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## Interactive comment on "Carbonate System Parameters of an Algal-dominated Reef along West Maui" by Nancy G. Prouty et al.

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Interactive comment on "Carbonate System Parameters of an Algal-dominated Reef along West Maui" by Nancy G. Prouty et al. Anonymous Referee #1 Received and published: 30 January 2018

R1: "General Comments" Overall, this is a very nice paper that is scientifically sound and contains very few technical errors. The authors measured seawater carbonate chemistry and nutrients at shallow fringing reefs around a submarine groundwater discharge site to show what's driving chemical variability at these shallow sites with local anthropogenic stressors. They showed that chemistry (salinity, carbonate chemistry, DO) was highly variable at the vent site and driven by SGD while most parameters had

C<sub>1</sub>

a diurnal signal on the reef due to benthic metabolism. They also showed that areas closest to the vent site experienced a shift in NCC and NCP that may relate to nutrients being discharged from the vent. This study is scientifically sound and addresses a critical knowledge gap of understanding natural drivers of seawater carbonate chemistry variability on reefs, which must be understood in order to predict the effects of long-term anthropogenic ocean acidification on reefs. My main critique of this paper is clarification of the terminology in order to more accurately draw conclusions about benthic metabolism from the available data they collected.

AR: We appreciate the valuable comments from Anonymous Referee #1 and believe we have conscientiously addressed the suggestions in the text and have detailed our responses below.

R1: "Specific Comments" Introduction This manuscript gave a nice introduction to the re- search and sets the reader up for understanding and interpreting the results. However, the research goals were stated twice and therefore seemed repetitive. Typically, the research objectives are listed near the end of the introduction. It also was difficult to tie different parts of the introduction together, but hopefully the specific comments below will help address the flow:

AR: We agree with the reviewer's critique regarding repetition in the introductory paragraph and we have omitted the research objectives stated earlier in the introductory paragraph.

R1: Lines 36-37: Need to define OA versus coastal acidification. I assume the authors are referring to OA as a long-term anthropogenic effect owing to uptake of CO2 while coastal acidification refers to natural processes.

AR: As noted by the reviewer, it is important to distinguish between ocean acidification (OA) and coastal acidification. Ocean acidification is largely driven by the uptake of atmospheric anthropogenic CO2 in oceanic waters (Orr et al., 2005) whereas coastal acidification is believe to be largely explained by processes such as contributions from

freshwater inflow, upwelling and/or eutrophication (Cai et al., 2011) whereby excess nutrient loading from human activities to coastal waters enhances respiratory processes that release CO2 and in turn increase coastal water acidity (e.g., see review by Strong et al., 2015). We have included a clarification statement in the revised manuscript in the Introduction section.

R1: Lines 36-40: These are nice introductions to stressors on reefs and community metabolism; however, the tie between the two is not clear as presently written. Perhaps consider adding a transition between these two statements stating how these stressors are affecting reefs (e.g. decreased calcification, increased dissolution, etc.) and then go into community metabolism.

AR: Per the reviewer's suggestion, we have modified these statements for greater clarity and have revised the introduction to include the following statement: "These stressors can lead to a decrease in reef health by removing grazing fish, decreasing calcification rates, and increasing nutrient and contaminant concentrations, thereby shifting the balance between reef accretion and bioerosion."

R1: Lines 52-53: Again, I felt like this was an abrupt transition. Could add "which may influence reef metabolism and community composition" at the end of the sentence. AR: Per the reviewer's suggestions we have modified this statement to include "...which may influence reef metabolism and community composition by changing coastal water quality."

R1: Line 57: add "calcium carbonate (CaCO3)" in front of dissolution

AR: Per the reviewer's suggestions we have inserted "calcium carbonate (CaCO3)" in front of dissolution

R1: Methods Lines 95-96: What is the other 90% of cover where there is 10% live coral cover? What is the community composition of the other 49% of hard-bottom area? This would help with interpretation of results and DIC/TA slopes as this relates

C3

to the community composition (corals vs algae vs sand, etc. See Page et al 2016 for reference on community composition influence on seawater carbonate chemistry.)

AR: A detailed discussion of seafloor-bottom type can be found in Cochran et al. (2014). In brief, the remaining 49% of available hardbottom consists of aggregate reef, spur-and-groove, patch reefs, pavement, and reef rubble, which as the reviewer points can influence seawater carbonate chemistry (Page et al., 2017). In addition to live coral cover, Cochran et al. (2014) observed macroalgae, corraline algae, seagrass, and turf in the area mapped (5 km2 of sea floor from the shoreline to water depths of  $\sim\!\!30$  m), however the sampling sites in our study were areas of live coral cover. We have included additional information in the Methods Section and reference to Page et al. (2017) in the Introduction Section.

R1: Lines 111-114: What was the approximate depth of the vent site? This would be valuable information in interpreting the variability (measured as daily range) of chemistry since depth can be such a strong control (Falter et al 2013).

