Biogeosciences

Ref. No.: bg-2020-232

Chemical characterization of Punta de Fuencaliente CO_2 seeps system (La Palma Island, NE Atlantic Ocean): a new natural laboratory for ocean acidification studies / Sara González-Delgado et al.

Responses to Peter Landschützer:

Comment: *"Dear authors, many thanks for responding to the referee comments. As you can see, the referee recommendations range from minor revisions to rejection. Overall, I decided that major revisions are necessary before the manuscript can be considered for publication. There are 2 major comments in particular that I am concerned about and that have been raised by multiple referees: 1) The novelty of the study and 2) the suitability of the study site as a natural laboratory. From your response(s) regarding point 1) I read that while some of the sites have been investigated in the peer-reviewed literature, your study provides new data from these sites plus additional sites that have not been investigated yet. Likewise from your response(s) regarding point 2) I read that you e.g. see some analogues to conditions described in future projections. In both cases I would advice you to make these points much clearer in the text, better link to existing studies that were conducted at the same sites (even though with other data) and give these other studies appropriate credit and be more precise about where you see the analogues and under what conditions/scenarios these analogues may emerge. I would also like to note that I intend to send the revised manuscript back to the same referees for their evaluation".*

- Response: Thank you very much for your comments. We have made the modification following your recommendations. We are submitting the manuscript with the clean version, including all the changes. Number of lines bellow refers to the clean version of the manuscript. Regarding the novelty of the study - point 1, we have included more details in Lines 57 – 60, 91 – 94 and 128 – 130. We have described in more detail the previous studies done in the area to avoid any confusion with the usage of data; and to highlight the novelty of the our work. We would like to remark that no previous work has used the data we are presenting in this work.

About the suitability of the study area as a natural laboratory - point 2, we have explained it better in Lines 252 – 257 and 258 – 262 and we have also want to highlight figure 6 which better show the location of the emission points, and where the different future pH scenarios can be found. This map can be very useful for researchers interested in performing their experiments in Fuencaliente (La Palma island).

We would like to highlight that all the reviewers comments have also been considered and most of them included. For more details please read our responses to each of the reviewers.
We really appreciate your time and recommendations to improve our work, and we believe that now we are presenting a more robust study that will be very interesting for Biogeoscience´s readers.
Thanks again for this opportunity.

Ref. No.: bg-2020-232 RC1

Referee #1

Thank you for your revision of our manuscript. Your comments have been essential in guiding our revision and we hope that we have satisfactorily dealt with the errors and clarify any point that were originally confusing. We very much appreciate your effort in refining our research and to improve our text. We also thanks that you have found the subject of the review manuscript interesting, as you state: "*This study provides a novel and comprehensive description of a location resembling future water chemistry conditions, as expected under ocean acidification scenarios. The authors provide a valuable dataset of measured and estimated parameters in seven sites, along the south of La Palma island, located in the North Atlantic Ocean. It is very interesting the explanation the authors provided about the origin/source of these acidified waters, also the discussion of the community assemblages inside the lagoons, where conditions behave different from coastal waters.*"

Responses to Referee's comments:

SPECIFIC COMMENTS (individual scientific questions/issues)

Referee #1; **comment 2**: *"Abstract: in the same way the authors presented the CO2 emission flux range in this section, it is advised to include the general range of measured and calculated parameters. This provides the reader with a general overview of the chemistry conditions in this location. - Please specify whether omega aragonite and calcite were measured or calculated."*

- Response: We agree with the comment and we have made the changes. Please see sentences between Line 18 and 21.

Referee #1; **comment 3:** *"Keywords: consider removing the word "area". Also, including the word "groundwater" to the list."*

- Response: We agree with you and we have made the changes. Check Line 28.

Referee #1; **comment 4:** "*Material and methods:- Was the VINDTA a 3C? If yes, please specify. - Authors are advice to include further details regarding water sampling and handling: sampling procedure (Niskin, SCUBA, etc), sampling containers for AT, CT and salinity (type of bottles), total number of samples (N per site, period, etc, consider present a summary of this information in a table as Supplementary material), samples fixed with HgCl2?, storing conditions. - There is no mentioned in this section of how they obtained the atmospheric CO2 values. This should be clarified.*"

- Response: We agree with your comments and we have added more details about the sampling and handling methods. Please go to Lines 105 - 109 and Lines 113 -115, 119 and Lines 123 - 124. Also, we now include a table with your suggestion (please see appendix A).

Referee #1; **comment 5:** "*Results: - The authors indicated they found important differences between tides. This is an important finding, in agreement with results previously reported by Manzello (2010) in a shallow tropical coral reef, therefore, the authors could include an additional graphic representation of it as supplementary material (box plot, scatter plot or other). – The authors indicated that "Los Potreros, is a continuation of Playa del Faro", however, according to Fig.1 Los Barqueros is located between these locations.*"

- **Response**: We agree with your suggestion and we have included a line graph with the tidal fluctuation of the minimum pH (see appendix B). We apologize for the confusion between "Los Porretos" and "Los Barqueros" both are the same site. We have made the correction in Figure 1.

Referee #1; **comment 6:** *" Figures: - It's unclear, what it is the purpose of the dashed-line square in the figures? In Figs.2, 4, 5 is used as division for different sites but in Fig. 3 represents a tide difference. The authors should try to standardize the use of this element among all figures and also be clearly indicated in the caption. - Fig.1: caption must include a description of the figures in each panel. - Fig.1: in order to facilitate reader's interpretation, ID letters from panel b and c should coincide. Currently, there is no clear whether the authors tried to make these panels complement of each other. For example, when interpreting the left map from panel c based in color/letter code (using yellow mark as reference to Playa Echentive), it seems there is a mixed up (the stars should be Lagoon1 and Lagoon 2, but currently are marked as Playa del Faro + Lagoon 2). Authors should carefully review the ID letters/colors from panels b and c. Another suggestion it's to merge both legends, by including the color code next to the letter in the legend* *from panel b. - Fig.1, Fig.5: it's unclear to which sampling period corresponds the panel "High tide". The authors should consider including tide initials (LT, HT) in all the panels/figures, maybe next to the sampling period title, and indicate it in the caption description. - Fig4: low and high tide labels are missing in the figure panels. - I would rather to see the order of the figures arranged by parameters. For example, move up Fig.5 after Fig.2, so all pH figures are shown together. This would facilitate following the figures, specially considering that arrangement per site does not follow the same order in all figures (Fig. 2 = Playa del Faro + Los Potreros but Fig. 3 = Los Potreros + Echentive Laggon 1, etc). - Fig. 8: caption requires minor modifications. "Selected" instead of "Select" and "Purpose" or "proposal" instead of "purpose".*

- **Response**: We agree with your comment and we hope that we have satisfactorily clarify this confusion. Figure 1 has been modified; the identification letters now match between panel a and b, and high and low tide are marked as HT and LT respectively. Figures 2, 3 and 4 have been modified in line with your comments: now Figure 2 has all pH interpolation graph. In Figures 3 and 4 we have added the initials LT and HT in the titles of each graph. Also, the dashed line has only one purpose, to separate each sampling site. Finally, we have corrected the caption of Figure 8 in Line 293.

TYPING ERRORS, ETC.

Referee #1; **comment 7:** *"General: values <10 must be written in letters. - Line 20: start new sentence with "This". - Line 30: move "Since the last decade" to the beginning of the paragraph. Otherwise, it seems that you are referring to the effects exclusively taking place during the last decade. - Paragraph 50: replace "are" by a "," and move "are" in front of "an oceanic". - Paragraph 55: add "," before "which". - Paragraph 70: last sentence, add "," before "what", and close the sentence with "?". - Paragraph 80: "were" instead of "where". - Study area: figures within the text are not mentioned in sequential order (1c comes prior 1b). Authors must either a) modify the order of the sentences in the text or b) exchange the panels order in the figure (swap 1b by 1c). - Line 100: "culometric" is missing an "o" after the "c" (typo). Tittle of Dickson's manual is incorrect. – Paragraph 105: remove "with" after "data using". - Paragraph 115: "during the last eruption" instead of "of the last eruption". - Paragraph 130, 240: use the same amount of decimal positions when reporting values (pH 8.0, omega calcite 5.0). - Paragraph 160: add "up" before "to". - Paragraph 165: "data only from" instead of "data from only". – Paragraph 190: add "," after "therefore". Remove "was" after "water"? - Paragraph 230: replace "a" by "an" before "unique". - Paragraph 240: remove "the" before "shore". – Paragraph 285: remove "s" in "predicts".*

- **Response**: We thank you very much for providing these text corrections. We have corrected the errors in Lines 22, 31, 51, 58, 77 - 78, 83, 92 – 96, 113, 115, 117, 121, 130, 136 – 253, 171, 174, 204, 205, 244 - 245, 252, 300.

Ref. No.: bg-2020-232 RC2

Referee #2

Thank you for reviewing our manuscript, we really appreciate your effort in refining our research. Your comments have been very constructive and help us to improve our research. We hope that we have satisfactorily dealt with the original confusing points. We also thanks that you have found our data worth publishing, even though there was a misunderstanding, caused by some typing errors and confusion in the figures.

