STORM-BASED FLUVIAL INPUTS: NUTRIENT, PHYTOPLANKTON, AND CARBON DIOXIDE RESPONSES IN A TROPICAL EMBAYMENT, KANE'OHE BAY, HAWAI'I

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAI'I AT MĀNOA IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF SCIENCE
IN
OCEANOGRAPHY
MAY 2010

By
Patrick S. Drupp

Thesis Committee:
Eric H. De Carlo, Chairperson
Fred T. Mackenzie
Paul Bienfang

We certify that we have read this thesis and that, in our opinion, it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Oceanography

THESIS COMMITTEE

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Chairperson

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To Mom, Dad, and Rob, whose continuous support made all this possible

Acknowledgements

I would like to acknowledge the University of Hawaii Sea Grant Program for funding this work. I would also like to thank my advisor Eric De Carlo and committee members Fred Mackenzie and Paul Bienfang for all of their help and guidance throughout this study. I would also like to thank the NOAA/PMEL carbon group, Dick Feely, Chris Sabine, Stacy Maennar- Jones, Sylvia Musielewicz, and Noah Lawrence for their work in maintaining our buoy network. Special thanks to Pat Caldwell for organizing and archiving many of our data sets through the NOAA Ocean Data Center, as well as the maintenance staffs at both the Hawaii Institute of Marine Biology and SOEST. Thank you to everyone who has helped in both the lab and the field, Didier Dumas, Rachel Solomon, KR MacDonald, Kristen Fogaren, Michelle Wong, Sara Thomas, Becca Simpson, Chip Young, Jeff Jaegger, Keo Lopes, and Derek Smith.

Abstract

This work describes use of a buoy system to monitor, autonomously, water quality responses to land-derived nutrient inputs and the physical forcings associated with local storm events. These data represent 2.5 years of near-real time observations at a fixed station, collected concurrently with spatially distributed synoptic sampling over larger sections of Kaneohe Bay. Nutrient loadings from direct rainfall and/or terrestrial runoff produce an immediate increase in the N:P ratio of bay waters up to 48, and drive phytoplankton biomass growth. Rapid uptake of nutrient input subsidies by phytoplankton causes a rapid decline of nitrogen levels, a return to N-limited conditions, and a subsequent decline of phytoplankton biomass over time scales ranging from a few days to several weeks, depending on the conditions and proximity to the sources of runoff. This work exemplifies the utility of combining synoptic sampling and real-time autonomous observations to elucidate the responses of coastal tropical coral reef systems to climatic perturbations over the array of time scales (hours to annual) on which they occur.

Many subtropical and tropical systems throughout the Pacific Ocean are similar to Kaneohe Bay and our work provides an important indication of the variability and range of CO_2 dynamics that are likely to exist elsewhere. Such variability must be taken into account in any analysis of the direction and magnitude of the air-sea CO_2 exchange for the integrated coastal ocean, both proximal and distal. Finally, it cannot be overemphasized that our work illustrates several examples of how high frequency sampling provided by a moored autonomous system can provide details about ecosystem responses to stochastic atmospheric forcing, which are commonly missed by traditional synoptic observational approaches.

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Preface

This thesis is presented in the form of an article for the journal, *Aquatic Geochemistry*. This paper details a 2.5 year study of near real time observations in a tropical embayment, Kaneohe Bay, Hawaii. Numerous biogeochemical parameters were measured, and this paper presents the data describing the effects of storm events on nutrient and chlorophyll concentrations and their relationship with water column pCO_2 and flux of CO_2 between the bay waters and the atmosphere. Results presented here, however, are non-inclusive and considerably more data can be found online as part of the NOAA/PMEL carbon group's website, the Hawaii Integrated Ocean Observing site, the NOAA Data Center archives, and the World Ocean Data Atlas (web links included in paper).

Two appendices have been added along with figures not included in the journal article. Appendix A contains additional figures which are primarily time-series profiles of two sites in Kaneohe Bay and serve to illustrate the evolution of the water column both on a long term (seasonal) and short term (storm events) time scale. Appendix B contains figures detailing the effects of storm events and nutrient subsidies on pCO_2 and the fluxes of CO_2 in the bay.

The goal of the journal paper is to show the importance and necessity of real-time continuous measurements (and synoptic spatial sampling) of multiple biogeochemical parameters, local weather patterns, and climatic forcings and evaluation of anthropogenic impacts in a highly temporally and spatially variable tropical coastal system. Most of the relationships and conclusions derived from this study would remain unknown without the availability of the data generated through the long-term, high frequency sampling methods utilized in this work. Many other similar understudied (or completely unstudied) environments exist in the tropical ocean, and this work will help to predict the geochemical dynamics of those systems as well as provide a proven framework for future studies.

Introduction

Fluvial nutrient inputs to coastal waters have been shown to have important impacts on temperate estuarine ecosystems (e.g., Fisher et al., 1988; Jordan et al., 1991: Hubertz and Cahoon, 1999; Billen et al., 2001; D'elia et al., 2003; Scavia et al., 2003; Rabalais 2004; Rabalais et al., 2004; Turner and Rabalais, 2004). However, much less is known about how, and on what time scales, such inputs may impact coastal ecosystems in subtropical or tropical areas. The work reported here is part of a larger collaborative effort to understand the carbon cycle in subtropical and tropical coral reef ecosystems that has been undertaken by our group and colleagues in the NOAA/PMEL CO_2 program (see Ringuet and Mackenzie, 2005; Fagan and Mackenzie, 2007; De Carlo et al., 2007; and Solomon et al., submitted).

Kaneohe Bay (Figure 1) is a sheltered tropical embayment located on the northeast (windward) coast of Oahu, Hawaii. It is one of the most studied coral reef ecosystems in the world (e.g., Cox et al., 1973; Smith et al., 1981; Taguchi and Laws, 1987, 1989; Jokiel et al., 1993; Hunter and Evans, 1995; Laws and Allen, 1996; Atkinson, 2000; Hearn and Atkinson, 2000; Kinzie et al., 2001; Falter et al., 2004; Ringuet and Mackenzie, 2005; Tanaka and Mackenzie, 2005; Hoover et al., 2006; De Carlo et al., 2007; Fagan and Mackenzie, 2007; Hoover and Mackenzie, 2009; Solomon et al., submitted). The bay receives significant freshwater input from eleven streams; of these, Kaneohe Stream is the most important freshwater source. Kaneohe Stream discharges into the southern sector of the bay, which has restricted circulation and accounts for more than 75% of the discharge into the embayment (Hoover 2002). The central and northern sectors of the bay, characterized by numerous patch reefs and a large barrier reef, comprise ~75% of the bay volume and have physical and biogeochemical properties similar to those of the oligotrophic open ocean surrounding the Hawaiian Islands (Smith et al. 1981; Hoover 2002).

Figure 1

The physical properties of Kaneohe Bay water are largely controlled by evaporation, precipitation, and wind, and stream runoff, with only minor effects from tides (Bathen 1968; Smith et al. 1981; Ringuet and Mackenzie, 2005; Ostrander et al. 2007). The first two processes affect the salinity, and rainfall (and subsequent stream discharge) influences both the dissolved and suspended particulate and nutrient loadings to the bay. Consistent northeast trade winds generally keep the bay well mixed, yet occasional periods of warmer temperatures and low wind speeds may cause the bay to stratify vertically (Smith et al. 1981). The bay is subject to mixed, semidiurnal tides, and submarine groundwater discharge into the bay appears to be impacted most strongly by tidal fluctuations.

Anthropogenic perturbations to Kaneohe Bay have been documented for at least 50 years, when urbanization of its watershed accelerated after WWII, and the southern sector of the bay received extensive amounts of sewage discharge. Sewage inputs were diverted out of the bay in 1978 (Smith et al., 1981), after which time phytoplankton and benthic biomass declined rapidly, and bay waters in the southern sector regained the N-limited conditions similar to the central and northern sectors of the bay (Laws and Allen; 1996). Southern Kaneohe Bay continues to receive nutrient-rich surface runoff and groundwater seepage, and remains on the EPA 303-d list of water quality limited segments in Hawaii (Hoover, 2002; Ringuet and Mackenzie, 2005; Hoover et al., 2006, De Carlo et al., 2007).

Storm events cause conditions in the relatively oligotrophic, N-limited southern sector to change rapidly (Smith et al. 1981; Laws and Allen, 1996; Hoover 2002: Ringuet and Mackenzie, 2005). Extensive rainfall in the watershed due to low pressure storms and orographic uplifting over the steep Koolau mountain range causes stream flow to increase rapidly (Tomlinson and De Carlo, 2003), flushing high levels of particulate and dissolved nitrogen, phosphorus and silica into the bay (Hoover, 2002; Ringuet and Mackenzie, 2005; De Carlo et al., 2007; Hoover and Mackenzie, 2009). Plumes of nutrient-enriched freshwater can cover up to a third of the southern sector of Kaneohe Bay, and subsequently trigger phytoplankton blooms (Laws and Allen, 1996; Ringuet and Mackenzie 2005; Hoover et al., 2006; De Carlo et al. 2007).

Methods

Study Site

This investigation focused on the southern sector of Kaneohe Bay. This sector has a relatively long mean residence time of 13 days and an average depth of 9.5 m (Smith et al., 1981). During most of the year, physical mixing in the bay is driven predominantly by tradewinds and to a lesser degree by semidiurnal tides. The southern sector is generally well-mixed except during periods of high rainfall, when water column stratification develops in response to freshwater inputs (Ringuet and Mackenzie, 2005; De Carlo et al., 2007); the duration and extent of such stratification are strongly dependent on wind forcing. Like most of windward Oahu, Kaneohe Bay receives abundant rainfall. Average long-term rainfall in the watershed is nearly 200 cm/yr, and ranges from 85 cm/yr to as high as 365 cm/yr (Giambelluca et al. 1986). During the December 2005 to June 2008 period of this study, annual rainfall varied from 150 - 300 cm/yr.

Field Methods

The Coral Reef Instrumented Measurement and CO_2 Monitoring Platform ($CRIMP-CO_2$) is a 1.5m diameter buoy, which extends 1 meter both above and below the surface of the water. The buoy houses a LICOR-820 infrared sensor, a MaxtecMAX^{TM} - 250 Series sensor measuring CO_2 and O_2, and a Sensirion for measuring humidity. A Sea-Bird Electronics MicroCat CT (37-SMP) attached to the buoy platform measures temperature and conductivity. Further details regarding the buoy instrumentation are reported in Solomon et al. (submitted). The $CRIMP-CO_2$ buoy takes measurements at 3hr intervals and the data are transmitted daily via Iridium satellite to servers at NOAA/PMEL. Data from the CRIMP-CO_2 buoy instruments and from our other buoys in Hawaii coastal environments can be viewed in "near real time" at: http://www.pmel.noaa.gov/co2/coastal/HI/ or http://www.soest.hawaii.edu/hioos/focus_area/water_quality.php.

The CRIMP-CO_2 buoy was deployed in the southern portion of Kaneohe Bay 300-400m southwest of both Coconut Island and Lilipuna Pier (Figure 1). This site was selected due to its proximity to coral reefs and because storm-derived freshwater plumes are normally advected over this site. The CRIMP-CO_2 buoy design allows deployment of autonomous instruments on its platform located ~1m below the surface. Throughout this study a YSI 6600 system was employed to measure chlorophyll-a (chl-a) fluorescence, dissolved O_2 saturation (DO), turbidity, pH, conductivity, temperature, and depth at 10 min intervals. This multi parameter sonde was deployed near the CRIMP-CO_2 intake tube, about 0.5 m below the sea surface, although the probes at the bottom of the sonde were in water closer to 1 m in depth. The sonde was recovered every 3-5 weeks for data download and replacement with another recalibrated unit. For certain deployments, sampling intervals varied between five and 15 minutes, depending on the length of the deployment and the anticipated battery life. These measurements by the autonomous instruments provided high temporal frequency data to complement the lower frequency CO_2 buoy measurements and synoptic sampling.

Synoptic sampling was carried out at nine locations in Southern Kaneohe Bay (Figure 1). Stations were chosen to give a mixture of near-shore and offshore locations, as well as sites that would be in the path of freshwater plumes from streams. The water column was profiled for biogeochemical parameters and near-surface (0.5 m) water samples were collected on a bi-monthly basis throughout the rainy season (October – May) and on a monthly basis in the dry season (June – September) to characterize background conditions. Following large storm events (defined as ≥5 cm rain in 24 h), the nine stations were sampled daily for five days or until the evidence of storm runoff and phytoplankton blooms was no longer apparent in water column properties, whichever was greater. Water column profiling was accomplished by use of a YSI 6600 sonde during storm periods, and discrete water samples were collected from a depth of 0.5 m for laboratory analyses. Samples for nutrients and chl-a were collected in 1L 10% HCl-washed 1L HDPE bottles and stored in a cooler while in the field. Additional water samples were collected in 300 mL, borosilicate glass bottles for Total Alkalinity (TA) analysis. TA samples were immediately poisoned with 200 µL of a saturated mercuric chloride ($HgCl_2$) solution to eliminate biological activity. TA samples were also collected monthly at the CRIMP-CO_2 buoy location. On selected dates, duplicate samples for dissolved inorganic carbon (DIC) analysis were collected, and stored at 4°C until filtration. Weather data were obtained from the Hawaii Institute of Marine Biology weather station on Coconut Island including solar radiation, both total and photosynthetically active, wind speed and direction, and rainfall. Rainfall data were also taken from the Luluku rain gauge (HI15), located near the base of the Koolau mountain range in the bay's watershed (Fig 1).

Lab Methods

Samples were refrigerated (dark), immediately filtered (GF/C membranes) and subsequently frozen until analysis following methods described by Hoover (2002), Ringuet and Mackenzie (2005), and De Carlo et al (2007). Samples were analyzed for chl-a, NO_3^-, NO_2^-, soluble reactive PO_4^{3-} (SRP), and $Si(OH)_4$. Samples collected from 11/26/05 to 7/31/07 were analyzed colorimetrically on a Technicon AutoAnalyzer (Parsons et al., 1984). Detection limits for N and P species were 0.1µM and 1µM for Si. Samples collected from 8/28/07 to 5/22/08 used an Autonomous Profiling Nutrient Analyzer (APNA) built by SubChem Systems, Inc., equipped with optical cells by WET Labs, Inc. and analyzed according to standard spectrophotometric methods (Strickland and Parsons 1972). APNA detection limits for NO_3, NO_2^-, PO_4^{3-}, and $Si(OH)_4$ were 0.04µM, 0.03µM, 0.06µM, and 0.44µM, respectively. Samples for chl-a were processed by filtering 70mL through 25mm Whatman GF/C filters. The filters were placed in glass vials, wrapped in foil, and stored at -20°C until analysis. Prior to analysis, 5mL of 90% acetone was added and the vials were vortexed, stored at -20°C for 24-72 hours to allow for full extraction, and analyzed using a Turner Designs 111 fluorometer using the acidification method (Strickland and Parsons 1972).

