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RESEARCH ARTICLE

Quantification of diffuse CO_2 flux emission from the crater lagoon of Vila Franca do Campo Islet (São Miguel, Azores)

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Abstract

To investigate unexplored areas and apply methodologies suitable for monitoring volcanic activity, a pioneer study was undertaken in the crater lagoon of Vila Franca do Campo Islet to identify possible CO_2 degassing zones in the marine environment. This study was carried out using a floating accumulation chamber, which to the best of our knowledge, has only been applied to lacustrine environments.

A survey was carried out in the crater lagoon in August 2017, resulting in a total of 143 CO_2 flux measurements. Other parameters, such as water temperature, pH, electrical conductivity, and depth, were also determined at each measuring point, covering a study area of 0.02 km^2. At one of the deepest sites with higher CO_2 flux values, water samples were collected at depth for determination of stable isotopic composition.

Water temperatures ranged between 21.0 and 27.0 °C, pH from 8.24 to 8.89, and electrical conductivity from 52.5 to 53.9 mS/cm. As expected, due to the marine water composition, sampled waters are of the Na-Cl type. CO_2 flux varied between 0.581 and 1.0 g m^{-2} d^{-1} (average = 2.967 g m^{-2} d^{-1}). A single CO_2 population, characterized by low CO_2 fluxes, points to a biogenic CO_2 origin ($\delta^{13}C = -9.62‰$). The estimated value for the total CO_2 emitted from the water surface is 0.05 t d^{-1}. CO_2 flux measurements were also compared with the structural features that cross the tuff cone, but no clear relation was observed with fractures/faults.

This methodology should be applied to other coastal marine areas, especially where anomalous gas emissions have been reported.

Keywords Surtseyan tuff cone · Volcanic monitoring · CO_2 flux · Hydrogeochemistry · Coastal water bodies · Oceanic islands

Introduction

The natural occurrence of CO_2 can have several origins such as outgassing from the mantle, from crustal carbonate rocks or result from biological activity (Toutain et al. 2002). Volatiles from the deep interior of the Earth are brought to the surface by volcanic activity, being CO_2 the predominant carbon species. CO_2 is the first major volatile to exsolve during magma ascent because of its low solubility in silicate melts. Moreover, magmas are already CO_2-saturated regarding a separate vapor phase at great crustal depths (Anderson 1975; Wyllie and Huang 1976; Mysen 1977; Wallace 2005).

The establishment of CO_2 budgets requires good estimates of both carbon sources and sinks; thus, the integration of inland waters in the overall terrestrial carbon budget has shown to be crucial (Sobek et al. 2003; Cole et al. 2007; Duarte et al. 2008; Rocher-Ros et al. 2017). Likewise, ocean

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and coastal carbon are of major importance for the global carbon cycling (e.g., Walsh et al. 1981; Smith and Hollibaugh 1993; Tsunogai et al. 1999; Borges et al. 2005; Cai et al. 2006; Chen and Borges 2009; Laruelle et al. 2010; Liu et al. 2010; Borges 2011; Cai 2011; Dai et al. 2013).

The carbon cycle in continental shelf seas has been disturbed by human activities since the beginning of the industrial revolution (Bauer et al. 2013; Regnier et al. 2013). Changes in carbon cycling results from the increasing amounts of organic and inorganic carbon coming from rivers (Meybeck 1982) and tidal wetlands (Cai 2011; Bauer et al. 2013), as well as from the variable intensity of CO_2 exchange at the air-water interface in coastal waters (Mackenzie et al. 2012). The exact magnitude of this change is still unclear (Cai 2011; Bauer et al. 2013; Regnier et al. 2013), and the present-day exchange of CO_2 between the atmosphere and continental shelf seas remains poorly constrained, with an uncertainty as large as 50–100% (Bauer et al. 2013).

Consequently, the coastal ocean has been poorly represented in Earth system models, in terms of understanding the processes involved and of temporal-spatial resolution (Holt et al. 2005; Bonan and Doney 2018). Recent studies have further highlighted the vulnerability of coastal systems to increasing anthropogenic perturbations (Bauer et al. 2013; Regnier et al. 2013), adding to the challenge of understanding the already complex coastal carbon cycle and projecting its changes into the future.

Estimates of global coastal sea-air CO_2 fluxes have improved significantly because of a rapid increase in regional flux measurements. Nevertheless, there is still a need to a better understanding of the CO_2 exchanges at the water-air interface in areas that act as carbon sinks (Degrandpré et al. 2002; Thomas et al. 2004; Borges et al. 2006) or as sources (Friederich et al. 2002; Cai et al. 2003; Shadwick et al. 2011). For example, the South China Sea basin is considered a carbon source, whereas the Oregon-California coast is a carbon sink (Cao et al. 2019). In many of these coastal systems, temporal and spatial changes in CO_2 fluxes remain to be resolved as large uncertainties are often associated with the presently reported CO_2 fluxes in individual systems, which impact on the estimation of global fluxes. There is an important gap in our understanding of the contribution of high CO_2 emission regions such as active volcanic systems, which may be important net contributors.

