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Spatiotemporal variability in seawater carbon chemistry for a coral reef flat in Kāneʻohe Bay, Hawaiʻi

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Running Head: Reef seawater carbon chemistry in Kāneʻohe Bay

Keywords: coastal biogeochemistry, coral reef, ocean acidification

Abstract

Coral reef community composition and ecosystem function may change in response to anthropogenic ocean acidification. However, the magnitude of acidification on reefs will be modified by natural spatial and temporal variability in seawater CO_2 chemistry. Consequently, it is necessary to quantify the ecological, biogeochemical, and physical drivers of this natural variability before making robust predictions of future acidification on reefs. In this study, we measured temporal and spatial physiochemical variability on a reef flat in Kāneʻohe Bay, Oʻahu, Hawaiʻi using autonomous sensors at sites with contrasting benthic communities and by sampling surface seawater CO_2 chemistry across the reef flat at different times of the day during June and November. Mean and diurnal temporal variability of seawater CO_2 chemistry were more strongly influenced by depth gradients (~0.5-10 m) on the reef rather than benthic community composition. Spatial CO_2 chemistry gradients across the reef flat reflected the cumulative influence from benthic metabolism, bathymetry, and hydrodynamics. Based on graphical assessment of TA-DIC data, reef metabolism in November was dominated by organic carbon cycling over inorganic carbon cycling, while these processes were closely balanced in June. Overall, this study highlights the strong influence of depth on reef seawater CO_2 chemistry variability through its effects on benthic biomass to seawater volume ratio, seawater flow rates,

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and residence time. Thus, the natural complexity of ecosystems where a combination of ecological and physical factors influence reef chemistry must be considered when predicting ecosystem biogeochemical responses to future anthropogenic changes in seawater CO_2 chemistry.

Introduction

The increase in anthropogenic carbon dioxide (CO_2) in the atmosphere since pre-industrial time has resulted in a range of environmental changes including warming of the troposphere and the upper ocean, and acidification of the surface ocean (Hartmann et al. 2013; Rhein et al. 2013). Ocean acidification (OA) is caused by uptake of anthropogenic CO_2, increasing concentrations of dissolved CO_2 and hydrogen ions [H^+] (i.e., lower pH) (Solomon et al. 2009; Bates et al. 2014). These changes in seawater CO_2 chemistry result in a decrease in carbonate ions [CO_3^{2-}] and the seawater saturation state (Ω) with respect to calcium carbonate ($CaCO_3$) minerals (e.g., aragonite and calcite; $\Omega =[Ca^{2+}][CO_3^{2-}]/K_{sp}^*$ where K_{sp}^* is the ion concentration solubility product at equilibrium). Ongoing OA has raised concerns about the potential impacts on marine calcifiers (i.e., shellfish, crustaceans, corals, and calcifying algae) because their ability to secrete calcareous shells or skeletons partly depends on seawater pH and Ω (Kleypas et al. 2006; Doney et al. 2009). Coral reefs are thought to be particularly vulnerable to OA due to experimental results under high CO_2 conditions showing: 1) decreased rates of calcification of corals and calcifying algae (Chan and Connolly 2012; Comeau et al. 2013;

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Johnson et al. 2014); 2) increased rates of carbonate dissolution and bioerosion (Andersson et al. 2009; Wisshak et al. 2012; Eyre et al. 2014, 2018); and 3) increased growth and competitive strength of fleshy macroalgae (McCook et al. 2001; Diaz-Pulido et al. 2011; Johnson et al. 2014). Combined with the effects of other environmental perturbations (e.g., warming, eutrophication, sedimentation, overfishing), these changes may scale up to ecosystem-wide impacts on coral reefs, resulting in shifts from net calcification and accretion towards net $CaCO_3$ dissolution and erosion (Silverman et al. 2009; Andersson and Gledhill 2013; Eyre et al. 2014, 2018), and shifts towards reefs dominated by fleshy macroalgae (Jokiel et al. 2008; Kroeker et al. 2013). However, the magnitude and timing of these shifts are currently uncertain and vary between different reefs.

To understand future impacts of OA on coral reefs, it is necessary to understand how reef seawater CO_2 chemistry will change. Many predictions of how coral reefs will respond to OA are based on projected acidification in the open ocean rather than the actual reefs (e.g., Silverman et al. 2009; Hoegh-Guldberg et al. 2007; Ricke et al. 2013). However, seawater CO_2 chemistry on coral reefs can be substantially different compared to the open ocean because of large natural variability owing to high biological activity, high biomass to water volume ratio (i.e., shallow depth), and variable flow rates (Hofmann et al. 2011; Andersson and Mackenzie 2012; Drupp et al. 2013; Andersson et al. 2014). Consequently, this large variability may confound the magnitude (Jury et al. 2013; Shaw et al. 2013) and effects of OA on reef organisms and ecosystems (Dufault et al. 2012; Cornwall et al. 2013; Rivest et al. 2017), and both the mean

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and/or extreme pH and Ω values may be important in determining these effects (Boyd et al. 2016). Hence, there is a need to understand when and where seawater pH and Ω will reach certain conditions within different coral reef habitats, as well as the specific set of properties and mechanisms leading to these conditions (Falter et al. 2013).

The variability of seawater CO_2 chemistry on coral reefs is influenced by a combination of ecological, biogeochemical, and physical properties and processes (e.g., Bates et al. 2010; Kleypas et al. 2011; Falter et al. 2012; Shaw et al. 2012; Albright et al. 2013; Drupp et al. 2013; Falter et al. 2013; Teneva et al. 2013; Koweek et al. 2015a, b; Lowe and Falter 2015). The major biogeochemical processes to consider include net community production (NCP=primary organic carbon production – autotrophic and heterotrophic respiration) and net community calcification (NCC=calcification – $CaCO_3$ dissolution), which affect the seawater dissolved inorganic carbon (DIC) and total alkalinity (TA) balance. NCP mainly affects DIC with positive NCP reducing DIC and increasing pH and Ω, whereas positive NCC results in a reduction of TA and DIC in a ratio of 2:1 leading to a decrease in pH and Ω (Zeebe and Wolf-Gladrow 2001; Andersson and Gledhill 2013). The balance of NCP and NCC contributes to the overall reef metabolism, which is strongly linked to diurnal and seasonal cycles in light and temperature, but also external input of organic material and nutrients via advection, upwelling, fluvial input, runoff, and internal waves (Kawahata et al. 2000; Bates et al. 2010; Jantzen et al. 2013; Eidens et al. 2014; van Hoytema et al. 2016). Air-sea CO_2 exchange also influences the reef seawater CO_2 chemistry,

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but for reefs with seawater residence times of a few hours to several days, this flux is typically minor relative to the influence of NCP and NCC (Frankignoulle et al. 1996; Yeakel et al. 2015).