Results

Responses of the nearshore marine environment to atmospheric and/or fluvial perturbations are presented here in graphical fashion. Only selected responses are described and this report is not inclusive of all situations encountered during our study. Readers are encouraged to peruse all profiling and sampling data collected during the study which are available at the URL given above and at from the NOAA data center at UH Manoa. (http://www.nodc.noaa.gov)

Temporal and Diel Cycles at CRIMP-CO_2

Time series concentrations of CO_2 and O_2 in the water and atmosphere measured at three hour intervals over the study period (Figure 2) reveal overall seasonal changes, i.e., higher CO_2 values in the summer and lower CO_2 values in winter. The dry (summer) season is shaded in gray in Figure 2. During the study period, the average concentrations of CO_2 in the atmosphere and near-surface seawater were 372 µatm and 448 µatm, respectively, exhibiting an overall imbalance between these two reservoirs. The mean winter and summer seawater CO_2 concentrations were 424 µatm and 485 µatm, respectively. The atmospheric CO_2 concentrations were consistent with the marine air surface annual mean data from Cape Kumukahi, Hawaii of 380 ppmv (Keeling, Piper et al. 2007). Periods during which atmospheric CO_2 levels were above the global marine surface air average were generally conditions of weakened trade winds and/or southerly winds (Solomon et al., submitted). Sea surface temperature (SST) and sea surface salinity (SSS) vary temporally, and both parameters show maxima in the summer (Figure 2). SST ranged from 22-28°C, with minima in January and February; SSS also showed minimal values in the winter, due to higher precipitation and fluvial discharges. The mean SSS values for the winter and summer periods were 33.63 and 34.91, respectively. Winter data were averaged over the 2006 and 2007 seasons, and the summer average is derived from 2007; other data not used in these mean calculations showed similar trends suggesting consistent year to year temporal variability.

Figure 2

Kaneohe Bay is characterized by strong diurnal cycles in water column properties as well as longer term temporal changes. Figure 3 shows diurnal changes in the concentrations of CO_2 in near surface seawater, chl-a, DO saturation and pH over a ten day period. The sensor based chl-a values (from ~1m) were on average slightly lower than those for discrete water samples, which were collected from a depth <0.5 m. The lower bottle values may reflect a slightly greater abundance of chl-a near the surface than at the bottom of the YSI probe, at a depth of nearly one meter. Peak chl-a concentrations usually occurred in the late afternoon (14:00-16:00 hrs), with daily fluctuations of about 1-3 µg/L during non event (background) conditions. As anticipated, peak chl-a levels correspond with maximum dissolved oxygen saturation and pH values since

$$CO_{2(aq)} + H_2O \leftrightarrow 2H^+ + CO_3^{-2} \leftrightarrow CH_2O + O_2.$$

Dissolved oxygen saturation ranged from ~80% (night) to 120% (near mid-day 14:00-16:00). The regularly observed declines in chl-a, DO, and pH, together with increasing CO_2 clearly show the switch from net autotrophy to net heterotrophy in the near surface waters of southern Kaneohe Bay sampled by CRIMP-CO_2.

Synoptic Sampling: Nutrients and Chl-a

Water column biogeochemistry was spatially quite variable among the nine sites. Nutrient and chl-a data (Table 1) vary widely from the generally oligotrophic reference site (SB) to the more estuarine sites proximate to stream mouths. All nutrient concentration trends showed minimum average values at sites SB and D, slightly higher values at sites E, LC, and CRIMP-CO_2, and maximum values at sites JD4, JD5, JD6, and KS. The predominant wind pattern normally produces a clockwise circulation in the southern sector of the bay, and this moves fluvial discharges northward along the shoreline. Under southwesterly wind conditions, stream inputs are advected directly seaward from Kaneohe stream mouth (Ostrander et al. 2007); during such conditions, fluvial inputs do not advect over sites JD5, JD6, D, and CRIMP-CO_2 and higher nutrient concentrations are observed at Sites JD4 and E

Table 1.

Average summer and winter concentrations of chl-a, NO_3^-, NO_2^-, NH_4^+,PO_4^{3-}, and $Si(OH)_4$ are given in Table 2. During the summer (dry), concentrations of nutrients and chl-a are lowest and are considered baseline; concentrations of dissolved N and P are generally less than <0.4µM and <0.2µM, respectively, and levels of chl-a rarely exceed 1.5 µg/L. Average and maximum concentrations of NO_3^- were generally higher at all sites during the winter. Concentrations of PO_4^{3-}, NO_2^-, NH_4^+ and $Si(OH)_4$, however, were more similar throughout the year at all sites. The nearshore sites (JD4, JD5, JD6 and KS), showed higher maximum NH_4^+ concentrations during winter, while the offshore sites showed higher maxima during the summer. Concentrations of chl-a are also related to solar radiation and turbidity. Mean chl-a concentrations were 2-5 times greater during winter than during the summer months when the range of chl-a concentrations is also narrowest. Lowest chl-a values occurred at the reference site (SB), and in the Lilipuna Channel (LC).

Table 2

Storm Events

Six storm events that were observed during this study occurred on 12/5/2005, 2/2006-4/2006, 9/25/2006, 10/29/2006, 11/4/2007, and 12/5/2007. Within 24 hours of ≥5 cm of rainfall being recorded at the Luluku rain gauge in the bay watershed, the water column was profiled and sampled. Figure 4, a time series plot of SSS between October 2007 and December 2007, illustrates how fluvial discharges to the bay are reflected in SSS at CRIMP-CO_2 station. Beginning in November 2007 a relatively cool, fresh plume developed over parts of the southern sector of Kaneohe Bay. This plume altered the physical properties (SSS, SST) and caused significant changes in the chemistry and biology within this portion of Kaneohe Bay. Nutrient-rich stream runoff discharged soils and groundwater from the watershed causing nutrient levels in the bay spike. Due to small amounts of NO_x scavenged from the atmosphere, direct rainfall into the bay also inputted nutrients to surface waters. Figure 5 and Table 1, showing nutrient concentrations from 11/25/2005 to 5/22/2008 at the CRIMP-CO_2 buoy location, are characterized by low baseline concentrations and sharp pulses of high concentrations associated with the rain events. Depending on weather and wind conditions, these input pulses may reach CRIMP-CO_2 buoy in 1-4 days (Ostrander et al., 2007). Figure 5 (right panels) highlights two storms that occurred in September and October of 2006. The first storm, with initial rainfall of 7.5 cm on 9/25/2006, produced a 25-fold increase in NO_3^- from a baseline of ~0.2 µM to ~5 µM and a commensurate increase in $Si(OH)_4$ to 285 µM on 9/27/2006. Most of this nutrient spike disappeared by 9/28/2006.

Intermittent rainfall from October 30th -November 2nd (6.35 cm on 10/30/2006 and 12.7 cm on 11/1/2006) produced another nutrient enriched plume at the mouth of Kaneohe Stream, with NO_3^- and PO_4^{-3} concentrations rising above baseline levels (25.19 µM and 1.14 µM on 10/31/2006). The plume reached the CRIMP-CO_2 location on 10/31/2006, resulting in nitrate, phosphate, and chlorophyll concentrations of 8.63 µM, 0.99 µM, and 1.49 µg/L, respectively. The next day, nutrient and chlorophyll values fell dramatically, as seen in Table 1, and the N:P ratio returned to near Redfield (17.86). More rainfall, beginning the afternoon of November 1 and continuing the next day caused another influx of nutrients to the bay. This plume caused a nearly threefold increase of NO_3^- to 10.56 µM and $Si(OH)_4$ levels rose to 42.16 µM. No significant spike in PO_4^{-3} occurred at either the CRIMP-CO_2 station or in the stream mouth. Nutrient levels declined rapidly and the next 6 days were characterized by a return to baseline conditions.

Figure 4

Figure 5

Figure 6 shows nutrient levels at the mouth of Kaneohe Stream during the study period. Baseline concentrations at this site are always higher than at other bay locations, and large pulses of nutrients from the stream mouth are clearly evident during each storm. The impacts of an abnormally long (40 d) storm that began in February of 2006 were recorded. This event caused elevated concentrations of both NO_3^- (~10-30 µM) and $Si(OH)_4$ (~ 300 µM) for nearly 5 months before returning to lower, more typical levels. In sharp contrast, PO_4^{-3} concentrations quickly returned to baseline values of ~0.25 µM after spiking to near 1 µM at the beginning of intense storm period.

Figure 6

Chl-a concentrations (Figure 7) show strong temporal fluctuations in response to nutrient inputs to southern Kaneohe Bay (Figure 5 and 6). Storm events caused phytoplankton biomass to increase by up to an order of magnitude (~7-10 µg chl-a /L) from baseline conditions typified by <1 µg chl-a /L in the summer and 1-3µg chl-a /L in the winter. In winter, chl-a concentrations rose sharply in response to storms, as shown by substantial albeit variable increases in chl-a concentrations above baseline following each major storm event (Dec 2005, Feb-Mar 2006, Oct 2006, and Nov-Dec 2007). Response to the 40 day storm (Feb-April 2006), however, was characterized by an abrupt chl-a spike followed by sustained high (>2 µg/L) chl-a levels throughout the late winter and early spring (Figure 7). High resolution sampling is of particular value in these tropical watershed systems because the response of streams to storms is very abrupt (Tomlinson and De Carlo, 2003) and receiving water conditions vary rapidly in response to freshwater inputs (De Carlo et al., 2007; Ostrander et al., 2007).

Figure 8 shows times series measurements of chl-a and turbidity taken at the CRIMP buoy from 10/25/07 – 4/2/08. Chl-a peaks are evident following the storms on November 4th and December 4th as well as increased levels in late January due to multiple days of continuous rainfall. Small increases in turbidity can be observed following each of these rain events as suspended solids discharged by the streams are advected over the buoy location. However, these pulses are relatively small, rarely increasing above 2 NTU's.

Figure 7

Figure 8

Figure 9 shows pCO_2 and NO_3^- levels at the CRIMP buoy from 9/27/07 – 12/10/07. Rainfall on both November 4th and December 4th caused plumes of fresh, nutrient rich water (see Figure 4) to spread over the bay towards CRIMP. NO_3^- levels spiked to 1.5μM and 0.5μM following the two storms. A rapid drawdown was apparent over the next few days, accompanied by a drawdown of pCO_2. Figure 10 shows that chlorophyll concentrations measured at the buoy location were substantially elevated during these periods of pCO_2 drawdown. Chlorophyll levels spiked to ~5μg/L following both storms, with the November storm exhibiting a brief sharp spike, while increased chlorophyll levels persisted for a longer period following the December storm.

Figure 9

Figure 10

Discussion

Seasonal variability in the geochemistry of southern Kaneohe Bay largely reflects influences of tropical climatic patterns prevailing in Hawaii. The dry season, characterized by dry, sunny days with near constant trade winds, maintains the bay waters relatively oligotrophic and well mixed (Bathen, 1968; Smith et al. 1981; Laws and Allen, 1996; Ringuet and Mackenzie, 2005; Ostrander et al., 2007). This is reflected in water column profiles of T, S, DO, turbidity and pH that are generally constant and surface nutrient levels that approach limits of detection (Table 2). During the wet season, local weather conditions are more dynamic (e.g., greater variability in winds, frequent intense but often brief storm events). Nutrient enriched freshwater enters the bay following intensified stream flow after such rain events (e.g., De Carlo and Tomlinson, 2003; Ringuet and Mackenzie, 2005; De Carlo et al., 2007). These inputs are manifested as distinct pulses in the time-series concentrations of nutrients at stations CRIMP-CO_2 and KS (Figure 5 and 6). Depending on conditions, surface nutrient concentrations away from the stream mouth may rise rapidly (e.g., <0.1 - 30 μM $N0_3^-$, <0.1 -1 μM PO_4^{3-} and <5 -250μM $Si(OH)_4$ (Table 2). Ringuet and Mackenzie (2005) reported similar ranges of nutrient variability at one of these stations sampled during their study.

The fate of storm water plumes in Kaneohe Bay, characterized by depressed SST and SSS, and elevated nutrient concentrations depends on several interacting processes. The low salinity, nutrient-rich runoff plumes initially form a surface layer overlying normal salinity bay waters. Differential water column mixing under differing wind conditions (i.e., velocity and direction), as well as the extent and duration of enhanced stream flow, figure prominently in the persistence of these plumes in the bay; tidal mixing appears to play a much more limited role (Ringuet and Mackenzie, 2005; Ostrander et al., 2007). Extended periods (a few days to one week) of low velocity winds following a large runoff event help maintain water column stratification and retain nutrients near the surface. This relieves nitrogen limitation and drives phytoplankton blooms. The occurrence of strong (i.e., ≥10 kt) tradewinds either during a rain event or subsequent to formation of a runoff plume causes rapid mixing of nutrients throughout the water column (De Carlo et al., 2007). This process effectively reduces nutrient concentrations and decreases the time during which non-limiting nutrient levels prevail. Mixing effectively decreases nutrient availability for uptake by primary producers by that portion of nutrients that become distributed to aphotic waters. Higher winds also enhance circulation and increase the northward advection of nutrients out of the southern sector of the bay. The persistence of plumes and maintenance of stratification are therefore key factors in determining the magnitude of the phytoplankton response to a given nutrient input. This in turn affects the pCO_2 of the water column via the combination of forcing mechanisms that impact gas exchange between the ocean and atmosphere, the physical and chemical properties of CO_2 (e.g., partial molal volume, solubility) and biological processes involving CO_2 such as primary productivity, heterotrophy, and calcification (Solomon et al., submitted).

Changes in the biogeochemistry of Kaneohe Bay waters in response to nutrient inputs affect the CO_2 concentrations on time scales ranging from daily to seasonal (Figure 2). The time series of buoy data during ten days in March 2008 (Figure 3) shows the diurnal covariance between chl-a, DO, and pH, and a negative correlation of these parameters with the water column CO_2 content. Typically a chl-a maximum occurs in the mid-late afternoon and is accompanied by a corresponding spike in DO; photosynthesis decreases CO_2 concentrations during the day. At night, when heterotrophy dominates the ecosystem, DO is used in respiration and CO_2 is produced, thereby driving the diurnal variations in the concentrations of these gases.

