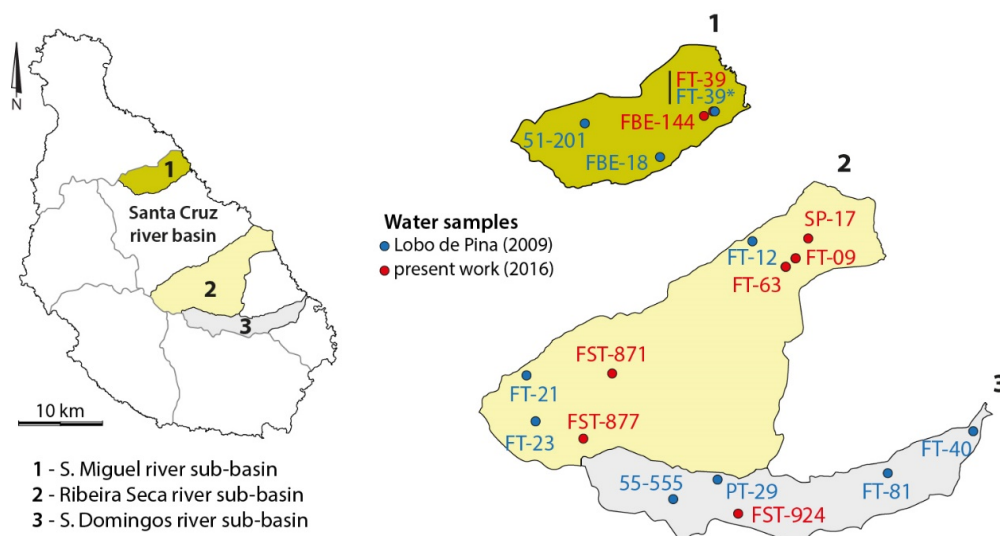


Figure 8. Distribution of sampling points for hydrochemistry study in S. Miguel, Ribeira Seca and S. Domingos river sub-basins. *—the FT-39 borehole is coincident in both works.

3.2.2. Hydrochemical Classification

Table 3 presents the general water properties in the river sub-basins, obtained from campaigns held in the summer of 2003 [29] and in the present work (summer 2016).

In general, mineralization is lower in the samples from the S. Miguel sub-basin, which have electrical conductivities between 525 and 1711 $\mu\text{S}/\text{cm}$. Between the two periods, an increasing trend can be observed in Ribeira Seca (with values above 975 $\mu\text{S}/\text{cm}$) and S. Domingos, where the two highest values are recorded (1927 and 2110 $\mu\text{S}/\text{cm}$, respectively, in the samples FST-924 and PT-29). This behavior follows the general tendency of the parameters Ca and Na. The same is observed for sulfate, with generally lower values in S. Miguel (4.6–82.8 mg/L), and higher values in Ribeira Seca (23.1–231 mg/L).

Nitrates and nitrites, typically associated with diffuse pollution phenomena, are present in all sub-basins, but with varying patterns. In the sub-basin of S. Domingos, the sample FST-924 stands out, with high concentrations of these anions. It should be noted that the values established in the Cape Verdean legislation are 50 mg/L and 0.3 mg/L, respectively, for nitrate and nitrite. Therefore, this well reveals the existence of a phenomenon of organic contamination. This can be of fecal, agricultural or even industrial origin, given its location in a heavily agricultural area (bananas, and sugar cane) and in the vicinity of a cane distillery. Agriculture should also be controlling the water chemistry in Ribeira Seca (the most cultivated sub-basin), as suggested by the systematic occurrence of nitrate and nitrite.

Table 3. Hydrochemistry in the most cultivated sub-basins of Santa Cruz river basin: T in °C; EC in $\mu\text{S}/\text{cm}$; ions in mg/L ; DL—detection limit of the analytical method. Rows in gray are from [29]; the others were obtained in the summer of 2016 (present work).