The degree of influence exerted by different biogeochemical processes (i.e., the balance between NCC and NCP) on seawater CO_2 chemistry is directly related to the benthic community composition including coral cover and the relative abundances of calcifiers and non-calcifiers (Anthony et al. 2011; Kleypas et al. 2011; Page et al. 2016). Early studies of reef productivity at Eniwetok Atoll (Marshall Islands) noted differences in seawater pH and oxygen depending on the relative abundance of algal turf (Johannes et al. 1972; Smith 1973) and more recently, flume and mesocosm experiments have quantified how different key benthic functional groups on reefs (e.g., corals, calcifying algae, carbonate sand, macroalgae, and mixed communities) modify seawater CO_2 chemistry differently (Anthony et al. 2011; Anthony et al. 2013; Jokiel et al. 2014; Page et al. 2016, 2017). Because of the differential influence of varying benthic communities on seawater pH and Ω, it has been proposed that some habitats may be able to alleviate OA while others may exacerbate it (Semesi et al. 2009; Anthony et al. 2011; Kleypas et al. 2011; Manzello et al. 2012; Anthony et al. 2013; Hendricks et al. 2014; Camp et al. 2016; Kwiatkowski et al. 2016).

In addition to the benthic community composition, the geomorphology, seawater depth, ratio of biomass to water volume, flow rates, and residence time are important factors that influence the variability of seawater CO_2 chemistry (Drupp et al. 2013; Falter et al. 2013; Lowe and Falter 2015). Longer residence time, shallower depth, and higher biomass allow biological

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processes to modify seawater CO_2 chemistry to a greater extent compared to shorter residence time, deeper depth, and lower biomass. However, the absolute changes in pH and Ω are dependent on the relative modification of DIC and TA as the influence of NCP and NCC on these parameters can counteract each other (Andersson and Gledhill 2013; Page et al. 2016, 2017). Previous studies based on coupled hydrodynamic-biogeochemical models parameterized with field data have emphasized the importance of both benthic metabolism and residence time in controlling the temporal and spatial variability in seawater CO_2 chemistry (Zhang et al. 2012; Falter et al. 2013).

We have previously conducted a number of mesocosm experiments at the Hawaiʻi Institute of Marine Biology (HIMB) in Kāneʻohe Bay to elucidate how OA may affect coral reef community metabolism and how different benthic communities modify the overlying seawater CO_2 chemistry (Andersson et al. 2009; Jokiel et al. 2014; Page et al. 2016, 2017). Some of our findings suggested that algal dominated areas and nighttime $CaCO_3$ dissolution could partially counteract reductions in pH at the local scale (Page et al. 2016) whereas communities with high coral cover experienced the lowest daily seawater pH, which was exacerbated at night due to the combined influence of negative NCP and positive NCC (Page et al. 2017). Although these mesocosm studies identified key relationships between community composition, benthic metabolism, and seawater CO_2 chemistry under controlled laboratory conditions, there is a need to bridge these results across natural functional, spatial, and temporal scales (Andersson et al. 2015; Edmunds et al. 2016). This requires comparison of experimental results with observations

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from the field to ascertain whether observed relationships hold true and can be extrapolated to the natural environment.

In this study, we built on the previous mesocosm experiments conducted at HIMB (Andersson et al. 2009; Page et al. 2016, 2017) to evaluate the spatio-temporal variations in seawater CO_2 chemistry for a reef flat in Kāneʻohe Bay, Oahu, Hawaiʻi (Fagan and Mackenzie 2007; Shamberger et al. 2011; Massaro et al. 2012; Drupp et al. 2013; Courtney et al. 2018). Our overarching research objectives were to better understand: 1) the natural temporal and spatial variabilities in seawater CO_2 chemistry for this reef flat; 2) how these variabilities relate to ecological (e.g., community composition), biogeochemical (NCP vs. NCC), and physical (e.g., depth and flow rates) properties; and 3) the relative importance of these drivers. Resolving these relationships will improve understanding of natural variability of CO_2 chemistry on coral reefs, identify reef areas that are more or less vulnerable to OA, and better parameterize regional models aimed at forecasting local and regional coral reef seawater CO_2 chemistry under changing ecological (Gardner et al. 2003; Wilkinson et al. 2008; Bruno and Valvidia 2016), and biogeochemical conditions.

Methods

Temporal and spatial variability in seawater CO_2 biogeochemistry was monitored over a barrier reef in Kāneʻohe Bay, Hawaiʻi (Figure 1) during June and November of 2016. Kāneʻohe Bay, which is located on the northeastern (windward) coast of Oahu, encompasses an area of 13

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km (alongshore) by 4 km (cross-shore). The bay contains a characteristic reef crest, reef flat, sand flat, and lagoon that includes 75+ patch reefs scattered throughout (Smith et al. 1981; Jokiel 1991). The shallow reef flat platform (< 4 m) contains a variety of benthic communities that are dominated by rubble, coral, or sand; much of the reef flat is classified as a "mixed community" with two or more of these functional groups equally present. The rubble community mainly consists of coral skeletons overgrown by a variety of benthic algae (CCA, *Halimeda* spp., and turf algae) with few coral colonies scattered throughout (Smith et al. 1981; Jokiel 1991).

Temporal variability was measured by deploying autonomous instruments on the benthos while surface seawater CO_2 chemistry was sampled via spatial surveys. In June, instruments deployed along one transect across the barrier reef platform (Figure 1; Stations 1-3) measured seawater conditions for 15 days. The spatial surveys (n=4) covered the southeastern portion of the reef flat, reef crest, and sand flat. In November, instruments were deployed at Stations 1-3 and along an additional transect that was perpendicular to the original transect (Figure 1; Stations 4-5) in order to capture any spatial gradients along the reef flat. The instruments were deployed for a shorter period of time (9 days) but more spatial surveys of surface seawater CO_2 chemistry were conducted (n=6). See Table 1 for a summary of the sampling effort for each month.

Autonomous sampling of seawater carbon biogeochemistry

Instruments were deployed on the reef flat to measure short-term variability in seawater temperature, salinity, pH, dissolved oxygen (DO), light, and currents. Each of the stations

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consisted of different benthic community compositions and seawater depths (Table 1). Instruments measured physical and chemical parameters of seawater every 30 minutes. In June, Stations 1-3 were sampled. Station 1, which was located over rubble closest to the reef crest, included a SeapHOx (Bresnahan et al. 2014) that measured seawater pH, DO, temperature, and salinity. Station 2, which was located at the midpoint of the transect and had a mixed community of rubble and coral, was equipped with a Seafet (pH) and Aquadopp High Resolution Current Profiler (Nortek Instruments). Three types of instruments were deployed between large coral colonies at Station 3: SeapHOx, Aquadopp Low Resolution Current Profiler (Nortek Instruments), and an ECO-PAR (photosynthetically active radiation) sensor (Wetlabs, Seabird Scientific). On June 24, the concrete block that held the PAR sensor tipped over, but it was placed upright again on June 29. Because the sensor did not receive full light due to this displacement, data for this time frame were excluded from further analysis.

During November, temporal variability was measured at five stations that formed a cross (i.e., two transects) that were intended to capture gradients across and along the reef flat. Station 1 (rubble community) included a SeapHOx and Aquadopp Low Resolution Current Profiler. A Seafet and Aquadopp High Resolution Current Profiler were deployed at Station 2 (mixed community). Station 2 also had a Seabird SBE 16plus V2 recorder (temperature and salinity) equipped with an oxygen optode (Aandera Oxygen Sensor 3835). Station 3 (coral community) consisted of a SeapHOx and ECO-PAR sensor. At Station 4, the benthic community contained mostly coral and sand. A Seabird SBE 16plus V2 recorder equipped with an oxygen optode

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(Aandera Oxygen Sensor 3835) was deployed at this station. Station 5 was also a mixed community of rubble and sand, where a third Seabird SBE 16plus V2 recorder was deployed.