On a seasonal scale, the increased phytoplankton biomass from elevated nutrient inputs can cause lower winter CO_2 levels (Figure 2), although the enhanced solubility of CO_2 in cooler and somewhat freshened water accounts for most of the difference between summer and winter values (Solomon et al., submitted). Temporary but sharp winter CO_2 decreases in bay waters are clearly the result of removal from the water column by enhanced primary productivity. These sharp decreases dampen the source strength of bay waters and on some occasions can switch the bay to a sink of CO_2 from the atmosphere. Higher winter primary productivity in Kaneohe Bay was also observed by Kinzie et al. (2001), Hoover (2002), and Ringuet and Mackenzie (2005). In addition to runoff, enhanced deposition of atmospheric NO_x could also contribute to higher primary productivity during the winter, although we can only provide circumstantial evidence to support this hypothesis (see below). The substantially higher winter chl-a concentrations at all stations (Table 2) support the hypothesis that phytoplankton blooms are the primary driver of the sharply decreased CO_2 content of bay waters during the winter when N-limitation is least severe.

N-limited conditions previously described for Kaneohe Bay (e.g., Smith et al. 1981; Laws and Allen, 1996; Hoover, 2002; Ringuet and Mackenzie, 2005) is substantiated by this current study. The N:P ratios during both the winter and summer (Table 2) show summer values that are well below the idealized Redfield Ratio of 16:1 at all but two sites, strongly indicating prolonged N-limitation over this 2.5 year study period. Only sites KS and JD6 do not show typically N-limited N:P ratios during the summer; KS is directly in line with the main source of nutrient subsidies (i.e., Kaneohe Stream) to the bay, and JD6 is only slightly north and in the direct path of the stream plume under trade wind conditions. Even in the winter, the average N:P ratios at bay sites that are not near the Kaneohe Stream mouth are indicative of N-limitation (Table 2). The availability of P for phytoplankton added to bay waters during storms is decreased by the highly adsorptive nature PO_4^{3-} by binding onto reactive particle surfaces. This would be consistent with prior reports that south Kaneohe Bay waters switched to P-limitation shortly after storms and after the N was rapidly drawn down by phytoplankton blooms (Ringuet et al., 2005). Yet, particle-bound P has also been shown to undergo a slow but progressive desorption, which can lower the N:P ratio in receiving waters (De Carlo and Dollar, 1997; De Carlo et al., 2007).

Winter runoff frequently drives the N:P ratio above the N-limitation range in Kaneohe Bay, and triggers brief phytoplankton blooms. N:P ratios at the CRIMP-CO_2 buoy commonly rise above 16 within 1-2 days of the initial rainfall from storm events (Table 1). An exception was the November 5, 2007 event that generated a plume of unusually small areal extent because the majority of rain fell directly over the bay, rather than into the watershed, and had less effect on land-derived nutrient subsidies. Subsequently, concentrations of NO_3^- rose only slightly, albeit sufficiently enough to cause a phytoplankton response (Figures 7,8,9). During most storms, chl-a levels increased rapidly to maximum values until the available NO_3^- was exhausted. Figures 5 and 8 illustrate the almost immediate decline of NO_3^- and PO_4^{3-} to background levels, and the reversion of water column conditions to a situation typifying an N-limited, low chl-a system.

Sharp pulses and collapses of nutrient and phytoplankton levels were observed at all the open water locations in southern Kaneohe Bay, but not at the nearshore Sites JD4 through JD6 and KS. Silica levels at KS are consistently elevated owing to groundwater inputs and runoff. This is reflected in average summer and winter values of ~216 µM $Si(OH)_4$, although a minimal winter value of 24.2 µM, and a minimal summer value of 33.5 µM were observed. Unlike the open bay, the enhanced NO_3^- levels at KS during the winter months persist for longer times and are not depleted rapidly by blooms; at this more brackish location, NO_3^- remains enriched long after any initial runoff input and well into the summer months.

Several physical factors combine to influence the extent and persistence of nutrient enrichment in the water column along the western shore of southern Kaneohe Bay near the stream mouth. In this area of enhanced stream inputs, the turbid, low salinity plume in the upper 0.5m may inhibit the growth of marine phytoplankton due to decreased light availability and/or suboptimal salinities. Conditions of lower productivity would prolong the period of elevated nutrient concentrations; additionally, the loss of inputs of PO_4^{3-} through adsorption onto terrigenous particles would tend to drive these sites toward P-limitation, thereby prolonging elevated NO_3^- conditions.

The extensive storm of February - March 2006 led to high NO_3^- levels which persisted into July (Figure 6); nutrients reached maximum values in late March, and elevated chlorophyll (~2µg/L) levels persisted throughout the southern sector of the bay

(Figure 7). During the first half of this storm event, normal (NE, 10-15mph) trade wind conditions prevailed, but on 15 March, the winds became more variable, and lighter, southerly winds dominated. This shift in winds caused increased stratification throughout the bay, and produced maximal levels of nutrients and chl-a. Water column CO_2 (Figure 2) subsequently decreased to levels below atmospheric conditions causing the bay to become briefly a sink of CO_2 (Solomon et al., submitted). Other than a brief two day period following the Nov 4th 2007 storm, this was the only time during the study period that the water column became a sink of CO_2 from the atmosphere. This was due to a combination of CO_2 drawdown (due to enhanced productivity) and high wind speeds which facilitated a gas transfer across the air-sea interface. Because dampened pCO_2 conditions are often associated with low winds (following Kona Storms), the source strength of the water column is often reduced to a state of no gas transfer, but does not switch to being a sink.

The late September 2006 storm caused a perceptible nutrient spike at the CRIMP-CO_2, KS and adjacent JD6 stations, but not at any other stations. This is thought to reflect a "first flush" effect that has been associated with the first storm of the season (e.g., De Carlo et al., 2007). Both NO_3^- and $Si(OH)_4$ accumulate in groundwater preferentially over PO_4^{3-} during the summer due to differing reactivities of these chemical species, leading to uptake and retention of P in solid phases. The spike of NO_3^- and $Si(OH)_4$ at CRIMP buoy can be seen in the right panel of Figure 5. Respiration of organic content in soils, and the attendant release of N and P is followed by retention of the P species onto Fe and Al oxyhydroxides of the lateritic soils characterizing Hawaiian basalts, while groundwater-basalt interactions release $Si(OH)_4$ to the groundwater (e.g., De Carlo et al. 2007). Given sufficient rainfall intensity, rain from the first storm of the season percolates most readily through soils, causing lesser surface runoff but flushing of the NO_3^-, NH_4^+ and $Si(OH)_4$ enriched groundwater from the aquifer to the bay. In late September 2006, strong tradewinds following such an input prevented stratification and allowed more of the flushed groundwater nutrients to be mixed vertically before reaching the offshore locations. Although only slightly elevated concentrations of chl-a were observed across the bay, the near surface seawater CO_2 content at the CRIMP-CO_2 buoy was significantly lower following the storm, suggesting enhanced productivity. Profiles show slightly elevated chl-a throughout the water column for the three days after this storm. This indicates that the ecosystem response to this late summer nutrient subsidy was broad-based spatially when N-limitation was relaxed, even though elevated nutrient levels were only evident at the stations nearest the shore and stream mouth. Warm temperatures, strong light conditions and relatively low turbidity allowed rapid uptake of nutrients and the prompt resumption of N-limited conditions (Table 1).

On the night of October 30, 2006 and into the next morning, approximately 11.4 cm of rain fell at the Luluku stream gauge. Concentrations of NO_3^- and PO_4^{3-} rose above baseline levels to 8.63 μM and 0.99 μM when sampled the afternoon of the 31st. The chl-a concentration was 1.49 μg/L, a slight increase from the baseline, although not nearly as high as observed during other rain-induced blooms. With an N:P ratio of 8.74 and phosphate levels nearly five times higher than average, the system was most likely nitrogen limited. The lack of a substantial increase in $Si(OH)_4$ (to only 2.40 μM) probably also inhibited diatom growth, which is quite common in bay waters following large storms (Ringuet an Mackenzie, 2005; Hoover et al., 2006).

Rainfall of 17.8 cm between November 1and 2, 2006, caused a ~2.5 fold increase in NO_3^- to 10.56 μM and $Si(OH)_4$ rose to 42.16 μM. Phosphate levels, however, were three times less (0.34 μM) as compared to those measured after the initial rainfall on October 31. This was most likely due to a flushing of phosphorus-enriched sediments after the first rainfall, leaving little phosphate remaining. The rise in silicate levels indicates a strong submarine freshwater discharge. After the rainfall on October 30 and 31, the soils were not saturated enough to create significant freshwater seepage, but with the additional rain two days later, freshwater was discharged nearshore, close to the CRIMP-CO_2 buoy. On November 2, N:P ratios reached 30.86, suggesting a phosphorus limited system. The following day, November 3, was characterized by a dramatic decline in all nutrient levels as concentrations of chlorophyll rose to 1.26 μg/L. Following this bloom, the environment returned to a low N:P ratio typical of the normally nitrogen limited system. This increase in chlorophyll was not as large as during some storms, but led to three times higher concentrations than baseline conditions for the month.

The 2006-2007 winter was relatively dry and there were no large storms until November of 2007. On 4 November, the bay received 25.4 cm of direct rainfall over a 24 hour period and 14 cm were recorded at the Luluku rain gauge in the upper watershed. In a few hours, salinity in the bay fell from 35.5 to 31.5 at CRIMP-CO_2 buoy (Figure 4). A large freshwater lens spread across the southern basin, augmented by stratification due to light winds and high solar radiation. Although nutrients never reached levels observed during other storm events, concentrations of chl-a increased nonetheless; the enhanced productivity caused significant decreases in pCO_2. Figure 9 shows this decrease of pCO_2 coupled with the rapid uptake of NO_3^- by phytoplankton. NO_3^- levels spiked to 1.5μM on

November 5th. Over the next 3 days, NO_3^- fell to its baseline conditions, as pCO_2 dropped by 100μatm. Chlorophyll levels (Figures 7, 8, 10) exhibited a sharp spike about ~2-3 times above baseline levels. The rapid uptake of nutrients resulted in a chlorophyll crash only 2 days after the initial increase. Another storm, only one month later, had very little effect on nutrient concentrations suggesting that the watershed soils did not have adequate time to restore N and P concentrations to previous levels. However, even with only a small nutrient increase, pCO_2 again exhibited a drawdown correlated with the utilization of the nitrate subsidy. Because of the persistence of rain over several days, rather than one short, intense rain period, nutrient levels remained slightly elevated for several days, leading to a more sustained bloom than in some prior storms (Figure 10). Increased turbidity (Figure 8) of ~2 NTU, associated with both storms, does not appear to have much of an effect (e.g. photoinhibition) on phytoplankton growth, as rapid mixing quickly removed suspended solids from the upper water column.

Conclusions

Southern Kane'ohe Bay is a very dynamic biogeochemical system, with many controlling factors. This study shows that high resolution time series data of multiple parameters, coupled with synoptic sampling, are necessary to understand short and long-term changes of the biogeochemistry of the water column in such a dynamic environment. Although nutrient runoff ultimately controls the intensity of phytoplankton blooms, it is obvious that many other factors are involved. Wind speed, incident solar radiation, and turbidity are all factors that control whether the environment can initiate and sustain a bloom, and the lapse period between storms has a significant effect on the concentrations of nutrients available for transport out of the immediate input area.

Carbon dioxide dynamics are strongly coupled with phytoplankton blooms and nutrient loading. Large bloom events are clearly capable of changing the direction of the air-sea flux of CO_2 from bay waters being a source to being a sink. While the periods of sink behavior are short in duration and not very frequent, in-situ observations and sampling are critical in characterizing the extremely variable nature of the CO_2 dynamics in this system. Coastal CO_2 air-sea exchange, release and uptake events are likely to be highly variable throughout the world's coastal ecosystems. Many subtropical and tropical systems throughout the Pacific Ocean are similar to Kaneohe Bay and our work provides an important indication of the variability and range of CO_2 dynamics that are likely to exist elsewhere. Such variability must be taken into account in any analysis of the direction and magnitude of the air-sea CO_2 exchange for the integrated coastal ocean, proximal and distal. Finally, it cannot be overemphasized that our work illustrates several examples of how high frequency sampling provided by a moored autonomous system can provide details about ecosystem responses to stochastic atmospheric forcing which are commonly missed by traditional synoptic observational approaches.

Tables

Table 1. Nutrients and Chl-a Concentrations and N:P Ratios at CRIMP Buoy

Date	**NO_X μM**	**Si μM**	**PO_4 μM**	**Chl μg/L**	**N:P**
11/26/2005	0.07	5.07	0.02	0.56	2.92
11/27/2005	0.35	4.53	0.02		14.8
11/28/2005	0.45	8.99	0.05	1.29	9
12/4/2005		3.96			
12/5/2005	0.06	0.95	0.08	3.75	0.77
12/6/2005	0.06	3.23	0.06	9.31	1.05
12/7/2005	0.06	0			
12/12/2005				0.96	
12/17/2005	0.56	6.54	0.09		6.22
1/6/2006				1.26	
1/20/2006	0.12	7.68	0.09	0.67	1.33
1/27/2006				0.52	
2/7/2006	0.04	11.25	0.08	0.75	0.5
2/20/2006	2.73	22.32	0.32	3.95	8.53
2/21/2006	6.23	39.39	0.52	2.63	12
2/22/2006	4.16	31.34	0.19	1.94	21.9
2/23/2006				4.63	
2/24/2006	0.17	4.22	0.12	4.07	1.42
2/25/2006	0.92	7.11	0.14		6.57
2/27/2006	0.72	7.78	0.15	1.26	4.8
2/28/2006	0.03	5.66	0.06	1.76	0.5
3/1/2006	0.4	8.1	0.07	2.81	5.71
3/2/2006				3.04	
3/4/2006				2.67	
3/5/2006				3.56	
3/6/2006	0.81	31.99	0.09	2.28	9
3/7/2006				2.89	
3/9/2006					
3/10/2006	0.49	9.94	0.06	1.98	8.17
3/16/2006	0.44	20.26	0.08	5.11	5.5
3/21/2006				7.87	
3/27/2006				2.35	
3/31/2006				5.42	
4/4/2006	0.03	3.94	0.07	6.97	0.43
4/12/2006	0.6	6.2	0.11	7.94	5.45
4/19/2006	0.48	5.24	0.06	0.44	8
5/12/2006	0.45	6.9	0.15	0.51	3
6/15/2006	0.11	11.11	1.44	0.19	0.08
7/14/2006	0.11	3.02	0.14	0.05	0.78
7/31/2006				0.11	
8/28/2006				0.91	
9/13/2006	0.22	11.72	0.12	0.62	1.84
9/26/2006	0.15	8.25	0.21	1.42	0.68
9/27/2006	5.08	285	0.16	0.67	32.5

