Chemical characterization of Punta de Fuencaliente CO₂ seeps system (La Palma Island, NE Atlantic Ocean): a new natural laboratory for ocean acidification studies

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Abstract. We present a new natural carbon dioxide (CO_2) system located off the southern coast of La Palma Island (Canary Islands, Spain). Like others CO_2 seeps, these seeps can be used as an analogue to study the effects of ocean acidification (OA) on the marine realm. With this aim, we present an accurate chemical characterization of the seeps system carbon emissions, describing the carbon system dynamics, by measuring pH, A_T and C_T, as well as, Ω aragonite and calcite. Our explorations on the area have found several emission points with similar chemical features. Here, the CO_2 emission flux varies between 2.8 kg CO_2 d^{-1} to 28 kg CO_2 d^{-1}, becoming a significant source of carbon. CO_2 seeps are of volcanic origin and the alteration of local ocean chemistry is due to acid brackish water discharges. Although this kind of acidified system is not a perfect image of future oceans, this area of La Palma island is an exceptional spot to perform studies aimed to understand the effect of different levels of OA on the functioning of marine ecosystems. These studies can then be used to comprehend how life has persisted through past Eras, with higher atmospheric CO_2, or to predict the consequences of present fossil fuel usage on the marine ecosystem of the future oceans.

Keywords. Volcanic area, hydrothermal, brackish water discharge, ocean acidification, ocean chemistry.

1 Introduction

Marine systems with natural carbon dioxide (CO_2) sources have been used as analogous of the acidified future oceans (OA) to understand its effects on organisms and marine ecosystems functioning since the last decade (IPCC, 2014; González-Delgado and Hernández, 2018). These areas are characterized by an extra-CO_2 input from volcanic (normally called CO_2 seeps), karstic or biological sources or originate from upwelling (González-Delgado and Hernández, 2018). Due to its origin, CO_2 vent systems are very common and can be found all over the world from mid-oceanic ridges to oceanic island and intra-plate magmatism (Tarasov et al., 2005). Moreover, there are marine shallow areas affected by CO_2 gas emissions that acidify the surrounding waters (Hall-Spencer et al., 2008).

Numerous advances in OA studies have been achieved using these systems, such as acidification effect on ecology interaction, physiological and genetic adaptations (Foo et al., 2018; González-Delgado and Hernández, 2018). Nowadays, it is possible to better understand the direct and indirect effects of OA in marine environments due to these acidified systems, for instance we now know that OA related changes will reflect in the services that ecosystems provide to us (Hall-Spencer and Harvey, 2019). Acidified systems can be also used to look back into the past of the Earth, and to study how early life could have originated

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on the planet (Martin et al., 2008). Understanding how life has adapted in the past acidified Eras, can be extremely useful to understand how current life will change in the expected future (Gattuso et al., 1998).

In general, the vent systems have emissions in the form of bubbles which are 90-99% CO_2. The remaining percentage corresponds to other gases or elements, such as methane (CH_4), sulfide (H_2S), heavy metals, and others. However, these
45 undesired gases or metals have had an insignificant effect on the studies performed in these areas (González-Delgado and Hernández, 2018). The most notable features of these acidified systems are the fluctuation of pH, the aragonite and calcite saturation states (Ω) (declining between 1 and 3) and dissolved inorganic carbon (DIC) which increases up to 3.2 mol C m^{-3} (González-Delgado and Hernández, 2018).

The Canary Islands are located in the North-Eastern Atlantic Ocean, an oceanic volcanic archipelago formed by numerous
50 hotspot island chains (Carracedo et al., 2001). The youngest islands are El Hierro with 1.1 million years and La Palma with an age of 2 million years (Carracedo et al., 2001). These islands are located to the west of the archipelago and it is where the last historical eruptions have taken place. The last two were the Teneguía volcano in La Palma in 1971, and the Tagoro volcano in El Hierro in 2011 (Padrón et al., 2015; Santana-Casiano et al., 2016).

Currently, in the historic volcanic area in the south of La Palma (Cumbre Vieja volcano complex), there is a continuous
55 degassing of CO_2 (Carracedo et al., 2001; Padrón et al., 2015). Correspondingly, on the nearby shore, CO_2 emissions have been detected recently in two different locations: Las Cabras site (Hernandez et al., 2016) and Punta de Fuencaliente which has already been used for OA ecological studies (Pérez, 2017; Viotti et al., 2019).

The local name "Fuencaliente", which translates into hot-springs, refers to the thermal fresh waters that emerge at the coast. Before the conquest of the islands in 1492, its waters were used by locals for its healing properties, and after that by visitors
60 from all over the world (Soler, 2007). However, these *thermas* were buried by the eruption of the San Antonio volcano in the 17th Century. These thermal waters have been so famous and important for Fuencaliente people, that there was an engineering project to dig up these special waters (Soler, 2007). The brackish water features measured by Soler (2007) showed high concentrations of bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), chloride (Cl^-), that together with high temperatures (almost 50 ºC) confirmed the influence of internal magmatic activity. Nearby, there are brackish lagoons located in the innermost part of
65 Echentive beach, about 200 m from the coastline with diameters of 30 m and depths of up to 4 m (Fig. 1). Measures of oxygen isotope ($\delta^{18}O$ SMOW) (Calvet et al., 2003) suggest a slight dilution of the seawater in the lagoons by inland groundwater flowing into it. This indicates that the system is affected by the submarine groundwater discharges (SGD), which probably originate from the thermal waters (Soler, 2007).

