

***Interactive comment on “Chemical
characterization of Punta de Fuencaliente CO₂
seeps system (La Palma Island, NE Atlantic
Ocean): a new natural laboratory for ocean
acidification studies” by
Sara González-Delgado et al.***

Sara González-Delgado et al.

saglezdel@gmail.com

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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.

C1

Responses to Referee's comments:

Referee #2; comment 1: “The Authors performed some measurements of the seawater carbonate chemistry around Punta de Fuencaliente 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 CO₂ vents or Puerto Morelos acidify system. All of them are special places because they present pH and pCO₂ 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.”

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- 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 CO₂ 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 $\mu\text{mol kg}^{-1}$ 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

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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

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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 Enchentive lagoons are two different sampling sites and we have corrected it on the figures and on the text.

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Las Cabras, as explained in the manuscript in Lines 59 - 60, is a CO₂ 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, pCO₂, CT, AT, Ω calcite and Ω 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 3). 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 3). 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, pCO₂, CT, AT, Ω calcite and Ω 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 supplementary material 2 and 3).

Referee #2; comment 11: "L 141. "During high tide, the anomalies almost disappeared.." which support the hypothesis about the role of the lagoon in the local beach

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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 CO₂ gases, from volcanic activity, are mixing with brackish groundwater that are discharged o seeped in the coast through the rock porosity.

Referee #2; comment 12: “L. 202. PFS. Please just write the location.”

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

Referee #2; comment 13: “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 CO₂ 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 CO₂ seep system, because the CO₂ emissions that altered the

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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 14: “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 15: “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

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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.

Please also note the supplement to this comment:
<https://bg.copernicus.org/preprints/bg-2020-232/bg-2020-232-AC2-supplement.zip>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2020-232>, 2020.

C9

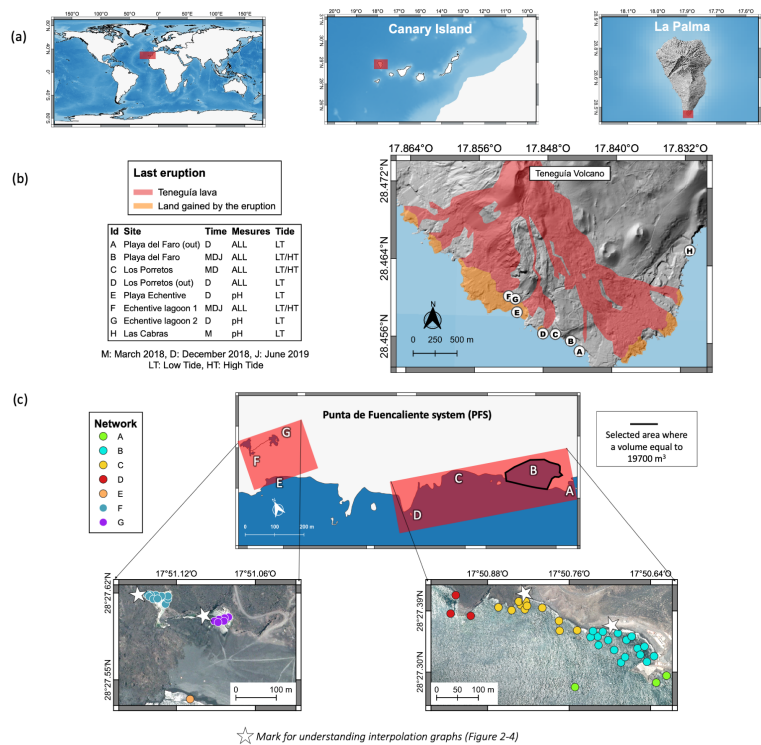


Fig. 1.

C10

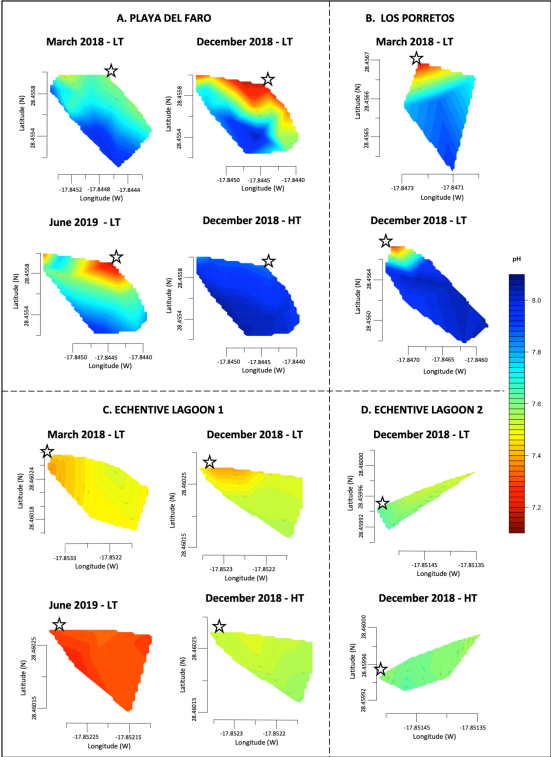


Fig. 2.