*0 values indicate below detection limit

Table 1. (continued)Nutrients and Chl-a Concentrations and N:P Ratios at CRIMP- Buoy

Date	**NO_X μM**	**Si μM**	**PO_4 μM**	**Chl μg/L**	**N:P**
9/28/2006	0.1	11.64	0.18	1.43	0.57
10/4/2006	0.17	9.93	0.22	1.2	0.8
10/17/2006	9.22	37.06	0.76	0.43	12.1
10/31/2006	8.63	2.4	0.99	1.49	8.74
11/1/2006	3.96	0.71	0.22	0.51	17.9
11/2/2006	10.6	42.16	0.34	0.57	30.9
11/3/2006	0.5	4.9	0.15	1.26	3.38
11/4/2006	0.15	11.32	0.16	0.85	0.98
11/5/2006	0.19	8.91	0.1	0.6	1.95
11/6/2006	1.6	10.88	0.11	0.55	14.6
11/8/2006	0.21	11.24	0.19	0.49	1.08
11/22/2006	0.34	11.56	0.14	0.47	2.41
12/1/2006				1.38	
1/4/2007	0.28	4.64	0.18	1.08	1.61
1/9/2007				1.01	
2/7/2007	0.51	7.01	0.14	0.7	3.55
2/28/2007				0.8	
3/7/2007	0.16	8.07	0.2	0.1	0.82
4/4/2007	0.32	8.64	0.23	1.65	1.38
4/27/2007				0.91	
5/14/2007	0.13	11.33	0.053	0.22	2.45
7/31/2007	0.39	11.1	0.142	1.27	2.77
8/28/2007	0.15	1.213	0.211	0.82	0.71
10/19/2007	1.47	8.581	0.283	1.2	5.19
11/5/2007	0.73	9.991	0.172	1.63	4.23
11/6/2007	0.1	0.465	0.091	0.27	1.15
11/7/2007	0.22	0.019	0.136	1.85	1.65
11/8/2007	0.09	0.65	0.061	0.8	1.4
11/9/2007	0.16	8.446	0.182	0.54	0.88
11/20/2007	0.02	1.225	0.128	0.94	0.15
12/6/2008	0.48	0.159	0.148	1.47	3.24
12/7/2008	0.31	0.737	0.176	0.02	1.75
12/8/2007	0.31	10.91	0.174	1.47	1.77
12/9/2007	0.25	1.173	0.016	1.74	15.6
12/10/2007	0.26	8.958	0.395		0.65
12/11/2007	0	0.628	0.178	2.25	0
1/11/2008	0.36	4.835	0.171	1.11	2.1
1/31/2008	0.13	2.306	0.131	0.94	0.95
2/13/2008	0.16	1.172	0.229	1.04	0.7
2/28/2008	0.18	6.475	0.243	1.07	0.74
3/12/2008	0	0.854	0.175	0.53	0
4/30/2008	0.16	6.589			
5/22/2008				0.44	

*0 values indicate below detection limit

Table 2. Winter and Summer Statistics of Nutrients, Chl-a, and N:P at all Sites

		SB	**D**	**E**	**JD6**	**JD5**	**JD4**	**KS**	**LC**	**CRIMP-CO2**
NO3 (Winter)	**Avg**	0.97	1.01	1.21	7.35	6.7	3.82	17	1.29	1
	Min	<0.04	<0.04	<0.04	0.06	0.06	<0.04	0.42	<0.04	<0.04
	Max	19.16	11.4	11.57	33.73	34.32	21.16	35.03	14.69	10.56
	St Dev	3.1	2.51	2.8	8.71	8.77	6.2	9.94	3.03	2.1
	n	47	47	50	48	50	46	51	34	52
NO3 (Summer)	**Avg**	0.21	0.49	1.19	3.86	2.4	3.68	11.03	0.85	1.15
	Min	<0.04	0.07	0.06	0.17	0.08	0.08	0.47	<0.04	0.1
	Max	0.65	4.12	14.7	15.84	16.03	20.26	25.19	7.96	9.22
	St Dev	0.17	1.05	3.88	3.53	4.38	5.62	8.5	2.06	2.65
	n	15	15	15	15	15	15	15	15	15
PO4 (Winter)	**Avg**	0.14	0.13	0.15	0.19	0.21	0.2	0.35	0.17	0.17
	Min	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
	Max	0.66	1.06	0.81	0.96	0.72	0.78	0.92	0.4	0.99
	St Dev	0.13	0.16	0.16	0.17	0.16	0.16	0.21	0.08	0.15
	n	48	48	50	46	47	46	49	34	50
PO4 (Summer)	**Avg**	0.12	0.19	0.2	0.22	0.25	0.34	0.32	0.19	0.28
	Min	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
	Max	0.23	0.63	0.88	0.82	0.99	2.41	1.14	0.61	1.44
	St Dev	0.07	0.14	0.2	0.19	0.23	0.59	0.27	0.13	0.37
	n	15	15	15	15	15	15	15	15	15
NO2 (Winter)	**Avg**	0.11	0.12	0.13	0.15	0.2	0.16	0.13	0.11	0.17
	Min	<0.03	<0.03	<0.03	<0.03	<0.03	0.05	<0.03	<0.03	<0.03
	Max	0.34	0.32	0.36	0.38	0.5	0.53	0.38	0.27	0.46
	St Dev	0.09	0.1	0.11	0.12	0.14	0.13	0.1	0.09	0.13
	n	18	18	18	18	18	18	18	18	18
NO2 (Summer)	**Avg**	0.13	0.17	0.13	0.14	0.16	0.13	0.09	0.13	0.18
	Min	0.11	0.11	<0.03	0.1	0.07	0.09	0.06	0.13	0.07
	Max	0.17	0.23	0.3	0.2	0.27	0.16	0.11	0.14	0.3
	St Dev	0.03	0.06	0.16	0.05	0.1	0.04	0.03	0.01	0.12
	n	3	3	3	3	3	3	3	3	3

Table 2. (continued) Winter and Summer Statistics of Nutrients, Chl-a, and N:P at all Sites

		SB	**D**	**E**	**JD6**	**JD5**	**JD4**	**KS**	**LC**	**CRIMP-CO2**
Si (Winter)	**Avg**	7.82	8.47	10.92	59.48	60.85	31.02	216.9	7.49	8.34
	Min	<0.44	<0.44	<0.44	1.41	0.88	0.52	24.2	<0.44	<0.44
	Max	82.19	47.01	67.42	247.19	252.71	142.05	457.8	39.13	42.16
	St Dev	12.65	9.19	12.82	64.56	71.35	38.32	101.19	7.36	9.4
	n	43	47	50	48	50	47	50	34	53
Si (Summer)	**Avg**	7.18	8.98	10.51	85.14	41.12	50.25	216.99	10.64	28.58
	Min	<0.44	1.03	0.61	8.27	2.46	0.79	33.46	<0.44	1.21
	Max	15.45	27.18	26.44	211.2	181.19	235.06	326.93	33.35	285.02
	St Dev	3.82	5.87	7.09	76.77	51.52	66.13	101.09	7.55	71.4
	n	15	15	15	15	15	15	15	15	15
NH4 (Winter)	**Avg**	0.83	0.91	1.07	1.41	1.27	1.2	1.73	0.79	0.75
	Min	<0.1	<0.1	<0.1	<0.1	<0.1	0.16	<0.1	0.2	<0.1
	Max	4.38	4.4	5.47	4.94	2.86	3.01	7.85	1.67	2.4
	St Dev	0.93	0.96	1.06	1.1	0.83	0.86	1.74	0.5	0.53
	n	25	25	27	25	27	24	28	16	29
NH4 (Summer)	**Avg**	0.7	0.83	1.08	1.76	1.72	2.05	3.5	0.82	0.82
	Min	0.37	0.33	0.29	0.47	0.5	0.78	1.33	0.35	0.36
	Max	2.17	1.69	4.14	5.11	6.02	5.57	7.81	1.39	1.73
	St Dev	0.51	0.45	1.05	1.29	1.56	1.47	2.06	0.34	0.49
	n	12	12	12	12	12	12	12	12	12
Chl-a (Winter)	**Avg**	1.91	2.44	2.29	2	3.37	2.41	1.29	1.46	2.02
	Min	0.22	0.29	0.25	0.06	0.38	0.34	0.12	0.15	0.02
	Max	7.87	12.17	10.69	8.05	68	11.56	8.46	7.59	9.31
	St Dev	1.51	2.48	2.21	1.69	8.77	2.4	1.47	1.67	2.02
	n	62	61	62	61	61	62	63	39	62
Chl-a (Summer)	**Avg**	0.48	0.67	0.73	1.13	1.01	1.06	0.74	0.55	0.76
	Min	0.07	0.05	0.11	0.3	0.11	0.13	0.07	0.11	0.05
	Max	0.94	2.25	1.4	4.26	2.55	3.41	2.25	1.06	1.49
	St Dev	0.28	0.56	0.41	0.97	0.77	1.04	0.57	0.36	0.5
	n	17	17	17	17	17	16	17	17	17

Table 2. (continued) Winter and Summer Statistics of Nutrients, Chl-a, and N:P at all Sites

		SB	D	E	JD6	JD5	JD4	KS	LC	CRIMP-CO2
N:P (Winter)	**Avg**	4.8	7.2	6.4	35	40.7	51.2	87.1	7	4.8
	Min	0.4	0	0	0	0	0.3	1.6	0	0
	Max	32.6	113	48.4	403.1	257.5	358.8	454.2	83.6	30.9
	StDev	6.7	16.3	9	74.1	59.6	75.4	106.4	15.7	6.1
	n	45	51	53	49	50	49	52	34	53
N:P (Summer)	**Avg**	1.74	1.87	4.3	29.73	11.89	31.26	92.75	3.11	4.84
	Min	0.5	0.4	0.33	0.66	0.46	0.86	1.28	0.17	0.55
	Max	5.99	6.54	29.44	323.67	116.89	226.29	788	12.98	32.45
	StDev	1.61	1.84	8.1	82.01	29.65	58.89	197.83	3.48	8.4
	n	14	14	15	15	15	15	15	15	15

Figures

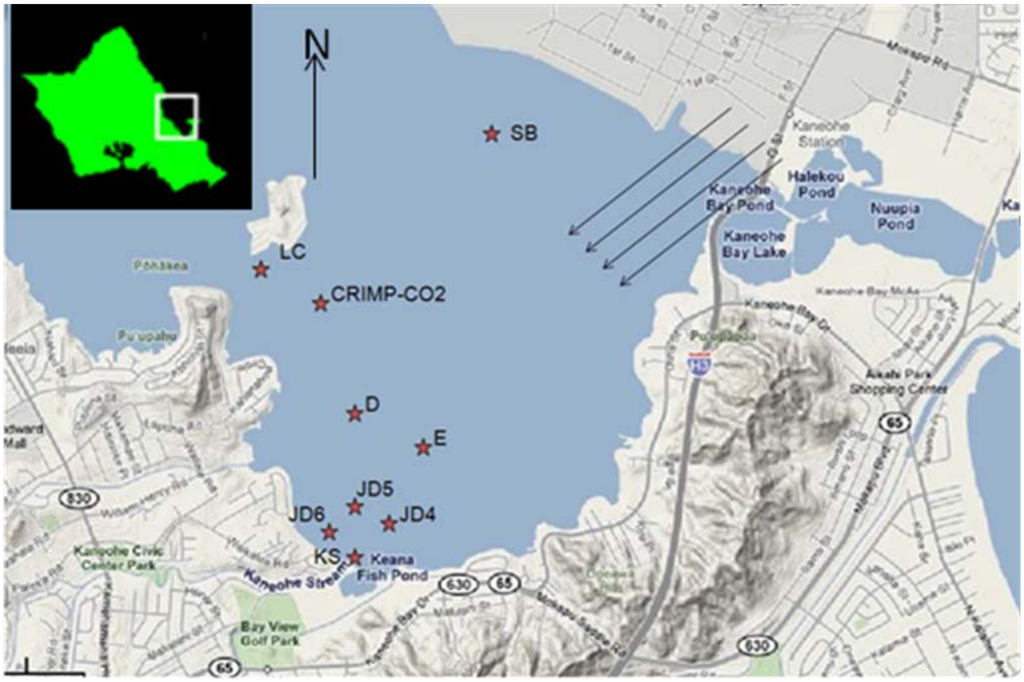

Figure 1: Southern Kane’ohe Bay and the 9 sample sites in the bay. Arrows show typical wind direction (magnitude not to scale)

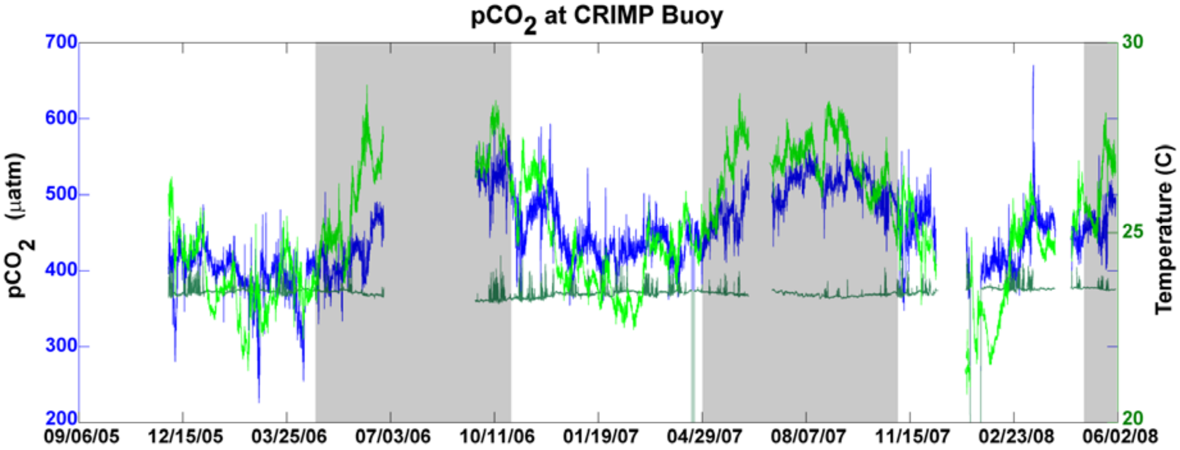

Figure 2: pCO$_2$ in water (blue) and atmosphere (dark green), along with SST (light green) recorded by CRIMP buoy over 2.5 years. Gray regions demarcate the dry season (May-October). SST and pCO$_2$ display a clear temporal trend, while atmospheric CO$_2$ remains nearly constant throughout the year.

