**Editorial Comments (EC) to the Author:**
The discussion phase of your manuscript is now over and I encourage you to submit a version revised along the lines of your replies to the referees' comments. Please also consider the following comments:

**EC:** Net respiration a suggested by referee #1 does not mean anything and could generate confusion. I recommend using dark respiration which is a commonly used expression.

**AR:** We understand this comment is in reference to describing the diurnal cycle as described in Section 4.0. This statement (line 240 in original manuscript), has been revised to "DIC decreased during the day due to photosynthesis, whereas at nighttime, pH decreased and DIC increased in response to dark respiration (Fig. 3)."

**EC:** For reporting date and time, use ISO 8601 (2018-03-21)

**AR**: Per the editor's suggestion, we have revised the reporting nomenclature in the revised manuscript.

**EC** When discussing DIC-TA plots, you may find the paper by Cyronak et al. (2018; PLoS ONE) useful. I believe it was published after you submitted your manuscript.

**AR**: During our revision process we accessed the paper by Cyronak et al. (2018) and have included reference to this recently published study in the context of using carbonate parameters to evaluate reef health.

**EC**: Finally, Biogeosciences strongly promotes the full availability of the data sets reported in the papers that it publishes in order to facilitate future data comparison and compilation as well as meta-analysis. This can be achieved by uploading the data sets in an existing database and providing the link(s) in the paper. Alternatively, the data sets can be published, for free, alongside the paper as supplementary information. The ascii (or text) format is preferred for data and any format can be handled for movies, animations etc...

**AR**: We have included a statement at the end of the Acknowledgement Section: " Additional data to support this project can be found in Prouty et al. (2017b)." This reference is a USGS data release.

**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 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 $CO_2$ 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 $CO_2$ 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 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 $km^2$ of sea floor from the shoreline to water depths of ~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 ± 0.55 micromole per kg SW. The average difference between 31 duplicate sample analyses was 0.76 ± 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 ±1.17micromole per kg SW. The average difference between 37 duplicate sample analyses was 1.9 ± 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 $pCO_2$ based on the DIC-pH pairs in the revised manuscript.

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-μm filter and 0.20-μm 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:** We have revised this statement for clarity. The revised manuscript now reads "…dark 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 *n*TA versus *n*DIC 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 *n*TA-*n*DIC 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 $CaCO_3$ precipitation and dissolution. The NCC:NCP ratio is defined as 1/[(2/m)-1] where m is the slope of the *n*TA-*n*DIC 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 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:** We have revised the manuscript to "net dissolution" and "net respiration" for greater clarity.

**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 *n*DIC and *n*TA 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.

***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.

**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 $\Omega_{arag}$ 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 $pCO_2$) 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).

**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 *n*TA 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 *n*DIC-*n*TA 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.

# Carbonate System Parameters of an Algal-dominated Reef along West Maui

Nancy G. Prouty[1], Kimberly K. Yates[2], Nathan Smiley[2], Chris Gallagher[3], Olivia Cheriton[1], and Curt D. Storlazzi[1]

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**Abstract**

Constraining coral reef metabolism and carbon chemistry dynamics are fundamental for understanding and predicting reef vulnerability to rising coastal $CO_2$ concentrations and decreasing seawater pH. However, few studies exist along reefs occupying densely inhabited shorelines with known input from land-based sources of pollution. The shallow coral reefs off Kahekili, West Maui, are exposed to nutrient-enriched, low-pH submarine groundwater discharge (SGD) and are particularly vulnerable to the compounding stressors from land-based sources of pollution and lower seawater pH. To constrain the carbonate chemistry system, nutrients and carbonate chemistry were measured along the Kahekili reef flat every 4 h over a 6-d sampling period in March 2016. Abiotic process - primarily SGD fluxes - controlled the carbonate chemistry adjacent to the primary SGD vent site, with nutrient-laden freshwater decreasing pH levels and favoring undersaturated aragonite saturation ($\Omega_{arag}$) conditions. In contrast, diurnal variability in the carbonate chemistry at other sites along the reef flat was driven by reef community metabolism. Superimposed on the diurnal signal was a transition during the second sampling period to a surplus of total alkalinity (TA) and dissolved inorganic carbon (DIC) compared to ocean end-member TA and DIC measurements. A shift from net community production and calcification to net respiration and carbonate dissolution was identified. This transition occurred during a period of increased SGD-driven nutrient loading, lower wave height, and reduced current speeds. This detailed study of carbon chemistry dynamics highlights the need to incorporate local effects of nearshore oceanographic processes into predictions of coral reef vulnerability and resilience.