In the last two decades, an increasing number of studies underlined the importance of SGD (Jeandel, 2016). SGD is an essential
70 but poorly recognized pathway of material transport to the marine environment (Szymczycha et al., 2014). The term SGD includes the discharge of fresh groundwater to coastal seas to which recirculation of seawater often contributes (Burnett et al., 2006, Charette et al., 2016). For issues related to oceanography, the term is restricted to fluid circulation through continental shelf sediments with emphasis on the coastal zone (Burnett et al., 2006, Jeandel, 2016). One aspect that has yet not been considered is what occurs in areas where SGD is enriched by the emissions of recent volcanism or by hydrothermal activity.
75 In this case, these discharges can also act as sources of gases and hydrothermal emission compounds to the ocean and become points of emission of CO_2 that contribute to the OA. However, shallow coastal beaches and intertidal lagoons are highly dynamic systems controlled by physical processes and subjected to marine and continental influences. Processes as the tide or the submarine groundwater discharges produce higher ranges of variation in physical and chemical parameters than in the open ocean water.

80 Hence, and with the purpose of using the Punta de Fuencaliente area as a natural acidified laboratory, an accurate physical and chemical characterization of this area is presented in this study. The main objectives where (1) determining the area affected by the emissions and detecting new emissions points for replication studies, (2) characterize the ocean chemistry of the area, and (3) to confirm the volcanic origin of the acidification.

2 Material and methods

2.1 Study area

The physical-chemical parameters were sampled across the south of La Palma island, located in the west of the Canary Islands (North-Eastern Atlantic Ocean) (Fig. 1a, supplementary material 1). Following the previous studies in the area (Hernández et al., 2016; Pérez, 2017; González-Delgado et al., 2018a; González-Delgado et al., 2018b; Hernández et al., 2018; Viotti et al., 2019), a sampling network was created. It is formed by 7 sites: Playa del Faro, Los Porretos and surroundings (that together with Las Cabras site, they are known as the Punta de Fuencaliente system or PFS), Playa de Echentive and the two Echentive lagoons (Fig. 1c). The sampling took places between 0 and 2 m depth, at three different times (March 2018, December 2018 and June 2019), and during low and high tide when it was necessary to assess the continuity of the natural emissions (Fig. 1b).
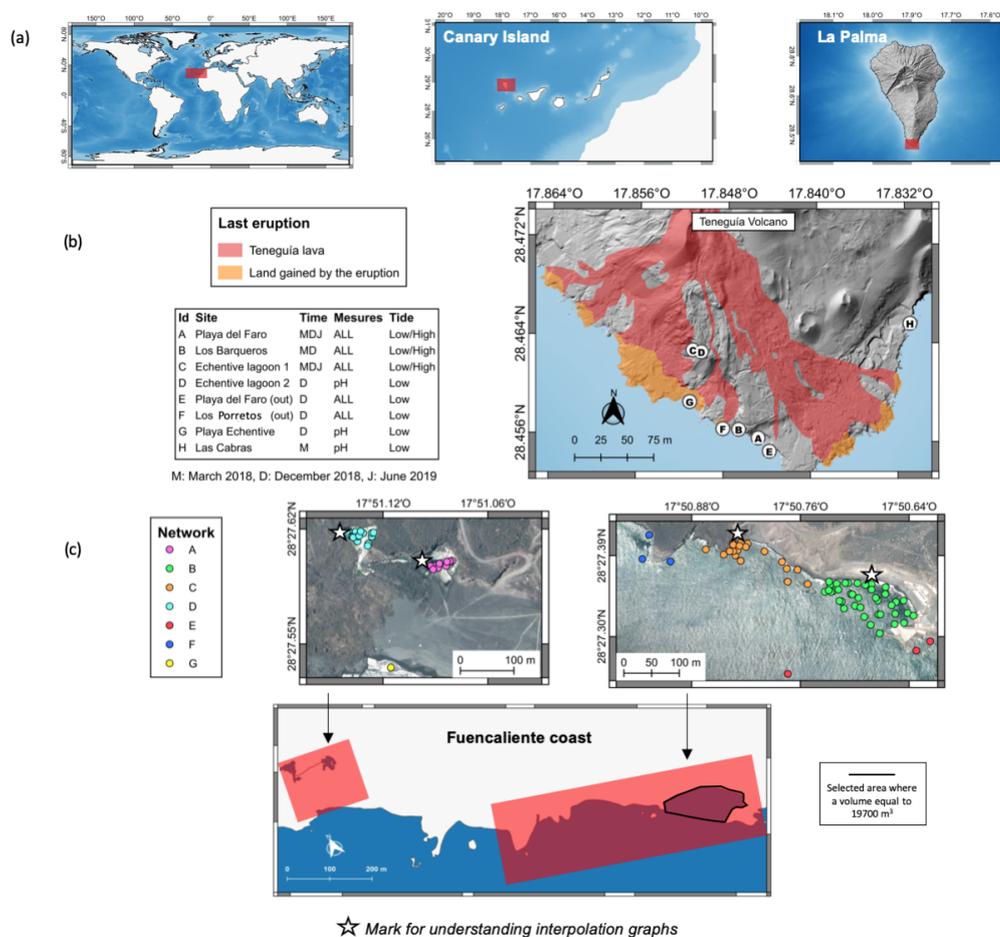

Figure 1: Location of the sampling network performed in this work around the 7 sampling areas (A-G) in the south of the island of La Palma. The location of Punta Las Cabras (H) considered in Hernández et al. (2016) is also included. The map and image base layers used are distributed under public domain (https://www.grafcan.es/).