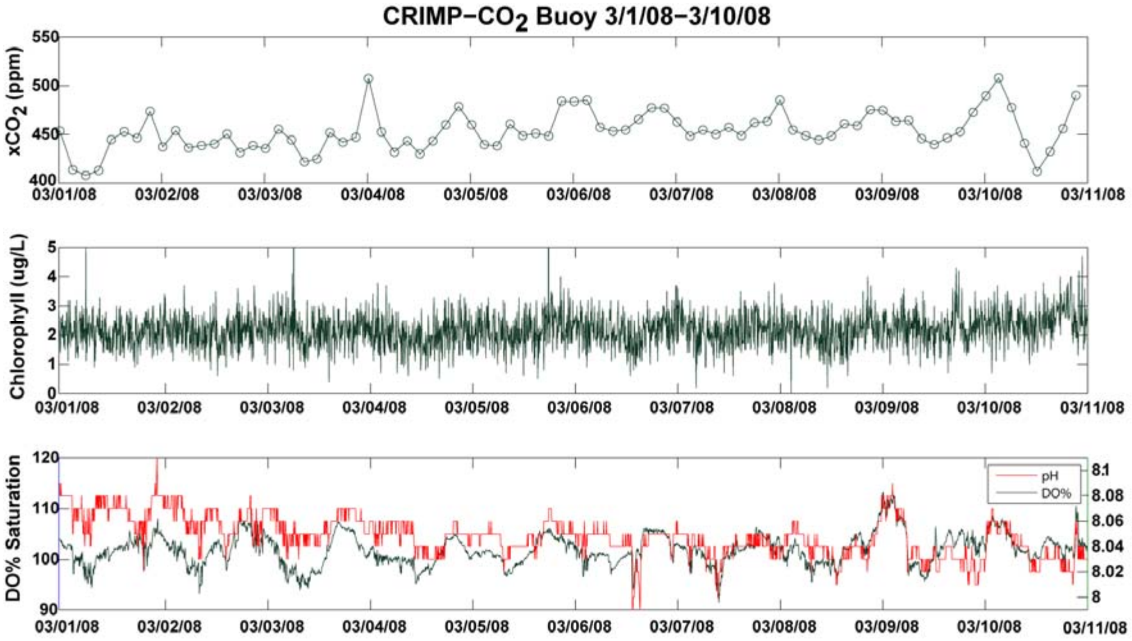

Figure 3: Diurnal fluctuations of xCO_2 (top), chlorophyll (middle), dissolved oxygen, and pH (bottom) from 3/1/08-3/10/08

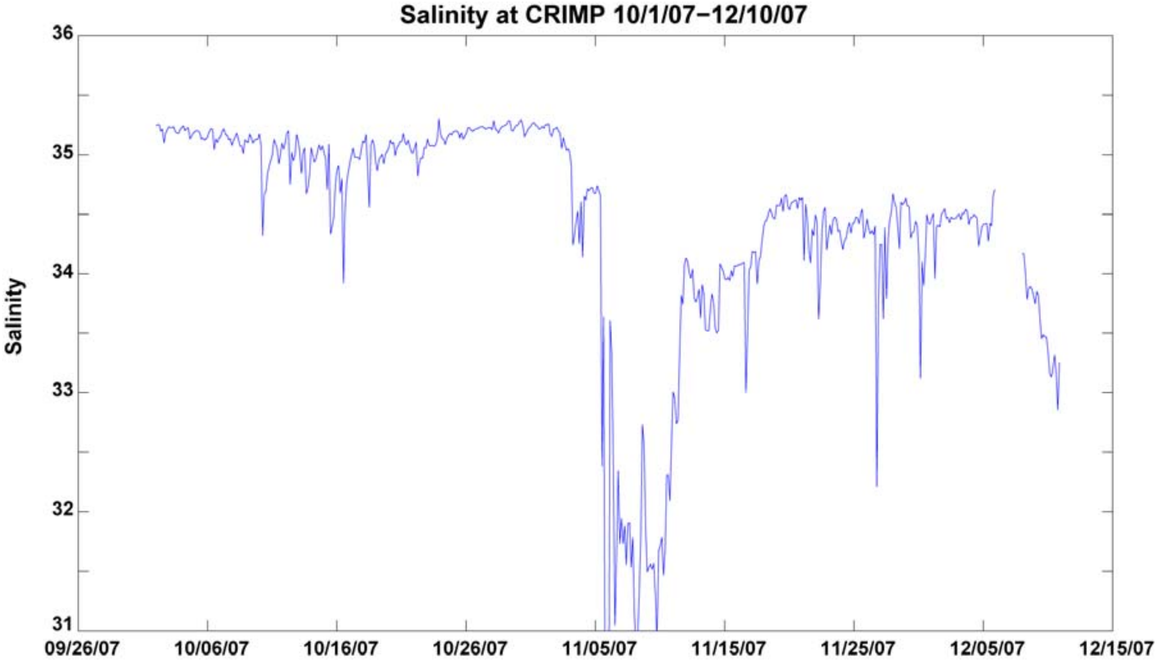

Figure 4: Time series of salinity at CRIMP buoy; 14 cm of rain fell in the watershed and 25 cm fell directly over the bay on 11/4/07 followed by another 25 cm in the watershed from 12/1/07 to 12/5/07.

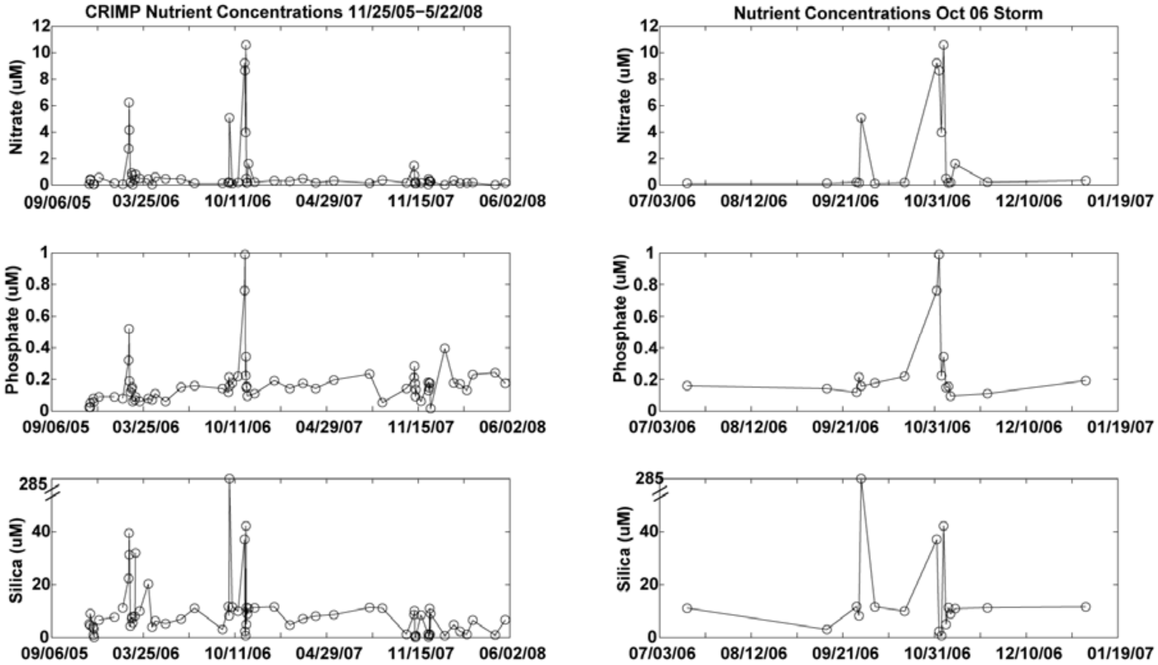

Figure 5: Time series plots of nitrate, phosphate, and silica at CRIMP-CO_2 over the 2.5 year study period (Left). Nutrient concentrations at CRIMP-CO_2 between July 2006 and January 2007 are presented on the right and show increased nutrient concentrations due to heavy rainfall on 9/25/06 and 10/29/06.

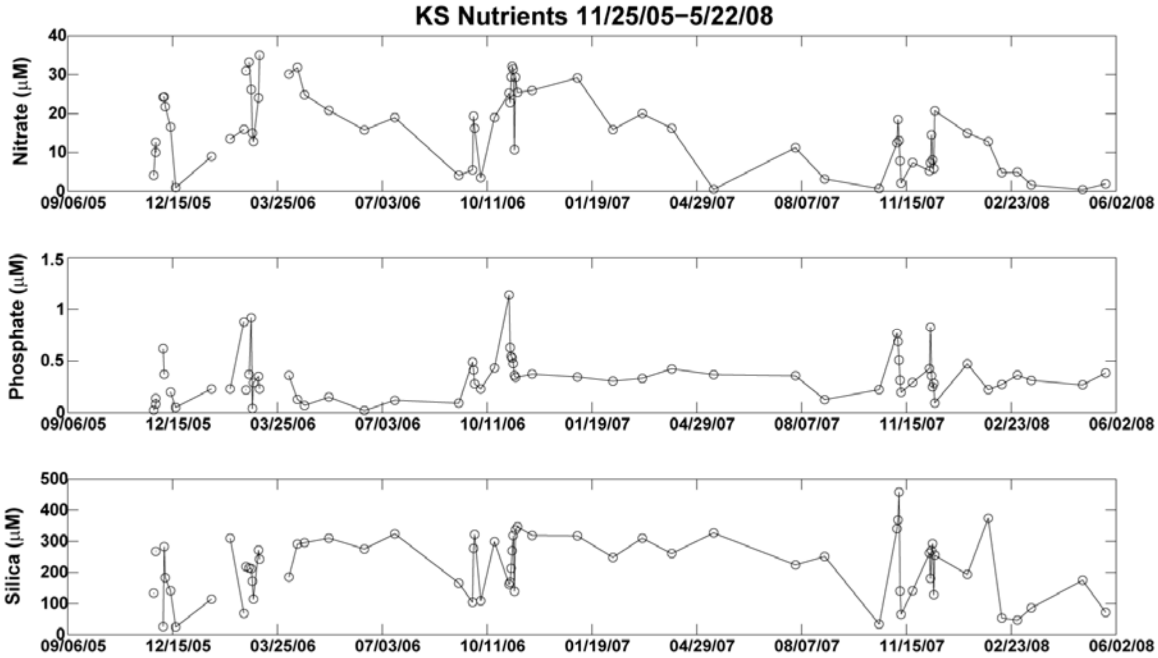

Figure 6: Nutrient concentrations at Kaneohe Stream Mouth (KS) over the study period. Each pulse of nutrients follows a large storm event.

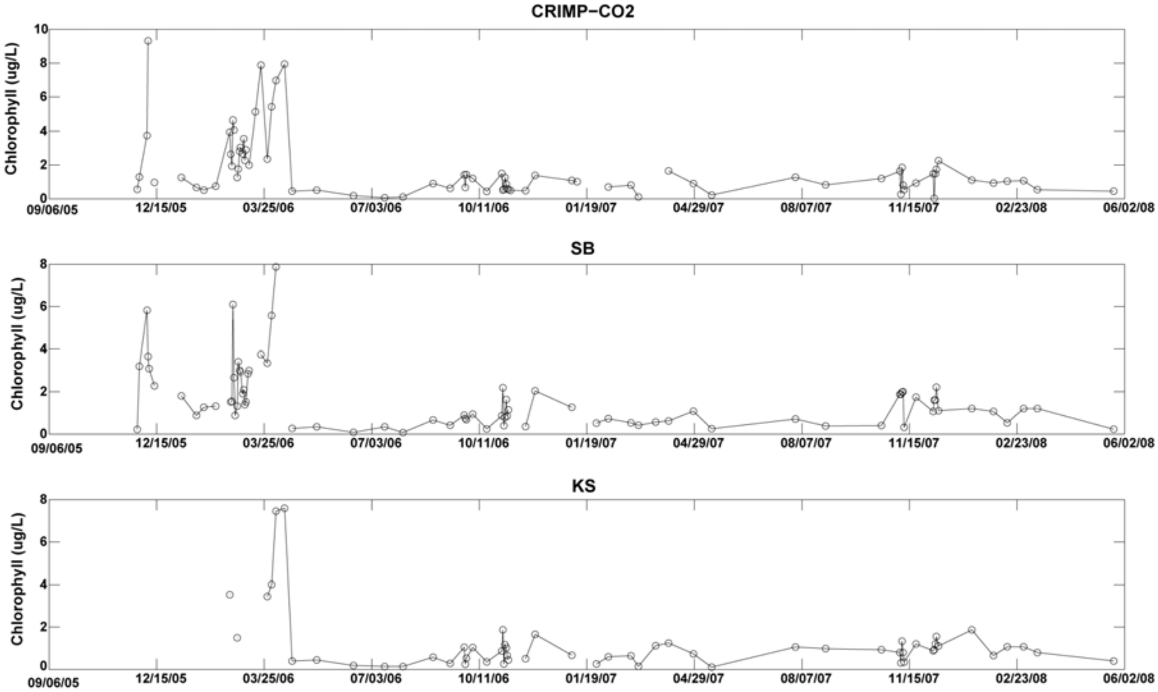

Figure 7: Chlorophyll concentrations from 11/25/05-5/22/08 at CRIMP-CO_2, SB, and KS stations in southern Kaneohe Bay.

