3841

UNIVERSITY OF HAWAII LIBRARY

BIOGEOCHEMICAL IMPACTS OF STORM RUNOFF ON WATER QUALITY IN SOUTHERN KANEOHE BAY, HAWAI'I

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

MASTER OF SCIENCE

IN

OCEANOGRAPHY

DECEMBER 2003

By
Stephanie Ringuet

Thesis Committee:

Fred Mackenzie, Chairperson
Eric DeCarlo
Jane Schoonmaker
Edward Laws

© 2003, Stephanie Ringuet

DEDICATION

I dedicate this thesis to my mother, Huguette Gagnon. Thank you for always having been so close to me despite the thousands of miles between us. Your constant support and encouragement played a major role in my achievement.

ACKNOWLEDGEMENTS

I would like to express profound gratitude to my advisor, Dr. Fred T. Mackenzie, for his support, supervision and useful suggestions throughout this research work. His enthusiasm for science was a constant source of inspiration for me. I am also highly thankful to Dr. Eric H. DeCarlo, Dr. Jane Schoonmaker, and Dr. Edward A. Laws for their valuable comments on my thesis.

I would like to extend my gratitude to my teachers, fellow graduate students and co-workers in the Department of Oceanography who have contributed, directly or indirectly, to the success of this project. The list is too long to be included here, but I will always be grateful to everyone who helped me one way or another. Special thanks are due to Daniel Hoover for sharing his knowledge of sampling and analytical methodologies appropriate for storm sampling. Special thanks are also due to Scott Narod for his precious help in the field, without which I would not have obtained such an extensive dataset. Throughout the past three years, I encountered fascinating people and places, and I will always cherish the memories of my time spent at the University of Hawaii.

I am, more than ever, indebted to my family and friends for their love and constant support. I am especially thankful to my mother, Huguette

Gagnon, for her precious assistance and encouragement during difficult times. Thank you also to my best friend Genevieve Tessier for always finding a way to bring a little bit of sun into my life. Special thanks are also due to Matthew Brown for his invaluable support and for making me realize that everything is possible in life.

This work was supported by NOAA Hawaii Sea Grant and Hawaii Coral Reef Initiative Research Program.

ABSTRACT

Fluvial impacts on water quality and ecosystem structure were evaluated in southern Kaneohe Bay, Oahu, Hawaii. Fluvial inputs occurred as small, steady baseflow interrupted by intense pulses of storm runoff. Baseflow impacted only restricted areas around stream mouths, but the five storm events sampled during this study produced transient runoff plumes of much greater spatial extent. Nutrient loading via runoff generally led to an increase of the phytoplankton biomass and gross productivity in southern Kaneohe Bay, but the rapid depletion of nutrients resulted in a fast decline of the algal population for all storm events considered in this study. Because of variability in export and mixing rates of runoff nutrients, the magnitude of the phytoplankton response was not proportional to nutrient loading. Under baseline conditions, water-column productivity in southern Kaneohe Bay is normally nitrogen-limited. However, following storm events, the high dissolved inorganic nitrogen to dissolved inorganic phosphorus (DIN:DIP) of runoff nutrients drive South Bay waters towards phosphorus-limitation. A depletion of phosphate (PO_4^{3-}) relative to nitrate (NO_3^-) in surface waters was observed following all storm events. Due to high flushing rates, recovery times of bay waters from storm perturbations ranged from three to eight days and appeared to be correlated with tidal range. Storm inputs can thus have significant impacts on the water column ecosystem and biogeochemistry in southern Kaneohe Bay, but the perturbations are only transient events.

TABLE OF CONTENTS

LIST OF TABLES

Table **Page**

Chapter 3

Table **Page**

Chapter 4

LIST OF FIGURES

Figure **Page**

Figure		Page

Figure		Page

CHAPTER 1 : INTRODUCTION

1.1 Coastal Zones

The coasts of the world's continents are the areas where the land meets the sea. The term coastal zone encompasses shoreline environments as well as adjacent open coastal waters, including unique ecosystems such as estuaries, coral reefs, mangroves and tidal marshes. In 1969, the US Commission on Marine Science, Engineering and Resources, proposed a definition of the coastal zone that takes into account both spatial and functional aspects:

"The coastal zone is the part of the land affected by its proximity to the sea, and that part of the sea affected by its proximity to the land as the extent to which man's land-based activities have a measurable influence on water chemistry and marine ecology (U.S. Commission on Marine Science, Engineering and Resources Govt. Print. Off, 1969)."

This definition emphasizes the importance of the coastal areas for humans, 40 to 60% of whom live within 60 km of the coastline. The presence of extensive and growing urban development along the world's coasts exerts an increasing pressure on these areas. For instance, point source and non-point source (NPS) pollution activities occurring far upstream can not only affect an entire watershed, but can also impinge on the surrounding coastal ocean waters. Hence, it is necessary to understand the linkages between the land and the sea to evaluate the impact of human activities in the coastal zones.

1.2 Fluvial Discharges

River basins are undoubtedly one of the major linkages between the land and the proximal ocean. Streams deliver freshwater, sediments and nutrients to adjacent waters. Excluding upwelling, stream runoff has been identified as the principal source of nutrients to numerous coastal zones (Meybeck, 2001). Natural fluvial inputs of nutrients stimulate the primary production of marine ecosystems, and are particularly important in estuarine environments. In addition to natural materials, however, anthropogenic substances are also carried by rivers. Nutrient pollution, principally nitrogen (N) and phosphorus (P), is widespread in coastal ecosystems. Nitrogen and phosphorus from land-based sources such as sewage, agricultural and urban runoff have increased the nutrient loading via rivers to the coastal ocean by 50 to 200% over the preindustrial fluxes (Mackenzie, 2003). Excess inputs of these nutrients stimulate the proliferation of algae, and can eventually lead to the problem of eutrophication. Therefore, although natural fluvial inputs are essential to fuel the productivity of estuaries, nutrient and sediment loading via stream runoff can also cause adverse effects.

1.3 Stream flow Variability

Stream water discharges to coastal environments are not constant; they typically vary with rainfall intensity. Consequently, fluvial inputs of terrigenous materials to the coastal ocean are also variable and are strongly a function of the stream flow conditions (Bostater and Biggs, 1985; Chanton and Lewis, 2002). Based on water flow data, river fluxes are often divided into baseflow and storm runoff contributions. Storm water runoff into the coastal ocean can have major impacts on a variety of oceanographic properties and processes that include coastal currents, coastal nutrient and optical characteristics, and contamination from heavy metals, organic compounds and microbial inputs (Jones and Washburn, 1998). Several studies have shown that flood events are particularly important for sediment transport, and can account for most of the sediment transfer to coastal waters (Puig and Palanques, 1998; Seitzinger et al., 2002). Moreover, storm runoff can greatly enhance nutrient loading in estuaries due to leaching of soluble materials under high rainfalls (Staver et al., 1996; Arhonditsis et al., 2000), contributing further to the problem of NPS pollution in coastal environments. However, flood events are highly episodic and virtually unpredictable, making them much harder to characterize and to manage. As a result, their contributions are often underestimated in sediment and nutrient budget calculations, and their impacts on coastal ecosystems are yet to be fully appreciated.

1.4 <u>Nutrients and Primary Productivity</u>

Estuarine environments, where rivers and streams flow into the ocean, are among the most productive on Earth, amounting to approximately 190 g of organic carbon per square meter per year (Mackenzie, 2003). The primary productivity of these ecosystems is largely controlled by the availability of light and nutrients in the water column. Nutrients are required to not only be present in sufficient amounts, but also in appropriate relative concentrations. Under nutrient balanced conditions, most healthy marine phytoplankton cells have a nitrogen-to-phosphorus ratio of approximately 16:1 (Redfield et al., 1963). While light limitation can be important seasonally, particularly in non-tropical climatic zones, and locally in turbid waters, nutrients are commonly the key limiting factor. Consequently, nearly all studies on limitation of primary production in estuarine ecosystems have focused on nutrients.

The concept of nutrient limitation, *a priori* straightforward, does not have any formal definition. As a result, it has been used differently in the scientific literature by various workers. Three common definitions are: (1) the restriction of growth rates of phytoplankton populations currently present in a water body by the low availability of a nutrient (Goldman et al., 1979; Fisher et al., 1995); (2) the limitation of the potential rate of net primary production, allowing for possible shifts in the phytoplankton community composition (Nixon et al., 1980; D'Elia et al., 1986); and (3) the nutrient limitation of net ecosystem production (Smith and Atkinson, 1984). Each of these definitions is relevant to discrete temporal and spatial scales; they should therefore be used accordingly to address specific questions.

The nutrient limitation of algal growth rates relates to small temporal and spatial scales such as days and liters of water. It also usually refers to production of new phytoplankton biomass prior to loss (Fisher et al., 1995). Because these scales are suitable to experimental manipulations, short-term bioassays have been the prevailing approach for assessing the nutrient status of marine ecosystems. However, this technique excludes important ecosystem processes such as changes in species composition and grazing. The nutrient limitation of biomass accumulation involves larger temporal and spatial time scales. It integrates growth rates, shift in phytoplankton community, and loss rates due to grazing and advection. This concept is obviously more relevant to real ecosystems but is much more complex to evaluate experimentally. According to Howarth (1988), the appropriate definition for one primarily concerned with eutrophication should be the "nutrient limitation of the potential rate of net primary production". In other words, if a nutrient is added and net primary production increases, regardless of the community composition, then the system is considered to be nutrient-limited. Unless otherwise noted, I will further employ this definition when using the term "nutrient limitation".

Although trace metals have been identified to be the primary limiting nutrients in certain open ocean areas (Martin, 1990; Smith et al., 2000; Zhang, 2000), micronutrients rarely limit the productivity in estuarine areas. Therefore, macronutrients such as nitrogen and phosphorus have been the focal point of virtually all eutrophication studies in coastal environments. Primary production in estuaries and marine ecosystems is conventionally thought to be nitrogen limited (Nixon and Pilson, 1983; Hecky and Kilham, 1988; Howarth, 1988). However, recent studies have shown that some estuaries are phosphorus-limited or switch seasonally between N and P limitation (Labry et al., 2001; Murrell et al., 2002; Sundareshwar et al., 2003). Thus, nitrogen limitation in coastal ecosystems should not be taken automatically as a fact; the question should be addressed on a case-by-case basis.

1.5 Temperate Versus Tropical/Sub-Tropical Systems

To date, most studies on the impacts of fluvial nutrients on coastal ecosystems have been carried out in temperate estuaries. Tropical regions, located between the Tropics of Cancer (23.5°N) and Capricorn (23.5°S), have received comparatively much less attention. Even though storm runoff is likely to affect both tropical and temperate systems in a similar manner, there are distinct differences between the two climate zones that may control biogeochemical processes following a flood event. Obvious differences are the higher average temperature and higher annual total light incidence in tropical estuaries, resulting in higher photosynthesis and no temperature limitation of primary productivity (Saenger and Holmes, 1992). More importantly, nutrient cycling seems to be fundamentally different in temperate and tropical environments.

Phosphorus and nitrogen concentrations are generally lower in tropical estuaries than in their temperate counterparts, particularly during the dry season (Hatcher et al., 1989; Eyre and Balls, 1999). While this view may be valid in a general sense, Furnas (1992) pointed out that the perception of low nutrient levels in tropical waters might simply be the result of the predominance of studies carried out in relatively pristine areas.

Nitrogen in the marine environment is found in several different forms, but the principal sources of fixed nitrogen for marine algae and bacteria are ammonium (NH_4^+) and nitrate (NO_3^-). Transformations between inorganic nitrogen species occur almost exclusively through biological processes. The oxidation of ammonium to nitrate (nitrification) and the dissimilatory reduction of nitrate to nitrogen gas (denitrification) are carried out by specialized microbial communities. Nitrifying bacteria have high optimum operating temperatures (>30 ^{0}C) (Antoniou et al., 1990), suggesting that rates of microbial processes could be higher in tropical ecosystems. Some free-living and symbiotic bacteria can convert atmospheric nitrogen (N_2) into ammonia through the process of nitrogen fixation, providing an additional source of biologically available N. Although significant N-fixation rates have been observed for coral reef, seagrass beds, and freshwater swamp ecosystems, they rarely contribute to more than a small fraction of N inputs to tropical coastal ecosystems (Furnas, 1992).

Unlike nitrogen, which has a large atmospheric reservoir (N_2), there is no significant gaseous source for phosphorus. As a result, the fluxes and storage of P in aquatic systems are dominated by exchanges between dissolved pools, biomass, and mineral-bound P on suspended particles and in sediments. As a result, P cycling between particulate and dissolved phases is strongly a function of mineralogical composition, implying fundamental differences between tropical and temperate systems. Because of higher temperature and precipitation in tropical regions, soils are generally highly weathered and are characterized by a large content of secondary aluminum and silicon-rich clay minerals and iron oxyhydroxides (Six et al., 2002). Because these minerals have a strong affinity for dissolved inorganic phosphorus (DIP), phosphorus ions commonly undergo a complex series of desorption-adsorption reactions in stream and coastal waters. On average, Froelich (1988) estimated that approximately 15 % of particle-bound P was rapidly desorbed (within minutes/hours) from fluvial material entering the coastal ocean. The released form of phosphorus (mostly PO_4^{3-}) is immediately available to biological uptake, and can then be added to the DIP pool delivered by rivers. The remaining fraction of mineral-bound P may be subsequently released to the water column during early diagenesis, enhancing the flux of biologically available P (Berner and Rao, 1994). However, carbonate sediments, common in tropical regions, can also act as a sink for phosphorus by sequestering permanently phosphorus during the formation of authigenic apatite (Short et al., 1985; Fisher et al., 1995). The relative contribution of processes that involve phosphorus has ultimately strong implications for nutrient limitation of primary production. Consequently, it has been suggested that phosphorus may play a more critical role than nitrogen in tropical ecosystems (Howarth, 1988; Fisher et al., 1995).

Interestingly, a comparative study between tropical and temperate estuaries concluded that silicate concentrations are significantly higher in tropical estuarine waters (Eyre and Balls, 1999). Moreover, because of the high concentrations of silicate generally found in tropical freshwaters, Furnas (1992) suggested it is unlikely that silicate is a major limiting nutrient in tropical coastal waters.

Another noteworthy distinction between tropical and temperate catchments is the difference in the variability of stream discharge. Although flood events are uncommon and occur only as a few short-lived events during the wet season, they can account for up to 80% of the total yearly load of nutrients and sediments to tropical estuaries (Milliman and Syvitski, 1992; Eyre, 1995). On the other hand, because freshwater inputs are generally more constant in temperate systems, high flow events do not account for such a high proportion of the total yearly transport (Correll et al., 1992; Eyre and Balls, 1999). Therefore, because forcing events in the tropics are commonly of short duration, nutrient levels in the water column will most likely be characterized by episodic short-term fluctuations. Unfortunately, because of the difficulty inherent in sampling sporadic runoff events, little work has been done to characterize the transient impacts of flood events on tropical ecosystems.

1.6 Importance of Storm Events in Hawaiian Islands

The Hawaiian Islands, located in the North Pacific Ocean between approximately 19 and 22 degrees north latitude, are more than 2000 miles away from the nearest continental land mass. Hawaii's mountainous topography strongly influences its weather and climate: the distribution and variable altitude of peaks, valleys, ridges and slopes cause marked variations in temperature, wind speed, cloudiness, and rainfall. Annual rainfall is extremely variable locally and seasonally. Annual precipitation typically averages 51-64 cm along the coast, 89 cm about two kilometers inland, and up to 152-178 cm about three kilometers inland in the mountainous areas

(Naval Pacific Meteorology and Oceanography Center, 2001). The main rain-producing mechanisms for Hawaiian Islands are orographic effects, frontal passages, Kona storms, and tropical cyclones.

Northeasterly winds, commonly referred to as trade winds, prevail throughout the year over the Hawaiian Islands. The orographic uplifting of moist trade wind air causes clouds to form and often results in brief intense rain events, especially where the mountains are steep. Rain produced by this process, called orographic rainfall, is very consistent in windward areas and leads to higher annual rainfall totals along the windward slopes.

Cold fronts, common between October and April, mark the leading edges of cold air masses associated with low-pressure systems moving north of the Islands (Juvik and Juvik, 1998). They typically bring widespread clouds, heavy rain, and occasional thunderstorms. The more vigorous fronts are often preceded by strong southwest winds and followed by gusty northerly winds. However, the frequency of the passage of cold fronts over the Islands varies from year to year.

Kona storms are another type of low-pressure system of subtropical origin that usually develop northwest of Hawaii during winter (Juvik and Juvik, 1998). Because they are virtually always associated with moist, southerly winds and heavy rainfall, Kona storms are synonymous with bad weather in Hawaii. Because the winds are usually relatively light, they can persist for a week or more, contributing greatly to the annual total precipitation. However, some winters have had no Kona storms, others five or more. As for cold fronts, the El Niño Southern Oscillation (ENSO) is believed to be an important cause of this year-to-year variability (Juvik and Juvik, 1998).

Because Hawaiian drainage basins are small and mountainous, streams respond rapidly to storm rainfall. Following an intense rain event, it takes no more than a few hours for the streams to reach maximum flow, delivering large amounts of sediments and nutrients to adjacent coastal waters. Thus, freshwater discharges into Hawaiian coastal waters are strongly a function of the frequency and magnitude of storm events. A study by Hoover (2002) based on the National Stream Quality Accounting Network (NASQAN) long-term records for Hawaii demonstrated that individual storm events are quantitatively important in terms of annual fluxes of water. For the seven NASQAN study sites, the largest flow day in an average year contributed 5 to 12 % of the annual total flow. Moreover, based on a study carried out in watersheds located on Oahu, Hoover (2002) demonstrated that gross nutrient fluxes (dissolved and particulate) are dominated by storm runoff fluxes.

1.7 Study Rationale

Traditionally, water quality monitoring has been performed by manual sampling at weekly, biweekly, or even monthly intervals. While this approach is appropriate for long-term monitoring in areas that are not subject to rapid changes in water quality, it is not well suited for examining coastal ecosystems in more variable environments. Water quality in Hawaii is known to vary significantly and rapidly in response to a number of phenomena, including wind, waves and particularly storm runoff (Hoover, 2002). Because of cost, effort and mainly time issues, the limitations of standard sampling have made it difficult to assess the degree to which land runoff may affect Hawaiian coastal ecosystems. To capture variability on time scales on the order of hours to days and to establish the timing of biological responses, frequent sampling of water quality parameters during and following storm events is necessary.

The primary goal of this study was to investigate the transient impacts of storm runoff events in Hawaiian coastal waters. Although runoff materials can affect estuarine ecosystems on time scales of months and years, the focus of this study was to evaluate the impacts on shorter time scales (hours, days). To distinguish baseline and storm-induced variability, another objective of this project was to gather the necessary data to characterize baseline conditions.

1.8 Study Site Selection

Because of the extensive record of data available for Kaneohe Bay, this embayment, situated on the windward side of the island of Oahu (Figure1.1), was selected to evaluate the impacts of storm runoff events. In addition, the Hawaii Institute of Marine Biology (HIMB), conveniently located on Coconut Island (Moku O Lo'e) in southern Kaneohe Bay (Figure 1.1), provided laboratory space and small boats. Land use in the vicinity of the southern basin is also shown in Figure 1.1. The Kaneohe watershed is mainly characterized by urban development, making its adjacent coastal waters a good site to investigate the impacts of urban runoff and non-point source nutrient pollution. Another advantage of this site is the relatively long mean residence time of water in the semi-enclosed southern basin (about 13 days, (Smith et al., 1981)), which is suitable to examine the transient effects of storm runoff on Bay ecosystems. Finally, the documented impacts of severe storm runoff in Kaneohe Bay (Banner, 1968; Jokiel et al., 1993) suggest that smaller storm events could also have a considerable influence on the biogeochemistry of Bay waters.

1.9 Overview of Southern Kaneohe Bay

1.9.1 Dimensions, water circulation and tides

Kaneohe Bay is the largest sheltered body of water in the Hawaiian Islands; it is about 12.7 km long and 4.3 km wide. The southern basin has a total area of approximately 8.4 km^2, a total volume of 80 x 10^6 m^3, and an average depth of about 9 m (Smith et al., 1981). South Bay, protected and semi-enclosed by the Mokapu Peninsula and Coconut Island, has a restricted circulation and limited exchange with the rest of the bay and oceanic waters. Circulation of water is mainly governed by tidal flow, wind-driven mixing and advection. In addition to wind speed, the direction of the wind can also influence circulation and material fluxes in southern Kaneohe Bay, especially when freshwater input is high (Kimmerer et al., 1981). Being less dense, freshwater floats on the higher salinity estuarine water and then disperses across the surface of the Bay. The pattern of the plume dispersion is a function of the wind direction; therefore stream runoff will move in a different direction depending on whether it is associated with "trade winds" (northeast) or "Kona winds" (southwest). When trade winds blow from 45^0-135^0, Kimmerer et al. (1981) showed that the plume flows through the Lilipuna Channel west of Coconut Island into the central sector. However, when north winds or southwest winds prevail, the plume is more likely to remain for a longer time in the southern basin, losing material by diffusion across the front. This has important implications for the fluxes of material in South Bay; the nutrients and sediments carried by storm runoff could be effectively advected out of the basin under the influence of strong trades. Thus, the impact of the plume is likely to be not only function of the volume of stream discharge, but also of the wind regime. In addition, tides in Kaneohe

Bay occur semi-diurnally, with a mean tidal amplitude of about 68 cm/day (Jokiel et al., 1993). The volume of water exchanged is a function of tidal height, and can be increased by more than 30% during a maximum tidal change of 112 cm.

1.9.2 Meteorology

Precipitation in the Kaneohe Bay watershed increases toward the mountains because of the orographic effect. Long-term average rainfall in the watershed is 193.1 cm per year (Western Regional Climate Center, Kaneohe Mauka station 781, 1949-1998). Annual precipitation shows substantial temporal variation: it can range from as low as 85 cm on unusually dry years, to up to 365 cm during the wettest ones. The wet season typically extends from October to May. The long-term annual mean temperature for the same station is 23.5 ^{0}C, with an average of only 4 ^{0}C difference between winter and summer months. As mentioned before, the prevailing winds in Hawaii come from the northeast, blowing more than half of the time from this direction in the Kaneohe Bay area (Smith et al., 1981).

1.9.3 Hydrology

The Kaneohe Bay watershed, naturally delineated by steep cliffs to the south (up to 800m), covers an area of approximately 97 km^2. Three perennial streams drain from the watershed into the southern basin of Kaneohe Bay: Kawa Stream, Keaahala Stream and Kaneohe Stream (Figure 1.1). Roughly 75% of total runoff in the southern basin originates from Kaneohe stream (Hoover, 2002), which is the outlet for one of the larger drainage systems on the windward side. Based on a 25-year record (1976-2000) of the USGS station (#16272200) located in the Kamooalii upper branch of Kaneohe Stream, the mean stream flow is approximately 0.293 m^3/s. However, runoff is highly variable; peak stream flow values of up to 183 m^3/s have been recorded at this site.

1.9.4 Biology

Kaneohe Bay is famous for its coral reefs, which have very high productivity and can provide habitat for more than 3000 species of fishes, invertebrates, benthic algae, and seagrasses. Although these groups of organisms are important in the Bay ecosystem, they will not be discussed further. The focus of this study was on the phytoplankton biomass; being the primary producers, they will be the first to respond to nutrient inputs. Moreover, plankton community structure can be a powerful indicator of eutrophication. The results of size fractionation studies in South Bay demonstrated that picoplankton (0.2-2.0 μm) accounts for 40 ± 14 % of the total Chl *a* (Taguchi and Laws, 1989). It is believed that cyanobacteria of the genus *Synechoccus* could account for more than half of this size fraction

(Laws and Allen, 1996). Based on pigment analyses, Laws and Allen (1996) also suggested that diatoms are an important component of the phytoplankton community in Kaneohe Bay, representing roughly 45 % of the total Chl *a*.

1.9.5 Water Quality

After Honolulu, the southern portion of the Kaneohe watershed is the most densely populated area in Hawaii. It comprises the municipalities of Kaneohe and Kailua, which have populations of approximately 37,700 and 36,100 people respectively. Urban development has had unambiguous influence on the watershed ecosystem. To name only a few, land clearing, stream channelization and dredging all have caused significant changes to the natural environment. A major impact of urbanization was the discharge of large volumes of sewage into the southern portion of the Bay between 1951 and 1977. Sewage outfall diversion completed in 1978 reduced the total nutrient fluxes (dissolved and particulate) in southern Kaneohe Bay by about 75% for nitrogen and 97% for phosphorus (Smith et al., 1981). The decreased nutrient loading in the southern basin had important impacts on the South Bay ecosystem, one of which was a reduction of the phytoplankton standing crop by about 59% in 1979 (Smith et al., 1981). More than ten years after the sewage diversion, the water column in South Bay had become even more oligotrophic, as evidenced by decreased phytoplankton biomass and inorganic nutrient levels (Laws and Allen, 1996). However, the present-day nitrogen and phosphorus budgets in southern Kaneohe Bay are still affected significantly by anthropogenic subsidies (Hoover, 2002). Dissolved reactive nitrogen and phosphorus fluvial fluxes are still clearly elevated compared to "pristine" conditions, suggesting that non-point-source pollution remains a problem in the watershed. In fact, Keahaala, Kawa and Kaneohe streams continue to be listed as moderately to severely impaired by the Hawaii Department of Health (HIDOH, 1998; Burr, 2003). Increased nutrient and sediment loading during storm runoff events could then be significant enough to have considerable impacts on water quality in southern Kaneohe Bay.

