

Comparison of CO₂ Dynamics and Air-Sea Exchange in Differing Tropical Reef Environments

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Abstract

An array of MAPCO₂ buoys, CRIMP-2, Ala Wai, and Kilo Nalu, deployed in the coastal waters of Hawaii have produced multiyear high temporal resolution CO₂ records in three different coral reef environments off the island of Oahu, Hawaii. This study, which includes data from June 2008-December 2011, is part of an integrated effort to understand the factors that influence the dynamics of CO₂-carbonic acid system parameters in waters surrounding Pacific high island coral reef ecosystems and subject to differing natural and anthropogenic stresses. The MAPCO₂ buoys are located on the Kaneohe Bay backreef, and fringing reef sites on the south shore of O'ahu, Hawai'i. The buoys measure CO₂ and O₂ in seawater and in the atmosphere at 3-hour intervals, as well as other physical and biogeochemical parameters (CTD, chlorophyll-a, turbidity). The buoy records, combined with data from synoptic spatial sampling, have allowed us to examine the interplay between biological cycles of productivity/respiration and calcification/dissolution and biogeochemical and physical forcings on hourly to inter-annual time scales.

Air-sea CO₂ gas exchange was also calculated to determine if the locations were sources or sinks of CO₂ over seasonal, annual, and interannual time periods. Net annualized fluxes for CRIMP-2, Ala Wai, and Kilo Nalu over the entire study period were 1.15 mol C m⁻² yr⁻¹, 0.045 mol C m⁻² yr⁻¹, and -0.0056 mol C m⁻² yr⁻¹, respectively, where positive values indicate a source or a CO₂ flux from the water to the atmosphere, and negative values indicate a sink or flux of CO₂ from the atmosphere into the water. These values are of similar magnitude to previous estimates in Kaneohe Bay as well as those reported from other tropical reef environments. Total alkalinity (A_T) was measured in conjunction with pCO₂ and the carbonic acid system was calculated to compare with other reef systems and open ocean values around Hawaii. These findings emphasize the need for high-resolution data of multiple parameters when attempting to characterize the carbonic-acid system in locations of highly variable physical, chemical, and biological parameters (e.g. coastal systems, reefs).

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Keywords: carbon dioxide, alkalinity, gas exchange, coral reefs, tropical

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9 46 **1 Introduction**

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12 47 Atmospheric concentrations of carbon dioxide (CO₂) have been on the rise for the past
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14 48 200 years due to human activities releasing more than 400 petagrams of carbon into the
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16 49 atmosphere since 1750. Approximately half of these emissions occurred during the past 40 years
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18 50 (CDIAC cdiac.ornl.gov/). Atmospheric concentrations of ~395 μatm, as observed at Mauna Loa
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20 51 in 2012 (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>), are significantly higher than those at any
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22 52 time in the past 800,000 years (Petit et al., 1990; Augustin et al., 2004; Siegenthaler et al., 2005).
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24 53 Although the atmospheric record is now well characterized, much work remains to be done in the
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26 54 oceanic realm especially on the strength of the CO₂ exchange flux and its future.

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28 55 The vast majority of research on the effect of the rise of atmospheric CO₂ on the oceans
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30 56 has been focused on the open ocean. (Andersson et al., 2007; Feely et al., 2004; Feely et al.,
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32 57 2008; Orr et al., 2005; Takahashi et al., 2009; Wanninkhof et al., 2012). The open ocean, in
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34 58 general, is regarded as a sink for atmospheric CO₂, meaning that the net flux of CO₂ presently is
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36 59 into the ocean. However, the global coastal ocean is quite variable with respect to the net flux of
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38 60 CO₂ into or out of the atmosphere. Values of coastal net CO₂ flux (mol C m⁻² yr⁻¹) range from
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40 61 438 and 3330 in some European estuaries (Frankignoulle et al., 1998) to -34.6 and -33.6 in both
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42 62 the Gulf of Biscay and the East China Sea (Frankignoulle and Borges, 2001; Wang et al., 2000)
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44 63 and as high as -87.6 (Hales et al., 2003) in a highly productive upwelling region off the Oregon
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46 64 coast. Massaro et al. (2012) reported a net flux of 1.80 mol C m⁻² yr⁻¹ in the southern sector of
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48 65 Kaneohe Bay. Positive values indicate a flux of CO₂ from the ocean into the atmosphere
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50 66 (source) and negative values indicate a flux into the ocean (sink). However, many of these flux
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52 67 estimates were obtained through periodic synoptic sampling of the surface waters of these
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54 68 systems and very few long-term, high resolution, *in-situ* studies on the CO₂-carbonic acid system
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56 69 and CO₂ exchange dynamics have been performed in coastal environments (e.g. De Carlo et al.,
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58 70 this volume; Drupp et al., 2011; Massaro et al., 2012).

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60 71 As atmospheric CO₂ levels continue to rise for (at least) the remainder of the 21st century,
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62 72 the global shallow ocean environment, which has been a source of CO₂ to the atmosphere for at

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4 73 least the past 300 years, may reverse its net flux to that of a sink for atmospheric CO₂ just like
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6 74 the open ocean (Andersson and Mackenzie, 2004; Andersson et al., 2006; Mackenzie et al.,
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8 75 2011; Wanninkhof et al., 2012).
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10 76 **2 Study Rationale**

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13 77 This study expands upon a 2.5 year *in-situ* high-resolution time series study that was
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15 78 carried out in southern Kaneohe Bay, Oahu, Hawaii (Figure 1a and 1b) through the use of the
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17 79 Coral Reef Instrumented Monitoring and CO₂ Platform (CRIMP-CO₂) buoy (Drupp et al. 2011;
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19 80 Massaro et al., 2012). Kaneohe Bay, in particular its southern sector, has been extensively
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21 81 studied for the past 40 years (e.g., Roy, 1970; Cox et al., 1973; Hollett, 1977; Smith et al., 1981;
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23 82 Taguchi and Laws, 1987, 1989; Jokiel et al., 1993; Hunter and Evans, 1995; Laws and Allen,
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25 83 1996; Atkinson, 2000; Hearn and Atkinson, 2000; Kinzie et al., 2001; Falter et al., 2004; Ringuet
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27 84 and Mackenzie, 2005; Tanaka and Mackenzie, 2005; Hoover et al., 2006; De Carlo et al., 2007;
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29 85 Fagan and Mackenzie, 2007; Hoover and Mackenzie, 2009; Drupp et al. 2011; Massaro et al.,
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31 86 2012; Shamberger et al., 2011). The bay is thought to be representative of other high-island
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33 87 tropical reef environments found throughout the Pacific Ocean.

34 88 The Coral Reef Instrumented and CO₂ Monitoring (CRIMP-CO₂) program, initiated in
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36 89 late 2005, was the first long-term, high resolution CO₂ monitoring program conducted in tropical
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38 90 coastal waters. The CRIMP-CO₂ buoy also served as a platform for deploying additional water
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40 91 quality sondes measuring a variety of standard physical and biogeochemical parameters. In June
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42 92 2008, the CRIMP buoy was relocated to its current location (CRIMP-2, Figure 1b) at a depth of
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44 93 3 m on the inside edge of the Kaneohe Bay barrier reef, in the central sector of Kaneohe Bay.
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46 94 Two additional buoys, Water Quality Buoys Ala Wai and Kilo Nalu (WQB-AW and WQB-KN,
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48 95 respectively, Figure 1c) were also deployed at that time, on the south shore of Oahu in ~12 m
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50 96 water depth on sand patches adjacent to fringing reefs in Mamala Bay, approximately 200 m
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52 97 offshore of urban Honolulu. These three buoys provide high frequency (3 hr) CO₂ and ancillary
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54 98 water quality parameters of conditions in differing coastal coral reef environments, and
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56 99 complementary data are obtained through periodic synoptic sampling.

57 100 **Figure 1**

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4 101 Periodic synoptic sampling, often performed during the day under favorable weather
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6 102 conditions (e.g. De Carlo et al., this volume), misses diel cycles and, frequently, changes induced
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8 103 by local rainfall and storm events. The latter have been shown to induce rapid and brief changes
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10 104 in stream flow (e.g., Tomlinson and De Carlo, 2003; Hoover and Mackenzie, 2009) and have a
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12 105 significant effect on short-term CO₂ variability and general biogeochemistry (e.g., nutrient
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14 106 concentrations) in the nearshore semi-estuarine environment of Kaneohe Bay (Ringue and
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16 107 Mackenzie, 2005; De Carlo et al., 2007; Fagan and Mackenzie, 2007; Hoover and Mackenzie,
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18 108 2009; Drupp et al., 2011; Massaro et al., 2012). Strong diel signals, due to water column and
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20 109 reef productivity/respiration and calcification/dissolution processes, have been observed by both
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22 110 Drupp et al. (2011) and Shamberger et al. (2011) in Kaneohe Bay. Seasonal and annual trends in
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24 111 water column pCO₂ were clearly evident in previous work by Fagan and Mackenzie (2007),
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26 112 Drupp et al. (2011), and Massaro et al. (2012). Based on these studies, it is evident that only a
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28 113 monitoring program that is both long-term (multiple years) and high resolution (multiple samples
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30 114 per day) can adequately characterize CO₂ exchange fluxes and processes controlling them in
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32 115 dynamic biogeochemical environments such as Kaneohe Bay and other tropical reef
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34 116 environments.

34 117 **3 Methods**

37 118 *3.1 Environmental Setting*

40 119 Kaneohe Bay, the location of the CRIMP-2 buoy, is the largest semi-enclosed body of
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42 120 water on the island of Oahu, Hawaii (Figure 1) and is located on the northeast (windward) coast.
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44 121 It is host to numerous fringing and patch reefs as well as a large barrier reef. The bay has a mean
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46 122 depth of 9.5 meters, with the barrier reef averaging ~2 meters depth (Bathen, 1968).
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48 123 Northeasterly tradewinds blow the majority (~80%) of the year and their speed is a major factor
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50 124 in governing the magnitude of air-sea CO₂ gas exchange fluxes (Massaro et al., 2012). Water
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52 125 residence time in the bay ranges from hours on the barrier reef to 30+ days in the more
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54 126 hydrologically isolated southern sector (Lowe et al., 2009a), where the original CRIMP buoy
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56 127 was deployed.

57 128 CRIMP-2 was deployed in 3 m of water over sandy sediment on the inside edge of the
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59 129 barrier reef (Figure 1b) in the central sector of Kaneohe Bay. The site was chosen due to its

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130 proximity to the barrier reef (~20 m distance from the backreef edge) and because the flow of
131 water at this site is nearly unidirectional, thereby allowing measurements of water chemistry and
132 its CO₂ content after the water flows across the barrier reef from the open ocean. Effectively, the
133 water chemistry at this site represents an end-member following the alteration of its chemistry
134 due to biological and physical processes during its transit across the barrier reef. It is important
135 to note that much of the reef may not have been exposed to the same water chemistry that is
136 measured at this buoy, as the water has been undergoing biogeochemical alteration continuously
137 during its transit across the reef. For example, data from Shamberger et al., 2011 (discussed
138 later) collected from a mid-reef location falls in between the open ocean values and our CRIMP-
139 2 end-member. The CRIMP-2 location is also generally isolated from direct terrestrial and
140 riverine inputs from the Kaneohe Bay watershed.

141 Recent work has shown that the biogeochemistry of the CRIMP-2 location is driven
142 largely by benthic productivity and calcification occurring on the barrier reef (Shamberger et al.,
143 2011). This is in sharp contrast to the original CRIMP location, where land runoff combined with
144 the physical characteristics of the site modified considerably the biogeochemistry of the water
145 and CO₂ exchange dynamics on various time scales (Ringuelet and Mackenzie, 2005; De Carlo et
146 al. 2007; Drupp et al., 2011; Massaro et al., 2012). At the CRIMP-2 location, runoff has very
147 little effect on the magnitude of the air-sea flux of CO₂ and the location also can be considered a
148 relatively healthy coral reef environment in which to study the CO₂-carbonic acid system and
149 CO₂ exchange.

150 Fringing reefs in Mamala Bay on the south shore of Oahu are rather unprotected. These
151 reefs are generally subject to the direct physical effects of tides, winds, and open ocean wave
152 action, and nearshore water exchanges readily with surrounding open ocean water. The two sites
153 (Ala Wai and Kilo Nalu) differ from each other in the presence or absence, respectively, of
154 riverine input from the Ala Wai Canal. The canal drains approximately 1/3 of urban Honolulu
155 (population ~850,000) and contributes significant amounts of fluvial discharge containing high
156 nutrient and suspended sediment loads to coastal waters. The effects of this discharge are
157 especially evident at the Ala Wai buoy following (large) storm events (Tomlinson et al., 2011).
158 Occasionally, depending on wind and swell conditions, this riverine signal can reach the Kilo
159 Nalu buoy, about 1.6 km to the west, although the impacts of the fluvial discharge on water

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160 quality at that site are typically highly attenuated. The substrate in Mamala Bay out to the 30m
161 isobaths consists mainly of sand, limestone pavement, and spur and groove coral reef.
162 Encrusting algae and coral dominates the reef with some *Porites lobata* and *Pocillopora*
163 *meandrina*. Macroalgae have 10-90% local coverage of the pavement (Battista et al., 2007,
164 Tomlinson et al., 2011).