2.2 Carbon dioxide system parameters

In March and December of 2018, the total dissolved inorganic carbon concentration (C_T), total alkalinity (A_T), pH, salinity and temperature were measured, whilst in June 2019 only the pH and temperature were measured. Total alkalinity and C_T were

100 respectively determined by potentiometric and culometric methods, using a VINDTA system (Mintrop et al., 2000). The
calibrations were made using certified reference material batch #163 (González-Dávila et al., 2007). The pH was measured at
a constant temperature of 25 °C using an Orion pH meter with a combined Orion glass electrode ($pH_{T,is}$). The calibration was
performed on the total seawater scale using a TRIS artificial seawater buffer (salinity 35) according to the manual Good
Measurement Practices of the Carbon Dioxide System in the oceans (Dickson et al., 2007, SOP 6a).

105 Salinity and temperature were measured *in situ* using a handheld conductivity meter (Hanna Instruments HI98192).
Furthermore, the salinity was also measured in the laboratory using a high-precision Portasal salinometer, accurate to ±0.001.
The pH under "*in situ*" conditions, the partial pressure of carbon dioxide (pCO_2) and the saturation states of calcium carbonate
forms (Ω aragonite and Ω calcite) were determined from A_T and C_T data using with the CO2sys program (Pierrot et al., 2006).
We used the linear interpolation method to represents the A_T, C_T, $pH_{T,is}$, Ω aragonite and calcite parameters measurement when

110 anomalies were found.

3 Results

After extensive sampling throughout the south of La Palma, we detected four areas where natural CO_2 emissions occur. These
four areas, Las Cabras, La Playa del Faro, Los Porretos and the two Echentive Lagoons (Fig. 1b), correspond to areas that
were not buried by the lava of the last eruption (Teneguía volcano 1971; Padrón et al., 2015, Fig. 1b). Las Cabras site was

115 discarded in subsequent samplings due to the difficult access, the poor sea conditions and the small size of the area affected
by the emissions (Hernández et al. 2016). In all cases, the anomalies were the highest during low tide.

3.1 Temperature and salinity

Temperature and salinity in Playa del Faro and Los Porretos do not present major changes between the different time points
(supplementary material 2). During March 2018, Playa del Faro had an average temperature of 19 ± 0.2 °C with colder values

120 of 18.7 °C near shore, Los Porretos was not measured this time. In December 2018, both Playa del Faro and Los Porretos
presented an average temperature of 21.5 ± 0.02 °C. However, salinity values present a minor diminution from 37.05-36.51 in
Playa del Faro and from 37.05-36.07 in Los Porretos (supplementary material 2). Both sites presented colder and slightly less
saline water near the coast. Regarding the Echentive lagoons, only the biggest lagoon was measured, where the salinity varied
from 31 to 32 units (supplementary material 2). The same lagoon presented warmer temperatures than the coastal waters during

125 June 2019, 26.4 ± 0.7 °C and 22 ± 0.1 °C, respectively.

3.2 Carbon dioxide system parameters

In both studied shore areas of PFS (Playa del Faro and Los Porretos) the parameters of the carbon dioxide system, $pH_{T,is}$ (Fig.
2), A_T, C_T and Ω aragonite and calcite (Fig. 3) were strongly affected by the entrance of water with less salinity.
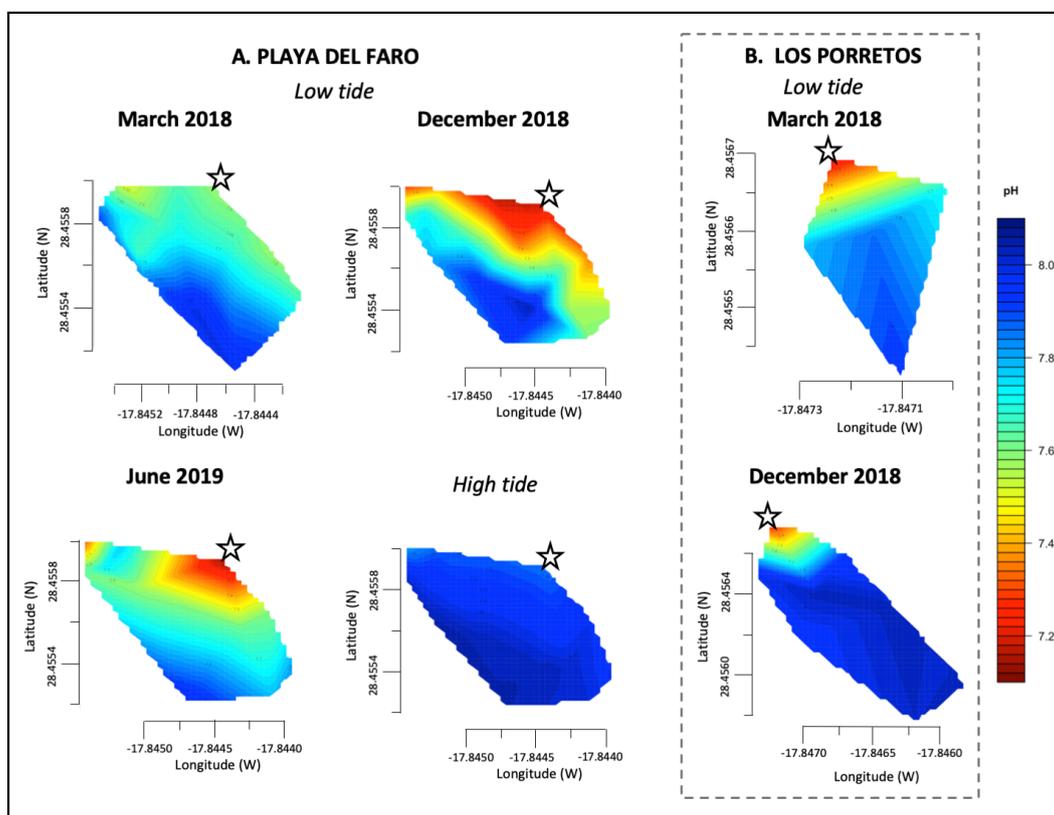
3.2.1 Playa del Faro

