



Radon (^{222}Rn) occurrence in groundwater bodies on São Miguel Island (Azores archipelago, Portugal)

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Abstract

A set of springs were sampled along São Miguel Island (Azores, Portugal) to proceed to the characterization of the major ion and radon (^{222}Rn) content. According to the selection criteria a total of 42 discharges were sampled, both during winter and summer periods, along major geological units, namely 3 springs at Sete Cidades Volcano, 4 at Nordeste Volcano, 17 at Fogo Volcano, and 18 at Furnas Volcano. Spring water temperature ranges from 12.8 to 78.1 °C in winter (mean = 23.6 °C), and from 12.6 to 76.7 °C in summer (mean = 23.9 °C), and the dataset comprehends 26 (winter) to 21 (summer) cold springs, 3 to 8 orthothermal springs, as well as 13 thermal discharges. Mean electrical conductivity is equal to 552.9 $\mu\text{S}/\text{cm}$ (winter) and 550 $\mu\text{S}/\text{cm}$ (summer), suggesting a short residence time, and waters are acidic to slightly basic in character ($\text{pH}_{\text{winter}}$: 4.16–7.16; $\text{pH}_{\text{summer}}$: 4.05–7.35). Groundwater chemistry is mainly controlled by silicate leaching, enhanced by the water temperature, seawater spraying and by the active volcanic environment. ^{222}Rn content ranges between 0.99 and 551.64 Bq/L (mean = 47.8 Bq/L) in winter and between 1.42 and 559.67 Bq/L (mean = 49.4 Bq/L) in summer. All the springs with anomalously higher values are located in Fogo Volcano, while the lowest radon concentrations are observed at Furnas Volcano. Groundwater temperature exerts a control over the ^{222}Rn concentration; thus, the lower content corresponds to the most mineralized thermal waters. Springs with the higher radon content show the radiogenic contribution from uranium-rich peralkaline syenite intrusive body. Furthermore, data reveal that besides this lithologic control some waters are influenced by ^{222}Rn migration from a deeper source towards shallower aquifers, carried by a volatile flux of CO_2 .

Keywords Radon · Groundwater · Hydrogeochemistry · Volcanic aquifers · Azores

Introduction

Radon is the heaviest among all the naturally occurring noble gases, being a product of the ^{238}U - (^{222}Rn), ^{235}U - (^{219}Rn) and ^{232}Th - (^{220}Rn) decay processes (Baskaran 2016). With a half-life time of 3.823 days, ^{222}Rn nuclide results from the direct decay of ^{226}Ra along the ^{238}U -series (Hambrook 1983).

In the last decades, ^{222}Rn has been recognized as the single major contributor to the ionizing radiation dose received by humans (Baskaran 2016). Several studies have attributed a carcinogenic effect to ^{222}Rn (Darby et al. 2005; Turner et al. 2011) being this effect was also recognized by the World Health Organization (WHO 2010). The exposition to ^{222}Rn is enhanced in active volcanic regions (Baxter et al. 1999; Linhares et al. 2018). The indirect exposition to radon due to the inhalation of ^{222}Rn released from tap water into indoor air (Cinti et al. 2019), as well as the direct ingestion of ^{222}Rn -rich water (UNSCEAR 2008; WHO 2011) also increases health hazard associated to radon.

Among all the nuclides resulting from U or Th decay, ^{222}Rn is the one presenting the highest specific activity in groundwater, remaining as a dissolved phase in groundwater (IAEA 2014). Major sources of ^{222}Rn in groundwater are the ^{226}Ra decay, congruent and incongruent dissolution of U-bearing minerals, as well as recoil and desorption, and in opposition maybe removed as a result of radioactive decay

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(Baskaran 2016). Usually, radon content in groundwater ranges between 10 and 100 Bq/L (Schubert et al. 2006), but may vary up to 5 orders of magnitude (Baskaran 2016).

The behaviour of ^{222}Rn in groundwater, coupled with the absence of a radon anthropogenic source and the easily detection, justifies that ^{222}Rn has been widely used as aqueous tracer in the last two decades (Schubert et al. 2006), mainly among other applications for dating and characterizing groundwater flow (Baskaran 2016). Studies have been published to characterize groundwater discharge to oceans (e.g., Rodellas et al. 2017), surface and groundwater bodies interaction (e.g., Khadka et al. 2017), precursor of seismic activity (e.g., Erees et al. 2007), non-aqueous phase liquid contamination (Schubert 2015) and groundwater dating and characterization of flow dynamics (e.g., Molin-Porras et al. 2017).

The Azores archipelago is made of nine volcanic islands spread along NW–SE trending lineaments distributed in a 600-km-wide area. The archipelago is emplaced near the triple junction between the America, Nubia, and Eurasia plates, resulting in a complex geodynamic setting characterized by several tectonic structures that affects the Azores region (Fernandes et al. 2006; Marques et al. 2013). Since the discovery and settlement of the archipelago in the early fifteenth century, a total of 28 submarine and subaerial volcanic eruptions occurred (Gaspar et al. 2015). In the Azores, groundwater is a key resource for human water supply which relies almost on abstraction in springs and drilled wells (Cruz and Coutinho 1998; DRA 2015), thus groundwater quality is an important subject of study.

The present study was carried out in São Miguel, the major island of the Azores archipelago, located between $37^{\circ} 54' 38'' \text{ N}$ and $37^{\circ} 42' 13'' \text{ N}$ of latitude and $25^{\circ} 08' 03'' \text{ W}$ and $25^{\circ} 51' 17'' \text{ W}$ of longitude. The island has an area of 744.6 km² and is the most populated in the archipelago (137 519 inhabitants; year 2017).

The occurrence of radon, as well as the associated health hazard, was first studied in the Azores archipelago by Baxter et al. (1999). The first attempt to proceed to a systematic characterization of radon occurrence in groundwater was made at Faial Island by Coutinho (2000), following the setup of an observation network planned to evaluate the influence of tectonics and seismic activity over ^{222}Rn release since the onset of a seismic swarm in the late 1992 (Coutinho et al. 1993). More recently, extensive radon surveys in soils were made at geothermally and tectonically active areas of Pico Alto Volcano (Terceira Island; e.g., Aumento 2002, 2010) and Furnas Volcano (São Miguel Island), first regarding soil gaseous emanations (Silva 2006; Silva et al. 2015a; 2015b) and after also encompassing groundwater discharges (Silva 2013; Silva et al. 2017). This latter study showed that regardless the important Rn emissions from soils, values observed in groundwater are under the World Health Organization

(WHO 2011) threshold value, being controlled by water temperature.

Several studies characterized ^{222}Rn occurrence and dynamics in groundwater had been done in other volcanic regions worldwide, such as in the Hawaii Island (Swarzenski et al. 2017), Italy (e.g., Cinti et al. 2013, 2019), Iceland (Óskarsson and Ásgeirsdóttir 2017), Reunion Island (Barillon et al. 1993), Jeju Island (Hwang et al. 2005) or the Canaries archipelago (Alonso et al. 2015).