S. Miguel													
Samples	T	pH	CE	Na	K	Ca	Mg	Si	Cl	HCO ₃	SO ₄	NO ₃	NO ₂
51-201	24.2	7.2	527	77.9	8.9	27.2	23.3	16.9	56.7	220.0	9.1	21.7	<DL
FBE-18	27.5	7.1	525	68.1	9.9	27.2	22.0	17.3	70.9	188.0	4.6	21.7	<DL
FBE-144	27.8	7.4	1289	78.8	8.8	77.1	60.3	23.1	218.8	285.8	35.7	23.6	<DL
FT-39	27.0	7.8	1711	130.0	12.7	79.5	82.3	24.7	315.1	327.5	82.8	13.6	<DL
FT-39*	26.0	6.9	1439	113.0	9.9	57.0	70.7	30.0	248.7	276.0	50.3	16.8	<DL
Ribeira Seca													
FT-21	26.7	7.1	1351	243.0	6.4	24.8	53.5	16.9	85.1	556.0	81.9	<DL	<DL
FT-23	26.7	7.2	1041	166.0	17.9	40.0	31.3	16.7	106.4	312.0	63.7	53.6	<DL
FST-877	27.9	7.8	1467	230.0	8.4	54.7	19.7	11.8	168.1	321.5	230.9	14.8	6.17
FST-871	32.0	7.3	1311	232.0	4.8	34.1	5.7	12.3	144.5	286.1	218.2	8.73	4.16
FT-12	25.2	7.1	1311	66.4	5.9	82.8	64.7	23.3	229.3	176.0	23.1	25.9	<DL
FT-63	28.6	7.9	1213	67.0	7.3	95.5	49.9	20.1	185.9	320.9	57.5	45.5	5.6
FT-09	27.9	7.9	975	54.7	5.7	82.0	42.0	19.5	134.0	286.2	44.4	46.9	3.9
SP-17	28.2	8.0	1370	67.2	7.4	111.0	56.2	19.0	232.7	320.9	63.7	41.5	5.8
S. Domingos													
FST-924	30.7	7.1	1927	281.0	8.7	61.5	69.2	17.6	26.3	546.1	172.9	317.0	9.8
55-555	22.8	8.0	433	34.2	6.6	19.3	21.0	20.8	41.2	176.0	7.2	7.5	<DL
PT-29	24.6	7.0	2110	438.0	9.9	8.0	43.7	21.7	127.6	661.0	227.6	21.7	<DL
FT-81	25.5	6.9	1282	84.5	7.5	85.7	50.9	24.4	198.0	288.0	38.4	52.3	<DL
FT-40	27.7	7.2	1394	93.0	5.7	82.2	63.3	22.6	259.3	193.0	36.8	15.9	<DL

In terms of hydrochemical classification, the previous work from [29] indicated bicarbonate-sodium ($\text{HCO}_3\text{-Na}$) waters in the highest areas of the island, where the intermediate aquifer formations appear (Figure 4). The same author indicated magnesian-chloride (Mg-Cl) or sodium-chloride (Na-Cl) classifications in the areas closest to the coast.

The results achieved in the present work with the most recent data (2016 summer campaign) in these three sub-basins indicate a general trend that is close to that detected in other works, namely, [40] for the whole Island, [59] for the Santa Cruz basin and [34] for the S. Domingos sub-basin.

Thus, Piper's diagram (Figure 9) suggests that waters of a mixed nature predominate (Group 1— $\text{Na+Ca+Mg-HCO}_3\text{+Cl}$, and Na+Ca+Mg-Cl ; Group 2— Na-Cl waters; Group 3—all samples are Na-HCO_3 ; the sample located out of groups is of Na+Ca+Mg-HCO_3 facies).

The author of [59] also showed this dispersion of facies in the valleys of S. Domingos, Ribeira Seca and S. Miguel, with a predominance of mixed classifications. According to this author, in S. Miguel, the waters are bicarbonate-sodium or sulfate or calcium-chloride or magnesium. Similarly, in S. Domingos, the same author indicated bicarbonate-sodium or sulfated or sodium-chloride waters. In the case of Ribeira Seca, the facies identified are sulfated-sodium or, also, calcium-chloride or magnesium.

In the present study, Piper's diagram (Figure 9) confirms this dispersion of classifications, not indicating a clear trend of differentiation between the three sub-basins. Sodium-chloride waters occur in all three cases, corresponding to the water points closest to the coast. In turn, the most bicarbonate sample was identified in the S. Domingos river sub-basin, at the furthest point from the coast (55-555, Figure 8), suggesting a geological control to the detriment of the marine one.