1.9.6 Nutrient Limitation

Smith et al. (1981) were interested in establishing which nutrient, phosphorus or nitrogen, limited phytoplankton biomass in the southern basin. Because sewage was characterized by a relatively low nitrogen-to-phosphorus ratio of about 6, they hypothesized that nitrogen would be the primary limiting nutrient. In fact, the results of their nutrient enrichment experiments demonstrated that nitrogen was the nutrient limiting the biomass of phytoplankton, for both the pre- and post-diversion periods. A decade after sewage diversion, Laws and Allen (1996) repeated the nutrient addition experiments and concluded that the Bay was still distinctly nitrogen limited. From 1998 to 2001, a long-term monitoring project named "Coastal Intensive Site Network" (CISNet) took place in Kaneohe Bay. The 3-year average dissolved inorganic nitrogen to dissolved inorganic phosphorus ratio (DIN:DIP) in the water column for this period of time is about 3.5, suggesting again that southern Kaneohe Bay is nitrogen limited.

1.9.7 Historical Storm Events

Impacts of two large historical runoff events have been documented in the watershed. In May 1965, extraordinarily heavy rains caused a thick layer of freshwater to spread over the surface of Kaneohe Bay. The low salinity layer persisted for several days, resulting in massive mortality of coral reef organisms in shallow water. Because of the influence of sewage nutrients in the water column at this time, the system was already eutrophic prior to the event. Nevertheless, a massive phytoplankton bloom occurred about one week after the event, most likely fueled by the nutrient loading from storm runoff and from the decay of dead organisms. Recovery of the coral community was slow, apparently because the eutrophic conditions sustained nuisance algae (Jokiel et al., 1993). On New Year's Eve of 1988, another flooding event produced similar effects in southern Kaneohe Bay. Again, this event resulted in a freshwater "reef kill". A spectacular phytoplankton bloom occurred during the two weeks following the runoff event, with Chl *a* concentrations more than 40 times higher than pre-flooding values (Jokiel et al., 1993). Water quality parameters returned to near normal conditions within approximately one month.

There has been at least one attempt to characterize the impacts of stream runoff in southern Kaneohe Bay (Jokiel and Cox, 1999). Unfortunately, a major ENSO occurred during the period of sampling (1997-1998), resulting in unusually dry conditions in the Kaneohe Bay watershed. Because no significant storms occurred during this period, the water quality data collected were inconclusive in terms of impacts on the ecosystem.

1.10 Research Hypotheses and Objectives

The fundamental hypothesis of this research project is that moderate runoff events have considerable impacts on water column properties and ecosystem dynamics in southern Kaneohe Bay. Each of the following hypotheses is based on this primary assumption.

Hypothesis 1: Storm perturbations of conservative water quality parameters such as salinity, temperature and turbidity are short-lived, and the duration of perturbations is determined by the amount of runoff discharged into southern Kaneohe Bay.

Rationale: Because residence time of water in southern Kaneohe Bay is on average 13 days, the perturbations induced by a moderate runoff event are not likely to persist for more than a few days. Being less dense than bay waters, runoff waters float at the surface. Smaller runoff volumes result in thinner freshwater layers and less “potential mixing” with bay waters, which should in turn result in a rapid restoration of baseline conditions. Thus, because flushing times are likely to be shorter for smaller discharge episodes, the duration of water-column perturbations should scale with the magnitude of the runoff events.

Hypothesis 2: Dissolved inorganic nutrient behavior during post-flood recovery in southern Kaneohe Bay is regulated by both physical processes (advection, mixing and dilution) and non-conservative processes (biological uptake).

Rationale: When entering southern Kaneohe Bay, freshwater plumes rapidly lose material by diffusion across the front of the plume and by sedimentation. Kimmerer et al. (1981) have shown that sewage outfall plumes can be directly advected out of the southern basin. Thus, rapid advection and mixing are likely to be major controls on post-flood nutrient dynamics. However, the relatively long residence time of water in southern Kaneohe Bay (~ 13 days) should make internal nutrient processing possible. Therefore, post-flood nutrient dynamics are likely to depart from the simple conservative mixing behavior.

Hypothesis 3: Moderate storm runoff events significantly enhance phytoplankton growth and productivity in southern Kaneohe Bay, and the magnitude of the ecosystem response is a function of nutrient loading.

Rationale: Historical flood events in southern Kaneohe Bay have resulted in massive phytoplankton blooms (Jokiel et al., 1993). While the ecosystem response is not expected to be as large for moderate runoff events, the retention time of runoff nutrients in the southern basin should still be long enough for significant biological uptake to occur. Under transient conditions of saturating nutrient concentrations, several algal species can build-up an intracellular nutrient storage pool which can later permit higher growth rates (Sommer, 1989). Because runoff waters are often characterized by high suspended loads (Hoover, 2002), the lag time between nutrient discharge and algal response is likely to be a function of light availability in the water column. Because the annual range of water temperature and solar radiation in Hawaiian coastal waters is very low, baseline primary production is comparable throughout the year and mostly limited by nutrient availability. Therefore, there should be a strong correlation between nutrient loading and the extent of post-flood algal proliferation.

Hypothesis 4: Post-flood phytoplankton blooms in southern Kaneohe Bay are primarily regulated by nitrogen availability.

Rationale: Previous nutrient enrichment experiments have demonstrated that phytoplankton growth in southern Kaneohe Bay is primarily limited by nitrogen (Smith, 1981; Laws and Allen, 1996). Moreover, the very low DIN to DIP ratios reported for the southern basin during the period of the CISNet study suggest that reactive inorganic P concentrations are well in excess relative to inorganic reactive N in Bay waters. Therefore, an increase in nitrogen availability will most likely result in an increase in algal biomass. As baseline conditions are reestablished during the post-flood recovery period, depletion of DIN in the water column should lead to a decline in phytoplankton population.

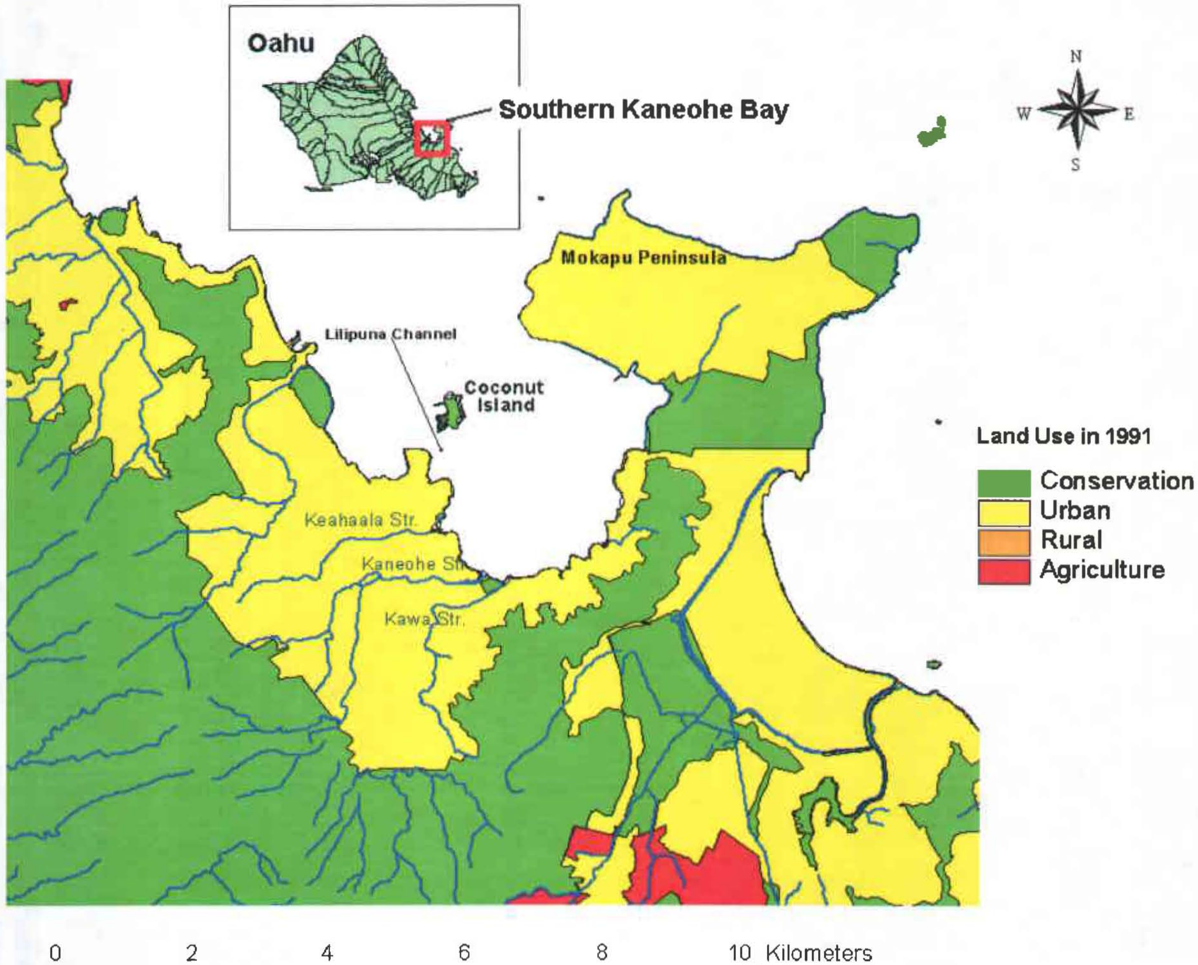


Figure 1.1. Land use and monitored streams adjacent to southern Kaneohe Bay located on the windward side of the island of Oahu.

CHAPTER 2 : METHODS

2.1 Field Methods

Data collection was accomplished using two main sampling strategies. The first consisted of establishing baseline conditions and monitoring the natural variability of a number of water quality parameters in southern Kaneohe Bay. The second sampling approach was designed to concentrate specifically on transient impacts of storm events.

Continuous monitoring was achieved using a YSI 6600 multi-parameter monitoring system. The YSI sonde was configured to measure temperature, salinity, dissolved oxygen, pH, turbidity and Chl-a fluorescence at intervals of 5 minutes. The sonde was deployed at two different sites in the course of this study. From July 2001 to September 2002, it was mounted to the pier located on the eastern side of Coconut Island (PP on Figure 2.1). From October 2002 to February 2003, the YSI sonde was deployed on the Kaneohe Yacht Club "D Buoy" (Figure 2.1). The sonde was retrieved every two to four weeks for servicing, data downloading and calibration of the probes.

Biweekly grab sampling and water column profiling with a second YSI sonde at seven sites in southern Kaneohe Bay (Figure 2.1) were also used to establish baseline conditions. Prior to sampling, the YSI sonde was calibrated in the laboratory as described in the manufacturer's operational manual. The YSI measurements of temperature, pH, conductivity, turbidity, Chl fluorescence, and dissolved oxygen at each station were taken every four seconds while lowering the sonde through the water column. Grab samples were mainly collected at the surface, with occasional depth profiles obtained at D Buoy using a Niskin sampler. Grab samples were processed in the laboratory for analysis of total suspended solids (TSS), turbidity, salinity, nutrients (phosphate, nitrate, nitrite, silica, ammonium, total nitrogen, total phosphorus) and chlorophyll *a*.

During the Fall of 2002, productivity measurements were introduced into the sampling scheme. The oxygen light-dark bottle method (Bender et al., 1987) was selected for a number of reasons: the protocol is relatively simple and inexpensive, an automated Winkler titration system was available in the Department of Oceanography at the University of Hawaii, and production rates measured with the ^{14}C technique have been shown to be significantly lower than those determined by the oxygen methods (Bender et al., 1987). Surface water was collected in an 8-liter HCl cleaned Nalgene bottle, typically around 0900 hours. Subsamples were taken within 30 minutes using silicon tubing to minimize bubble formation and intrusion of atmospheric oxygen. The flasks were divided into three categories: time zero, light bottles, and dark bottles. Each subset consisted of at least five replicates. For the incubation period of 24 hours, the light and dark bottles were put in a tank at Coconut Island with a continuous flow of seawater pumped from the bay. The incubation conditions were therefore nearly those of *in situ* conditions: the light availability was virtually the same as in south Kaneohe Bay surface waters, and the temperature difference between bay waters and the incubation tank was found to be no more than 0.3 ^{0}C. The "time zero" subsamples were fixed as soon as the incubation started. The procedure for sample fixation is summarized in section 2.2.

Based on previous observations (Jokiel and Cox, 1999), the threshold for storm sampling was fixed at 2.0 inches (5.1 cm) of rainfall recorded at the National Weather Service (NWS) Luluku rain gage (Figure 2.1) in a 24-hour period. During sampling of storm runoff, the baseline sampling scheme was repeated, and additional field measurements were taken at selected sites. At least 20 liters of surface water were collected at D Buoy for productivity incubations, nutrient enrichment experiments, filtration for HPLC analyses, and standard filtrations. When visible, the locations of the boundaries of the freshwater plume were recorded using a Garmin GPS 76 receiver. In addition, salinity gradients within the plume were determined by towing the YSI conductivity probe in the surface water while slowly moving the boat. All samples were collected in acid-cleaned bottles and refrigerated until processing in the laboratory.

2.2 Laboratory Methods

In the laboratory, grab samples were processed for analysis of dissolved nutrients, chlorophyll *a* (Chl *a*), total suspended sediments (TSS), and precision salinity. Filtrations for Chl *a* content were carried out on the day of collection, and filtrations for nutrients were completed within 24 hours of collection. Because of the large number of samples collected during storm events, filtrations for TSS were generally not performed until a few days to weeks after collection, and samples were kept refrigerated at 4 ^{o}C until that time.

For dissolved nitrogen (N), phosphorus (P) and silica (Si) analyses, samples were filtered through acid-rinsed and deionized water-rinsed Whatman GF/C filters (nominal pore size of 1.2 um). The filtrate was frozen for subsequent analyses. Samples were analyzed within six months using standard colorimetric methods on commercial autoanalyzers at the University of Washington Oceanography Technical Services Laboratory and at the University of Hawaii.

For Chl *a* determinations, approximately 100 ml of seawater from each sample were filtered through a glass-fiber Whatman GF/C filter (nominal pore size of 1.2 um). To be consistent with the procedures previously used in our laboratory for Chl *a* filtrations, GF/C filters were used instead of GF/F filters (pore size of 0.7 um). To determine any differences in the retention capability between the two filter types, a few random samples from southern Kaneohe Bay were filtered using both filter types. The small differences between the two filters were not found to be statistically significant ($t = 0.0569$, $df = 9$, $P = 0.9559$). Chl *a* pigment analyses were also made to determine the size distribution of Chl *a*. For that purpose, approximately 250 ml of sample were filtered through a 2.0 μm Isopore membrane filter, and 100 ml of the filtrate were subsequently filtered through a 0.2 μm membrane filter. Picoplankton Chl *a* was considered to be the Chl *a* collected on the 0.2 μm filter (Laws and Allen, 1996). The samples were frozen and kept in the dark until extraction. Prior to analyses, the filters were placed in 90% acetone, and pigments were extracted in a freezer at –20 °C for 24 hours as described by Strickland and Parsons (1972). Chl *a* assays were made on a Turner Designs AU-10 fluorometer. The instrumental detection limit was 0.05 μg/l, and the percent relative standard deviation never exceeded 5%.

Samples for salinity measurements were transferred directly from the sampling bottles to 125 ml Nalgene bottles sealed and kept refrigerated until analysed. Bottles made of flint glass are usually recommended for storage of salinity samples, but plastic bottles were used to be consistent with the methods previously used in our laboratory. The material effect on salinity is believed to be minor, and can be considered negligible when comparing samples with significant differences in salinity. The bottles were "overfilled" to minimize evaporation. Samples were analyzed within six months on a Guildline AUTOSAL Model 8400 B autoanalyzer in the University of Washington Oceanography Technical Services Laboratory.

For oxygen determinations, the samples were fixed using the standard protocol for Winkler titrations (Carpenter, 1965). After adding 1 ml of each fixing reagent (manganese chloride and alkaline iodide solutions) to the sample, the glass stopper was carefully replaced without trapping air bubbles. If any bubbles were present, the sample was discarded. The flask was then shaken vigorously to disperse the precipitate uniformly. To avoid bubble formation during storage, the flared mouths of the flasks were filled with seawater, and the bottles were stored at room temperature in the laboratory where temperature fluctuations were minimized. The dissolved oxygen concentrations were measured using a computer-controlled potentiometric titration system. The computer program interfaces and operates with a microburet Dosimat (model 665) and a pH meter (Orion model 720A). The program parameters were chosen to optimize the equivalence point determination based on the computer addition of microliters of thiosulfate titrant. A blank determination and a standardization of the thiosulfate titrant against a potassium iodate certified reference standard were performed at the beginning of each analysis. The coefficient of variation for standards was 0.3%, and the coefficient of variation for triplicate samples was 1 % or better.

For total suspended solids (TSS) determinations, an aliquot of well-mixed sample was filtered onto a pre-weighed, combusted Whatman GF/C glass fiber filter. The filters were dried overnight at $60^{0}C$, and then cooled to room temperature in a dessicator. The filters were subsequently reweighed, and the weight difference and the filtrate volume were used to calculate the concentration of TSS. These samples were also used for particulate C and N determinations on a commercial Carlo Erba NC2500 Elemental Analyzer (Isotope Biogeochemistry Laboratory, University of Hawaii). Prior to C and N analyses, the filters were acidified with 1N HCl to dissolve inorganic carbon contained in carbonate phases.

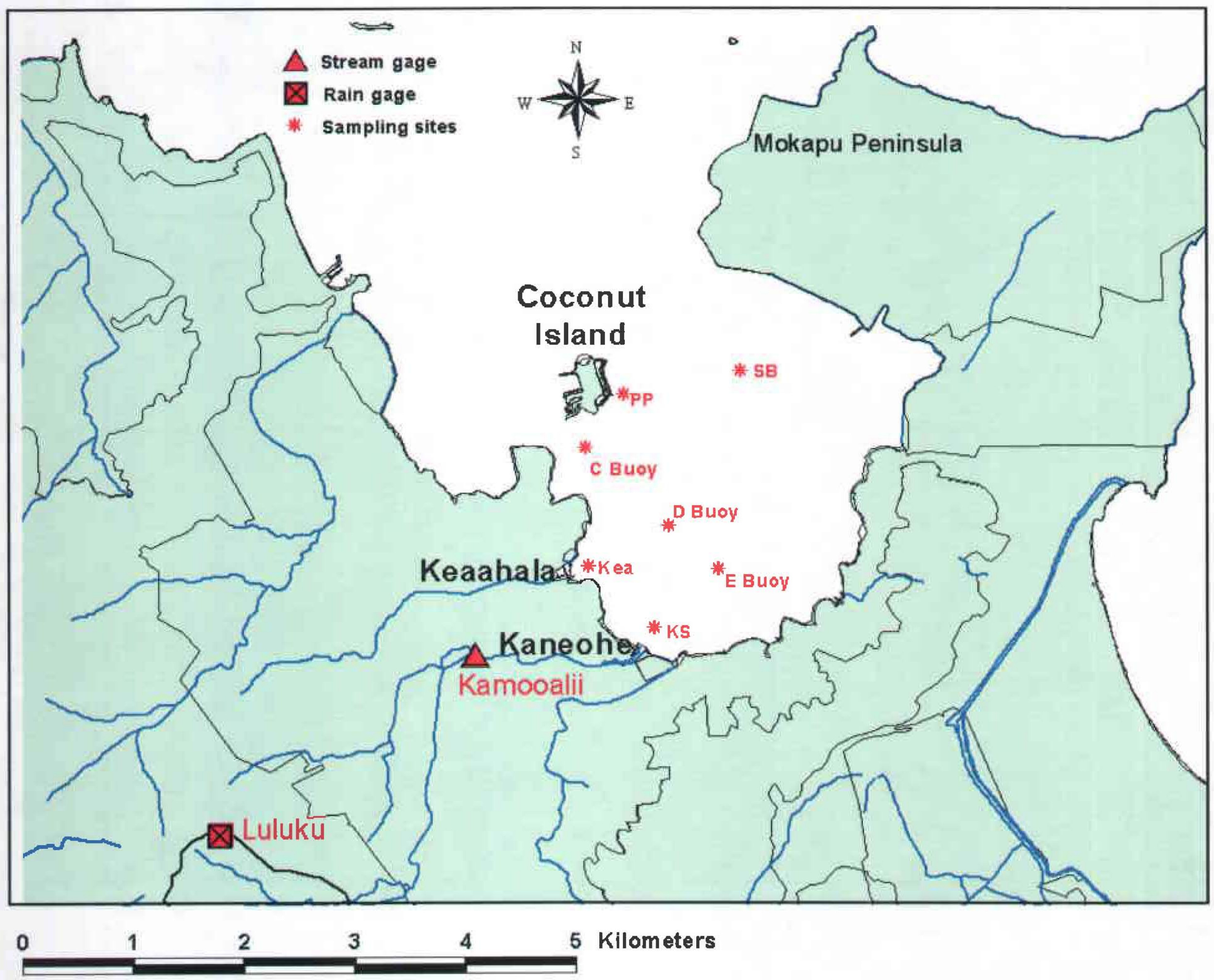


Figure 2.1. Monitoring sites in southern Kaneohe Bay for this study. The locations of the NWS Luluku rain gage and the USGS Kamooalii stream gage in the adjacent watershed are also shown.

CHAPTER 3 : BASELINE VARIABILITY OF WATER QUALITY PARAMETERS IN SOUTHERN KANEOHE BAY

3.1 Introduction

Baseline water quality conditions for the seven sampling sites in southern Kaneohe Bay (Figure 3.1) were established using data obtained mainly between November 2001 and March 2003. In addition, water quality data obtained at biweekly intervals for the duration of the Coastal Intensive Site Network (CISNet) monitoring project in Kaneohe Bay (November 1998 to July 2001) were used for comparison with nearby sites. The locations of the CISNet sampling sites in southern Kaneohe Bay are also shown in Figure 3.1. Table 3.1 on next page summarizes information about all the sites.

Table 3.1. Information on sampling sites in southern Kaneohe Bay.

Site	GPS Coordinates	Average Water Depth (m)	Bottom substrate type	Distance from Kaneohe stream mouth (km)
Kea	N 21.4182 W 157.7899	2.0	Mud	———
KS	N 21.4140 W 157.7840	1.5	Mud	0.17
E Buoy	N 21.4189 W 157.7808	10.3	Mud	0.55
D Buoy	N 21.4228 W 157.7845	8.8	Mud	0.91
C Buoy	N 21.4277 W 157.7882	14.0	Mud	1.74
PP	N 21.4330 W 157.7863	2.0	Reef	2.29
SB	N 21.4345 W 157.7787	13.7	Mud	2.83
MP (CISNet)	N 21.4157 W 157.7852	———	———	———
SB (CISNet)	N 21.4357 W 157.7775	———	———	———
OF (Smith et al 1981)	Not available (close to MP)	———	———	———

Rainfall data were obtained from the National Weather Service (NWS) Hydronet Luluku station (HI-15) located in the upper part of the Kaneohe watershed (Figure 2.1). Because stream flow can be directly related to rainfall in mountainous areas (Smith et al., 1981), rainfall collected at Luluku rain gage is a reasonable indicator of runoff in Kaneohe Bay. High discharge periods for Kaneohe stream (greater than 2.0 m^3/s) are usually associated with rainfall greater than 5.3 cm in a 24-hour period (Jokiel and Cox, 1999). To ensure that a runoff event would not be missed, the lower rainfall threshold for storm sampling was set to roughly 5.1 cm in a 24-hour period (see section 2.1). On the other hand, by definition baseline conditions are characterized by low runoff influence. Total rainfall at Luluku station was calculated for the five days preceding each baseline sampling (Figure 3.2). The upper limit for baseline conditions was arbitrarily set to 4.1 cm of rainfall in a period of five days. The amount of rainfall was above the threshold for only one sampling day (4/24/02). Data collected that day were not included in the baseline calculations.

3.2 <u>Results</u>

3.2.1 Fluorometric Chlorophyll a

Chlorophyll *a* (Chl *a*), contained in all photosynthetic organisms, is commonly used as a proxy for total phytoplankton biomass in marine waters. Table 3.2 summarizes the average concentrations of Chl *a* for baseline conditions in southern Kaneohe Bay.

Table 3.2 Average Chl *a* baseline concentrations in µg/l for the sites in southern Kaneohe Bay for the period of November 2001 to February 2003. All concentrations are in µg/l. n is the number of samples.

Station	Mean	Median	Standard deviation	Range	n
D Buoy	0.82	0.80	0.35	0.17-1.40	25
E Buoy	0.72	0.64	0.34	0.08 -1.33	18
C Buoy	0.71	0.73	0.27	0.19 -1.05	16
PP	0.53	0.53	0.21	0.14 – 1.05	25
SB	0.50	0.37	0.28	0.18 – 0.98	12
Kea	1.69	1.51	0.87	0.45 – 4.2	15
KS	1.38	1.16	0.94	0.42 – 4.02	16

The same baseline Chl a concentration data are shown as boxplots for each site in Figure 3.3. The two sites located near the stream mouths, KS and Kea, show a greater mean Chl *a* concentrations and a greater range of Chl *a* concentrations than the bay sites. The variability appears to decrease with distance from Kaneohe stream mouth (Figure 3.4), suggesting that the influence of stream discharge on Chl a concentrations is rather localized during baseflow conditions. Statistical analyses of the Chl *a* baseline concentrations revealed that the sites can be divided into three significantly different groups: (A) KS and Kea, (B) C, D, and E Buoys, (C) PP and SB. Using the non-parametric Wilcoxon test (also known as the Mann-Whitney U test), no statistically significant differences were found between the sites within each group. The differences in Chl a medians between the three groups were all found to be statistically significant ($P < 0.05$).