Cross-validation between instrument temperature and salinity measurements was performed by measurements using a YSI Professional Plus multi-meter probe (Texas Instruments, Inc.). Agreement was observed within the accuracy of the YSI (±0.2°C and ±0.1 salinity) at all stations except for temperature at Station 5, which was corrected accordingly. DO values are reported relative to mean conditions at each station (ΔDO) since no calibration samples were collected to verify absolute DO concentrations. Autonomous pH measurements were cross-calibrated at *in situ* conditions measured after a two-day conditioning period. Seawater samples were taken near the intake valve of the SeapHOx and Seafet instruments while the instruments were measuring for laboratory analysis of DIC and TA (see below for sampling protocol) to verify instrument pH measurements. Seawater pH was calculated from *in situ* temperature, salinity, pressure, DIC, and TA using CO2sys (Lewis and Wallace 1998) and stoichiometric dissociation constants (K^*_1 and K^*_2) defined by Mehrbach et al. (1973) as refit by Dickson and Millero (1987). pH was defined on the total hydrogen ion scale (pH_T). Repeated samples taken throughout the sampling periods confirmed that there was no drift in the instrument pH measurements over time.

Temporal variations in additional environmental conditions were assessed from publically available data from NOAA. Water level relative to Mean Lower Low Water (MLLW) was measured at Moku o loʻe, HI by the NOAA Tides and Currents program

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(https://tidesandcurrents.noaa.gov/waterlevels.html?id=1612480). Wave height data for

Kāneʻohe Bay (Station 225) was obtained from the Coastal Data Information Program

(https://cdip.ucsd.edu/themes/?zoom=auto&tz=UTC&r=999&un=0&pb=1&d2=p70&u2=s:225:s

t:1:v:pm_download_table:dt:201809). Hourly wind speed and direction data for Station

MOKH1 (Moku o loʻe, HI) were downloaded from the NOAA National Buoy Data Center

(https://www.ndbc.noaa.gov/station_history.php?station=mokh1).

Spatial sampling of surface seawater CO_2 chemistry

Seawater CO_2 chemistry was measured via boat over a spatial grid covering ~1.45 km by

~1.25 km area of the barrier reef in Kāneʻohe Bay (Figure 1) in the morning and afternoon to

capture spatial variability throughout the diurnal period. This spatial area was selected to

encompass a variety of benthic habitats including the reef crest (also referred to as "outer reef"),

reef flat (mostly rubble), backreef, and a carbonate sand flat. Each spatial survey took

approximately 60-90 min, which is shorter than the water residence time that ranges of the order

of <1 day to a few days (Lowe et al. 2009).

At each sampling location, *in situ* temperature (±0.2°C), salinity (±0.1), and DO (±0.2 mg

L^{-1}) were measured using an YSI Professional Plus multi-parameter probe (Texas Instruments,

Inc.) approximately 0.25 m below the sea surface. Once again, ΔDO is reported relative to mean

conditions for each spatial survey in order to assess the relative changes over space. In addition,

seawater from each site was collected into 250 mL Pyrex glass bottles and immediately poisoned

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with a saturated solution of mercuric chloride ($HgCl_2$) to halt any biological activity in the sample. These samples were shipped to Scripps Institution of Oceanography where they were analyzed for DIC and TA using an Automated Infrared Inorganic Carbon Analyzer (AIRICA, Marianda Inc.) equipped with a LI-COR 7000 CO_2/H_2O gas analyzer and open-cell potentiometric acid titrations, respectively, according to standard protocols for seawater CO_2 measurements (Dickson et al. 2007).

The accuracy and precision of the DIC and TA instruments were checked periodically using certified reference material from the laboratory of A. Dickson (Scripps Institution of Oceanography). Accuracy was calculated as the average (± 1 sd) offset from certified values of DIC and TA. During June, DIC had an accuracy of -0.55 ± 2.05 μmol kg^{-1} (n=25) and TA had an accuracy of -1.77 ± 1.45 μmol kg^{-1} (n=10). During November, the accuracy of DIC and TA were -1.84 ± 1.73 (n=72) and -0.35 ± 2.41 μmol kg^{-1} (n=24), respectively. Because DIC measurements on occasion were subject to slight systematic drift, CRM was analyzed every 5 samples in order to capture any potential drift and enable corrections (note though that the reported accuracy represents the accuracy of uncorrected data). Seawater pCO$_2$, pH, and Ω_a were calculated from *in situ* temperature, salinity, pressure, DIC, and TA using CO2sys (Lewis and Wallace 1998) as previously described for the instrument calibration samples.

In order to visualize the spatial variability in measured and calculated parameters of seawater chemistry, data were interpolated between sampling sites using a triangulation-based cubic interpolation in MATLAB. A graphical analysis of TA and DIC vectors (Deffeyes 1965;

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Andersson and Gledhill 2013) was also performed as an additional method for visualizing

seawater chemistry changes on the reef flat due to benthic metabolism (NCC and NCP). Surface

DIC and TA (mean ± 1 sd) measured at Station ALOHA as part of the ongoing Hawaii Ocean

Time Series (Karl and Lukas 1996) were included as an "offshore" reference

(http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html). To compare regression slopes with

mesocosm experimental results of Page et al. (2016), we calculated the ΔTA and ΔDIC relative

to the average TA and DIC for the "outer reef" sites, which most closely represents the source

water for this reef flat. Type II linear regressions, which assume error for both the y and x axes,

were fit to TA and DIC data for June and November using the 'lmodel2' package within R

v3.3.1 software (R Development Core Team 2008). The slopes produced by the major axis

method are reported.

Results

Temporal variability based on autonomous sensors

Seasonal variability

Distinct differences in wave height and light intensity (PAR) were observed in Kāneʻohe

Bay between June and November while other environmental and oceanographic properties (e.g.,

wind, tidal range, salinity, and currents) showed less variation (Figure 2). November sampling

dates experienced larger swell (mean significant wave height (H_s) ± 1 sd = 2.58 ± 0.30 m)

compared to June sampling dates (H_s = 1.73 ± 0.37 m) (Figure 2), which likely generated shorter

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residence times in November relative to June (Lowe et al. 2009; Courtney et al. 2018). Photosynthetically active radiation (PAR) levels on average were higher during June (daily integrated mean $\pm$ 1 sd = 432 $\pm$ 476 μmol photons m^{-2} s^{-1}) compared to November (278 $\pm$ 269 μmol photons m^{-2} s^{-1}). Maximum daily light levels ranged from 1311-1655 μmol photons m^{-2} s^{-1} in June while maximum levels reached 415-1206 μmol photons m^{-2} s^{-1} in November with higher maximum irradiance during the last few days of sampling (Figure 2).