165 *3.2 In-situ Measurements*

166 The buoys are equipped to make a broad range of measurements. A LICOR-820 infrared sensor
167 and a MaxtexMAX™-250 Series sensor measuring CO₂ and O₂, respectively, are located within
168 the buoy body, as well as a Sensirion humidity sensor. Data are collected every 3 hours and
169 transmitted daily via Iridium satellite to NOAA/PMEL (Pacific Marine Environmental
170 Laboratory). The accuracy of the LICOR-820 is conservatively estimated to be 2.5% of the
171 measured value. Details regarding the analytical scheme of the buoy can be found in Massaro et
172 al. (2012) and Shamberger et al. (2011). CO₂ and O₂ data from all three buoys can be viewed in
173 “near real time” at <http://www.pmel.noaa.gov/co2/coastal/HI/>

174 Both WQB-AW and KN buoys are also equipped with Sea-Bird Electronics SeaCat16
175 v2plus CTD’s (Conductivity, Temperature, Depth) and WET Labs FLNTUS ECO
176 fluorometer/turbidity sensors. Temperature, conductivity (salinity), dissolved oxygen,
177 chlorophyll, and turbidity are measured at 20 minute intervals. SBE16 data from WQB-AW and
178 WQB-KN are transmitted every 20 minutes via a Satlantic STOR-X data logger and cell phone
179 modem. A Yellow Springs Instrument (YSI) 6600 Multi-Parameter sonde and a Sea-Bird
180 Electronics MicroCat CT (37-SMP) are attached to the CRIMP-2 buoy and measure temperature,
181 conductivity, dissolved oxygen, chlorophyll, turbidity, and pH. Water quality data from the
182 SBE16’s can be viewed in real time on the Pacific Islands Ocean Observing System (PacIOOS)
183 website.

184 http://oos.soest.hawaii.edu/pacioos/data_product/WQ/

185 Wind and tidal data were obtained from the NOAA National Ocean Service (NOS)
186 Station OOUH1 in downtown Honolulu (for south shore buoys) and from the Hawaii Institute of
187 Marine Biology (HIMB) weather station on Coconut Island (for CRIMP-2). Rainfall data for the
188 windward coast were obtained from gauges at the Hawaii Institute of Marine Biology (HIMB) on

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189 Coconut Island in southern Kaneohe Bay and the National Weather Service (NWS) HI15 Luluku
190 gauge in the Kaneohe Stream watershed. South shore rainfall was measured at the NWS HI-18
191 Manoa Lyon Arboretum and NWS HI-20 Nuuanu Valley gauges (in the upper watersheds which
192 drain much of Honolulu) and from NWS HI-26 Aloha Tower within Honolulu harbor.

193 *3.3 Sample Analysis*

194 Discrete water samples were collected at each location, during periods of routine
195 equipment maintenance, usually every 4 weeks. Samples for total alkalinity (A_T) were collected
196 from the surface waters in 300 mL borosilicate bottles. Each sample was fixed with 200 μ L of
197 saturated $HgCl_2$ to inhibit any biological activity. The bottles were sealed with Apiezon-greased
198 ground glass stoppers. Total alkalinity was determined using the open cell potentiometric
199 titration method (Dickson et al., 2007) on a Metrohm Titrando 905. The accuracy of the A_T
200 determinations was evaluated using certified reference materials (CRM) from the Scripps
201 Institution of Oceanography (Dickson et al., 2001; Dickson et al., 2003; Dickson et al., 2007)
202 and found to be $1.37 \mu\text{mol kg}^{-1}$ (n=26). The precision between replicates was $1.52 \mu\text{mol kg}^{-1}$
203 (n=63).

204 *3.4 Calculations*

205 Concentrations of CO_2 measured by the LICOR-820 were corrected using the relative
206 humidity in the equilibrator to calculate a dry xCO_2 (mole fraction at 0% humidity). Using the
207 methods from Zeebe and Wolf-Gladrow (2001), originally developed by Weiss and Price (1980).
208 pCO_2 was calculated utilizing ambient water vapor pressure, dependent on T and S, and
209 assuming that the air directly above the sea surface was 100% saturated.

210 Calculations of air-sea fluxes were made using Equation (1) below:

$$211 \quad \mathbf{F=k\alpha\Delta pCO_2,} \quad \mathbf{(1)}$$

212 where k is the CO_2 gas transfer velocity, α is the solubility of CO_2 in seawater at the specified
213 temperature and salinity, and ΔpCO_2 is the difference between atmospheric and seawater pCO_2
214 concentrations (Weiss, 1974; Liss, 1983; Wanninkhof, 1992). The gas transfer velocity, k, was
215 calculated using the Ho et al. (2006) parameterization shown in equation (2):

$$k_{(600)} = (0.266 \pm 0.019) (U_{10})^2, \quad (2)$$

where U_{10} is the wind speed measured at (or corrected to) ten meters above sea level. Error bars for fluxes were calculated by error propagation, using a 2.5% error for the CO_2 measurement and an uncertainty of 0.019 in the Ho et al. parameterization.

Normalization of pCO_2 to an average seawater temperature was performed according to Takahashi et al. (1993, 2002) assuming a 4.23% change in pCO_2 per 1°C change in temperature (equation 3). The effect of only temperature on pCO_2 at a given time was also calculated (equation 4) from Takahashi et al. (1993 and 2002) using the mean pCO_2 of the study period. This represents the pCO_2 changes induced by temperature fluctuations under isochemical conditions.

$$\text{pCO}_2 \text{ at } T_{\text{mean}} = \text{pCO}_{2\text{obs}} * \exp(0.0423*(T_{\text{mean}}-T_{\text{obs}})) \quad (3)$$

$$\text{pCO}_2 \text{ at } T_{\text{obs}} = \text{pCO}_{2\text{mean}} * \exp(0.0423*(T_{\text{obs}}-T_{\text{mean}})), \quad (4)$$

where T_{obs} and $\text{pCO}_{2\text{obs}}$ are the measured *in-situ* temperature and pCO_2 , and T_{mean} and $\text{pCO}_{2\text{mean}}$ are the annual mean values of temperature and pCO_2 .

Dissolved inorganic carbon (C_T), pH (total scale), and calcium carbonate saturation state (Ω) were calculated using CO2SYS (Lewis and Wallace, 1998) with carbonic acid constants by Mehrbach et al. (1973) refit by Dickson and Millero (1987).

Nutrient analyses were performed on a Seal Analytical AA3 HR Nutrient Autoanalyzer. Nitrate (NO_3^-) and nitrite (NO_2^-) were analyzed according to the methods of Armstrong et al. (1967) and Grasshoff et al. (1983) with a detection limit of $0.006 \mu\text{mol L}^{-1}$ and a relative standard deviation (CV) of 0.3%. Silicate ($\text{Si}(\text{OH})_4$) was analyzed based on the methods of Grasshoff et al. (1983) with a detection limit of $0.350 \mu\text{mol L}^{-1}$ and a CV of 0.5%. Soluble reactive phosphate (PO_4^{3-}) was analyzed according to the colorimetric method of Murphy and Riley (1962) with a detection limit of $0.018 \mu\text{mol L}^{-1}$ and a CV of 0.4%.

4 Results

Figure 2a shows the pCO_2 of seawater at all three buoy locations over the entire study period of June 2008-December 2011. A seasonal trend is evident in all three data sets; however,

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243 CRIMP-2 (blue) shows much greater short term variations in pCO₂. The solid yellow line in this
244 figure indicates 377 μatm, which was the mean air pCO₂ during the study period. When
245 seawater pCO₂ is above this line, the location is a source of CO₂ to the atmosphere and when
246 seawater pCO₂ is below the line, the location is a sink for CO₂ from the atmosphere. However,
247 source or sink activity is dependent upon the instantaneous flux, which was calculated from the
248 *in-situ* measured atmospheric pCO₂ at the time of the seawater measurement. The mean seawater
249 pCO₂ values at CRIMP-2, Kilo Nalu, and Ala Wai were 439 ± 11 μatm, 379 ± 10 μatm, and
250 389 ± 10 μatm, respectively. Minimum and maximum values are reported in Table 1. CRIMP-2
251 displayed the largest variation with a range of 780 μatm. The standard deviation of the mean
252 was 83.4 μatm at CRIMP-2 compared to values of 18.2 and 25.3 μatm for KN and AW,
253 respectively, further demonstrates the greater short-term variations which occur at the CRIMP-2
254 location.

255 Figure 2b displays the pCO₂ normalized to average T during the entire study period, as
256 calculated by Equation 3. Even when normalized to the mean temperature of 25°C, pCO₂ still
257 exhibits large short term fluctuations at all three buoys. The T-normalized pCO₂ also displays a
258 seasonal trend (albeit much less than in the raw pCO₂ data shown in Figure 2a) which can be
259 difficult to discern due to the short term variations.

260 *Figure 2*

261 *Table 1*

262 Monthly mean pCO₂ was calculated at each location and is shown in Figure 3a. The
263 trend of higher pCO₂ in the summer and lower pCO₂ in the winter was also observed at the
264 original CRIMP location (Drupp et al., 2011; Massaro et al., 2012). Figure 3b shows the weekly
265 temperatures throughout the study period. All three locations follow the same trend of maximum
266 temperatures (~27 °C) during the summer and minimum temperatures (~23-24 °C) in the winter.
267 Water at CRIMP-2 does become slightly cooler than water at AW and KN during the winter
268 months, but does not become warmer than water at AW and KN during the summer.

269 *Figure 3*

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The daily range of pCO₂ was also calculated for each day throughout the study period. Table 2 shows statistics for the daily ranges at all three buoys, as well as the original CRIMP buoy. CRIMP-2 exhibited a mean daily range of 196 ± 16 μatm, four times greater than observed at the Ala Wai location. The maximum daily ranges at AW and KN are considerably lower than the mean daily range at CRIMP-2. At each location, pCO₂ dropped throughout the day reaching a minimum value in the afternoon, around ~14:00 hrs. Maximum daily pCO₂ values occurred late at night to the early morning (~4:00-8:00 hrs). The pCO₂ varied in the opposite direction of oxygen concentrations, which peaked in the mid-afternoon and reached minimum concentrations during the night. Pearson correlations between pCO₂ and pO₂ at each buoy are shown in Table 3. An anti-correlation of -0.75 was observed at CRIMP-2: negative, albeit weak, correlations were also observed at Ala Wai and Kilo Nalu. An example of the diel anti-correlation cycle is shown in Figure 4, which displays pCO₂ and pO₂ at CRIMP-2 from April 22 to May 12, 2010.

Table 2

Table 3

Figure 4

Autocorrelation was also evaluated for each buoy data set to determine the periodicity of pCO₂. This value indicates the correlation between all points separated by specific time intervals in the same data set. A strong autocorrelation was found at a period of 24 hours for each location. An autocorrelation plot for CRIMP-2 is shown in Figure 5. This correlation stayed relatively strong for 48 and 72 hours but dropped off (<0.5) over greater multiples of 24 hours. The correlation of 0.74 at 24 hrs observed at CRIMP-2 was the highest of the three locations during the study period (see Table 3). A correlation greater than 0.50 existed out to 72 hours (24 hr intervals), meaning that even points 72 hours (3 days) apart had a correlation value of greater than 0.50. A much lower (and sometimes negative) correlation occurred between points 12 hours apart.

Figure 5

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4 297 Instantaneous CO₂ fluxes at the three buoy sites are presented in Figure 6 in units of
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6 298 mmol C m⁻² hr⁻¹ during the entire study period of June 2008 to December 2011. Statistics for
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8 299 these fluxes are shown in Table 4. As expected from the larger range of pCO₂ values, CRIMP-2
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10 300 displayed the largest range of flux and had a mean instantaneous flux of 0.13 ± 0.030 mmol C m⁻²
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12 301 hr⁻¹. The mean flux at Kilo Nalu was 0 and 0.005 ± 0.005 at Ala Wai. Percentage of time spent
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14 302 as a source and a sink was also computed for the three sites. The CRIMP-2 and Ala Wai water
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16 303 columns were CO₂ sources to the atmosphere 78% and 66% of the study period, respectively.
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18 304 The Kilo Nalu location was a source 51% of the time.

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20 305 Net annualized fluxes for all three locations are also shown in Table 4 in units of mol
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22 306 C/m²/yr. CRIMP-2 was a source of 1.15 ± 0.27 mol C m⁻² yr⁻¹, while Ala Wai and Kilo Nalu
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24 307 were essentially neutral at 0.045 ± 0.048 mol C m⁻² yr⁻¹ and -0.0050 ± 0.072 mol C m⁻² yr⁻¹,
25
26 308 respectively. For comparison, CRIMP displayed an annualized flux of 1.76 ± 0.37 mol C m⁻² yr⁻¹
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28 309 for the time period of December 2005 to June 2008 (Massaro et al., 2012).