Five vertical profiles for Chl *a* determinations were obtained at D Buoy during baseline conditions (Figure 3.5). Because of the relatively coarse and uneven sampling intervals, the profiles are difficult to compare. However, some general observations can be made of Chl *a* distributions with depth. First, there seems to be a persistent increase in Chl *a* concentrations near the bay bottom. This could be due to the presence of clay particles which have a fluorescence in a range similar to that of Chl *a*. Although the probability of any clay particle interference was minimized by the filtration of the sample, the amount of particles smaller than 1 μm in size could have been significant. Another explanation for the elevated Chl *a* values near the bottom would be the accumulation of sinking phytoplankton cells. Diatom cells, having a rigid silica wall, tend to be heavy and are commonly maintained near the surface by turbulence. Periods of low turbulence characteristic of baseline conditions in the bay could enhance the sinking of diatom cells toward the bottom. Except for the profile obtained on 1/24/02, another general feature of the vertical distributions of Chl *a* concentrations is that they are roughly constant in the upper 4 meters of the water column, suggesting that the upper layer is generally well-mixed.

Filtrations for Chl *a* size fractionation were carried out on five occasions on surface samples collected at D Buoy during baseline conditions. Results are shown in Figure 3.6. Chl a concentrations for phytoplankton larger than 2.0 μm range from 0.16 to 1.04 μg/l, while the Chl *a* concentrations for picoplankton (0.2 – 2.0 μm size fraction) range only from 0.14 to 0.40 μg/l. This suggests that most of the variability in total Chl *a* concentrations can be accounted for by larger phytoplankton. Two previous studies also evaluated the size distribution of Chl *a* in southern Kaneohe Bay, and selected information is summarized in Table 3.3.

Table 3.3. Percentage of Chl *a* accounted for by picoplankton determined by different studies in southern Kaneohe Bay. Errors for the estimated percentages correspond to one standard deviation. n is the number of samples.

Study	Period of sampling	Sampling site	Percentage of Chl a accounted for by picoplankton (%)
This study	November 2002 – March 2003	D Buoy	21 ± 11 (n = 5)
CISNet	November 1998 – July 2001	MP	32 ± 15 (n = 57)
Laws and Allen (1996)	October 1989 – June 1992	OF	39

The average percentage of picoplankton is smaller for this study than that for previous studies, but this could be an artifact of the small number of samples in this study. The fact that the samples were collected only during winter for this study could also have had an effect on the percentage of picoplankton. Thus, the average of 32% obtained with the larger CISNet dataset is likely to be a more reliable estimate of the contribution of picoplankton to total Chl *a*.

3.2.2 Accessory Photosynthetic Pigments

High-performance liquid chromatography (HPLC) pigment analysis is a useful tool for estimating the relative abundances of different algal groups, allowing one to partition total Chl *a* concentrations into contributions from the major phytoplankton classes. HPLC analyses were carried out on three samples collected in southern Kaneohe Bay during baseline conditions. Given the small number of samples obtained for this study, selected pigment data from Laws and Allen (1996) and the CISNet study were included for establishing the baseline phytoplankton community. Box plots of the baseline concentrations for the pigments fucoxanthin, zeaxanthin, chlorophyll *b* (Chl *b*), 19'-hexanoyloxyfucoxanthin (hex), and peridinin are shown in Figure 3.7. Fucoxanthin, zeaxanthin and Chl b, which are the diagnostic pigments for diatoms, cyanobacteria and chlorophytes respectively, have the highest median concentrations. Their concentrations are also quite variable; a difference of up to a factor of three can be observed between samples. On the other hand, hex and peridinin show considerably less variability. Because the absolute pigment concentrations are inherently related to the amount of Chl *a*, pigment data were normalized to total Chl a and are also shown as box plots in Figure 3.7. Interestingly, fucoxanthin normalized to Chl *a* shows less variability than zeaxanthin and Chl b, suggesting that fucoxanthin might be more tightly coupled to total biomass than the other pigments. Baseline pigment data for southern Kaneohe Bay are summarized in Table 3.4.

Few data exist concerning the structure of the phytoplankton community in southern Kaneohe Bay. In 1981, Smith et al. reported that the phytoplankton community was composed primarily of diatoms and secondarily of dinoflagellates, with few chlorophytes. More than a decade later, Laws and Allen (1996) concluded that diatoms continued to be an important component of the phytoplankton community. Using a Chl *a*/fucoxanthin ratio of 4.16 (Laws et al., 1994), they estimated that diatoms accounted for approximately 45% of the Chl *a*. They also concluded that the cyanobacteria *Synechococcus,* an important component of the picoplankton, was abundant in southern Kaneohe Bay. Assuming a Chl *a*/zeaxanthin ratio of 2.1 (Letelier et al., 1993), Laws et al. (1994) estimated that cyanobacteria make up approximately 25 % of the phytoplankton biomass. Pigment data given in Table 3.4. suggest that the phytoplankton community is now primarily composed of diatoms, cyanobacteria and chlorophytes. Because the ratios used in Laws and Allen (1996) were not determined using pigment data from Kaneohe Bay or a comparable estuarine system, they are not used in this study to calculate percentages.

Table 3.4. HPLC pigment data for southern Kaneohe Bay during baseline conditions. Data are from Laws and Allen (1996, n=13), the CISNet study (n=2) and this study (n=3).

Pigment	Associated algal group	Median concentration (ng/l)	Standard deviation (ng/l)	Median pigment:Chl*a*
Fucoxanthin	Diatoms	89	98	0.19
Zeaxanthin	Cyanobacteria	169	76	0.20
Chl *b*	Chlorophytes	137	100	0.18
19'-hexanoyloxyfuco-xanthin	Prymnesiophytes	57	125	0.08
Peridinin	Dinoflagellates	5	10	0.01

3.2.3 Dissolved Nutrients

Dissolved nutrients in surface water samples collected in southern Kaneohe Bay during baseline conditions are summarized in Table 3.5. Boxplots of phosphate (PO_4^{3-}), nitrate (NO_3^-), ammonia (NH_4^+) and silica ($Si(OH)_4$) concentrations for all sites are shown in Figure 3.8. Boxplots of dissolved organic phosphorus (DOP), dissolved organic nitrogen (DON) and the dissolved inorganic nitrogen to dissolved inorganic phosphorus ratio (DIN:DIP) are shown in Figure 3.9. Except for DON, nutrient concentrations are considerably higher at Kea than at other sites due to its proximity to Keaahala stream mouth. For this reason, the Kea site is discussed separately.

At all sites except Kea, PO_4^{3-} concentrations are very low during baseline conditions, with medians ranging from 0.08 to 0.15 μM. There appears to be more variability in NO_3^- concentrations between sites, with medians ranging from 0.06 to 0.47 μM. Except for the PP site, NH_4^+ concentrations are generally slightly higher than those of NO_3^- during baseline conditions, with medians ranging from 0.12 to 0.34 μM. Concentrations of $Si(OH)_4$ are comparatively high and fairly constant for the "bay" sites, ranging from 6.21 to 7.09 μM. In contrast, $Si(OH)_4$ is much more variable and abundant at the KS site which is located closer to the stream mouth. Concentrations of DOP are very low and do not vary much throughout the bay. Median concentrations of DON range from 7.23 to 9.13 µM and seem to be more variable than DOP. Again excluding the Kea site, DIN:DIP ratios are low in the southern basin, with medians ranging from 2.41 to 6.08. Because of variability in stream discharge and associated DIN, ratios are higher and more variable for the nearshore site KS.

The Kea site has an obvious stream signature with concentrations of $Si(OH)_4$ one order of magnitude higher than those observed at other sites. Interestingly, all dissolved nutrients, except for DON, are much higher at the Kea site than at other sites, suggesting that stream discharge is not a significant source of DON to southern Kaneohe Bay. DIN:DIP ratios are five to ten times higher at the Kea site than at other sites, implying that Keaahala stream delivers more dissolved reactive nitrogen than dissolved reactive phosphorus to southern Kaneohe Bay.

Statistical analyses revealed that the division of sampling sites used for Chl *a* is not valid for dissolved nutrients. Using the non-parametric Wilcoxon test, no statistically significant differences were found between D Buoy and site SB for all nutrients, suggesting that during baseline conditions nutrient concentrations are relatively constant over a distance of roughly 2 kilometers. Between sites SB and KS, which are separated by a distance of 2.5 km, the only statistically significant difference was for silicate ($P<0.05$). Interestingly,

PO_4^{3-} and NO_3^- concentrations at PP are statistically significantly higher ($P<0.05$) than at other sites. Because no significant difference in $Si(OH)_4$ was found and site PP is located more than 2 km from the stream mouth, stream discharge is unlikely to be the cause of elevated nutrients at site PP. On the other hand, because site PP is located below the pier off the south-eastern part of Coconut Island, an "island effect" could be responsible for the higher nutrient levels at site PP. Since PP has an average depth of 2 meters and has a coral reef bottom substrate, another possible explanation would be that the elevated surface nutrient concentrations are the result of nutrient fluxes coming out of the reef. High NH_4^+ excretion rates have been reported for several coral species (Uthicke, 2001). Corals are also known to release large amounts of DOC and DON (Ferrier-Pages et al., 1998). Uthicke (2001) also observed that small amounts of PO_4^{3-} can be released by holothurian coral species and concluded that the only important N-excretion product was NH_4^+. Therefore, because NH_4^+ concentrations at site PP were not significantly different than those at other sites, nutrient regeneration within the coral reef is most likely not the cause of elevated PO_4^{3-} and NO_3^- concentrations at site PP.

Surface water samples were also collected biweekly from October 1998 to July 2001 at two sites in southern Kaneohe Bay for the CISNet monitoring program. The CISNet SB site is essentially located at the same place as the SB site from this study, for which baseline surface samples were collected from March 2001 to January 2003. Using the non-parametric Wilcoxon test, statistically significant differences were found for NO_3^-, NH_4^+, DOP and DIN:DIP between the two periods ($P < 0.05$). The data are summarized in Table 3.6. Despite the fact that the number of samples in this study is considerably smaller than that for CISNet, the data suggest that there was more dissolved inorganic nitrogen in Southern Kaneohe Bay in 2001-2002 than in 1998-2000. Statistical analyses of CISNet MP data and D Buoy data revealed that NO_3^-, NH_4^+ and DIN:DIP ratios were significantly higher at D Buoy even though site MP is located closer to Kaneohe stream mouth. This observation also suggests that there was more DIN in 2001-2002 than in 1998-2000 in southern Kaneohe Bay.

Table 3.5. Baseline dissolved nutrient concentrations in surface water of southern Kaneohe Bay. All concentrations are in μM. The upper numbers are the medians and the numbers in parentheses correspond to one standard deviation. n is the number of samples.

Site	PO_4^{3-}	NO_3^-	NH_4^+	$Si(OH)_4$	DOP	DON	DIN:DIP
D Buoy (n=29)	0.09 (0.05)	0.15 (0.16)	0.17 (0.24)	6.44 (2.83)	0.16 (0.04)	9.13 (2.63)	4.2 (4.9)
E Buoy (n=18)	0.10 (0.07)	0.07 (0.10)	0.12 (0.21)	7.09 (3.49)	0.17 (0.05)	8.75 (3.27)	2.8 (2.7)
C Buoy (n=16)	0.10 (0.07)	0.06 (0.10)	0.12 (0.21)	6.94 (2.68)	0.15 (0.06)	7.92 (2.93)	2.4 (8.0)
PP (n=31)	0.15 (0.07)	0.47 (0.43)	0.25 (0.89)	6.73 (2.40)	0.10 (0.09)	7.74 (3.15)	4.9 (3.5)
SB (n=12)	0.08 (0.03)	0.18 (0.11)	0.18 (0.16)	6.21 (1.84)	0.16 (0.04)	7.36 (4.45)	5.3 (2.9)
KS (n=19)	0.10 (0.05)	0.27 (0.38)	0.34 (0.36)	10.13 (17.44)	0.17 (0.06)	7.23 (2.03)	6.1 (7.3)
Kea (n=14)	0.44 (0.38)	11.37 (6.05)	2.60 (1.50)	168.65 (63.41)	0.48 (0.21)	6.95 (5.79)	30.4 (32.1)

Table 3.6. Median nutrient concentrations in μM for CISNet SB (1998-2001) and site SB of this study (2001-2003). Shaded boxes correspond to statistically different values using the Wilcoxon non-parametric test for P<0.05. n is the number of samples.

	CISNet SB (n=70)	**This study SB** (n=12)
PO_4^{3-}	0.07	0.10
NO_3^-	0.02	0.18
NH_4^+	0.10	0.18
$Si(OH)_4$	6.93	6.21
DOP	0.25	0.16
DON	6.96	7.36
DIN:DIP	1.80	5.29

The dataset for baseline conditions collected during this study is not large enough to assess seasonality in nutrient concentrations. However, with samples collected biweekly over a period of nearly three years, the CISNet dataset is more suitable to evaluate seasonality. Dissolved nutrient concentrations at site MP were divided into four seasons and compared using the Wilcoxon non-parametric test. Summer levels of NO_3^- and PO_4^{3-} were statistically lower ($P<0.05$) than concentrations during winter, fall and spring, most likely due to low-runoff conditions prevailing during summertime. No other significant difference was found between the other seasons.

Six vertical profiles of dissolved nutrients determined at D Buoy are shown in Figure 3.10. Except for a single value on 6/03/02, NO_3^- concentrations are very low and constant throughout the water column. In general, a slight increase in NH_4^+ concentrations was observed with increasing depth, most likely due to remineralization of organic matter both in the water column and in the sediments. Concentrations of PO_4^{3-} also appear to increase slightly with depth in some profiles. However, this may not be a general feature because PO_4^{3-} is more or less constant with depth in the other profiles. Except for the profile from 6/03/03, there seems to be a tendency for $Si(OH)_4$ concentrations to be slightly lower at depth. This could be due to the presence, near the surface, of silica-rich buoyant freshwater. DOP varies little with depth, with variations in each profile mostly within the analytical precision of ±0.04 μM. DON concentrations with depth do not appear to have a definite trend. For some profiles (1/24/02, 6/22/02, 6/03/02), DON concentrations decrease with depth, most likely due to remineralization of dissolved organic matter in the water column. In addition, the same profiles are associated with an increase of NH_4 with depth. However, this is not a general feature of the vertical gradient in DON, since DON concentrations also increase with depth for other profiles (3/01/02, 4/11/02).

3.2.4 Total Suspended Solids

Table 3.7 summarizes the total suspended solid (TSS) concentrations during baseline conditions for the seven sites in southern Kaneohe Bay. The same data are shown as box plots in Figure 3.11. The two sites located near the stream mouths (Kea and KS) have a larger range of values than the other stations, suggesting again that generally only nearshore sites are affected by stream flow variability during baseflow conditions. The general trend for TSS is a decrease with increasing distance from Kaneohe Stream mouth. On average, TSS concentrations for the group B sites (C, D, E Buoys) are roughly half of the TSS concentrations for the group A sites (KS and Kea). TSS concentrations for the sites located farther offshore (group C, SB and PP) are on average about one third of the TSS concentrations of the sites in group A.

Table 3.7 Concentrations of TSS during baseline conditions at the sampling sites in southern Kaneohe Bay for the period of November 2001 to December 2002. All concentrations are in mg/l. n is the number of samples.

Station	**Mean**	**Median**	**Standard deviation**	**Range**	**n**
D Buoy	2.66	2.42	1.42	1.05 – 5.77	15
E Buoy	2.64	2.03	2.40	0.28 – 9.12	14
C Buoy	1.93	1.18	1.89	0.25 – 7.14	14
PP	1.74	1.54	0.83	0.64 – 3.85	17
SB	1.57	1.37	1.31	0.32 – 4.42	8
Kea	5.57	4.01	4.37	0.81 -15.22	12
KS	4.23	2.93	3.20	1.01 - 9.68	13

3.2.5 YSI Multi-parameter Sonde Measurements

Surface measurements

Surface measurements of turbidity, pH, dissolved oxygen (DO) and salinity data from the YSI sonde vertical profiles at each sampling site were compiled for baseline conditions. Box plots are shown in Figure 3.12. Turbidity readings were higher and more variable for nearshore sites (Kea and KS), indicating again a greater influence of stream discharge on those sites. However, medians for turbidity are about two nephelometric turbidity units (NTU) or less for all sites, implying that turbidity is generally low in southern Kaneohe Bay during baseline conditions. All sites have comparable baseline pH, with medians narrowly constrained from 8.03 to 8.07. Because dissolved oxygen saturation (DO) levels vary significantly over a few hours (see section 3.1.7), it is difficult to do a cross-site comparison. Sampling was usually carried out in the following order: E Buoy – KS – D Buoy – Kea – C Buoy – SB – PP, which could be the reason why the last sites exhibit greater DO median concentrations. On average, the oxygen saturation measured with the YSI probe in southern Kaneohe Bay is about 120 % near 11:00 am.

The two nearshore sites (Kea and KS) show a considerable range of salinities during baseline conditions. Variability in stream flow undoubtedly affects salinity levels at sites located closer to the stream mouth. In addition, tidal effect also seems to play a role. The relationship between the water level and salinity for both Kea and KS is shown in Figure 3.13. Because the water discharge is much smaller for Keaahala stream than for Kaneohe stream, it is likely that its contribution to variations in salinity levels would be less significant. In addition, the distance of Kea site relative to Keaahala Stream mouth is shorter than the distance of KS site relative to Kaneohe Stream mouth. This could explain the better correlation between tide and salinity obtained for the Kea site.

Precision salinity measurements were carried out on selected samples during this study (n = 82). There is an overall excellent correlation between the salinity measurements taken with the YSI sonde and the precision salinity analyses, with R^2 = 0.986 (Figure 3.14). A predictive Model I regression analysis (Ricker, 1973) was performed using the SigmaPlot software, with the constraint y (0) = 0. The resulting equation, y = 0.9754x, can be used to predict the precision salinity values from the YSI measurements taken during baseline conditions. The results are summarized in Table 3.8. Excluding the Kea and KS sites, the average surface salinity in southern Kaneohe Bay during baseline conditions is approximately 34.3.

Table 3.8. YSI surface salinity measurements and corresponding predicted precision salinity values for each site in southern Kaneohe Bay during baseline condition. n is the number of surface salinity measurements taken with the YSI sonde.

Station	Median YSI Salinity	Predicted Precision Salinity	n
D Buoy	35.26	34.39	18
E Buoy	35.21	34.34	14
C Buoy	35.18	34.31	13
PP	35.05	34.19	7
SB	34.90	34.04	9
Kea	22.40	21.85	13
KS	34.81	33.95	14

Vertical profiles

Because of its position relative to Kaneohe and Keaahala stream mouths, the existing D Buoy maintained by the Kaneohe Yacht Club was selected to be the primary sampling site in southern Kaneohe Bay for this study. Hence, only the baseline vertical profiles for this station will be discussed in detail.

Vertical profiling using the YSI multi-parameter sonde was carried out on several occasions at D Buoy. Eighteen profiles of temperature, salinity, dissolved oxygen, pH and turbidity taken during baseline sampling are shown in Figure 3.15. Nearly all temperature and salinity profiles show no evidence of distinct stratification, suggesting that bay waters are well-mixed most of the time. Information on the accuracy of the YSI sonde is summarized in Table 3.9. Because the differences between nearly all pH measurements are within the instrumental error of ± 0.2, no assessment can be made of the temporal variability of this parameter. However, the overall shape of the profiles suggests that pH is relatively constant with depth. Most of the differences in turbidity measurements between sampling days were also within instrumental error of ± 2 NTU. However, turbidity was usually substantially higher in deeper waters than in bay surface waters. Overall, turbidity profiles during baseline conditions are characterized by low near surface values and a slight increase with depth. Dissolved oxygen concentrations typically decrease with depth, but remain above saturation in most of the profiles. To verify that this trend was not an artifact of the YSI probe, an experiment was performed at D Buoy on February 2003. The sonde was submerged just below the surface waters for approximately five minutes to allow the probes to equilibrate. The sonde was next slowly lowered into the water column until the bottom was reached, and brought back up at the same rate of approximately 5cm/sec. The descending and ascending DO profiles are shown in Figure 3.16. DO saturation is higher at the surface than at depth for both profiles, implying that this trend is not an instrumental artifact. The wide range of dissolved oxygen saturation values (108-143%) in surface waters in Figure 3.15 most likely reflects variations in bay productivity and differences in time of sampling (see section 3.1.7).

Table 3.9. Accuracy values reported by the manufacturer for the parameters measured with the YSI 6600 multi-parameter sonde.

Parameter	Accuracy
Temperature	± 0.15 ^{0}C
Salinity	± 0.35 ppt
pH	± 0.2
Dissolved Oxygen saturation	± 2 %
Turbidity	± 2 NTU

As mentioned previously, vertical profiles of water quality parameters were also obtained for the other sites in southern Kaneohe Bay. To illustrate the variability among sites during baseline conditions, representative profiles of temperature, salinity, pH, dissolved oxygen and turbidity were selected for KS, D Buoy and SB (Figure 3.17). Surface salinities (upper 4 meters) were essentially constant throughout the bay; the differences observed over a distance of 2.7 km from the stream mouth were within the instrumental error of ± 0.35. For deeper stations, the salinity and temperature profiles suggest that the southern basin is fairly well-mixed vertically. However, a slight decrease in salinity near the sediments was observed at both D Buoy and SB site, possibly indicating a groundwater flux. Turbidity appears to be higher nearshore, probably due to resuspension of sediments at the shallower sites.

3.2.6 Primary Productivity Rates

Primary productivity measurements were made in surface water samples collected at D Buoy on four occasions besides storm sampling periods. Net community productivity was calculated by taking the difference between the dissolved oxygen (DO) concentrations in the light bottles after a 24-hour incubation and the DO concentrations in the "time zero" (t_O) bottles. Community respiration was determined by subtracting the O_2 concentrations in the dark bottles from those in the t_O bottles. Gross production is the sum of net community production and respiration, assuming that light and dark algal respiration rates are similar (Bender et al., 1987). Results are shown in Figure 3.18. Net productivity rates for the three first measurements are all below 10 µM O_2 day^{-1}, whereas the net productivity rates measured on 3/17/03 are above 20 µM O_2 day^{-1}. A significant rain event (3.58 cm) occurred the day prior to sampling for the incubation experiment of 3/17/03, suggesting that this day may not be representative of baseline conditions. Moreover, Chl *a* concentrations at the start of the incubation (1.78 µg/l) were significantly higher than the baseline median of 0.80 µg/l. As a result, the rates measured on 3/17/03 will be excluded from baseline productivity rates.

Productivity measurements are usually expressed in terms of carbon fixed. The conversion of oxygen to carbon can be made using stoichiometric photosynthetic quotients, which are ratios indicating the relative amounts of oxygen and carbon involved in photosynthesis. The photosynthetic quotients (PQ) for new and recycled production are estimated to be 1.4 ± 0.1 and 1.1 ± 0.1, respectively (Laws, 1991). New production is commonly described as the production associated with newly available nitrogen, typically NO_3^-. On the other hand, recycled production involves regenerated forms of nitrogen such as NH_4^+. Previous studies demonstrated that most of the nutrient uptake in Kaneohe Bay is supported by internal recycling (Caperon et al. 1979, Smith et al. 1981, Laws and Redalje 1982). If most of the production is recycled, one would expect the net production to be roughly equal to respiration. Because the results shown in Figure 3.18 indicate that net production is higher than respiration for the measurements carried out for this study, a PQ of 1.4 was used to convert the oxygen to carbon under baseline conditions.

Primary productivity rates have been previously measured in southern Kaneohe Bay and data are summarized in Table 3.10. Average rates in

Caperon et al. (1971) were reported as hourly photosynthetic rates. To estimate 24-hr net production, the rates were multiplied by a factor of 8.4 and adjusted downward by 15 percent to account for nighttime respiration [Laws and Redjale 1979, Smith et al. 1981). Unfortunately, all previous productivity estimates were made using the ^{14}C method, making it difficult to compare these rates with those obtained with the O_2 method. It has been demonstrated that the rates of ^{14}C production are often lower than the rates measured with the O_2 method, and that the difference can be as high as a factor of two (Grande et al., 1989). Losses of ^{14}C as a result of remineralization, $DO^{14}C$ excretion and incomplete collection of $PO^{14}C$ cause discrepancies between the two methods. The extent of ^{14}C losses is therefore more likely to increase with the length of incubation. This could explain why the productivity rates measured by Taguchi and Laws (1989) are considerably lower than the other estimates. Prior to sewage diversion in 1978, net community productivity rates were significantly higher than present rates, reflecting the eutrophic state of the ecosystem. Interestingly, present-day community productivity rates are comparable with post-diversion rates measured in 1978 when the mean Chl *a* concentrations were considerably higher in South Bay. Although this is likely to be the result of the higher rates measured with the O_2 method, this could also indicate that the decrease in phytoplankton biomass was not necessarily associated with an equivalent decrease in primary productivity.

Table 3.10 Net community productivity rates in southern Kaneohe Bay evaluated in different studies from 1971 to 2003. (pre) and (post) correspond to pre- and post- sewage diversion.

Study	Net production (mg C m^{-3} day^{-1})	Method	Length of incubation (hrs)	Mean Chl a (mg m^{-3})
Caperon et. al (1971)	181	^{14}C	5	2.21
Smith et al (1981)	(pre) 294 (post) 54	^{14}C	3	(pre) 4.67 (post) 1.33
Taguchi and Laws (1989)	36	^{14}C	24	1.2
This study	60	O_2	24	0.89

3.2.7 Short-term Variability

To evaluate short-term variability of water quality parameters during baseline conditions in southern Kaneohe Bay, the YSI multi-parameter sonde was deployed at sites PP and D Buoy to record automatically measurements at five-minute intervals. In addition, grab sampling and vertical profiling were carried out on two occasions over a period of approximately 24 hours.