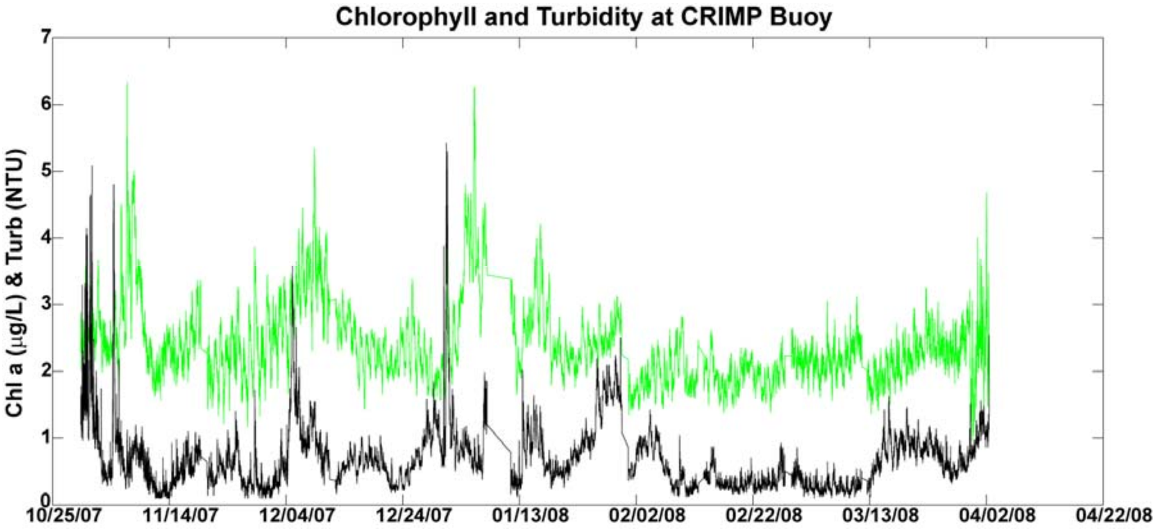

Figure 8: Chlorophyll (green) and turbidity (black) taken at CRIMP Buoy from 10/26/07-4/2/08.

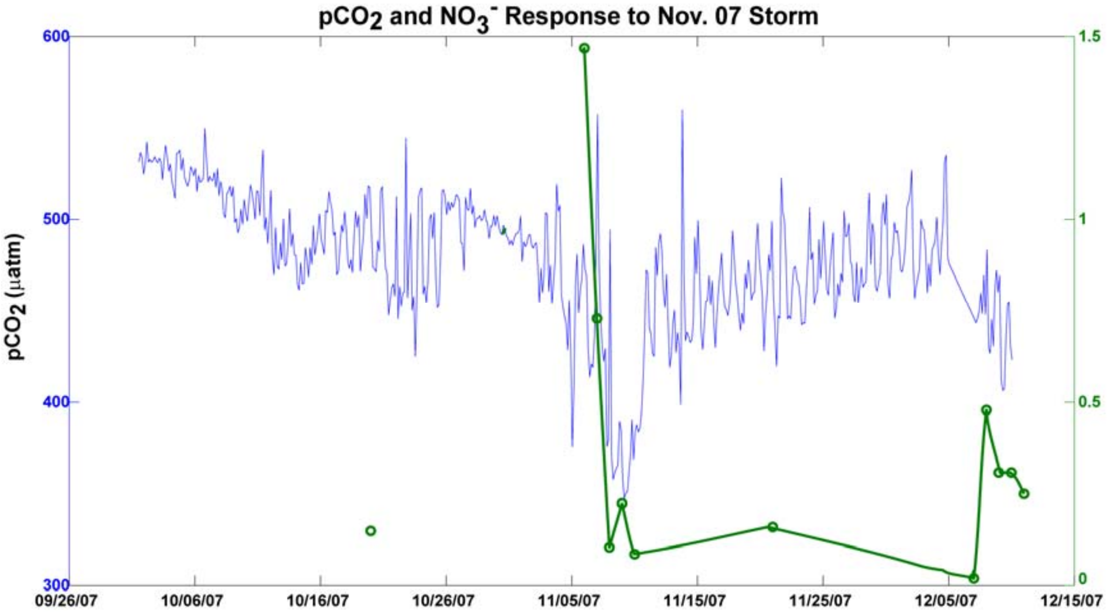

Figure 9: pCO_2 levels and nitrate concentrations from 9/27/07 – 12/10/07. Storm events on 11/4 and 12/4 lead to a spike in nitrate and a corresponding drawdown of pCO_2 due to phytoplankton blooms in response to the nutrient subsidy.

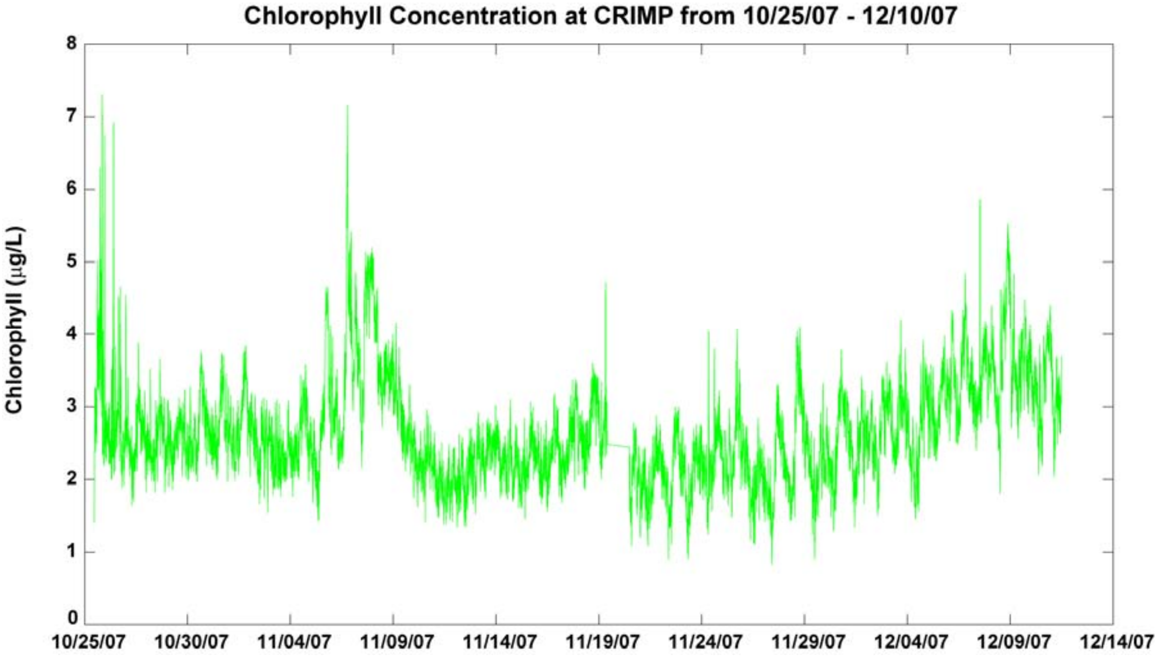

Figure 10: Chlorophyll levels at CRIMP buoy during both the 11/4 and 12/4 storms of 2007. An intense but brief bloom occurred on 11/7 and a more sustained, but smaller intensity, bloom occurred beginning 12/5.

Appendix A – Time Series Profiles of Water Column

Appendix A contains figures (mainly time series profiles) from the winter of 2007-2008. Large storm events occurring on 11/4/07 and 12/4/07 dramatically affected the physical and biogeochemical properties of the Kaneohe Bay water column. These figures show the evolution of the physical (e.g. salinity and temperature) and biochemical (e.g. dissolved oxygen and chlorophyll) parameters in the water column.

Salinity at CRIMP-CO2 from November 2007-May 2008

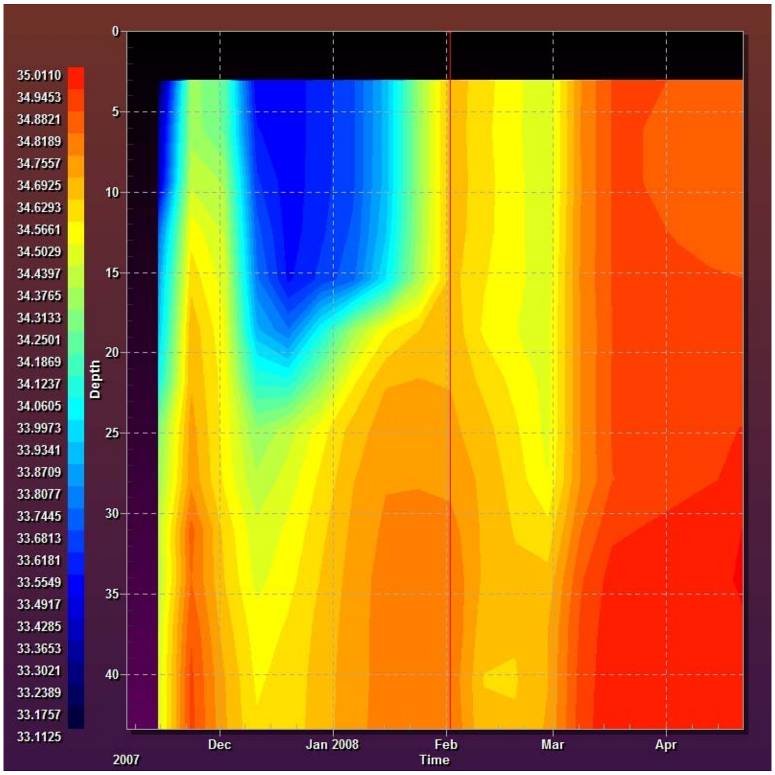

Figure 1: This time series profile of salinity, created from multiple profiles at the CRIMP-CO_2 location, shows an obvious freshening of the upper water column during the winter months of Nov 07 – May 08.

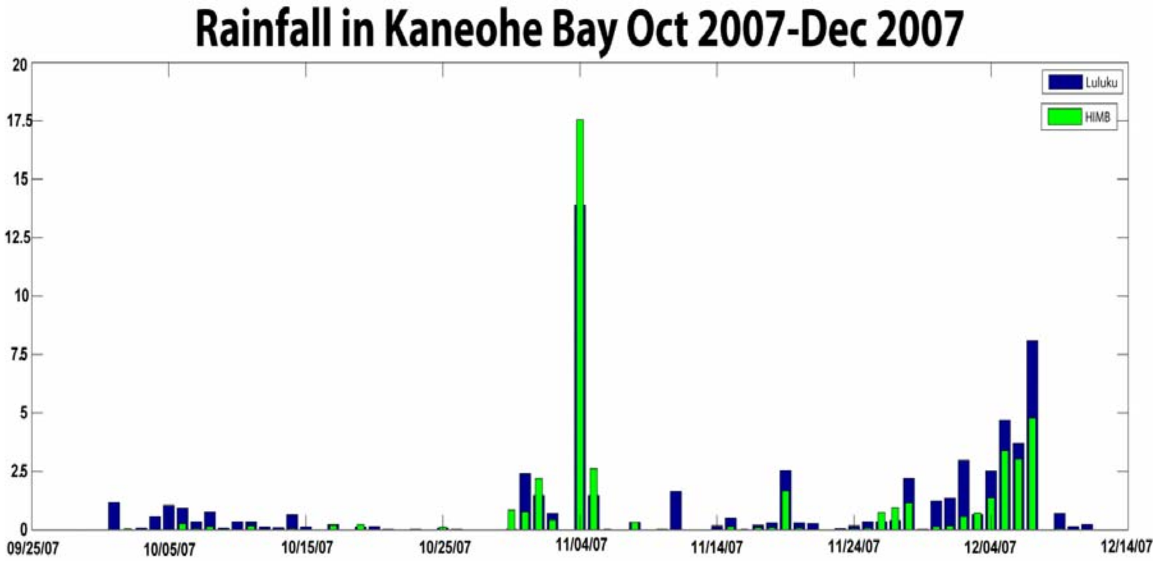

Figure 2: Daily rainfall totals from the USGS Luluku Rain gage and HIMB weather station. High rainfall totals beginning in November 2007 and continuing through December 2007 were the cause of upper water column freshening (as seen in Fig 1) and contributed to the lower water column temperatures during this time period.

Temperature at CRIMP-CO2 from November 2007-May 2008

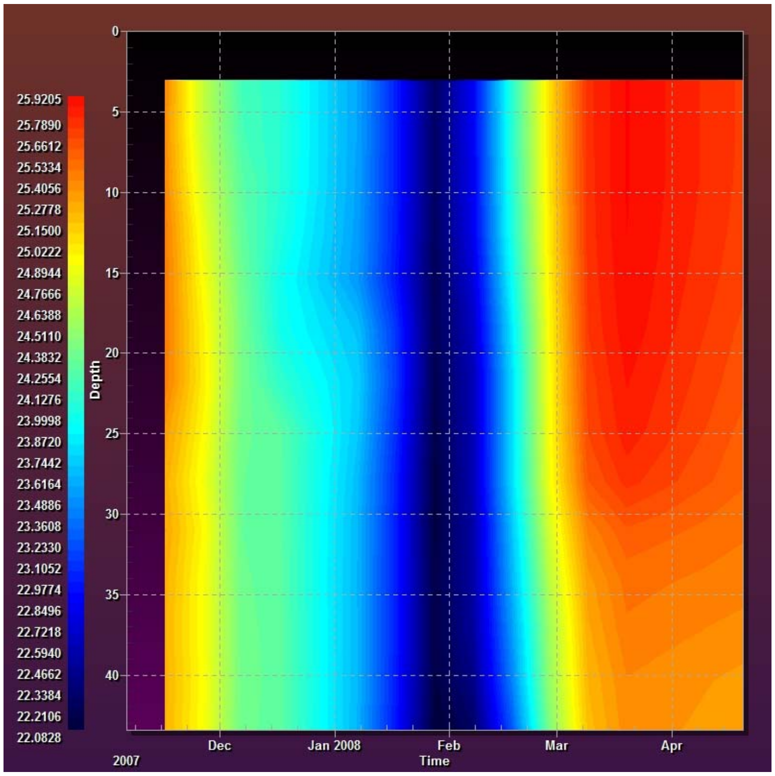

Figure 3: Although a fresher surface layer formed during the 2007-2008 winter, the water column never became temperature stratified, cooling fairly uniformly into February, before warming back up in early summer.

Dissolved Oxygen Saturation at CRIMP-CO2 from Nov 2007-May 2008

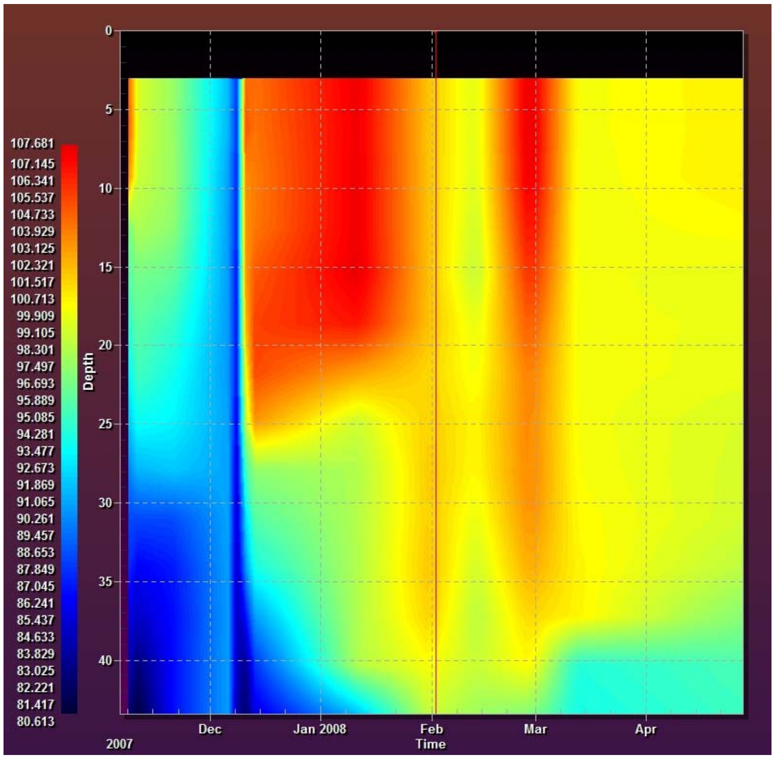

Figure 4: Dissolved oxygen reflects the salinity of the water column. Freshening of the water column (as seen in Figure 1) enhances solubility of oxygen and leads to supersaturated with respect to DO.