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30 310 Table 5 shows net annualized fluxes (in mol C m⁻² yr⁻¹) for each year (2008-2011) of the
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32 311 study period as well as for each season of the study period. Seasons are separated as summer dry
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34 312 periods from May through October and the winter wet periods from November through April.
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36 313 The water at CRIMP-2 was a source of CO₂ to the atmosphere every year of the study period
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38 314 (1.39 ± 0.25 mol C m⁻² yr⁻¹, 0.82 ± 0.20 mol C m⁻² yr⁻¹, 1.10 ± 0.28 mol C m⁻² yr⁻¹, and 1.31 ±
39
40 315 0.36 mol C m⁻² yr⁻¹). The water at Ala Wai was initially a source of CO₂ in 2008 and 2009,
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42 316 switched to a sink of CO₂ (albeit a small sink) in 2010 of -0.003 ± 0.013 mol C m⁻² yr⁻¹ and back
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44 317 to a source of 0.092 mol C m⁻² yr⁻¹ in 2011. Initially, in 2008, the Kilo Nalu environment was a
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46 318 source (0.073 ± 0.081 mol C m⁻² yr⁻¹) but from 2009-2011, the surface seawater most likely
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48 319 transitioned to a sink (-0.018 mol C m⁻² yr⁻¹, 0.00 mol C m⁻² yr⁻¹, and -0.032 mol C m⁻² yr⁻¹,
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50 320 respectively. Because of the small value of ΔpCO₂ and resulting high relative uncertainty, it is
51
52 321 not possible to classify at present the Kilo Nalu location as a CO₂ source or sink. Each location
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54 322 also displayed a seasonal trend in flux. At CRIMP-2, waters oscillate between strong sources in
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56 323 the summers (mean of 1.66 mol C m⁻² yr⁻¹) and weaker sources in the winter (mean of 0.66 mol
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58 324 C m⁻² yr⁻¹). The same trend was observed at both the Ala Wai and Kilo Nalu locations, as the
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60 325 water column switched between source and sink behavior on a summer to winter time scale.

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326 Data are not shown from the Kilo Nalu buoy for the winter of 2010-2011 or the summer of 2011
327 due to problems with the equilibrator.

328 *Table 4*

329 *Table 5*

330 Total alkalinity at the buoy locations ranged from a mean of 2225 $\mu\text{mol kg}^{-1}$ at CRIMP-2
331 to 2306 and 2298 at Kilo Nalu and Ala Wai, respectively. A_T data from synoptic sampling are
332 shown in Figure 7. C_T and pH (total scale), calculated from A_T and $p\text{CO}_2$, were lower at
333 CRIMP-2 (1960 $\mu\text{mol kg}^{-1}$ and 7.99) than at Ala Wai and Kilo Nalu (~1993 $\mu\text{mol kg}^{-1}$ and
334 ~8.06). Carbon system parameters and statistics are shown in Table 6. The Kilo Nalu
335 environment displayed the least amount of variability, while the water at CRIMP-2 and at Ala
336 Wai had similar absolute variability, despite differences in the mean values. Data from surface
337 waters at Station ALOHA, from the Hawaiian Ocean Time-series (HOT,
338 <http://hahana.soest.hawaii.edu/hot/hot-dogs/>), during the same time period, are also shown and
339 are most comparable with Kilo Nalu. Data from Shamberger et al. (2011) taken from 3 separate
340 synoptic experiments at the CRIMP-2 site and a mid-reef site, during 6/08, 8/09, and 2/10, are
341 consistent with the data from this study. Figure 8 shows the relationship between A_T and C_T at
342 each location. Both A_T and C_T have been normalized to a salinity of 35 (nA_T and nC_T) to help
343 reduce the effects of mixing of water masses with different properties. HOT data from 2008-
344 2011 (<25m) are also shown as an end-member point included in each regression.

345 *Table 6*

346 *Figure 7*

347 *Figure 8*

348 **5 Discussion**

349 *5.1 Physical Controls of $p\text{CO}_2$*

350 During the 3.5 year study period, all three buoy environments displayed temporal cycles
351 of $p\text{CO}_2$ on time scales ranging from daily to seasonal. Data (in Figure 2a), collected every three
352 hours, from all three buoys show the long term seasonal variability, due in part to temperature

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353 changes, as well as the short term (hourly-weekly) variability due to both biological activity and
354 physical forcing.

355 Monthly mean pCO₂ is shown in Figure 3a to clarify the seasonal trends of pCO₂. The
356 summer dry period, from May-October, is marked by warmer water and air temperatures and
357 significantly less precipitation, resulting in less nutrient-rich land runoff (Ringuet and
358 Mackenzie, 2005; De Carlo et al. 2007, Hoover and Mackenzie, 2009; Drupp et al. 2011).
359 CRIMP-2 exhibited a seasonal amplitude of pCO₂ of ~100 μatm, while seasonal amplitudes at
360 Kilo Nalu and Ala Wai were ~ 35 μatm. These amplitudes are based on monthly mean data in
361 order to eliminate large transient increases or decreases unrelated to seasonal variation. Because
362 increasing temperature raises seawater pCO₂ (and vice versa) by 4.23% per degree Celsius
363 (Takahashi et al. 1993), pCO₂ is elevated in the summer and depressed in the winter at all three
364 locations. Temperature changes, however, are not the only cause of pCO₂ changes in the water
365 column at any of these locations. If temperature was the only factor, the annual seasonal
366 amplitudes (based on monthly means) should be nearly twice the observed ranges at Kilo Nalu
367 and Ala Wai, and slightly less than the observed range at CRIMP-2. The other main factors
368 driving long-term pCO₂ trends include biological processes, residence time (a function of
369 mixing), and air to sea gas exchange (a function of wind speed and ΔpCO₂). These processes are
370 discussed below.

371 In order to separate the effects of temperature and biological processes on pCO₂, two
372 different normalizations were applied (Takahashi et al., 1993). Equation 4 was used to derive the
373 temperature-dependent effects on pCO₂. The values are calculated based on a mean pCO₂ at
374 each location for the entire study period, and are representative of temperature-induced changes
375 under isochemical conditions (i.e. no biological/mixing effects on water chemistry). On short
376 time scales, greater variation is observed at CRIMP-2 than at either Kilo Nalu or Ala Wai, due to
377 larger daily temperature fluctuations, the shallow depth of the reef and the longer water residence
378 time of water in Kaneohe Bay. On a seasonal to annual scale, greater variation (~1.5 times) is
379 also observed at CRIMP-2 compared to the other locations. This enhanced variation in pCO₂ is
380 caused by an annual temperature range at CRIMP-2 approximately 1.5 times larger than at either
381 Kilo Nalu or Ala Wai (Figure 3b). Temperature is the strongest contributor to long-term pCO₂
382 variations, and it even has a daily effect (mean daily range of 21 μatm), but it is not the only

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4 383 physical factor affecting pCO₂.
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7 384 Residence time is another important physical factor impacting pCO₂, as it controls the
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9 385 amount of time the water column is exposed to biological processes. Longer residence times
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11 386 allow for an accumulation of CO₂ from continuous respiration and calcification by the biological
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13 387 community. The residence time of water in Kaneohe Bay is controlled by wave action and wind
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15 388 speed and less by tidal mixing. Tradewinds blow from the northeast approximately 80% of the
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17 389 year with a mean speed of 4.9 m s⁻¹, and wave action is considered to be the dominant control on
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19 390 current speed across the reef (Lowe et al., 2009b). Water takes only a few hours to travel across
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21 391 the reef flat, although during light winds (and the consequent low wave action), the water can
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23 392 take more than a day to flow across the reef (Shamberger et al., 2011). Lowe et al. (2009 a/b)
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25 393 also show some model runs with residence times exceeding 24 hours. An example of longer
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27 394 residence time leading to increased pCO₂ is shown in Figure 4. Beginning on May 1, 2010 and
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29 395 lasting until May 5, wind speeds were dramatically lower (<2 m s⁻¹) than typical (~4-6 m s⁻¹).
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31 396 The current speed across the reef, based on offshore significant wave height using the
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33 397 relationship developed for the Kaneohe Bay barrier reef by Lowe et al. (2009b) immediately
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35 398 prior to this period was approximately 30 cm s⁻¹ and dropped to a low of ~10 cm s⁻¹ on May 3.
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37 399 The reduction in wind/current speed significantly increased the water residence time on the reef,
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39 400 resulting in an accumulation of CO₂ derived from calcification and respiration. In addition, low
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41 401 wind speeds reduce air-sea gas exchange, thereby lowering gas evasion rates, and further
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43 402 enhancing the accumulation of CO₂ in the water column (Massaro et al., 2012). In a related
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45 403 study on the Kaneohe Bay barrier reef, Shamberger et al. (2011) found that daily cycles of A_T
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47 404 were enhanced and pCO₂ was elevated on days when wind speeds were low and residence time
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49 405 was long (13+ hours). The higher mean pCO₂ at CRIMP in southern Kaneohe Bay, despite
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51 406 considerably lower rates of calcification (Drupp et al., 2011; Massaro et al., 2012), was attributed
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53 407 primarily to a longer residence time of approximately 15-30 days (Ostrander et al., 2008; Lowe
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55 408 et. al, 2009a), which further supports our findings.
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59 409 The chemistry of water at Kilo Nalu, in stark contrast to Kaneohe Bay, displays little
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61 410 short- or long-term variability. It is reasonably representative of the surrounding open ocean
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63 411 water, with a mean pCO₂ of 378 μatm for the study period and a standard deviation that is four
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65 412 times less than that at CRIMP-2. The Kilo Nalu location is very weakly stratified and

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4 413 consistently flushed by tides, currents, and waves. Stratification of the water column at Kilo
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6 414 Nalu is mainly caused by daily heating and is relatively weak, if present at all, while convective
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8 415 mixing destabilizes the site at night (Hamilton et al., 1995; Sevadjan et al., 2010). Water
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10 416 column productivity is generally low and chlorophyll-a concentrations rarely exceed 0.5-1.0 μg
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12 417 L^{-1} (Tomlinson et al., 2011). Benthic productivity is also likely low as the bottom substrate is
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14 418 primarily sand over limestone pavement with very little coral or algal cover. This deeper
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16 419 (relative to CRIMP-2), fairly well mixed water column masks much of the CO_2 signal, which is
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18 420 low to begin with at this site. The Ala Wai buoy location experiences similar physical forcings as
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20 421 Kilo Nalu, which contribute to a similar mean pCO_2 of 389 μatm , although its proximity to the
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22 422 mouth of the Ala Wai Canal results in stronger land-ocean interactions at this site due to
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24 423 enhanced fluvial runoff and nutrient inputs (discussed below).

25 424 5.2 Biogeochemical Controls of pCO_2

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28 425 The water column at CRIMP-2 (blue in Figure 2) exhibits the largest short-term
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30 426 variability of pCO_2 observed at all three locations owing to high rates of daily calcification and
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32 427 productivity on the reef flat (Shamberger et al., 2011). A similar trend of short-term variability
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34 428 was described by Drupp et al. (2011) at the CRIMP location in southern Kaneohe Bay.

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36 429 Normalization of pCO_2 to both mean temperature and mean pCO_2 separates the effects of
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38 430 temperature-independent and temperature-dependent processes on pCO_2 (Takahashi et al. 1993,
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40 431 2002). Temperature normalization (equation 3) alone removes the effect of temperature on pCO_2
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42 432 and provides a value that Takahashi (1993) refers to as reflective of the “net biology effect.” It is
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44 433 clearly evident in Figure 2b that T-normalized pCO_2 (“net biology effect”) accounts for the vast
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46 434 majority of short-term variability of pCO_2 and even displays a slight seasonal trend. The
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48 435 standard deviation at all three study locations barely changes between the *in-situ* pCO_2 and the
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50 436 T-normalized value, indicating that the majority of the variance in the *in-situ* pCO_2 values cannot
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52 437 be attributed to temperature. The CRIMP-2, Kilo Nalu, and Ala Wai sites have T-normalized
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54 438 standard deviations of 84.5 μatm , 17.5 μatm , and 24.4 μatm , respectively, nearly identical to the
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56 439 standard deviations of the *in-situ* values of 83.4 μatm , 18.2 μatm , and 25.3 μatm , respectively.

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58 440 Figure 9 shows the A_T at CRIMP-2 versus salinity. The conservative mixing line (black
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60 441 dashed line) was derived by Massaro et al. (2012) for Kaneohe Bay, using offshore seawater and

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4 442 a zero salinity intercept derived from water samples collected at the mouth of Kaneohe Stream,
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6 443 the major river flowing into Kaneohe Bay. All of the CRIMP-2 samples, except for 11/14/2009,
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8 444 fall below the mixing line supporting the hypothesis that calcification/productivity processes
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10 445 across the reef are the main drivers of temporal changes in $p\text{CO}_2$ and A_T . The only sample that
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12 446 does not fall below the mixing line was taken on a day with stronger than average trade winds
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14 447 (gusts up to 9 m s^{-1}) resulting in faster current speeds (short residence time), as well as below
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16 448 average solar radiation reducing photosynthetic and calcification rates. The point falls virtually
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18 449 on the mixing line ($A_T=2297 \mu\text{mol kg}^{-1}$) suggesting that the seawater sampled at that time may
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20 450 have represented open ocean water.