Diffuse CO_2 degassing studies on the surface of lakes, and other water bodies, in which spatial and temporal flux variations are quantified, provide important information that can be used to map hidden active faults and monitor active volcanic systems (Baubron et al. 1990; Pérez et al. 1996; Aiuppa et al. 2004; Werner and Cardellini 2006; Toutain et al. 2009; Mazot et al. 2014; Andrade et al. 2016), as well as contribute to improve the Earth's carbon budget (e.g., Kusakabe et al. 2008; Padrón et al. 2008; Mazot and Taran 2009; Hernández et al. 2011; Mazot et al. 2011; Pérez et al. 2011; Caudron et al. 2012; Chiodini et al. 2012; Arpa et al. 2013; Mazot and Bernard 2015; Andrade et al. 2016).

The study of CO_2 emission from the surface of volcanic lakes in the Azores has gained expression in the last decade and showed that the CO_2 emitted from most of these water bodies is mainly biogenic (Cruz et al. 2015; Melián et al. 2016; Andrade et al. 2016; Tassi et al. 2018; Andrade et al. 2019a, 2019b, 2019c, 2019d). To date, no diffuse CO_2 degassing studies using the floating accumulation chamber method have been carried out in coastal waters or in the open sea. Thus, this paper presents the first systematic study on CO_2 degassing at the seawater surface, through detailed flux measurements performed in the crater lagoon of Vila Franca do Campo Islet (São Miguel, Azores). The islet corresponds to a Surtseyan-type tuff cone located 500 m offshore the south coast of São Miguel Island. Despite being dismantled by marine erosion and highly fractured, it shows a well-preserved crater flooded by seawater that forms a shallow circular lagoon with a surface area of only 0.02 km^2.

The main objectives of the present study are to (1) estimate for the first time the CO_2 flux in the crater lagoon of Vila Franca do Campo Islet, (2) identify potential anomalous degassing areas associated to structural features, (3) assess the CO_2 sources, and (4) test the floating accumulation chamber as an adequate methodology to measure CO_2 fluxes in coastal-marine environments.

Geological setting

The Azores archipelago is a group of nine volcanic islands located in the Atlantic Ocean between latitudes 36.9°N–39.7°N and longitudes 24.9°W–31.3°W (inset of Fig. 1A). From a geodynamic point of view, this area of the North Atlantic corresponds to the triple junction of the North American, Eurasian, and Nubian lithospheric plates (Madeira et al. 2015 and references therein).

São Miguel is the largest (744 km^2) of the Azorean islands and it is formed by seven volcanic systems: three active central volcanoes (Sete Cidades, Fogo – also known as Água de Pau – and Furnas), separated by two active fissure systems (Picos and Congro). Two extinct volcanic systems (Povoação and Nordeste) form the eastern part of the island (Pacheco et al. 2013; Gaspar et al. 2015).

Vila Franca do Campo Islet

Vila Franca do Campo Islet is located offshore the south flank of Fogo Volcano, approximately 500 m from the town of Vila Franca do Campo (Fig. 1A). The islet is an emergent Surtseyan-type tuff cone resulting from a