Responses to Referee's comments:

Referee #2; **comment 1**: "*The Authors performed some measurements of the seawater carbonate chemistry around Punta de Fuencalente CO2 seeps. It focused on the role of groundwater discharge in the acidification of the local beaches. The aim was to describe a new natural analogue to study future (and past) conditions. While the description of such a system is welcome as each extreme site could add insight toward a better understanding of the mechanisms involved in the stress response, this system is far to be a natural analogue to study the effect of OA. With this in mind, I suggest the Authors to revise the ms according to what they recognised to be central in their study (L 273), and improve the methods description, figure legends, which make this ms hard to be follow. However, I think the data are good and merit to be published.*"

- **Response**: We disagree with "this system is far from being a natural analogue for studying the effect of OA", as we have shown in this manuscript, this Fuencaliente area is acidified due to the volcanic activity which is altering the groundwater that is continuously being discharged into the shore. Please note that being "analogue" is not the same as being "equal", we consider La Palma system an "analogue" and similar to other natural analogues, such as Ischia seeps system, Papua New Guinea CO_2 vents or Puerto Morelos acidify system. All of them are special places because they present pH and pCO_2 values similar to future IPCC predictions, as we have demonstrated for La Palma seeps system, and despite the anomalies that all of these natural systems present (see Table 2 from González-Delgado and Hernández, 2018). On the other hand, regarding the description of the methods as well as the legend of the figure, we have followed your recommendations and those of the Referee #1 and have made the appropriated changes to better explain these sections.

Referee #2; **comment 2**: *" I do not understand the sentence in L 20. Both CO2 seeps and acid brackish water contribute to change the seawater chemistry! Wow! Authors should be more cautious about certain ideas.*"

- Response: We agree with you and we have changed the sentence for better understanding (see Line 22 - 23). In this manuscript, we have demonstrated that volcanic CO_2 emissions alter the brackish groundwater that is discharged into the coast of La Palma, changing the chemistry of the water (see Figure 5 for understand the process and Figure 2 to 4 for the data).

Referee #2; **comment 3**: *"It is hard to think that these kind of systems could be used to understand how life persisted through past Eras. Ok for potential future scenarios, but with several assumptions..*"

- Response: We disagree with the comment in general. As we have already mentioned in the manuscript, within La Palma system we have found a very extreme environment in the Echentive lagoons. These extreme chemical characteristics (for example, Ct values of 10817.12 µmol kg-1 and pH of 7.12 unit) could be used to understand how life has persisted in these extreme conditions, similar to Rio Tinto in Spain or the hot springs in Yellowstone. The study of the extremophiles organisms that live there can help us to understand how was the beginning of life on earth. We believe this is an interesting research topic and worth to mention in the manuscript.

Referee #2; **comment 4**: *"L 31 and 34. The best references for this general sentence are Hall-Spencer et al 2008 and Dando et al 1999 respectively. Note for the Authors. It would be great to see here the relevant literature instead of Gonzales-Delgado and Hernandez 2018 only. For instance, Vizzini et al 2016, Pichler et al 2019 should be cited with regard to the potential biases of trace elements at seeps."*

- Response: We agree with your suggestion and we have included more relevant literature. Please go to Lines 32-33, 36, 39, 47-48.

Referee #2; **comment 5**: *"L 64-68. This part is not clear. It suggests that the lagoons receive fresh inland ground water and a slight dilution of the seawater in the lagoons, so it receive water from both. Then the author state that "this indicate that the system is affected by the submarine groundwater, which probably originate from the thermal waters". What exactly the Authors want to say? And, without the data found (we are in the introduction) is it quite speculative, isn't it?"*

- Response: We agree that it is possible to clarify this part. In this section, we try to explain that there is a mixture of seawater with brackish groundwater in the Echentive Lagoons and there are previous evidences of this finding since Soler (2007) and Calvet et al., (2003) studies. We apologize for the confusion and we have made the changes to Line 69 - 70.

Referee #2; **comment 6**: "*L 65. "there are brackish lagoon located .. about 22m from the coastline", actually within 50 m in Fig. 1, and 100 m in L 229."*

- Response: We agree that there was a problem in figure 1 and in the text and we have changed both (see Figure 1 and Line 243). Line 68 is the correct one "...at about 200 m from...".

Referee #2; **comment 7**: *"Methods. This section needs to be deeply improved. The sampling methods and analyses need to be described."*

- Response: We agree with your comments and we have added more details about sampling and handling methods following your comment and those of Referee #1. Please go to Line 92 - 124.

Referee #2; **comment 8**: **"***Fig. 1. I understand that panel left in c represents the lagoon, but what about panel right? The legend should contain more details and the figure should be self-explained. What is the role of the two identical stars in panel right which are repeated in fig 2 in all the sites? Are the figures with colour? It is difficult to read the pH etc. Nice work putting lat & long but meters would be better to directly appreciate the extension of the area."*

- Response: We agree that the caption figures needed more details and we made the modifications accordingly (see Line 97 - 102 and Line 184 - 193). We believe that now the figures are self-explanatory. The stars was included to better interpret and locate the interpolation graphics from Figure 2 - 4. All the figures have vivid colors for a better interpretation of the elements. For the interpolations graphs, it is possible to see the anomaly using a color gradient from red to blue. We have corrected some errors in the legend and scales of some panels in Figure 1. Now, you can see the extension of the affected area in meters (see Figure 1).

Referee #2; **comment 9**: *"Authors wrote that sampling were performed between 0 and 2 m depth (need details in the methods). Is the sites so shallow everywhere? Considering the 2 m oscillation in the tide, why the Authors only sampled the intertidal zone?"*

- Response: We agree with your comments and we have further explained the sampling process (please see Line 104 - 108). In figure 1 you can see that we took samples from the shore up to 50 m inland (and one control point up to 200 m). Scuba dive was used to take the water samples with the bottles between 0 and 2 m depth. This samples were taken in the beach, no at the intertidal zone.

Referee #2; **comment 10**: *"Fig. 1 vs results. Well it is hard. Ok, sites Playa del Faro, Los Porretos, Lagoon 1 and 2 (also Enchentive, called Playa Echentive in Fig 1 table b); Las Cabras?? Last eruption was in the 17th century? L 116. "In all cases, the anomalies were the highest during low tide." Please change the word anomalies. So what? Where are the seeps? On the beach? Their extensions? Their depth? Salinity was 31 in the lagoons and normal near the coast. These measurements did not suggest any link between lagoon and the beach. So, L 127-128 how the Authors can state that the SW carbonate chemistry was strongly affected by the entrance of water with less salinity?"*

- Response: Previous figures have been improved to avoid misunderstanding regarding the location of the samples and the anomalies. The errors you highlighted have been corrected (please see Figures 1, 2, 3 and 4). Playa Echentive and Echentive lagoons are two different sampling sites and we have corrected it on the figures and on the text. Las Cabras, as explained in the manuscript in Lines 59 - 60, is a CO_2 seep recently described by Hernández et al., 2016, and it was sampled again for us (see Line 92 - 104 and Figure 1). However, as we already explained in the manuscript, "*Las Cabras site was 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)"*. Furthermore, as it explained in the manuscript "*These four areas, Las Cabras, La Playa del Faro, Los Porretos and the two Echentive Lagoons (Fig. 1b,c), correspond to areas that were not buried by the lava during the last eruption (Teneguía volcano 1971; Padrón et al., 2015, Fig. 1b)"*, so the last eruption was in the 20th century.

We do not understand why we might have to change the word "anomalies". Anomaly means " *a…thing that is different from what is usual…"* (Cambridge Dictionary). So, we think that it is a good word to use when the salinity, pH, pCO_2, C_T, A_T, $\Omega_{calcite}$ and $\Omega_{aragonite}$ exceed the normal values for seawater; as it happens in the seeps found in the beaches of Las Cabras, La Playa del Faro, Los Porretos and the two Echentive Lagoons (please see Figure 2, 3 and 4 and supplementary material 3). With regard to salinity, the lowest values found in the Echentive lagoon are 31 - 32 units of salinity. However, it has also been detected, as it been said in the manuscript *"... slightly less saline water near the coast."* with value of 36.51 – 36. 07 during low tide (see supplementary material 2). It can be thought that this is a normal value of salinity, nonetheless we see that, during the high tide and in the control areas, the salinity is always higher (37.05 units) (please see supplementary material 2). For this reason, we disagree with the last sentence of your comment and we want to remark that *"…the entrance of water with less salinity"* with very extreme values of pH, pCO_2, C_T, A_T, $\Omega_{calcite}$ and $\Omega_{aragonite}$ near the coast, especially during low tide in Playa del Faro and Los Porretos exist and strongly change the chemistry of seawater. All our results demonstrated this fact (see Figure 2, 3, 4 and appendix A, supplementary material 2).

Referee #2; **comment 12**: *"L 141. "During high tide, the anomalies almost disappeared.." which support the hypothesis about the role of the lagoon in the local beach acidification. But, if they exist, what about the CO2 seeps it was supposed to acidify the area? Fig. 7 the figure is fairly useless and does not describe the role of the lagoons."*

- Response: Again, we believe there is a misunderstanding. At no point we have suggested that the lagoons play a role in the acidification of beaches. Our hypothesis would be, as it been said in the manuscript, *"….what occurs in areas where SGD is enriched by the emissions of recent volcanism or by hydrothermal activity?... these discharges can also act as sources of gases and hydrothermal emission compounds to the ocean and become points of emission of CO2 that contribute to the OA*". Therefore, what we have defended in this paper is that a source of brackish groundwater that is affected by volcanic emissions, seeps through the soil and rocks into the sea (see Figure 5). On the way, it accumulates forming the Echentive lagoons where it mixes with seawater. The old Figure 7, now Figure 5 shows us a drawing of the process of acidification of the beaches. It seems clear then that CO_2 gases, from volcanic activity, are mixing with brackish groundwater that are discharged o seeped in the coast through the rock porosity.