The aforementioned studies, among others, showed the importance of measuring ^{222}Rn in groundwater discharging in volcanic regions, which is closely associated to the fact that if volatile magmas accumulate beneath a volcano, then an anomalous change in the radon values in aqueous bodies should be expected (Segovia 1991). Taking in account this relevance, the objectives of the present work are (1) to determine radon content over a set of groundwater discharges spread along the main geological units in the São Miguel Island (Azores archipelago), (2) to evaluate any seasonal differences and (3) to characterize the relationship with the overall water chemistry. This work is the first comprehensive survey of radon content in groundwater in the Azores archipelago, as the previous research made on this topic was limited to smaller areas or to specific targets, as mineral water discharges (Silva 2013; Silva et al. 2017).

Study area

Geological setting

The island of São Miguel is a 65-km-long volcanic ridge interspersed by large central volcanoes. Six volcanic systems are here present namely, from the east to the west Nordeste and Furnas volcanoes, Congro fissure system, Fogo Volcano, Picos fissure system and Sete Cidades Volcano. We conducted field work at Nordeste, Furnas, Fogo and Sete Cidades, therefore only these volcanic systems will be further considered.

Nordeste Volcano is an eroded edifice constituting the easternmost part of the island. Its first products are dated back to ~ 850 ka (Sibrant et al. 2015), thus younger than the previous dating range proposed a few decades earlier (950 ka–4 Ma; Abdel-Monen et al. 1975). The early-stage magmatism, with a basaltic composition, was possibly related to the activity of a fissure zone. During later stages, volcanic activity centralized and evolved magmas have been emitted (Moore 1990).

Furnas Volcano is located in the central-east part of the island, and according to Moore (1991) is the youngest of the three polygenetic volcanoes of São Miguel, with a sub-aerial activity starting 93 ± 9 ka ago (McKee and Moore 1992). This volcano is indeed constituted by a large polygenetic

caldera formed during several episodes of collapse (Guest et al. 1999). Two eruptions occurred here since the settlement of the island: the first in 1439–1443 AD, from historical accounts and geological findings (Queiroz et al. 1995), and the last in 1630 AD, in the southern rim of the caldera (Cole et al. 1995).

Fogo Volcano is a central volcano topped by a lake-hosted caldera. The oldest activity of Fogo yields an imprecise age of 280 ± 140 ka on a submarine sample in the northern flank (Muecke et al. 1974) and a consistent age of 181 ± 15 ka for a subaerial lava flow (Gandino et al. 1985). Geochronological data indicated that two summit collapses occurred probably between 26.5 ± 0.5 and 46 ± 6 ka (McKee and Moore 1992). The activity of the last 5000 years consisted in explosive trachyte pumice emission from the summit (from plinian to sub-plinian eruptions) and basaltic to mugearitic lava emissions from the lateral vents, being the last one dated in 1563–1654 AD.

Sete Cidades is the westernmost volcano whose growth started 210 ± 8 ka ago (McKee and Moore 1992). The summit presents a 5×4.7 km composite caldera, with an average depth of 300 m that resulted from several stages of collapse at 36, 29 and 16 ka, caused by concomitant tectonic activity and magma emissions (Queiroz et al. 2008). Over the past 5000 years at least 17 explosive eruptions took place at Sete Cidades, and according to precise ^{14}C dating the last one occurred in 1440 BP (Conte et al. 2019). At the same time, basalts were emitted from lateral vents on the lower and submarine NW slopes of the volcano (Beier et al. 2006).

Syenites are the product of late crystallization of trachyte magma in shallow reservoirs. They are widespread among the products of all central volcanic systems except for Nordeste, therefore syenites are obviously absent in lavas of the fissure zones, confirming the absence of shallow magma storage systems (Zanon 2015). These rocks are particularly frequent in the lavas and pyroclastic products of Fogo Volcano (Osann 1888; Cann 1967; Widom et al. 1993) where they show a high degree of interaction with the host lava (Storey et al. 1989; Widom et al. 1993; Elliott et al. 2007). As a matter of fact, some hybrid rocks from Fogo with clear signs of syenite and/or trachyte pumices partial assimilation are plotted on mixing lines between basalt and trachyte in major element diagrams (Storey et al. 1989). Only the syenites at Fogo are peralkaline and contain 2.9–18.3 ppm of uranium (Ridolfi et al., 2003). This element is dominantly contained in pyrochlore, where it can reach 3–5 wt% as UO_2 , in thorite (0.2–0.3 wt% UO_2) and in the rarer chevkinite and dalyte (tens to hundreds of ppm).

Hydrogeological setting

Mean annual precipitation in São Miguel is equal to 1722 mm (DROTRH/INAG 2001), being generally higher

in the eastern area and in the north flank of the island (Bettencourt 1979; DROTRH-INAG 2001). The mean annual runoff in São Miguel is equal to 686 mm, mainly of torrential character, corresponding to a total discharge of $511 \text{ Mm}^3/\text{yr}$ (DROTRH/INAG 2001; DRA 2015).

According to the River Basin District Plan of the Azores six groundwater bodies are delimited at São Miguel Island, corresponding to the major geological systems. Groundwater extraction on São Miguel is equal to $25.3 \text{ Mm}^3/\text{yr}$, being $23.7 \text{ Mm}^3/\text{yr}$ for human public supply, exceeding by far the annual volume of surface water abstracted for various uses ($0.52 \text{ Mm}^3/\text{yr}$) (DRA, 2015; Cruz and Soares 2018).

Groundwater in the Azores occurs in two major aquifer systems, namely the basal aquifer system and perched-water bodies (Cruz 2003, 2004). The former is coastal aquifer, corresponding to fresh-water lenses floating on underlying saltwater, with a very low hydraulic gradient. The latter is confined or leaky aquifers at altitude, drained out by numerous springs in the volcano slopes, and the last surveys have counted a total of 1106 springs spread in almost all the groundwater bodies in São Miguel Island (1.48 springs/ km^2 ; DRA 2015). Spring discharge reflect a seasonal control, being higher in winter period comparing to the summer season (Coutinho et al. 2015), as well as a lithological control, being higher in lava flow aquifers comparing to springs discharging from pyroclastic formations (Paradela 1980).

Specific capacity at São Miguel ranges between 0.49 and 100 L/s/m , with a median value of 1.1 L/s/m (Cruz 2004; DRA 2015). Transmissivity range is 5.98×10^{-4} – $1.22 \times 10^{-1} \text{ m}^2/\text{s}$, with a median value of $1.35 \times 10^{-3} \text{ m}^2/\text{s}$, and the median value is one order of magnitude lower than the median value for the archipelago (Cruz 2004; Coutinho et al. 2015).

Numerous mineral water discharges are found at São Miguel Island, corresponding mainly to springs discharging from perched-water bodies (55 springs), being also observed 10 boiling pools, and 10 drilled and hand-dug wells (Cruz et al. 2010a; Freire et al. 2015). These discharges are located in the area dominated by the active central volcanoes of Sete Cidades (5 discharges), Fogo (24) and Furnas (45). Despite the dominance of the Na-HCO_3 water type, mineral water discharges present a wide geochemical diversity, from cold CO_2 -rich springs to thermal waters of diverse temperature and water type (Na-Cl ; Na-SO_4 ; Na-HCO_3) (Cruz et al. 2010a, 2013; Freire et al. 2015). Other hydrothermal manifestations are observed along Furnas and Fogo volcanoes, such as low temperature fumaroles and steaming ground (Viveiros et al. 2015).