<u>24-hr sampling</u>

The first "24-hr sampling" was performed on 22 June to 23 June 2002. Surface grab samples were collected and YSI measurements were made at D Buoy and KS sites five times during a 21-hr period. The results are shown in Figure 3.19. Except for dissolved oxygen percent saturation (DO%), all parameters were nearly constant at D Buoy for the period of sampling. On the other hand, there was much more variability at the nearshore site KS. Stream discharge at Kaneohe stream varied little during the 24-hr period, presumably not enough to account for the variability observed at KS. Fluctuations in silica and salinity seem to be related to tidal effects. Results from the circulation model of the Bay waters (SPECIES, Hearn 2000) indicate that during low tide the currents are predominantly directed offshore, presumably bringing fresher waters to the Bay. This may explain the four-fold increase in silica concentrations and the decrease in salinity observed during the falling tide cycle. Nitrate and phosphate concentrations appear to be higher during low tides, but do not follow the same trend as that for silica. On the other hand, only a slight increase in silica was observed at D Buoy, suggesting that the tidal effect is restricted to nearshore areas. Chl *a* concentrations at KS varied significantly throughout the day. Because the doubling time of phytoplankton cells is typically on the order of one day at low nutrient levels, this variability is most likely due to tidal movement rather than reflecting net algal growth. There is a considerable range in dissolved oxygen saturation values at both sites. Higher concentrations of DO were observed during periods of higher solar radiation, showing that primary productivity plays an important role in regulating oxygen concentrations at both sites.

Another "24-hr sampling" was performed on 22-23 August 2002. Surface grab samples were collected and YSI measurements were made eight times over a 24-hour period. Surface data for D Buoy are shown in Figure 3.20. NO_3^-, NH_4^+, and PO_4^{3-} concentrations varied by a factor of two to five during the period of sampling. While NO_3^- and PO_4^{3-} appear to co-vary, $Si(OH)_4$ clearly shows a different trend. The increase in $Si(OH)_4$ concentrations at D Buoy is associated with a slight decrease in salinity (0.9). However, because no significant salinity decrease was observed at the same time at site KS and because stream flow at Kaneohe stream remained relatively constant for the period of sampling, this is probably not the result of a change in runoff. There was a very small rain event of 0.1 cm at night, but it is probably insignificant to explain the decrease in salinity. Moreover, it is unlikely that rainfall would be responsible for an increase of 5 µM in silica levels. A significant input of groundwater in the bay could possibly be the explanation. Although both NO_3^- and NH_4^+ concentrations decrease throughout the sampling period, NH_4^+ seems to be depleted earlier than NO_3^-. This may be due to the fact that NO_3^- assimilation by phytoplankton is often hampered by the presence of NH_4^+ (Harvey and Caperon 1976, Lindell et al. 1999, Varela et al. 1999), and that the phytoplankton uptake rates are higher for NH_4^+ than NO_3^- (Maguer et al., 2000). Dissolved oxygen saturation values appear to correlate with the amount of solar radiation, suggesting again that DO levels are mainly controlled by the daily cycle in primary production. Data collected during both sampling events provide a good indication of the short-term variability in water quality parameters during baseline conditions. Table

3.11 summarizes the range of values observed for selected parameters measured during the 24-hr sampling experiments.

Table 3.11. Range of values for the water quality parameters measured during 24-hr sampling experiments carried out in June and August 2002. n.a. = not available

Parameter	24-hr Sampling	Site	
		KS	D Buoy
NO_3^- (μM)	June 2002 August 2002	0.08 – 1.42 n.a.	0.08 – 0.20 0.24 – 0.60
NH_4^+ (μM)	June 2002 August 2002	0.02 – 0.89 n.a.	< 0.10 0.01 – 0.47
PO_4^{3-} (μM)	June 2002 August 2002	0.03 – 0.17 n.a.	0.10 – 0.11 0.08 – 0.22
$Si(OH)_4$ (μM)	June 2002 August 2002	9.98 – 36.37 n.a.	11.20 – 14.48 7.81 – 16.72
Chl *a* (μg/l)	June 2002 August 2002	0.46 – 2.54 n.a.	0.64 – 0.97 n.a.
YSI Salinity	June 2002 August 2002	31.91 – 35.47 22.35 – 32.78	- 35.50 34.61 – 35.62
DO %	June 2002 August 2002	85.1 – 129.4 91.5 – 118.7	96.3 – 136.7 96.8 – 116.4

YSI Multi-parameter sonde deployments

Deployments of the YSI sonde provided a valuable record of water quality parameters (temperature, salinity, pH, dissolved oxygen, turbidity) in southern Kaneohe Bay. Data representative of baseline conditions collected during one-week deployments are shown for Point Pier (Figure 3.21, 12/27/01-1/10/02) and for D Buoy (fig 3.22., 12/27/02-1/10/03). Wind speed and solar radiation measurements obtained at HIMB are also shown in Figures 3.21 and 3.22.

Variations in salinity were very small for both sites, mostly within instrumental accuracy of 0.35. Temperature readings show a distinct daily cycle, typically with a difference of 0.3 to 1.0 ^{0}C between nighttime and daytime. DO saturation levels also show a pronounced daily cycle. Percent saturation of DO usually peaks in the mid-afternoon and dips around midnight, confirming that variations in DO are mostly driven by primary productivity. There is, however, a noteworthy difference in the DO amplitude between PP and D Buoy sites. Values range from 78 to 140% at PP and from 87 to 112 % at D Buoy. The higher daily maximum and greater range in DO observed at Point Pier are probably due to the fact that the sonde was located about 1.5 m away from the reef, thereby allowing the YSI probe to pick up a strong productivity signal from the reef community. On the other hand, the sonde at D Buoy was located approximately 8 m above the muddy bottom, suggesting that the DO signal was the result of phytoplankton productivity. For both sites, pH correlates with DO trends, suggesting that daily variations in pH are also driven by respiration and photosynthesis. At nighttime, the free CO_2 released during respiration reacts with water to produce carbonic acid, which then decreases pH. Nonetheless, variations in pH are small, ranging from about 7.90 to 8.1 at both sites. Turbidity data were noisier than other parameters. Because most of the turbidity values recorded were in the low range and within the range of the specified instrumental accuracy of 2 NTU, it is difficult to differentiate true variability from instrumental noise, especially for PP site. Overall, turbidity was low at both sites, with values ranging mostly from 0 to 4 NTU. Turbidity was slightly higher at D Buoy, and increased turbidity seems to be associated with strong wind episodes.

3.3 Discussion

In many respects the southern basin of Kaneohe Bay can be considered as an oligotrophic estuarine environment during baseline conditions. Except for $Si(OH)_4$, inorganic nutrient concentrations are generally very low and often below the detection limits of traditional colorimetric methods. The high proportion of picoplankton cyanobacteria provides further evidence of the oligotrophic state of the bay. Because of their large surface-to-volume ratio, picoplankton are well suited to compete for nutrients at low concentrations and are typically found in abundance in oligotrophic environments (Stockner, 1988).

Because concentrations of both PO_4^{3-} and DIN are generally low, there is probably co-limitation of productivity by phosphorus and nitrogen during baseline conditions. Except for the sites located around stream mouths, ratios of DIN-to-DIP in southern Kaneohe Bay are well below the

Redfield ratio of 16 for phytoplankton growth. Assuming that nitrogen fixation rates are negligible, this suggests that nitrogen is probably the primary limiting nutrient during baseline conditions. Another way to infer nutrient limitation is to compare ambient nutrient levels with the half-saturation constant for nutrient uptake (K) derived from the Michaelis-Menten equation for enzyme kinetics (Fisher et al., 1995). K corresponds to the nutrient concentration at which the phytoplankton growth rate would equal half the maximum growth rate. Table 3.12 summarizes the range of half-saturation constants for planktonic populations (Fisher, 1995) and the ambient median DIN and DIP baseline concentrations at D Buoy. Although very low, PO_4^{3-} levels at D Buoy approximate the lower range of K values reported in the literature. On the other hand, both NO_3^- and NH_4^+ baseline concentrations at D Buoy are at least three times smaller than the K values for planktonic populations. This is again indicative of primary N-limitation of phytoplankton growth in southern Kaneohe Bay during baseline conditions.

Table 3.12 Range of half-saturation constants (K) reported for planktonic populations and median baseline inorganic nutrient concentrations in µM at D Buoy.

	K	D Buoy Median
PO_4^{3-}	0.1 - 0.2	0.09
NO_3^-	0.5 - 1.0	0.15
NH_4^+	0.5 - 1.0	0.17

Phytoplankton biomass in South Bay seems to have remained practically constant for the past 10 years. For the period of October 1989 to June 1992, (Laws and Allen, 1996) reported median Chl *a* values ranging from 0.58 to 0.76 µg/l for the southern basin, which are comparable to the median Chl *a* concentrations of 0.37 to 0.80 µg/l obtained in this study. Because of the different methods used to estimate photosynthetic rates, it is difficult to evaluate long-term changes in southern Kaneohe Bay. Net community productivity rates in southern Kaneohe Bay for 1985-1986 were reported to average 36 mg C m^{-3} day^{-1}, while net community productivity rates obtained during this study average 60 mg C m^{-3} day^{-1}. Because both ^{14}C and O_2 methods can differ by up to a factor of 2 (Bender et al., 1999), the apparent discrepancy may simply be an artifact of the methods used.

Low turbidity and total suspended solid concentrations, even around the stream mouths, suggest that primary productivity is virtually never light-limited during baseline conditions. While variations in solar radiation most likely modulate photosynthetic rates, primary productivity in southern Kaneohe Bay is mainly limited by the low availability of inorganic nutrients during baseline conditions.

Except for the nearshore sites, another noteworthy feature of the baseline dataset is that surface dissolved nutrients seem to be relatively uniformly distributed over a distance of 2 kilometers. In general, vertical nutrient profiles do not show large variations with depth, and salinity and temperature profiles are virtually constant with depth. All together, this indicates that generally there is no distinct stratification in the southern basin and that the water column is relatively well-mixed during baseline conditions.

3.4 Summary and Conclusions

Results presented in this chapter indicate that during baseline conditions bay waters exhibit characteristics of oligotrophic estuarine environments. Surface dissolved inorganic nutrient concentrations are low in the southern basin; inorganic nitrogen and phosphate concentrations border on the detection limits of standard colorimetric methods. Median Chl *a* concentrations at the bay sites did not exceed 0.80 mg/l during baseline conditions and more than 20% of the Chl *a* is accounted for by picoplankton. Photopigment analyses indicate that the phytoplankton community is primarily composed of diatoms, cyanobacteria and chlorophytes. Surface net primary production rates in the bay waters were on average 60 mg C m^{-3} day^{-1} during baseline conditions. TSS concentrations and turbidity levels were generally very low, indicating that primary productivity in southern Kaneohe Bay is most likely not limited by light availability during baseline conditions. However, the low DIN:DIP ratios observed in the bay (2.4 to 4.9) suggest N-limitation of bay productivity. Results also demonstrate that the spatial extent of stream influence on water quality parameters is very limited under baseflow conditions.

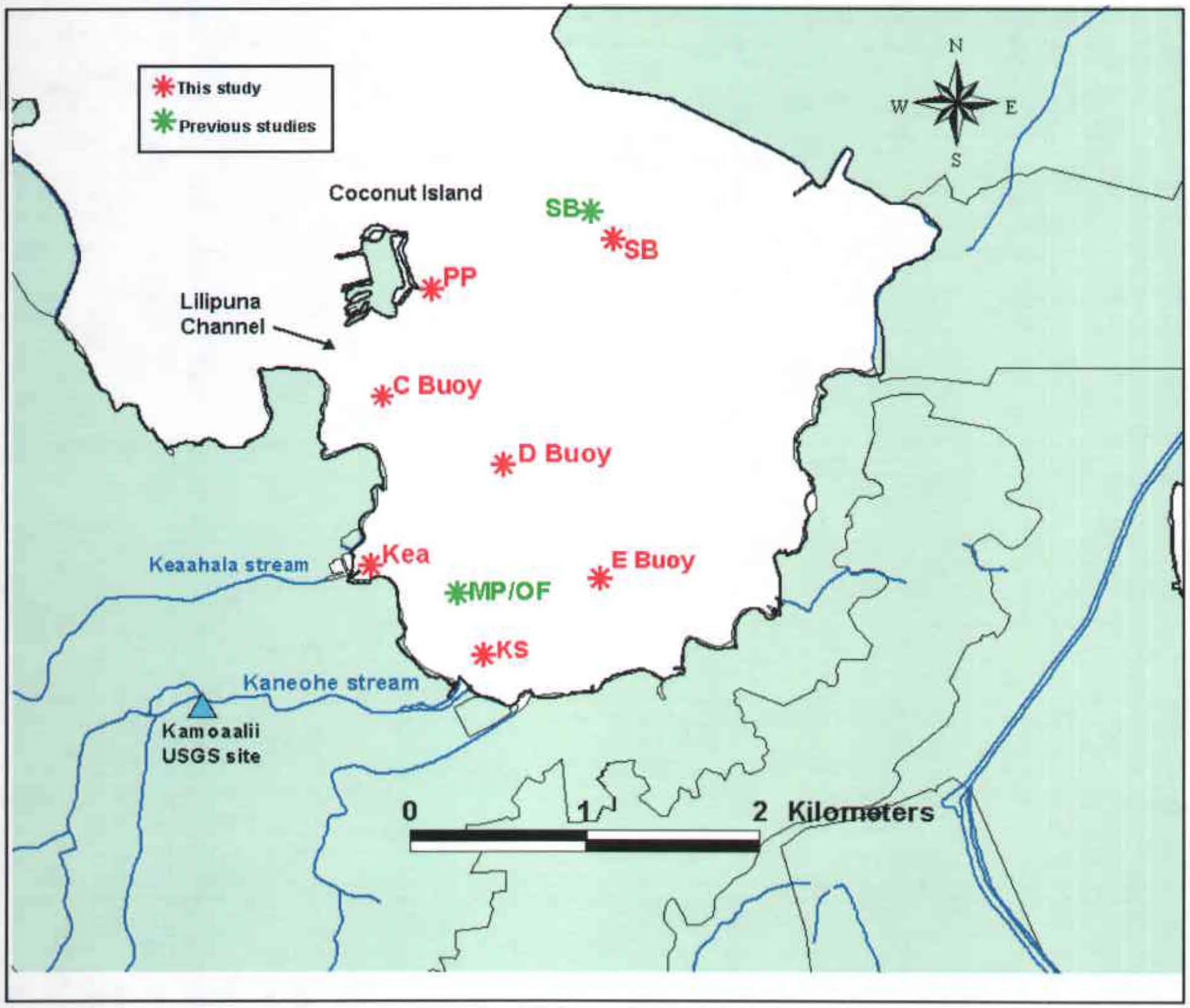


Figure 3.1. Location of sampling and monitoring sites in southern Kaneohe Bay.

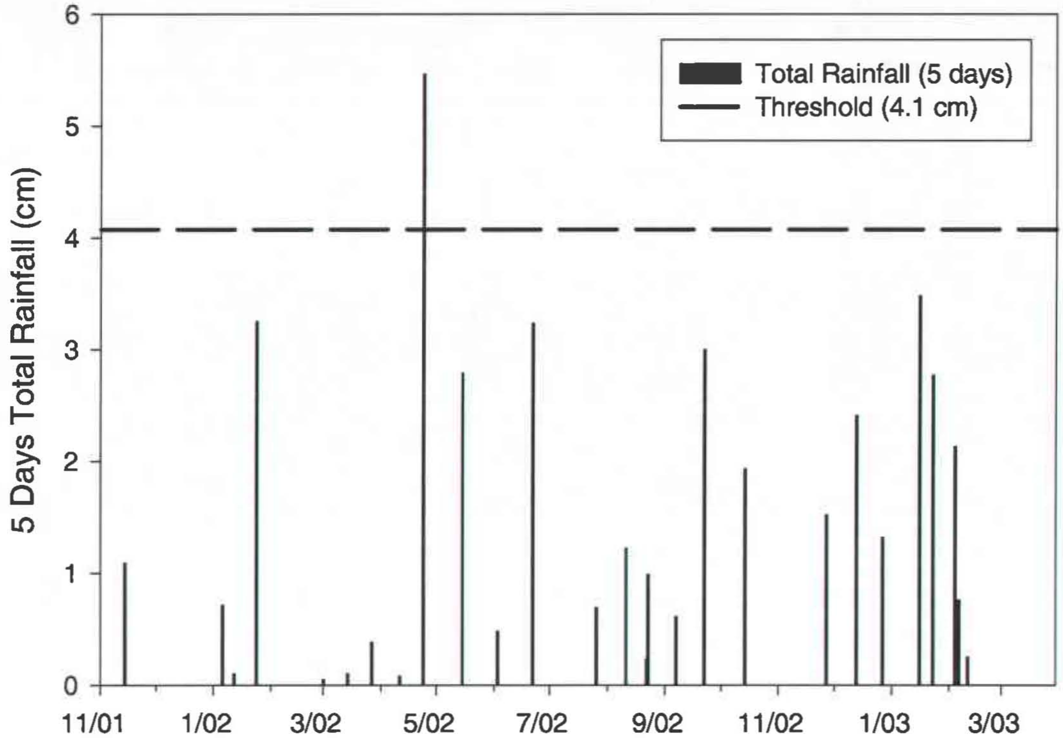


Figure 3.2. Total rainfall for the five days preceding each baseline sampling in southern Kaneohe Bay (N=28). Dashed line represents the total rainfall threshold of 4.1 cm.

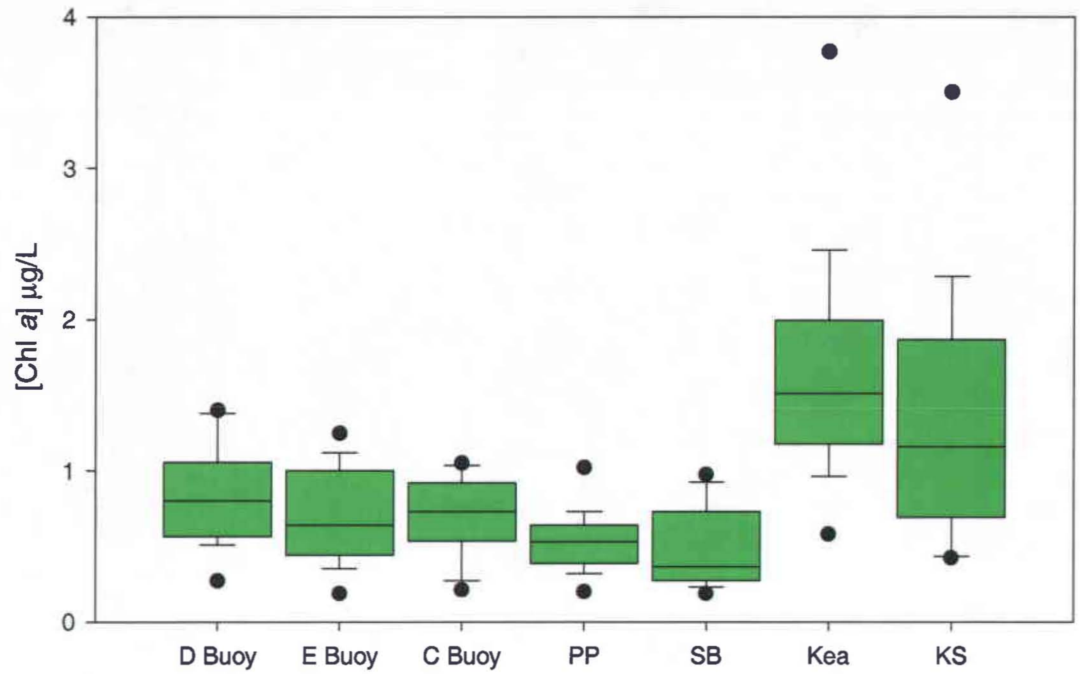


Figure 3.3. Box plots for Chl *a* concentrations for the sites in southern Kaneohe Bay. Lines within the boxes mark the median, the boundaries of the boxes indicate the 25th and the 75th percentiles, the whiskers mark the 10th and 90th percentiles, and the dots correspond to the 5th and 95th percentiles.

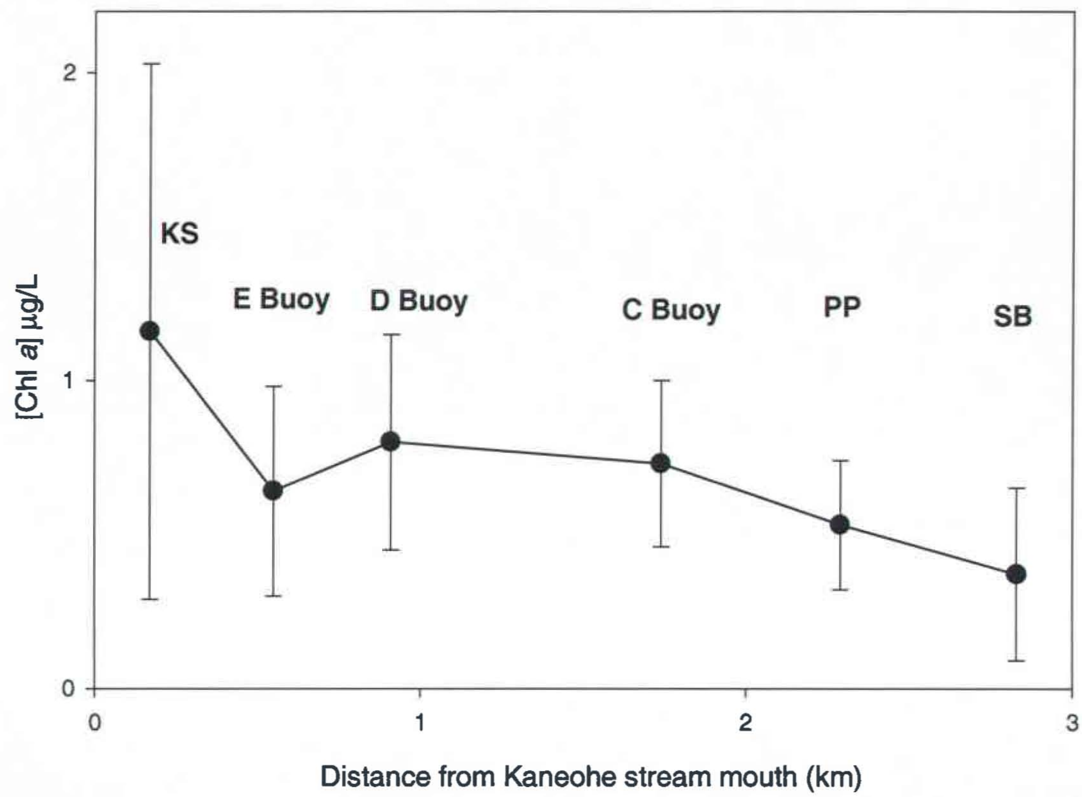


Figure 3.4. Median baseline Chl a concentrations for the sites in southern Kaneohe Bay as a function of the distance from Kaneohe stream mouth. Error bars represent one standard deviation.

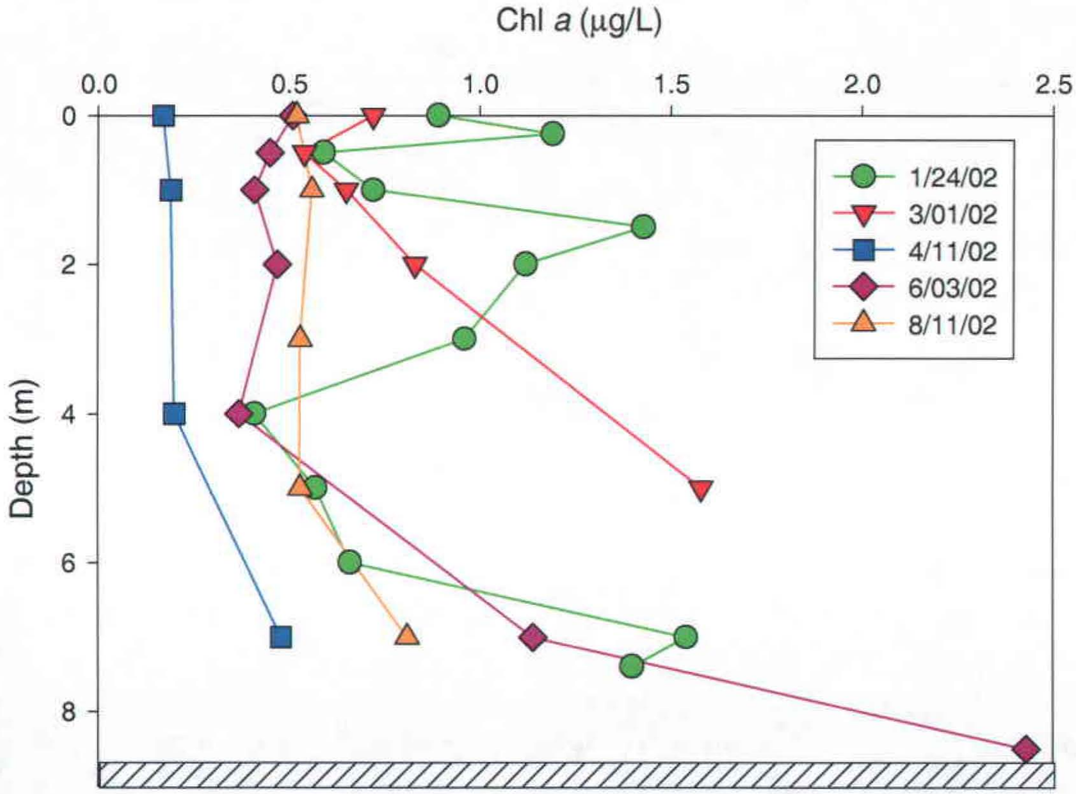


Figure 3.5. Vertical profiles of Chl a concentrations at D Buoy during baseline conditions. Hatchured box represents the bottom of the bay.