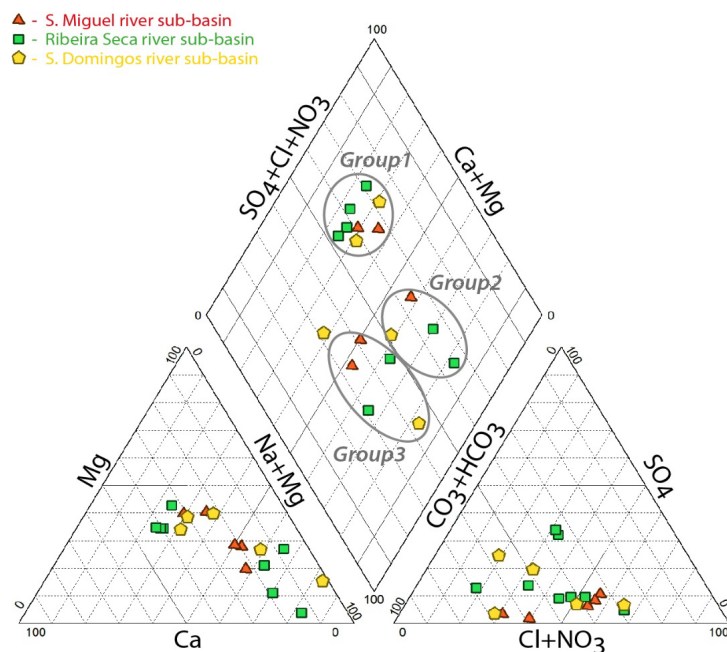


Figure 9. Hydrochemistry classification (Piper diagram) of the S. Miguel, Ribeira Seca and S. Domingos river sub-basins for summer of 2016.

The hydrochemical processes that control the chemistry in these sub-basins can be inferred from the relationships represented in Figures 10–12. These relationships propose the contribution of major ions to the mineralization (expressed through the EC). For this representation, the Na, Mg, Si, Cl, HCO_3^- and SO_4^{2-} ions were selected in order to evaluate the type of signature: predominantly marine, geological (water–rock interaction) or anthropic.

In the S. Miguel river sub-basin (Figure 10), there are high correlations between EC and Na ($R^2 = 0.7406$), EC and Mg ($R^2 = 0.9984$) and EC and Cl ($R^2 = 0.9968$). In turn, the EC–Si correlation is lower ($R^2 = 0.4329$). This pattern could be indicating a marine contribution that could be associated with saline intrusion, or deposition and leaching of marine aerosols. This signature is also recognized by the high Na–Cl correlation ($R^2 = 0.7438$). Similar trends were observed by [40], for samples from the main valleys of Santiago Island and, also, by [7], in a study carried out in islands of the Azores Archipelago.