Groundwater resources in São Miguel are estimated at $370 \text{ Mm}^3/\text{yr}$, with recharge rates between 16 and 45%, the latter at the Ponta Delgada–Fenais da Luz aquifer system (Cruz 2004).

Methodology

A set of 42 spring discharges were selected along São Miguel to proceed to the collection of groundwater samples for major-ions and radon (^{222}Rn) analysis (Fig. 1). The selection of the springs to be sampled was based on several criteria, as the total discharge, the abstraction for public supply and the diversity on geological and hydro-geological environment. As so, springs that discharge from trachytic and basaltic aquifers, as well as mineral water springs (thermal and cold CO_2 -rich springs), were considered taking in account previous data sets from Coutinho (1990), DROTRH/INAG (2001), Cruz (2004), Cruz et al. (2010a), DRA (2015) and Freire et al. (2015). Thus, the number of springs selected was variable, in the range of 3 discharges at the Sete Cidades Volcano, 4 at the Nordeste Volcano, 17 at Fogo Volcano, and 18 at Furnas Volcano.

Sampling collection was made in the winter (December–February 2017) and summer (July–August 2017) periods to access any seasonal effects over radon content. Immediately after sampling, measurements of temperature, pH and electrical conductivity were made, using

specific portable equipment (WTW pH/Cond 340i), as well as alkalinity and dissolved CO_2 titrations using current methods (APHA/AWWA/WPCF 1985). Major-cation content was determined by atomic absorption spectrometry, over acidified samples using concentrated nitric acid, and major-anion composition through ionic chromatography. In both cases, samples were also filtered in the field ($0.45\ \mu\text{m}$ cellulose membrane filter). Silica was analysed by spectrophotometry, using the silicomolybdic method.

To measure the radon concentration in groundwater, two samples per survey were taken at each discharge. Samples were collected at each spring through a tube with one extremity placed inside the outlet and the other in the sampling flask, which is in turn located inside a bucket full of water of the discharge, thus avoiding contact with atmospheric air and ^{222}Rn loss. This procedure at each groundwater discharge lasted for about 10 min to assure the representativeness of the sample.

Subsequently, a radon detector equipment (RAD7 Radon Detector from DURRIDGE Company, Inc.) coupled with the water analysis set RAD H_2O was used in the laboratory, being the analysis made in the same day of the field work. The RAD H_2O includes silicone tubing, an aeration system, a filter, and

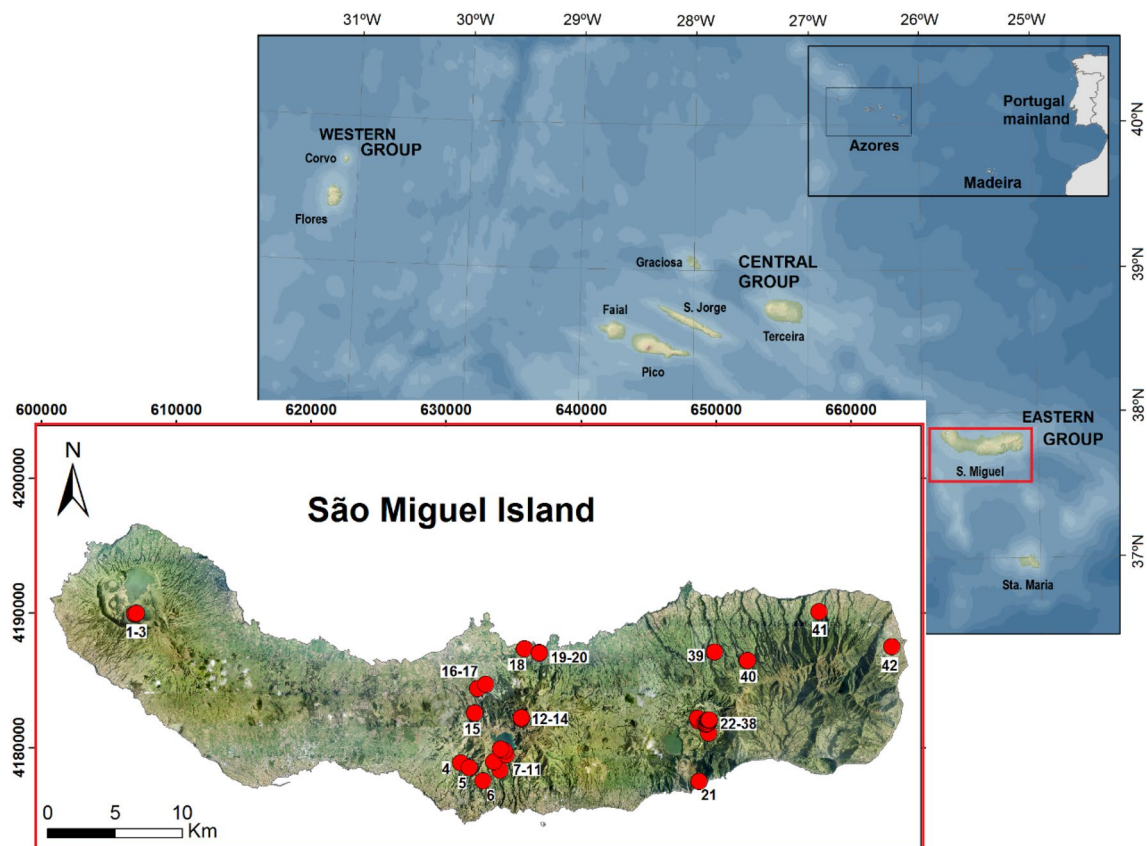


Fig. 1 Location of the Azores archipelago in the North Atlantic Ocean; in the foreground the location of the 42 sampled springs along the island of São Miguel is shown

a desiccant unit, the latter two to prevent, respectively, impurities and humidity inside the detector. Before the beginning of each measurement the detector is purged of radon through the injection of air, in open circuit, for 10 min or until the humidity inside drops below 6%. RAD 7 allows fast, inexpensive, and versatile radon measurements in water (Burnett et al. 2001; Lee and Kim 2006).

For this purpose, 250-mL samples were used for radon concentrations below 100 Bq/L and 40 mL aliquots for higher radon concentrations, according, respectively, the measurement protocols WAT250 and WAT40 (Durrige Company 2011). The procedure for determination of the radon concentration is done in closed loop for 30 min, being the sample aerated through the introduction of air into the sample during the first 5 minutes to remove the dissolved radon. During the aeration process more than 95% of the available radon is removed from the water. After this step, and following a 5-min-long waiting interval, measurements are made along four 5-minute-long cycles. The final radon concentration for each sample corresponds to the mean reading from the four cycles counted (Durrige Company 2011) and the final value for each spring is the mean value from the two samples collected in the discharge. The correction of the humidity within the detector as well as the overall data validation was performed using Capture software. The radon concentrations were also corrected for radon decay through the application of a decay correction factor (DCF). Therefore, results are multiplied by the DCF, which is obtained taking into account the average lifetime of radon atoms and the time between sample collection and the analysis. The final radon concentration of each discharge was calculated averaging the concentration obtained after the corrections applied at the two samples of each survey.