21
22 451 **Figure 9**

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24 452 Daily $p\text{CO}_2$ values at CRIMP-2 on the reef fluctuate widely with a mean range four times
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26 453 greater than the two other buoys. Chlorophyll measured at all three buoys is low (mean $< 0.6 \mu\text{g}$
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28 454 L^{-1}), implying that most of the photosynthesis/respiration and calcification/dissolution signals
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30 455 observed at CRIMP-2 are driven by the benthic reef flat organisms, rather than organisms in the
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32 456 water column. Average values of total nitrogen ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_3$) were $0.55 \mu\text{mol}$ at sites
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34 457 across the reef and $0.46 \mu\text{mol}$ at CRIMP-2, and inorganic phosphate was below detection levels
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36 458 ($0.29 \mu\text{mol L}^{-1}$ for all samples. Water column production was likely nutrient limited as
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38 459 previously shown by Ringuelet and Mackenzie (2005) and Drupp et al., (2011). A study
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40 460 performed by Shamberger et al. (2011) found that net ecosystem production (NEP) on a daily
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42 461 basis ranged from $-378 \text{ mmol m}^{-2} \text{ d}^{-1}$ to $80 \text{ mmol m}^{-2} \text{ d}^{-1}$ (negative values indicate net respiration,
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44 462 positive values indicate net production). The reef varied from net autotrophic during the day to
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46 463 net heterotrophic at night during this study, a characteristic of many reef systems.

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48 464 Daily cycles of $p\text{CO}_2$, typical of what would be expected from daytime photosynthesis
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50 465 and nighttime respiration, are characterized by a maximum $p\text{CO}_2$ occurring at night/early
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52 466 morning, usually between 04:00-08:00, with a corresponding minimum $p\text{CO}_2$ occurring in the
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54 467 mid-afternoon, $\sim 14:00-17:00$. This cycle mirrors that of $p\text{O}_2$, which peaks in the late-afternoon
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56 468 and reaches a minimum in the early morning. This same cycle, caused by photosynthesis
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58 469 consuming CO_2 and producing O_2 during the day while respiration at night consumes O_2 and
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60 470 produces CO_2 , was also observed at CRIMP (Drupp et al., 2011 and Massaro et al., 2012).

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4 471 Autocorrelations, highlighted in the results and Table 3 shows that points separated by
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6 472 multiples of 24h (same time each day) are highly correlated even up to 72h apart (all points
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8 473 separated by 72h have correlations of ~0.56). After 72h, no points have a correlation better than
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10 474 0.50. Because of this, CO₂ levels at the buoy locations can be fairly accurately predicted
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12 475 approximately three days into the future under normal conditions. All points separated by 12h
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14 476 show weak or negative correlations. Because the points 12h apart are not strongly anti-
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16 477 correlated, daytime pCO₂ values are not an indication of what the nighttime values will be and
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18 478 vice versa. This is due to daytime photosynthesis and calcification being controlled primarily by
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20 479 solar radiation and nutrient availability, which change day to day. In addition, the water
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22 480 chemistry is affected by changes in residence time, which is primarily a function of wind speeds
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24 481 and forereef wave action. Because many of these factors are transient in nature, it is difficult to
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26 482 predict pCO₂ more than 2-3 days in advance. This makes long-term high resolution monitoring
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28 483 all the more valuable.

29 484 Although the data at CRIMP-2 are consistent with P/R cycles, Shamberger et al. (2011),
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31 485 in a complementary study on the barrier reef, showed that calcification increases during the day,
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33 486 with some dissolution occurring at night, and daily net ecosystem calcification ranged from 174
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35 487 to 331 mmol CaCO₃ m⁻² d⁻¹ (positive values indicate net calcification, negative values indicate
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37 488 net dissolution). The release of CO₂ during calcification would counter its uptake during
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39 489 photosynthesis. Because of this, the observed pCO₂ is a **net concentration** that would be much
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41 490 lower were it not for calcification concurrent with photosynthesis. The opposite can be true at
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43 491 night when the uptake of CO₂ during dissolution counters the release of CO₂ from respiration.

44 492 The subdued seasonal trend remaining in the T-normalized pCO₂ data is different
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46 493 between CRIMP-2 and the south shore buoys, Kilo Nalu and Ala Wai. T-normalized pCO₂ at
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48 494 CRIMP-2 decreases during the winter (Nov.-Apr.) and increases in the summer (May-Oct.).
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50 495 This trend, however, is reversed in both Kilo Nalu and Ala Wai where T-normalized pCO₂
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52 496 decreases during the summer months and increases in the winter. The trend on the south shore is
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54 497 consistent with summer/winter photosynthetic/respiration cycles (and a relative lack of
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56 498 calcification), as shown, for example, by De Carlo et al. (this volume) in the Bay of Villefranche
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58 499 in the NW Mediterranean. Decreasing SST lowers the rate of water column primary production
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60 500 during the winter, leading to a slight increase in pCO₂ at Kilo Nalu and Ala Wai. In addition, at
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501 Ala Wai, increased organic rich runoff in the winter can cause periods of elevated pCO₂.
502 However, at CRIMP-2 on the barrier reef, where calcification exerts a major biological control
503 on pCO₂, decreased wintertime temperatures also favor lower rates of calcification (e.g. Jokiel
504 and Coles, 1977; Coles and Jokiel, 1978; Marshall and Clode, 2004; Langdon and Atkinson,
505 2005), driving the T-normalized pCO₂ down. However, this effect may be somewhat mitigated
506 by the simultaneous temperature-driven decrease in primary productivity (raising pCO₂ via
507 increased respiration).

508 Although the mean pCO₂ and seasonal pCO₂ trends at the Ala Wai buoy are similar to
509 those at the nearby Kilo Nalu site, seawater does experience greater short-term variability
510 (evident as a slightly higher standard deviation), owing to its location near the mouth of the Ala
511 Wai canal. This canal drains a considerable portion of the Honolulu urban watershed and its
512 waters are enriched both in nutrients and organic matter as well as a number of pollutant
513 chemical species (e.g., De Carlo et al., 2004, 2005; Tomlinson et al., 2011). This continuous and
514 occasionally strong supply of nutrients and organic matter from the Ala Wai canal contributes to
515 an enhanced daily photosynthesis/respiration cycle. During periods of heavy rainfall, the Ala
516 Wai delivers large pulses of freshwater, sediment, and nutrients (Tomlinson et al., 2011).
517 Tomlinson et al. (2011) described a storm in the Honolulu watershed that occurred on 13 March
518 2009 resulting in elevated chlorophyll at the Ala Wai buoy, peaking at 3-5 times the baseline
519 values observed during the week following this intense 24-hour storm. In the two days following
520 this storm, daily pCO₂ cycles, measured by WQB-AW, were significantly dampened due to an
521 increase in photosynthesis. However, the large amount of terrestrial organic matter, introduced
522 by runoff, also enhanced respiration, driving pCO₂ levels back up at night. On 17 March 2011,
523 pCO₂ reached its highest value of the season, 505 µatm. The following two days were marked by
524 a phytoplankton bloom with chlorophyll levels 4.5 times greater than baseline values (Tomlinson
525 et al., 2011), most likely caused by an increased nutrient subsidy following the remineralization
526 of runoff derived organic matter. This same trend was also observed at the Kilo Nalu location,
527 albeit on a considerably smaller scale. Following this storm, Kilo Nalu experienced daily cycles
528 of pCO₂ of ~65 µatm, with maximum pCO₂ above 400 µatm from March 15 to 19. In
529 comparison, the Kilo Nalu location had not shown pCO₂ over 400 µatm in more than a month.
530 The response of Kilo Nalu to runoff from the Ala Wai canal is not typically this strong but

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4 531 particularly large amounts of rain in the Ala Wai watershed and overland flow near the buoy
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6 532 location undoubtedly contributed to additional non-point source runoff and an influx of organic
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8 533 material. Runoff-induced phytoplankton blooms and subsequent remineralization were also
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10 534 shown to affect similarly the pCO₂ levels in southern Kaneohe Bay at the original CRIMP
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12 535 location (Drupp et al., 2011).

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14 536 Even under baseline conditions, the effect of remineralization of runoff derived organic
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16 537 matter can be observed at the Ala Wai location. Figure 8 shows nA_T versus nC_T at the three
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18 538 buoy locations. After normalization, the sample values, especially those from Kilo Nalu, cluster
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20 539 around values similar to the open ocean. Mean HOT surface (<20 m depth) samples have
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22 540 nA_T=2307 μmol kg⁻¹ and nC_T=1986 μmol kg⁻¹ (updated from Keeling et al., 2004;
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24 541 <http://hahana.soest.hawaii.edu/hot/hot-dogs/>) and have been added as an end-member point
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26 542 included in the regression. Some of the Ala Wai samples have elevated C_T due to the higher
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28 543 levels of pCO₂ derived from net respiration and remineralization of organic rich runoff from
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30 544 land. The elevated A_T concentrations at Ala Wai, relative to the HOT data may reflect
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32 545 dissolution within the water column as it is very unlikely that sufficient alkalinity is being added
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34 546 from the land runoff. In contrast, the nA_T vs nC_T plot for CRIMP-2 is scattered due to the variety
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36 547 and greater variability of physical and biological processes previously discussed. Residence time
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38 548 is an important factor affecting A_T, as current speed and, on the rare occasion, direction across
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40 549 the reef are not always constant. Future plans include the deployment of acoustic Doppler current
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42 550 profilers (ADCP) to understand more fully the effects of residence time on pCO₂ and A_T in these
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44 551 different reef settings.

44 552 *5.3 Air-Sea Gas Exchange*

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47 553 Instantaneous CO₂ fluxes are shown in Table 4 and Figure 6a-c. CRIMP-2 shows the
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49 554 largest range from 3.08 mmol C m⁻² hr⁻¹ to -1.00 mmol C m⁻² hr⁻¹. Although this range was
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51 555 nearly two times greater than the CRIMP range reported by Massaro et al. (2012), the mean
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53 556 instantaneous flux was 0.128 mmol C m⁻² hr⁻¹, only about half that of the CRIMP mean. This
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55 557 can be attributed to the latter location having higher average pCO₂ concentrations despite having
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57 558 smaller variations in pCO₂ and lower levels of biological activity (including very little
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59 559 calcification). The lower variation, but higher mean concentration, is a result of the longer
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61 560 residence time of the south bay waters, which is on the order of days to weeks rather than a few

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4 561 hours as observed over the barrier reef. The waters surrounding all three buoys during parts of
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6 562 the study period acted as CO₂ sources to the atmosphere (positive flux), as well as sinks from the
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8 563 atmosphere (negative flux) during other time periods due to seasonal and diel variations in water
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10 564 column pCO₂ and transient events (often storms), resulting in phytoplankton blooms (pCO₂
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12 565 drawdown) or organic matter respiration (pCO₂ increase). The net annualized fluxes for
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14 566 CRIMP-2, Ala Wai, and Kilo Nalu were 1.15 mol C m⁻² y⁻¹, 0.045 mol C m⁻² y⁻¹, and -0.0056
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16 567 mol C m⁻² y⁻¹, respectively. The flux at CRIMP-2, on the barrier reef, is consistent with, but
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18 568 lower than the flux obtained by Massaro et al. (2012) at CRIMP of 1.76 mol C m⁻² y⁻¹ in
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20 569 southern Kaneohe Bay from 2006-2008, and Fagan and Mackenzie's (2007) value of 1.45 mol C
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22 570 m⁻² y⁻¹ for the entire Kaneohe Bay lagoon. However, these three flux estimates are considerably
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24 571 greater than those calculated for the fringing reefs of Honolulu.

25 572 The Ala Wai study site is strongly influenced by mixing with open ocean seawater.
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27 573 However, it remains a net annual source of CO₂ to the atmosphere due to its proximity to
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29 574 frequent nutrient- and organic carbon-rich freshwater discharges and to respiration of labile
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31 575 organic matter in the water column (previously discussed). Waters near the Ala Wai buoy do,
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33 576 however, switch between source and sink seasonally. In the rainy winter months, enhanced
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35 577 nutrient-rich discharge from the watershed stimulates primary productivity during the day,
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37 578 although delivery of pre-existing organic matter also can increase respiration at night.
38
39 579 Furthermore, the enhanced solubility of CO₂ at lower seawater temperature during the winter
40
41 580 leads to a lower seawater pCO₂ relative to the atmosphere, resulting in air-sea gas exchange.
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43 581 This seasonality is reflected in the data in Table 5.

