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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 #2 Received and published: 21 February 2018

R2: This is a very interesting and very well-written paper that will definitely be a nice contribution to the field. There are a few major and minor comments below that I feel need to be addressed prior to publication.

AR: We appreciate the valuable comments from Anonymous Referee #2 and believe we have conscientiously addressed the suggestions in the text and have detailed our responses below.

R2: My biggest criticism is that the authors did not account for TA and DIC fluxes from the SGD itself. This is an important step to interpret how much of the delta TA or delta DIC is due to reef metabolism. The authors also need to add a data analysis section to the methods and state all their statistical approaches and programs used to analyze the data. The remaining comments are relatively minor.

AR: As recommended by the reviewer, we calculated the contribution of TA and DIC from SGD at all four reef flat sites for the time period when salinity was lowest at the vent site (10.64) and the greatest contribution of SGD water likely occurred. The average residuals (calculated as the difference between the measured and non-zero salinity normalization following Richardson et al., 2018) for TA and DIC were 12±6 and 26±12 μmol kg-1, respectively. The range of TA at the reef flat sites over the course of the experiment was 706 μmol kg-1, and the range of DIC was 460 μmol kg-1. The maximum contribution from SGD (at lowest vent site salinity) could have accounted for 1.7% of the variability, and SGD DIC could only have accounted for 5.7% of DIC variability. At the S1 site, closest to the vent, the range of TA and DIC variability over the course of the experiment was 192 and 459 μmol kg-1, respectively with SGD accounting for 6.3% and 5.7% of the variability in TA and DIC, respectively.

Per the reviewer's suggestion, we have expanded the methods section to include a brief overview of the statistical methods.

R2: Line 52: There are other carbonate data for Kahekili (see, Silbiger et al. 2017 Ecology), but it is extremely limited. This is by far the most comprehensive study at this site, but "no field-based measurements" is inaccurate.

AR: Thank you for bringing this to our attention. This statement has been revised to "Building upon these studies, we present a comprehensive study to characterize the carbonate system parameters from the reefs in this area." We have also included reference to Silbiger et al. (2017) in the revised manuscript.

R2: Line 81: Change "plants" to calcifying algae

AR: Per the reviewer's suggestion "plants" has been changed to "calcifying algae". R2: Line 85: This is the first at Kahekili, but not the first to constrain carbonate chemistry in response to SGD (see Richardson et al. 2017 L&O). I would remove this sentence.

AR: We have modified this statement given previous work at Black Point, Oahu where proximal on-site sewage disposal has been identified as a nutrient source to groundwater discharge (Richardson et al., 2017). In addition, we have included this reference in the revised manuscript (Introduction Section 1).

R2: Line 124: Put both accuracy and precision of the instruments.

AR: Per the reviewer's comment, we have included both accuracy and precision in the measurements presented in Section 2.2.

"TA and DIC sample accuracy were within 0.56 ±0.55 and 1.50 ± 1.17 μmol kg-1 of certified reference material respectively. Precision for TA based on replicate sample analyses was 0.76 ± 0.83 μmol kg-1. Precision for DIC based on replicate sample analyses was 1.9 ± 1.5 μmol kg-1."

R2: Line 168: Why did you use the TA-pH pairs rather than the TA-DIC pairs for the omega calculations? TA-pH is fine, but TA-DIC has less error propagation for calculating omega and it seems that you have those data.

AR: We measured all three carbonate parameters and found the calculated Ωarag 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 Ωarag (and pCO2) based on the DIC-pH pairs in the revised manuscript.

R2: Line 171: It is not clear which TA, DIC values you are talking about here.

AR: For clarification, we have inserted "along the reef flat" in this statement.

R2: Add a data or statistical analysis section at the end of the methods and discuss how you analyzed your data here. What program did you use for your stats?

AR: Per the reviewer's suggestion, we have included a brief overview of the statistical methods/approach in a new section (2.4).

2.4 Statistical Analysis (new section) Slope of salinity normalized total alkalinity (nTA): salinity normalized dissolved inorganic carbon (DIC), net community calcification: net community production ratio (NCC:NCP=2ΔDIC/ΔTA-1) (Suzuki and Kawahata, 2003), correlation coefficients (r2), analysis of variance (ANOVA), and standard error of difference (SEdif) were calculated in Excel v. 14.7.6. Histogram plots and cubic spline fits were made in KaleidaGraph 4.1.3. As described in Section 2.3, the full seawater CO2 system was calculated using an Excel Workbook Macro translation of the original CO2SYS program (Pierrot et al., 2006).