The spring discharge was also measured in the field during sampling collection whenever the physical conditions allow it (90.5% of the 42 springs). The mean value during the winter sampling campaign is equal to 166.5 m³/day (range: 1.47–972 m³/day), being as expected slighter higher comparing to values measured during summer (mean = 121.5 m³/day; range: 1.23–528.1 m³/day). The median values are much lower than the mean, showing that some springs present very high discharges comparing to the remaining ones, and are equal to 56.6 and 40.3 m³/day, respectively in winter and summer periods. In two springs where discharge measurements were not made possible the mean daily discharge estimated by the municipality of Ponta Delgada is about 4363 m³/day.

Data presentation and discussion

Hydrogeochemical outline

A summary of the main physico-chemical parameters (temperature; pH; electrical conductivity; dissolved CO₂)

as well as the major-ion and SiO₂ content is given in Table 1.

The temperature of the studied discharges is highly variable, being in the range of 12.8–78.1 °C in winter (mean = 23.6 °C), and between 12.6 and 76.7 °C in summer (mean = 23.9 °C). Considering a mean annual air temperature of 17.5 °C in São Miguel (AEME-IM 2011), and applying the criteria proposed by Schoeller (1962), 26 springs may be classified as cold, 3 as ortothermal and 13 as thermal waters in winter. The summer dataset comprehends 21 cold springs, 8 ortothermal and 13 thermal discharges. Thermal discharges are mainly located at Furnas (temperature winter range: 14.6–78.1 °C; summer range: 14.6–76.7 °C) and Fogo (winter range: 12.8–29.7 °C; summer range: 13.0–31.1 °C) volcanoes. The highest temperature is observed at Caldeirão spring (No. 35), located at Furnas.

Electrical conductivity (EC) is on the range of 99 to 1662 μS/cm in winter (mean = 552.9 μS/cm), and between 101 and 1657 μS/cm in summer (mean = 550 μS/cm). The lower values are observed in the cold springs of Nordeste (winter range: 99–180 μS/cm; summer: 101–179 μS/cm), Sete Cidades (winter: 176–194 μS/cm; summer: 174–199 μS/cm), as well as in the cold discharges of Fogo Volcano (winter: 94–173 μS/cm; summer: 95–198 μS/cm). The highest EC values are observed at Furnas Volcano (winter: 194–1379 μS/cm; summer: 199–1657 μS/cm). The lowest EC values suggest a short residence time, as well as a high water–rock ratio (Langmuir 1997) and is typical of cold springs discharging from perched-water bodies in the Azores (Cruz and Amaral 2004; Cruz et al. 2010b; Cruz and Andrade 2015). Instead, the highest values are consistent with the occurrence of thermal waters, in which temperature enhances water–rock interaction (Cruz et al. 2010a; Freire et al. 2014, 2015).

Sampled waters are acidic to slightly basic in character, being pH values in the range of 4.16 to 7.16 in winter (mean = 5.57), and between 4.05 and 7.35 in summer (mean = 5.72). During the winter sampling campaign, a set of samples in Fogo (No. 13–17; 19) and Furnas (No. 33–36) volcanoes depict pH values lower than the mean value (5.57), corresponding to cold springs presenting the highest dissolved CO₂ content (494–993.5 mg/L), well above the mean value (365.1 mg CO₂/L). The cold CO₂-rich springs correspond to waters with very low EC, thus suggesting a short residence time in areas where the CO₂ release from volcanic origin is anomalously higher (Cruz et al. 2006, 2010a; Viveiros et al. 2010). Dissolved CO₂ range is similar for winter (9.5–993.5 mg/L; mean = 365.1 mg/L) and summer (4.1–960.3 mg/L; mean = 378 mg/L).

Most of the waters are mainly from the Na–HCO₃, Na–HCO₃–Cl and Na–Cl–HCO₃ types, although some samples from Fogo Volcano are from the Na–Cl water type, and generally no major seasonal differences are

Table 1 Spring water chemical data statistics: main variables (temperature, pH, electrical conductivity (EC), dissolved CO₂, major-ion composition and SiO₂ and ²²²Rn content

Geological unit	Season	Value	T °C	pH	EC µS/cm	CO ₂ mg/L	HCO ₃ mg/L	Cl mg/L	SO ₄ mg/L	F mg/L	NO ₃ mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	SiO ₂ mg/L	Rn Bq/L	
Fogo	Winter	Max	29.70	7.61	550.00	918.00	228.75	89.50	49.83	3.40	7.07	93.38	4.90	45.00	15.32	108.85	551.64	
		Min	12.80	4.16	94.00	2.30	4.88	16.53	2.07	0.27	0.18	0.18	13.33	0.13	2.58	0.24	34.50	2.96
		Mean	17.99	5.84	200.82	258.62	52.85	29.82	16.87	13.48	0.75	2.85	21.21	1.22	11.09	4.03	59.63	94.11
		St. Dev	5.79	1.17	116.81	314.47	60.61	34.77	25.70	4.61	0.65	1.90	21.03	1.33	6.42	2.63	21.97	151.41
		Median	15.00	5.87	161.00	10.90	34.77	298.29	96.39	50.91	7.50	7.80	42.04	3.53	35.23	9.19	144.22	559.67
		Max	31.10	7.70	542.00	960.30	2.70	31.11	16.45	1.19	0.24	0.32	9.62	0.10	2.48	0.26	65.89	3.20
	Summer	Min	13.00	4.05	95.00	2.70	31.11	16.45	1.19	0.24	0.32	9.62	0.10	2.48	0.26	65.89	3.20	
		Mean	18.21	5.89	202.59	286.65	76.66	31.04	10.21	1.32	1.32	3.28	19.10	1.27	10.43	3.03	90.41	92.60
		St. Dev	6.16	1.20	113.78	339.83	78.51	18.37	13.87	1.79	1.79	2.97	7.92	0.90	7.88	2.57	23.24	156.11
		Median	14.90	6.28	162.00	20.20	38.43	25.50	4.63	0.63	0.63	2.95	16.45	1.20	7.86	2.25	82.30	15.07
		Max	78.10	7.16	1662.00	993.50	957.09	158.18	89.22	5.03	5.03	8.24	373.55	14.73	53.92	62.78	222.19	38.27
		Min	14.60	4.69	194.00	11.20	70.76	23.08	6.45	0.69	0.69	1.00	25.21	1.60	12.47	4.73	56.21	0.99
Furnas	Winter	Mean	32.19	5.73	764.33	363.76	385.79	73.12	26.52	2.86	4.23	149.89	6.35	30.05	21.92	123.46	7.11	
		St. Dev	19.59	0.73	522.92	292.39	324.88	52.98	22.24	1.36	2.73	124.37	4.70	11.15	17.97	50.33	8.81	
		Median	20.90	5.97	492.00	264.65	241.87	47.63	15.92	2.67	2.67	4.78	98.71	3.51	27.67	11.41	93.28	3.75
		Max	76.70	7.01	1657.00	827.40	894.87	164.42	95.52	5.95	5.95	8.09	260.13	13.62	51.20	55.90	278.33	31.38
		Min	14.60	4.46	199.00	8.10	19.30	24.12	5.79	0.74	0.74	2.96	19.94	1.93	10.39	6.12	73.19	1.42
		Mean	32.89	5.85	760.72	361.39	366.54	72.26	25.88	2.89	2.89	5.36	107.62	6.03	29.20	25.22	146.70	9.76
	Summer	St. Dev	19.26	0.81	519.30	301.51	310.36	53.52	22.89	1.50	1.50	1.95	86.60	4.11	11.69	16.44	55.12	10.09
		Median	22.35	6.22	485.50	317.05	243.78	45.52	15.90	2.35	2.35	5.75	67.01	2.99	27.50	17.13	123.95	5.32
		Max	15.70	6.86	180.00	19.10	39.65	33.45	9.48	0.54	0.54	19.29	18.62	4.88	8.37	5.59	38.97	43.03
		Min	12.80	6.31	99.00	9.50	23.18	25.49	4.98	0.12	0.12	2.30	12.61	1.57	2.78	3.73	26.27	13.75
		Mean	14.58	6.55	148.75	12.83	32.48	28.83	6.90	0.33	0.33	10.06	15.93	2.92	4.63	4.59	32.13	25.52
		St. Dev	1.31	0.25	34.84	4.36	7.00	3.74	1.95	0.30	0.30	7.11	2.73	1.58	2.55	0.89	5.22	13.91
Nordeste	Winter	Median	14.90	6.52	158.00	11.35	33.55	28.20	6.57	0.33	9.32	16.26	2.61	3.70	4.53	31.65	22.65	
		Max	15.70	7.35	179.00	17.90	39.65	168.53	19.22	0.25	28.65	16.02	6.50	5.65	4.52	66.02	36.73	
		Min	12.60	6.68	101.00	4.10	21.45	31.34	4.77	0.16	0.16	2.24	12.23	1.40	3.31	2.89	46.86	9.51
		Mean	14.50	7.00	148.25	13.48	30.98	70.22	8.96	0.20	0.20	12.99	14.23	3.33	4.52	3.97	55.14	22.37
		St. Dev	1.40	0.31	34.33	6.43	7.93	65.69	6.87	0.06	0.06	11.16	1.98	2.21	1.05	0.73	8.47	11.99
		Median	14.85	6.98	156.50	15.95	31.42	40.50	5.93	0.20	0.20	10.54	14.34	2.72	4.57	4.23	53.84	21.62