44 582 At all three locations, the seasonality in CO₂ flux (source in summer, sink in winter) is
45
46 583 further enhanced by the seasonality of atmospheric CO₂. In the winter, CO₂ in the Hawaiian
47
48 584 atmosphere is significantly higher than during the summer
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50 585 (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>). The higher atmospheric winter concentrations are
51
52 586 part of the annual northern hemisphere P/R cycles. Because the seasonal variability of
53
54 587 temperature and pCO₂ in the water column and in the atmosphere are in opposite directions, the
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56 588 ΔpCO₂ is affected throughout the entire year. For example, lower atmospheric CO₂, coupled
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58 589 with higher temperature-driven water column pCO₂ during the summer, enhances gas exchange
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60 590 by increasing the concentration gradient between the two reservoirs. In the winter, high

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4 591 atmospheric CO₂ and lower water column pCO₂ reduce the size of the ΔpCO₂ term. These
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6 592 opposing effects contribute to the seasonality in the source/sink function. At CRIMP-2, the
7
8 593 ΔpCO₂ during the summer is driven even higher by calcification. Despite the finding from a
9
10 594 recent short-term Kaneohe Bay barrier reef study of Shamberger et al. (2011) that did not show a
11
12 595 significant increase in summertime calcification, many other studies support this conclusion. It
13
14 596 has been found that corals in Hawaii and at other reef sites reach a maximum calcification rate at
15
16 597 approximately 26°C, the ambient temperature of Hawaiian summers (Jokiel and Coles, 1977;
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18 598 Coles and Jokiel, 1978; Marshall and Clode, 2004; Langdon and Atkinson, 2005). Thus in
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20 599 general, we would anticipate higher calcification during the warm summertime. In contrast, at
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22 600 both Kilo Nalu and Ala Wai, the biological processes (higher summertime productivity)
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24 601 counteract the temperature seasonality (see Figure 6a-c), causing a decrease in ΔpCO₂. In
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26 602 addition to the changes in the CO₂-carbonic acid system chemistry of the water, Hawaiian
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28 603 summers typically have stronger and more persistent tradewinds, which increase the rate of the
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30 604 gas exchange. It is these additive effects that lead to CRIMP-2 being a significant net annual
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32 605 source, and opposing effects that lead to Ala Wai and Kilo Nalu being a very mild source and
33
34 606 mild sink, respectively.

35 607 Flux values presented here compare well to previous studies. Above we already
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37 608 compared the fluxes reported in Kaneohe Bay by Fagan and Mackenzie (2007) and Massaro et
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39 609 al. (2012). The fluxes estimated in this study are also of similar magnitude to those reported for
40
41 610 other tropical reef environments. Ohde and Van Woesik (1999) calculated a flux of 1.8 mol C
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43 611 m⁻² yr⁻¹ for an Okinawan reef in Japan. Comparable reef environments in Bermuda (1.2 mol C
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45 612 m⁻² yr⁻¹ at Hog Reef Flat, Bates et al., 2001) and the northern Great Barrier Reef (1.1 to 1.5 mol
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47 613 C m⁻² yr⁻¹ on Yonge Reef, Frankignoulle et al., 1996) also exhibited comparable fluxes.

48 614 **6 Conclusions**

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51 615 Coastal tropical reef surface waters at multiple buoy moorings around the island of Oahu,
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53 616 Hawaii, exhibit highly variable CO₂-carbonic acid system chemistry and magnitude and
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55 617 direction of CO₂ exchange due to differences in land/ocean interactions, water column and
56
57 618 benthic (CRIMP-2) photosynthesis/respiration, and residence time. Data from this study and
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59 619 previous work in Kaneohe Bay (De Carlo et al., 2007; Drupp et al., 2011; Ringuet and

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Mackenzie, 2005; Massaro et al., 2012) demonstrate the utility of long-term, high-resolution sampling to characterize accurately the carbon chemistry of the coastal surface waters of Hawaii and other similar tropical reef environments where diel cycles, land-derived runoff, and seasonal changes and physical characteristics can all combine to alter the CO₂-carbonic acid system chemistry of the water column on multiple time scales

Seasonal biological and temperature effects on the pCO₂ of the water column were in phase at CRIMP-2, due to vigorous benthic calcification, but at the Ala Wai and Kilo Nalu, where there is much less of an overall calcification signal, these seasonal effects were out of phase, leading to a smaller range of pCO₂. Total alkalinity data showed that the carbon chemistry of surface waters at the Ala Wai and Kilo Nalu buoy sites is primarily controlled by water mass mixing that is driven by tides and waves. At these locations, A_T and C_T values are very similar to open ocean values, with slightly elevated pCO₂ due to increased remineralization of organic matter derived from land runoff and respiration of organic matter produced *in situ* during nutrient-rich pulses of land runoff. A_T and C_T at the CRIMP-2 barrier reef location are primarily controlled by biological activity and the residence time of water on the reef.

Air-sea CO₂ exchange also showed seasonality. Both the Ala Wai and Kilo Nalu buoy locations became a sink during the winter months as cooler temperatures and brief phytoplankton blooms drew down pCO₂. While waters at CRIMP-2 never became a net sink during the winter months, it did display periods of sink activity causing an overall reduction in source strength in winter. During the summer months, high temperatures coupled with lower atmospheric CO₂ and stronger winds, as well as enhanced calcification (at CRIMP-2), led to each location acting as a source of CO₂ to the atmosphere. However, as previously stated, the processes controlling pCO₂ at CRIMP-2 are in phase, likely amplifying the net air-sea gas exchange by increasing seasonal variability, whereas, at Ala Wai and Kilo Nalu these processes are competing (out of phase) and likely reduce the net air-sea gas exchange. Currently Kaneohe Bay, both within the inner lagoon (Fagan and Mackenzie, 2007; Massaro et al., 2012) and its barrier reef, is a net source of CO₂ to the atmosphere, while the Ala Wai and Kilo Nalu areas are a weak source and weak sink of this gas, respectively.

It is important to note that this study along with the previous studies in southern Kaneohe Bay detailed by Drupp et al. (2011) and Massaro et al. (2012) have found significant differences

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650 in CO₂-carbonic acid system chemistry and CO₂ exchange between four Hawaiian reef settings
651 located in close proximity to each other. It is critical that we do not over-extrapolate results from
652 one setting to a global perspective as more and more studies show that CO₂ dynamics in coral
653 reef environments are highly variable and often quite different between various locations.

654
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21 873 **Figure Captions**

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24 874 **Figure 1a:** The island of Oahu, highlighting Kaneohe Bay on the windward (East) coast and the
25 875 Honolulu watershed on the southern coast (Figure courtesy of Mike Tomlinson).
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27 876 **Figure 1b:** Kaneohe Bay on the windward coast, highlighting the CRIMP-2 buoy (yellow circle)
28 877 on the backside of the barrier reef (right). The original CRIMP location is marked as a red circle
29 878 in the left figure (Images modified from Digital Globe).
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32 879 **Figure 1c:** Two buoys are located 200m offshore of urban Honolulu above fringing reefs.
33 880 Ala Wai buoy (WQB-AW) is located near the mouth of the Ala Wai canal, which drains
34 881 part of the Honolulu city watersheds. The Kilo Nalu buoy (WQB-KN) is located ~2 km
35 882 west of WQB-AW (Images from Google Earth modified by Mike Tomlinson).
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38 883 **Figure 2a:** pCO₂ data, taken every 3 hours, from all 3 buoys shows the long term
39 884 seasonal variability, due largely to temperature changes, as well as the short term (hourly-
40 885 weekly) variability, due to both biological and physical forcings. CRIMP-2 (blue) located
41 886 on the Kaneohe Bay barrier reef exhibits the largest variability owing to the reef flat's
42 887 high rates of calcification and productivity. Kilo Nalu (red) shows little variability and is
43 888 fairly representative of the surrounding open ocean water. The yellow line indicates the
44 889 mean air pCO₂ of 377 µatm over the study period. .
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47 890 **Figure 2b:** pCO₂ was normalized to a mean temperature to show temperature
48 891 independent (net biology) effects on pCO₂. Normalizations were calculated according to
49 892 Takahashi et al. (2002).
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52 893 **Figure 2c/d:** pCO₂ data and normalized pCO₂ data from Ala Wai and Kilo Nalu is
53 894 shown.
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56 895 **Figure 3:** Monthly mean pCO₂ (top panel) was calculated for each buoy clearly showing a
57 896 seasonal trend. Temperature changes affect seawater pCO₂ by 4.23% per degree Celsius
58 897 (Takahashi et al. 1993). The warmer “dry” season from May-Oct. Weekly mean water
59 898 temperatures (bottom panel) display a typical summer/winter seasonal trend.
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Figure 4: pCO₂ and pO₂ at CRIMP-2 buoy are anti-correlated (see Table 3) since the reef is highly productive. Photosynthesis during the day decreases pCO₂ while increasing pO₂, with a max O₂ saturation resulting at ~14:00. Respiration at night drives pCO₂ up, with maximum values measured around 04:00-07:00. Elevated pCO₂ from 5/2-5/4 was caused by low wind period (0-2 m s⁻¹ rather than normal 6-8 m s⁻¹) increasing residence time and lowering the gas transfer velocity resulting in a buildup of CO₂ from respiration and calcification.

Figure 5: Autocorrelation of hourly pCO₂ at CRIMP-2 clearly shows a daily cycle which is highly correlated even up to 72 hours.

Figure 6: Instantaneous air-sea gas exchange of CO₂ at all 3 buoy locations is shown. Note that positive values represent a source of CO₂ to the atmosphere, while negative values represent a sink of CO₂ from the atmosphere. Each environment displays a seasonal trend of source activity in the summer and sink activity in the winter.

Figure 7: Total alkalinity measured at each buoy location from 2009-2011 is displayed. A_T at the CRIMP-2 buoy is consistently lower, due to calcification as open ocean water flows across the barrier reef. Water at the Ala Wai and Kilo Nalu sites is more representative of open ocean water, showing only a small change from typical offshore water, which far less variability over time.

Figure 8: A_T and C_T have been normalized to S=35 to remove mixing effects and show the relationship between the two parameters. Regression lines include the HOT mean data from 2008-2011 to serve as an end-member point. A system controlled solely by photosynthesis and respiration would have a theoretical slope of 1, while a system controlled only by calcification and dissolution would have a slope of 2. The data for Ala Wai and Kilo Nalu cluster around typical open ocean values, although a small addition of pCO₂ from organic matter remineralization results in higher C_T values at Ala Wai. CRIMP-2 is highly variable due to the combined effects of P/R, calcification/dissolution and residence time across the reef.

Figure 9: The A_T vs salinity plot can help identify whether alkalinity was added or removed as water flowed across the reef as water moved towards CRIMP-2. Because all but one of the samples fall below the conservative mixing line, alkalinity was biogeochemically removed across the reef flat. The black square is the open ocean end member point used to calculate the conservative mixing line.