Referee #2; **comment 13**: "*L. 202. PFS. Please just write the location."*

- Response: We agree with the comment and made the change in Line 216.

Referee #2; **comment 14**: "*L. 205. I agree with the fact that this system is similar to the Ojos in Mexico. The latter has been a highly debated "natural analogue" to future conditions since the groundwater discharge profoundly change the seawater chemistry and do not mimic what we should expect in the future. CO2 seeps are more "realistic" in some ways and with limitations. I invite the Authors to pay attention about this potential caveat when using the PFS as a natural lab to study the effect of ocean acidification."*

- Response: We agree that CO_2 seep can be more "realistic" than the Ojos system in Mexico when studying the effect of ocean acidification. Nevertheless, as we have emphasized in the manuscript and throughout the responses to your comments, PFS can be considered a CO_2 seep system, because the CO_2 emissions that altered the groundwater comes from volcanic activity. The PFS clearly mimic what we should expect in the future, as it has been demonstrated with our study. To improve this interpretation, we have made changes to Lines 220 and 226. We also wants to clarify, again, that we have pay attention to potential caveat and it have been highlighted in the manuscript (please go to Line 256 to 276). Therefore, and although not perfect (as the rest of the natural acidified systems already described), PFS is an analogue of future oceans and it can be used to understand the impact of OA on marine organism or ecosystem functioning.

Referee #2; **comment 15**: "*Paragraph 4.3. Sorry but La Palma is not similar to other natural acidified systems, and I do not believe it is a very useful spot for large-scale long-term adaptation experiments: : :to be used as an analogue of climate change scenarios. Please, be objectives. For instance, although the data are nice and I understand the effort put in such a sampling, from this data set it is not clear what is the real variability in time and space (L 238: PFS have been characterized from the shore to offshore.. is not really true, at least from what I understood by reading the few details given in the methods). The Authors suggested some of these caveats in the 20 lines from L244, which is good.* "

- Response: We think that you have misinterpreted our work, possibly because of some errors found in the previous version of the manuscript, that have led to several confusions when interpreting the results. The lack of some details in the methodology or the figures did not help either. We hope that now our clarifications may help you to have a better interpretation of our work.

Referee #2; **comment 16**: *"In the discussion (paragraph 4.2) some speculative observations about the community are described. It is complicate to appreciate the site as a natural lab with only such a scarce description of the biota. Then, L 259 the Authors added this sentence: "only one type of rocky benthic habitat is present.." Well, we know that OA will affect the marine organisms (maybe) but I think this is too much! Maybe there are some caveats in using this interesting site as a natural analogue. The last sentence (L 273) is, in my opinion the best one describing the aim of this study. I invite the Authors to revise the paper in the direction they finally described. Conclusions. I disagree with most of its content."*

- Response: In section 4.2, we consider that we have not made any "speculative observations". It is true that there is little description of the biota, yet we consider this work to be purely about the chemical and physical characteristics of the area. We are in the process of publishing another manuscript with a detailed description of the flora and fauna from the PFS. Therefore, in the old

Line 259 there was another misunderstanding, so that this will not happen again, we have made the corresponding changes and added the missing reference (see Line 273). When we say that "*only a type of rocky benthic habitat is present*", we refer in a general sense to the typical habitat found in the south of La Palma Island, not to the marine communities presents.

Ref. No.: bg-2020-232 RC3

Referee #3

Thank you for the review our manuscript and for your comments and constructive criticism. We have considered them and add more information to clarify the confusing points.

Responses to Referee's comments:

Referee #3; **comment 1**: "*The authors describe the chemistry of a "new" CO2 vent system. Due to the extreme variability at all sites and the change in alkalinity, the relevance of these sites as a laboratory for future ocean acidification seems limited. Most of the locations seems to have already been described in previous publications. Perhaps the only new location is the lagoon site but its use as a natural analogue for past and future oceans is questionable due to the addition of brackish and groundwater. The other locations were already reported, following the nomenclature in Figure 1:*

** site H is reported in Hernández, C. A., C. Sangil, and J. C. Hernández. 'A New CO2 Vent for the Study of Ocean Acidification in the Atlantic'. Marine Pollution Bulletin 109, no. 1 (15 August 2016): 419–26. https://doi.org/10.1016/j.marpolbul.2016.05.040.*

** Site A, B are reported in Viotti, Sofía, Carlos Sangil, Celso Agustín Hernández, and José Carlos Hernández. 'Effects of Long-Term Exposure to Reduced PH Conditions on the Shell and Survival of an Intertidal Gastropod'. Marine Environmental Research 152 (1 December 2019): 104789. https://doi.org/10.1016/j.marenvres.2019.104789.*

** E,F,G data are not reported in this manuscript as far as I can see. As it is not evident what data is novel, please clearly state what part of the data is unpublished and novel data and which one is not. Also please clearly highligt what does the additional chemistry data add to the previously published studies. At the moment I have difficulties in recommending this manuscript for publication.*"

- Response: We agree with you that there is some caveats in these type of natural acidified system, however these cavities exists in all of the already described systems. We recommend you to see the Table 2 of our review paper (González-Delgado and Hernández 2018 - Advances in Marine Biology) where we do a comparison between natural acidified systems worldwide. Although, not perfect, these systems with their cavities are very useful to study the impact of OA on marine organisms and its capacity of adaptation, among other things. And, are by far more realistic than OA *in vitro* experiments. Therefore, we do not agree with you and these systems can be considered natural analogues of future oceans.

It is true that site H (Las Cabras), as well as, sites B and C (Playa del Faro and Los Porretos) have been previously reported. However, this study is the first detailed chemical characterization of the whole area and include new seeps (Echentive Lagune and Los Porretos). For the present study, we include data that have not been used before and that have been collected on the long-term and in a larger scale. Additionally, for this study pH, pCO_2, temperature, alkalinity and salinity have been measured accurately using proper apparatus (e.g. VINDTA 3C for alkalinity).

Therefore, we consider to be a novelty:

(1) The precise chemical description of this acidified system composed of several CO_2 seep points and, as you said, the description of the Echentive Lagoons (F and G).
(2) All the data presented, and its spatial and temporal variability.
(3) And the description of the process of acidification of the coastal area of Fuencaliente (Origin of the seeps).

We would like to clarify, again, that all the measurements in this work (see supplementary material 2) are unpublished data. And we believe that we have not at anywhere in the text given any indication to the contrary. It is true that there are pH and pCO_2 measurements at Las Cabras and La Playa del Faro in the previous two papers. We have included this information in Lines 60 and 94. However, these measurements were made at another time and with a different, less precise, methodology and only at the sampling points.

Sara González Delgado
Universidad de La Laguna, Tenerife, Canary Islands, Spain

Chemical characterization of Punta de Fuencaliente CO_2 seeps system (La Palma Island, NE Atlantic Ocean): a new natural laboratory for ocean acidification studies

Sara González-Delgado[1], David González-Santana[2,3], Magdalena Santana-Casiano[2], Melchor González-Dávila[2], Celso A. Hernández[1], Carlos Sangil[1], José Carlos Hernández[1].

[1] Departamento de Biología Animal, Edafología y Geología, Facultad de Ciencias, Universidad de La Laguna, Canary Islands, Spain.
[2] Instituto de Oceanografía y Cambio Global, IOCAG-ULPGC. Universidad de Las Palmas de Gran Canaria, Canary Islands, Spain.
[3] Univ Brest, CNRS, IRD, Ifremer, LEMAR, F-29280 Plouzane, France.

Corresponding author: Sara González-Delgado (sgonzald@ull.edu.es)

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, and calculating Ω aragonite and calcite. Our explorations on the area have found several emission points with similar chemical features. Here, the C_T varies from 2120.10 to 10784.84 µmol kg-1, A_T from 2415.20 to 10817.12 µmol kg-1, pH from 7.12 to 8.07, Ω aragonite from 0.71 to 4.15 and Ω calcite from 1.09 to 6.49 units. Also, 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. These CO_2 emissions, which are of volcanic origin, acidify the brackish groundwater that is discharged into the coast and alter the local seawater chemistry. 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.

Eliminado: as well as,

Eliminado: seeps

Eliminado: and the alteration of local ocean chemistry is due to acid …

Eliminado: s

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

Eliminado: area

1 Introduction

Since the last decade, 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 (IPCC, 2014; Hall-Spencer et al., 2008; Foo et al., 2018; 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 (Dando et al., 1999; 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).

Eliminado: M

Eliminado: since the last decade

Numerous advances in OA studies have been achieved using these systems, such as acidification effect on ecology interaction (ej. Nagelkerken et al., 2016), physiological (ej. Migliaccio et al., 2019) and genetic adaptations (ej. Olivé et al., 2017). 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-

Eliminado: Foo et al., 2018; González-Delgado and Hernández, 2018)…

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 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 undesired gases or metals have had an insignificant effect on the studies performed in these areas (Boatta et al., 2013; Vizzini et al., 2013; Agostini et al., 2015; Pichler et al., 2019). 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, are an oceanic volcanic archipelago formed by numerous 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 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). However, in these works only the pH and pCO_2 were measured, in localised points where certain samples were taken.