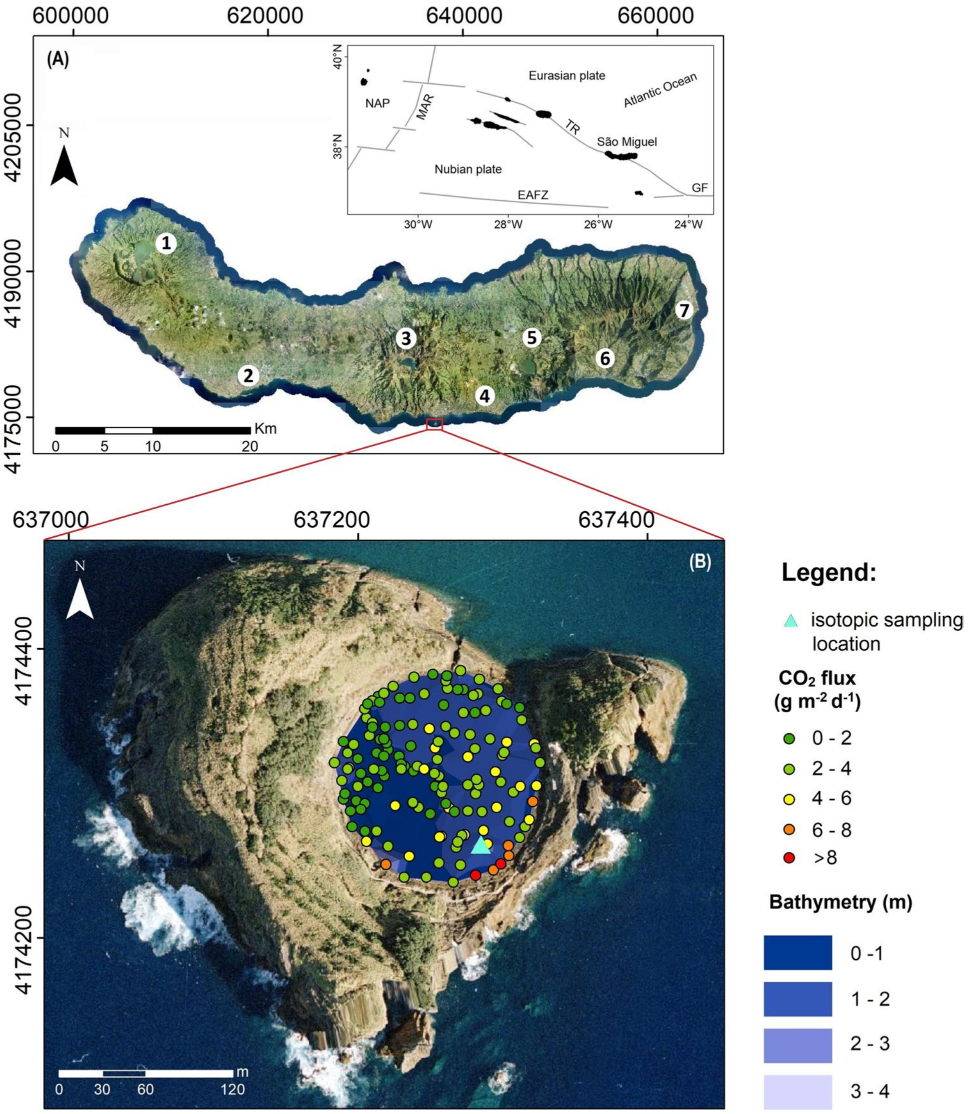

Fig. 1 (**A**) Location of the Vila Franca do Campo Islet offshore the south coast of São Miguel Island. Identification of the volcanic systems that form the island (1—Sete Cidades volcano; 2—Picos Fissural volcanic system; 3—Fogo volcano, also known as Água de Pau volcano; 4—Congro Fissural Volcanic System; 5—Furnas volcano; 6—Povoação volcano; 7—Nordeste Volcanic System, after Gaspar et al., 2015). Inset shows the geodynamic setting of the Azores archipelago and main tectonic features of the region (NAP—North American plate; MAR—Mid-Atlantic Ridge; TR—Terceira Rift; EAFZ—East Azores Fracture Zone; GF—Gloria Fault). (**B**) Bathymetry and CO_2 flux sampling points measured and isotopic sampling location (UTM—WGS1984, zone 26S)

hydromagmatic basaltic eruption that took place in shallow seawater (20–30 m depth). Its age is poorly constrained between 5000 and 10,000 years (Moore 1991), as the cone is partially capped by the Fogo A pumice fall deposit (c. 4600 years BP; Wallenstein et al. 2015) that erupted from the nearby Fogo Volcano.

The tuff cone is asymmetric being the western side wider and higher (maximum height of 62 m a.s.l.) than the eastern side of the edifice. The outer flanks are largely dismantled by marine erosion and crossed by many fractures, some of which wide enough to allow seawater to flow through. This significantly reduced the original size of the volcanic edifice and resulted in several rocky bodies found in the south and eastern parts. The tuff cone has a 10-m wide artificial opening on the north side, which allows the entry of small boats. Despite being eroded and fractured, the inner flanks show a well-preserved crater that is flooded by seawater, creating a circular lagoon with a diameter of 150 m and a surface area of approximately 0.02 km^2.

The rocks forming the cone consist of fine-grained diffuse-stratified to stratified tuffs, with variable proportions of *lapilli* and ash. Numerous basaltic lava bombs and angular blocks are scattered throughout the outcrops. These rocks are highly lithified due to the extensive palagonitization and zeolitisation of the pyroclastic deposits, increasing their brittle behavior in response to stress changes.

Methodology

Diffuse CO_2 degassing measurements and statistical approach

Measurements of CO_2 flux on the water surface of the crater lagoon were made in the summer of 2017 (7th of

August), in a total of 143 measurements, covering an area of 0.02 km^2.

Determinations of water temperature, pH, and electrical conductivity were carried out at each measurement location using specific portable devices (a testo 925 meter was used to measure water temperature and a WTW 340i meter for pH and electrical conductivity). The bathymetry was also determined with a Garmin ECHO^{TM} 500c bathymetric probe at each point.

A set of samples for the determination of stable isotopic contents ($\delta^{18}O$, δ^2H, and $\delta^{13}C$) was collected at the bottom of the water column (Fig. 1B). The water was stored in HDPE bottles for the $\delta^{18}O$ and δ^2H (‰ vs. V-SMOW) analyses according to a standard procedure (Clark and Fritz 1997). The analysis was 0.999 accurate and the maximum error interval was 3‰. The procedure proposed by the International Atomic Energy Agency (IAEA 2017) was used to sample for the dissolved inorganic carbon (DIC) $\delta^{13}C$ (‰ vs. V-PDB). The accuracy of the analysis was 0.999 and the maximum error interval was 0.15‰. Further details about the experimental protocol and the equipment used can be found in Andrade et al. (2019b). Water was also collected for isotopic analysis and some physical and chemical parameters (temperature, pH, and electrical conductivity), outside the islet NE of the main entrance, to compare the values with those inside the crater.

For the measurement of the CO_2 flux on the water surface, the accumulation chamber method was used. This method has shown to be an adequate way to measure CO_2 fluxes in volcanic and geothermal regions, since it is an absolute method that requires neither suppositions nor correlations that depend on the characteristics of the soil or the water (Chiodini et al. 1998; Bernard et al. 2004; Mazot 2005). This method is not only simple to apply but also quick, what allows to perform a high density of points in the sampled areas.