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1 Figures

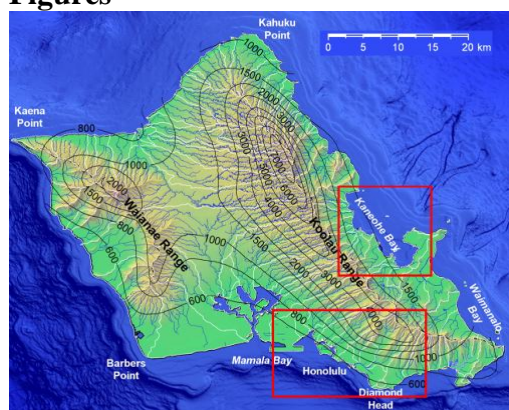


Figure 1a

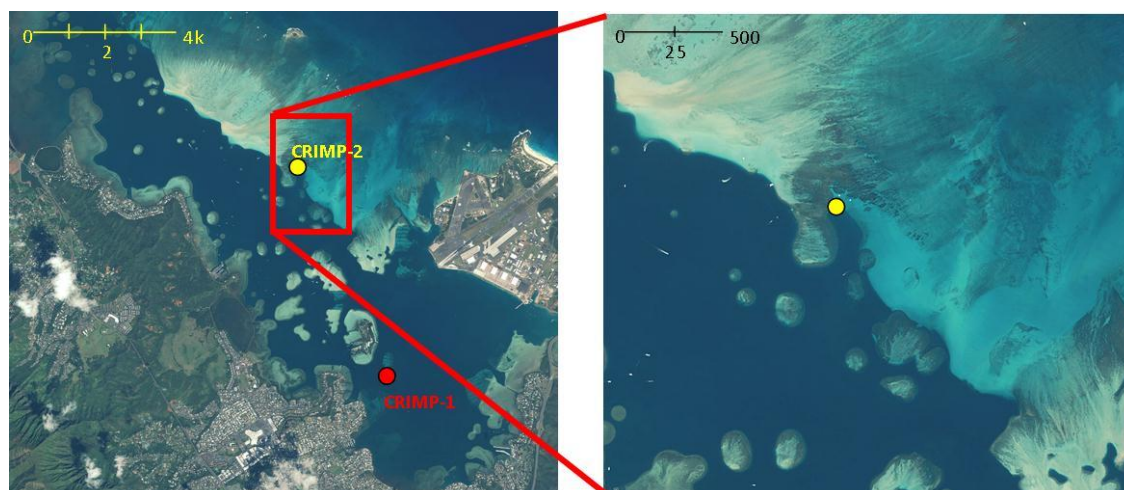


Figure 1b

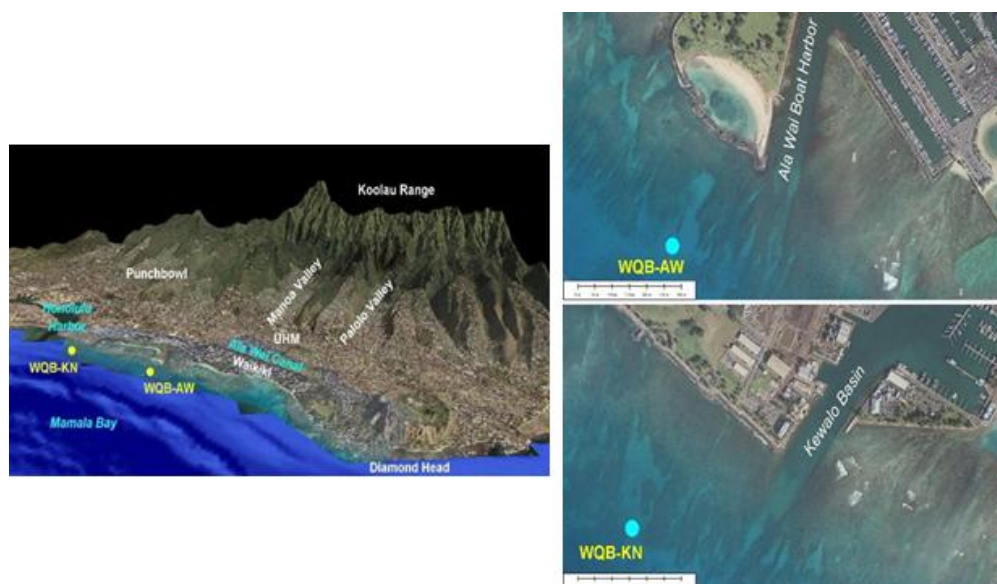
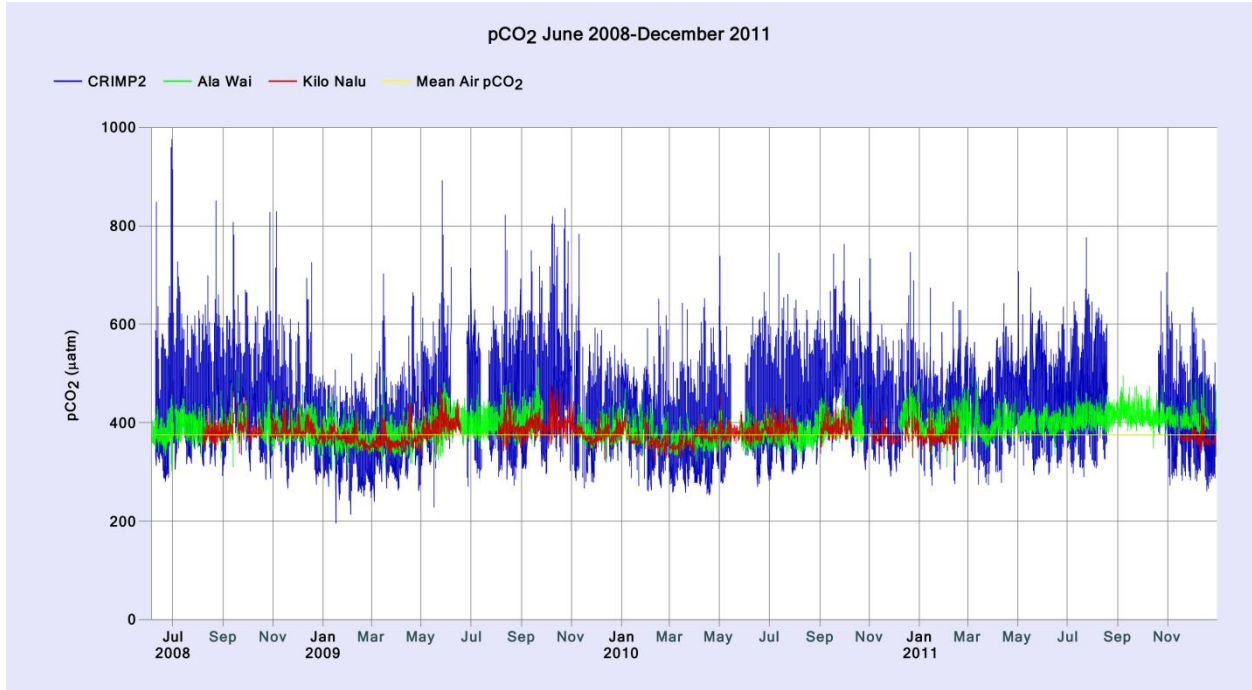


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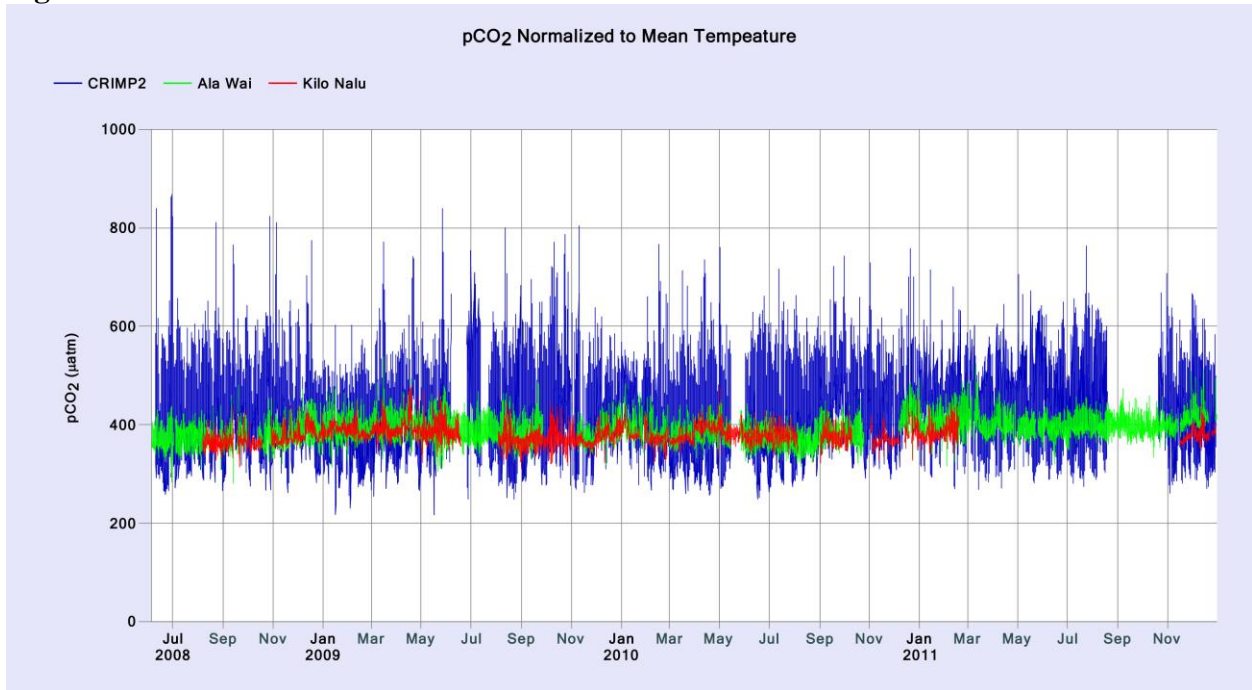
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Figure 2a

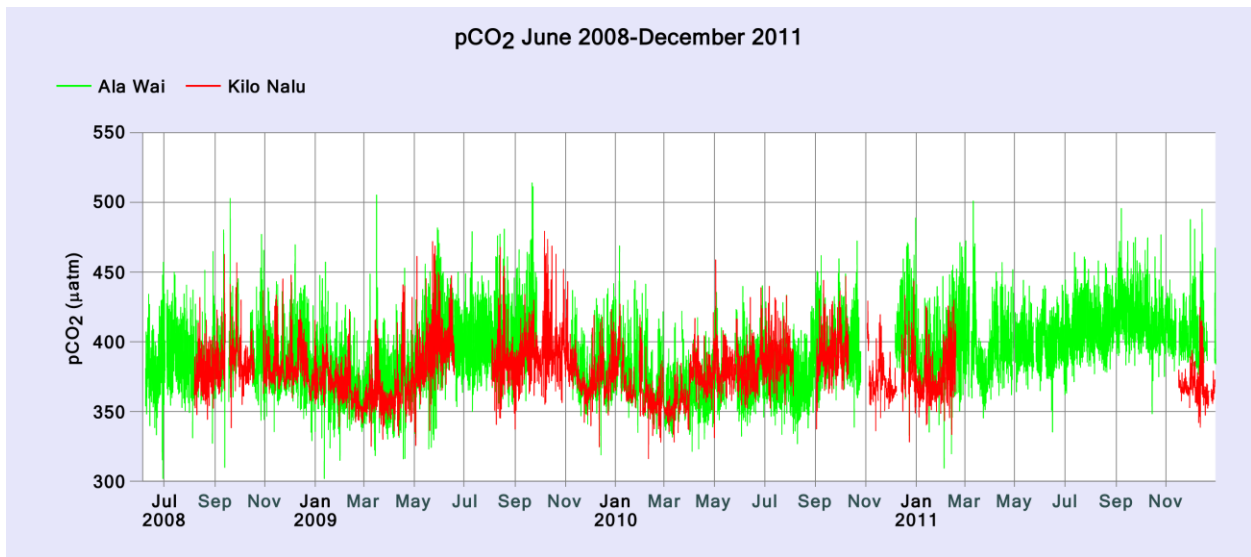


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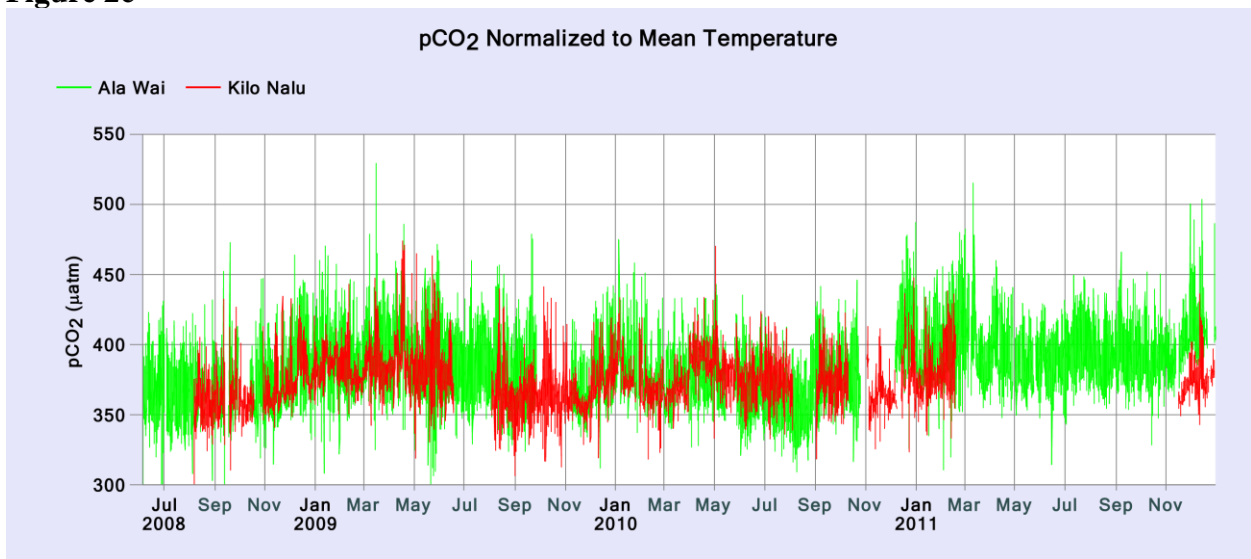
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Figure 2b