## 1. Introduction

Coral reefs provide critical shoreline protection and important ecosystem services, such as marine habitat, and support local economies through tourism, fishing, and recreation (Hughes et al., 2003; Ferrario et al., 2014). However, coral reefs are being threatened by global climate change processes, such as increasing temperatures, sea-level rise and ocean acidification (OA, caused by uptake of atmospheric carbon dioxide into the ocean (Orr et al., 2005). These effects are often compounded by local stressors such as over-fishing, sedimentation, land-based sources of pollution and coastal acidification (Knowlton and Jackson, 2008) that can result from freshwater inflow, eutrophication, and/or coastal upwelling. 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 erosion. However, isolating the effects of these stressors is difficult without establishing the biological and physical controls on community calcification and production. This is particularly challenging for coral reefs adjacent to densely

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inhabited shorelines, where freshwater fluxes can deliver excess nutrients. In turn, this can lead to coastal acidification caused by eutrophication and enhanced respiratory processes that release $CO_2$ and increase coastal water acidity (e.g., Cai et al., 2011; Strong et al., 2014), outbreaks of harmful algal blooms (Anderson et al., 2002), and decreased coral abundance and diversity (Fabricius, 2005;Lapointe et al., 2005). In many cases, eutrophication can alter ecosystem function and structure by shifting reefs from coral- to algae-dominated (Howarth et al., 2000; Andrefouet et al., 2002; Hughes et al., 2007). Changes in community structure can have profound impacts on coral reef metabolism and reef carbon chemistry dynamics (e.g. Page et al., 2016), which are ultimately linked to reef health and the ability to predict future responses to rising $pCO_2$ levels (Andersson and Gledhill, 2013). Understanding the local drivers of ecosystem function and reef community metabolism is critical for gauging the susceptibility of the reef ecosystem to future changes in ocean chemistry.

Numerous efforts have been conducted along west Maui, Hawaii, USA, to characterize and quantify submarine groundwater discharge (SGD) and associated nutrient input (Dailer et al., 2010;Dailer et al., 2012;Glenn et al., 2013;Swarzenski et al., 2013;Swarzenski et al., 2016;Silbiger et al., 2017), which may influence reef metabolism and community composition by changing coastal water quality. Building upon these studies, we present a comprehensive study to characterize the carbonate system parameters from the reefs in this area. The carbonate chemistry system is sensitive to changes in photosynthesis, respiration, calcification, and calcium carbonate ($CaCO_3$) dissolution, and can be characterized by measuring total alkalinity (TA), dissolved inorganic carbon (DIC), pH, $pCO_2$, nutrients, salinity, and temperature. Analysis of these parameters yields valuable information on ratios of net community calcification and production, and can be used to identify biological and physical drivers of reef health and ecosystem function (Silverman et al., 2007; Shamberger et al., 2011; Lantz et al., 2014; Albright et al., 2015; Muehllehner et al., 2016; DeCarlo et al., 2017; Richardson et al., 2017; Cyronak et al., 2018). This is particularly important given growing concern that coastal and ocean acidification may shift reef ecosystems from net calcification to net dissolution by the mid to end of the century (Silverman et al., 2009; Andersson and Gledhill, 2013) with an overall reduction in calcification rates and increase in dissolution rates (Shamberger et al., 2011; Shaw et al., 2012; Bernstein et al., 2016) that can contribute to reef collapse (Yates et al., 2017).

The health of many of Maui's coral reefs has been declining rapidly (Rodgers et al., 2015), with recent coral bleaching events leading to increased coral mortality (Sparks et al., 2016). The decline in coral cover along the shallow coral reef at Kahekili has been observed for decades (Wiltse, 1996; Ross et al.,

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2012), along with a history of macro-algal blooms (Smith et al., 2005). The shift in benthic cover from abundant corals to turf- or macro-algae (primarily *Ulva fasciata*) and increased rates of coral bioerosion have been linked to input of nutrient-rich water via wastewater injection wells (Dailer et al., 2010;Dailer et al., 2012; Prouty et al. 2017a). Treated wastewater is injected through these wells into groundwater that flows toward the coast where it emerges on the reef through a network of small seeps and vents (Glenn et al., 2013;Swarzenski et al., 2016). Changes in coastal water quality observed off west Maui can impact the balance of production of $CaCO_3$ skeletons by calcifying algae and animals on the reef, cementation of sand and rubble, and $CaCO_3$ breakdown and removal that occurs through bioerosion, dissolution, and offshore transport. Here, a high-resolution seawater sampling study was conducted to constrain the carbonate chemistry system and evaluate the biological and physical processes altering reef health along the shallow coral reef at Kahekili in Kaanapali, west Maui, Hawaii, USA (Fig. 1). This study characterizes the diurnal and multi-day variability of coral reef carbonate chemistry along a tropical fringing reef adjacent to a densely inhabited shoreline with known input from land-based sources of pollution, and identifies the controls on carbon metabolism. Ultimately, understanding carbonate system dynamics is essential for managing compounding effects from local stressors.

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## 2. Methods

### *2.1 Study Site*

The benthic habitat along the shallow reef at Kahekili in Kaanapali, West Maui (Fig. 1) consists of aggregate reef, patch reef, pavement, reef rubble and spur and groove (Cochran et al., 2014), with persistent current flow to the south (Storlazzi and Jaffe, 2008). Only 51% of the hardbottom at Kahekili is covered with at least 10% live coral, with the remaining hardbottom consisting of aggregate reef, spur-and-groove, patch reefs, pavement, and reef rubble (Cochran et al., 2014). The shallow fore reef experiences algae blooms in response to inputs of nutrient-rich water via wastewater injection wells (Dailer et al., 2010;Dailer et al., 2012). Groundwater inputs occur from both natural sources (rainfall and natural infiltration) and from artificial recharge (irrigation and anthropogenic wastewater). The inland Wailuku Basalt, consisting of a band of unconsolidated sediment along the coast and a small outcrop of Lahaina Volcanics, dominates the geology of the area surrounding the study site, controlling the flow of groundwater. Mean annual precipitation rates are up to 900 cm $yr^{-1}$ (Giambelluca et al., 2013), with natural recharge the greatest in the interior mountains.