AR: The vent site was located at a comparable depth to the two shallow (<1.5 m) sites (S1 and S2). We have inserted the water depth in the revised manuscript.

R1: I do wonder about any algae, bacterial films, etc. that may have grown on the inside of the tubing and possibly influenced carbonate chemistry and nutrients. Were there any tests (e.g. sampling carbonate chemistry near the intake and at the outtake) to assess whether the tubing was clean throughout the entire field study?

AR: Sampling tubes were flushed for a minimum of 20 minutes to remove residual seawater before collecting data and water samples. In addition, the tube intakes were fitted with a stainless steel screen cap to prevent uptake of large particulates. We also inspected the tubes upon extraction and found no significant algal growth. The revised manuscript includes this additional information.

R1: Thanks for providing the approximate precision of the TA and DIC measurements.

It would be great to see the actual precision and accuracy (as mean plus/minus sd) of pH, TA, and DIC though.

AR: In the revised manuscript we have reported accuracy and precision as determined from repeat analyses of CRM; For TA, precision of the data set is reported as one standard deviation determined from 56 replicate measurements of CRM Batch 154 and was 0.79 micromole per kg SW. Accuracy of TA for the data set is reported as average difference (abs(measured - known value)) between measured and known value of the same 56 replicate measurements of CRM Batch 154, and was 0.56  $\pm$  0.55 micromole per kg SW. The average difference between 31 duplicate sample analyses was 0.76  $\pm$  0.83 micromole per kg sw.

For DIC, precision of the data set is reported as one standard deviation determined from 49 replicate measurements of CRM Batch 154 and was 1.91 micromole per kg SW. Accuracy of DIC for the data set is reported as average difference (abs(measured - known value)) between measured and know value of the same 49 replicate measurements of CRM Batch 154 and was  $1.50 \pm 1.17$ micromole per kg SW. The average difference between 37 duplicate sample analyses was  $1.9 \pm 1.5$  micromole per kg SW.

We have included this information in the revised manuscript in the methods section.

R1: What carbonate parameters are actually used for the pCO2 and saturation state calculations? This was unclear to me at this point of the manuscript but later it states they were calculated from TA-pH pairing. Please clarify in the methods.

AR: We measured all three carbonate parameters and found the calculated  $\Omega$  arag values similar between the DIC-pH and TA-pH pairs, not surprising given that solubility is highly pH dependent. We did however observe differences between the measured and calculated TA. Processes unrelated to calcification can impact TA values that are not accounted for in calculations but may contribute to the TA measurements. Therefore, to be conservative, we have chosen to present  $\Omega$  arag and pCO2 based on the DIC-pH pairs in the revised manuscript.

C5

R1: What kind of filters were used for nutrients and carbonate chemistry sampling? Some filters may alter the values due to reactions between seawater and the material of the filters.

AR: A cellulose nitrate 0.45- $\mu m$  filter and 0.20- $\mu m$  polyethersulfone syringe filter were used to provide sterile sampling (i.e., low extractables) to ensure sample integrity and reduce the risk of contamination with pipetting. We have included this information in the revised manuscript.

R1: Results The results are very well-written. Just one clarification: Line 215: What range of dates were used to calculate values for the open ocean site?

AR: We reported a range of open ocean data from HOT station that was measured from 10/31/1988 to 12/9/2015 that can be accessed at http://hahana.soest.hawaii.edu/hot/products/products.html. We have included this additional information in the revised manuscript.

R1: Discussion Line 240: Respiration also occurs during the day, not just at night. Could state "net respiration" rather than just "respiration"

AR: The reviewer makes a valid point, we have revised this statement for clarity. The revised manuscript now reads "...net respiration."

R1: Lines 249-251: How can both NCP and NCC dominate? It's unclear whether the authors are trying to say they are more balanced compared to the 2nd sampling or whether they mean "net photosynthesis (+NCP)" and "net calcification (+NCC)."

AR: The reviewer brings up an important point, we have clarified this paragraph in the revised manuscript to: "To further understand the temporal variability in carbonate chemistry over the 6-d sampling period along the reef flat, diagrams of nTA versus nDIC were plotted according to Zeebe and Wolf-Gladrow, (2001), along with vectors indicating theoretical effects of the organic carbon (NCP) and inorganic carbon (NCC) cycle on seawater chemistry (Kawahata et al., 1997;Suzuki and Kawahata, 2003) (Fig

5). As presented here, NCP refers to the balance of photosynthesis and respiration, and NCC refers to the balance between calcification and dissolution (see review by Cyronak et al., 2018). Diagrams of nTA-nDIC indicate the dominance of net photosynthesis (+NCP) and net CaCO3 precipitation (+NCC) during the first sampling period (16-19 March)." R1: Lines 252-254: Please use NEC/NEP or NCC/NCP to maintain consistency with the scales used in this study. Also, please define these terms either here or in the introduction. AR: For consistency this ratio is reported as NCC:NCP in the revised manuscript. As described in the previous author response, NCP refers to the balance of photosynthesis and respiration, and NCC refers to the balance between calcification and dissolution (see review by Cyronak et al., 2018).