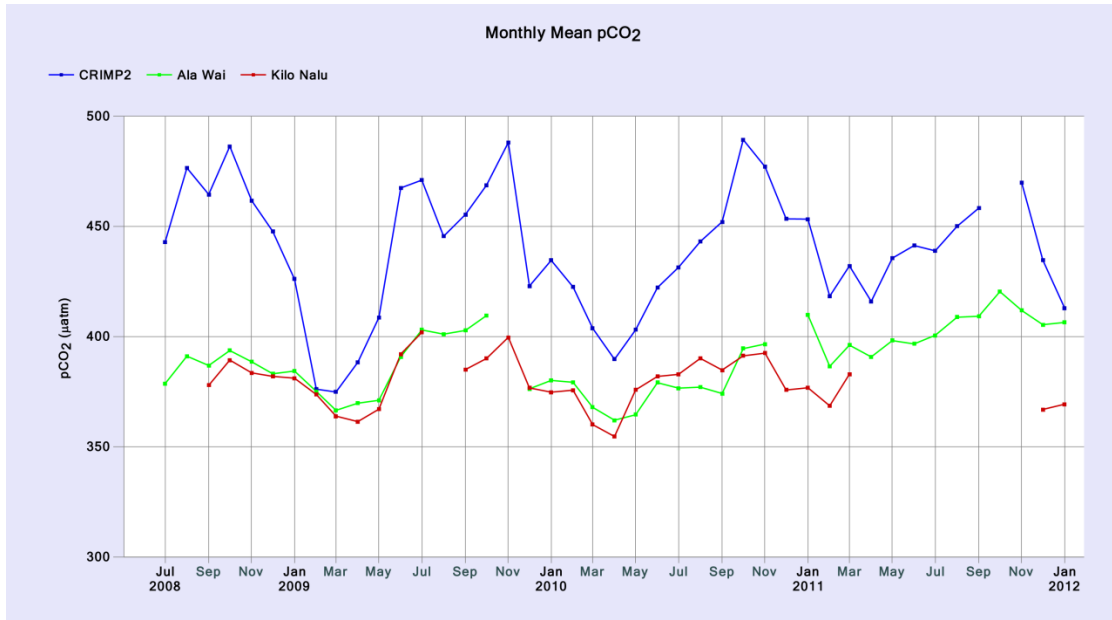
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Figure 2c

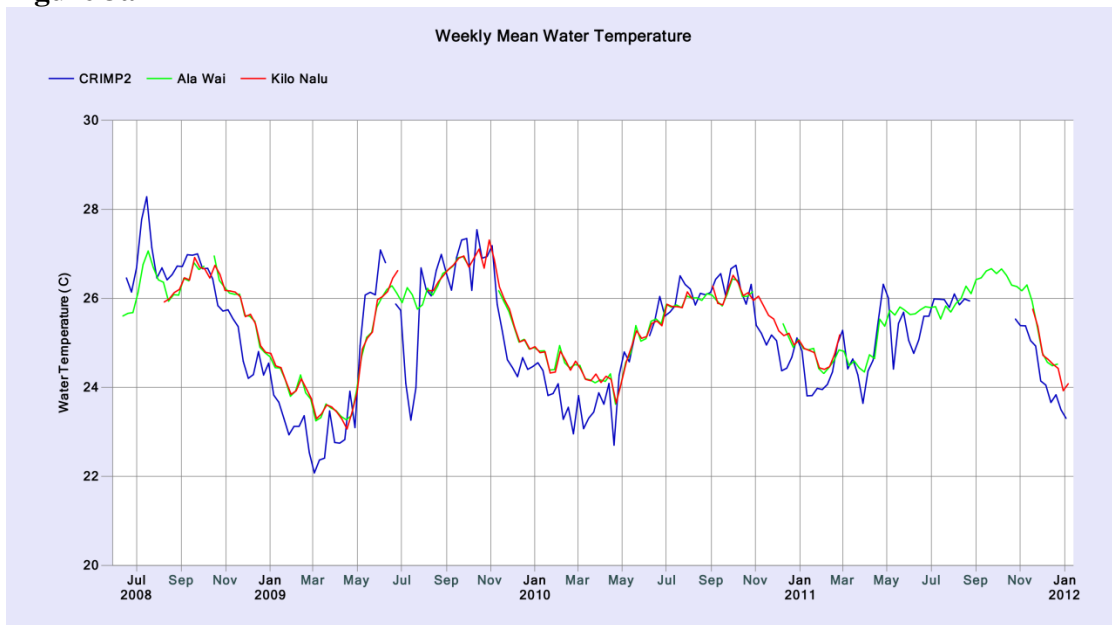


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Figure 2d

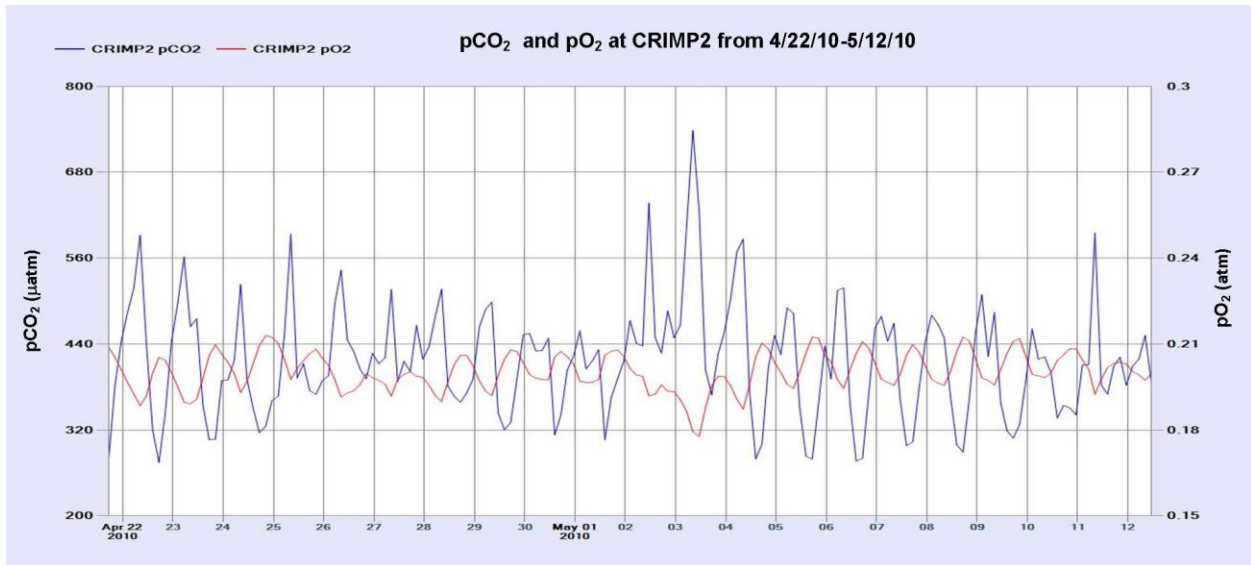


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19 **Figure 3a**



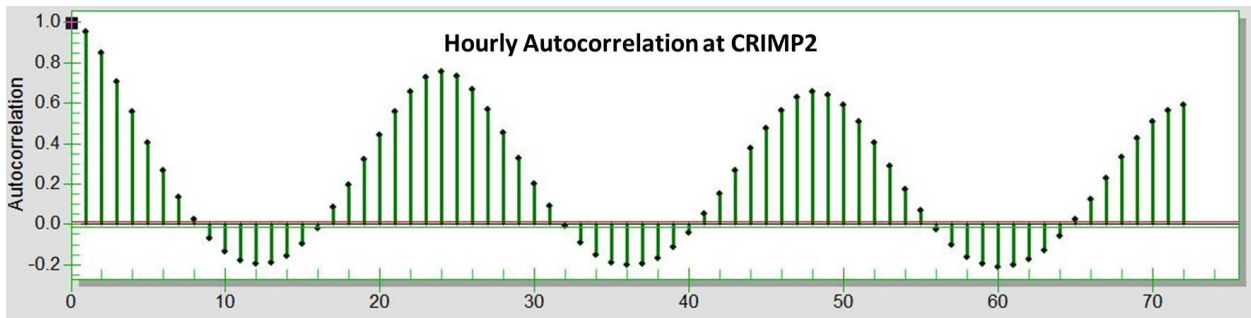
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21 **Figure 3b**

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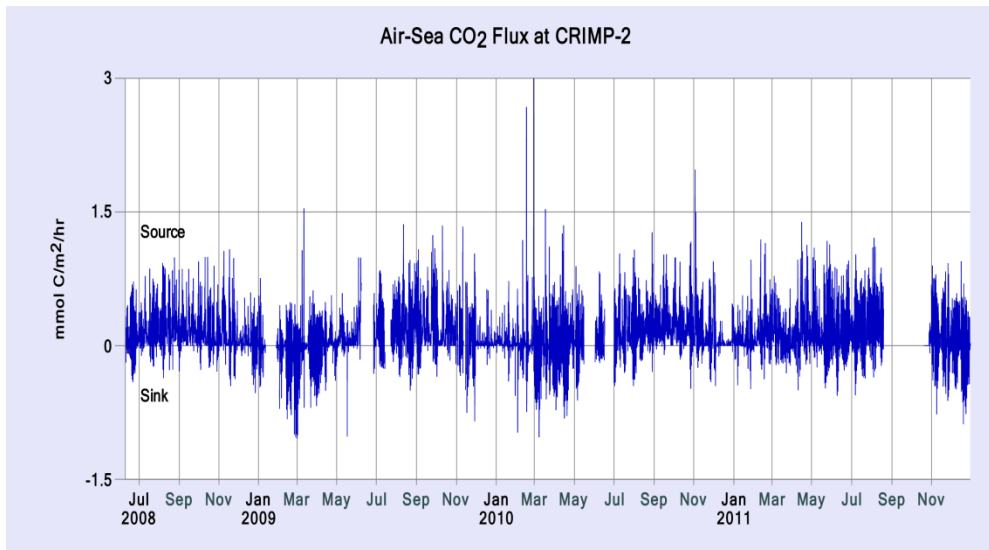
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Figure 4

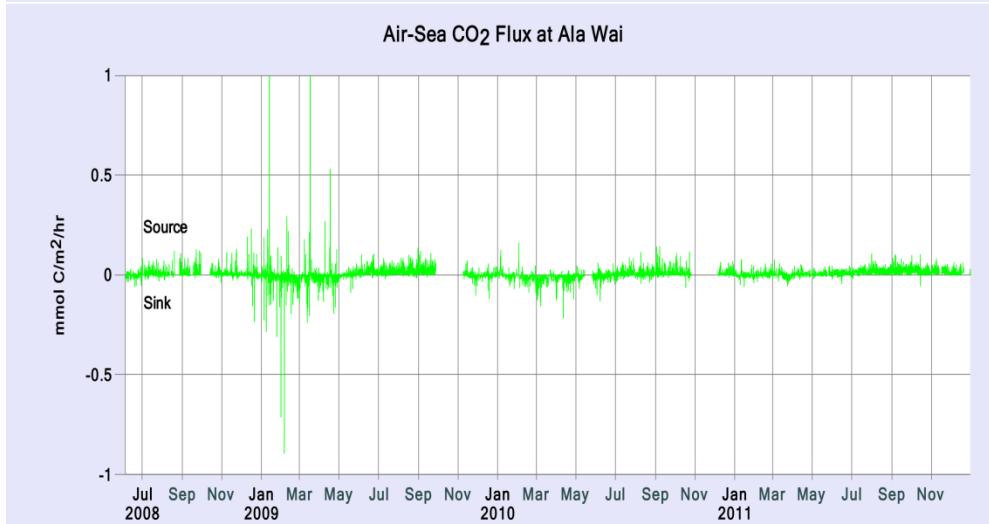


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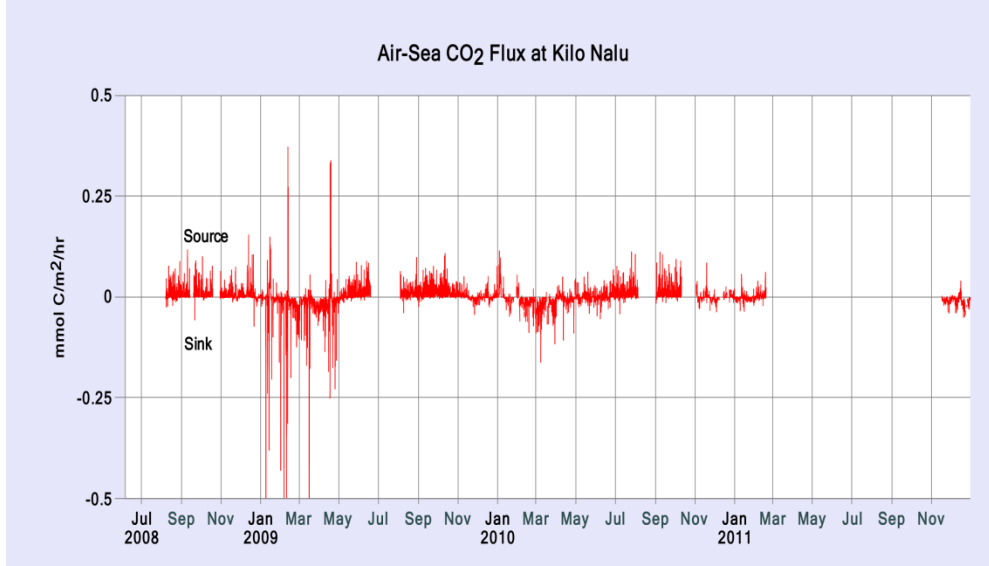
Figure 5