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### *2.2 Field Sampling*

Two intensive sampling periods were carried out during the 6-d period between 2016-03-16 to 2016-03-24 along the reef flat with live coral cover. Seawater nutrients and carbonate chemistry variables were collected every 4 h during each sampling period from the primary vent site and in adjacent coastal waters along the shallow reef at Kahekili (Fig. 1). The first sampling period was from 15:00 on 2016-03-16 to 15:00 on 2016-03-19, and the second sampling period was from 15:00 on 2016-03-21 to 11:00 on 2016-03-24 (all reported times in local [HST]). There were five sampling sites: two shallow (<1.5 m) sites (S1 and S2) located approximately 10 m offshore, two deeper (5 m) sites (S3 and S4) located approximately 115 m offshore, and a shallow site located approximately 20 m offshore and within 0.25 m of an active SGD vent (vent site; <1.5 m) (Glenn et al., 2013;Swarzenski et al., 2016). Sampling tubes (ranging from approximately 100 to 200 m in length) were installed at each site by affixing the tube to a concrete block located approximately 20 cm above the seafloor, or by attaching the tubing directly to dead reef structure using zip ties. Tube intakes were fitted with a stainless steel screen cap to prevent uptake of large particulates. The remaining length of each tube was positioned along the seafloor to the adjacent beach by weighting the tube with a 1 m piece of chain, or by weaving the tube through dead reef structure approximately every 20 m. The tube outflow ends were labeled for each sampling site, bundled in a common location, and located above the high water line on the beach for sampling access. A peristaltic pump was used to pump seawater from the seafloor. Sampling tubes were flushed for a minimum of 20 minutes to remove residual seawater before collecting data and water samples. Sampling tubes were inspected upon extraction and no significant algal growth was observed. Temperature salinity, and dissolved oxygen of water samples were measured using a YSI ProPlus multimeter that was calibrated daily with an accuracy of ± 0.2°C, ± 0.1 psu, and ± 0.2 mg $L^{-1}$, respectively. However, due to temperature change during water transit time within the sampling tube, in-situ temperatures were also recorded from Solonist CTD Divers installed at the intake of each sampling tube. An upward-looking 2-MHz Nortek Aquadopp acoustic Doppler profiler (ADP) was deployed at the southern deeper site (S4). The ADP sampled waves at 2 Hz for 17 min every hour and currents at 1 Hz every 10 min in 1-m vertical bins from 1 m above the seabed up to the ocean surface.

*2.3 Seawater Analyses*

Samples for dissolved nutrients ($NH_4^+$, Si, $PO_4^{3-}$, and [$NO_3^-$+$NO_2^-$]) were collected in duplicate by filtering water with an in-line 0.45-µm cellulose nitrate filter and 0.20-µm polyethersulfone syringe filter, and were kept frozen until analysis. Nutrients were analyzed at the Woods Hole Oceanographic Institution's nutrient laboratory and University of California at Santa Barbara's Marine Science Institute Analytical Laboratory via flow injection analysis for $NH_4^+$, Si, $PO_4^{3-}$, and [$NO_3^-$+ $NO_2^-$], with

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precisions of 0.6-3.0%, 0.6-0.8%, 0.9-1.3%, and 0.3%-1.0% relative standard deviations, respectively. Select samples were collected and analyzed for nitrate isotope ($\delta^{15}N$ and $\delta^{18}O$) analyses at the University of California at Santa Cruz using the chemical reduction method (McIlvin and Altabet, 2005;Ryabenko et al., 2009) and University of California at Davis' Stable Isotope Facilities using the denitrifier method (Sigman et al., 2001). The isotope analysis was conducted using a Thermo Finnigan MAT 252 coupled with a GasBench II interface; isotope values are presented in per mil (‰) with respect to AIR for $\delta^{15}N$ and VSMO for $\delta^{18}O$ with a precision of 0.3-0.4‰ and 0.5-0.6‰ for $\delta^{15}N$-nitrate and $\delta^{18}O$-nitrate, respectively.