The accumulation chamber method was initially used for flux measurement in soils, which was modified (added a buoy attached to the accumulation chamber) to allow it to float, and thus take measurements at the water surface (Fig. 2). Nevertheless, following the first diffuse degassing measurements performed in crater lakes using the floating accumulation chamber technique (Kling et al. 1991), the application of this method to volcanic crater lake emissions started to be applied afterwards (Bernard et al. 2004; Bernard and Mazot 2004; Mazot 2005; Mazot and Taran 2009; Hernández et al. 2011; Arpa et al. 2013; Andrade et al. 2016; Melián et al. 2016).

This method was already used in previous studies in water bodies the Azores archipelago (Andrade et al. 2016, 2019a, 2020). More details about the methodology, as well as the main advantages and constraints associated with the selected approach, are described by Mazot and Bernard (2015). Other specific procedures, such as the calibration routine, are described in Andrade et al. (2016) and Andrade et al. (2019a).

Two statistical methods were applied to process the data: the Graphical Statistical Approach (GSA) (Chiodini et al. 1998) and the sequential Gaussian simulation (sGs) (Deutsch and Journel 1998; Cardellini et al. 2003). These approaches allowed the estimation of the overall diffuse CO_2 emission from the crater

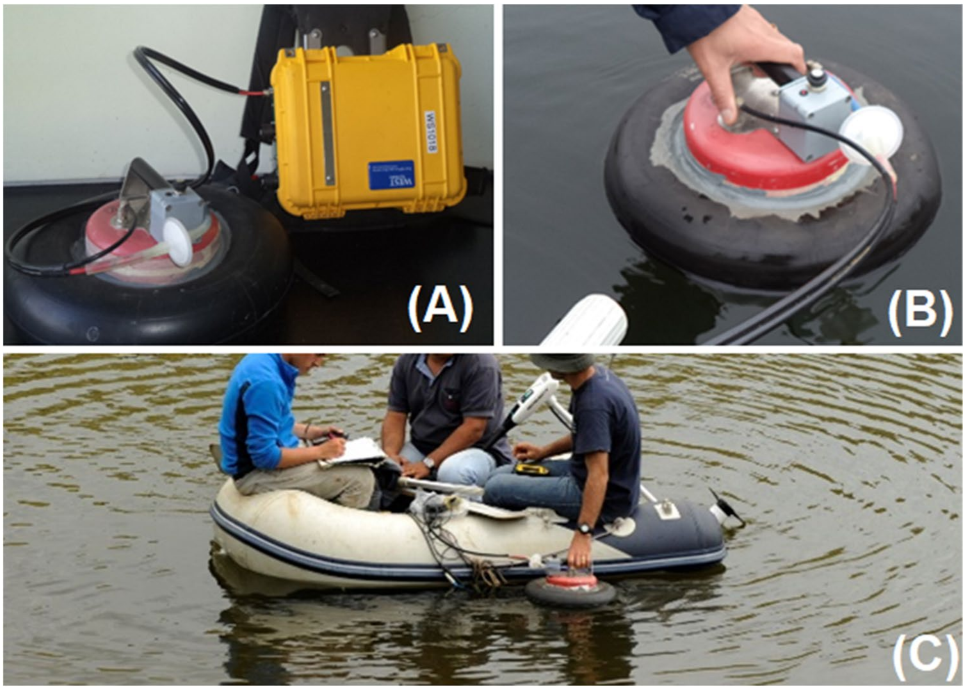

Fig. 2 (**A**) Portable CO_2 flux instrument + modified accumulation chamber. (**B**) Floating accumulation chamber. (**C**) Measurements at the water surface, using the modified accumulation chamber method.

lagoon of Vila Franca do Campo Islet. Further details about these two procedures can be found in Sinclair (1974), Chiodini et al. (1998), Deutsch and Journel (1998), Cardellini et al. (2003), and Andrade et al. (2019a).

Structural analysis

Field observations were combined with aerial photo interpretation to map and characterize the structural features present at Vila Franca do Campo Islet, following the methodology in Zanon et al. (2009). The orientation of 98 fractures was measured with a geological compass at eight stations (Fig. 3). Seven of the eight stations were located on the inner flanks around the crater, where the measured features were more protected against marine erosion. Station 8 was located on the northern outer flank of the cone, but as it faces the south coast of São Miguel Island, it is less exposed to wave action. Rose diagrams of the collected data are shown in Fig. 3.

Results and discussion

Water physico-chemical parameters and stable isotopic content

Descriptive statistics of the physico-chemical parameters of the lagoon water is provided in Table 1. Water physico-chemical maps for the several variables (temperature, pH, and electrical conductivity) in each measurement point are presented in Fig. 4.

The surface temperature of the water in the crater lagoon ranged from 21.6 to 27.0 °C, being this 5.4 °C-gradient mainly associated with the depth of the water column. The influence of depth is shown by the contrast between the shallower area (<1 m) where the highest temperatures (>26 °C) were recorded and the deepest areas (>3 m) where the lower temperatures (<22 °C) were measured (Figs. 1B and 4A). These values are in the same scale of the one measured in the coastal waters outside the islet (25.8 °C) in the same day.