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 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 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 brackish groundwater flowing into it. This indicates that in the system there are groundwater discharges, which probably comes from the thermal waters studied by Soler, (2007).

In the last two decades, an increasing number of studies underlined the importance of submarine groundwater discharges (SGD) (Jeandel, 2016). SGD is an essential 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?. 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.

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 were (1) determining the area affected by

Eliminado: González-Delgado and Hernández, 2018

Con formato: Subíndice

Eliminado: is affected by the submarine

Eliminado: (SGD),

Eliminado: originate

Eliminado: (

Eliminado: ,

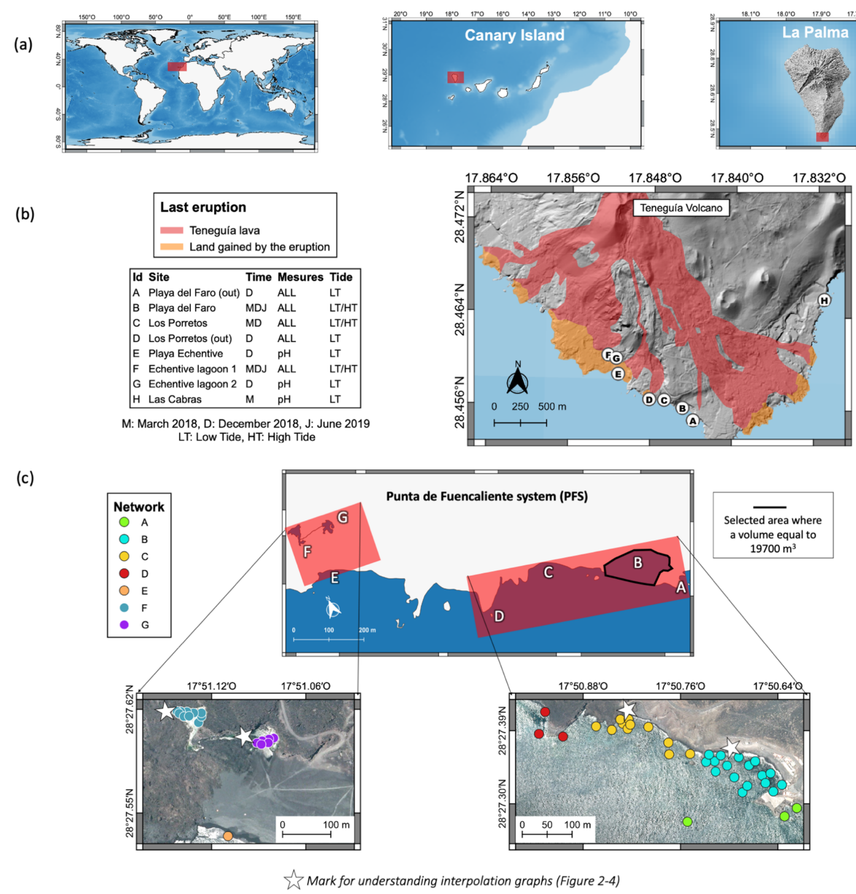
Eliminado: h

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). 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, appendix A). 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 for the first time. It is formed by seven sites: Playa del Faro, Los Porretos and surroundings (that together with Las Cabras site, they are known as Punta de Fuencaliente system or PFS), Playa Echentive and the two Echentive lagoons (Fig. 1c).



Movido (inserción)[1]

Eliminado: ,

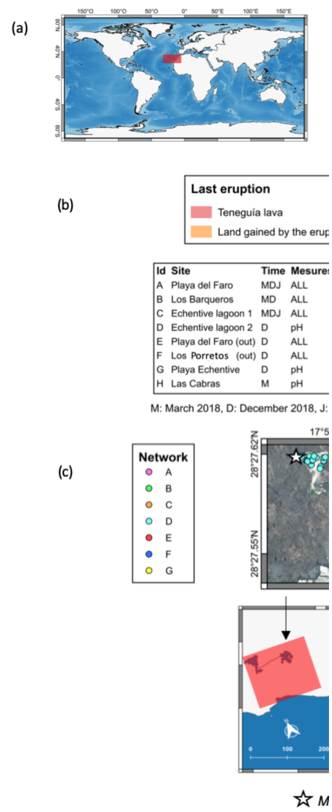
Eliminado:

Eliminado: 7

Eliminado: the

Eliminado: de

Movido hacia arriba[1]: 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).



Eliminado:

Con formato: Centrado

Figure 1: (a) Location of study are on North-Eastern Atlantic Ocean, in the west of the Canary Island, in the South of La Palma Island. (b) Location of the seven sampling sites (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 area covered by the last volcanic eruption, Teneguía volcano, is also indicated. (c) Location of sampling network performed in this work around the Punta de Fuencaliente system (PFS) and the selected area where the volume was calculated to CO2 flux calculation. The stars are included as a help to better interpret and locate the interpolation graphics from Figure 2-4. The map and image base layers used are distributed under public domain (https://www.grafcan.es/).

Scuba diving was used for sampling all bottles unless the reference station out of Playa del Faro (Fig. 1c A) where a CTD rosette was used. For the scuba sampling, the bottle was previously rinsed three times at the sampling location and then the bottle was immersed with the mouth down and turned at 1 m depth for sampling. Samples were poisoned with 100 µl of saturated $HgCl_2$ solution, sealed, kept at darkness, and analysed on the lab. In March 2018 this was done the same day while in December it was done two days later. For pH 100 ml borosilicate glass bottles were filled with seawater.

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 respectively determined by potentiometric and coulometric methods, using a VINDTA3C 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 thank to a thermostated at 25 °C in less than one hour, 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 Guide to best practices for ocean CO_2 measurements (Dickson et al., 2007, SOP 6a). Salinity and temperature were measured *in situ* using a handheld conductivity meter (Hanna Instruments HI98192). Furthermore, 200 ml salinity bottles were measured on the laboratory in less than two days an 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 the CO2sys program (Pierrot et al., 2006).

Atmospheric CO2 concentrations used for fluxes calculations were those measured at the Izaña station at the island of Tenerife (IZO site and available in the World Data Centre for Greenhouse Gases).

We used the linear interpolation method to represents the A_T, C_T, $pH_{T,is}$, Ω aragonite and calcite parameters measurement when 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 (both first measured by Hérnandez et al., 2016, and Pérez, 2017 and Viotti et al. 2019, respectively), Los Porretos and the two Echentive Lagoons (Fig. 1b,c), correspond to areas that were not buried by the lava during the last eruption (Teneguía volcano 1971; Padrón et al., 2015, Fig. 1b). Las Cabras site was 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 (appendix B).

3.1 Temperature and salinity

Eliminado: sampling network performed in this work around the 7…

Eliminado: areas

Con formato: Color de fuente: Texto 1

Con formato: Fuente: 10 pto, Color de fuente: Texto 1, Inglés (británico)

Con formato: Color de fuente: Texto 1

Con formato: Color de fuente: Texto 1, Subíndice

Con formato: Color de fuente: Texto 1

Con formato: Fuente: Sin Negrita

Eliminado:

Eliminado: of

Eliminado: the manual Good Measurement Practices of the Carbon Dioxide System in the oceans

Eliminado: the

Eliminado: as also

Eliminado: i

Eliminado: with

Eliminado: of

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 19.00 ± 0.20 ºC with colder values of 18.70 ºC near shore, Los Porretos was not measured this time. In December 2018, both Playa del Faro and Los Porretos presented an average temperature of 21.50 ± 0.02 ºC. 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 31.00 to 32.00 units (supplementary material 2). The same lagoon presented warmer temperatures than the coastal waters during June 2019, 26.40 ± 0.70 ºC and 22.00 ± 0.10 ºC, 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. 2A, B), A_T, C_T and Ω aragonite and calcite (Fig. 3, 4B) were strongly affected by the entrance of water with less salinity.

3.2.1 Playa del Faro

In March 2018, the pH changed from 8.06 in offshore samples to 7.50 nearshore, reaching 7.16 and 7.13 during December 2018 and June 2019, respectively (Fig. 2A). 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 2132.13 µmol kg^{-1} and 2418.38 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 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 1.50 (Fig. 3c, d).

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 2692.13 and 2512.35 µmol kg^{-1}, respectively) (Fig. 3a, b) and pH values of 7.75 - 7.85 in the sampling points closest to the coast (Fig. 2A).

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. 2B, Fig. 4B). 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 3456.6 µmol kg^{-1} (corresponding with carbon dioxide pressure values of 5200 µatm), pH values of 7.27, and 1.45 and 0.95 values of Ω calcite and aragonite, respectively (Fig. 2B, Fig. 4B, supplementary material 2).