Seawater samples for determining carbonate chemistry variables (pH on the total scale, TA, and DIC) were collected from the 5 sampling sites using a peristaltic pump and pressure filtering seawater through a 0.45-µm filter. Samples for pH (0.007±0.017) were filtered into 30-mL optical glass cells and analyzed within 1 hr of collection using spectrophotometric methods (Zhang and Byrne, 1996), an Ocean Optics USB2000 spectrometer, and thymol blue indicator dye. Samples for TA and DIC were filtered into 300-ml borosilicate glass bottles, preserved by adding 100 µL saturated $HgCl_2$ solution and pressure sealed with ground glass stoppers coated with Apiezon grease. TA samples were analyzed using spectrophotometric methods of Yao and Byrne (1998) with an Ocean Optics USB2000 spectrometer and bromocresol purple indicator dye. DIC samples were analyzed using a UIC carbon coulometer model CM5014 and CM5130 acidification module fitted with a sulfide scrubber, and methods of Dickson et al. (2007). In-situ temperatures recorded from Solonist CTD Divers were reported and used to temperature-correct pH and perform CO2SYS calculations as described below.

Certified reference materials (CRM) for TA and DIC analyses were from the Marine Physical Laboratory of Scripps Institution of Oceanography (Dickson et al., 2007). 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 $kg^{-1}$. The full seawater $CO_2$ system was calculated with measured salinity, temperature, nutrients (phosphate and silicate), TA, DIC, and pH data using an Excel Workbook Macro translation of the original CO2SYS program (Pierrot et al., 2006). Given the enriched nutrient setting of the study site, TA values were nutrient corrected in CO2SYS (Dickson, 1981). The aragonite saturation state ($\Omega_{arag}$) and $pCO_2$ are reported based on DIC-pH pairs, with dissociation constants $K_1$ and $K_2$ from Mehrbach et al. (1973) refit by Dickson and Millero (1987) and KSO4 from Dickson (1990). The TA and DIC values were normalized to salinity

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(by multiplying by a factor of 35/S, where S is the measured salinity value) to account for variations in TA and DIC along the reef flat driven by evaporation and/or precipitation (Friis et al., 2003) and are reported as *n*TA and *n*DIC as previously established in reef geochemical surveys (e.g., Suzuki and Kawahata, 2003; Yates et al., 2014; Muehllehner et al., 2016) where TA and DIC exhibit non-conservative behavior with respect to salinity. However at the vent site the TA and DIC data was not normalized to salinity given the contribution of TA and DIC from SGD.

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*2.4 Statistical Analysis*

Slope of salinity normalized total alkalinity (*n*TA): salinity normalized dissolved inorganic carbon (DIC), net community calcification: net community production ratio (NCC:NCP=2ΔDIC/ΔTA-1) (Suzuki and Kawahata, 2003), correlation coefficients ($r^2$), analysis of variance (ANOVA), and standard error of difference ($SE_{dif}$) 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 $CO_2$ system and was calculated using an Excel Workbook Macro translation of the original CO2SYS program (Pierrot et al., 2006).

## 3. Results

*3.1 Submarine Groundwater Endmember*

The magnitude of change and absolute values in the carbonate chemistry, nutrients, and salinity were greatest at the primary vent site relative to the four sites along the reef. The salinity ranged from 10.64 to 36.72 over the 6-d period (Fig. 2A), with the most dramatic decrease in salinity on 2016-03-22 when salinity decreased from 32.45 to 12.47 within 4 hr. The reduction in salinity was sustained over a 32-hr period. A rapid change was also observed in the pH, DO, TA, DIC, and nutrient concentrations (Fig. 2). For example, nitrate concentrations at the vent site ranged from 0.45 to over 70 µmol $L^{-1}$, with an average nitrate concentration of 117 (SD 0.09) µmol $L^{-1}$ measured directly from the discharging seep water. The $\Omega_{arag}$ values decreased to less than 1 and $pCO_2$ values increased to 2000 µatm when salinity values dropped to less than 15 (Fig. 2D). No diurnal pattern was detected in the seawater carbonate chemistry at this site. Instead, these results are consistent with earlier work documenting lower pH, nutrient enriched freshwater endmember values tightly coupled to SGD ( Swarzenski et al., 2012; Glenn et al., 2013;Swarzenski et al., 2016).