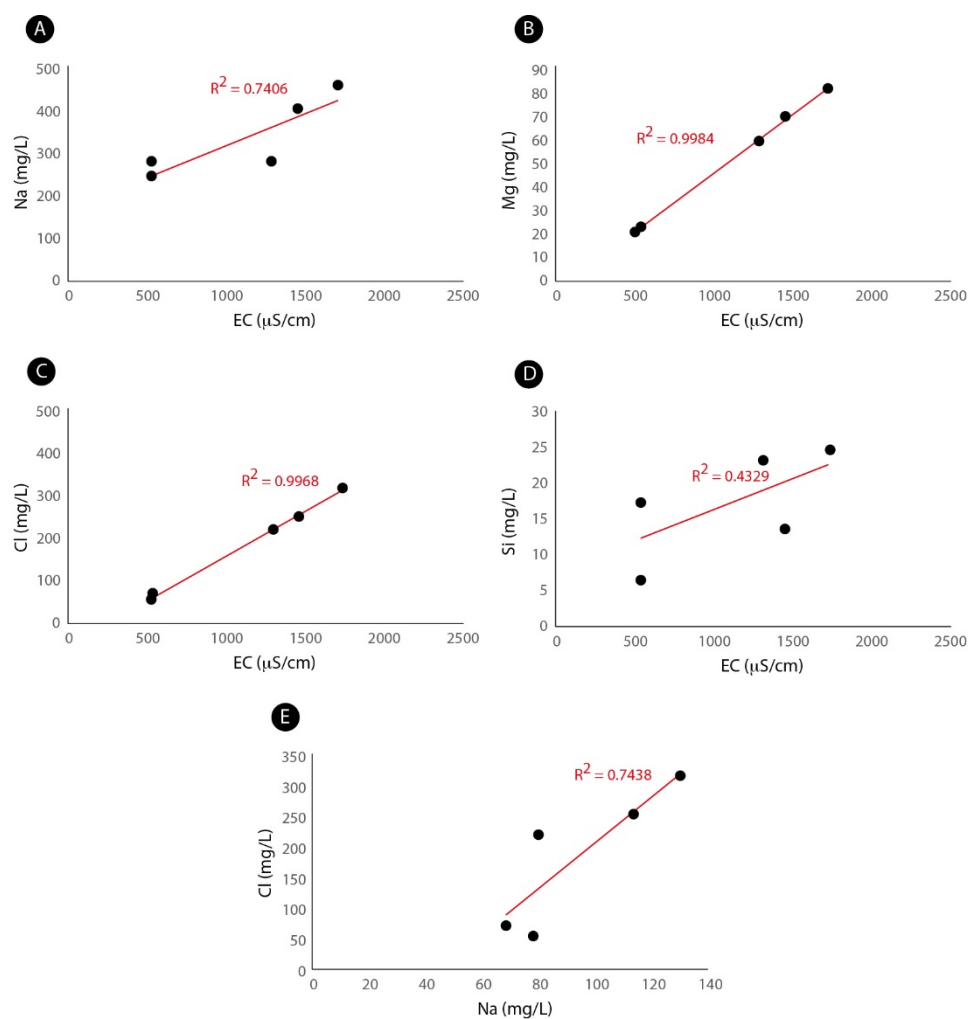


Figure 10. Relations between electrical conductivity (EC) and major ions in the S. Miguel river sub-basin. (A) EC–Na; (B) EC–Mg; (C) EC–Cl; (D) EC–Si; (E) Na–Cl.

In the Ribeira Seca river sub-basin (Figure 11), the correlations do not highlight specific mechanisms of hydrochemical control. The highest correlation is observed between Na and Cl ($R^2 = 0.382$) (Figure 11E), possibly indicating some marine contribution. The low correlations between EC and Si and Si and HCO_3^- (Figure 11C,D) could suggest a reduced influence of water–rock interaction processes. It should be noted that the EC measured here is higher than in the other two sub-basins. Additionally, the intense agricultural activity in this area may be responsible for this apparent anomaly.