During both sampling periods in June and November, the bay experienced northeasterly trade winds and the amplitude of the mixed semi-diurnal tides was less than 1.0 m (Figure 2). Mean seawater temperature ($\pm$ 1 sd) was 26.5 $\pm$ 0.4°C in June and 26.1 $\pm$ 0.2°C in November. Salinity was similar across seasons and most stations, averaging 34.80 $\pm$ 1.40 in June and 34.96 $\pm$ 0.14 in November. Current speeds were variable but never exceeded 0.3 m s^{-1} during both months (Figure 3). In June, seawater flowed predominantly towards the southwest at Stations 2 and 3 with slightly higher flow rates at Station 2, which was deeper than Station 3. The same flow direction was observed at Station 2 in November whereas currents at Station 1 flowed predominantly to the southeast (Figure 3). Drifters that were deployed over the reef in November corroborated this finding as they were observed to turn toward the southeast in the proximity of Station 1 (Figure 1). During both months, daily cycles of seawater temperature, pH, and DO closely followed light levels with higher values during the day and lower values at night (Figure 2).

Daily and spatial variability in June

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In June, seawater temperature averaged $26.5 \pm 0.5°C$ at Station 2 (mixed community) and $26.5 \pm 0.7°C$ at Station 3 (coral community) (Figure 2). Each station experienced higher seawater pH and DO during the day and lower values at night. Station 1 had a mean seawater pH of 8.01 ± 0.04 over the 12-day study period. This station was located closest to the outer reef and the benthos was dominated by rubble. Station 2, which was also covered in rubble with few scattered coral colonies (mixed community), experienced a similar mean pH but higher variability (8.01 ± 0.06). The innermost station located in an active coral reef community (Station 3) had the lowest mean and highest variability in seawater pH of 7.98 ± 0.07. The lower overall mean at this station was attributed to lower seawater pH during night.

Because the DO sensor on one of the SeapHOxes failed, only the DO data for the coral community at Station 3 are reported (Figure 2); this station experienced relatively consistent variability throughout the study period. Dissolved oxygen was as low as 100 μmol kg^{-1} below mean conditions at night and then increased to ~150 μmol kg^{-1} above mean conditions by midday when light levels were the highest. The mean daily range at this station was 188 ± 32 μmol kg^{-1}.

Daily and spatial variability in November

November was slightly cooler than June with average temperatures ranging from $25.9 \pm 0.6°C$ (Station 3) to $26.1 \pm 0.6°C$ (Station 4). The shallowest stations (Stations 4 and 5) experienced the highest diurnal variability and Station 5 also experienced the highest daytime (maximum) seawater temperatures (Figure 2).

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Mean seawater pH was similar across all stations with Station 1 (rubble community) experiencing lower variability (8.02 ± 0.04) compared to the mixed community (Station 2) and the coral community sites (Station 3) which were similar (8.01 ± 0.07) (Figure 2). During the first few days of sampling, each station experienced similar daytime maximum seawater pH. However, during the last three days of sampling, daytime maximum seawater pH was highest at the outermost station (Station 1) and lowest at the innermost coral-dominated station (Station 3).

Similar to seawater pH, DO was higher during the day and lower at night (Figure 2). The diurnal variability of DO was smaller than observed in June with lower daytime elevation and lower nighttime depression relative to the mean. The daily variability of DO at each station ranged from 74 ± 39 μmol kg^{-1} (Station 1; rubble community) to 111 ± 46 μmol kg^{-1} (Station 4; mixed community).

Spatial variability based on boat surveys

Seasonal variability

There were distinct spatial gradients in measured (T, ΔDO, DIC, TA) and calculated (pCO$_2$, pH, Ω$_a$) parameters of seawater CO$_2$ chemistry across the reef flat during both June and November (Figures 4-7). The spatial sampling also revealed seasonal differences in mean temperature, salinity, DIC, and TA (Table 2). Seawater temperature and salinity were slightly higher in June (26.8 ± 0.6°C and 35.08 ± 0.08) compared to November (26.2 ± 0.7°C and 34.82 ± 0.24). In contrast, June experienced lower mean DIC (1914 ± 39 μmol kg^{-1}) and TA (2216 ± 35

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µmol kg^{-1}) compared to November (DIC: 1960 ± 50 µmol kg^{-1}; TA: 2261 ± 28 µmol kg^{-1}). Mean pH, pCO$_2$, and Ω_a were relatively similar between June and November (Table 3).

Daily and spatial variability in June

In general, seawater temperature in June was lower in the morning (26.5 ± 0.4°C) than in the afternoon (27.2 ± 0.5°C). The shallower sandy stations to the west were warmer than the other stations (Figure 4). Dissolved oxygen generally followed the same pattern as temperature whereas DIC mirrored the oxygen distribution. Mean DIC was ~30 µmol kg^{-1} lower in the afternoon (1897 ± 38 µmol kg^{-1}) than during the morning (1931 ± 38 µmol kg^{-1}) surveys. Mean TA was relatively similar between surveys regardless of the time of day (morning surveys: 2217 ± 35 µmol kg^{-1}; afternoon surveys: 2215 ± 36 µmol kg^{-1}), but there was always drawdown of TA from the outermost to the innermost stations with the lowest TA observed at the coral community stations (Figure 9). Seawater pCO$_2$ was higher in the morning compared to the afternoon while pH and Ω_a had the opposite trends. There was a pattern of increasing pCO$_2$ and decreasing pH and Ω_a from northwest to southeast during the majority of surveys, particularly in the afternoon (Figure 5).

Daily and spatial variability in November

Similar to our observations in June, seawater temperature was generally higher in the afternoon (26.5 ± 0.5°C) compared to the morning (25.6 ± 0.4°C). The shallowest stations over the sand flat experienced the coolest temperatures during the morning and warmest temperatures

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in the afternoon, typically leading to a spatial gradient from southwest to northeast of increasing temperature during the morning and decreasing temperature in the afternoon. DO displayed smaller spatial gradients in November compared to June. The highest DIC values were observed during the November morning surveys (2005 ± 25 μmol kg^{-1}) while the lowest values were observed during the afternoon surveys (1937 ± 44 μmol kg^{-1}). The lowest values were observed over the shallow sand flat, resulting in a spatial gradient of higher to lower DIC from southwest to northeast. Similar to June, mean TA across the entire survey area was relatively consistent between morning and afternoon (2263 ± 21 μmol kg^{-1} and 2260 ± 31 μmol kg^{-1}, respectively), but with the largest TA drawdown observed over the coral community stations during the afternoon (Figure 6). As observed in June, seawater pCO_2 was higher in the morning compared to the afternoon while pH and Ω_a showed the opposite pattern. The sand flat had the lowest pCO_2 and highest pH and Ω_a during the afternoon (Figure 7).

Effects of depth and benthic community composition

During both months, spatial gradients in seawater physical and chemical parameters appeared to reflect a combination of depth (Figure 8), benthic community composition (Figure 9) and the integrated influence of biogeochemical processes on seawater as it flowed over the reef (i.e., the chemical memory of its flow trajectory; Figure 10). The lowest mean DIC and the highest mean temperature, pH, and Ω_a were all associated with the shallowest depths of the reef flat (Figure 8). The largest changes in these parameters occurred between 0 and 2 m while they

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remained fairly constant beyond 2 m depth. Furthermore, the shallowest sites experienced the

greatest variability in these parameters, which was especially pronounced in November. In

contrast, there were no clear trends with respect to seawater TA as a function of depth, but TA

was always lower at the coral community sites compared to the other communities (Figures 8-9).

Based on the spatial measurements in June, there were qualitatively small differences in

mean DIC and TA between the outer reef, rubble, and mixed communities whereas the coral

community had lower mean DIC and TA, and also exhibited greater variability (Figure 9).