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*3.2 Reef Flat*

In contrast to the vent site, the overall magnitude of carbonate chemistry variation at the other four sites along the reef flat was less, and the signal was coherent among these sites. This coherency is captured in the pH time series (Fig. 3B), where the pH data from the four sites were significantly ($p$<0.05) positively correlated with each other (with $r \sim 0.5$). The lowest salinity value along the reef flat was 33.51, indicating minimal freshwater influence on reef flat salinity. As a result, the carbonate system parameters measured along the reef were non-linear with respect to salinity (Supplemental Fig. 1), instead a diurnal pattern dominated the signal (Fig. 3). Lowest pH values occurred around midnight (23:00); and highest pH values occurred in the afternoon (~14:00-15:00). This diurnal pattern was also apparent in the DIC data, with lowest values in the afternoon and increasing around midnight, with a cubic spline fit (Press et al., 1988) highlighting diurnal cycle from all four sites along the reef flat. Likewise, the diurnal signal was identifiable in the $\Omega_{arag}$ and $pCO_2$ time-series, with $\Omega_{arag}$ values increasing and $pCO_2$ decreasing during the mid-day hours (Fig. 3). The diurnal signal in the $n$TA time-series was similar to the signal for $n$DIC. At the shallow (<5 m) sites, pH and DO covaried ($r^2$=0.43-0.87; $p$<0.001). The range in pH and $\Omega_{arag}$ was largest at the shallow sites; however, the average values were similar along the reef, 3.02 to 3.06 and 8.00 to 8.01, respectively, and were elevated relative to the average values recorded at the vent site, 7.85 (SD 0.17) and 2.28 (SD 0.81) for pH and $\Omega_{arag}$, respectively (Prouty et al., 2017b). No diurnal pattern was observed for the nutrient data; however, there was an offshore gradient in nutrient concentrations with enriched nutrients at the shallow sites compared to the deeper sites. Nutrient concentrations (Si, $PO_4^{3-}$, and $NO_3^-$) from the two shallow sites were statistically greater than the two deeper sites according to pairwise multi-comparison one-way ANOVA with a *post hoc* Tukey HSD ($p$>0.05). For example average nitrate concentrations at the two shallow sites were 0.71 (SD 0.35) and 0.41 (0.18 SD) compared to 0.17 (SD 0.10) and 0.19 (SD 0.11) μmol $L^{-1}$. Deficits and surpluses of $n$TA and $n$DIC, with respect to open ocean conditions, were calculated as Δ$n$TA and Δ$n$DIC using values from Station HOT (Dore et al., 2009), located approximately 250 km offshore as reported from 1988 to 2015 (http://hahana.soest.hawaii.edu/hot/products/products.html). The Δ$n$TA values ranged from -332 μmol $kg^{-1}$ to 85 μmol $kg^{-1}$ and -171 μmol $kg^{-1}$ to 141 μmol $kg^{-1}$ Δ$n$DIC. The standard error of difference ($SE_{dif}$) was calculated for Δ$n$TA and Δ$n$DIC values to evaluate whether the deficits and surpluses of $n$TA and $n$DIC were significant. Histogram plots reveal statistical ($p$=0.05; critical t value of 1.68; df=37) deficits and surpluses as well as differences between the first and second half of the sampling period (Fig. 4). Results show a shift from a deficit in Δ$n$TA to a surplus in Δ$n$TA at all stations, as well as a shift from a deficit in Δ$n$DIC to a surplus in Δ$n$DIC, suggesting a shift in the second sampling period from net $CaCO_3$ production to net $CaCO_3$ dissolution, and from net photosynthesis to net

respiration. This change was most distinct at the two shallow sites. The *n*TA and *n*DIC values from the second sampling period were also enriched relative to a range of values reported from nearshore Oahu sites (Drupp et al., 2013) but consistent with coastal sites from Maunalau Bay, Oahu with known inputs of SGD (Nelson et al., 2015; Richardson et al., 2017).

## 4. Discussion

The diurnal pattern observed at the four sampling sites along the reef flat is typical of a reef environment where biotic processes involving coral reef community metabolism (e.g., respiration/photosynthesis and calcification/dissolution) dominate the carbonate chemistry system (e.g., Smith, 1973). The non-linear relationship between salinity and carbonate chemistry parameters further supports the notion that biotic processes are driving carbonate chemistry variability along the reef flat (Millero et al., 1998; Ianson et al., 2003). The lower amplitude *n*TA diurnal signal supports previous observations that the region was algal-dominated (Smith et al., 2005). In this case, the lower biomass of calcifying organisms leads to conditions that favor respiration-photosynthesis processes relative to calcification-dissolution (Jokiel et al., 2014). Elevated pH values during mid-day, coincident with elevated sea surface temperature (SST) and peak solar irradiance, are consistent with maximum photosynthetic activity. DIC decreased during the day due to photosynthesis, whereas at nighttime, pH decreased and DIC increased in response to dark respiration (Fig. 3). This pattern is in stark contrast to the primary vent site where no diurnal pattern was observed, and abiotic controls on the carbonate system dynamics explain the strong linear relation to salinity. Variability at the vent site is driven by SGD rates, which are elevated during low tide when hydraulic gradients are the steepest (Dimova et al., 2012;Swarzenski et al., 2016). This spatial pattern is consistent with offshore transects from Maunalua Bay where sites closest to shore incorporated greater contribution of SGD derived TA and DIC than offshore sites (Richardson et al., 2017).

To further understand the temporal variability in carbonate chemistry over the 6-d sampling period along the reef flat, diagrams of *n*TA versus *n*DIC were plotted according to Zeebe and Wolf-Gladrow, (2001), along with vectors indicating theoretical effects of net community production (NCP) and net community calcification (NCC) 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 *n*TA-*n*DIC indicate the dominance of net photosynthesis (+NCP) and net $CaCO_3$ precipitation (+NCC) during the first sampling period (2016-03-16 to 2016-03-19). The slope values