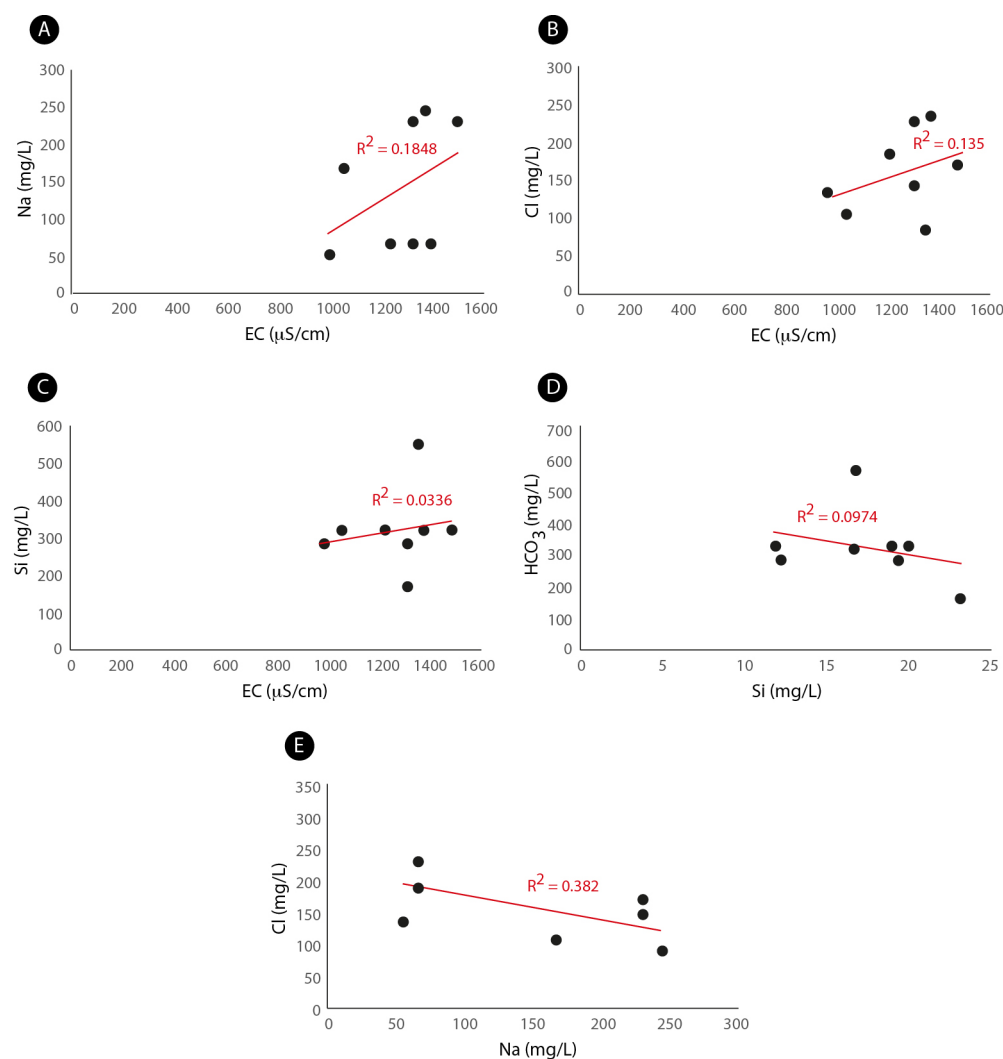


Figure 11. Relations between electrical conductivity (EC) and major ions in the Ribeira Seca river sub-basin. (A) EC–Na; (B) EC–Cl; (C) EC–Si; (D) Si–HCO₃; (E) Na–Cl.

In the S. Domingos river sub-basin (Figure 12), the marine signature is not evident, although there is a high EC–Na correlation ($R^2 = 0.7625$). The low EC–Cl and Na–Cl correlations seem to corroborate higher geological and/or anthropic contributions. In turn, the bicarbonate ion appears here with a high correlation (EC–HCO₃ of $R^2 = 0.7487$), suggesting the influence of phenomena of water–rock interaction associated with the weathering of silicate volcanic rocks, with release of alkaline and alkaline earth metals and production of alkalinity. As [60] and [7] stated, the Mg/Ca relationship may also help clarify this predominance of geological control over the marine influence. In fact, in this sub-basin, the ratio varies between 5 and 0.8, with the lowest values being near the coast (FT-81 and FT-40, Figure 8). The cited authors indicated that Mg/Ca ratios of ≥ 1 , in the context of volcanic rocks, are in agreement with the contribution from the parental rock.