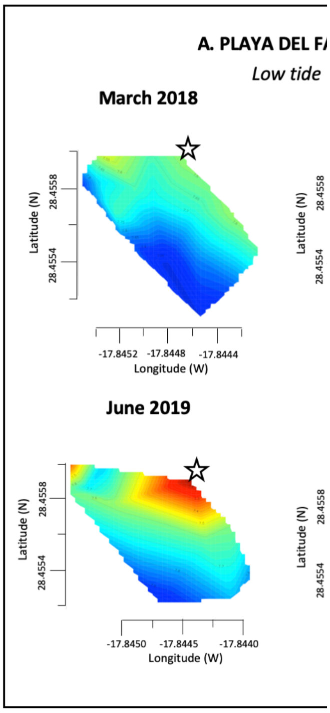
In both beaches, the emission is acting as an important source of CO_2 into the atmosphere. In Playa del Faro, the partial pressures of CO_2 in surface waters reached up to 5000 µatm in low tide (the values in the atmosphere were between 405 and 410 µatm) (supplementary material 2). This produced high concentration gradients that combined with high-intensity winds 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 up to 150 tons of CO_2 per year.

3.2.3 Echentive lagoons

Eliminado: ¶

Eliminado: 2500

Eliminado: µmol kg^{-1}



Eliminado:
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.¶ ... [1]

Eliminado: 600

Eliminado: 3

Eliminado: 8

Eliminado: ¶ ... [2]

The two lagoons at Playa 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 only from the big lagoon) (Fig. 2C, D). Similarly, the C_T was above 9700 µmol kg^{-1}, with comparable values for A_T (Fig. 4Ca, b). These C_T and A_T concentration together with the low pH values counteracted the saturation states of calcite and aragonite that were, respectively, never below 4.35 and 2.79 (Fig. 4Cc, d). Furthermore, when both lagoons were sampled during December 2018, similar concentrations were measured at low and high tide (Fig. 2C, D). 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. 2C, D, supplementary material 2). The rest of the big lagoon 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. 2C, D). 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.

Eliminado: Nueva in

Eliminado: from

Eliminado: 5

Eliminado: 6

Eliminado: 5

Eliminado: 5

Eliminado: 5

Con formato: Centrado

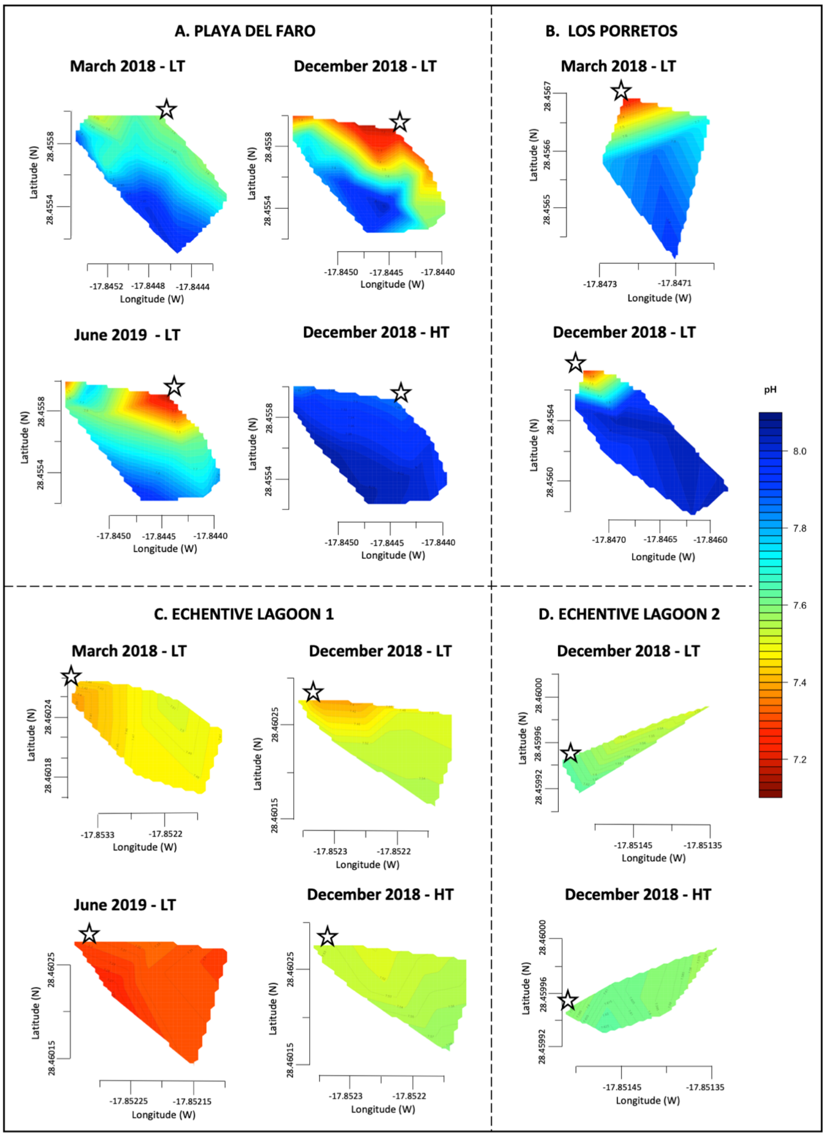


Figure 2: Linear interpolation graphs of pH values that were collected in March 2018, December 2018 and June 2019 during low tide (LT) and high tide (HT) in Playa del Faro (A), Los Porretos (B), Echentive lagoon 1 (C) and Echentive lagoon 2 (D). The star symbol is the reference mark on the map in Figure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

Con formato: Fuente: 9 pto, Negrita

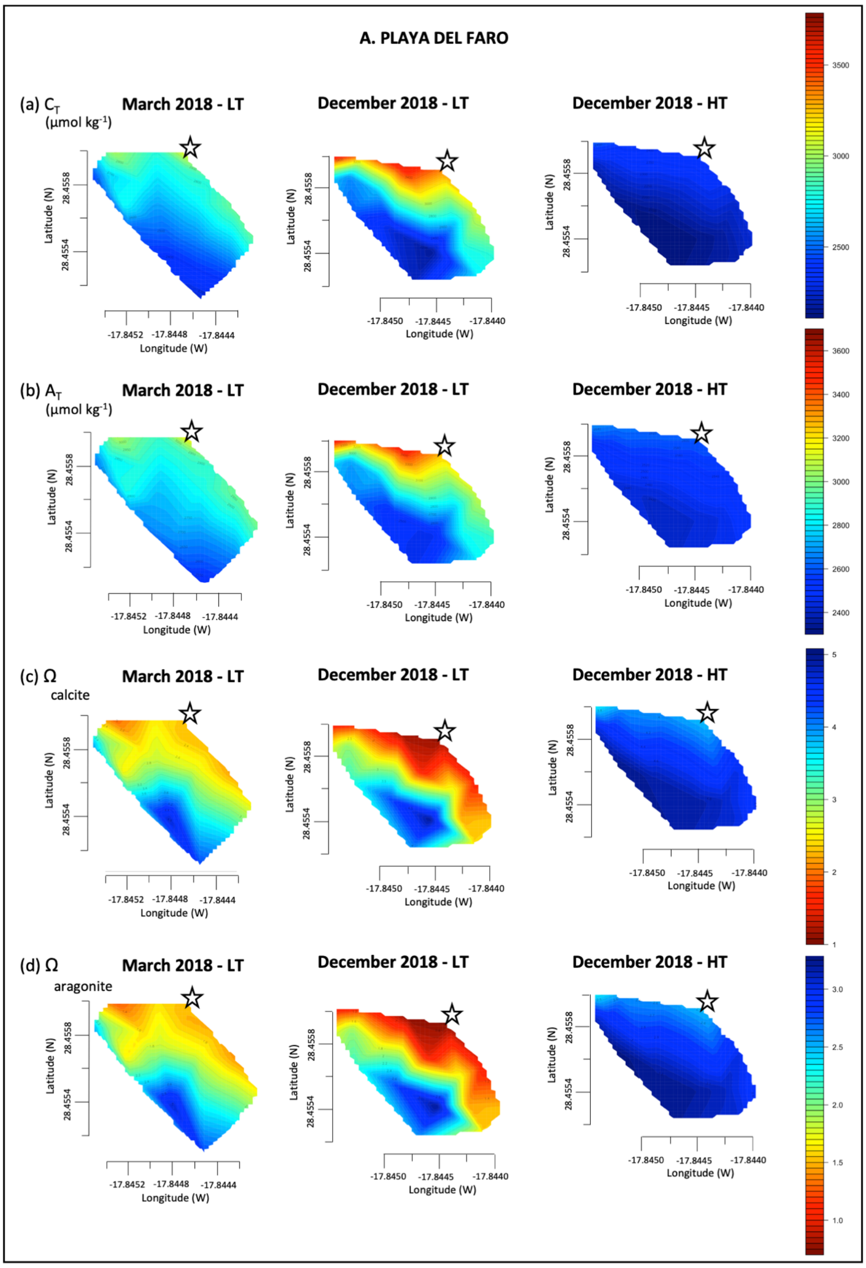


Figure 3: Linear interpolation graphs of CT (a), AT (b), Ωcalcite (c) and Ωaragonite (d) values during March 2018, December 2018 during low tide (LT) and high tide (HT) in Playa del Faro. The star symbol is the reference mark on the map in Figure 1c.