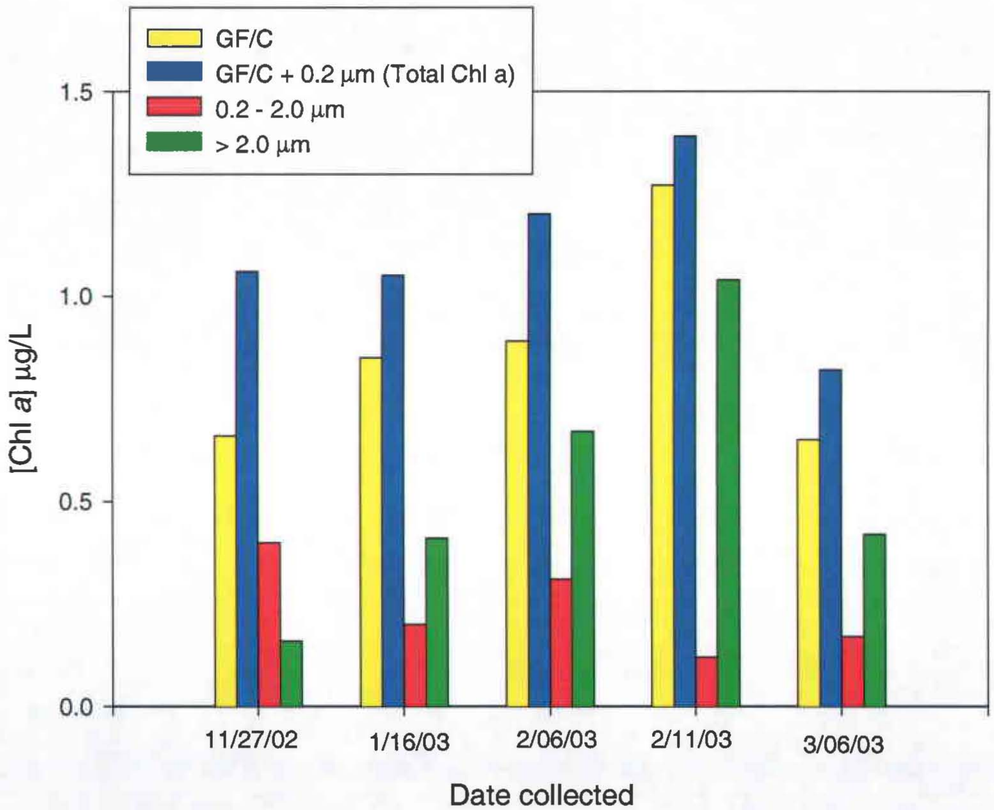


Figure 3.6 Chl *a* size fractionation of surface samples collected at D Buoy. Each set of bars represents Chl *a* concentrations for the same sample filtered through different filter pore sizes.

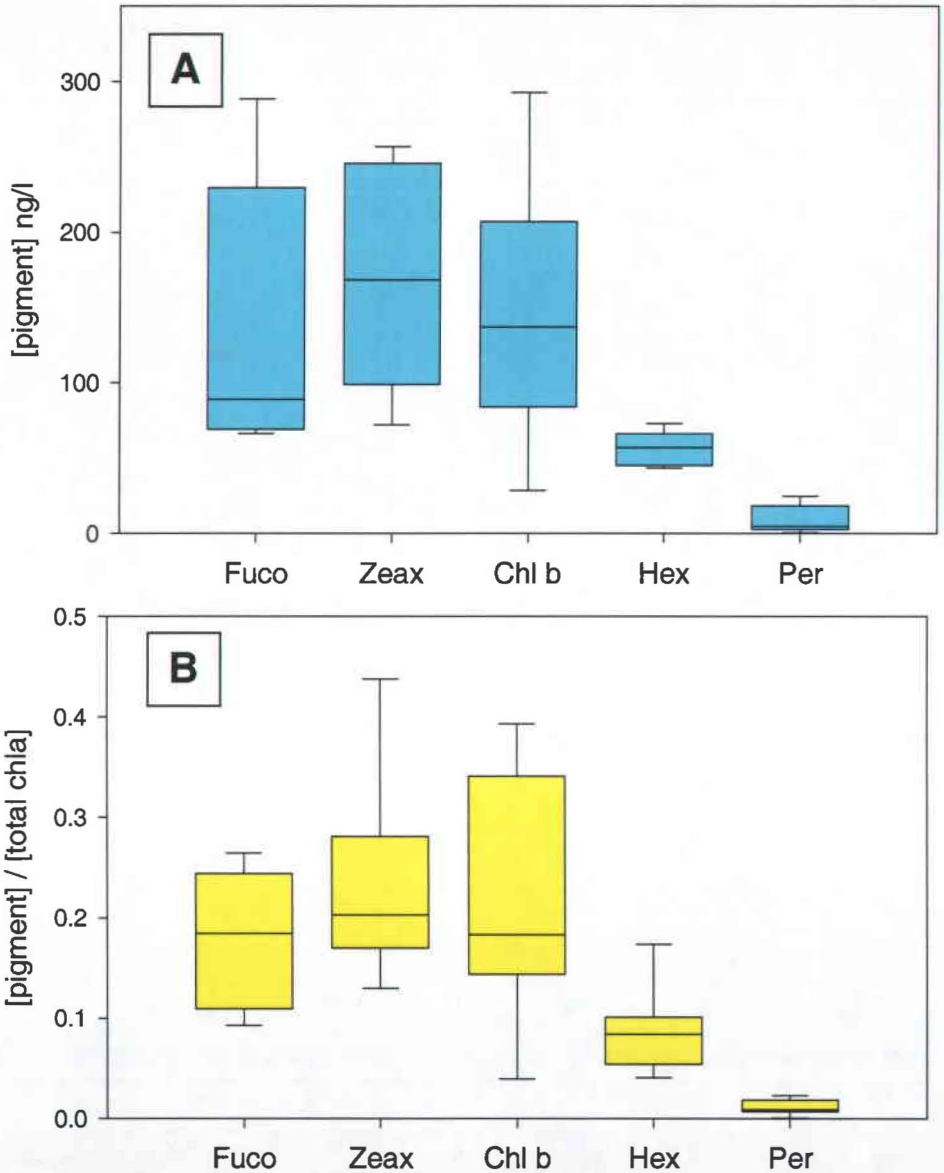


Figure 3.7. Box plots of HPLC pigment data in southern Kaneohe Bay during baseline conditions. (A) Pigment concentrations in ng/l. (B) Pigment concentrations normalized to Chl *a* concentrations. Fuco = Fucoxanthin, Zeax = Zeaxanthin, Chl b = chlorophyll b, Hex = 19'-hexanoyloxyfucoxanthin, Per = Peridinin. Lines within the boxes mark the median, the boundaries of the boxes indicate the 25^{th} and the 75^{th} percentiles, and the whiskers mark the 10^{th} and 90^{th} percentiles.

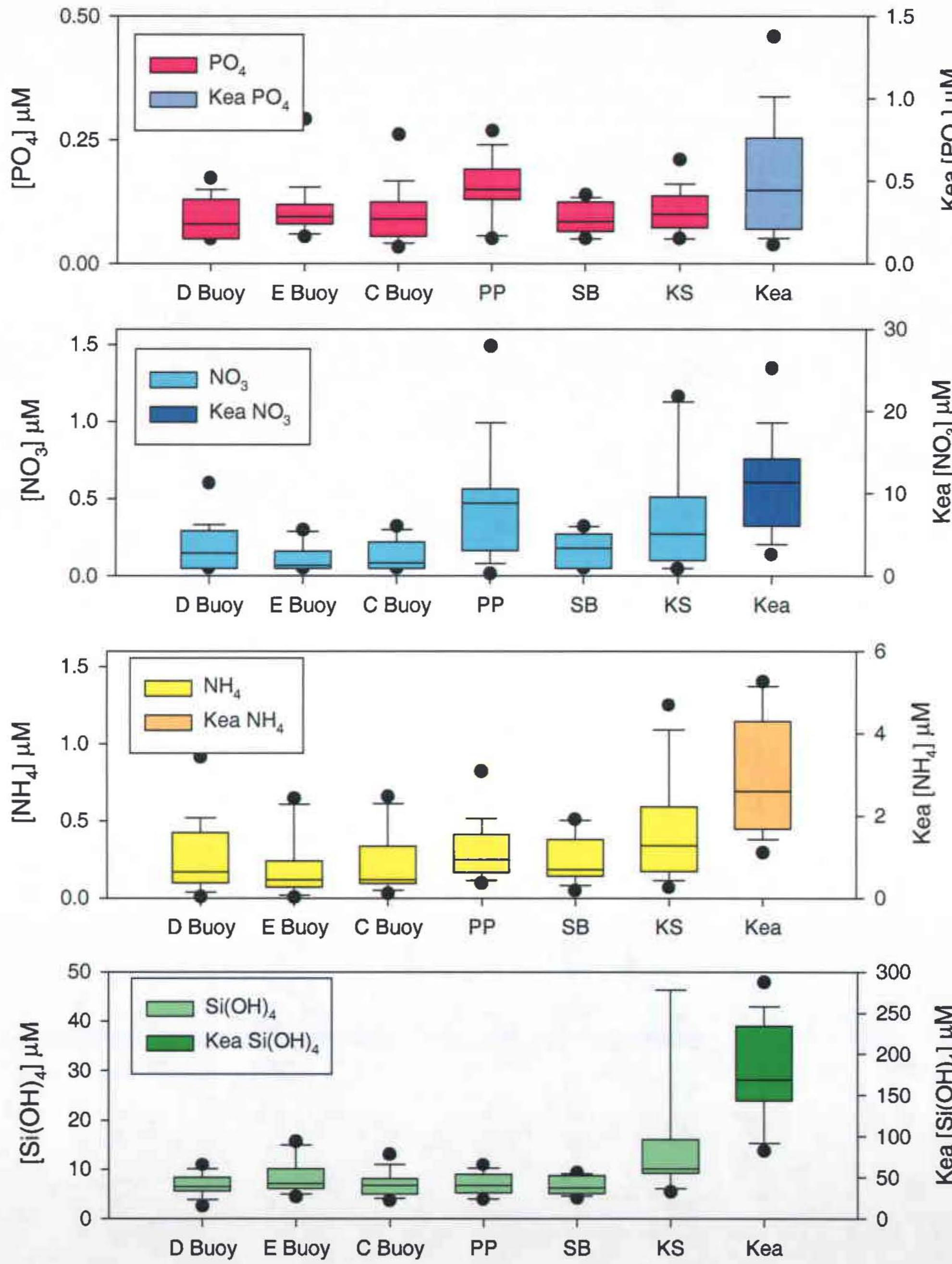


Figure 3.8. Boxplots for surface dissolved inorganic nutrient concentrations at all sites in southern Kaneohe Bay during baseline conditions. Note the different scale for site Kea. Lines within the boxes mark the median, the boundaries of the boxes indicate the 25th and the 75th percentiles, the whiskers mark the 10th and 90th percentiles, and the dots correspond to the 5th and 95th percentiles.

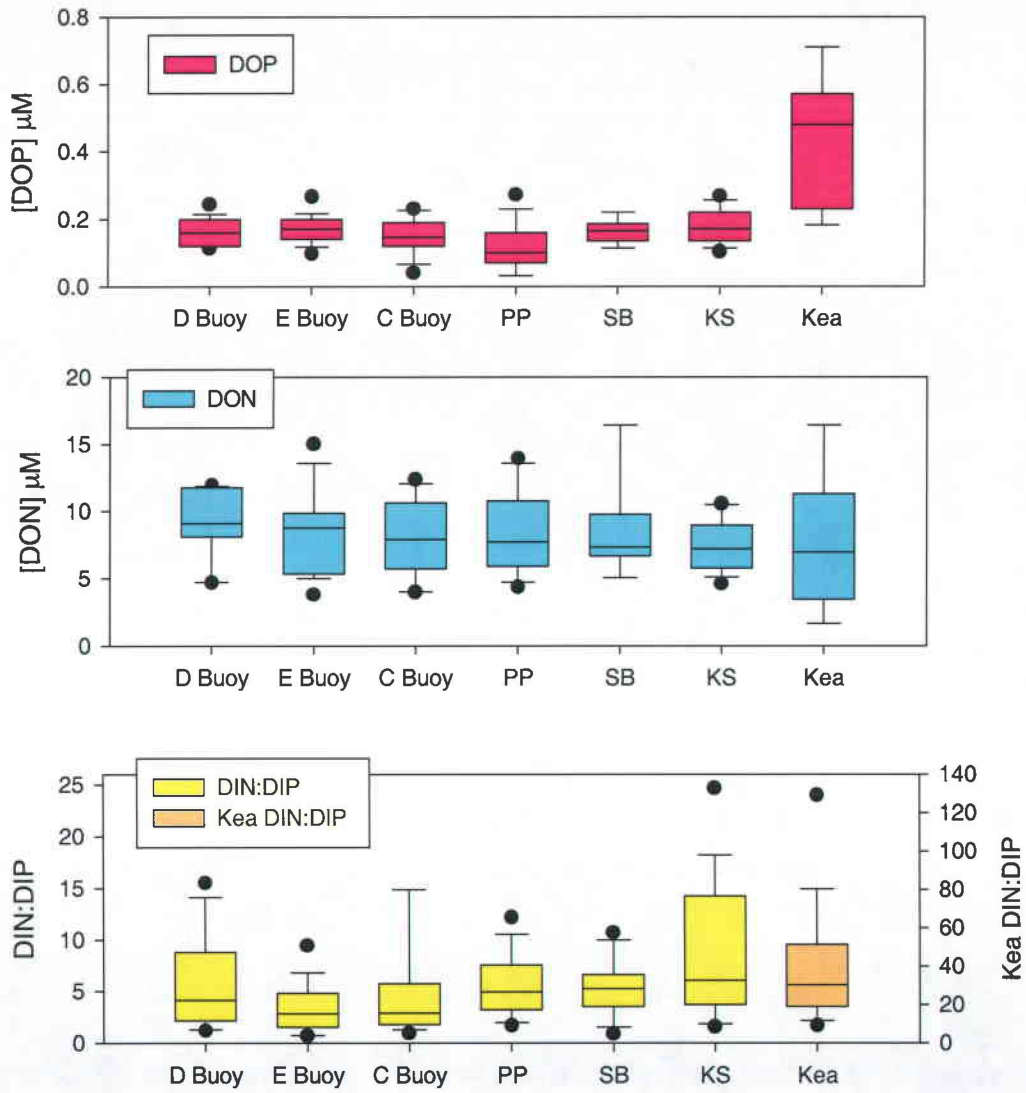


Figure 3.9. Boxplots of dissolved organic nutrients and DIN-to-DIP ratios at all sites in southern Kaneohe Bay during baseline conditions. Note the different DIN:DIP scale for site Kea. Lines within the boxes mark the median, the boundaries of the boxes indicate the 25th and the 75th percentiles, the whiskers mark the 10th and 90th percentiles, and the dots correspond to the 5th and 95th percentiles.

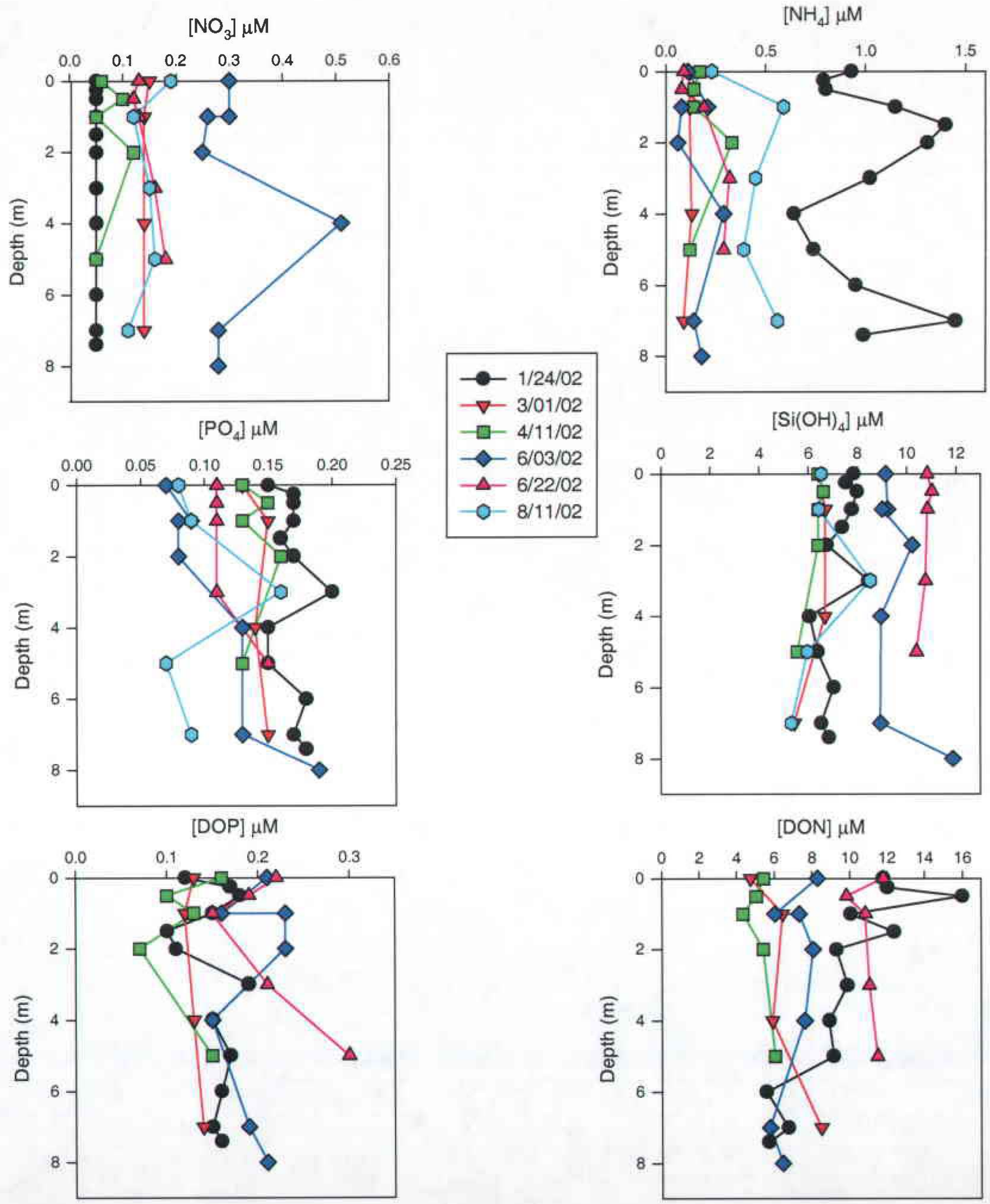


Figure 3.10. Vertical profiles of dissolved nutrient concentrations at D Buoy during baseline conditions. Analytical precision is ± 0.04 μM (error bars were omitted for clarity).

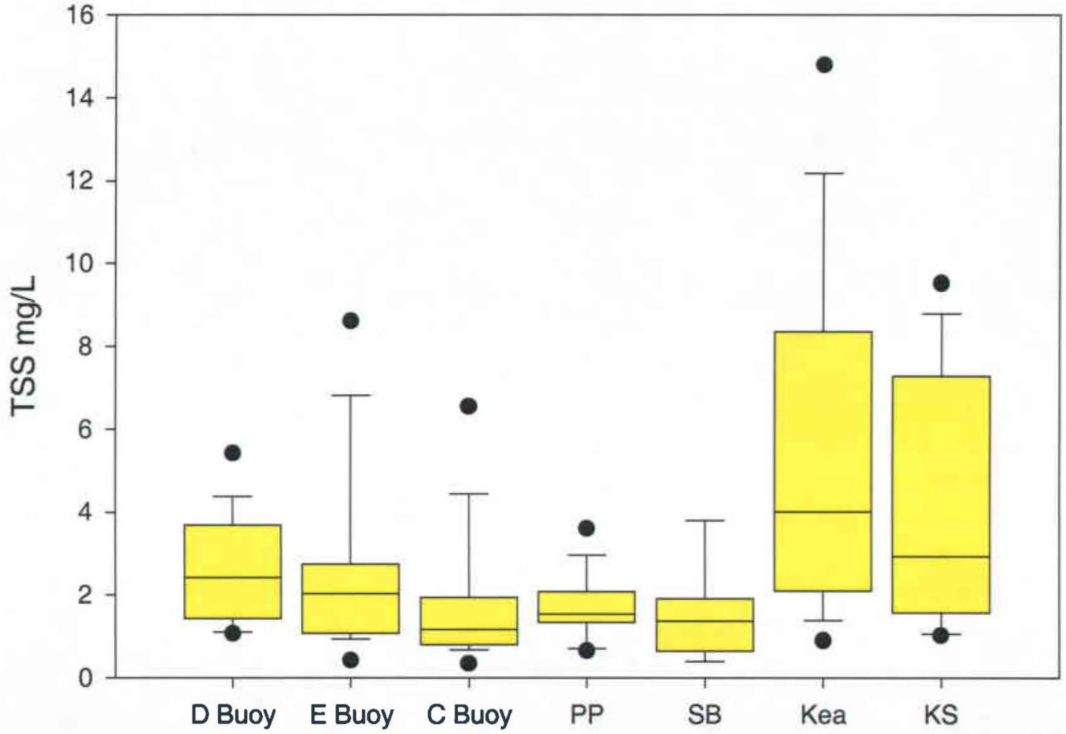


Figure 3.11. Box plots for total suspended solids (TSS) concentrations for the sites in southern Kaneohe Bay. Lines within the boxes mark the median, the boundaries of the boxes indicate the 25th and the 75th percentiles, the whiskers mark the 10th and 90th percentiles, and the dots correspond to the 5th and 95th percentiles.

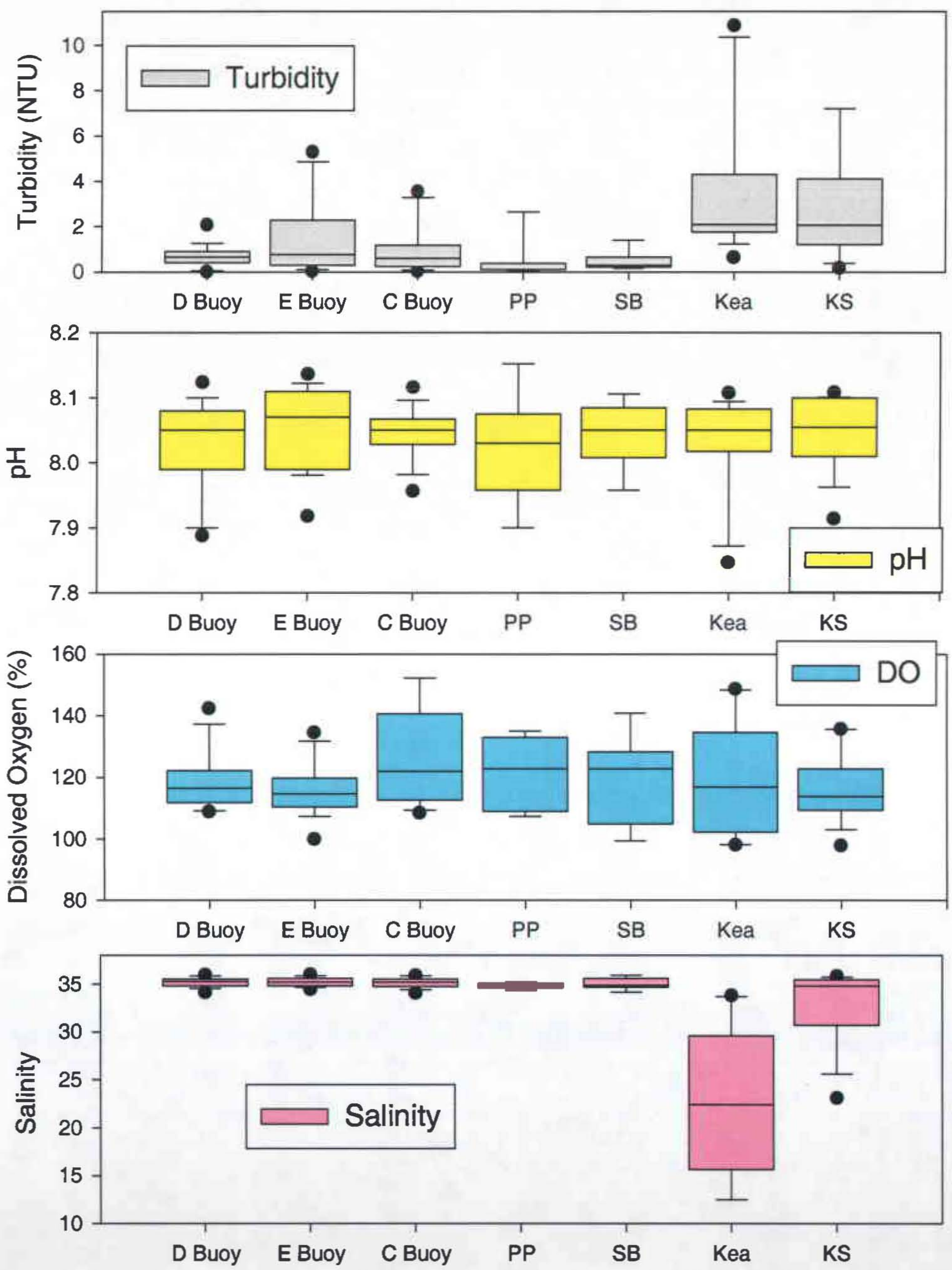


Figure 3.12. Surface YSI measurements of turbidity, pH, dissolved oxygen (DO), and salinity taken during baseline sampling for the period December 2001 – January 2002. Lines within the boxes mark the median, the boundaries of the boxes indicate the 25th and the 75th percentiles, the whiskers mark the 10th and 90th percentiles, and the dots correspond to the 5th and 95th percentiles.