The correlation coefficient between the water temperature and pH points out to a weak inverse linear relationship

Table 1 Descriptive statistics of the water physico-chemical data: main variables (temperature, pH, and electrical conductivity) and CO_2 flux data in the crater lagoon of the Vila Franca do Campo Islet

Water surface	Statistics	T (°C)	pH	Cond. (mS/cm)	CO_2 flux ($g\ m^{-2}\ d^{-1}$)
	Max.	27.00	8.49	53.9	10.99
	Min.	21.60	8.02	52.5	0.58
	Mean	24.51	8.24	53.7	2.97
	St. Dev.	1.29	0.11	0.2	1.71
	Median	24.30	8.24	53.7	2.55

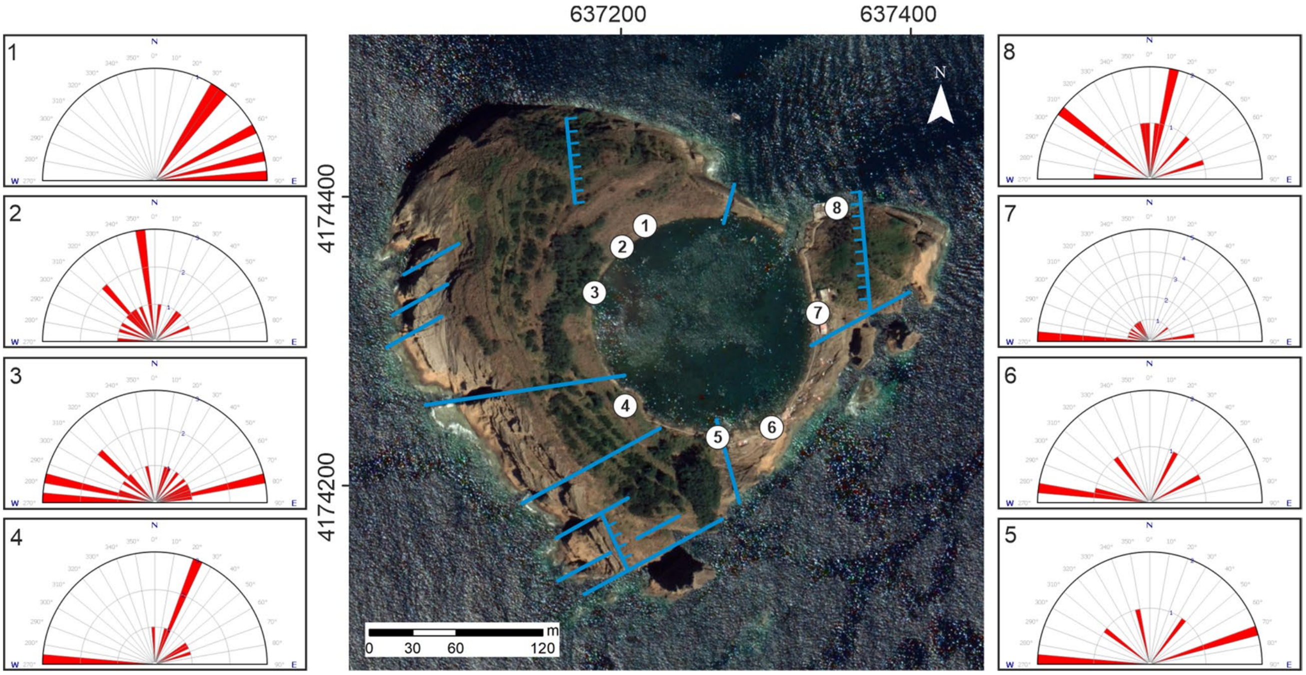

Fig. 3 Main structural features of the Vila Franca do Campo Islet and location of stations (1 to 8) where fractures were measured. Hatched lines correspond to normal faults, while solid lines to all other types of fractures. Half circle rose diagrams show the orientation of the fractures on each station (the length of the red bars is proportional to the number of fractures with the same direction)