Table 1 (continued)

Geological unit	Season	Value	T °C	pH	EC μS/cm	CO ₂ mg/L	HCO ₃ mg/L	Cl mg/L	SO ₄ mg/L	F mg/L	NO ₃ mg/L	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	SiO ₂ mg/L	Rn Bq/L
Sete Cidades	Winter	Max	15.30	6.99	194.00	6.60	56.12	36.87	6.24	2.34	4.45	33.11	0.98	2.94	4.68	39.46	10.30
		Min	15.00	6.45	176.00	2.80	47.58	29.29	5.20	1.92	1.74	31.91	0.47	2.74	3.55	34.72	2.25
		Mean	15.13	6.74	185.00	4.97	52.87	32.11	5.60	2.20	2.81	32.34	0.66	2.83	3.99	37.60	7.55
		St. Dev	0.15	0.27	9.00	1.96	4.62	4.15	0.56	0.24	1.45	0.67	0.28	0.10	0.61	2.53	4.59
	Summer	Max	15.40	7.82	185.00	5.40	59.78	38.65	5.19	2.60	3.78	24.49	0.83	4.22	4.58	65.42	10.11
		Min	15.30	6.59	174.00	2.10	56.73	31.25	4.26	1.70	1.55	23.15	0.41	2.88	3.76	60.51	1.51
		Mean	15.33	7.33	185.67	3.50	58.15	33.97	4.86	2.21	2.73	23.75	0.58	3.40	4.11	62.38	5.32
		St. Dev	0.06	0.65	12.58	1.71	1.54	4.07	0.51	0.47	1.12	0.69	0.22	0.72	0.42	2.65	4.59
		Median	15.30	7.58	184.00	3.00	57.95	32.00	5.12	2.34	2.85	23.60	0.49	3.08	3.98	61.22	4.04

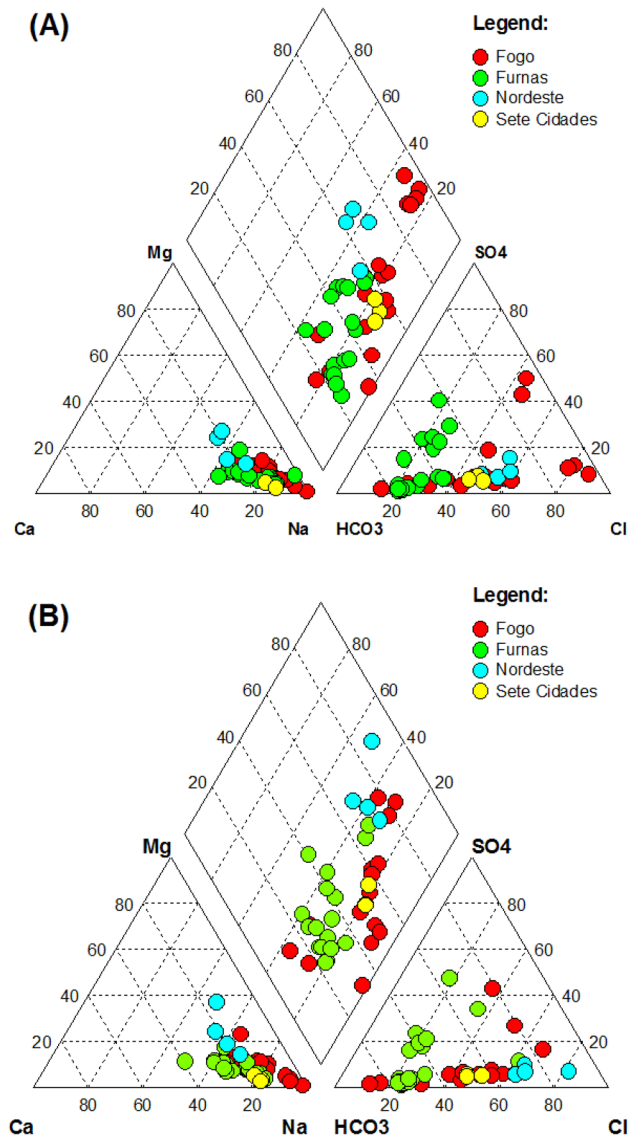


Fig. 2 Relative major-ion composition represented by means of a Piper-type diagram (A—winter survey; B—summer survey), showing that most of the samples are from the Na-HCO₃, Na-HCO₃-Cl and Na-Cl-HCO₃ types, although some samples from Fogo Volcano are from the Na-Cl water type, and a few discharges depict a SO₄-enrichment. Spring waters are represented according to their geological setting

observed between the winter (Fig. 2A) and summer surveys (Fig. 2B). A small number of springs depict a slight SO₄ enrichment, both in Furnas and Fogo volcanoes. Nevertheless, the dominant Na-HCO₃ water type corresponds to the most common composition found in perched-water bodies in the Azores archipelago (Cruz and Amaral 2004; Cruz and Andrade 2015), as well as to the dominant type regarding mineral waters composition in the archipelago (Cruz et al. 2010a; Freire et al. 2015).