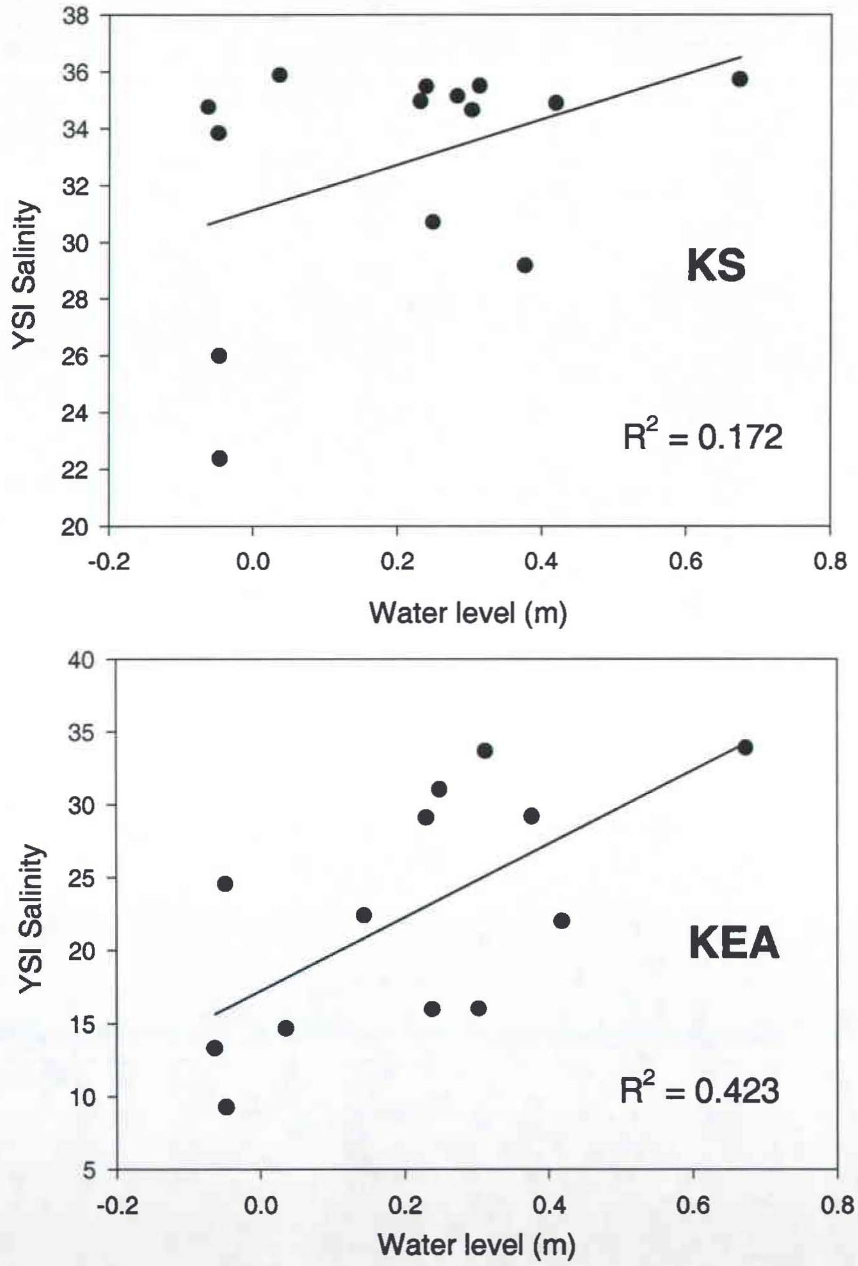


Figure 3.13. Water level versus its corresponding YSI salinity measurement for KS and Kea sites. Water height was recorded at NOAA Mokuoloe station in Kaneohe Bay (# 1612480) relative to the mean lower low water (MLLW).

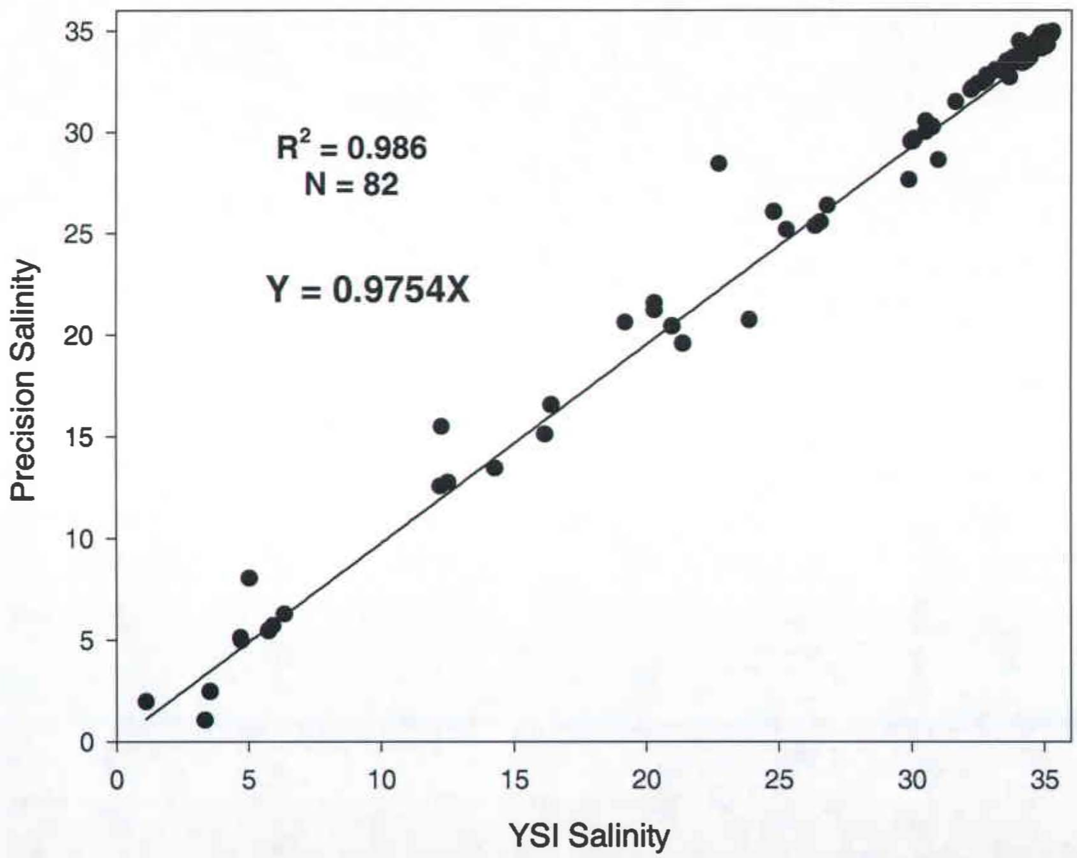


Figure 3.14. Salinity measurements taken with the YSI sonde versus corresponding precision salinity analyses of surface grab samples. Predictive regression was calculated using the software SigmaPlot 2000, with the constraint y(0)=0.

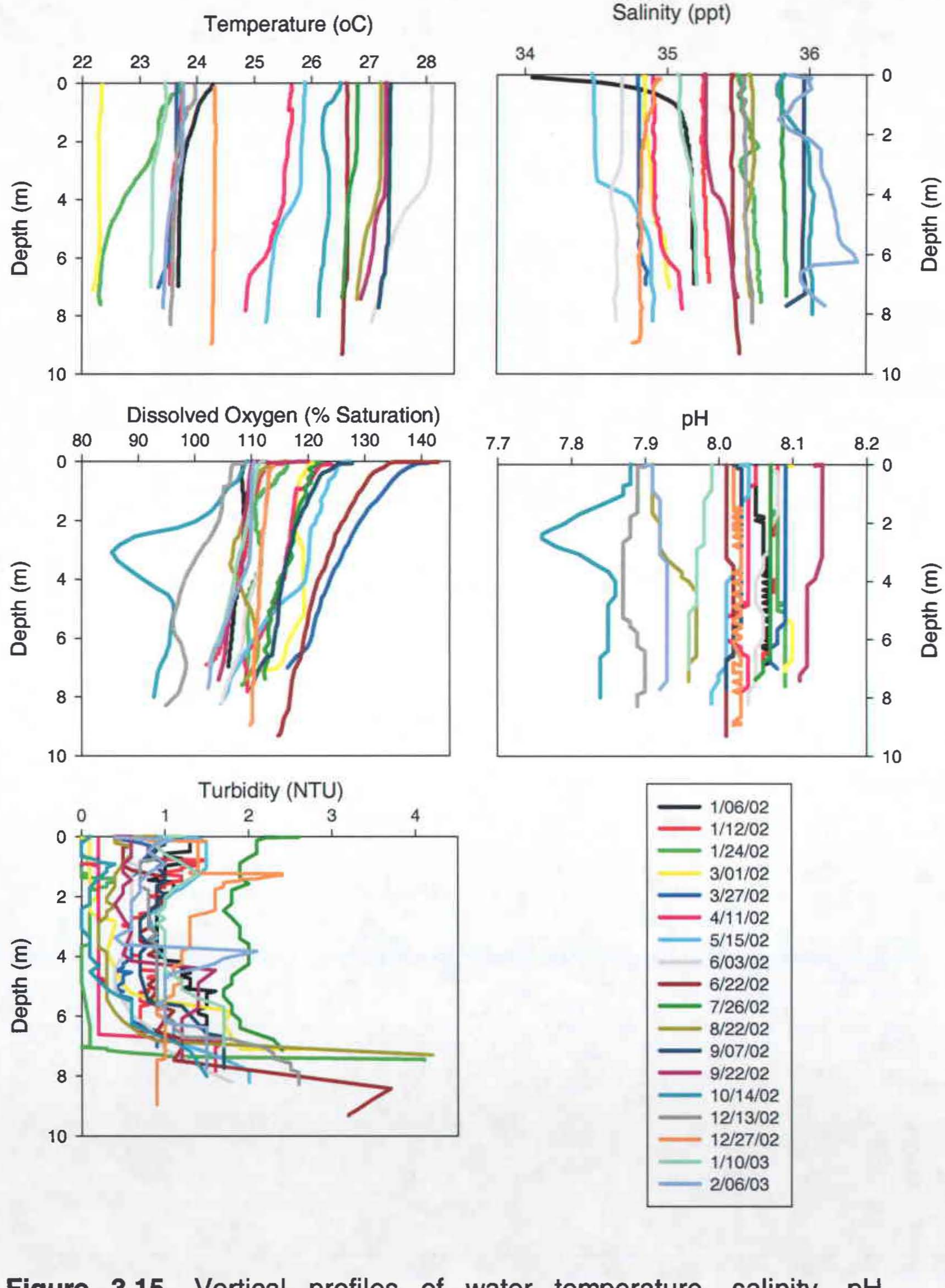


Figure 3.15. Vertical profiles of water temperature, salinity, pH, dissolved oxygen and turbidity at D Buoy during baseline conditions for the period of January 2002 – February 2003.

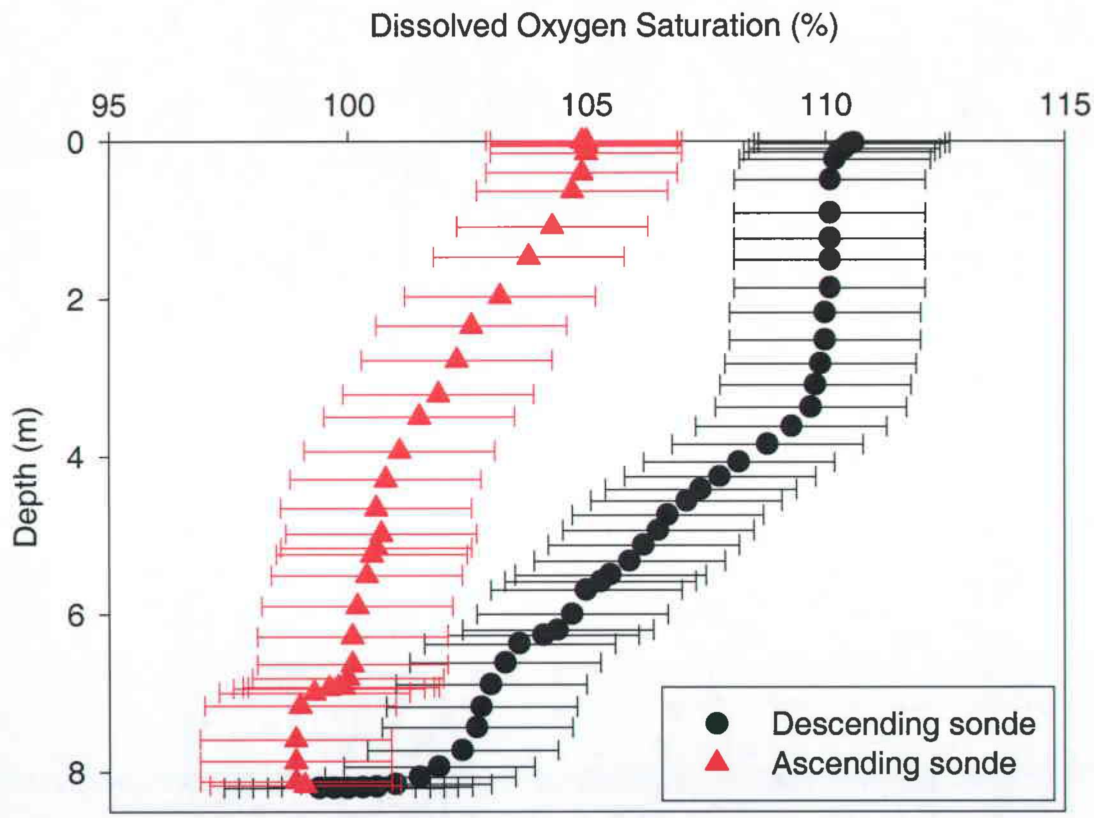


Figure 3.16. Dissolved oxygen saturation profile measured with the YSI sonde at D Buoy on 2/06/03. Black dots represent the DO values recorded while the sonde descends. Red triangles represent the DO values recorded while the sonde ascends. Error bars correspond to the accuracy as reported by the manufacturer (2%).

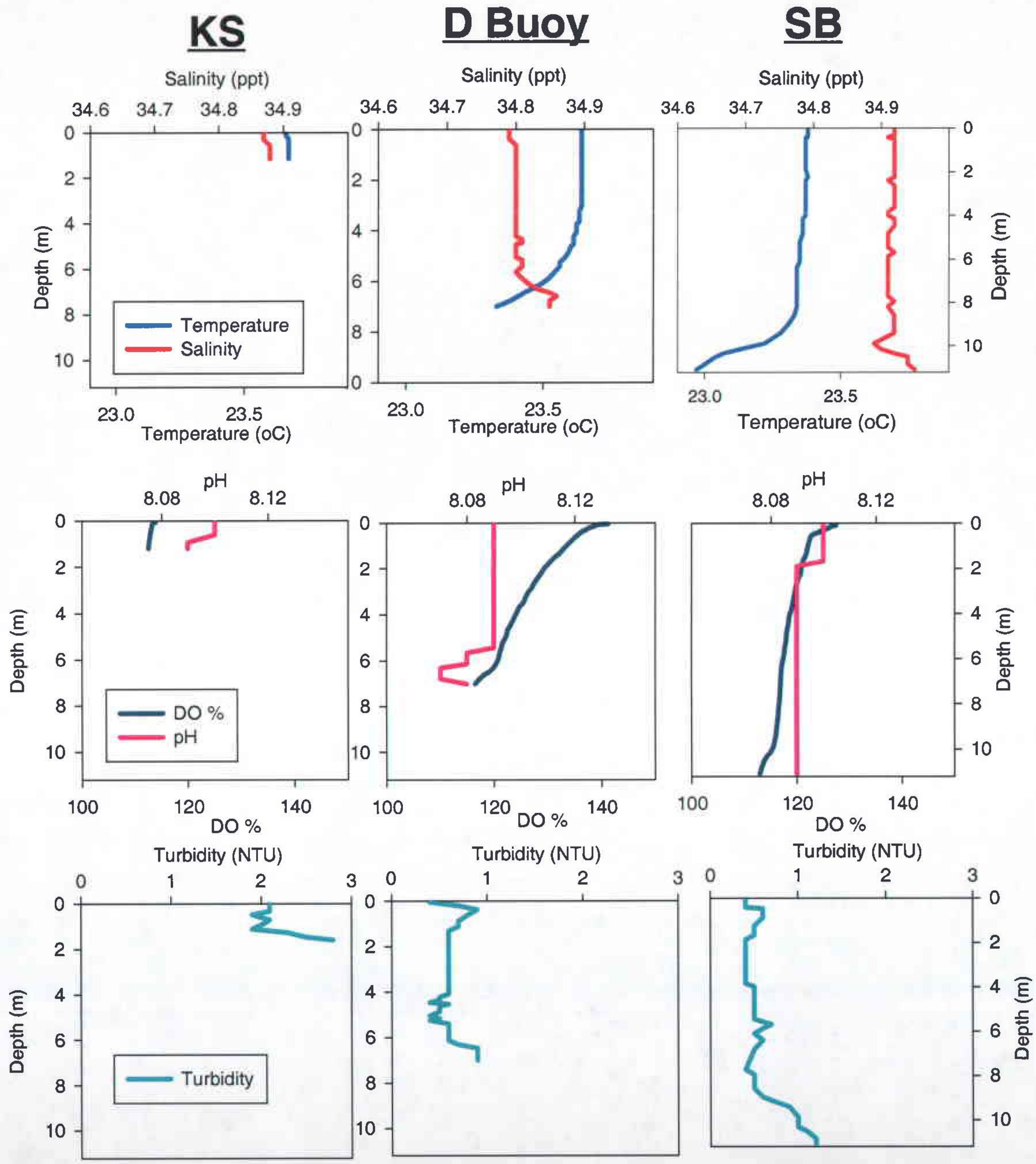
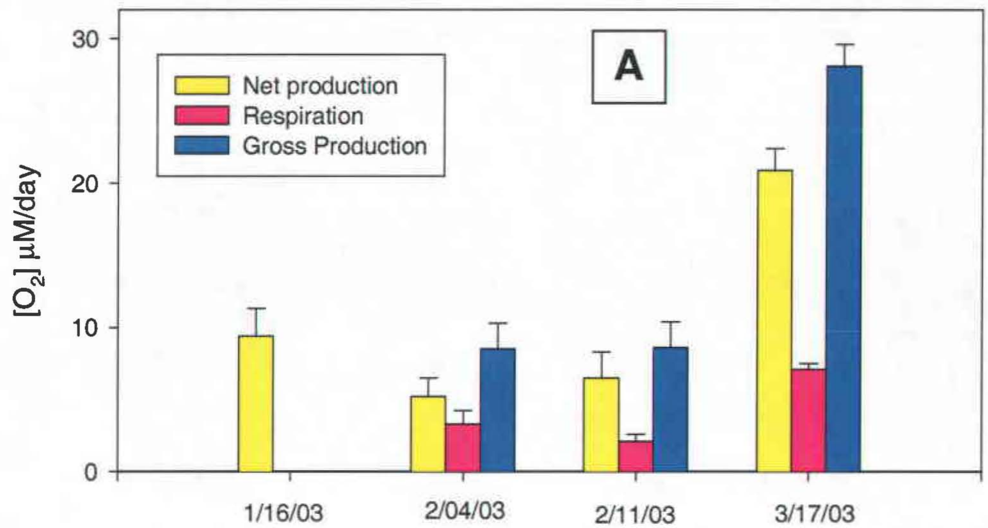


Figure 3.17. Vertical profiles of YSI measurements for KS, D Buoy and SB sites taken during baseline sampling on 3/27/02. The first column corresponds to the parameters for KS, the second column for D Buoy, and the third column for SB. The scales used are the same for all sites.



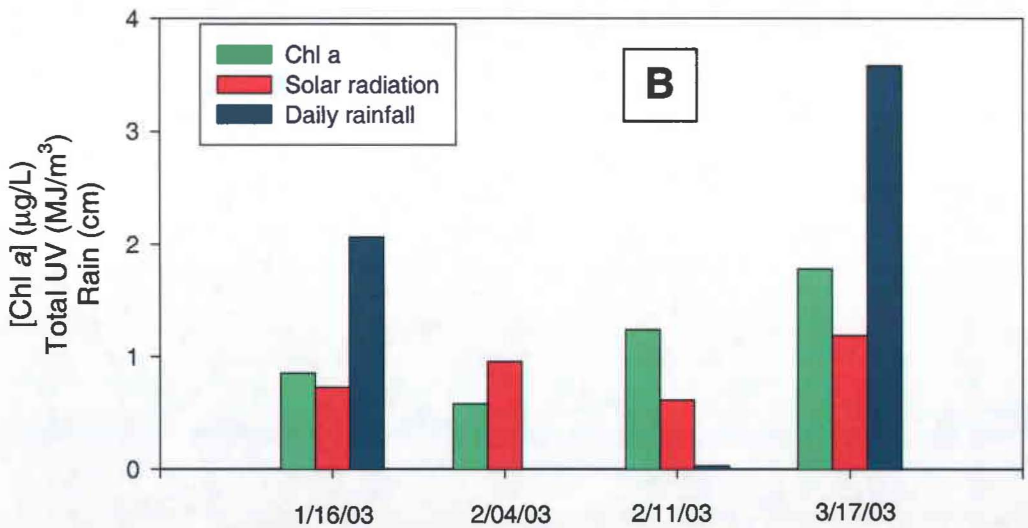


Figure 3.18. (A) Daily primary production rates measured at D Buoy on four different days. Respiration rates are not available for the incubation carried out on 1/16/03. Number of replicates is no less than 3 for each set. The error bar corresponds to one standard deviation between the replicates. **(B)** Chl *a* concentrations and meteorological parameters for the corresponding dates. Chl *a* corresponds to the concentrations at the start of the incubation, solar radiation is for the time of incubation, and the daily rainfall is the total precipitation for the day preceding the incubation.

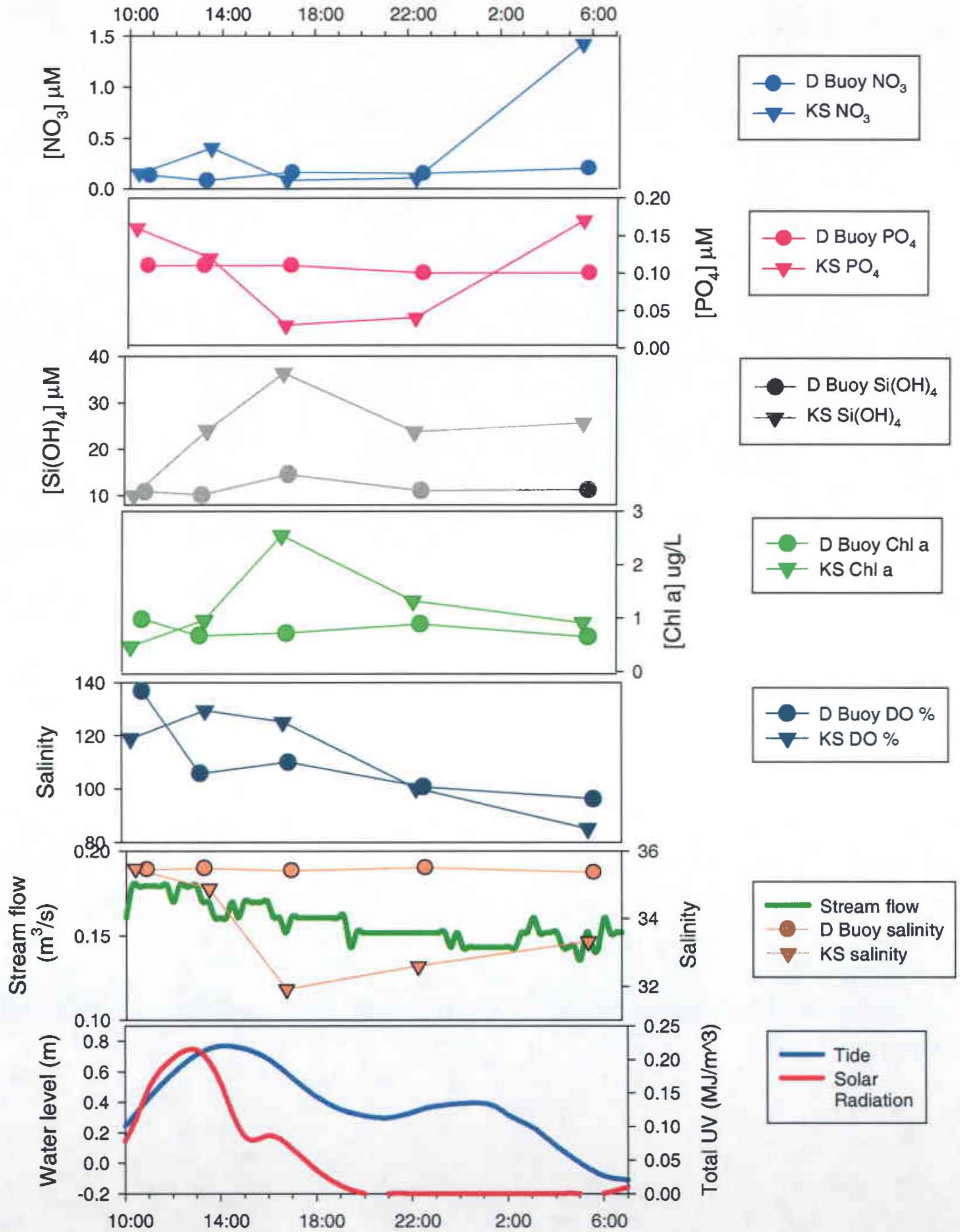


Figure 3.19. Grab sampling and YSI parameter surface water data for the sampling performed on 6/22/02-6/23/02. Samples were collected five times at D Buoy and KS sites over a 21-hr period. Tide and solar radiation data are from the HIMB meteorological station (Coconut Island) and stream flow data are from the USGS Kamooalii stream station located in the upper branch of Kaneohe stream.