130 In March 2018, the pH changed from 8 in offshore samples to 7.5 nearshore, reaching 7.16 and 7.13 during December 2018
and June 2019, respectively (Fig. 2). Similarly, high A_T and DIC were measured throughout Playa del Faro. In March 2018,
the ocean data obtained in the furthest coast station of Playa del Faro reached typical values of 2132 μmol kg^{-1} and 2418 μmol
kg^{-1}, respectively for C_T and A_T (supplementary material 2). As we approached the shore, both factors increased to values that
exceeded 3100 μmol kg^{-1}, following an inverse distribution observed with salinity, with an increase in the C_T:A_T ratio close to

135 1:1, indicating an important contribution of bicarbonate along the area (Fig. 3a, b). In December 2018, the anomaly increased
to over 3500 μmol kg^{-1} in both parameters. As a direct consequence of the low pH values, although compensated by the high

C_T, A_T and dissolved calcium contents (determined by ICP-MS, data not presented), the calcite and aragonite saturation states were also affected. It was observed that the area nearest to the shore presented saturation values of calcite and aragonite that were below 1.5 (Fig. 3c, d).

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During high tide, the anomalies almost disappeared, which means that the tide acts as a pressure plug of the flow of this water to the coastal area. Nevertheless, we still found a mild increase in A_T and C_T (reaching 2500 µmol kg^{-1}) (Fig. 3a, b) and pH values of 7.75 - 7.85 in the sampling points closest to the coast (Fig. 2).

145 **Figure 2: Linear interpolation graphs of pH values that were collected in March 2018, December 2018 and June 2019 during low and high tide in Playa del Faro (A) and Los Porretos (B). The star symbol is the reference mark on the map in Figure 1c.**

Figure 3: Linear interpolation graphs of C_T (a), A_T (b), Ω_{cal} (c) and Ω_{ara} (d) values during March 2018, December 2018 during low and high tide in Playa del Faro. The star symbol is the reference mark on the map in Figure 1c.

150 **3.2.2 Los Porretos**

Los Porretos, is a continuation of Playa del Faro that is also affected by the emission of water with high C_T and low pH. This emission was first observed during March 2018. The measured C_T exceeded 3400 µmol kg^{-1} and the pH$_{T,is}$ reached 7.25 at the emission station (Fig. 2, Fig. 4). In December, the sampling was repeated, observing that the most anomalous values occurred in the stations closest to the coast. The emission point presented C_T concentrations of 3600 µmol kg^{-1} (corresponding with

155 carbon dioxide pressure values of 5200 µatm), pH values of 7.2, and 1.3 and 0.8 values of Ω calcite and aragonite, respectively (Fig. 2, Fig. 4, supplementary material 2).

In both beaches, the emission is acting as an important source of CO_2 into the atmosphere. In Playa del Faro, the partial pressures of CO_2 in surface waters reached up to 5000 µatm in low tide (the values in the atmosphere were between 405 and 410 µatm) (supplementary material 2). This produced high concentration gradients that combined with high-intensity winds