R2: What were the TA values coming directly out of the seep?

AR: As shown in the Figure 2 and available in Prouty et al. (2017a,b) the TA values measured at the vent site ranged between 2300 to 2700 μmol kg-1.

R2: When calculating delta TA and DIC, the SGD endpoint needs to be taken into account. SGD can have a dramatically different TA and DIC concentrations than seawater (see Nelson et al. 2015 Marine Chem). A good portion of the TA and DIC fluxes are thus likely due to SGD and the remainder after accounting for these fluxes are due to bio- logical processes (e.g., calcification, dissolution, P,R). Examples of studies that have accounted for fluxes of TA and/or DIC from freshwater sources are Paquay et al 2007 Aquatic geochem or Richardson et al. 2017 L&O

AR: The reviewer is correct; SGD can dramatically impact the TA and DIC concentrations (e.g., Nelson et al., 2015), and this is clearly captured in the fact that all carbonate parameters adjacent to the primary seep site behaved conservatively with respect to salinity (Prouty et al., 2017a,b). Similarly, freshwater fluxes in a river-estuary system can alter TA and DIC, for example Paquay et al. (2007) noted that TA and DIC in an estuary on the Big Island of Hawaii were conservative with respective to salinity. Therefore, the conservative behavior of DIC and TA with respect to salinity highlights the influence of freshwater on the carbonate chemistry system and should be accounted for in reef areas exposed to freshening from SGD (e.g., Richardson et al., 2017).

As discussed above, we calculated the contribution of TA and DIC from SGD at all four reef flat sites for the time period when salinity was lowest at the vent site (10.64) and the greatest contribution of SGD water likely occurred. The maximum contribution from SGD could have accounted for 1.7% of the variability, and SGD DIC could only have accounted for 5.7% of DIC variability. At the S1 site, closest to the vent, the range of TA and DIC variability over the course of the experiment was 192 and 459 μmol kg-1, respectively with SGD accounting for 6.3% and 5.7% of the variability in TA and DIC, respectively. We observed a very typical biotic response in the DIC and TA data, as shown in the diurnal DIC and TA plots in Figure 3 and lack of conservative behavior with respect to salinity (see new Figure S1). Adjacent to the vent site, abiotic processes, specifically SGD is driving changes in TA and DIC variability however along the reef flat biotic process dominated the TA and DIC signal.

R2: Line 234: The TA amplitude could also be indicative of high dissolution rates or a biproduct of the TA flux from the SGD onto the reef.

AR: We agree with the reviewer's comment that higher dissolution rates would drive higher TA concentrations (as well as DIC concentrations), however we only observed lower amplitude in the nTA diurnal range, rather than an increase in total concentration.

R2: Line 251: Put this information in the methods and explain how you did the calculation in addition to citing the paper.

AR: Per the reviewer's suggestion, we have expanded the methods section to include a brief overview of the statistical methods, including how we calculated the slope values of the nDIC-nTA plots.

R2: Line 290: remove “on the short term” at the end of the sentence. There is no physiology data in this study, so this sentence is a bit of a stretch. It does however look at ecosystem functioning of reefs.

AR: Per the reviewer's suggestion, we have removed the text “on the short term” in the revised manuscript.

R2: Line 297: add a citation after “environment.”

AR: Per the reviewer's suggestion we have included a reference in this statement (Sunda and Cai 2012).

R2: In the discussion, it would be interesting if the authors compared their results to with other studies that also measured carbonate chemistry at SGD sites (e.g., Nelson et al. 2015 Marine Chem and Richardson et al. 2017). Are the patterns similar or different?

AR: The reviewer brings up an important point and we have expanded the manuscript to include comparisons to previously published studies, particularly those from Maunalua Bay (e.g., Nelson et al., 2015; Richardson et al., 2017). For example, the spatial gradient observed in net dissolution at sites closest to the SGD in Maunalua Bay are consistent with results from Kahekili where lower NCC:NCP ratios at the shallow sites highlights the greater vulnerability of the shallow sites to net dissolution (-NCC) under lower pH conditions relative to the deeper sites.

R2: Figures: make the colors more contrasting in the figures so that people printing in black and white can see the differences.

AR: Figures 2-5 were originally submitted as black and white and per the editor's suggestion we revised the figures to color.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2018-35/bg-2018-35-AC2-supplement.pdf

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