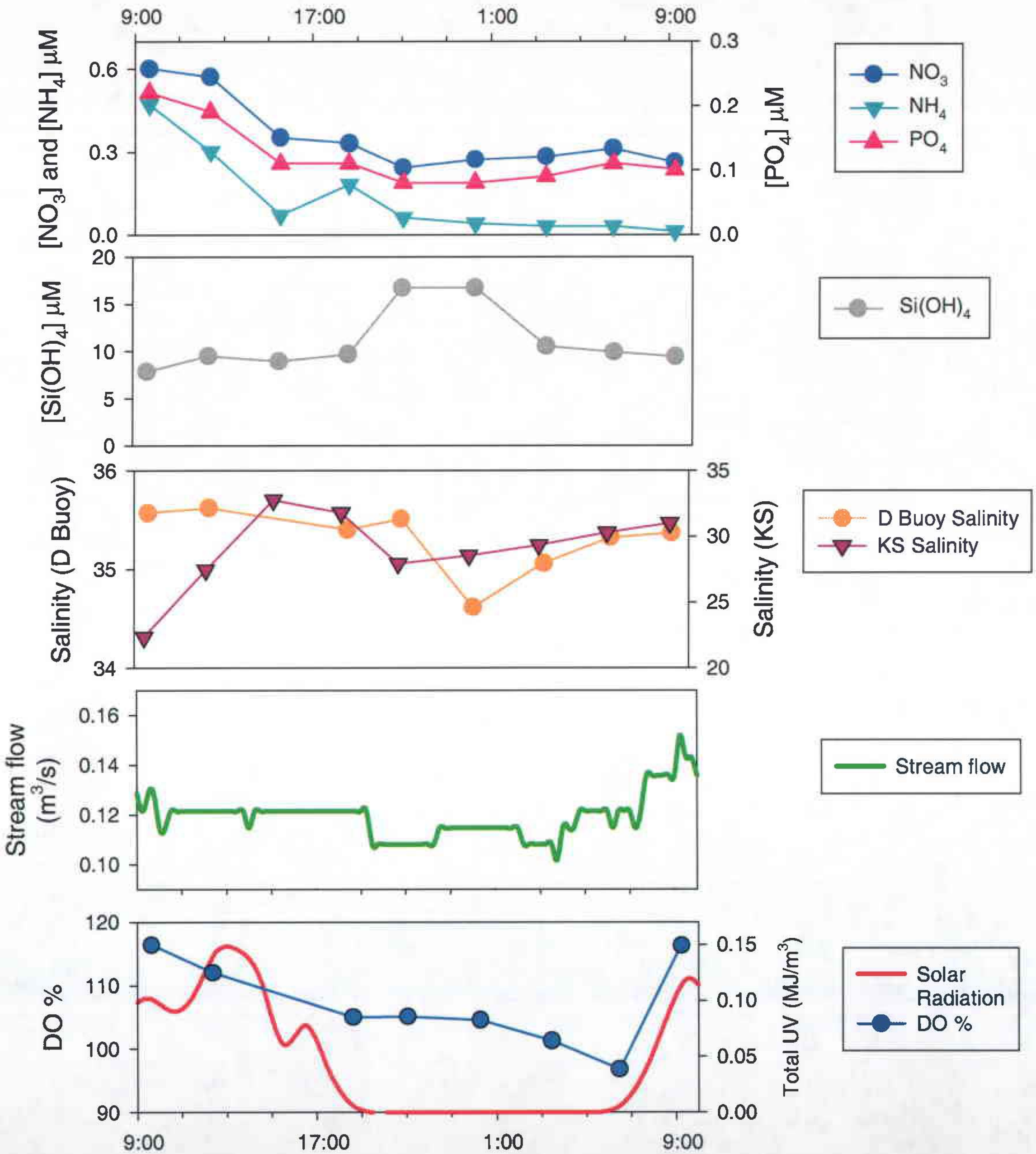


Figure 3.20. Grab sampling and YSI parameter surface water data at D Buoy for the sampling performed on 8/22/02-8/23/02. Samples were collected eight times over a 24-hr period. Rainfall and solar radiation data are from the HIMB meteorological station (Coconut Island) and stream flow data are from the USGS Kamooalii stream station located in the upper branch of Kaneohe stream.

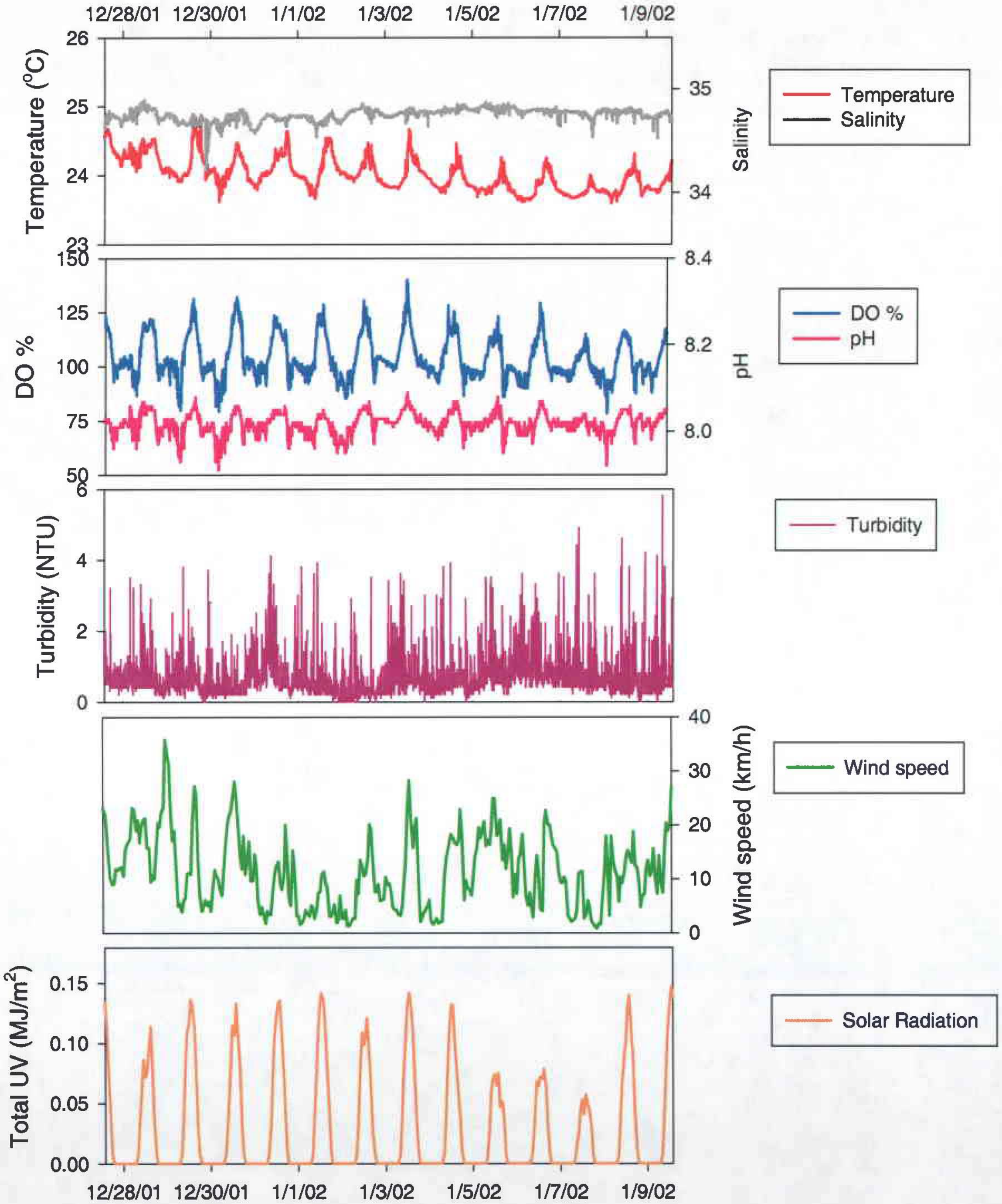


Figure 3.21. YSI sonde deployment at site Point Pier (PP) during baseline conditions from 12/27/01 to 1/10/02. Measurements were recorded at 5-minute intervals. Hourly wind speed and solar radiation data were obtained from the meteorological station located at HIMB.

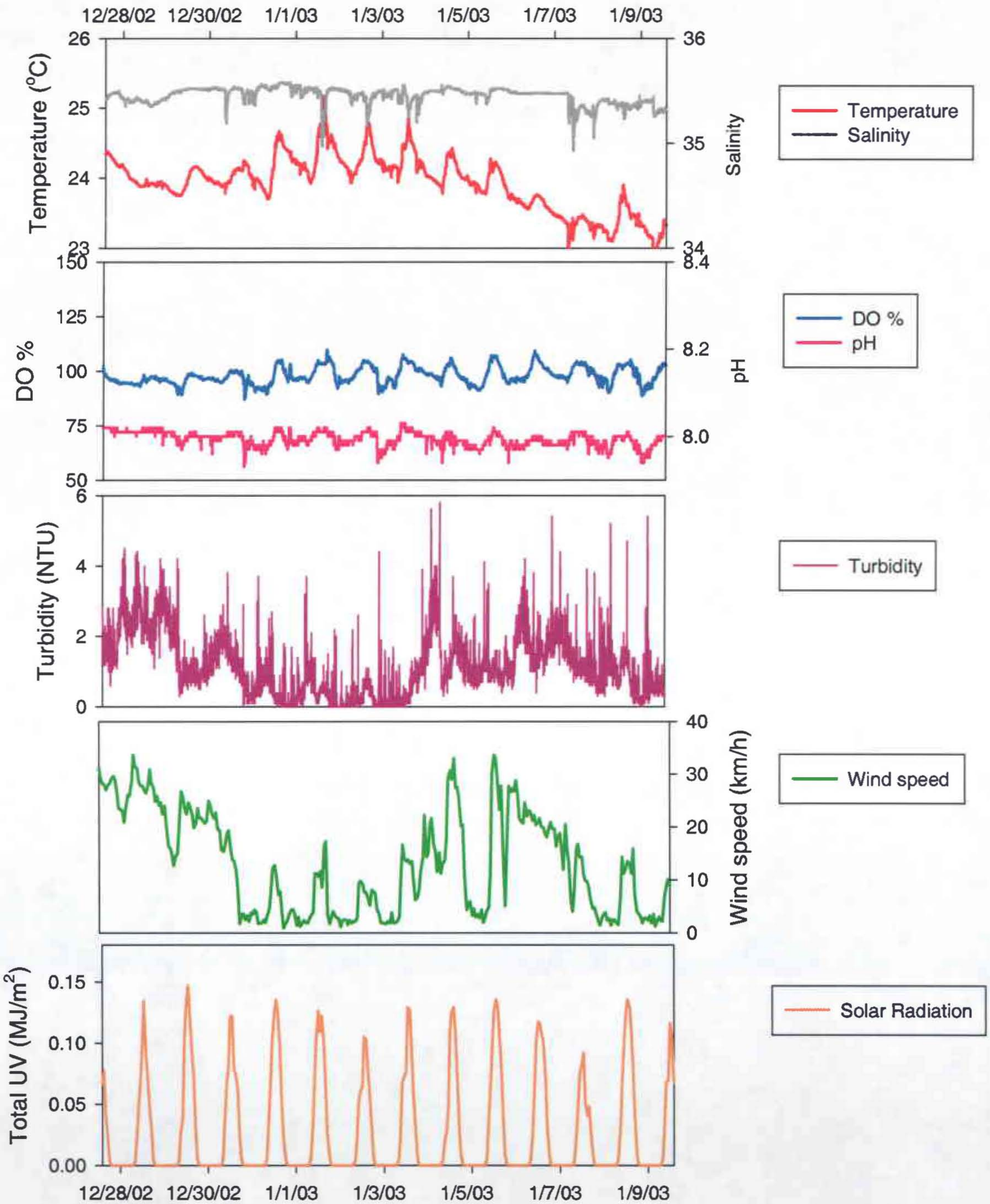


Figure 3.22. YSI sonde deployment at site D Buoy during baseline conditions from 12/27/02 to 1/10/03. Measurements were recorded at 5-minute intervals. Hourly wind speed and solar radiation data were obtained from the meteorological station located at HIMB.

CHAPTER 4 : IMPACTS OF STORM RUNOFF EVENTS IN SOUTHERN KANEOHE BAY

4.1 Introduction

The primary goal of this study was to characterize the biogeochemical impacts of storm runoff in southern Kaneohe Bay relative to the baseline conditions described in Chapter 3. Unfortunately, precipitation in the Hawaiian Islands was unusually low during the period of study (November 2001 to February 2003) due to the drought Oahu has been experiencing since 2000 (Commission of Water Resource Management, State of Hawaii, http://www.state.hi.us/dlnr/cwrm/drought/). Nevertheless, daily rainfall exceeded the sampling threshold of 5.1 cm a few times during the study (Figure 4.1), and sampling was carried out during five runoff events. Because of the variability of precipitation, stream discharge, ground saturation state and meteorological conditions among the events, results for each runoff episode are first described separately. This presentation is followed by a discussion that synthesizes data from events sampled in this study and selected historical storm events in Kaneohe Bay.

4.2 Results

4.2.1 November 2001 Storm Event

The first storm event for the period of study occurred during a Kona low that developed on 27 November 2001. Several hydrological studies have emphasized the importance of antecedent soil moisture conditions on runoff generation (Van Dijk and Kwaad, 1996; Brown et al., 1999; Dykes and Thornes, 2000). As a rough estimate of the relative ground saturation state between runoff events, the number of days with less than 2.54 cm (1 inch) total rainfall preceding each episode was calculated. The number of "dry" days preceding this event was 20. Because sampling sites had not yet been selected prior to this event, the November 2001 storm is only discussed briefly.

The highest daily rainfall during this episode was recorded on 27 November 2001, with 9.42 cm recorded at the Luluku rain gage. Five-days total precipitation for this event was 13.68 cm. Southwest and southeast winds typically associated with Kona lows were light to moderate, averaging about 17.7 km/h. Sampling was carried out three times following this event: on November 27, 29 and 30 (Figure 4.2). Boundaries of the freshwater plume were visible on the first day of the event but were not mapped. On 29 November, northeasterly trade winds returned and there was no further observable evidence of runoff.

YSI profiles were taken on 27 November in the middle of the freshwater plume and selected parameters are shown in Figure 4.3. The GPS coordinates for this site, called "mid-plume", were close to the location of E Buoy, suggesting that the plume was spreading eastward in the southern basin rather than following the typical course through the Lilipuna Channel described by Kimmerer et al. (1981). The cooler freshwater layer at mid-plume was only approximately 25 cm in thickness. Turbidity was high near the surface (up to 38 NTU) and turbidity values greater than 2 NTU extended to a depth of about one meter, suggesting that suspended sediments were sinking out of the freshwater layer. The dissolved oxygen profile indicates an area of undersaturation around 50 cm depth, which most likely reflects oxygen consumption due to high biological oxygen demand (BOD) associated with sinking land-derived organic material. YSI profiles for the same parameters were also taken at D Buoy on 27 and 30 November (Figure 4.4). Near surface salinities were not as high at D Buoy as at the mid-plume site, but there was still evidence of freshwater runoff. The impacted surface layer extended to about a depth of 1.3 m, with an average salinity of 32.65 and a temperature approximately 0.5 ^{0}C cooler than that of deeper waters. Dissolved oxygen was undersaturated throughout the water column, with saturation values as low as 86% observed at a depth of about 5 meters. Turbidity levels were only about 1 NTU higher than baseline conditions. On 30 November, depth profiles for all parameters were typical of the baseline conditions described in

Chapter 3, suggesting that the physical parameters in southern Kaneohe Bay returned to normal values within three days after the runoff event.

Dissolved nutrient concentrations in surface water following the runoff event for the Mid-plume and D Buoy sites are shown in Figure 4.5. On 27 November, NO_3^- concentrations were significantly higher than baseline values, with more than a 30-fold increase observed at D Buoy. PO_4^{3-} and $Si(OH)_4$ concentrations were also elevated, with approximately a 3-fold increase for PO_4^{3-} and a 5-fold increase for $Si(OH)_4$ at D Buoy relative to baseline values. Because of the larger NO_3^- loading relative to PO_4^{3-}, ratios of DIN to DIP were increased relative to baseline values and were close to the Redfield ratio of 16. Two days after the runoff event, NO_3^- and PO_4^{3-} concentrations were significantly lower. However, for both D Buoy and Mid-plume sites, PO_4^{3-} was depleted more efficiently than NO_3^- and DIN:DIP ratios remained above the baseline ratio. $Si(OH)_4$ concentrations were below average baseline levels. $Si(OH)_4$ removal is likely due to diatom uptake, but because there are no Chl *a* data available for this event, this hypothesis cannot be verified from just these data alone.

4.2.2 January 2002 Storm Event

The storm event that occurred in late January 2002 was noteworthy because of the occurrence of two distinct weather systems within a short period of time. An upper level trough southwest of the state began to affect island weather on 24 January 2002 and was associated with moderate trade winds. Orographically anchored heavy showers developed during the late afternoon of 26 January over the windward slopes of Oahu, resulting in a total daily rainfall of 8.51 cm measured at Luluku rain gage on 27 January. Subsequently, a Kona low that developed west of Kauai brought heavy rains across the state from 28 to 30 January 2002 and was accompanied by moderate southeasterly winds. The heaviest rainfall occurred on 29 January with a daily total of 8.92 cm recorded at Luluku rain gage. Five-days total precipitation for this event was 20.41 cm. The number of "dry" days prior to this event (less than 2.5 cm of rain per day) was 29.

Sampling was carried out five times over a week from 1/24/02-2/01/02 (Figure 4.6). Each rainstorm resulted in a distinct peak in the Kaneohe stream hydrograph, with a maximum stream flow of 8.02 m^3/s recorded for both events. No evidence of a freshwater plume was observed on 27 January, but the plume boundaries were clearly visible on 29 January (Figure 4.7). Because the amount of soil material leached is often a function of the ground saturation state (Hubertz and Cahoon, 1999), it is likely that this is the reason why no storm plume was observed on 27 January. Another possible explanation is the time of sampling relative to the peak in water discharge. Sampling was carried out 16 hours after the peak on 27 January while the freshwater plume was observed 2 hours after the maximum stream flow on 29 January. In addition, the advection of the storm plume through the Lilipuna Channel might have been hampered by the northerly component of the winds (23^{o}) prevailing during the early morning of 29 January.

YSI profiles were taken four times during this event at all sampling sites and selected parameters recorded at D Buoy are shown in Figure 4.8. Surface salinity values on 27 January 2002 were within the range of those from baseline conditions, suggesting again that the effects of runoff were minor at the time of sampling. On 29 January, the cooler surface layer diluted by freshwater extended down to a depth of about 0.8 m, with an average salinity of 24.5. Turbidity values were as high as 34 NTU near the surface and 10 NTU at a depth of 5 meters, suggesting that suspended sediments were sinking out of the runoff plume. Total suspended solid (TSS) concentrations in surface waters were typical of baseline values on 27 January (0.9 mg/l), but were significantly higher on 29 January (18.5 mg/l). On 30 January, salinity, temperature and turbidity profiles had nearly returned to baseline conditions, except for a slight salinity depression in the upper meter of the water column. Undersaturated concentrations of dissolved oxygen observed throughout the water column on 30 January indicate that either net primary productivity was inhibited, or that the biological oxygen demand associated with runoff waters was high, or a combination of both.

Dissolved nutrient and Chl *a* concentrations in surface waters following runoff at site D Buoy are shown in Figure 4.9. Nutrient concentrations were not significantly different from baseline values on 27 January, implying that the freshwater plume was rapidly diluted or carried offshore. On 29 January, all dissolved nutrient concentrations were significantly increased, with NO_3^-, PO_4^{3-} and $Si(OH)_4$ reaching concentrations of 12.39 µM, 0.79 µM and 75.56 µM, respectively. The DIN to DIP ratio of 18 observed on 29 January implies greater nitrogen than phosphorus loading in the bay. One day later, surface nutrient concentrations were much lower, but still slightly above baseline values. The prevailing southeast winds (average direction of 125^0) most likely caused the storm plume to flow through the Lilipuna Channel (Kimmerer et al., 1981). Typical moderate trade winds were reestablished on 31 January, and surface nutrient concentrations returned to baseline values by 1 February, only three days after the second runoff episode. Chl *a* concentrations remained near or below baseline values during this event, suggesting that phytoplankton did not respond rapidly to the nutrient loading on the timescale of sampling. It appears that nutrients did not remain in the southern basin long enough for significant biological uptake to occur, or that increased algal growth occurred shortly after the last day of sampling.

Ratios of the dissolved nutrient and Chl *a* concentrations during the storm event relative to the baseline concentrations are shown for all sites in

Figures 4.10 and 4.11. For all sites located within the freshwater plume observed on 29 January, the increase in runoff concentrations relative to baseline was greater for NO_3^- than for other nutrients, up to two orders of magnitude above pre-storm concentrations. On 30 January, surface NO_3^- concentrations at all bay sites were still significantly elevated relative to baseline, while surface PO_4^{3-} and $Si(OH)_4$ concentrations were nearer their baseline values. Interestingly, DON concentrations at the bay sites on 29 January were not significantly different from baseline conditions, while DOP concentrations were only slightly higher. These observations suggest that storm runoff is probably not a significant source of dissolved organic nutrients for southern Kaneohe Bay. At all sites, Chl *a* concentrations on 30 January were notably lower than baseline levels. High turbidity levels observed on 29 January may have inhibited primary productivity, resulting in a decrease in phytoplankton biomass. The undersaturated dissolved oxygen values observed in the southern basin on 30 January (Figure 4.8) also suggest that net community productivity was lower than normal.

4.2.3 May 2002 Storm Event

A strong upper level trough during the first week of May 2002 produced intense thundershowers over the Koolau Range of Oahu. Winds associated with this weather system were variable, switching from moderate trades to light southwesterly winds. Total daily rainfall recorded at Luluku rain gage for

6 May was 19.89 cm, and the five-days total precipitation for this event was 27.13 cm. The number of "dry" days preceding the event was 12.

Sampling was carried out eight times during the period of 5/06/02-5/15/02 (Figure 4.12). On the afternoon of 6 May, water in southern Kaneohe Bay was very turbid, and the freshwater plume was so large that it extended beyond Coconut Island (Figure 4.13). At that time, the winds were light and the plume was traveling eastward instead of the typical westward flow through the Lilipuna Channel. The maximum stream flow of 21.47 m^3/s for Kaneohe stream was recorded on the night of 6 May. Moderate trades were reestablished early on 7 May, causing the runoff plume to flow towards the Lilipuna Channel. The margins of the plume were discernible on the morning of 7 May as shown in Figure 4.13.

YSI profiles were taken at D Buoy on eight occasions during this event and selected parameters are shown in Figure 4.14. Profiles obtained on the morning of 6 May were representative of baseline conditions, indicating that significant stream discharge had not yet occurred. By late afternoon of 6 May, considerable amounts of runoff had reached D Buoy. The thin surface freshwater layer was approximately 30 cm-thick, with an average salinity of 25.8 and a temperature 0.5 ^{o}C cooler than the bay waters. YSI turbidity values approached 20 NTU near the surface, with a TSS concentration of

9.64 mg/l. On 7 May, moderate winds enhanced mixing of the water column, extending the runoff layer down to a depth of about 2 meters. Surface waters were still murkier than normal, with an average turbidity of 5 NTU. On 12 May, surface salinities were still slightly lower than baseline conditions (by about 1 unit), implying that runoff waters had not been completely flushed out of the southern basin six days after the event. Dissolved oxygen was below saturation for the first four days of the event, suggesting that bay productivity was lowered and/or that BOD was high. Baseline conditions for all YSI parameters were reestablished by 15 May, nine days after the initial runoff-induced perturbation.

Surface dissolved nutrient and Chl *a* concentrations following runoff for the site D Buoy are shown in Figure 4.15. On the afternoon of 6 May, all dissolved inorganic nutrients in surface waters were enriched considerably, with NO_3^-, PO_4^{3-} and $Si(OH)_4$ reaching concentrations of 7.35 μM, 1.02 μM and 43.60 μM, respectively. The DIN to DIP ratio was about 10. Subsequently, all nutrient concentrations decreased but remained above baseline values for several days, except for PO_4^{3-}. PO_4^{3-} concentrations dropped to baseline values on 9 May and then below analytical detection limits on 10 May, while NO_3^- and $Si(OH)_4$ were still in excess of baseline levels. Chl *a* concentrations remained near baseline values for the first few days, but then increased by a factor of 3 on 10 May, suggesting that runoff nutrients were actively taken up by phytoplankton. However, because of a rapid PO_4^{3-} depletion, Chl *a* concentrations were back to normal two days later.