Con formato: Centrado

Con formato: Fuente: 9 pto, Negrita

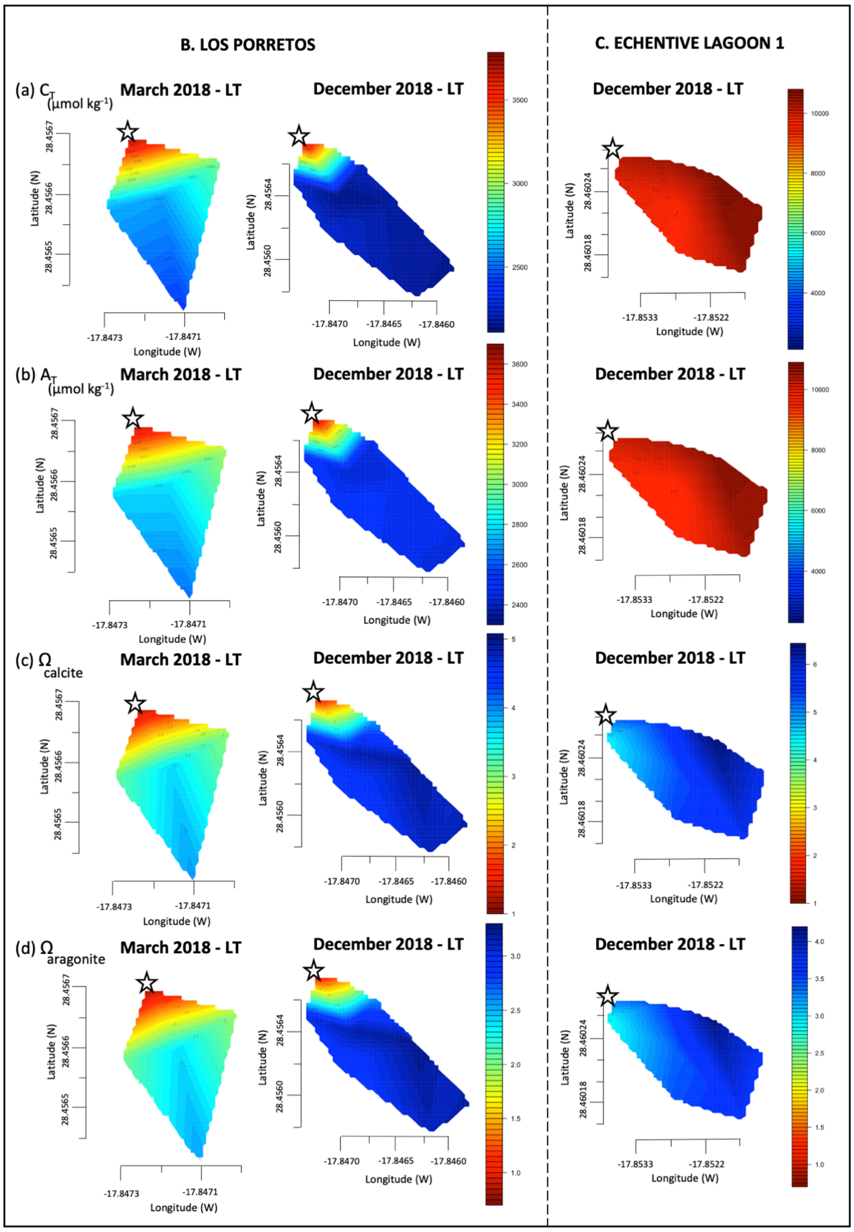


Figure 4: Linear interpolation graphs of CT (a), AT (b), Ωcalcite (c) and Ωaragonite (d) values during March 2018 and December 2018 during low tide (LT) in Los Porretos (B) and Echentive Lagoon 1 (C). The star symbol is the reference mark on the map in Figure 1c.

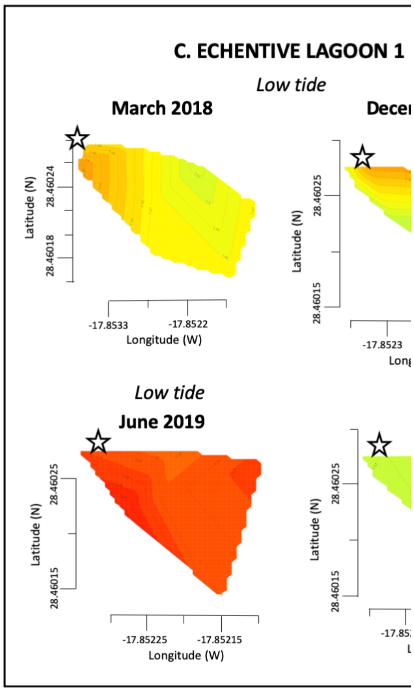
3.3 CO_2 flux calculation

Con formato: Centrado

Con formato: Fuente: 9 pto, Negrita

Con formato: Justificado

Eliminado: ¶



Eliminado: 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.¶

The CO_2 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, 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 36.93 (equivalent to 745.80 Tons of sea sat) at low tide to 37.02 at high tide (747.50 Tons of sea salt). The decrease in salinity at low tide could be accounted for by the emission of 57m^3 of brackish groundwater.

Eliminado: 27

Eliminado: 19

The brackish groundwater was also responsible for the A_T and C_T changes (Fig. 3a, 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, 4.40 kmol of alkalinity was 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 caused the increase of 6.70 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. 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 5.70 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 2.80 kg CO_2 d^{-1} to 28 kg CO_2 d^{-1}.

Eliminado: 2

Eliminado: was

4 Discussion

4.1 The origin of the CO_2 seeps

Our results reveal the influence of brackish water discharge in the acidification process of Punta de Fuencaliente System (PFS) (Fig. 5). 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 and seep systems worldwide (references within González-Delgado and Hernández, 2018). Moreover, the presence of acidic water flow of La Palma also has a slight 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).

Eliminado: 7

Eliminado: greater

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 due to underground volcanic activity, 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).

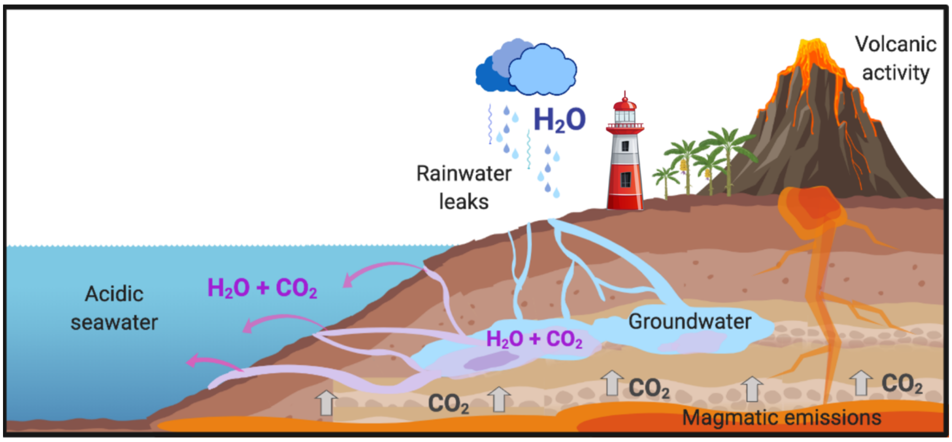


Figure 5: Acidification process representation of Punta de Fuencaliente system (PFS) (made with Biorender).

Eliminado: 7

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, 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, 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 200 m distance from the coast (Fig. 1), have a salinity of 32 and C_T and A_T concentrations five times 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 an 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 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.

Eliminado: 1

Eliminado: 5

4.3 La Palma as a natural laboratory for marine research

The natural CO_2 gradients south of La Palma have been characterized from shore to offshore, varying for C_T from 2120.10 to 3794.00 µmol kg^{-1}, for pH from 7.12 to 8.07, for Ωaragonite from 0.71 to 3.28 and Ωcalcite from 1.09 to almost 5.02. Which is similar 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 (2014) (Fig. 6). Nevertheless, several caveats for future prediction experiments should be considered.

Eliminado: the

Eliminado: 8.7

Eliminado: 76.7

Eliminado: 1

Eliminado: 9

Eliminado: 8

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. 6).

Eliminado: 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, the most typical community of Canary island, is present at the PFS (Sangil et al., 2018). 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. 6). These studies could allow us to disentangled adaptation and evolution of marine life to the changing carbonate conditions over time (Gattuso et al., 1998).

Eliminado: 8

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).

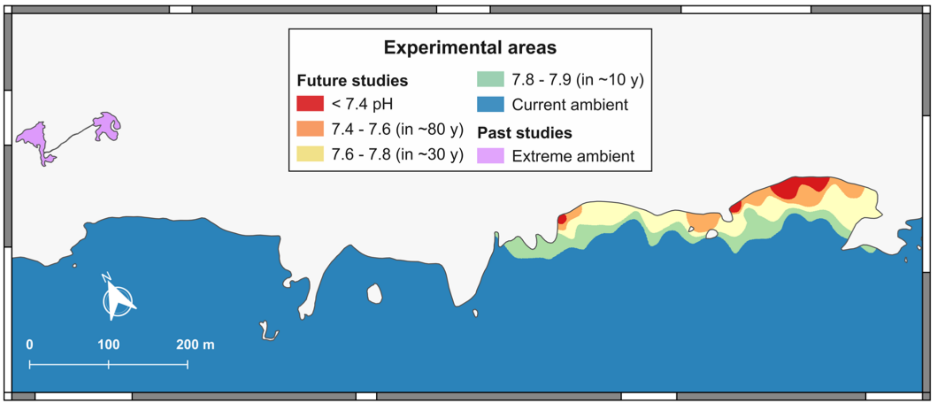


Figure 6: Selected areas for experimental purpose (Interpolation IDW, 4.0 of correlation with Qgis).