160 characteristic of the area, produced CO_2 fluxes that can reach up to 1 mol m^{-2} day^{-1} (considering its main effects during low tide and Wanninkhof, 2014 for the gas transfer velocity coefficient) that amount to 150 tons of CO_2 per year.
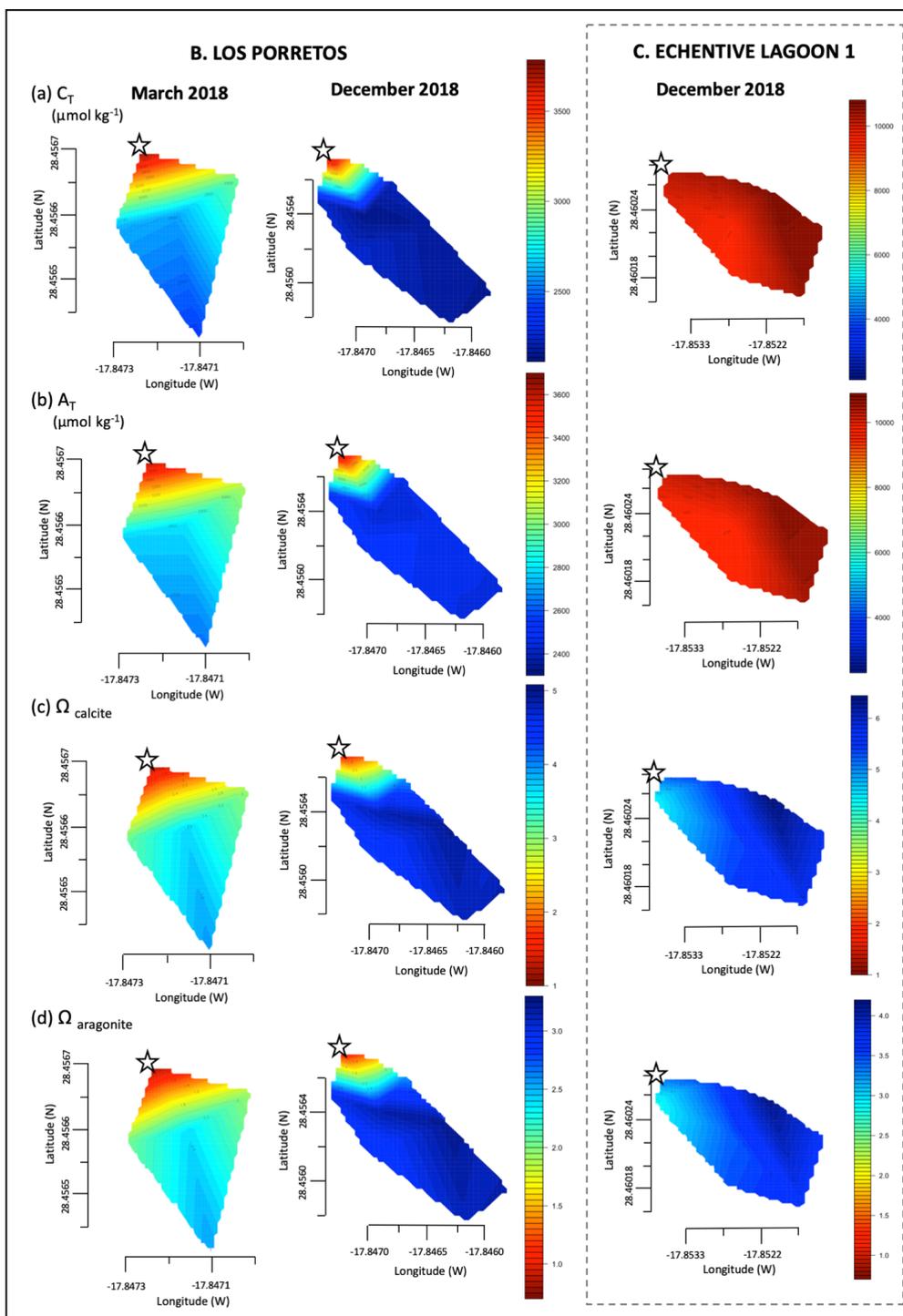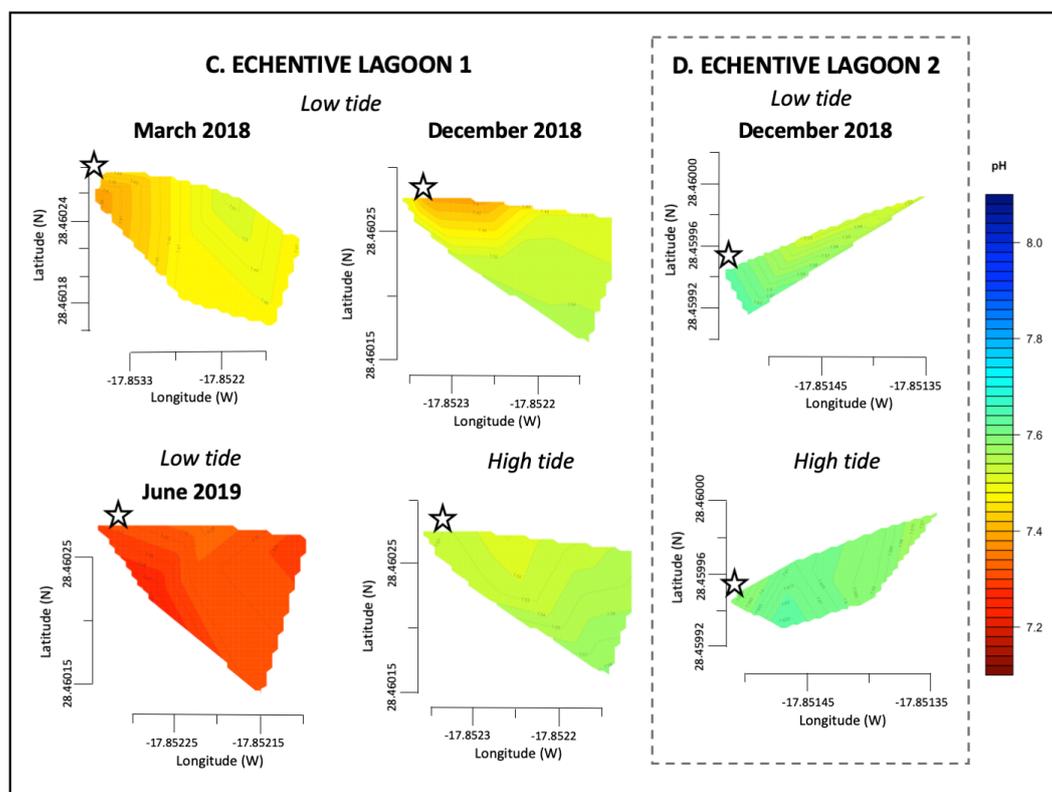
Figure 4: Linear interpolation graphs of C_T (a), A_T (b), Ω_{cal} (c) and Ω_{ara} (d) values during March 2018, and December 2018 during low and high tide in Los Porretos (B) and Echentive Lagoon 1 (C). The star symbol is the reference mark on the map in Figure 1c.