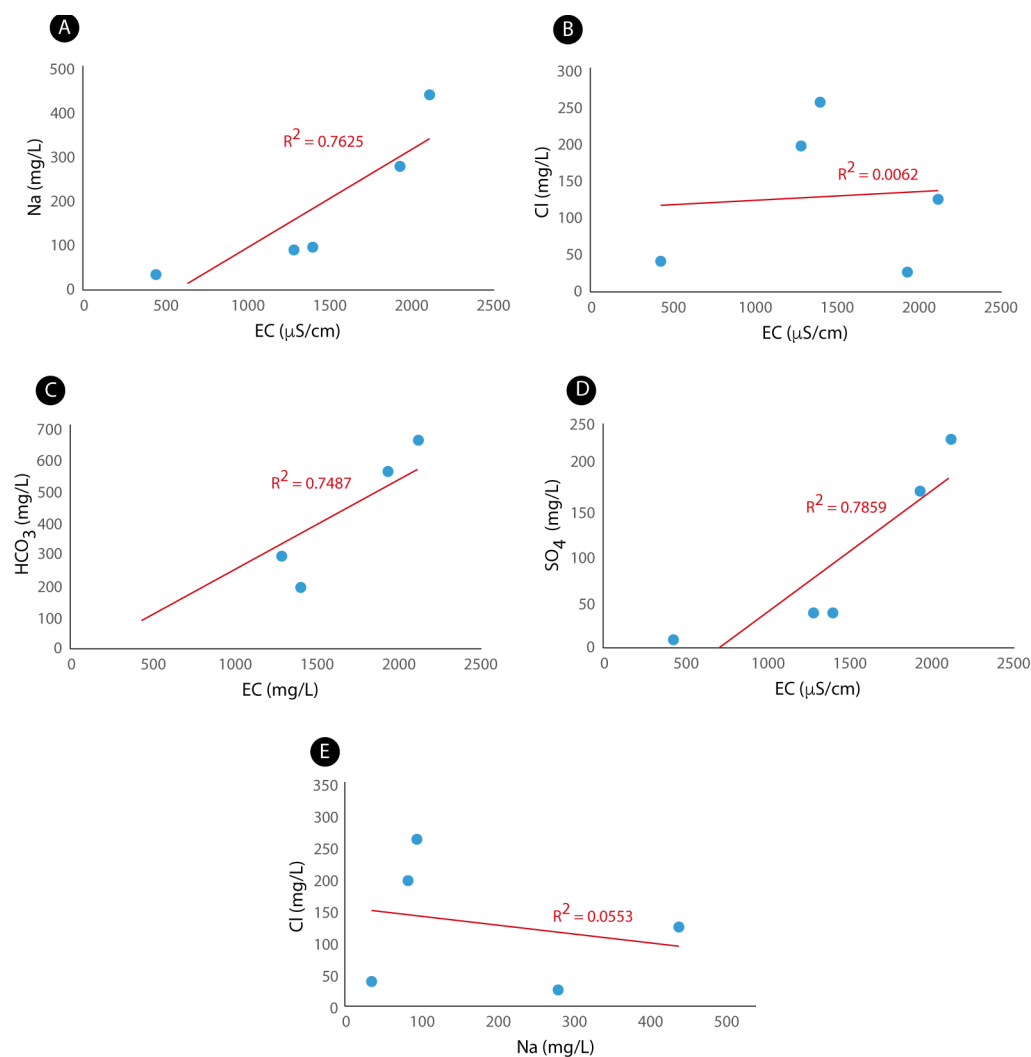


Figure 12. Relations between electrical conductivity (EC) and major ions in the S. Domingos river sub-basin. (A) EC–Na; (B) EC–Cl; (C) EC–HCO₃; (D) EC–SO₄; (E) Na–Cl.

The highest correlation is observed between EC and SO₄ ($R^2 = 0.7859$). Thus, in addition to geological control, high sulfate and nitrate concentrations may indicate pollution associated with agricultural and industrial activity, in agreement with the location mentioned above.

3.2.3. Water Quality and Risk of Soil Salinization

The data presented in Table 3 can serve, in an expeditious manner, to evaluate the evolution of water quality between the summer of 2003 and 2016. Figure 13 shows a set of quality parameters, which aim to show the evolution over time and from upstream to downstream, i.e., in order to detect differences with the proximity to the coastline.

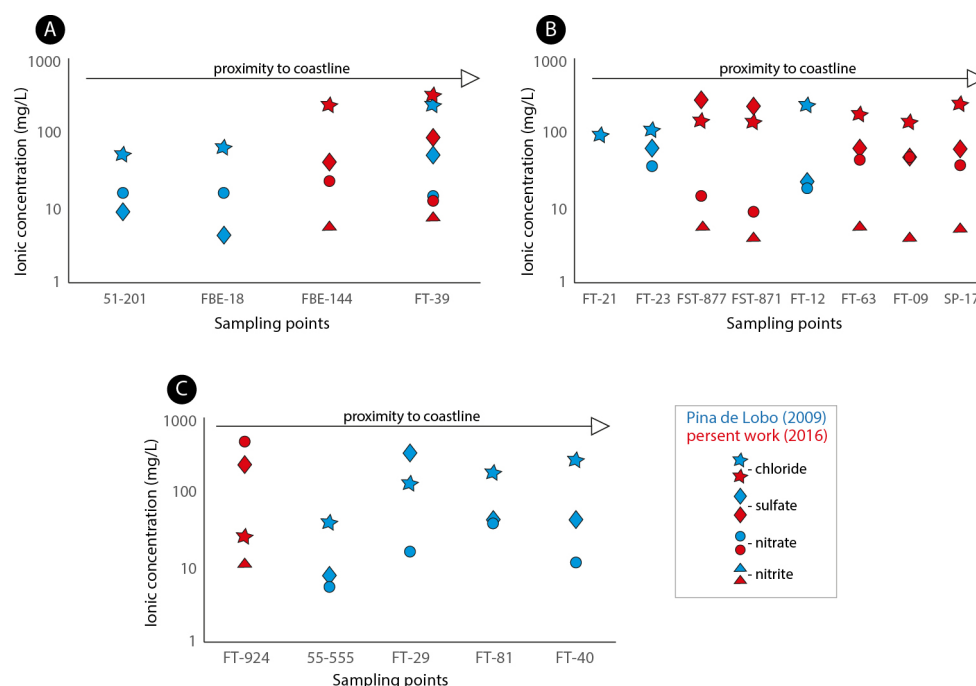


Figure 13. Pattern of temporal and spatial evolution of anion indicators of water quality in the S. Miguel (A), Ribeira Seca (B) and S. Domingos (C) river sub-basins. The graphs show the evolution from upstream to downstream, i.e., from the valleys' highest quotas to the lowest and widest sections of the valleys, which end at the eastern coastline.