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of the *n*DIC-*n*TA plots were used to calculate ratios of NCC:NCP (Table 1) using methods of Suzuki and Kawahata (2003) to estimate the relative contribution of these processes to reef biogeochemistry. In the absence of reliable water mass residence time, ratios were used rather than metabolic rates. The NCC:NCP ratios for the first sampling period ranged from 0.50 to 0.87 indicating a dominance of NCP relative to NCC. Plots of *n*DIC-*n*TA (Fig. 5) indicate that these sites were dominated primary by net photosynthesis and net calcification. This pattern was observed at all four sites along the reef flat. The lower NCC:NCP ratios at the shallow sites highlight the greater vulnerability of the shallow sites to net dissolution (-NCC) under lower pH conditions relative to the deeper sites. These results are in agreement with Richardson et al. (2017) that found net dissolution at reef sites closet to groundwater vents in Maunalua Bay, Oahu. A shift occurred at all sampling sites after the first sampling period. Elevated *n*DIC and *n*TA values from 2016-03-21 to 2016-03-22 indicate a shift to respiration and net dissolution in the *n*TA-*n*DIC diagrams (Fig. 5). At the shallow sites, S1 and S2 (Fig. 5A and B), the NCC:NCP ratios were 0.56 and 0.39 during the second sampling period (Table 1), respectively, indicating the dominance of NCP relative to NCC. Net dissolution and net respiration contributed nearly equally with NCC:NCP ratios near 1.0 during the second sampling at sites S3 and S4 located further offshore. Given the salinity range along the reef flat (34 to 36), traditional salinity normalization (e.g., Friis et al., 2003) could potentially overestimate the *n*DIC and *n*TA concentrations by ~20 to ~10 µmol $kg^{-1}$ respectively, according to non-zero normalization described in Richardson et al. (2017). However, rather than reflecting an artifact of the salinity normalization, given the non-linear relation of DIC and TA to salinity along the reef flat (Fig. S1), this shift is interpreted as a reef community response. As shown in Figures 4 and 5, this change captures a shift from a reef community dominated by net calcification and net photosynthesis to one dominated by net respiration and net dissolution.

The shift from net photosynthesis (P) to net respiration (R) as captured in the Δ*n*DIC histogram plots (Fig. 4), suggests that the coral-algal association consumed more energy than it produced during the second sampling period. As a proxy for autotrophic capacity, the change in P:R ratio may reflect an increase in coral heterotrophic feeding relative to autotrophic feeding (Coles and Jokiel, 1977;Hughes and Grottoli, 2013). Typically, stored lipid reserves in the tissue are utilized when the stable symbiotic environment is disturbed (e.g., Szmant and Gassman, 1990; Ainsworth et al., 2008). Although short-lived, thermally-induced bleaching has been linked to depletion of coral lipid reserves (e.g., Hughes and Grottoli, 2013), excess nutrient loading can also shift the stability of the coral-algae symbiosis, thereby reducing stored tissue reserves (Wooldridge, 2016). According to Glenn et al. (2013), up to 11

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$m^3$ $d^{-1}$ of dissolved inorganic nitrogen are discharged onto the West Maui reef as the result of receiving and treating over 15,000 $m^3$ $d^{-1}$ of sewage. Using a SGD flux rate of 87 cm $d^{-1}$ at the primary seep site (Swarzenski et al., 2016), and SGD nitrate end-member concentration of 117 μmol $L^{-1}$ (Prouty et al., 2017b), the nitrate flux from the primary vent site is 712 mol $d^{-1}$, clearly demonstrating excess nutrient loading. Elevated SGD end-member nutrient concentrations are consistent with those observed from Black Point, Maunalua Bay where effluent from proximal on-site sewage disposal is linked to excess nitrogen loads (Nelson et al., 2015; Richardson et al., 2017). As described above, an offshore gradient in nutrient concentrations was observed with enriched nutrients at the shallow sites compared to the deeper sites, consistent with a decrease in coral $\delta^{15}N$ values away from the vent (Prouty et al., 2017a). Coral tissue thickness was also negatively correlated to coral tissue $\delta^{15}N$ values ($r$ = -0.66; $p$ = 0.08), with the latter serving as a proxy for nutrient loading in alga samples along the reef flat (Dailer et al., 2010). It is possible that a reduction in coral tissue reflects preferential heterotrophic feeding under high nutrient loading, with nutrient enrichment by sewage effluent increasing primary production and biomass in the water column (e.g., Smith et al., 1981; Pastorok and Bilyard, 1985). While assessing the impacts of nutrient loading on coral physiology may be long term and subtle in some cases, results from our study highlight the potential short-term impacts of nutrification.

Identifying the exact mechanism(s) responsible for driving this shift is difficult given the complexity of the reef system. Possible explanations include warmer SSTs, suspension of organic matter, as well as secondary effects of nutrification from contaminated SGD (D'Angelo and Wiedenmann, 2014). Given that microbial communities rapidly take up inorganic nutrients (Furnas et al., 2005), there could be increased respiration as a result of increased microbial remineralization of organic matter in the nutrient-loaded environment (Sunda and Cai 2012). In other words, enhanced SGD-driven nutrient fluxes during the second sampling period could have increased microbial growth and remineralization, shifting the reef community metabolism, as captured in a shift in the carbonate chemistry system. In addition to community metabolism, local oceanographic effects such as the wind and wave regime can also drive carbonate chemistry by altering air-sea exchange and water mass residence times. During the first sampling period, the wave height increased from 0.4 m to 1.6 m over the first 2 d and mean current speeds were 1.6 cm $s^{-1}$ (Fig. S2). In comparison, during the second sampling period, wave height declined to less than 0.4 m and mean current speeds were 1.0 cm $s^{-1}$. Together, the reduced wave height and reduced wind speeds favor slower release of $CO_2$ generated by calcification and respiration processes from the water column (Massaro et al., 2012), resulting in higher $pCO_2$ and lower pH.