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3.2.3 Echentive lagoons

The two lagoons at Playa Nueva in Echentive (Fig. 1c) show the maximum anomalies in the south of La Palma. They presented low salinities and low pH, below 7.5 in all stations, and reaching 7.39 in the northwest during March 2018 (data from only the big lagoon) (Fig. 5). Similarly, the C_T was above 9700 µmol kg^{-1}, with comparable values for A_T (Fig. 4a, b). These C_T and A_T

170 concentration together with the low pH values counteracted the saturation states of calcite and aragonite that were, respectively, never below 4.6 and 2.9 (Fig. 4c, d). Furthermore, when both lagoons were sampled during December 2018, similar concentrations were measured at low and high tide (Fig. 5). The northwestern part of the big lagoon presented the highest C_T concentration (greater than 10000 µmol kg^{-1}) and the lowest pH reached 7.38 in low tide and 7.55 at high tide that coincided with a decrease in salinity and a mild temperature increase (Fig. 5, supplementary material 2). The rest of the big lagoon

175 remained at pH 7.58, similar to the small lagoon with a maximum pH of 7.63. However, the small lagoon presented a lower pH range, with a minimum of 7.50 in low tide and a maximum of 7.64 in high tide in the northern part (Fig. 5).

The water levels in both lagoons were tide dependent. The entry of salty marine water during high tide reduced the anomaly caused by the intrusion of lower salinity water rich in C_T and A_T.

180 **Figure 5: Linear interpolation graphs of pH during March 2018, December 2018 and June 2019 during low and high tide in Echentive Lagoon 1 (C) and Echentive Lagoon 2 (D). The star symbol is the reference mark on the map in Figure 1c.**

3.3 CO₂ flux calculation

The CO₂ flux was calculated for Playa del Faro. We assumed two end members, the open ocean endmember and an aquifer endmember. Soler (2007) discovered an aquifer near this area with brackish water (salinity = 30). Considering the bathymetry,

185 the volume occupied by seawater was 19700 m^3. We also assumed that groundwater discharge only occurred at low tide. The

average salinity changed from 36.927 (equivalent to 745.8 Tons of sea sat) at low tide to 37.019 at high tide (747.5 Tons of sea salt). The decrease in salinity at low tide could be accounted for by the emission of 57m^3 of brackish groundwater.

The brackish groundwater was also responsible for the A_T and C_T changes (Fig. 2a, b). Alkalinity increased by 219 µmol kg^{-1} from high tide (2465 µmol kg^{-1}) to low tide (2684 µmol kg^{-1}). Considering 57 m^3 of brackish water, 4.4 kmol of alkalinity was

190   required therefore the brackish groundwater had an A_T concentration of 76 mmol kg^{-1}. Similarly, the C_T in the beach increased by 333 µmol kg^{-1}, from high tide (2190 µmol kg^{-1}) to low tide (2523 µmol kg^{-1}). The brackish water was caused the increase of 6.7 kmol of inorganic carbon to the beach and therefore had an endmember concentration of 116 mmol kg^{-1}.

Considering the *in situ* temperature (20.67 ºC), the pH$_{T,is}$ decreased by 0.25 from 8.01 in hight tide to 7.76 in low tide. This meant that the acidity increased by 80%. This pH reduction meant that the water discharged on the beach had a pH of 5.57.

195   The medium partial pressure of carbon dioxide for the area increased from 459 µatm at high tide to a value of 988 µatm at low tide. Considering an average wind speed at the beach of 7 m s^{-1} (https://datosclima.es/Aemethistorico/Vientostad.php), La Playa del Faro acts as a strong source of CO_2, emitting 5.7 mmol CO_2 m^{-2} d^{-1} at high tide and increasing an order of magnitude at low tide (57 mmol CO_2 m^{-2}d^{-1}, Wanninkhof, 2014). Consequently, La Playa del Faro with its small area of only 0.01 km^2, is responsible for an atmospheric CO_2 emission flux varying between 2.8 kg CO_2 d^{-1} to 28 kg CO_2 d^{-1}.

200   **4 Discussion**

4.1 The origin of the CO₂ seeps

Our results reveal the influence of brackish water discharge in the acidification process of PFS (Fig. 7). Similar to aerial remnant volcanic activity in La Palma that generates high CO_2 atmospheric concentration (Padrón et al., 2015), submarine remnant volcanic activity causes the acidification process found here. This activity is comparable with other CO_2 vent systems

205   worldwide (references within González-Delgado and Hernández, 2018). Moreover, the presence of acidic water flow of La Palma has a greater resemblance with the acidification phenomenon found in Mexico, originating from a karstic groundwater discharge (Crook et al., 2012). Furthermore, the highly alkalized and bicarbonate waters found in Echentive lagoons are an artefact of water discharge from the hydrothermally affected aquifers of the area (Soler, 2007), as found in Las Cañadas del Teide, in Tenerife (another island of the same archipelago) (Marrero et al., 2008).