During June, mean TA at the sand community was also slightly lower than the mixed community

whereas mean DIC was similar between these two communities. A slightly different pattern was

observed in November with respect to both DIC and TA. Mean DIC exhibited a gradual

decrease from the outer reef, rubble, and mixed communities towards coral and sand

communities. Mean TA was lower for the coral community but similar between the other

communities (Figure 9).

TA-DIC relationships

In June, there was mostly a drawdown of TA and DIC across the reef flat compared to

offshore surface waters measured at Station ALOHA (Figure 10), indicating +NCC (net

calcification) and +NCP (net organic carbon production). In November, there was still mostly a

drawdown of TA, but DIC was both higher and lower on the reef compared to offshore. The

salinity-normalized TA drawdown was greater in June ($\Delta nTA = nTA_{ALOHA} -$ mean $nTA_{reef} =$

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99±32 μmol kg^{-1}) compared to November (ΔnTA = 34±30 μmol kg^{-1}) while the mean salinity-normalized DIC drawdown was 81±39 μmol kg^{-1} and 22±51 μmol kg^{-1} for June and November, respectively. The slopes of the TA-DIC regressions were less than 1 for each season indicating that carbon cycling across the reef flat was dominated by organic carbon cycling (NCP) versus inorganic carbon cycling (NCC) (Andersson and Gledhill 2013; Cyronak et al. 2018). However, the regression slopes differed between seasons with June having a greater slope (0.85) compared to November (0.24), indicating a potential shift in the relative importance of organic and inorganic carbon cycling between seasons. These regression slopes were slightly lower based on salinity-normalized TA and DIC (0.73 and 0.20 for June and November, respectively). However, based on the 95% confidence intervals, these were not significantly different from the non-salinity normalized slopes. In general, the lowest TA and DIC values were measured over the coral communities within the study area during both June and November.

Discussion

This study used a combination of field research approaches to understand temporal and spatial variabilities in seawater CO_2 chemistry for a coral reef flat in Kāneʻohe Bay, Hawaiʻi. Here, we first discuss the seasonal differences in environmental conditions and seawater biogeochemistry, and then the relative importance of ecological, biogeochemical, and physical drivers of daily temporal and reef-scale spatial variabilities. The results are then compared to previous work highlighting the importance of assessing experimental manipulations and results

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in the context of the dominant properties and forcings that occur in the natural environment, which we discuss in the context of an era of changing coral reef ecosystems and ocean conditions.

Seasonal differences in seawater biogeochemistry

Seasonal differences in light intensity (PAR) and, to a lesser extent, seawater temperature were associated with lower diel variability in DO, higher mean DIC and TA, and higher daytime spatial variability in seawater pH and Ω_a across the reef flat in November compared to June. These differences were most likely due to overall lower TA and DIC drawdowns on the reef and a relative shift in favor of organic carbon cycling (NCP) over inorganic carbon cycling (NCC) during November (Figure 10; Cyronak et al. 2018). The lower TA and DIC drawdowns observed in November may be due to shorter residence time and/or lower rates of NCC and NCP for the reef metabolism to alter the overlying seawater chemistry. Although we did not explicitly estimate residence time during this study, the higher significant wave height observed in November likely resulted in shorter residence time (~5 days) across the reef flat during this month compared to June (~7 days) according to the numerical circulation model developed for Kāneʻohe Bay by Lowe et al. (2009) (the given estimates were based on results for the area denoted "zone 2" in Table 4 in Lowe et al. 2009). Shorter residence time produce shorter contact time between the seawater and benthos, and thus, less alteration of seawater chemistry for a fixed rate of biogeochemical fluxes. This is consistent with a lower drawdown of TA and DIC in November compared to June. However, it is important to recognize that alterations to the

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seawater chemistry are cumulative and represent the net effect of all biogeochemical fluxes affecting the chemistry along a water parcel's flow trajectory across the reef (i.e., the chemical memory). Consequently, the observed lower drawdown of TA and DIC in November could also have been achieved by reduced rates of NCC and NCP or a combination of this and reduced residence time. Based on the observed average drawdown of nTA and nDIC across the reef and the approximate residence times, NCC decreased from 7.1 ± 2.3 to 3.4 ± 3.0 μmol kg^{-1} day^{-1} and NCP from 4.6 ± 3.3 to 0.9 ± 7.2 μmol kg^{-1} day^{-1} between June and November. However, it is important to recognize that these are very rough estimates that need to be viewed with caution as multiple factors that are not accounted for could affect these estimates, especially deviations from the true residence time that is affected by alterations to the wave height, wind and wave direction, wind speed, and tidal amplitude (Lowe et al. 2009). Irrespective of these caveats, in November, lower PAR most likely depressed photosynthesis of marine autotrophs (Chalker 1981; Comeau et al. 2017), which was evident from the smaller daily DO variability compared to June. Seasonal differences in temperature may also have influenced metabolic rates with cooler temperatures repressing respiration and thus DO consumption (Coles and Jokiel 1977; Gillooly et al. 2001), but given the small difference observed between the two study periods (26.5 ± 0.4°C vs. 26.1 ± 0.2°C), this is expected to have had a minor influence (i.e., based on a typical Q10 of 2 to 3 for biological systems, a 0.5°C change in temperature is expected to result in a 3-6% change in metabolic rates; e.g., Newell 1969). Consequently, the large difference in PAR and small difference in seawater temperature between June and November reflect a phase lag between

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these parameters that produce a scenario where seasonal differences in reef metabolism are only weakly influenced by temperature (Falter et al. 2012; Courtney et al. 2017). Seasonal differences in reef metabolism may thus be exacerbated during months of maximum and minimum seawater temperatures, which typically occur in August-September and January-February in Kāneʻohe Bay, respectively. Consequently, in addition to the influence of longer residence time, the greater drawdown and lower mean TA observed in June compared to November may also be due to higher rates of NCC resulting from higher energy availability fueling calcification from primary production (Muscatine 1990; Davies 1984; Rinkevich 1989; Marubini et al. 2001; LaVelle 1979; de Beer and Larkum 2001), higher light intensity possibly stimulating light sensitive ion pumps involved in the process of calcification (Al-Horani et al. 2003; Cohen et al. 2016), but with negligible influence from warmer seawater temperature (Courtney et al. 2017). These findings, however, contrast those from previous studies reporting relatively consistent rates of NCC across seasons in mesocosms (Langdon and Atkinson 2005; Page et al. 2016) and from field studies in Kāneʻohe Bay (Shamberger et al. 2011; Courtney et al. 2018). In particular, Courtney et al. (2018) observed no difference in NCC based on measurements conducted close in time to the present study, but was based on samples from a much greater area of Kāneʻohe Bay compared to the present study. Furthermore, the day-to-day variability can be large in response to changing physical and environmental conditions, and quantifying rates of NCC is typically associated with large uncertainty due to the difficulty of constraining hydrodynamics and quantifying the residence time (Venti et al. 2012; Zhang et al. 2012; Teneva et al. 2013; De Carlo et al. 2017;

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Courtney et al. 2018). From the current study, it was evident that the temporal and spatial variabilities in seawater CO_2 chemistry across the reef flat were due to a combination of factors ranging from environmental conditions (e.g., light and temperature), physical properties (e.g., geomorphology and depth), benthic community composition (e.g., coral vs. rubble vs. sand communities), reef metabolism (NCP vs. NCC), and seawater hydrodynamics (e.g., seawater flow rates, flow trajectory, and residence time) as previously highlighted by Falter, Lowe, Zhang and colleagues (Falter et al. 2012, 2013; Zhang et al. 2012; Lowe and Falter 2015 and references therein).