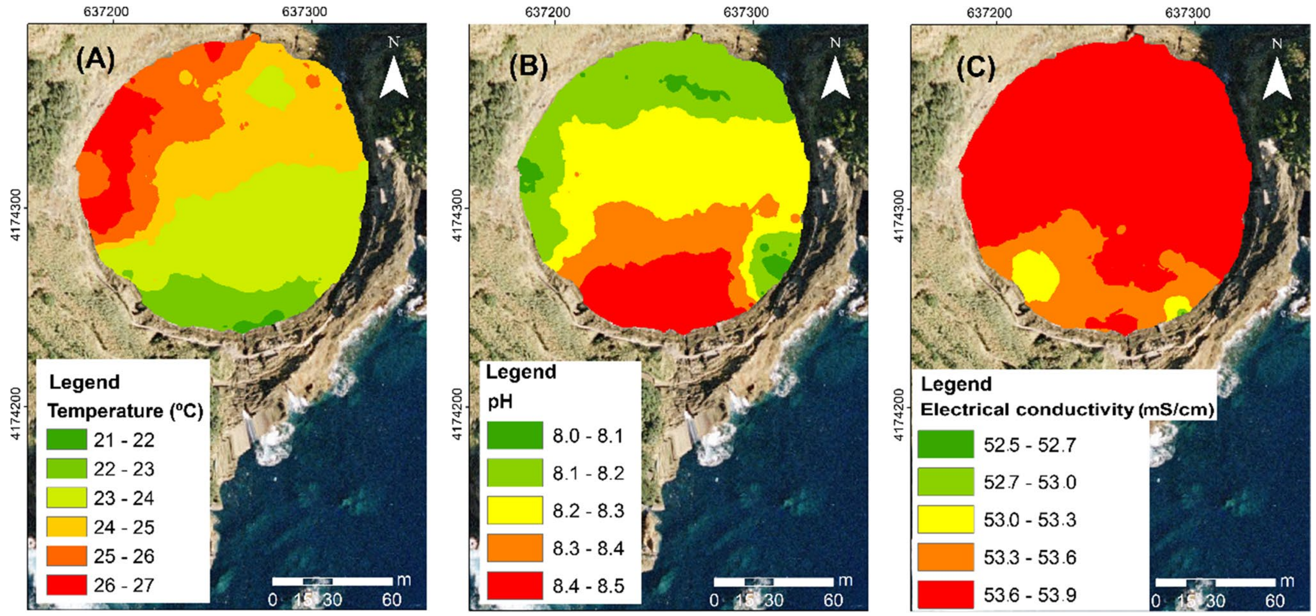

Fig. 4 (**A**) E-type surface water temperature map. (**B**) E-type surface water pH map. (**C**) E-type surface water electrical conductivity map

between both variables (r = -0.532), also explained by the influence of depth. In fact, the depth of the water column also explains the low variation observed for pH (Fig. 4B), with slightly alkaline values in the range between 8.02 and 8.49 (mean = 8.24), with the lowest values measured near the artificial opening on the north side of the tuff cone, and the highest values recorded in the south part of the lagoon (Fig. 4B).

The electrical conductivity ranged between 52.5 and 53.9 mS cm^{-1}, with the higher values measured also in the southern area of the lagoon, far from the artificial opening (Fig. 4C). Lagoon water is from the Na-Cl type, typical of marine environments. A positive relationship between conductivity and water temperature is shown by the correlation coefficient (r = 0.578), while in turn, as expected from the observed inverse relationship between temperature and pH, conductivity also depicts a weak negative linear relationship with pH (r = -0.524).

The $\delta^{18}O$ and $\delta^{2}H$ stable isotopic content is equal to 0.82‰ and 6.00‰, respectively, values that are in the same range of the ones from a sample taken in the coastal waters outside the islet (equal to 0.64‰ and 5.70‰, respectively). The slight difference between the $\delta^{18}O$ and $\delta^{2}H$ content inside and outside the islet may suggest some influence from evaporation in the lagoon due to the also slightly higher temperature and lower depth. These results are within the expected values for waters of the Atlantic Ocean that have enriched isotopic values ($\delta^{18}O > 0$‰ and $\delta^{2}H > 5$‰; Lécuyer et al. 1998; Xu et al. 2012; Werner et al. 2015). Likewise, Benetti et al. (2017) refer to comparable seawater isotopic compositions ($\delta^{18}O \sim 1$‰ and $\delta^{2}H \sim 7$‰) west of the Azores Islands.

The $\delta^{13}C$ content ranges between -9.62‰ (crater lagoon water) and -9.11‰ (coastal waters outside the islet), values slightly lower than those found in the literature for seawater in Atlantic Ocean ($\delta^{13}C$ = -8.64‰; Longinelli et al. 2013). The contribution from a marine organic matter source ($\delta^{13}C$ -10.0‰; Petterson and Walter 1994) is the most probable explanation to the measured values.

CO_2 flux in the crater lagoon

CO_2 flux values measured in the crater lagoon of Vila Franca do Campo Islet (Fig. 1B) ranged between 0.58 g m^{-2} d^{-1} and 11.0 g m^{-2} d^{-1}, with a mean value of 2.97 g m^{-2} d^{-1} (Table 1). Flux values have a negative linear relationship with temperature and conductivity (respectively r = -0.578 and r = -0.464) and a low positive correlation coefficient with pH (r = 0.410).

Cumulative probability graphics were used to plot the data of the CO_2 flux survey, depicting a lognormal population, which points to a single source for the CO_2 being released (Fig. 5). Taking in account the low CO_2 flux and the carbon isotopic values, a biogenic origin may be inferred with no evidence of volcanic/hydrothermal input, where no visible also, gas manifestations have been identified (gas bubbles in the water column). Biogenic source in this area should be related mainly to the presence of algae and some macrophytes. This is also favored by the fact that the lagoon is more protected from high waves and the algae may be trapped in the studied site. Accumulation and decomposition of organic matter (e.g., algae) in the sea bottom can also increase the release and emission of CO_2. A CO_2-fractionated biogenic source may be contributing to the water composition as it is depleted relative to the actual atmospheric value ($\delta^{13}C = -8.3‰$; Clark 2015) and far from a possible volcanic/hydrothermal signature ($\delta^{13}C$ in the range from $-3.5‰$ to $-6‰$; Cartigny et al. 2001).

The spatial diffuse CO_2 emission distribution map was elaborated following the sGs procedure, as described by Cardellini et al. (2003). The maps were made based on experimental variograms, which in this case was modeled integrating a spherical and hole effect structure (Isaaks and Srivastasa 1989) with different ranges and nugget values (Fig. 6).