Temperature at D-buoy from Dec 5, 2007-Dec 12, 2007

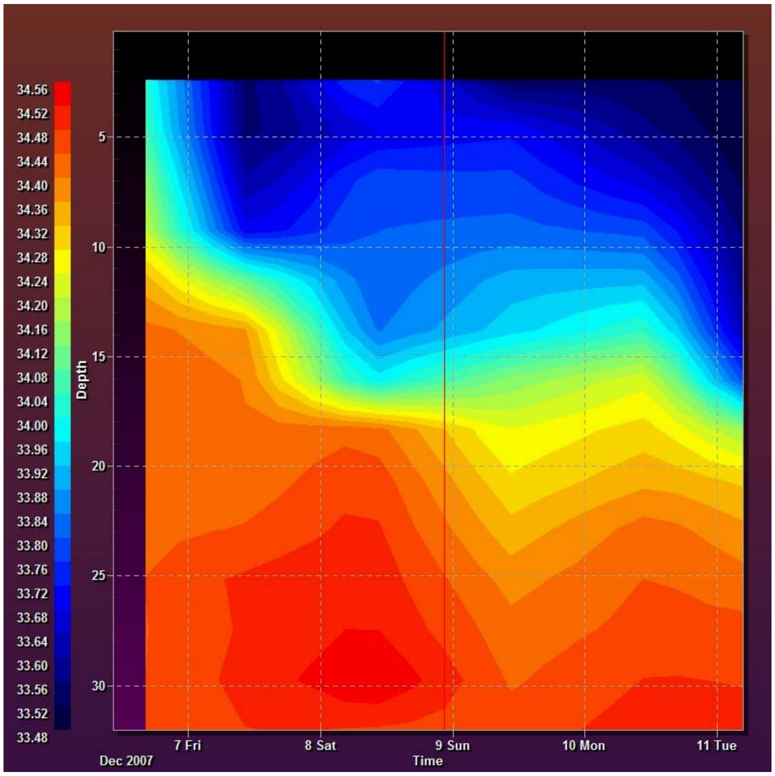

Figure 5: Heavy rainfall beginning 12/4/07 created a low salinity plume at D-buoy site and increased nutrient concentrations. As the wind direction switched to strong NE trade winds on 12/10, the plume was mixed deeper into the water column.

Chlorophyll at D-buoy from Dec 5, 2007-Dec 12, 2007

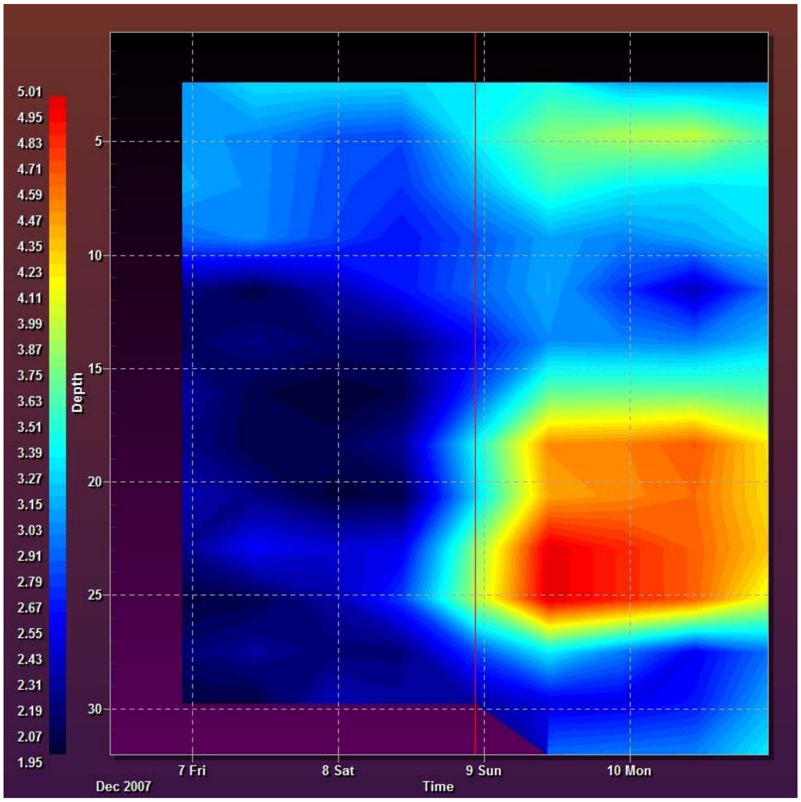

Figure 6: On 12/10/07 local winds switched from light southerlies ("Kona") to stronger NE trade winds, enhancing mixing of nutrients from the surface layer as well as transporting nutrients from Kaneohe Stream to D-buoy location. Enhanced mixing of nutrients through the water column, coupled with an increase in solar radiation allowed for a subsurface chlorophyll bloom to form, just below the low salinity surface water.

Appendix B: pCO_2 and CO_2 Flux Variability

Appendix B consists of graphs showing pCO2 variability in Southern Kaneohe Bay. The variability is due to temperature, respiration, photosynthesis, calcification, dissolution, and stream runoff. Several graphs attempt to remove one of more of these variables in an effort to isolate each individual signal. The effects of nutrient inputs on pCO_2 levels is also shown, as well as the effects of these drawdowns on air-sea CO_2 flux in the bay.

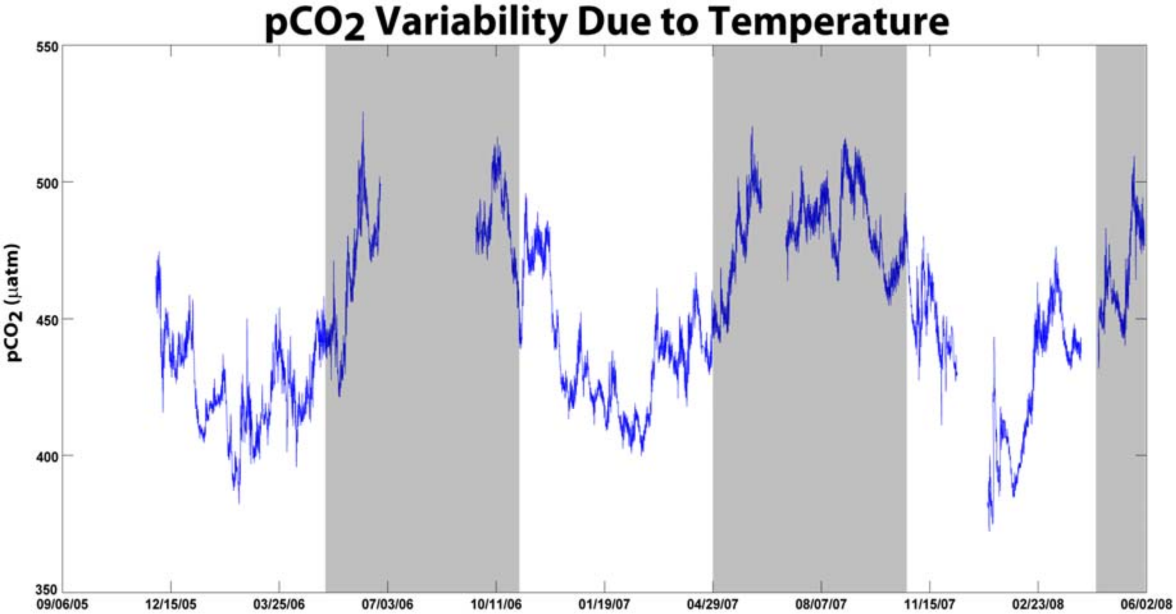

Figure 1: Changes in concentrations of CO_2 due to biological effects (respiration, photosynthesis, and calcification) as well as high pCO_2 runoff have been removed to show the variation in pCO_2 due only to temperature changes. Normalization was done using the equation:

(pCO_2 at T_{obs}) = $(pCO_2)_{mean}$ x $\exp[0.0423(T_{obs}-T_{mean})]$ from Takahashi et al., 1993.

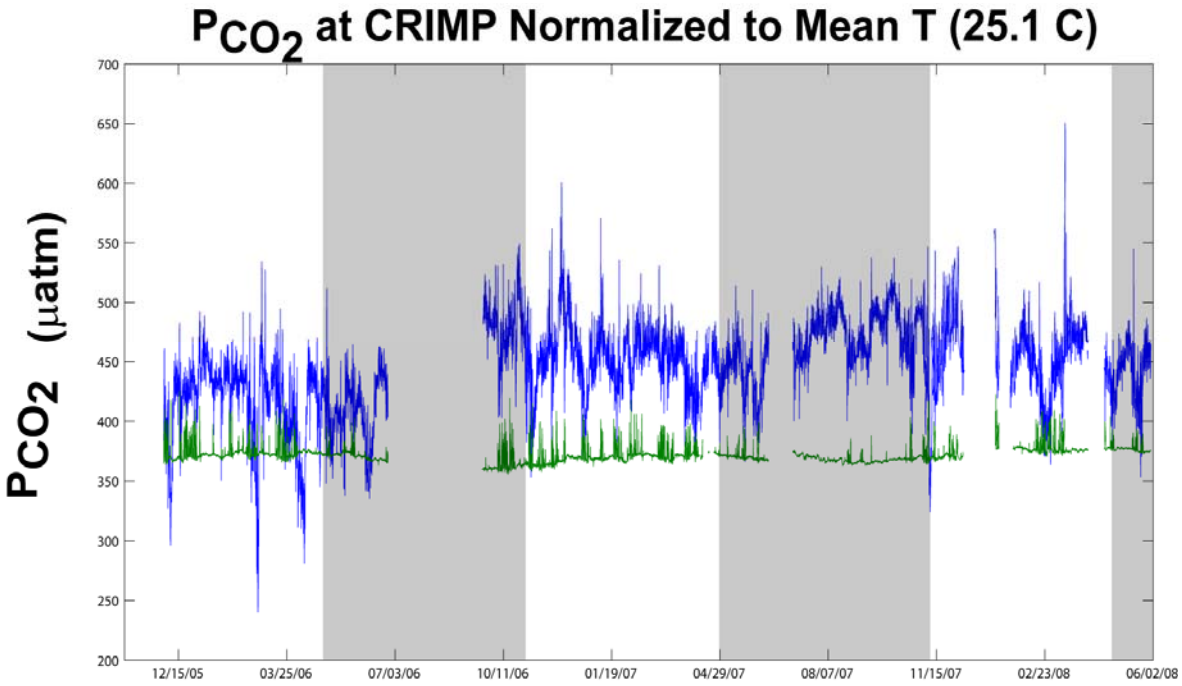

Figure 2: The temperature effect on pCO2 has been removed using the equation:

(pCO_2 at T_{mean}) = $(pCO_2)_{obs}$ x $\exp[0.0423(T_{mean}-T_{obs})]$ from Takahashi et al., 1993. This graph shows only changes in pCO_2 due to direct changes in CO_2 concentration. The blue line is the water column pCO_2 while the green line is atmospheric CO_2. Note that the atmospheric CO_2 has not been normalized to a mean temperature. The resulting variation in this graph is due to changes in biology and runoff with varying pCO_2 levels.

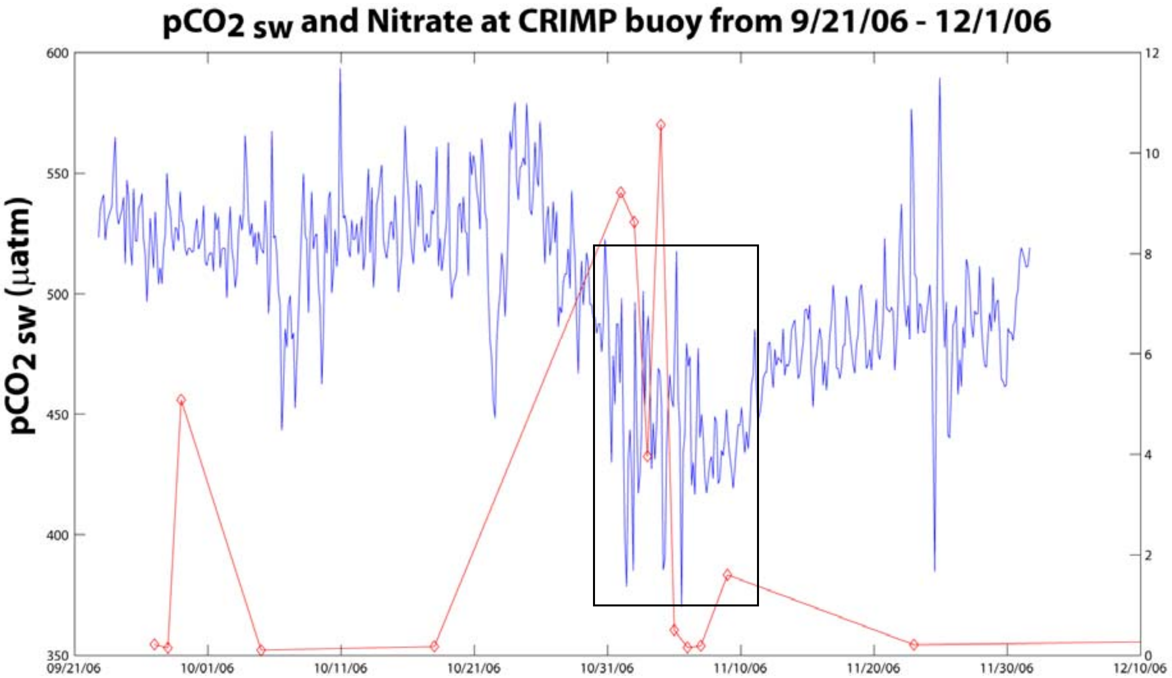

Figure 3: Nitrate concentrations (red) spike following a storm event from Oct 30-Nov 2. An immediate drawdown of nitrate by phytoplankton is accompanied by a 100μatm drawdown of pCO_2. The boxed region corresponds to the boxed region in Figure 4.