Drivers of daily variability across the reef

The daily light cycle was clearly the dominant driver of diel variability of seawater temperature and biogeochemical properties with minor influences from semi-diurnal tidal flow (Figure 2). This is consistent with observations from many other shallow coral reef environments (e.g., Hofmann et al. 2011; Guadayol et al. 2014; Koweek et al. 2015a, b; Takeshita et al. 2016; De Carlo et al. 2017). In the current study, day-to-day variations in seawater chemistry for a given location were likely due to variations in solar irradiance, tidal cycles, wind speed, and swell size and direction; these properties all influence the rates of reef metabolism (i.e., NCC and NCP), the timing of low and high tides, and/or the water circulation on the reef (Falter et al. 2013; Lowe and Falter 2015). The circulation of the reef flat in Kāneʻohe Bay is mainly driven by breaking waves and the associated wave setup at the reef crest, which drives shoreward water

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flow over the reef flat with modifications from geomorphology and depth gradients (Lowe et al. 2009; Falter et al. 2013; Lowe and Falter 2015). Some general trends emerged, however, from the different measurement approaches that provide insight to the influence of different factors such as benthic community composition, depth gradients, and hydrodynamics on the Kāneʻohe Bay reef flat CO_2 chemistry.

Benthic community composition

Based on the observed lower TA over the coral community during both months (Figure 9), it appears that only the coral community had sufficiently high enough rates of net calcification to distinguish its influence on TA and DIC from the other communities under the prevalent conditions. However, one also has to question whether the observed lower TA and DIC could result from re-entrainment of lower salinity lagoon water at the coral reef sites, but TA-salinity plots refute this possibility as the observed changes in salinity were too small to account for the observed changes in TA. Despite differences in TA and DIC between the communities, however, pH and Ω_a values were relatively similar across communities in June (Figure 9), which can be attributed to the close balance between organic and inorganic carbon metabolism (Figure 10; Andersson and Gledhill 2013). In contrast, mean pH and Ω_a and the variability of these parameters in November gradually increased from the outer reef towards the rubble, mixed, and sand communities owing to higher dominance of organic carbon cycling (Figure 10). The pH measurements from autonomous sensors also showed increasing variability associated with the coral and mixed communities compared to the rubble community but no clear differences in

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mean pH were observed for either month. Differences between spatial and autonomous

measurements result from the fact that spatial measurements were only conducted during the day

at multiple locations while sensors measured continuously throughout both day and night, albeit

at single locations. Although only the coral dominated community's influence on seawater CO_2

chemistry clearly stood out among the different communities, all communities may have exerted

a different influence on seawater chemistry (Page et al. 2016). However, these community-

specific influences on seawater chemistry may have been masked by the influence of more

dominant factors such as seawater depth, flow rates, and flow trajectory.

Physical properties: water depth, flow rates and distance from the outer reef edge

The highest mean seawater temperature, the lowest mean DIC minima, the highest mean

pH and Ω_a maxima, as well as the largest range of variability were all associated with the

shallowest depths of the reef flat, which for water depth less than 2 m changed non-linearly with

decreasing depth (Figure 8). The only exceptions were TA and observations associated with the

coral dominated community. No clear trends were apparent with respect to seawater TA as a

function of depth, but TA was always lower at the coral community compared to the other

communities (Figure 9), which we speculate is attributed to higher rates of calcification within

this community (Anthony et al. 2013; Page et al. 2016). Also, the depth for the coral reef

community is somewhat misrepresented as the immediate area surrounding the sample location

is extremely shallow with depths < 1 m (Figure 1). The explanation for the observed trends as a

function of depth was twofold; first, shallower depth likely resulted in increasing biomass to

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water volume ratio, and thus, greater modification of seawater chemistry owing to

biogeochemical processes (i.e., NCP and NCC) (Falter et al. 2013; Takeshita et al. 2018).

Similarly, shallow depths have higher heat gain or loss per volume of water compared to deeper

parts of the reef, and consequently, experienced greater temperature extremes and variability

(Lowe and Falter 2015). Second, the frictional resistance of the benthos increases non-linearly at

depths < 1 m leading to reduced flow rates and increased contact time between the water and the

benthos, and thus, greater modification of physical and chemical properties (Falter et al. 2013).

Based on water flow measurements from drifters and current profilers, it was evident that flow

rates were on average higher on the outer part than the inner part of the reef flat and deflected

southward due to the shoaling of the seafloor in an east to west direction of the study area

(Figures 1 and 3). Consequently, in addition to higher biomass to water volume ratio, slower

flow rates on the inner part of the reef flat allowed reef metabolism to have a larger influence on

seawater chemistry and also led to greater variability (Zhang et al. 2012; Falter et al. 2013;

Mongin and Baird 2014; Koweek et al. 2015a, b). The proposed underlying influence of depth is

strongly supported by our observations, although the bulk of observations was biased towards

daytime observations.

Although it is evident that depth, flow rates and biomass to water volume ratio all played

important roles on the seawater CO_2 chemistry of the Kāneʻohe Bay reef flat, superimposed on

these effects were those associated with distance from the outer reef edge and the seawater flow

trajectory (i.e., the chemical memory of the water as it transited the reef). As water flowed across

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the reef during the day, the cumulative influence of reef metabolism contributed to a sequential

drawdown of DIC in both June and November, and TA in June (e.g., as shown in Courtney et al.

2018). This partly explains the observed spatial trends in mean pH and Ω_a (Figures 5 and 7). The

combined influences of depth, flow rates and flow trajectory, however, were likely responsible

for the two-directional-gradients in the spatial distribution of chemical properties tracking both

depth gradients and distance from the reef edge (Figures 4 and 6). At night, we would expect the

opposite trends compared to daytime, although the spatial dataset lacks adequate representation

of nighttime conditions. This is partly corroborated by the November (early) morning datasets

(Figures 6-7) and also illustrated in the numerical simulations for an idealized reef flat described

by Falter et al. (2013).

Comparing field observations with experimental results

Any direct comparison between mesocosm experiments and field observations needs to

be viewed with caution due to inherent differences in the two approaches; yet, such a comparison

is critical to better interpret results from both the field and mesocosm experiments (Falter et al.

2012; Andersson et al. 2015). While mesocosm results represent the influence of distinct benthic

communities on seawater chemistry under roughly identical conditions, all results from field

communities essentially represent the influence of mixed communities on seawater chemistry

that is potentially affected by different water depth, biomass to water volume ratio, flow rates,

residence times, and chemical memory. Mean seawater pH values observed in the field were

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elevated relative to mesocosms in both summer and winter (Figure 11), which may be attributed

to differences between the locations (i.e., reef flat field study vs. south bay mesocosm source

water), timing of the studies, and/or the deeper (~3 m) water intake for the mesocosms in the

southern part of Kāneʻohe Bay. Furthermore, diel seawater pH extremes (maxima and minima)

in the field appeared slightly delayed and had similar or greater ranges relative to the

mesocosms. These differences were likely due to the larger spatial scale (100s of m to km),

longer residence time (hours to days; Lowe et al. 2009), and the cumulative influence from

multiple communities for the field observations compared to a residence time of < 1 hour for the

1 m × 1 m flow-through mesocosms (Page et al. 2016, 2017). The influence of residence time

was also apparent in TA-DIC analyses for which the total ranges of changes in TA and DIC were

much smaller in mesocosm experiments compared to field observations due to the shorter

duration for interaction between the benthos and the seawater (Figure 11).