Some major-ion contents depict a very high correlation coefficient towards EC, such as Na ($r=0.981$; Fig. 3A), HCO_3 ($r=0.993$; Fig. 3E), Cl ($r=0.946$; Fig. 3G) and Mg ($r=0.981$; Fig. 3D). High correlation coefficients are also obtained for SiO_2 ($r=0.886$; Fig. 3I), F ($r=0.820$; Fig. 3F), K ($r=0.805$; Fig. 3B) and Ca ($r=0.717$; Fig. 3C). These close relationships are representative of the main processes that control groundwater chemistry in the perched-water bodies at the Azores, such as silicate leaching and a marine source. Silicate leaching explains the alkali and alkali-earth metals content, as well as the release of HCO_3 , thus contributing to fluid acidity neutralisation, while marine source is the result of seawater spraying (Cruz and Amaral 2004; Cruz and Andrade 2015). Nevertheless, other factors may exert control over groundwater chemistry, such as the saturation state of primary minerals, the precipitation of secondary minerals and the acidic character of the environment (Aiuppa et al. 2000). Studies made in the Azores have also shown that in some springs discharging from perched-water bodies silica and fluoride solubility may be influenced by the saturation state regarding a few solid phases (Cordeiro et al. 2012; Freire et al. 2014).

The relationship between SO_4 and EC depicts a very low correlation coefficient ($r=0.092$; Fig. 3H), as a result of the abnormal sulphate enrichment observed in a few samples from Furnas and Fogo volcanoes (ref. 34, 32, 17, 33, 38, 15). This sulphate enrichment suggests mixture with waters that

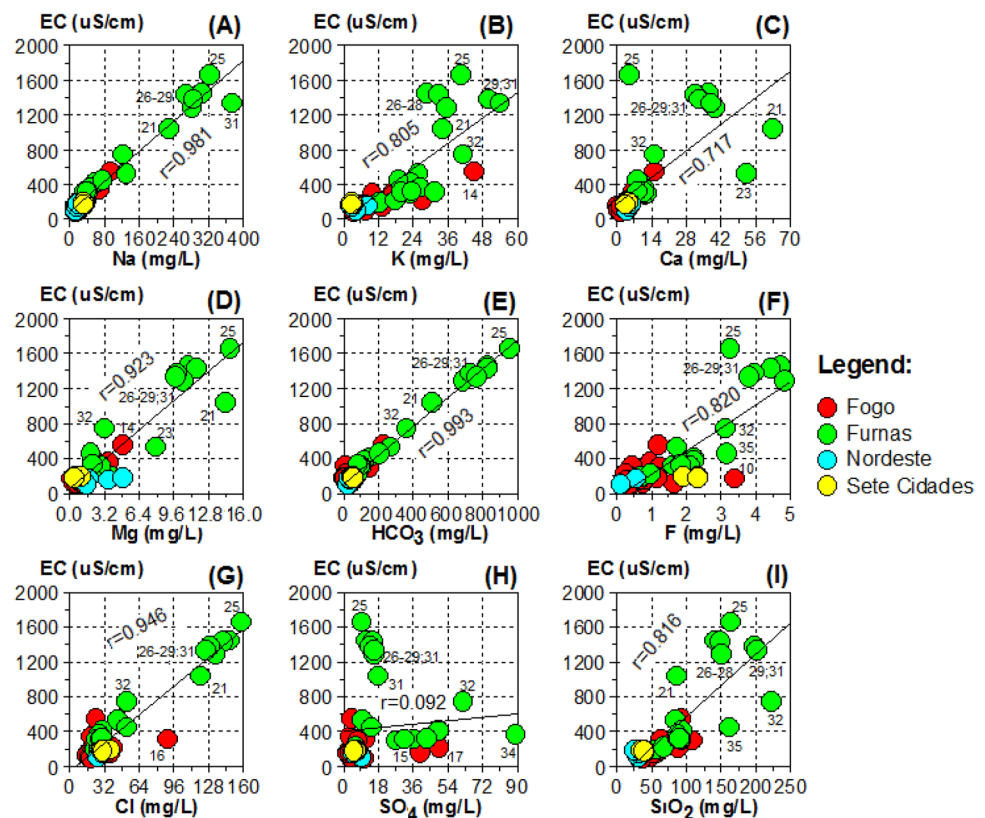
have been influenced by a steam heating process (Cruz and França 2006; Cruz et al. 2010a). This process, also described in other volcanic areas (Nordstrom et al. 2009; Varekamp et al. 2009), results in the oxidation of S-reduced gaseous emanations derived from a deeper-seated source, and also influences river water composition in the Azores (Freire et al. 2013).

Radon occurrence in groundwater

^{222}Rn content in groundwater ranges in winter between 0.99 and 551.64 Bq/L (mean = 47.8 Bq/L), while in summer values are in the range of 1.42 to 559.67 Bq/L (mean = 49.4 Bq/L) (Table 1). The median values for winter and summer sampling campaigns are, respectively, equal to 9.6 and 9.5 Bq/L, suggesting that some anomalously high ^{222}Rn measurements were observed. The geographic distribution of the radon content is shown in Fig. 4 (a detailed view is presented as an Online Resources file respectively for winter and summer surveys).

The highest ^{222}Rn content was measured at springs 19 (winter: 551.64 Bq/L; summer: 559.67 Bq/L) and 20 (winter: 388.37 Bq/L; summer: 401.63 Bq/L), thus presenting values well above most of the samples. Springs 5 (winter: 128.8 Bq/L; summer: 154.31 Bq/L) and 8 (winter: 155.9 Bq/L; summer: 130.31 Bq/L) also present high ^{222}Rn concentrations comparing to values in the dataset, which

Fig. 3 Relationship between major-ion and SiO_2 content with electrical conductivity (EC) for the winter survey data (correlation coefficients are shown for each plot). As a result of the main processes that control groundwater chemistry species as Na, HCO_3 , Cl, Mg, SiO_2 , F, K and Ca depict high to very high correlation coefficients towards EC