Figure 7 shows the spatial distribution of the CO_2 flux in the lagoon water. Overall, the CO_2 flux is low and without significant variations across the water surface, being the highest values measured in the southeast area. The influence of this area over the CO_2 emission is not significant, as only five measurements showed values higher than 6 g m^{-2} d^{-1}. It should be noted that in this area, there is a small pier, where it is possible to find, at times in the summer, large groups of bathers jumping and diving into the water. The month of August is usually the period of higher concentration of tourists on Vila Franca do Campo islet, which has a maximum limit of 400 visitors per day. On the day of the survey, the islet reached its maximum daily capacity, with more than 90% of the visitors going into the water at least once. For these reasons, the water from the lagoon is analyzed monthly by the Regional Directorate for Sea Affairs to determine its quality and the presence of bacteria (*Escherichia Coli* and *Intestinal Enterococci*).

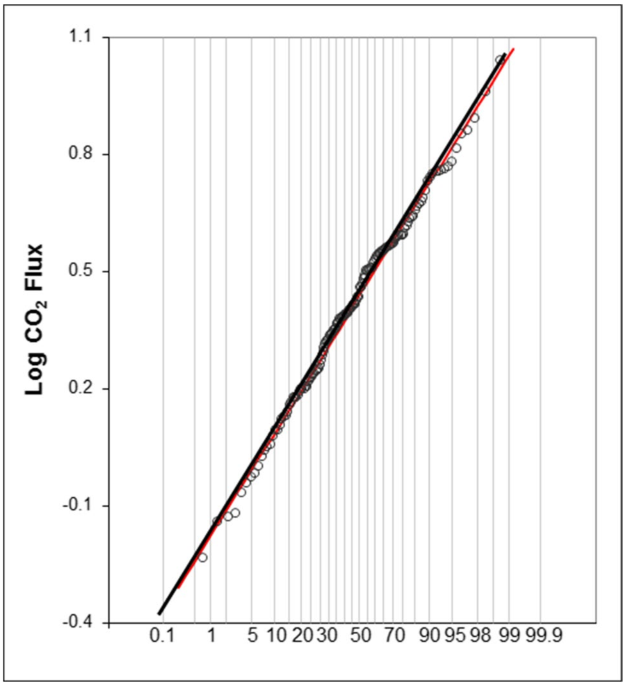

Fig. 5 CO_2 flux probability plot for the survey carried out in the crater lagoon of the Vila Franca do Campo Islet

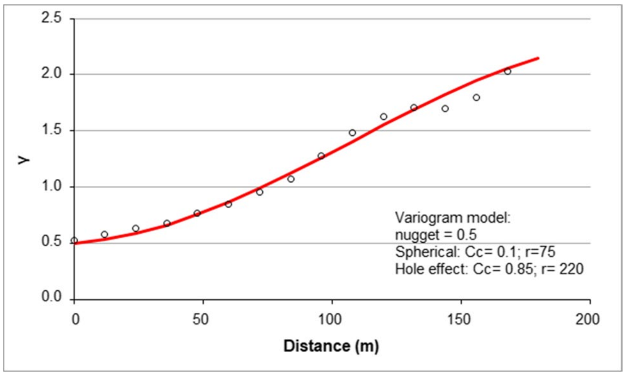

Fig. 6 Experimental and modeled variogram for the CO_2 flux normal scores in the crater lagoon of the Vila Franca do Campo Islet. Values for Cc (sill) and range (r; in m) are also shown for the variogram

Bathing in the lagoon has been forbidden several times in the last years due to failures in complying with bathing water quality criteria. For example, in June 2020, microorganisms content reached 5600 CFU/100 ml (*Intestinal Enterococci*) and 7100 CFU/100 ml (*Escherichia coli*), thus exceeding by far the threshold values of 300 CFU/100 ml (*Intestinal Enterococci*) and 1000 CFU/100 ml (*Escherichia coli*) from Directive 2006/7/EC (CEC 2006), respectively. However, at the time of the survey, values were ≤15 CFU/100 ml for both bacteria.

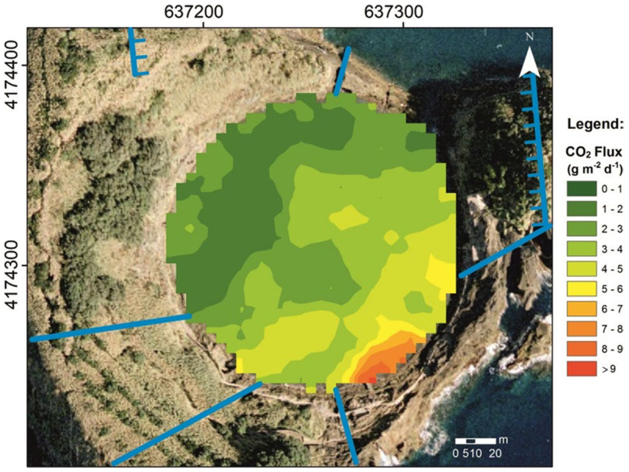

Fig. 7 E-type CO_2 flux map for the crater lagoon of the Vila Franca do Campo Islet, and main structural features. Hatched lines correspond to normal faults, while solid lines to all other types of fractures. (UTM—WGS84, zone 26S; interpolation method—sGs)

As mentioned above, the current study does not reveal the existence of volcanic CO_2 released at the bottom of this crater lagoon. Therefore, this susceptibility to contamination also indicates high biological activity in the seawater, which may contribute to the increase in biogenic CO_2, which is supported by the CO_2 fluxes and the isotopic analysis.