The strong differences between different communities on their influence on seawater

chemistry observed in mesocosms were not apparent in field observations, except for the coral

and sand dominated communities. This was likely due to the more similar composition of field

communities compared to mesocosm communities, and the stronger influence of depth, flow

rates, and cumulative changes in chemistry across communities present in the field (Falter et al.

2013). Observed changes in the balance between inorganic and organic carbon cycling in the

field, however, reaffirmed results from the mesocosms that communities with balanced NCP and

NCC have dampened influence on seawater pH whereas communities dominated by organic

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carbon cycling experience greater overall variability and more extreme pH values (Andersson and Gledhill 2013; Falter et al. 2013; Page et al. 2016; Cyronak et al. 2018). In general, most areas on the reef appeared similarly influenced by organic carbon cycling, but unfortunately there was no distinct area that was markedly dominated by autotrophs such as turf and/or macroalgae necessary to assess their stronger potential to elevate daily mean pH as inferred from mesocosm results (Figure 11). In the mesocosms, these results were partly due to the fact that nighttime influence on pH from respiration was similar across different communities so that the strong positive influence of daytime NCP in algal communities resulted in overall higher daily mean pH. In the field, however, all areas experiencing elevated daytime pH from positive NCP appeared to experience a comparable suppression of pH at night owing to a negative NCP of similar magnitude (Figure 11). This reaffirms the strong control exerted by depth, flow rates, and the cumulative modification of seawater chemistry due to reef metabolism as water flows across the Kāneʻohe Bay reef flat. This influence was especially pronounced during the November spatial surveys, where a gradual decrease in mean DIC and increase in variability were observed across the outer reef, rubble, mixed, and sand communities (Figure 9).

Whether $CaCO_3$ dissolution played a role in buffering nighttime seawater pH or not across the reef flat as indicated in acidified mesocosm experiments (Page et al. 2016) was not clear from the present study due to a lack of nighttime observations. Also, seawater pH and Ω_a remained well above the treatment levels of the mesocosm experiment where net dissolution was observed. Similarly, Shamberger et al. (2011) only observed a few instances of alkalinity

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repletion and net dissolution at night in approximately the same area during winter and summer. In contrast, benthic chamber incubations conducted in the sediments of Kāneʻohe Bay have reported some of the highest net $CaCO_3$ dissolution rates among a range of reef locations in the Atlantic and Pacific Oceans (Eyre et al. 2018) but are obviously limited to this specific benthic community. However, ΔTA-ΔDIC analyses based on spatial samples calculated relative to mean offshore DIC and TA for the "outer reef" sites (n=4) for each survey (n=10), indicated occasional TA repletion across the reef flat suggesting net dissolution (Figure 11), particularly in an area dominated by sand. The latter is consistent with results reported by Drupp et al. (2016) and Eyre et al. (2018). This finding of TA repletion over the shallow sandbar also was observed due to net dissolution of carbonate minerals in the sandy sediments at the CRIMP-2 station (Eyre et al. 2018) and for a larger spatial CO_2 chemistry survey conducted across Kāneʻohe Bay in June 2016 (Courtney et al. 2018).

A comparison was made between the overall net reef metabolism in the field and mesocosm results. Slopes for ΔTA-ΔDIC of 0.23 for the reef flat compared to 0.35 for a mixed mesocosm community in winter, although slopes ranged from 0.02 to 0.55 for individual communities (macroalgae: 0.02, crustose coralline algae: 0.40, corals: 0.41, and carbonate sand: 0.55; Page et al. 2016). Although no statistically significant differences were observed in net metabolism between summer and winter for mesocosm communities (Page et al. 2016), the ΔTA-ΔDIC slope for the reef flat in June exceeded one, indicating a relative increase in the relative importance of inorganic carbon cycling and net calcification compared to organic carbon

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cycling (Figure 11). Environmental conditions (e.g., higher light levels) during June were certainly more favorable for calcification, contributing to the more balanced ratio of inorganic to organic carbon cycling. It has been clearly demonstrated, however, that studies conducted on larger spatial scales tend to have higher TA-DIC or ΔTA-ΔDIC slopes due to integration of processes across multiple habitats and longer timescales over which NCP tends to approach zero (i.e., primary production is roughly balanced by total respiration; Falter et al. 2013; Cyronak et al. 2018).

Seawater CO_2 chemistry on coral reefs under climate change

Based on the results of this study and others (e.g., Shamberger et al. 2011; Falter et al. 2013; Drupp et al. 2016; Eyre et al. 2018), it is evident that different areas and habitats on coral reef flats experience different means and variabilities of CO_2 chemistry linked to a range of factors. Although these properties are partly related to the benthic community composition, in Kāneʻohe Bay, shallow depths ranging from < 0.5 m to 4 m combined with long water residence times (i.e., multiple days) appear to be the most influential factor of CO_2 chemistry extreme values and variability due to the associated increase in biomass to water volume ratio and reduction in flow rate with seafloor shoaling (Drupp et al. 2013; Falter et al. 2013). Consequently, the shallowest parts of the reef were the areas with the strongest potential for exacerbating and/or alleviating OA. However, areas with the most elevated pH conditions during the day also experienced the most suppressed pH conditions at night, which casts doubts on the

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effectiveness of localized seawater buffering over complete diel cycles in these habitats. Indeed, Drupp et al. (unpubl.) demonstrated that the amount of alkalinity produced through sedimentary dissolution of carbonate minerals would be insufficient to buffer reef waters under future OA conditions. In a future high-CO_2 world, the daily range between extreme pH values is also predicted to increase due to reduced buffering capacity (Shaw et al. 2011), further exacerbating these extremes. It is currently unknown whether marine organisms sensitive to seawater CO_2 chemistry have differential susceptibility between day and night, but if so, the range of variability and extreme values may play a role in their overall fitness and response to OA (Rivest et al. 2017). On diel timescales and for individual habitats, organic carbon cycling has the largest influence on seawater CO_2 chemistry, but on longer temporal and larger spatial scales NCP is close to balanced (i.e., primary production and respiration are close to balanced) on coral reefs. The mean and median production to respiration ratio (P:R) for a range of coral reef environments (n=20) are 1.24±0.38 and 1.09, respectively (Falter et al. 2013). Consequently, on longer temporal and larger spatial scales, the influence of inorganic carbon cycling on CO_2 chemistry becomes increasingly important, and the ecosystem scale balance of NCP and NCC ultimately control the offset between mean reef and open ocean TA and DIC, (Figure 11; Cyronak et al. 2018). Hence, ecosystem scale changes in benthic community composition in response to long-term environmental forcing mechanisms and/or short-term disturbances will influence the local seawater CO_2 chemistry properties (for example, compare June to November in Figure 10; see also Andersson et al. 2014 and Cyronak et al. 2018).