Eliminado: 8

Eliminado: ro

5 Conclusions

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 gradient analogous to future oceans conditions. Consequently, they can be used as natural laboratories to predict 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.

Eliminado: s

Appendix A

Eliminado: Acknowledgements
This research received a grant from the Fundación Biodiversidad of the Ministerio para la Transición Ecológica of the Spanish Government and help from the Ministerio de Economía y Competitividad through ATOPFe project (CTM2017-83476). We thank the researchers, the officers and crew of the R/V Ángeles Alvariño from Instituto Español de Oceanografía (IEO) for their help during the sampling process. Also, we want to thank Adrián Castro for his help during the water sample analysis in the laboratory of QUIMA group (ULPGC) and Enrique Lozano-Bilbao from the University of La Laguna for his comments and feedback. Finally, we very much appreciate all the help offered by the Fuencaliente town hall (La Palma).

Table A1: Summary of the sampling methodology, with the locations sampled ("Sites"), the date of each sampling ("Date"), whether the sampling was done during the low (LT) or high (HT) tide and whether the parameters measured ("Measures") were all (ALL) or only the pH (pH).

Sites	Date	Tide	Nº	Measures
Playa del Faro	mar-18	LT	23	All
Playa del Faro	dec-18	HT	17	All
Playa del Faro	dec-18	LT	19	All
Playa del Faro	jun-19	HT	11	pH
Playa del Faro	jun-19	LT	11	pH
Los Porretos	mar-18	LT	5	All
Los Porretos	dec-18	LT	14	All
Los Porretos	dec-18	HT	10	All
Echentive lagoon 1	mar-18	LT	8	All
Echentive lagoon 1	dec-18	LT	10	All
Echentive lagoon 1	dec-18	HT	10	All

Echentive lagoon 1	jun-19	LT	6	pH
Echentive lagoon 2	dec-18	LT	6	pH
Echentive lagoon 2	dec-18	HT	6	pH

Appendix B

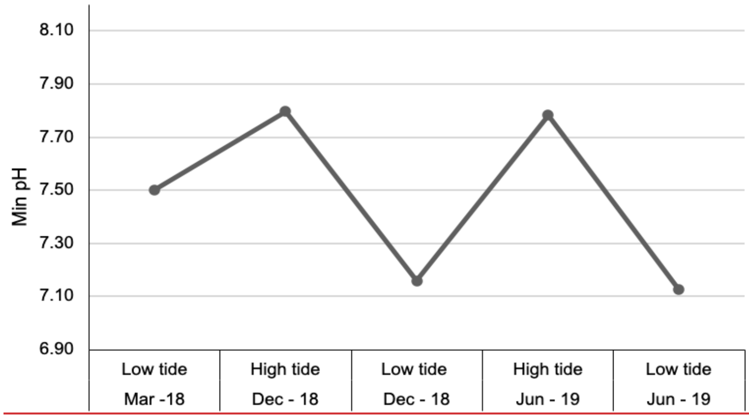


Figure B1: Line graph representing the tidal fluctuation of the minimum pH values (Min pH) at Playa del Faro, during March 2018 (Mar-18), December 2018 (Dec-18) and June 2019 (Jun-19).

Data availability

All measures obtained and used in this work will be published as supplementary material.

Con formato: Ninguno, Espacio Antes: 0 pto, Después: 0 pto

Con formato: Fuente: Sin Negrita

Author contribution

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.

Acknowledgements

This research received a grant from the Fundación Biodiversidad of the Ministerio para la Transición Ecológica of the Spanish Government and help from the Ministerio de Economía y Competitividad through ATOPFe project (CTM2017-83476). In March 2018, we thank to the officers, crew and researcher of the R/V Ángeles Alvariño from Instituto Español de Oceanografía (IEO) for their help during sampling process, specially Dr. E Fraile and F. Domingo (from VULCANA-II-0318 project). Also,

Con formato: Ninguno, Espacio Antes: 0 pto, Después: 0 pto

we want to thank Adrián Castro for his help during the water sample analysis in the laboratory of QUIMA group (ULPGC) and Dr. Enrique Lozano-Bilbao from the University of La Laguna for his comments and feedback. Finally, we very much appreciate all the help offered by the Fuencaliente town hall (La Palma).

Con formato: Fuente: Sin Negrita

References

Agostini, S., Wada, S., Kon, K., Omori, A., Kohtsuka, H., Fujimura, H., Tsuchiyaa, Y., Satoa, T., Shinagawaa, H., Yamadaa, Y., Inaba, K. Geochemistry of two shallow CO_2 seeps in Shikine Island (Japan) and their potential for ocean acidification research. Reg. Stud. Mar. Sci. 2, 45–53, 2015.

Boatta, F., D'Alessandro, W., Gagliano, A. L., Liotta, M., Milazzo, M., Rodolfo-Metalpa, R., Hall-Spencer, J. M., Parello, F. Geochemical survey of Levante Bay, Vulcano Island (Italy), a natural laboratory for the study of ocean acidification. Mar. Pollut. Bull. 73 (2), 485–494, 2013.

Burnett W. C., Aggarwal, P. K., Aureli, A., Bokuniewicz, H., Cable, J. E., Charette, M. A., et al. Quantifying submarine groundwater discharge in the coastal zone via multiple methods. Sci. Total Environ. 367, 498-543 https://doi.org/10.1016/j.scitotenv.2006.05.009, 2006.

Calvet, F., Cabrera, M. C., Carracedo, J. C., Mangas, J., Recio, C. and Travé, A. Beachrocks from the island of La Palma (Canary Islands, Spain). Mar. Geol., 197(1-4), 75-93, https://doi.org/10.1016/S0025-3227(03)00090-2, 2003.

Carracedo, J. C., Rodríguez-Badiola, E., Guillou, H., de la Nuez and Pérez-Torrado, F. J. Geology and volcanology of La Palma and El Hierro, Western Canaries. Estudios Geológicos, 57, 5-6, 2001.

Charette, M.A., Lam, P.J., Lohan, M. C., Kwon, E. Y., Hatje, V., Jeandel, C., Shiller, A. M., Cutter, G. A., Thomas, A., Boyd, P. W. and Homoky, W. B. Coastal ocean and shelf-sea biogeochemical cycling of trace elements and isotopes: lessons learned from GEOTRACES. Philos. Trans. R. Soc. A, 374(2081), p.20160076, https://doi.org/10.1098/rsta.2016.0076, 2016.

Código de campo cambiado

Crook, E. D., Potts, D., Rebolledo-Vieyra, M., Hernandez, L. and Paytan, A. Calcifying coral abundance near low-pH springs: implications for future ocean acidification. Coral Reefs, 31(1), 239-245, https://doi.org/10.1007/s00338-011-0839-y, 2012.

Código de campo cambiado

Dando, P. R., Stüben, D., & Varnavas, S. P. Hydrothermalism in the Mediterranean sea. Prog. Oceanogr., 44(1-3), 333-367, https://doi.org/10.1016/S0079-6611(99)00032-4, 1999.

Dickson, A. G., Sabine, C. L. and Christian, J. R. Guide to best practices for ocean CO_2 measurements. North Pac. Mar. Sci. Organ., p.191 http://hdl.handle.net/11329/249, 2007.

Código de campo cambiado

Foo, S. A., Byrne, M., Ricevuto, E. and Gambi, M. C. The carbon dioxide vents of Ischia, Italy, a natural system to assess impacts of ocean acidification on marine ecosystems: an overview of research and comparisons with other vent systems. Oceanogr. Mar. Biol. Annu. Rev., 56: 237-310, 2018.

Gattuso, J. P., Frankignoulle, M., Bourge, I., Romaine, S., and Buddemeier, R. W. Effect of calcium carbonate saturation of seawater on coral calcification. Glob. Planet. Change, 18(1-2), 37-46, https://doi.org/10.1016/S0921-8181(98)00035-6, 1998.

Código de campo cambiado

González-Dávila, M., Santana-Casiano, J. M. and González-Dávila, E. F. Interannual variability of the upper ocean carbon cycle in the northeast Atlantic Ocean. Geophys. Res. Lett., 34, L07608, doi:10.1029/2006GL028145, 2007.

González-Delgado, S. and J. C. Hernández. The importance of natural acidified systems in the study of ocean acidification: what have we learned?. Adv. Mar. Biol. 80, 57-99, DOI: 10.1016/bs.amb.2018.08.001, 2018.

González-Delgado, S., Hernández, J. C., Epherra, L., Hernández, C., Alfonso, B. Effect of a natural CO_2 gradient on egg characteristics of *Arbacia lixula*. Program & Abstracts: 16th International echinoderm Conference, Nagoya, pp 165, 2018b (Abstract).

González-Delgado, S., Hernández, J. C., Wangensteen, O., Alfonso, B., Soto, A. Changes in echinoderm populations due to a natural CO_2 gradient. Program & Abstracts: 16th International echinoderm Conference, Nagoya, pp 58, 2018a (Abstract).

Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D. and Buia, M. C. Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature, 454(7200), 96–99, https://doi.org/10.1038/nature07051, 2008.

Código de campo cambiado

Hall-Spencer, J. M. and Harvey, B. P. Ocean acidification impacts on coastal ecosystem services due to habitat degradation. Emerg. Top. Life Sci., 3(2), 197-206, https://doi.org/10.1042/ETLS20180117, 2019.