210   In PFS there is a decrease in salinity due to brackish water discharges. Hence, there is a constant filtration of brackish acidified waters through high permeable volcanic rocks (Carracedo et al., 2001, Marrero et al., 2008), with chemical features such as a 5.57 pH, a concentration of 76 mmol Kg^{-1} of A_T and 116 mmol Kg^{-1} of C_T. However, the effect on the surrounding seawaters depends upon tidal pressure and, more likely, other oceanic forces such as wind and waves (Moore, 2010; Mulligan et al., 2019).
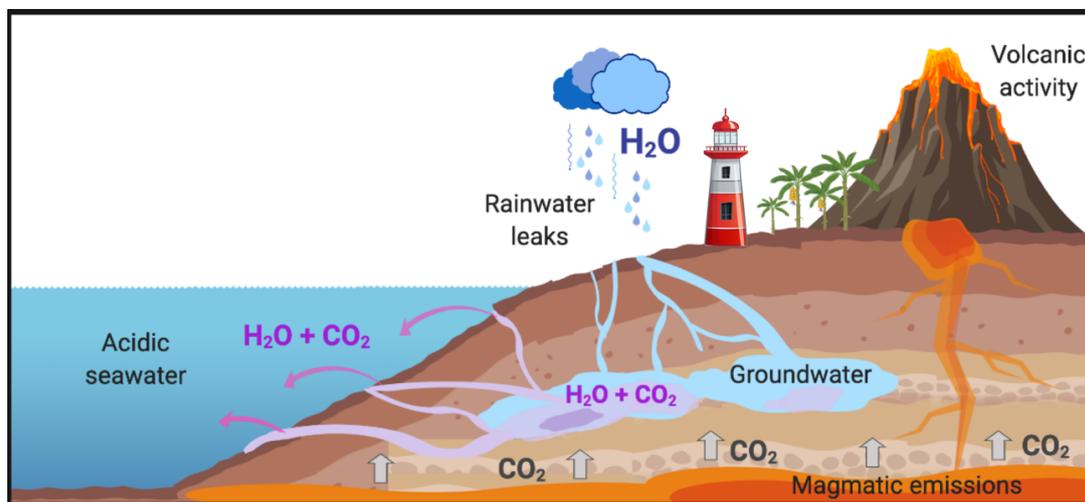
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Figure 7: Acidification process representation of Punta de Fuencaliente system (PFS) (made with Biorender).

4.2 Alteration of the carbon chemistry system and organism's assemblages

In the case of PFS, the water with lower salinity (36.79 - 36.45) and high concentration of C_T and A_T affect the surroundings,
220 decreasing the seawater pH up to 0.8 and reducing the carbonates saturation state up to 1.1 of calcite and 0.7 of aragonite. This
situation generates a carbon imbalance affecting carbonated organisms, especially those that precipitate aragonite on their
calcareous structures (Kroeker et al., 2010). When the saturation values are below one, the formation of carbonates is not
thermodynamically possible, although certain species require much higher saturation levels (Kroeker et al., 2010). The
calcifying organisms that could live in these acidified areas may present weaker shells, skeletons and/or others solid structures,
225 as we have recently observed in the mollusc *Phorcus sauciatus* (Viotti et al., 2019), as well as in the rest of calcifying organisms
(Pérez, 2017). This excess of CO_2 has also modified the community composition and trophic structure, causing a loss of
ecological and functional diversity on the benthic marine ecosystem (González-Delgado et al., in press).

In the case of Echentive lagoons, the anomaly is amplified due to a lower tidal influence and insulation. These acidified
lagoons, which are at around 100 m distance from the coast (Fig. 1), have a salinity of 32 and C_T and A_T concentrations 5 times
230 higher than normal ocean values. The C_T and A_T concentrations are so high that they compensate the decrease in pH with the
content of carbonates in the water. These singular characteristics create a unique marine ecosystem. The environment is
dominated by a biofilm of microorganisms predominantly microalgae, cyanobacteria and diatoms (Sangil et al., 2008), and
probably other bacteria and fungi. Nonetheless, some marine invertebrates persist, such as the common errant polychaete
Eurythoe complanata and the anemone *Actinia* sp. (Sangil et al., 2008). A more in-depth physiological study of these species
235 could help us to better understand their adaptation process to these conditions and to give insights of what we might expect in
future ocean acidification conditions, especially at the PFS area.

4.3 La Palma as a natural laboratory for marine research

The natural CO_2 gradients south of La Palma have been characterized from the shore to offshore, varying for C_T from 2128.7
to 3776.7 µmol kg^{-1}, for pH from 7.2 to 8.0, for Ωaragonite from 0.7 to 3.2 and Ωcalcite from 1.1 to almost 5. Which is similar
240 to other natural acidified systems worldwide (references within González-Delgado and Hernández, 2018). These chemical
features make PFS a very useful spot for large-scale and long-term adaptation experiments, where the natural CO_2 gradient
can be used as an analogue of climate change scenarios predicted by the IPCC (2019) (Fig. 8). Nevertheless, several caveats
for future prediction experiments should be considered.

First, there is a clear tidal influence, this is an important force that controls the acidified brackish water discharges. Although
a fluctuation of the emission is observed, normal ocean conditions can occur for a short time, about 2-4 hours per day, during
high tide, and depending on the oceanic conditions (Viotti et al., 2019). The $pH_{T,is}$ is severely affected by the location, reaching
down to ~7.2 in the emissions points, so a careful selection of the study sites is recommended, depending on the study
objectives (Fig. 8).