Nitrates and nitrites are analyzed here as potential indicators of agricultural and fecal contamination. All samples analyzed in 2003 show nitrite values below the detection limit of the method (therefore, they do not appear in the graphs of Figure 13). On the contrary, those analyzed in 2016 have concentrations above the legal limit (0.3 mg/L). The same situation applies to nitrate, sulfate and chloride, which generally occur with higher concentrations in the 2016 samples. This behavior can be seen in sample FT-39, which is the only well coincident in the two campaigns, with the exception of nitrate that is smoothly greater in the 2003 campaign. This assessment should be carefully analyzed, taking into account the small number of samples and the fact that, although close, they are not coincident water points (except FT-39, in the S. Miguel river sub-basin). Nevertheless, the pattern, visible in all three sub-basins, generally seems to indicate a decrease in water quality between the two periods under consideration.

The S. Miguel sub-basin reveals some oscillation in the spatial evolution of anthropic indicators, specifically nitrate and sulfate (Figure 13A). However, chloride reveals a growing trend along the valley, from upstream to downstream. This could be confirming the marine influence pointed out by other authors (e.g., [40, 61]).

The Ribeira Seca sub-basin (Figure 13B) is intensely cultivated in all its extensions, although with great variation in intensity and in the more or less rudimentary type of practices. This may explain the irregularity detected in the indicators, namely, nitrite and sulfate, avoiding the observation of a clear pattern of spatial variation.

In the S. Domingos sub-basin (Figure 13C), the spatial behavior seems to be controlled by the location of sample FST-924, which, as mentioned above, is located in the vicinity of an industrial plant and in a heavily farmed area. Thus, nitrite, nitrate and sulfate have the highest concentrations upstream. On the other hand, chloride increases steadily with proximity to the coastline, revealing the marine influence.

The water quality in such agriculture areas is a key issue for potential soil degradation, namely, by salinization. According to [62], salinization may not significantly influence the soil texture. However, the occurrence of superficial saline crustification processes affects water and air circulation, with consequences on

productivity, since they create unfavorable conditions for root penetration and water retention capacity. The authors of [63] also pointed out that saline soils have imbalances in nutrient availability, thus interfering with fertility.

The SAR diagram (Figure 14) suggests quality problems, in this case associated with the risk of salinization and sodification caused by the use of this water for irrigation purposes. The projection in this diagram puts all the samples at high risk of salinization, although at low to medium risk of sodium absorption, with the exception of one of the samples from the S. Domingos sub-basin (PT-29), in agreement with the high sodium concentration obtained in this sample (Table 3). The samples with a lower risk of sodification are located in the S. Miguel sub-basin, in concordance with what has already been described in terms of hydrochemistry.

Saline deposition (white efflorescence of sodium chloride) and retraction cracks are recurrently observed in the irrigated fields of these river sub-basins (Figure 15).

With increasing irrigation practices, salinization tends to continue and even intensify, especially with the persistence of dry conditions.