Hernández, C. A., Epherra, L., Alfonso, B., González-Delgado, S., Hernández, J. C. Characterization of a CO_2 vent in La Palma (Canary Islands) and its effects on the calcified structures of *Arbacia lixula*. Program & Abstracts: 16th International echinoderm Conference, Nagoya, pp 63, 2018 (Abstract)

Hernández, C. A., Sangil, C. and Hernández, J. C. A new CO_2 vent for the study of ocean acidification in the Atlantic. Mar. Pollut. Bull. 109(1), 419–426, https://doi.org/10.1016/j.marpolbul.2016.05.040, 2016.

IPCC. In: Core Writing Team, , Pachauri, R.K., Meyer, L.A. (Eds.), Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, p. 151. Geneva (Switzerland), 2014.

Jeandel, C. Overview of the mechanisms that could explain the 'Boundary Exchange' at the land–ocean contact. Philos. Trans. A. Math. Phys. Eng. Sci., 374(2081), 20150287, https://doi.org/10.1098/rsta.2015.0287, 2016.

Kasting, J. F. Earth's early atmosphere. Science, 259(5097), 920-926, DOI: 10.1126/science.11536547, 1993.

Kroeker, K. J., Kordas, R. L., Crim, R. N. and Singh, G. G. Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. Ecol. Lett., 13: 1419-1434, https://doi.org/10.1111/j.1461-0248.2010.01518.x, 2010.

Ma Y., Aichmayer B., Paris O., Fratzl P., Meibom A., Metzler R. A., Politi Y., Addadi L., Gilbert P. U. and Weiner S. The grinding tip of the sea urchin tooth exhibits exquisite control over calcite crystal orientation and Mg distribution. Proc. Natl. Acad. Sci. 106(15), 6048-53, https://doi.org/10.1073/pnas.0810300106, 2009

Marrero, R., López, D. L., Hernández, P. A., and Pérez, N. M. Carbon dioxide discharged through the las Cañadas aquifer, Tenerife, Canary Islands. Pure and Appl. Geophys., 165(1), 147-172, https://doi.org/10.1007/s00024-007-0287-3, 2008.

Martin, W., Baross, J., Kelley, D. and Russell, M. J. Hydrothermal vents and the origin of life. Nat. Rev. Microbiol., 6(11), 805, https://doi.org/10.1038/nrmicro1991, 2008.

Marty, B. and Tolstikhin, I. N. CO_2 fluxes from mid-ocean ridges, arcs and plumes. Chem. Geol. 145(3-4), 233-248, https://doi.org/10.1016/S0009-2541(97)00145-9, 1998.

Migliaccio, O., Pinsino, A., Maffioli, E., Smith, A. M., Agnisola, C., Matranga, V., Nonnis, S., Tedeschi, G., Byrne, M., Gambi, M. C. and Palumbo, A. Living in future ocean acidification, physiological adaptive responses of the immune system of sea urchins resident at a CO_2 vent system. Science of The Total Environment, 672, pp.938-950, 2019.

Mintrop, L., Pérez, F. F., González-Dávila, M., Santana-Casiano, J. M. and Körtzinger, A. Alkalinity determination by potentiometry: Intercalibration using three different methods, Cienc. Mar., 26, 23–37, http://hdl.handle.net/10261/25136, 2000.

Moore, W. S. The effect of submarine groundwater discharge on the ocean. Ann. Rev. Mar. Sci. 2, 59-88, https://doi.org/10.1146/annurev-marine-120308-081019, 2010.

Mulligan, A. E., Charette, M. A., Tamborski, J. J. and Moosdorf, N. Submarine Groundwater Discharge. Elsevier, 108-119, https://doi.org/10.1016/B978-0-12-409548-9.11482-4, 2019.

Nagelkerken, I., Russell, B. D., Gillanders, B. M., Connell, S. D. Ocean acidification alters fish populations indirectly through habitat modification. Nat. Clim. Chang. 6, 89–93, 2016.

Nakamura, K., and Kato, Y. Carbonatization of oceanic crust by the seafloor hydrothermal activity and its significance as a CO_2 sink in the Early Archean. Geochim. Cosmochim. Acta, 68(22), 4595-4618, https://doi.org/10.1016/j.gca.2004.05.023, 2004.

Paasche, E. Silicon and the ecology of marine plankton diatoms. II. Silicate-uptake kinetics in five diatom species. Mar. Biol., 19(3), 262-269, https://doi.org/10.1007/BF02097147, 1973.

Padrón, E., Pérez, N. M., Rodríguez, F., Melián, G., Hernández, P. A., Sumino, H., Padilla, G., Barrancos, J., Dionis, S., Notsu, K. and Calvo, D. Dynamics of carbon dioxide emissions from Cumbre Vieja volcano, La Palma, Canary Islands. Bull. Volcanol., 77, 1-15, https://doi.org/10.1007/s00445-015-0914-2, 2015.

Pérez, C. Effects of a Natural CO_2 Gradient on Benthic Coastal Populations, Degree Project, University of La Laguna, 2017. https://riull.ull.es/xmlui/handle/915/6758.

Pichler, T., Biscéré, T., Kinch, J., Zampighi, M., Houlbrèque, F., and Rodolfo-Metalpa, R. Suitability of the shallow water hydrothermal system at Ambitle Island (Papua New Guinea) to study the effect of high pCO_2 on coral reefs. Mar. Pollut. Bull., 138, 148-158, 2019.

Pierrot, D., Lewis, E. and Wallace, D.W.R.. MS Excel program developed for CO_2 system calculations. In ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 2006.

Sangil, C., Clemente, S. and Francisco, L. C. Ambientes litorales marginales en las islas Canarias: estructura y composición de las comunidades bentónicas en las Lagunas de Echentive (La Palma). Vieraea, 36, pp.143-162, 2008.

Sangil, C., Martins, G. M., Hernández, J. C., Alves, F., Neto, A.I ., Ribeiro, C., León-Cisneros, K., Canning-Clode, J., Rosas-Alquicira, E., Mendoza, J.C. and Titley, I. Shallow subtidal macroalgae in the North-eastern Atlantic archipelagos (Macaronesian region): a spatial approach to community structure. Eur. J. Phycol., 53(1), pp.83-98, https://doi.org/10.1080/09670262.2017.1385098, 2018.

Santana-Casiano, J. M., Fraile-Nuez, E., González-Dávila, M., Baker, E. T., Resing, J. A. and Walker, S. L. Significant discharge of CO_2 from hydrothermalism associated with the submarine volcano of El Hierro Island. Sci. Rep. 6, p.25686, https://doi.org/10.1038/srep25686, 2016.

Smith, A. M., Berman, J., Key Jr, M. M., and Winter, D. J. Not all sponges will thrive in a high-CO_2 ocean: Review of the mineralogy of calcifying sponges. Palaeogeogr. Palaeoclimatol. Palaeoecol., 392, 463-472, https://doi.org/10.1016/j.palaeo.2013.10.004, 2013.

Smith, A. M., Clark, D. E., Lamare, M. D., Winter, D. J., and Byrne, M. Risk and resilience: variations in magnesium in echinoid skeletal calcite. Mar. Ecol. Prog. Ser., 561, 1-16, https://doi.org/10.3354/meps11908, 2016.

Smith, A. M., Key Jr, M. M. and Gordon, D. P. Skeletal mineralogy of bryozoans: taxonomic and temporal patterns. Earth-Sci. Rev., 78(3-4), 287-306, https://doi.org/10.1016/j.earscirev.2006.06.001, 2006.

Soler-Liceras, C. La historia de la Fuente Santa. Editorial Turquesa. Santa Cruz de Tenerife, 2007.

Szymczycha, B., Maciejewska, A., Winogradow, A. and Pempkowiak, J. Could submarine groundwater discharge be a significant carbon source to the southern Baltic Sea?. Oceanologia, 56(2), 327-347, https://doi.org/10.5697/oc.56-2.327, 2014.

Tarasov, V. G., Gebruk, A. V., Mironov, A. N. and Moskalev, L. I. Deep-sea and shallow water hydrothermal vent communities: two different phenomena?. Chem. Geol. 224 (1–3), 5–39, https://doi.org/10.1016/j.chemgeo.2005.07.021, 2005.

Viotti, S., Sangil, C., Hernández, C. A. and Hernández, J. C. Effects of long-term exposure to reduced pH conditions on the shell and survival of an intertidal gastropod. Mar. Environ. Res., 152, p.104789, https://doi.org/10.1016/j.marenvres.2019.104789 , 2019.

Vizzini, S., Di Leonardo, R., Costa, V., Tramati, C. D., Luzzu, F., Mazzola, A. Trace element bias in the use of CO_2 vents as analogues for low pH environments: implications for contamination levels in acidified oceans. Estuar. Coast. Shelf Sci. 134, 19–30, 2013.

Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean revisited. Limnol. Oceanogr.-Meth., 12(6), 351-362, https://doi.org/10.1029/92JC00188, 2014.

Weber J. N. The incorporation of magnesium into the skeletal calcites of echinoderms. Am. J. Sci. 267: 537−566, doi: 10.2475/ajs.267.5.537, 1969.

Página 5: [1] Eliminado	**Microsoft Office User**	**15/10/20 17:46:00**

Página 5: [2] Eliminado	**Microsoft Office User**	**15/10/20 17:48:00**