Kāneʻohe Bay has a documented history of both short-term and long-term disturbances affecting water column and reef metabolism as well as community composition in response to both natural and human activities (Banner and Bailey 1970; Cox et al. 1973; Smith et al. 1981; Hunter and Evans 1995; Laws and Allen, 1996; Hoover et al. 2006; De Carlo et al. 2007; Drupp et al. 2011; Bahr et al. 2015a, 2017). For example, storm events and the associated input of terrestrially derived nutrients have been observed to initially reduce seawater pCO_2 across the bay due to phytoplankton blooms, followed by a gradual increase in pCO_2 as the organic detritus is decomposed and the bay returns to baseline conditions (Fagan and Mackenzie 2007; Drupp et al. 2011). In 2014 and 2015, abnormally warm seawater temperatures led to widespread coral bleaching and mortality across the bay (Bahr et al. 2015b, 2017). During the 2015 event, a transition towards net heterotrophy and net $CaCO_3$ dissolution was recorded at the reef scale, which consequently modulated net changes in seawater pH (Courtney et al. 2018). Due to limited coral mortality and rapid recovery of symbiotic algae, the reef recovered to pre-bleaching rates of NCC in less than 1 year. Similar modulation in seawater pH was reported by Andersson et al. (2014) under a range of modeling scenarios for the Bermuda carbonate platform in response to a decrease in NCC and increase in NCP, which was most effective in areas of long residence time reflecting the integrated chemical memory of the reef water.

The largest and most significant perturbation of Kāneʻohe Bay to date includes sewage input to the bay which began in the 1950s but accelerated considerably in the period from the late 1960s to the late 1970s (Banner and Bailey 1970; Smith et al. 1981). This caused increased

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sediment and nutrient inputs to the bay causing eutrophication, particularly in its southern sector and supporting a much higher abundance of filter and suspension feeders and the green bubble algae *Dictyosphaeria cavernosa* at the expense of coral cover, which decreased radically during this time period (Banner and Bailey 1970; Hunter and Evans 1995; Bahr et al. 2015a). In addition to the changes in benthic community composition, reefs shifted towards net heterotrophy and net $CaCO_3$ dissolution due to increased respiration, lower calcification, and higher chemical dissolution rates, and these changes were pronounced at reefs located closest to the two primary sources of sewage effluent in the southern sector of Kāneʻohe Bay (Smith et al. 1981). Once sewage was diverted away from the bay in 1978, coral populations recovered and the abundance of *D. cavernosa* decreased (Smith et al. 1981; Hunter and Evans 1995; Laws et al. 1996).

As coral reefs respond to future warmer temperatures, OA, sea level rise, and local perturbations such as eutrophication (i.e., due to both land runoff and occasional sewage spills) and overfishing, the net metabolism and the benthic community composition will continue to change, consequently changing seawater CO_2 chemistry. The current study highlights that results derived under controlled experimental conditions need to be carefully examined in the light of the dominant properties and processes occurring in the natural environment (Falter et al. 2012; Andersson et al. 2015). Although experimental results reveal the operational function of different properties (e.g., community composition), the relative importance of these properties in a natural setting may be easily misinterpreted or misunderstood unless they are specifically evaluated in

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the proper context of the particular setting. In the case of coral reefs, this study reiterates the statements previously expressed by Falter, Lowe, Zhang and colleagues (Falter et al. 2012, 2013; Zhang et al. 2012; Lowe and Falter 2015) that geomorphology and hydrodynamics need equal attention as the biogeochemical processes in characterizing and interpreting the controls of reef seawater CO_2 chemistry. Resolving the quantitative relationships between these varied factors, as well as their controls (e.g., wave height and depth control on flow rates and residence times; light, temperature and community composition on biogeochemical fluxes) will allow for improved predictions of seawater CO_2 chemistry conditions and variability. This is important at present reef habitats with limited CO_2 measurements and global reef locations undergoing changing ecological (Gardner et al. 2003; Wilkinson et al. 2008; Bruno and Valvidia 2016) and biogeochemical conditions in response to OA, climate change, and other potential disturbances.

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Figure Legends

Figure 1. Study site in Kaneohe Bay, Hawaii (left) showing each of the sampling stations on the reef flat. The stars (1-5) indicate locations of the instruments on the benthos while the circles show sites where seawater surface chemistry was measured. The survey area encompassed a variety of benthic habitats (reef break: orange; rubble: yellow; mixed community: magenta; coral: cyan; sand: blue) and depths ranging from 0 to 8 m (contour intervals of 2 m). The black arrows show the dominant direction of water flow as measured using drifters.

Figure 2. Temporal variability in environmental conditions and seawater chemistry for June (left panel) and November (right panel) with vertical black lines indicating the times of the spatial surveys. Wind, tide, and wave height data were obtained from the NOAA National Buoy Data Center (Moku o loʻe, HI station), Tides and Currents Program (Moku o loʻe, HI station), and Coastal Data Information Program (Kāneʻohe Bay station). PAR, temperature, pH, and DO were measured by our sensors on the reef flat. DO is reported relative to mean DO measured at each station.

Figure 3. Current data integrated across depth for June and November. Current speeds ranged from 0 to 0.3 m s^{-1} with dominant directions varying by station and season.

Figure 4. Spatial variability in seawater T, ΔDO, DIC, and TA for June morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 0.2°C or 25 μmol kg^{-1} for ΔDO, DIC, and TA.

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Figure 5. Spatial variability in pCO_2, pH, and Ω_a for June morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 25 µatm pCO_2, 0.05 pH, or 0.2 Ω_a.

Figure 6. Spatial variability in seawater T, ΔDO, DIC, and TA for November morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 0.2°C or 25 µmol kg^{-1} for ΔDO, DIC, and TA.

Figure 7. Spatial variability in pCO_2, pH, and Ω_a for November morning and afternoon with color gradients representing the range of values. Contour intervals (white lines) show 25 µatm pCO_2, 0.05 pH, or 0.2 Ω_a.

Figure 8. Seawater chemistry as a function of depth with shapes and colors representing the benthic communities (reef break: orange circle; rubble: yellow square; mixed community: magenta diamond; coral: cyan triangle; sand: blue inverse triangle) and instrument measurements (black). The open cyan triangle represents an estimated depth since this site is located on a slope. In general, seawater flowed from the outer reef (deeper sites) over rubble and mixed communities before reach coral and sand.

Figure 9. Seawater chemistry (mean $\pm$ 1 sd) as a function of benthic community with colors representing data collected from the spatial surveys and open black symbols showing data from the instruments on the benthos.

Figure 10. Seawater TA and DIC of the reef relative to offshore waters at Station ALOHA (mean $\pm$ 1 sd) with Type II linear regressions for June (blue) and November (orange). The larger regression slope during June (0.85) reflects nearly balanced NCC and NCP while NCP was dominant during November (0.24). The shapes represent different benthic communities and show the biggest TA and DIC drawdown for coral communities. pH isolines are shown as the grey lines.

Figure 11. Comparison to previous mesocosm experiments (Page et al. 2016) showing seawater pH (mean $\pm$ 1 sd) over 24 hours (top) and seawater ΔTA:ΔDIC regressions (bottom). The ΔTA and ΔDIC values for the present study were calculated as the offset from mean values at Station ALOHA.