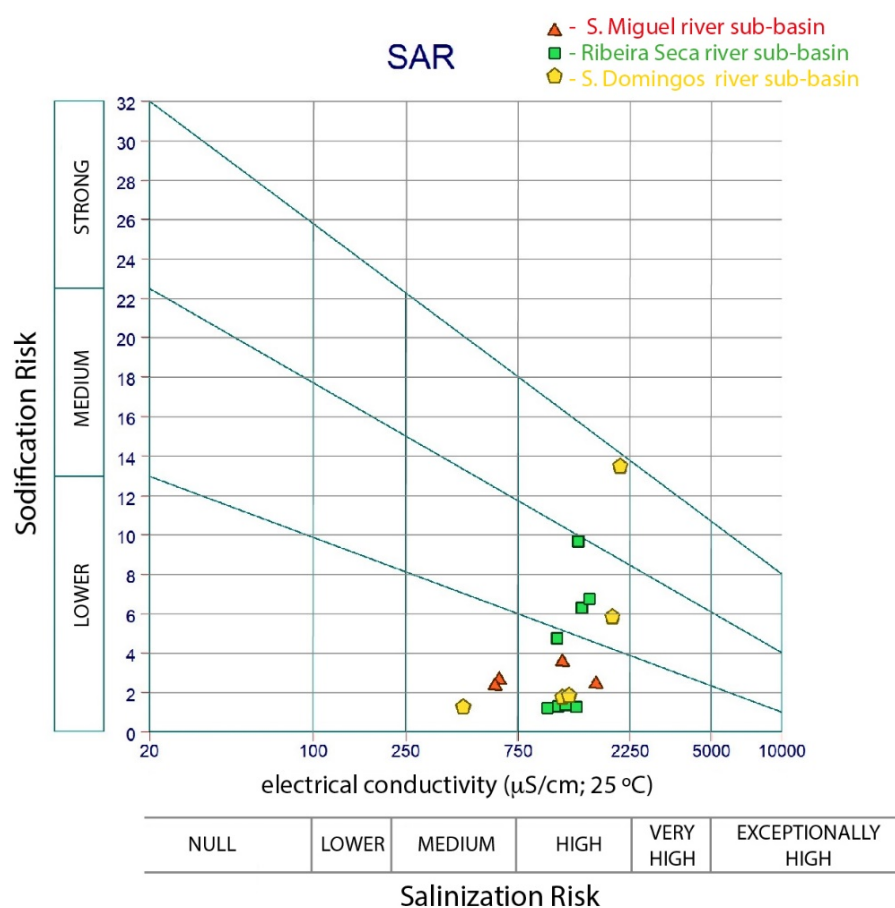


Figure 14. Soil salinization and sodium absorption risk (SAR diagram)—S. Miguel, Ribeira Seca and S. Domingos river sub-basins.



Figure 15. Image of deposition of salts and retraction cracks in the ground (Ribeira Seca river sub-basin).

4. Conclusions

The present study characterized three river sub-basins that are subject to agriculture pressure in Santiago Island, which is facing recurrent droughts and increasing aridity. Hydrochemistry and water quality were assessed through data obtained from wells used for drinking and irrigation purposes in the region with a higher intensity of agriculture practices.

In general, mineralization was lower in the samples from the S. Miguel sub-basin, which was indicated by the electrical conductivity, with lower values than those observed in Ribeira Seca and S. Domingos. This behavior followed the general tendency of the parameters Ca and Na. The same was observed for sulfate, generally with lower concentrations in S. Miguel and higher concentrations in Ribeira Seca.

Nitrates and nitrites, typically associated with diffuse pollution, were present in almost all river sub-basins (except the nitrite samples of the S. Miguel river sub-basin), but with varying patterns. In S. Domingos, one of the samples (FST-924) stood out, indicating the occurrence of organic pollution.

The hydrochemical classification revealed dispersion, not indicating a clear differentiation between the three sub-basins. Na-Cl waters occurred in all cases, corresponding to the water points closest to the coastline. In turn, a bicarbonate-magnesium sample was identified in the S. Domingos sub-basin, at the furthest point from the coastline, suggesting a geological control to the detriment of the marine contribution.

The evolution of water quality was performed by comparing data from the bibliography with results from a recent sampling campaign. This assessment, between

2003 and 2016, aimed to show the evolution over time and from upstream to downstream, i.e., in order to detect differences with the proximity to the coastline. Nitrates and nitrites were analyzed as potential indicators of agricultural and/or fecal contamination. All samples analyzed in 2003 showed nitrite values below the detection limit of the analytical method. On the contrary, most of the samples analyzed in 2016 had concentrations above the legal limit (0.3 mg/L). The same situation applies to nitrate, sulfate and chloride, which generally occurred with higher concentrations in the 2016 samples. This behavior can be seen for the parameters in sample FT-39, except for nitrate, which represents a well coincident in the two campaigns. This pattern, visible in the three river sub-basins, suggests a decrease in water quality between the two periods under consideration.

The three river sub-basins are at high risk of salinization, although at low to medium risk of sodium absorption, with the exception of one of the samples from the S. Domingos sub-basin, in agreement with the high sodium concentration obtained in this sample.

The increase in the irrigation area, due to the persistence of dry weather conditions, may promote an intensification of the salinization risk. Thus, water monitoring in these three sub-basins is an essential aspect to counteract the potential environmental degradation, with the threat of soil quality loss, with strong implications for food productivity.

The present results intend to contribute with knowledge that could be applied in similar insular territories, for helping decision making on water and soil resources management in arid and semi-arid contexts.

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