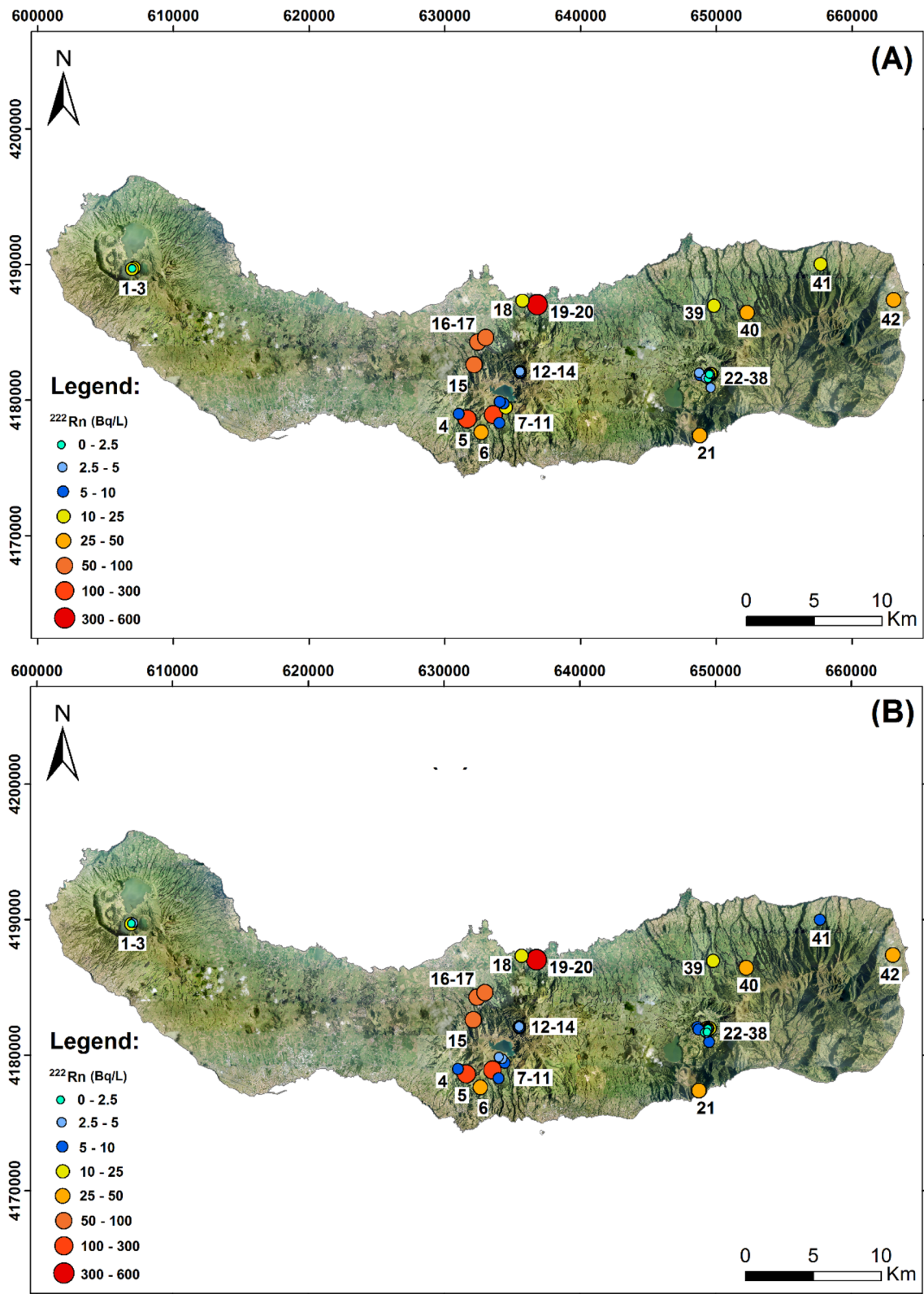


Fig. 4 Geographical distribution of the ^{222}Rn content in the studied springs (**A**—winter survey; **B**—summer survey), showing that all anomalously higher values are located in Fogo volcano, while low radon concentrations are observed at Furnas Volcano

generally have values as high as 90 Bq/L. All the springs with anomalous values are located in Fogo Volcano, which present higher values compared to other geological units both in winter (Fig. 4A) and summer periods (Fig. 4B). Low radon concentrations are observed at Furnas Volcano, where samples 22 to 38, all located inside the caldera complex, present lower measurements comparing to spring 21, located near the coast, as well as at Sete Cidades Volcano (samples 1 to 3). Intermediate values are observed at Nordeste (samples 39, 40).

The winter ^{222}Rn measurements in springs from the Fogo Volcano range between 2.96 and 551.64 Bq/L (mean = 94.11 Bq/L) and in summer between 3.2 and 559.67 Bq/L (mean = 92.6 Bq/L). Instead, the maximum values observed in the other geological units are as high as 43.03 Bq/L in winter and 36.73 Bq/L in summer, both values observed in Nordeste (winter mean = 25.52 Bq/L; summer mean = 22.37 Bq/L). In Furnas Volcano, values are as high as 38.27 Bq/L in winter (mean = 7.11 Bq/L) and 31.38 Bq/L in summer (mean = 9.76 Bq/L). The lowest maximum measurements were made over samples from Sete Cidades Volcano, both in the winter period (10.3 Bq/L; mean = 7.55 Bq/L) and summer (10.42 Bq/L; mean = 5.32 Bq/L).

Groundwater temperature exerts a control over the overall water composition, as shown by the relationship with

EC (Fig. 5A). Water temperature enhances water–rock interaction, thus as expected SiO_2 content in waters depicts a close linear relationship with temperature (Fig. 5B). The temperature vs. SiO_2 content relationship has been identified in previous studies made in the Azores archipelago (Cruz et al. 2010a; Freire et al. 2014, 2015; Cabral et al. 2015). The ^{222}Rn concentration in the most mineralized waters is very low, and samples with EC higher than 1200 $\mu\text{S}/\text{cm}$ have contents in the range from 1.36 to 4.41 Bq/L in winter and from 1.42 to 4.78 Bq/L during summer (Fig. 5C). This trend is mainly explained by the water temperature, which controls ^{222}Rn solubility (Roba et al. 2010; Cinti et al. 2013), thus samples with temperatures above 35 °C present very low concentrations, in the range of 1.36 to 6.04 Bq/L in winter, and from 1.42 to 24.69 Bq/L in summer (Fig. 5D). The latter value is observed in spring 32, and this abnormal value, compared to the range presented by the latter group of waters excluding this spring (1.42–4.78 Bq/L), may suggest the effect of mixing between shallow and deeper groundwater, a process that affects radon content in groundwater from volcanic aquifers (Cinti et al. 2013) and corresponds to a driver of the mineral waters chemistry in São Miguel Island, and namely in Furnas and Fogo volcanoes (Cruz et al. 2006, 2010a). Therefore, it is suggested that in

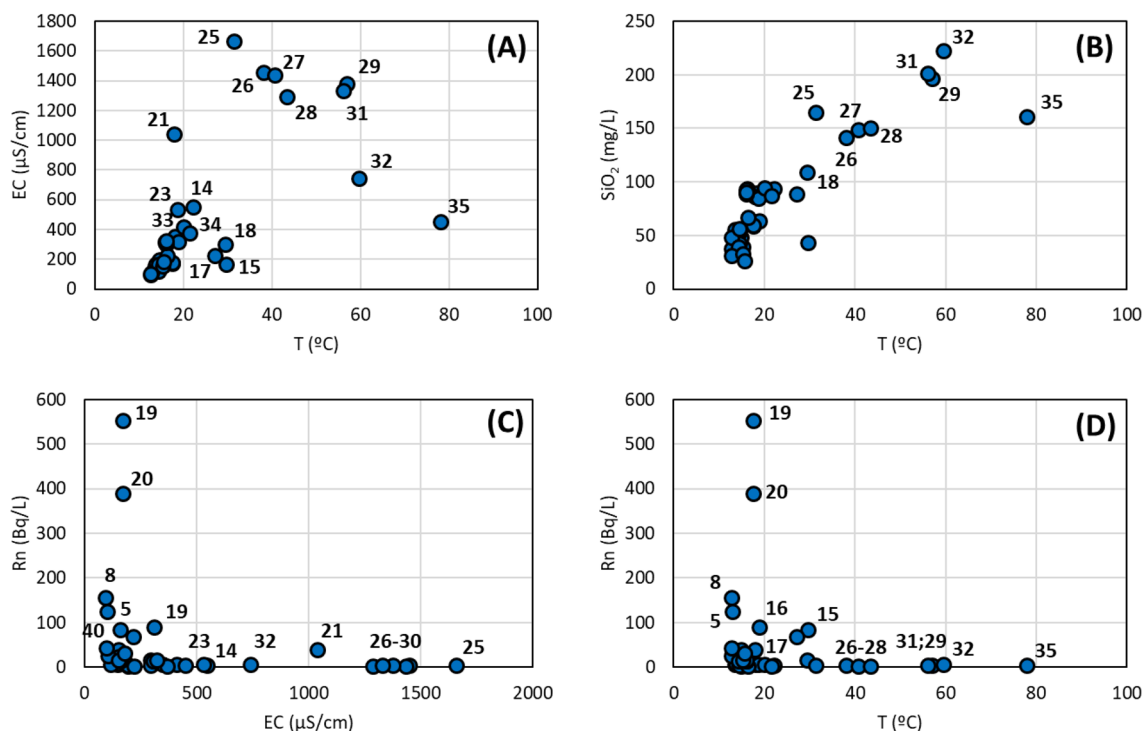


Fig. 5 Bivariate plots between **A** water temperature and EC, **B** temperature and SiO_2 content, **C** EC and ^{222}Rn content, and **D** water temperature and ^{222}Rn content for the winter data. All plots depict the control of water temperature over the overall dissolved species