It should be noted that the degassing values in the current study are very low when compared to the ones measured with the same methodology in Azorean volcanic lakes with a deep-derived (volcanic-hydrothermal) CO_2 source (Furnas Lake, Andrade et al. 2016; Furna do Enxofre Lake, Andrade et al. 2019b) (Table S1, electronic supplementary file). Moreover, no submarine hydrothermal vents have been identified in the surroundings of the Vila Franca do Campo Islet (Couto et al. 2015 and references therein). However, ongoing inland CO_2 surveys (João Pimentel, personnel communication) point to the existence of anomalous CO_2 degassing sites located in the south flank of Fogo Volcano, probably associated to tectonic structures and magnetotelluric anomalies (Kiyan et al. 2019). The current study does not show any extension of these anomalies to the Vila Franca islet.

The total amount of CO_2 emitted into the atmosphere from the water surface at the crater lagoon of Vila Franca do Campo Islet was estimated as 0.05 t d^{-1}. This value was computed with the sGs approach and is equal to the one obtained using the GSA, which again confirms the usefulness of both methodologies to estimate the final CO_2 emission, especially when only one population is identified. When this output is standardized by the sampling area (2.94 t km^{-2} d^{-1}), the computed value is one of the lowest when compared, for example, to volcanic lakes with similar areas in the Azores archipelago or in other parts of the world, and where the main source of CO_2 is also biogenic (Pérez et al. 2011; Andrade et al. 2021a). The very low values can be eventually explained by the continuous exchange of water between the crater lagoon and the coastal waters outside the islet through the artificial opening and the numerous fractures that cut the tuff cone.

Structural features

Vila Franca do Campo Islet is crossed by different types of structural features. The measured fractures are typically 0.5 to 1 cm wide, but a few of them are up to 50 cm wide. From strike and dip variations, it was possible to distinguish radially arranged and tangentially arranged fractures.

Radially arranged fractures are the most common type. They are long enough to cut through the entire tuff cone and deep enough to allow seawater to flow into the lagoon. Most radial fractures reveal only minor vertical displacements of a few centimeters. Others show horizontal movements, with major displacements, or show a transtensional component with minor vertical displacement. The latter fractures correspond to faults. The dominant strike of radially arranged fractures is E-W, followed by the N140° regional tectonic trend and its conjugate N80°. The N20° system is also present and marks the trend of dissection of the eastern part of the cone.

Tangentially arranged fractures are less common and correspond to groups of parallel joints with no displacement or very minor displacements with only a small vertical component. These groups of joints are located both on the inner and outer flanks of the tuff cone. They are usually associated with small collapses. The directions of tangentially arranged joints span 360°. However, the dominant strike is the E-W, followed by N70°.

Traces of two normal faults trending N175° were found on the northern side of the cone (Fig. 3). From their dip (~50°), they define a very shallow graben structure that could recall the path followed by magma upon intrusion. Dense vegetation on the southwest flank and the removal of a large portion of the southeast flank prevented further observations. The entire cone is cut by a set of parallel sub-vertical transtensive faults trending N60°. Their horizontal displacement component is higher than the vertical. These faults do not deform the pyroclastic deposits building the cone, meaning they formed after the deposits were lithified and therefore after volcanic activity.

Conclusions

This first study on CO_2 degassing in the marine environment, namely, in the crater lagoon of Vila Franca do Campo Islet (São Miguel, Azores), resulted on a detailed geochemical and hydrogeochemical characterization of the inner water of this islet.

The emission of CO_2 in the crater lagoon seems to be essentially associated with a biogenic source. Overall, the CO_2 flux is low (<11.0 g m^{-2} d^{-1}) and without significant variability across the water surface. The application of the GSA methodology enables the identification of just one population. The low CO_2 fluxes together with the $\delta^{13}C$ signature suggest a biogenic source for the CO_2 released from the crater lagoon. No clear relation was observed between CO_2 emission in the crater lagoon and the numerous fractures and faults that cross the tuff cone, further supporting its biogenic origin.

The total CO_2 emission from the crater lagoon of Vila Franca do Campo Islet amounts to approximately 0.05 t d^{-1}, being low, when compared to the values measured on many volcanic lakes in the Azores, previously studied by Andrade et al. (2021b).

Considering that in the Azores there are some places in the marine environment with secondary manifestations of volcanism, this study also stresses the need to develop similar studies in other marine areas. These can contribute not only to better understand the CO_2 emission from coastal waters and improve the volcanic carbon budget in the archipelago but also to evaluate the future impacts of ocean acidification.

The results gathered from the current study are useful in developing a better understanding of the carbon budget in coastal sea environments, close to active volcanic systems. Moreover, this study is complementary to other studies carried out in the Azores (e.g., inland diffuse degassing studies), which are important for the seismovolcanic surveillance of the archipelago. Nevertheless, further studies should be made in order to strengthen our conclusions, namely, regarding the CO_2-sources, by increasing the sampling network for the determination of the elemental and isotopic composition, and adding other analytical tools, such as using noble gasses tracers.

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Author contribution CA, JVC, and FV designed the investigation; CA collected data in field and in the laboratory and performed the data processing and analysis as well as wrote most of the manuscript; JVC, FV, VZ, and AP collaborated on the original draft preparation; CA, JVC, FV, VZ, AP, and RC revised the paper; all authors have read and approved the manuscript.

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Declarations

Conflict of interest The authors declare no competing interests.

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