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Despite being situated in an oligotrophic region with naturally occurring, low nutrient concentrations, anthropogenic nutrient loading to coastal waters via sustained SGD is driving nearshore eutrophication (Dailer et al., 2010; Dailer et al., 2012; Bishop et al., 2015; Amato et al., 2016; Fackrell et al., 2016), with algal $\delta^{15}N$ signatures at Kahekili Beach Park indicative of wastewater effluent (Dailer et al., 2010;Dailer et al., 2012). In response, there has been a shift in benthic cover from abundant corals to turf- or macro-algae over the last two decades. Areas of discrete coral cover loss up to 100% along the shallow coral reef at Kahekili have been observed for decades (Wiltse, 1996; Ross et al., 2012), with a history of macro-algal blooms (Smith et al., 2005). More recently, Prouty et al. (2017a) found accelerated nutrient driven-bioerosion from coral cores collected along the Kahekili reef flat in response to land-based sources of nutrients. This is consistent with earlier work showing nutrification-mediated increase in plankton loads can trigger increases in filter feeders and bioeroders that endanger reef structure integrity (e.g., Fabricius et al., 2012). Eutrophication from nutrient enriched SGD may contribute to an already compromised carbonate system (i.e., reduced pH and $\Omega_{arag}$) by increasing net respiration and remineralization of excess organic matter, and increasing bioerosion. Therefore, secondary effects of nutrient-driven increase in phytoplankton biomass and decomposing organic matter are also important considerations for coral reef management (D'Angelo and Wiedenmann, 2014).

As discussed above, SGD rates are elevated during low tide when the relative pressure head between terrestrial groundwater and the oceanic water column is greatest (Dimova et al., 2012;Swarzenski et al., 2016). Relative SGD is greater in the shallows close to shore where the tidal height is larger relative to the depth of the water column. Higher islands, therefore, have the potential for not only greater orographic rainfall and thus submarine groundwater recharge, but also greater potential pressure head and thus enhanced SGD- driven nutrient fluxes. There is also greater potential for enriched nutrient sources and reduced water quality with fast-growing population and development (Amato et al., 2016;Fackrell et al., 2016). Thus, SGD represents a key vector of nutrient loading in tropical, oligotrophic regions (e.g., Paytan et al., 2006). At the same time, closer to shore, current speeds are generally slower resulting in longer water mass residence times (Storlazzi et al., 2006); longer residence times would also be expected closer to the seabed, compared with upper water column flows (Storlazzi and Jaffe, 2008). Together, these suggest that the resulting exposure (= intensity x residence time) of coral reefs to nutrient-laden, low pH submarine groundwater is greater for coral reefs closer to shore off high islands than along barrier reefs or on atolls. This heightened

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vulnerability therefore needs to be taken into account when evaluating vulnerability of nearshore fringing reefs to changes in carbonate chemistry system given evidence of nutrient driven-bioerosion from land-based sources of pollution.

## 5. Conclusion

Field based measurements of carbonate chemistry variability were made along a shallow coral reef off Kahekili, west Maui, and captured differences in the relative importance of inorganic and organic carbon production over a 6-d period in March 2016. Submarine groundwater discharge fluxes controlled the carbonate chemistry adjacent to the primary vent site, with nutrient-laden freshwater decreasing the pH levels and favoring undersaturated $\Omega_{arag}$ conditions. In contrast, reef community metabolism dominated the carbonate chemistry diurnal signal at sites along the reef flat. Superimposed on the diurnal signal was a transition during the second sampling period, yielding a surplus of *n*TA and *n*DIC compared to ocean endmember measurements indicating a shift from net photosynthesis and calcification to net respiration and carbonate dissolution. This shift could be interpreted as a direct response to increased nutrient loading, and subsequent enhancement of organic matter remineralization. Predictions of reef response to elevated $pCO_2$ levels assume reef water tracks open-ocean pH, however local effects are equally important (e.g., Cyronak et al., 2013; 2018), particularly along densely-inhabited shorelines with known input from land-based sources of pollution. Building on previous work documenting the input of nutrient laden, low-pH freshwater to the reefs off Kahekili, results presented here offer a first glimpse into how anthropogenic-driven eutrophication might add an additional stressor to thresholds tipping the balance between net carbonate accretion and net carbonate dissolution, thus altering carbonate system dynamics.

## Author contribution

NGP and KKY designed the experiments and NGP, KKY, NS and CG carried them out. NGP and KKY completed the chemical measurements and OC compiled the oceanographic data. NGP prepared the manuscript with contributions from all co-authors.

The authors declare that they have no conflict of interest.