content and water–rock interaction, respectively represented by EC and SiO_2 content, as well as over ^{222}Rn , which solubility decreases in thermal waters

summer the mixing proportion of the most enriched ^{222}Rn shallower groundwater increases in relation to the deepest hydrothermal end-member contribution, which explain the higher value observed in this period in springs 32 and in 33.

If the lithology control over ^{222}Rn concentration in groundwater is masked by the spring water temperature, it may explain the abnormal values observed in springs 5 (winter: 123.81 Bq/L; summer: 154.31 Bq/L) and 8 (winter: 155.99 Bq/L; summer: 130.31 Bq/L), both located in the southern flank of Fogo Volcano. Despite the low EC measured at these springs, suggesting a short residence time, it appears that the elevated ^{222}Rn concentration has been supplied by a radiogenic source such as a peralkaline syenite body. The presence of such an intrusive body below Fogo volcano at a relative shallow depth is a valuable source for ^{222}Rn due to its elevated uranium content. In opposition, the scattered syenite xenoliths found at Sete Cidades and Furnas volcanoes do not contain uranium-bearing minerals.

Peralkaline syenites are found in many lavas and pyroclasts at Fogo Volcano and due to their petrographic characteristics, they may come from a single and large intrusive body rather than from a network of sills and dikes. The tectonics acting in this area since the cooling of this body and the onset of Fogo magmatism deeply dissected this intrusion, generating important vertical displacements which justify the presence of syenites close to the surface on the upper southern flank of the volcano. On the northern flank the syenite body is deeper, therefore the rather small half-life time of radon prevents that springs in the area present a high ^{222}Rn .

Considering springs 5 and 8 as representative of a ^{222}Rn enrichment associated to a lithologic source, it is possible to show that a sharp difference is observed regarding other cold springs with high ^{222}Rn concentrations such as 19 and 20, as well as discharges 15 to 17, all located in Fogo Volcano. In the dissolved CO_2 vs. ^{222}Rn plot, the latter springs present high dissolved CO_2 comparing to discharges 5 and 8, as well as comparing to perched-water bodies in the Azores without a volcanic imprint (Cruz and Amaral 2004), suggesting that gaseous phases releasing from depth enhances ^{222}Rn migration toward shallower aquifers, despite a contribution from a lithologic source (Fig. 6). The role of carrier gases, such as CO_2 , as drivers of the ^{222}Rn and other gases migration to the surface has been already characterized (Etiope and Martinelli 2002). CO_2 has been considered a carrier gas due to its large amount in several geological environments (Morner and Etiope 2002), including volcanic systems (Werner et al. 2018), carrying environments in which the potential hazardous effect of CO_2 itself is associated to the radioactivity of the ^{222}Rn (Rodrigo-Naharro et al. 2017). Another evidence of such a gas drag effect is the water chemistry itself, as for example springs 15 and 17, both located in the NW flank

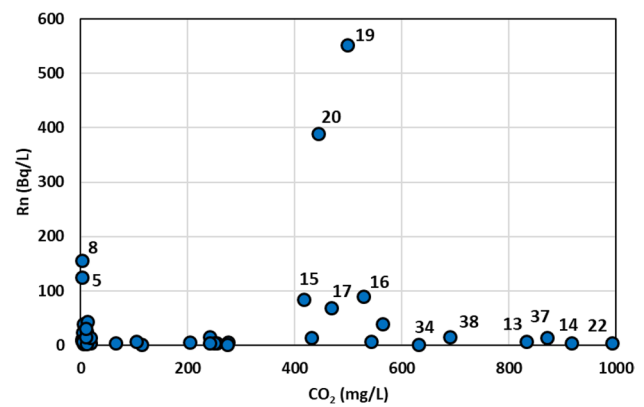


Fig. 6 Relationship between dissolved CO_2 and ^{222}Rn content for the winter survey data, suggesting that despite a contribution from a lithologic source (represented by 5 and 8) gaseous phases released from depth, such as CO_2 , enhances ^{222}Rn migration toward shallower aquifers, explaining the highest ^{222}Rn content observed in the cold springs 19 and 20

of Fogo, are part of the group that depict SO_4 -enrichment (Fig. 3H), thus indirectly influenced by steam-heating processes (Cruz and França 2006; Cruz et al. 2010a).

Conclusions

Radon, the heaviest among all the naturally occurring noble gases, may present a highly variable content in groundwater. The present study was made to determine radon content over a set of groundwater discharges spread along the main geological units in São Miguel, the major island of the Azores archipelago. For that purpose, a set of 42 springs were sampled during winter and summer seasons, mainly corresponding to cold and thermal discharges, of low mineralization, as shown by the mean EC values, not higher than 552.9 $\mu\text{S}/\text{cm}$ (winter) and acid to slightly basic in character. The radon content range between 0.99 and 551.64 Bq/L during winter (mean = 47.81 Bq/L), and between 1.42 to 559.67 Bq/L (mean = 49.37 Bq/L) in summer. The geographical distribution of data suggests that the highest radon concentrations are observed in Fogo Volcano, being mainly controlled by water temperature, and the main radon sources are generated by a shallow source (a uranium-bearing minerals peralkaline syenite) and a deeper source, of mantle origin. In the latter case, the carrier effect of mantle-derived gaseous phases, such as CO_2 , enhance the transport of radon toward the shallower aquifers.

All springs comply with the threshold value in the Portuguese law (500 Bq/L; Decree-Law 23/2016, from 3rd June), and are far from the value that according to the same normative requires any remediation measures (1×10^3 Bq/L). Nevertheless, from the overall set of data from both surveys,

springs 5, 8, 19 and 20 present ^{222}Rn content higher than the threshold value of 100 Bq/L, therefore requiring treatment if used as a drink-water supply source according to the World Health organization (WHO 2008, 2011). Therefore, results point out to the need to develop further assessments on drinking-water supply sources spread all over the Azores archipelago, made to assess ^{222}Rn content in groundwater, but as well to increase awareness among water managers and authorities toward any remediation measure to be taken, as similar studies have shown (Martins et al. 2019).

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Data availability All relevant data have been analyzed and presented as figures or tables in the manuscript. Moreover, the authors declare that all data and materials support their published claims and comply with field standards.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare they have no financial interests and any conflicts of interest/competing interests directly or indirectly related to the work submitted for publication.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication All authors agreed with the content and that all gave explicit consent to submit.

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