Second, there is an extra supply of different elements such us Mg that comes from groundwater (Soler, 2007). Magnesium
plays an important role in the calcification of marine organisms that have magnesite-calcite, such as echinoderms (Weber,
1969) and some bryozoans' species (Smith et al., 2006). Similarly, Hernández et al. (2016) found an increase in silicates in
the nearby area of Las Cabras. In these cases, Si could participate in the calcification of diatoms (Paasche, 1973) as well as in
many sponges (Smith et al., 2013). The increase of these essential elements for certain calcifying species can allow their
survival and growth in PFS while buffering the effects of acidification (Smith et al., 2016; Ma et al., 2009).

The high concentration of bicarbonate in the brackish waters also implies an extra contribution of alkalinity and carbonate that
can buffer the effect of acidification in the area, so it is necessary to take this into account when making predictions of the
future. These values together with calcium content are especially important factors in the case of the saturation state for both
calcite and aragonite, that shows high values for seawater with low pH values. Finally, only one type of rocky benthic habitat
is present at the PFS. Therefore, all conclusions derived from this acidified system should be interpreted with caution. Hence,
it is crucial to establish a collaborative network of researchers who are working in other natural acidified systems worldwide
to have a more realistic interpretation of future ocean scenarios.

The Echentive lagoons are an oversaturated carbonate system. Like hydrothermal alkalinity vents (Martin et al., 2008), it could
help us to understand the early life on Earth from the Precambrian, 4000 million years ago, when the atmosphere was rich in
CO_2 (Kasting, 1993; Nakamura and Kato, 2004) (Fig. 8). These studies could allow us to disentangled adaptation and evolution
of marine life to the changing carbonate conditions over time (Gattuso et al., 1998).

Additionally, and to our knowledge, it is the first time that a brackish water discharge altered by volcanic activity has been
studied. Each studied beach with a contribution of 150 tons of CO_2 per year becomes an important source of carbon into the
sea. Correspondingly, La Playa del Faro it is emitting 28 kg CO_2 d^{-1} in each tidal flow to the atmosphere. It may seem very
scarce compared to volcanic eruptions such as the most recent in the Canaries that occurred in the neighbouring island, El
Hierro, in 2010, which was emitting $6.0 \ 10^5 \pm 1.1 \ 10^5$ kg d^{-1} and now the emissions are unappreciated (Santana-Casiano et al.,
2016). However, the flux of CO_2 from La Palma island seems to have been started before the islands were conquered in 1493
(Soler, 2007), being in a more advanced degassing phase than el Hierro, with fewer emissions, but continued over time.
Therefore, if we consider its timescale, La Palma becomes a significant CO_2 source. For all these reasons, PFS and the lagoons
are an interesting area for future hydrological and oceanographic research, helping in new studies focusing on groundwater
fluxes, the oceanic water cycle and oceanic carbon fluctuation (Moore, 2010; Santana-Casiano et al., 2016; Mulligan et al.,
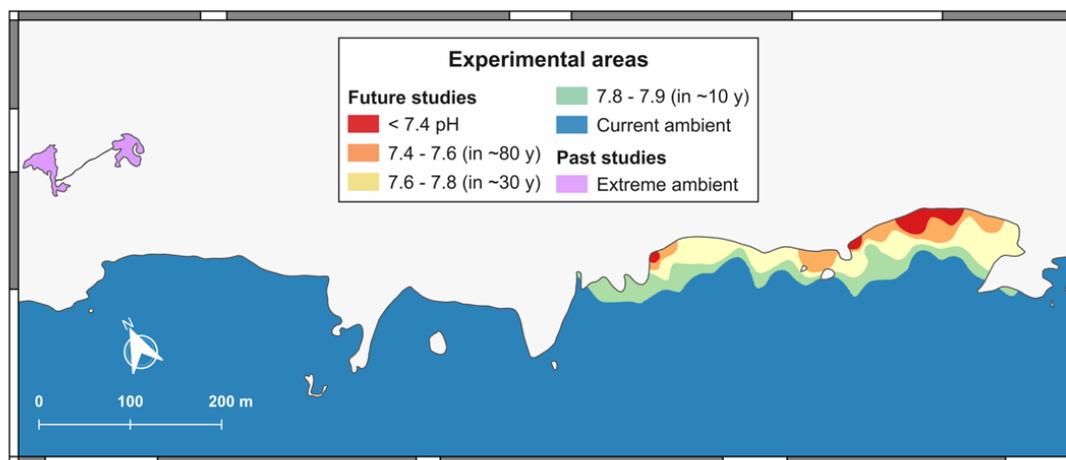2019).

Figure 8: Select areas for experimental propose (Interpolation IDW, 4.0 of correlation with Qgis).

5 Conclusions

280   The studies carried out show the existence of natural acidification in the southern coast of La Palma. This acidification process is caused by two natural phenomena: the discharge of submarine brackish waters from the aquifer and the magmatic emissions of CO_2 gas. Therefore, the monitoring of both sources is important not only from the biological point of view but also from an atmospheric, oceanographic, volcanologist and hydrological perspective. The emission found in Playa del Faro and Los Porretos (PFS) have similar chemical properties (even when alkalinity does not remain constant) that create a natural pH

285   gradient analogous to future oceans conditions. Consequently, they can be used as natural laboratories to predicts the effects of OA on the functioning of future oceans. The interior Echentive lagoons where the chemical alterations are intensified, present the conditions capable of disentangling how life has persisted during higher atmospheric CO_2 periods on planet Earth.

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Author contribution

295   Sampling and data analysis were performed by all authors. SGD and JCH lead the paper writing and all authors contributed to the interpretation of the results and writing.

Competing interests

The authors declare that they have no conflict of interest.

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