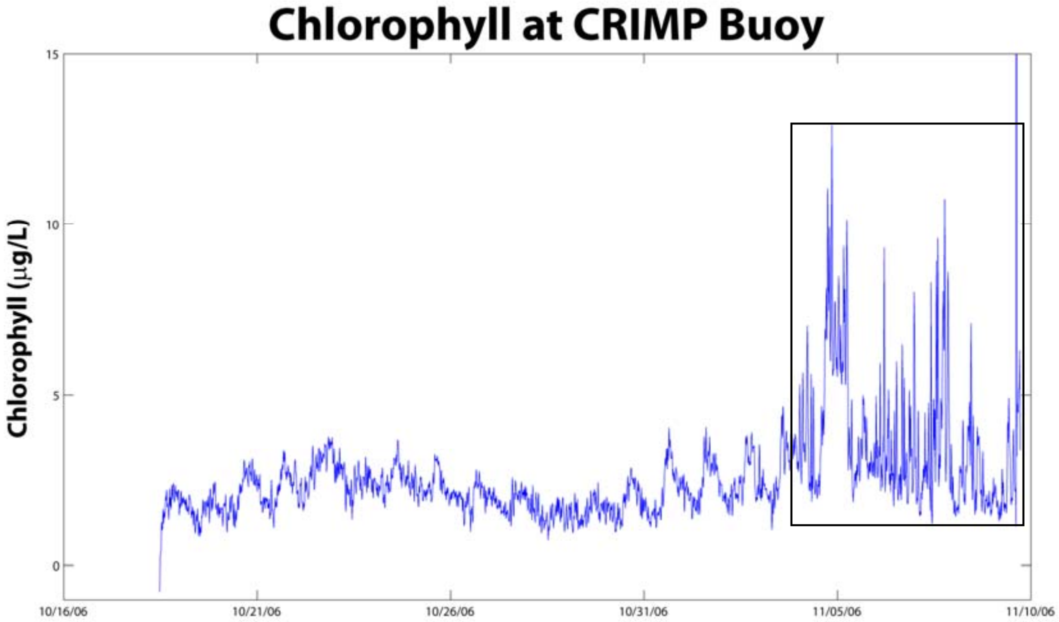

Figure 4: Chlorophyll values show a daily cycle with a baseline of ~2mg/L until the storm induced bloom on Nov 2nd. The boxed region shows enhanced chlorophyll and corresponds with the pCO_2 drawdown marked in Figure 3.

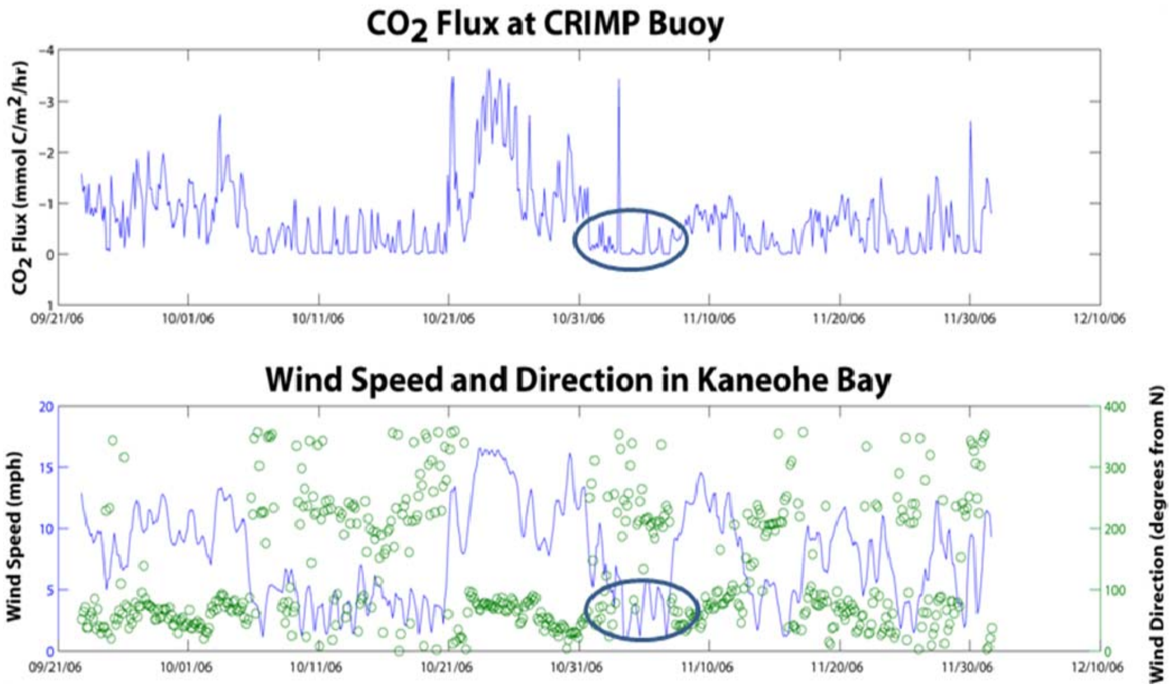

Figure 5: The top panel of Figure 5 shows CO2 flux from the bay, with negative values indicating a source of CO2 to the atmosphere. The circled regions demarcates the storm even describe in Figures 3 and 4. The large pCO2 drawdown dampened the source strength of the bay waters. The bottom panel shows wind speed (blue) and wind direction (green dots). Typical northeast trade wind conditions correspond to wind directions from 0-90°. These winds are typically higher speeds than the light variable southerly Kona winds. Low wind conditions immediately following the storm inhibited gas transfer across the air-sea interface and bay water fluxes were effectively 0.

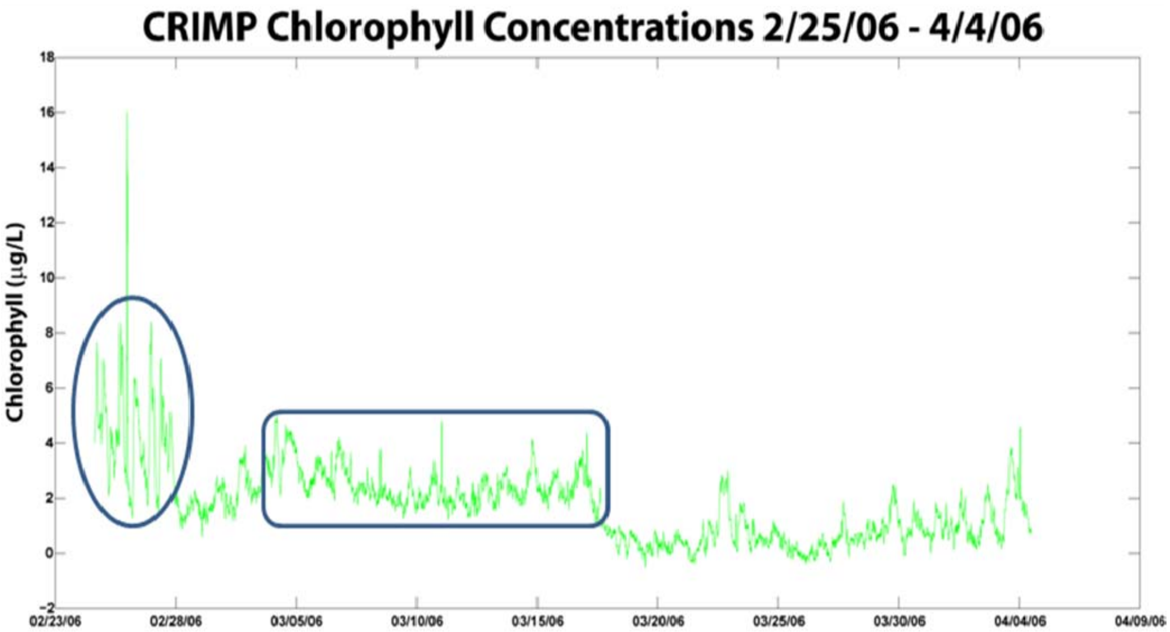

Figure 6: Chlorophyll during the 40 day storm from mid February to Apri of 2006 is elevated above baseline conditions. Chlorophyll response to the initial pulse of nutrients from the first rainfall is highlighted by the circle on the left. Consistent rainfall throughout March led to a persistence of nutrients in the water column and a sustained month-long bloom (rectangle).

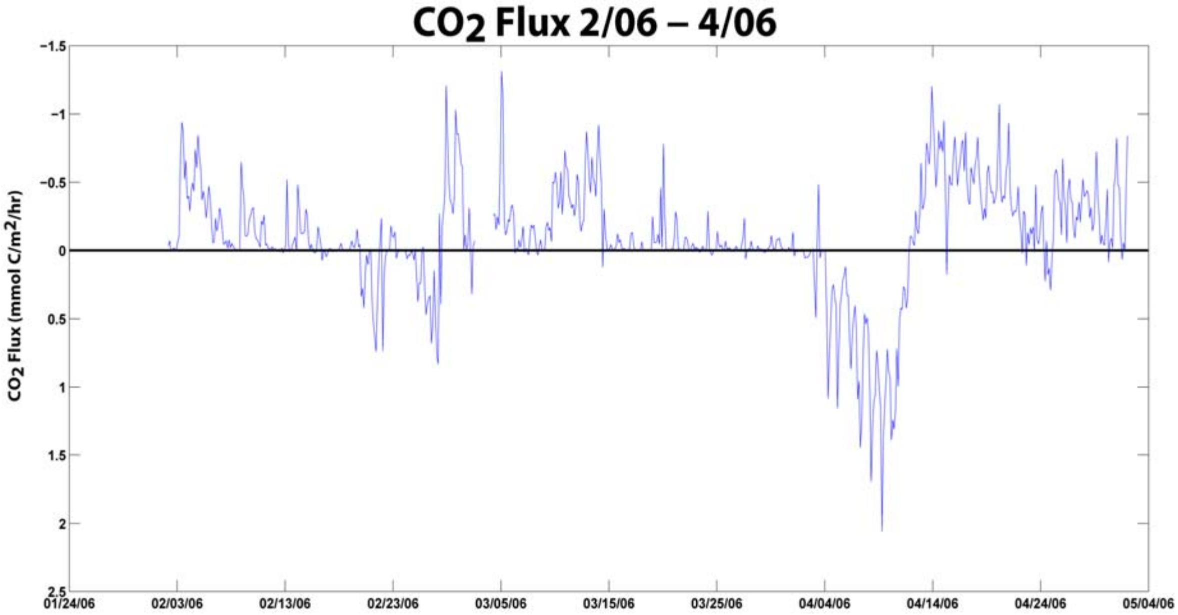

Figure 7: The persistent bloom shown in Figure 6 caused multiple significant pCO_2 drawdowns resulting in bay waters becoming a sink of CO_2 for brief periods of time as seen in this figure. Values above the solid line indicate source activity, while values below the line indicate sink activity.

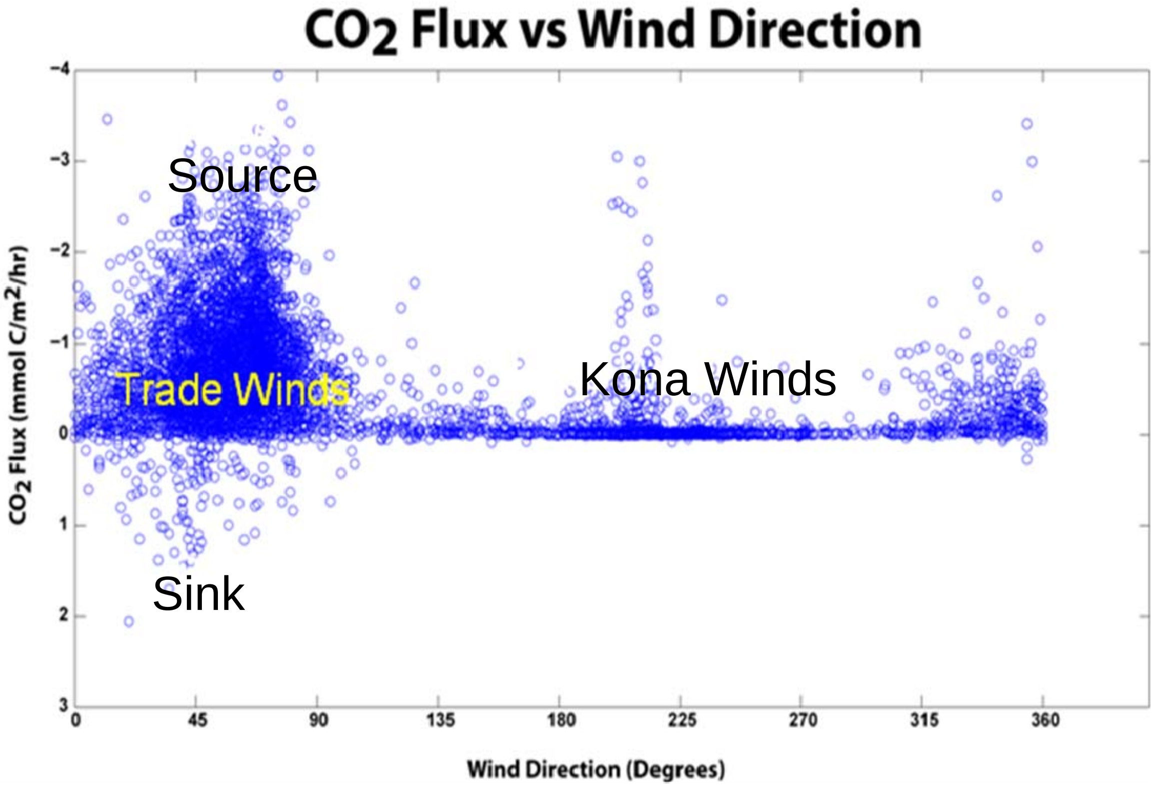

Figure 8: This figure shows the effect of wind on the CO_2 flux. The majority of samples are taken under trade wind conditions, and these conditions result in the strongest source signals of the study period. Kona Winds, typically associated with storm events are much more infrequent. Because of the relatively low speeds of Kona Winds, flux is typically suppressed, even though Kona Winds often occur during phytoplankton blooms following a storm and subsequent nutrient input. Only during periods of pCO_2 drawdowns and strong tradewinds does the bay switch from source to sink.

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