C11

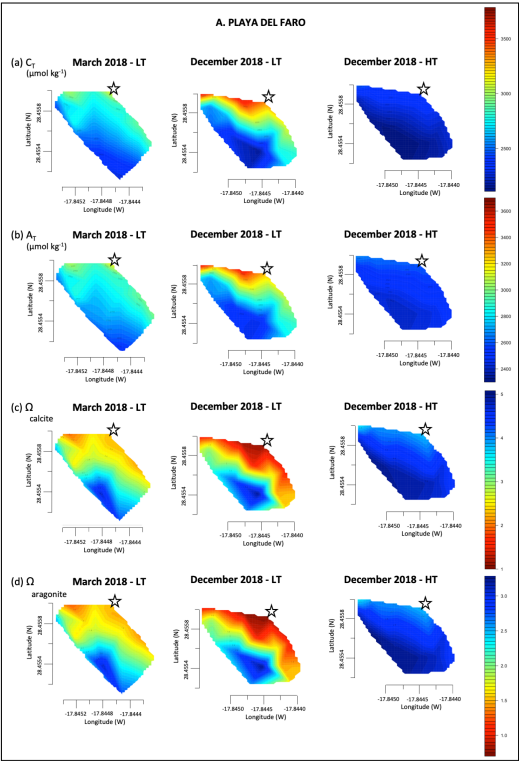


Fig. 3.

C12

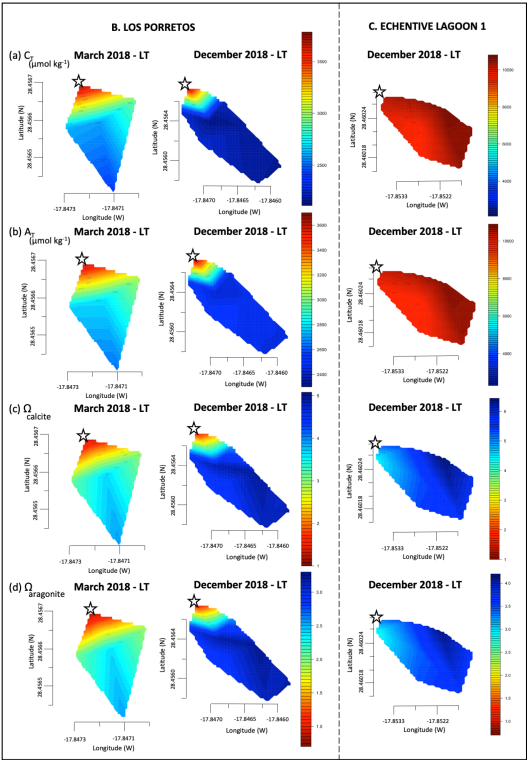


Fig. 4.

C13

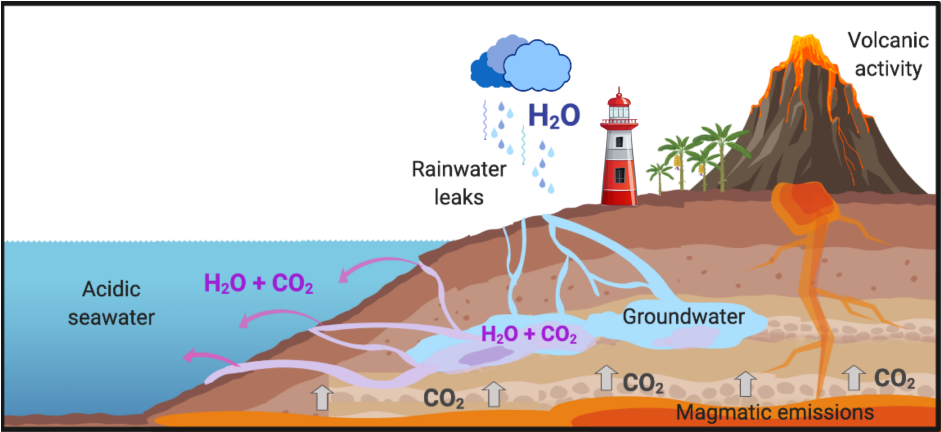


Fig. 5.

C14