R1: Lines 254-255: These should be "net calcification" and "net photosynthesis" to more accurately reflect what is actually measured. NCC and NCP can indicate net processes (calcification-dissolution or photosynthesis-respiration).

AR: The reviewer brings up an important point. For clarification and accuracy, we have revised the manuscript to "net calcification" and "net photosynthesis".

R1: Line 260: The lower NCC:NCP ratio only indicates dominance by organic carbon cycling (vs inorganic carbon cycling), not which process (photosynthesis, respiration, calcification, dissolution) is actually dominating.

AR: As the reviewer points out, NCP is controlled by the organic carbon cycle (regulated by photosynthesis and respiration) whereas NCC reflects the inorganic carbon cycle, in response to CaCO3 precipitation and dissolution. The NCC:NCP ratio is defined as 1/[(2/m)-1] where m is the slope of the nTA-nDIC plot. Therefore, changes in the NCC:NCP ratio are inferred to represent changes in the balance between the various process that influence the organic and inorganic carbon cycle. This has been reworded in the revised manuscript for clarification.

R1: Lines 260-262. This statement seems a little out of place and I'm not sure what point the authors are trying to convey. Why are the slopes in this study higher than

C7

Heron Island? Does this reflect differences in benthic community composition, ecosystem function, or a combination?

AR: We understand the reviewer's concern regarding the comparison of our NCC:NCP ratios to those at Heron Island given potential differences in community composition, water depth, etc. Therefore, we have removed this statement from the revised manuscript.

R1: Line 262: Again, "net dissolution" and "net respiration" since actual rates are not measured using this methodology

AR: In a similar response to above, we have revised the manuscript to "net dissolution" and "net respiration" for accuracy.

R1: Does the nitrate end member at the vent site vary temporally? I appreciate using the available data to show the SGD but wonder how closely it represents discharge during the time of this study.

AR: The SGD end-member nitrate concentration was similar at both high and low tide, 117.26 and 117.13  $\mu mol$  L-1 respectively, demonstrating consistency over a tidal range from water sampled directly from the vent using a piezometer inserted into the vent. However, interannual variability is possible given the range reported by Swarzenski et al. (2016) from collections in 2010 and 2013, 41.3 and 91.5  $\mu mol$  L-1, respectively. However, evaluating multi-year variability is outside the scope of this present study. R1: Figures/Figure Captions Line 389: "seep site AND on the nearshore. . .

AR: We thank the reviewer for brining to our attention this typo, the revised manuscript has been corrected accordingly.

R1: Line 393: So were TA and pH used to calculate pCO2 and saturation state? This was not clear in the methods.

AR: As described above we have chosen to present  $\Omega arag$  and pCO2 DICbased on the DIC-pH pairs in the revised manuscript.

R1: Figure 5: Please show error bars for the open ocean since this presumably represents a mean. NCC and NCP need to be defined either in the caption or text. In part E, these should all be shown as "net. . ." Rather than just showing the arrows for part E, could you put it on a TA/DIC plot? It can even be shown right on the plots for A-D. Given your discussion of the data, I personally would rather see the processes as small arrows on a subplot (or just in the corner of a plot) and then have dashed lines indicating the transitions between +NCC/-NCC and +NCP/-NCP. I think this would make it easier for the reader to go back and forth between the figure and discussion.

AR: Given the small error bars for the average open ocean nDIC and nTA values, we have chosen to report these values in the revised figure caption as adapted from Dore et al. (2009) since it would be difficult to view in the figure. Per the reviewer's suggestion we have revised Figure 5 and have embedded the information from Part E to Parts A-D. NCC and NCP are defined in the Discussion Section.

R1: "Technical Corrections" Line 47: no comma necessary Line 97: no comma necessary Line 112: Is 115 a typo? Should it be 15? Lines 154 and 157: parentheses just around the year Line 297: no space in SGD-driven

AR: Thank you for brining to our attention these technical corrections. We have made these corrections in the revised manuscript. However, the distance of the two deeper sites, S3 and S4 were located 115 m offshore therefore no change has been made.

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C9

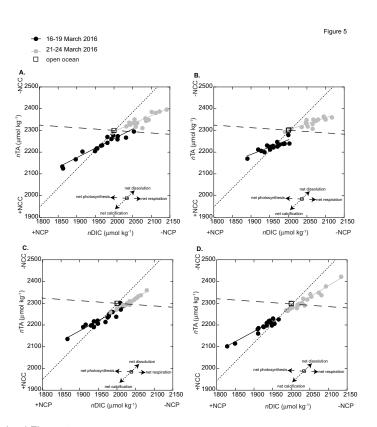


Fig. 1. Revised Figure 5