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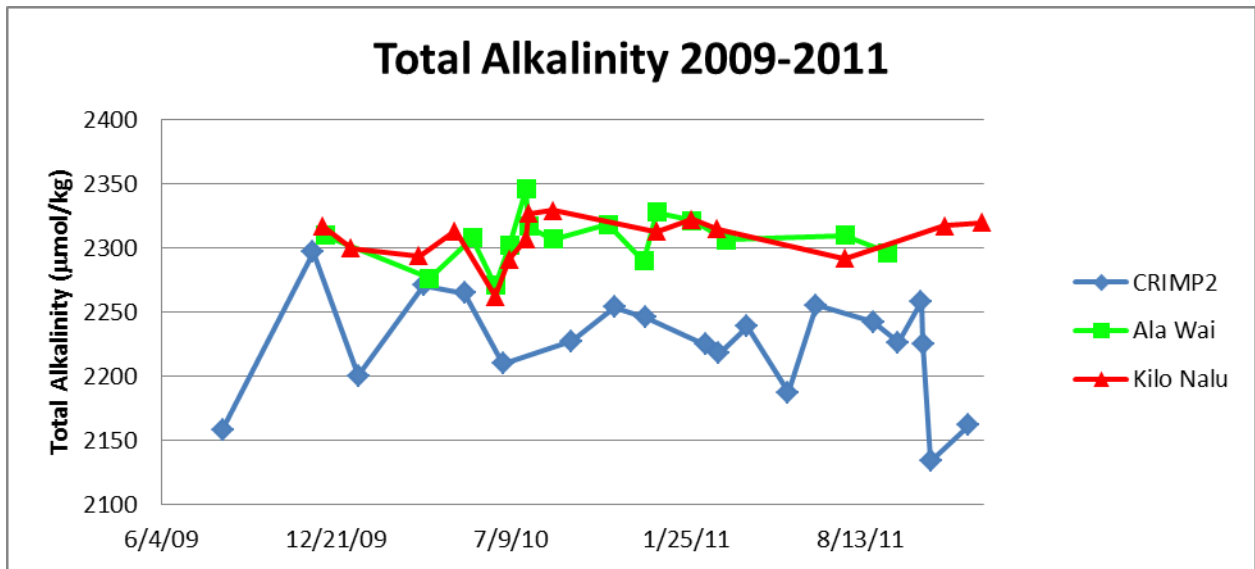


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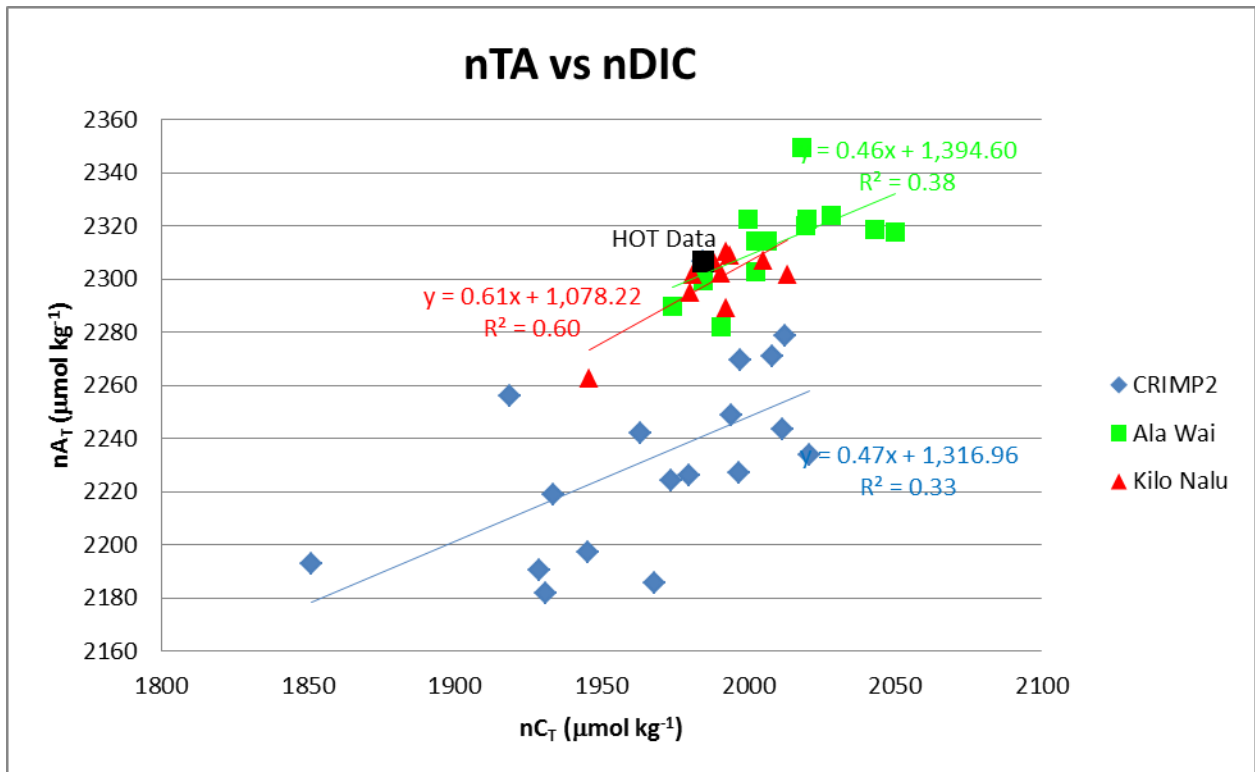
Figure 6



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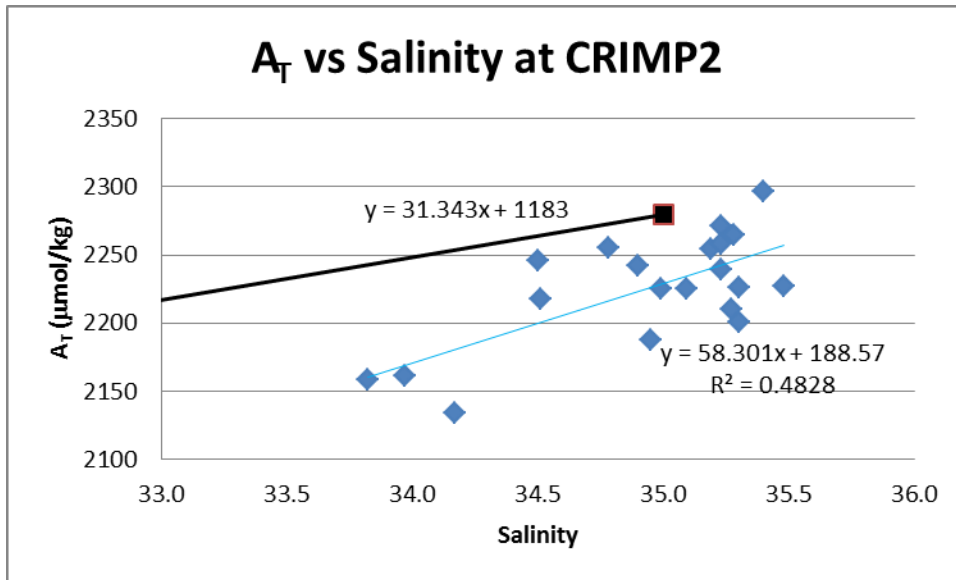
Figure 7



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Figure 8



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Figure 9

Tables

$pCO_{2\ sw}$	Min (μatm)	Max (μatm)	Mean (μatm)	St. Dev
CRIMP-2	196	976	439	83.4
Kilo Nalu	316	479	378	18.2
Ala Wai	302	514	389	25.3
CRIMP-1	225	671	448	50.8

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Table 1: pCO_2 statistics are shown for each of the three buoys from 6/10/08-12/31/11, as well as from the original CRIMP-1 buoy in southern Kaneohe Bay from 11/30/05-5/17/08.

pCO _{2 sw}	Daily Range Mean (µatm)	Daily Range Max (µatm)	Daily Range St. Dev
CRIMP-2	196	557	72.2
Ala Wai	52	146	21.3
Kilo Nalu	30	124	19.3
CRIMP-1	42	204	25.4

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61 **Table 2:** Daily ranges of pCO₂ for each buoy over the study period were calculated and a mean,
62 min, max, and standard deviation of the ranges were calculated. Daily pCO₂ values at CRIMP-2
63 on the reef fluctuate widely with a range 4x greater than any other buoy due to elevated levels of
64 productivity, respiration, calcification, and dissolution.
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Buoy	pCO ₂ vs pO ₂ Correlation	pCO ₂ Autocorrelation		
		12hrs	24hrs	72hrs
CRIMP-2	-0.75	-0.20	0.76	0.59
Ala Wai	-0.29	0.31	0.72	0.62
Kilo Nalu	-0.23	0.48	0.75	0.59

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78 **Table 3:** A negative (albeit weak for AW and KN) anti-correlation is exhibited between pCO₂
79 and pO₂. Autocorrelation shows a strong 24 hour periodicity indicative of P/R cycles.
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June 2008 - Dec 2011	Max Source	Max Sink	Mean	% Time As Source	% Time As Sink	Net Annualized Flux
	mmol C m ⁻² hr ⁻¹					mol C m ⁻² yr ⁻¹
CRIMP-2	3.25	-1.04	0.13	78.0%	21.3%	1.15
Ala Wai	1.72	-0.89	0.005	66.0%	33.9%	0.045
Kilo Nalu	0.373	-1.56	0.00	51.4%	48.4%	-0.0056
CRIMP-1*	1.34	-0.71	0.20	94.2%	5.5%	1.78*

82 **Table 4:** Instantaneous flux ranges are shown for each buoy as well as the percentage of time
83 spent as a source and a sink. Note that these values do not add up to 100% due to periods of no

84 wind or of $p\text{CO}_{2\text{sw}}$ equaling the $p\text{CO}_{2\text{air}}$. Net annualized flux measurements show that the
 85 CRIMP-2 buoy environments is a significant source of CO_2 to the atmosphere (positive values
 86 indicate sources), while the Ala Wai and Kilo Nalu environments are barely a net source and
 87 sink, respectively.

88 *CRIMP-1 data set from 11/05-6/08

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	2008		2009		2010		2011
CRIMP-2	1.39		0.82		1.10		1.31
Ala Wai	0.064		0.027		-0.003		0.092
Kilo Nalu	0.073		-0.018		0.00		-0.032
	Summer '08	Winter '08-'09	Summer '09	Winter '09-'10	Summer '10	Winter '10-'11	Summer '11
CRIMP-2	1.60	0.31	1.63	0.56	1.71	1.12	1.71
Ala Wai	0.069	-0.035	0.12	-0.057	0.049	0.028	0.13
Kilo Nalu	0.074	-0.082	0.086	-0.040	0.055	N/A	N/A
Fluxes in mol $\text{C m}^{-2} \text{ yr}^{-1}$							

92 **Table 5:** Annualized fluxes for each year of the study period as well as broken into the summer
 93 and winter (dry and wet) seasons. Note that positive values indicate source behavior of CO_2 to
 94 the atmosphere while negative (and red) values indicate sink behavior of CO_2 from the
 95 atmosphere. Because the buoys were deployed in June 2008, the annualized flux for 2008 is only
 96 calculated from June 2008-December 2008. Each buoy oscillates between source behavior in the
 97 summer and weak source or sink behavior in the winter. Summer (dry season) is defined as
 98 May-October and winter (wet season) is November-April.

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Location	nA _T (μmol kg ⁻¹)		nC _T (μmol kg ⁻¹)		pH		Ω _{Ar}	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
CRIMP-2 (this study)	2229.53	2181.63- 2278.55	1966.79	1850.94- 2020.93	7.99	7.90-8.13	2.96	2.40-3.77
Ala Wai (this study)	2305.53	2166.87- 2349.53	2001.44	1879.57- 2050.10	8.05	7.99-8.09	3.40	3.04-3.73
Kilo Nalu (this study)	2301.75	2262.85- 2335.35	1988.35	1945.80- 2013.35	8.06	8.03-8.08	3.50	3.26-3.63
HOT (2009- 2011)	2306.53	2298.03- 2317.14	1984.74	1969.02- 1998.93	8.07	8.06-8.08	3.63	3.56-3.71
CRIMP-2 (Shamberger et al., 2011)							2.83	2.50-3.07
K-Bay Midreef (Shamberger et al., 2011)							3.18	3.08-3.25

112 **Table 6:** Carbon system parameters C_T, pH, and Ω_{Ar} were calculated from A_T and pCO₂ samples
113 collected at each buoy. Both A_T and C_T have been normalized to salinity=35 (nA_T and nC_T). Ω_{Ar}
114 data from other studies in Kaneohe Bay compare well with the values calculated for CRIMP-2
115 during this study. Data from Station ALOHA and the HOT program also agree with our findings
116 that the water column at Ala Wai and Kilo Nalu represents open ocean water that has been
117 slightly altered by respiration and organic matter remineralization.