## Acknowledgements

This research was carried out as part of the US Geological Survey's Coral Reefs Project in an effort to better understand the effects of geologic and oceanographic processes on coral reef systems in the USA and its trust territories, and was supported by the USGS Coastal and Marine Geology Program.

The authors gratefully acknowledge the vital partnership and expert logistics support provided by the State of Hawaii Division of Aquatic Resources. We thank T. DeCarlo (UWA), H. Barkley (NOAA), two anonymous reviewers, and J.P. Gattuso for their valuable reviews, A. Cohen (WHOI) for helpful discussions, and K.R. Pietro and K. Hoering (WHOI), C. Moore (USGS), and G. Paradis (UCSB) analytical assistance, M. Dailer (U. Hawaii) for field assistance. The use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government. Additional data to support this project can be found in Prouty et al., (2017b).

**Figure Captions**

**Figure 1.** Location map of the island of Maui, Hawaii, USA, and the study area along west Maui. Bathymetric map (5-m contours) of study area showing seawater sampling locations (blue closed circle) along Kahekili Beach Park, and the primary seep site (blue open circle) superimposed on distribution of percent coral cover versus sand.

**Figure 2** Results of time-series of seawater chemistry variables over a 6-d period collected from the seep site located on the nearshore reef every 4 hr. (A) Salinity, (B) dissolved nutrient (nitrate+nitrite, phosphate, and silicate) concentrations (µmol $L^{-1}$), and nitrate stable nitrogen isotopes ($\delta^{15}$N-nitrate; ‰), (C) total alkalinity (TA) and dissolved inorganic carbon (DIC) (µmol $kg^{-1}$), (D) calculated carbonate parameters for aragonite saturation state ($\Omega_{arag}$), and $pCO_2$ (µatm; inverted) based on DIC-pH pairwise and measured salinity, temperature, nutrients (phosphate and silicate) data, (E) dissolved oxygen (DO; mg $L^{-1}$), and (F) temperature corrected pH (total scale). End-of-century projections according to IPCC-AR5 RCP8.5 "business as usual" scenario for pH (reduction by 0.4 units), $\Omega_{arag}$ (2.0; blue dashed), and $pCO_2$ (750 µatm; red dashed).

**Figure 3** Carbonate chemistry parameters and sea surface temperature (SST) composite from S1, S2, S3 and S4 along the shallow reef flat of Kahekili, Maui and cubic spline fits highlighting diurnal cycle for the first (2016-03-16 to 2016-03-19; solid line) and second (2016-03-21 to 2016-03-24; dashed line) sampling period for (A) Temperature, (B) pH, (C) *n*DIC and (D) *n*TA (µmol $kg^{-1}$), (E) $\Omega_{arag}$ and (F) $pCO_2$ (µatm).

**Figure 4** Histogram Δ*n*TA and Δ*n*DIC capturing deficits and surpluses of *n*TA and *n*DIC with respect to open ocean conditions. Overall a transition from net $CaCO_3$ production to net $CaCO_3$ dissolution and net photosynthesis to net respiration occurred between the first (2016-03-16 to 2016-03-19; blue)

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and second (2016-03-21 to 2016-03-24; red) sampling period for the shallow sampling sites (A)-(B) S1 and (C)-(D) S2, and the two deeper sites (E)-(F) S3, and (G-H) S4. Statistical ($p$=0.05) deficit and surplus values (±) for Δ$n$TA and Δ$n$TA shown in parentheses.

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**Figure 5** Seawater carbonate chemistry system along the reef flat off Kahekili as a function of $n$DIC and $n$TA for the shallow sampling sites (A). S1 and (B) S2, and two deeper sites (C) S3, and (D) S4 for the first (blue) and second (red) sampling periods and their respective slopes (solid lines) of $n$DIC and $n$TA (Table 1) and theoretical slope (dashed lines) given the predicted net effects of photosynthesis, respiration, calcification, and dissolution as shown in (E) and the respective change in net community calcification (NCC) and net community production (NCP). The relative position of the open ocean $n$DIC and $n$DIC values are reported as 1977 (SD 11) and 2304 (SD 5) μmol $kg^{-1}$ (adapted from Dore et al., 2009).

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| Site | *n*TA-*n*DIC Slope | NCC:NCP | $r^2$ |
|---|---|---|---|
| 2016-03-16 to 2016-03-19 | | | |
| S1 | 0.88 | 0.78 | 0.94 |
| S2 | 0.67 | 0.50 | 0.75 |
| S3 | 0.93 | 0.88 | 0.89 |
| S4 | 0.93 | 0.87 | 0.92 |
| 2016-03-21 to 2016-03-24 | | | |
| S1 | 0.72 | 0.56 | 0.78 |
| S2 | 0.56 | 0.39 | 0.77 |
| S3 | 0.99 | 0.98 | 0.95 |
| S4 | 1.04 | 1.08 | 0.94 |

**Table 1**

Slope of salinity normalized total alkalinity (*n*TA): salinity normalized dissolved inorganic carbon (DIC), net community calcification: net community production ratio (NCC:NCP=2ΔDIC/ΔTA-1) (Suzuki and Kawahata, 2003) and correlation coefficients ($r^2$).

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