Ratios of the May storm event dissolved nutrient and Chl *a* concentrations relative to the baseline concentrations for all sites are shown in Figures 4.16 an 4.17. Similar to the January event, the increase in runoff concentrations at all sites relative to baseline levels was greater for NO_3^- than for other nutrients. NO_3^- levels at all "buoy" sites (D, E and C) remained significantly above baseline for the six days following the event. However, PO_4^{3-} concentrations were decreased to near baseline values by 8 May, and were clearly below normal levels on 10 May for all "bay" sites. DIN to DIP ratios were considerably above baseline values for the five first days of the event, peaking sharply on 10 May at the time of strong PO_4^{3-} depletion. Similar to the January event, DON concentrations during this event did not differ from baseline values. DOP concentrations appear to have been more variable during this event, with higher concentrations relative to baseline observed at the nearshore site KS. Except for a few high values on the day of the runoff event, Chl *a* concentrations remained near baseline values for the first few days at most of the sites. However, on 10 May there was a 2-fold increase over baseline Chl *a* concentrations at all bay sites, suggesting that phytoplankton growth was enhanced. Results of t-tests (after verification that the populations were normally distributed using the Jarque-Bera test) indicate that the Chl *a* concentrations at the peak of the bloom for all bay sites were statistically significantly different from their respective baseline values at $P < 0.001$.

4.2.4 October 2002 Storm Event

The October event was initiated by a passage of a band of heavy showers and isolated thunderstorms moving across the island during the afternoon and nighttime hours of 14 October. This event was associated with very light southerly winds. The rain event was rather small: total daily rainfall recorded at Luluku rain gage for 15 May was 3.48 cm, and the five-day total precipitation for this event was 6.93 cm. However, because of the extent of dry conditions prior to the rain episode (over 160 "dry" days), this event was considered to be potentially significant.

Sampling was carried out daily during the period of 10/14/02-10/20/02 (Figure 4.18). On 15 October, eight hours following the peak of Kaneohe stream discharge, there was no visible evidence of runoff in southern Kaneohe Bay. The bay waters were in fact quite clear, indicating that sediment loading was not significant. Stream flow in Kaneohe stream reached a maximum of only 1.05 m^3/s during this event.

Profiles of selected parameters at D Buoy during this event are shown in Figure 4.19. Following the rain event of 15 October, surface waters in the bay were fresher than usual. The upper fresher layer was approximately 2 meters thick, with an average salinity of 33.3. Five days after the rain event, surface waters in southern Kaneohe Bay were still considerably fresher than bottom waters, by about 2 salinity units. The winds associated with this event were unusually light: westerly winds averaging only 5 km/h prevailed until 18 October mid-day, when light trades of about 10 km/h were reestablished. The calm conditions most likely contributed significantly to an increase in the residence time of the freshwater plume in the southern basin. At no time during this event did turbidity levels differ significantly from the baseline conditions. In addition, the low TSS concentrations of 1.31 mg/l following the peak in water discharge indicate that no large amounts of sediments were delivered into the bay during this event. Dissolved oxygen saturation values on the runoff day were quite low (below 80%).

Dissolved nutrient and Chl *a* concentrations in surface waters at site D Buoy for the period of 10/14/02-10/20/02 are shown in Figure 4.20. Unfortunately, because nutrient data for 15 October are not available, it is difficult to evaluate the extent of nutrient loading due to runoff. The elevated concentrations of NO_3^- and $Si(OH)_4$ above baseline values observed on 16 October suggest that there was a significant increase in dissolved inorganic nutrient concentrations following the small rain event. However, PO_4^{3-} concentrations were not above baseline values on 16 October. Dissolved nutrient concentrations essentially returned to baseline levels on 18 October, only 3 days after the rain event. A two-fold increase in Chl *a* concentrations was observed the day following the event. This suggests that phytoplankton responded rapidly to nutrient loading, possibly due to the low turbidity levels and the quiet conditions prevailing during the event. However, as observed for nutrients, Chl *a* concentrations returned to normal by 18 October.

Ratios of the rain event dissolved nutrient and Chl *a* concentrations relative to the baseline values are shown for all sites sampled in Figures 4.21 and 4.22. No nutrient data are available for 15 October. However, the increase of NO_3^- concentrations relative to baseline values at all sites on 16 October suggests that considerable nutrient loading due to runoff occurred the day before. Except for nearshore site KS, PO_4^{3-} concentrations in the southern basin were near or below baseline levels on 16 October. $Si(OH)_4$ concentrations were above baseline values during the whole sampling period. Because of the depletion of dissolved phosphorus relative to nitrogen, DIN-to-DIP ratios were considerably higher than baseline values during the first days of this event. Except for site PP, DON and DOP concentrations did not significantly differ from baseline values. Chl *a* concentrations were significantly elevated throughout the bay on 16 October, suggesting that the nutrient loading enhanced phytoplankton growth.

During the October 2002 storm event, surface water was also collected at D Buoy for diagnostic photopigments analyses. Selected pigment data are shown in Figure 4.23. On 16 October, the day during which a two-fold increase in Chl *a* concentrations was observed, the phytoplankton community was relatively diverse. The HPLC data indicate that the assemblage included significant contributions from each of these algal groups: diatoms, chlorophytes, prymnesiophytes, cyanobacteria and dinoflagellates. The largest increase in any photopigment relative to baseline values was observed for peridinin, with concentrations more than twenty times higher than baseline values. Therefore, dinoflagellates likely played an important role in the bloom event. Chl *b* and 19'-hexanoyloxyfucoxanthin pigments (indicative of chlorophytes and prymnesiophytes) also displayed elevated concentrations, approximately three times the average baseline levels. However, pigment data for 18 October indicate that the "typical" phytoplankton community was reestablished by this time.

Particulate material collected from surface waters at D Buoy during this event was used for particulate organic C and N determinations. Particulate material in bay water includes land-derived sediments, organic detritus and plankton. Smith et al. (1981) performed a number of analyses on particulate organic material (POM) in southern Kaneohe Bay. They calculated an average particulate organic carbon to nitrogen ratio (C:N) of 5.0 for the southern basin. Smith et al. (1981) also estimated that the standing crop of phytoplankton could account for roughly 33% of total POM (the rest being largely detritus) and as much as 88% of the living carbon. (Taguchi and Laws, 1989) calculated a long-term average C:N of 5.2 ± 0.5 for southern Kaneohe Bay and concluded that the C:N was remarkably constant during this 12-year period. In addition, based on three independent estimates, Taguchi and Laws (1989) concluded that phytoplankton carbon (C_p) on average probably accounts for 50-70% of total particulate carbon (TPC) in this system. Because these estimates were derived from samples taken mostly during baseline conditions, it seems reasonable to assume that the contribution of phytoplankton carbon to TPC would be higher during the time of a bloom. One could further hypothesize that the day-to-day changes in C:N would more likely be driven by changes in C_p. However, it should be kept in mind that zooplankton could also make a significant contribution to TPC. C:N ratios obtained for the October 2002 are shown in Figure 4.24. Because the TSS concentrations were very low during this event, the contribution of land-based material is presumed to be minor. C:N ratios were about 5.8 at the time of the bloom, but then increased to 7.3 as phytoplankton biomass decreased. Assuming that most of the changes in C:N can be attributed to changes in algal cellular ratios, this indicates that phytoplankton cells on 10/17/02 were depleted in N by 25 % relative to those on 10/16/02. A few days later, C:N ratios were back to values of 5.8 whereas Chl *a* concentrations typical of baseline conditions were observed.

4.2.5 February 2003 Storm Event

A. General Conditions

A storm system consisting of a shear line supported by an upper level trough swept across the island chain on 12 through 14 February 2003. Light southerly winds were associated with this system, although trade winds returned shortly after the storm event. On Oahu, heavy rains affected mainly the northeastern slopes of the Koolau Mountains, causing small stream flooding. Total daily rainfall recorded at Luluku rain gage for 14 February was 11.25 cm, and the five-days total precipitation for this event was 13.49 cm. The number of "dry" days preceding the rainstorm was 14.

Sampling at D Buoy was carried out nine times during the period of 2/14/03-2/21/03 (Figure 4.25). The maximum stream flow of 13.39 m^3/s for Kaneohe stream was recorded in the early morning of 14 February, only a few hours before sampling. The boundaries of the runoff plume were distinctly visible in the southern basin (Figure 4.26). On the morning of 14 February, strong trade winds averaging 28 km/h forced the runoff plume to flow towards the Lilipuna Channel. On 15 February, the plume boundaries were no longer discernible, but the bay waters were still turbid. The plume was most likely dispersed by the strong prevailing trade winds averaging 36 km/h on 15 February.

Profiles of selected parameters at D Buoy during the February 2003 event are shown in Figure 4.27. Around 9:00 am on 14 February (approximately three hours after peak stream flow), the cooler surface freshwater layer was approximately 50 cm thick with an average salinity of 17.22. Three hours later, the fresher water layer extended down to a depth of about 1.3 meter. An average salinity of 24.89 indicates rapid mixing of the runoff plume with Bay waters. At 9:00 am on 14 February, the high surface turbidity of 74.7 NTU and the TSS concentrations of 44.07 mg/l indicate significant transport of runoff sediments into the southern basin. Three hours later, surface turbidity and TSS concentrations were considerably lower (22.3 NTU and 15.38 mg/l, respectively) due to both mixing and sedimentation of runoff material. The upper 2.5 meters of the water column remained considerably fresher, cooler and murkier for the following two days. On 17 February, turbidity was down to baseline values, while there was still a slight depression in surface salinity and temperature. The entire water column was undersaturated with respect to dissolved oxygen on the first day of the event. Unfortunately, due to rough conditions, no reliable measurements of DO could be obtained on 15 and 16 February. Baseline conditions for all parameters were reestablished by 18 February 2003, four days after the rainstorm.

Dissolved nutrient and Chl *a* concentrations in surface waters during and following the February 2003 runoff event at site D Buoy are shown in Figure 4.28. On the morning of 14 February, all dissolved inorganic nutrient concentrations were greatly elevated, with NO_3^-, PO_4^{3-} and $Si(OH)_4$ reaching concentrations of 25.42 μM, 0.99 μM and 87.99 μM, respectively. Interestingly, three hours later surface NO_3^- and PO_4^{3-} concentrations were comparable to the morning values (27.27 μM and 1.26 μM respectively), while $Si(OH)_4$ concentrations were significantly lower (26.94 μM). This indicates that silica levels might have a different relationship with runoff discharge than NO_3^- and PO_4^{3-}. The DIN-to-DIP ratios of 26 and 22 measured on the morning of 14 February are clearly above the Redfield ratio, indicating greater N than P loading of bay waters. Subsequently, all nutrient concentrations decreased but remained above baseline values for two days after the runoff event, except for PO_4^{3-}. PO_4^{3-} concentrations were below analytical limits one day after the rainstorm. Three days later, on 18 February, all dissolved inorganic nutrients were depleted relative to baseline. Surface Chl *a* concentrations were near baseline values for the first two days of the event, but then increased by a factor of 3 on 16 February. Elevated Chl *a* concentrations persisted on 17 February, suggesting that phytoplankton growth was enhanced by the nutrient loading. However, the rapid depletion in surface nutrients most likely caused the decline in the algal population observed on 18 February. Chl *a* size fractionation data indicate that larger phytoplankton cells dominated the bloom. Picoplankton (0.2–2.0 μm) concentrations remained essentially constant throughout the event.

Ratios of dissolved nutrient and Chl *a* concentrations during the February 2003 storm event relative to baseline values for selected sites are shown in Figures 4.29 and 4.30. Following runoff, dissolved inorganic nutrient concentrations were considerably elevated relative to baseline values at all sites except for SB. The observation indicates that the runoff plume did not reach the northeastern part of the southern basin, most likely because of the effect of prevailing strong winds shortly after the rainstorm. The high surface salinity observed at SB on the runoff day (34.5) also supports this hypothesis. NO_3^- concentrations remained above baseline values for all other sites until 18 February, while PO_4^{3-} appears to have been depleted sooner. After the first three days, $Si(OH)_4$ concentrations were unusually low in southern Kaneohe Bay, most likely due to substantial uptake by diatoms. Except for SB, DIN to DIP ratios were considerably above baseline values at all sites for the first four days of this event. DON concentrations measured during this event were slightly higher than baseline values, particularly for the nearshore site KS, suggesting an enrichment of DON in stream runoff during the February 2003 event. However, DOP concentrations did not differ from baseline. Chl *a* concentrations at SB were already higher than baseline values on the primary runoff day, and remained elevated for most of this event. However, the elevated biomass is presumably not related to runoff because the runoff plume apparently did not reach this portion of the basin. Chl *a* concentrations at the other sites were relatively low at the beginning of the event, but then increased significantly a few days later.

During the February 2003 event, surface water was also collected at D Buoy for diagnostic photopigments analyses. Selected pigment data are shown in Figure 4.31. The phytoplankton bloom was largely dominated by diatoms, as evidenced by the 10-fold increase in fucoxanthin concentrations relative to baseline. With the exception of dinoflagellates, the biomass of other species characteristic of the baseline community did not increase following runoff. Zeaxanthin concentrations were below average baseline values, suggesting a small decrease of the cyanobacteria population. Microscopic examination of storm water samples revealed that several species of large chain-forming and pennate diatoms of the genus *Chaetoceros* were the more numerically abundant algal groups present in the phytoplankton community (R. Scheinberg, pers. comm.). In addition, the presence of the dinoflagellate *Ceratium* was also noteworthy. Combined with the Chl *a* size fractionation data, the HPLC analyses and microscopic examination indicate that the post-runoff bloom was mostly dominated by large diatoms.

Particulate material collected from surface waters at D Buoy during the February 2003 event was analyzed for particulate organic C and N. Carbon to nitrogen ratios (C:N) are shown in Figure 4.32. TSS concentrations and turbidity levels were typical of baseline conditions during the time of the bloom, suggesting a minor contribution of land-based material to total POM. During the time of the bloom, C:N averaged 7.4, but then reached values of 8.4 while Chl *a* concentrations were significantly decreased. Assuming that the change in C:N is mostly accounted for by a change in cellular ratio, this indicates that the algal cells on 18 February were depleted in N by 17 % relative to the first day of the bloom. A few days later C:N ratios decreased to values similar to the average ratio of 5.0 reported in previous studies, and typical baseline Chl *a* concentrations were observed.

B. Primary productivity

Primary productivity measurements were carried out three times in surface water samples collected at D Buoy during the February 2003 storm event: on days 1, 3 and 5 (Figure 4.33). Net community productivity and respiration were determined for 24-hr incubations. On the peak runoff day, oxygen concentrations in all light bottles decreased by the end of the incubation period, implying negative net community productivity. Consistent with low total daily solar radiation and high turbidity observed on 14 February 2003, primary productivity in southern Kaneohe Bay was most likely limited by light availability during the first day of the event. Two days later, on the first day of the phytoplankton bloom, net community productivity reached values more than eight times average baseline values. On 18 February, coincident with the decline of the phytoplankton population, net community productivity was barely above zero. The high daily solar radiation and the low turbidity on this day suggest that productivity was most likely not light-limited. Although there was a decrease in algal biomass relative to bloom conditions, Chl *a* concentrations remained slightly above baseline. However, both surface NO_3^- and PO_4^{3-} concentrations were depleted. Falkowski and Raven (1997) demonstrated that the effects of nutrient limitation are not only manifested in growth, but also in photosynthetic processes. For example, there appears to be a significant reduction in the photochemical efficiency of the reactive centers under nutrient-limited conditions (Falkowski et al., 1989). In addition, the limitation of nucleic acid synthesis can effectively be a negative feedback on photosynthesis (Falkowski and Raven, 1997). Thus, the low net productivity rates observed in southern Kaneohe Bay on 18 February could result from nutrient limitation. Interestingly, respiratory rates varied little during the event and were comparable to baseline rates. As expected, there was a slight increase in respiration on the day of the bloom, but the increase in respiration did not scale with the increase in productivity. Because dark respiration rates can vary by as much as a factor of two between different phytoplankton species (Laws et al., 2000), a shift in the phytoplankton community could account for the relatively low respiration rates observed during the bloom. In addition, because large grazers were not removed prior to incubations, differences in zooplankton density could considerably affect the respirations rates measured in the dark bottles.

Because the main source of nitrogen during storm events is NO_3^-, the conversion of oxygen concentrations to carbon was made using a PQ of 1.4 (Laws, 1991). Results of gross production rates are shown in Table 4.1. There is a large variability in the productivity indices (PI) calculated for this event, most likely resulting from an uncoupling of primary production from the total algal biomass. Harris (1984) demonstrated that many of the species present in the water column at any given time are not contributing significantly to total community productivity. Therefore, Harris suggested that the production rate expressed per unit of biomass (equivalent to PI) may change dramatically for reasons such as shifts in species composition.

Table 4.1. Surface gross productivity rates and productivity indices in southern Kaneohe Bay measured at D Buoy during the February 2003 storm event. Numbers in parentheses correspond to one standard deviation between replicates.

Date	Gross Production (mg C m^{-3} day^{-1})	Productivity Index (mg C m^{-3} day^{-1} mg Chl*a*$^{-1}$)
2/14/03	-16 (± 63)	-18
2/16/03	483 (± 29)	174
2/18/03	41 (± 4)	31

Production rates and biomass can be used to estimate potential community growth rates (Tilzer, 1984). The primary production rate (P) is expressed in mg C m^{-2} d^{-1} and the biomass at time t (B_t) in mg C m^{-2} at time t. As pointed out by Tilzer (1984), the main difficulty in this method is the conversion of phytoplankton cell Chl *a* to carbon, which depends on growth rates and light regimes (Goldman, 1980). Taguchi and Laws (1989) demonstrated that the 95% confidence interval for the C:Chl *a* ratio in southern Kaneohe Bay in 1978-1979 was about 85-141. The mid-point value from Taguchi and Laws (1989) was selected as a reasonable value for this study. Accordingly, phytoplankton biomass in southern Kaneohe Bay was estimated as 113 times the Chl *a* standing crop. On the following day, the biomass would be $B_{t+1} = B_t + P$, if no phytoplankton losses occurred. Assuming exponential growth ($B_{t+1} = B_t e^{\mu^*}$), the maximum rate of biomass increment in the absence of losses is:

$$\mu^* = \ln (1 + P/B_t)$$

and the doubling time is:

$$T = \ln 2 / \mu^*$$

Results of such a calculation performed for the baseline and storm samples are shown in Table 4.2.

Table 4.2 Estimated potential community growth rates (μ^*) and doubling times (T) for baseline samples (2/04/03, 2/11/03) and storm samples (2/14/03, 2/16/03, 2/18/03).

Date	μ^* (day^{-1})	T (day)
2/04/03	0.7	0.9
2/11/03	0.4	1.6
2/14/03	— **	—
2/16/03	0.9	0.7
2/18/03	0.2	2.9

** Because gross productivity was negative on 2/14/03, no growth rate was calculated.

Tilzer (1984) demonstrated that the rates of algal production calculated from productivity always greatly exceed apparent growth rates, indicating significant losses of photo-assimilated carbon. Nonetheless, the approach is suitable to compare qualitatively maximum potential growth rates during a given period of study. Potential growth rates calculated for the baseline samples average 0.6 day^{-1} and the uncertainty is estimated to be ± 30%. This seems to be in agreement with the community growth rates of 0.74 day^{-1} estimated by Smith et al. (1981) for the southern basin. Because of the negative net productivity following runoff on 14 February, no growth would occur, resulting in a decrease of the algal biomass. On 16 February, the first day of the bloom, potential community growth rates were high, suggesting the presence of species with high reproductive rates. Two days later, the average community growth rates were considerably lower. The fact that the crash in the phytoplankton population was observed after that day supports results of this calculation. The observed rates of biomass change were noticeably different from those predicted by the potential μ^*, indicating that losses due to grazing, sedimentation, excretion and wash-out are significant. In reality, observed biomass changes are more likely caused by small variations in the balance between growth and losses rather than by the absolute magnitudes of either processes.

4.3 Discussion

4.3.1 Inter-comparison of Storm Events

Extensive historical flow data for Kaneohe stream collected by the USGS at the Kamooalii site (http://water.usgs.gov/nwis, site #16272200) are available to assess the significance of the storm runoff events sampled during this study. Figure 4.34 shows the peaks in stream flow for the period of 1977-2002. Assuming that the magnitude of a given runoff event is proportional to the maximum instantaneous flow, the May 2002 event ranks twelfth in relative importance over this 25-year period. The maximum stream flow for the

February 2003 event (13.39 m^3/s) is comparable with peaks recorded for several years. Thus, some of the runoff events investigated during this study appear to be representative of "typical" large runoff events for Kaneohe Bay. Although this approach is probably suitable to evaluate roughly the significance of a given event, it should be kept in mind that river discharges do not necessarily correlate with peaks in instantaneous flow.

Storm runoff contributions to stream discharges were estimated for each event using the USGS 90%/10% criterion. This method is based on observed shifts in flow duration plots from Hawaiian streams (Hill, 1996). For the 25-year period of available data, daily flows were ranked and the lower 90% of flows is considered to represent baseflow, with the highest 10% representing runoff. The resulting flow break used for separation of baseflow and storm runoff contributions for the Kamooalii site is 0.45 m^3/s. This value is higher than the flow break of 0.34 m^3/s estimated by Hoover (2002). The discrepancy is most likely due to the unusually low flow conditions for the period of his study. Using the flow break of 0.45 m^3/s, storm runoff contributions to total discharge for the period of study were about 4%, which is significantly lower than the long-term average estimated with the USGS 90%/10% criterion. Hoover (2002) estimated that the total Kaneohe stream discharge into the southern basin is about 15% higher than the discharge data collected at Kamooalii site. Therefore, for each event the total storm runoff contributions were multiplied by a factor of 1.15 and results are shown in Table 4.3. Although the maximum stream flow was higher for the May 2002 event, the January 2002 event had a greater total storm discharge. This indicates that the duration and the intensity of rainfall are both equally important controls for runoff generation. There appears to be a good relationship between the five-days total rainfall and the storm discharge for a given event (Figure 4.35, R^2 = 0.85). This supports the assumption that rainfall is a reasonable indicator of runoff in southern Kaneohe Bay (see Chapter 3).

Table 4.3. Estimated storm runoff discharge (stream flow > 0.45 m^3/s) in southern Kaneohe Bay for each storm event.

Storm event	Storm runoff discharge (10^3 m^3)
November 2001	171
January 2002	741
May 2002	656
October 2002	25
February 2003	343

Elevated particulate carbon to nitrogen ratios were observed at D Buoy on the first day of each runoff episode except for the October 2002 event (Figure 4.36). It is well-known that there are major differences in the overall chemical composition between terrestrial systems and marine systems. Because of the extensive production of structural compounds of carbon such as cellulose, lignin and waxes, terrestrial plants are markedly enriched in carbon relative to other elements. Typical C:N ratios for terrestrial plants are around 104 (Bolin et al., 1983). Because the turbidity levels at D Buoy following runoff were high for all events except for the October 2002 event, this indicates that land-derived suspended materials have an elevated C:N relative to baseline ratios in the bay. The relationship between TSS and C:N for storm samples (Figure 4.36) supports the conclusion. Hoover (2002) reported a median C:N of 13.7 for storm runoff samples collected in Kaneohe stream. Therefore, elevated C:N ratios in southern Kaneohe Bay following rainfall result from sediment-laden runoff.

Because the time between sampling and the peak of water discharge differed between storms, it is difficult to compare the maximum absolute nutrient concentrations between runoff events. Samples were collected twice at D Buoy over a period of three hours following the February 2003 runoff event and nutrient data indicate that the system is very dynamic and changes on timescales of hours, perhaps even minutes. Therefore, unless samples are collected at similar stages of the storm hydrograph, absolute nutrient concentrations from synoptic sampling are not suitable to evaluate nutrient loading. Following a three-year study, Hoover (2002) calculated average concentrations of dissolved nutrients in Kaneohe stream during storm flow. The average concentrations for NO_3^- and PO_4^{3-} are 28 μM and 1.2 μM (n=61), respectively. Using the average concentrations and the storm discharge values, the amount of NO_3^- and PO_4^{3-} loading from Kaneohe stream during storm flow into southern Kaneohe Bay can be estimated for each storm event. Results are shown in Table 4.4 and Figure 4.37 (because of limited data, the November 2001 event was omitted from the following discussion). However, it should be kept in mind that because leachable material can accumulate during a prolonged dry period (Eyre and Balls, 1999), the average nutrient concentrations in storm runoff may vary with ground saturation state.

Table 4.4. Estimated NO_3^- and PO_4^{3-} loading into Kaneohe Bay due to storm runoff contribution from Kaneohe Stream (stream flow > 0.45 m^3/s).

Storm event	NO_3^- -loading (moles)	PO_4^{3-} -loading (moles)
January 2002	20755	889
May 2002	18379	788
October 2002	695	30
February 2003	9593	411

An average factor of increase in algal biomass was estimated for each event by dividing the maximum Chl *a* yields at the "bay" sites by their respective Chl *a* baseline concentrations described in Chapter 3. Results are shown in Figure 4.37. Factors of increase in biomass are not proportional to estimates of nutrient loading: the smallest event (October 2002) resulted in a doubling of the phytoplankton biomass throughout South Bay whereas the largest event (January 2002) did not result in a significant increase over baseline. This could be the result of the coarse sampling resolution. However, because phytoplankton doubling times in southern Kaneohe Bay approximate one day (Smith et al., 1981), daily sampling following runoff should be appropriate to detect changes in biomass.

However, the processing time of nutrients in southern Kaneohe Bay is likely to be more important for biological uptake than the magnitude of nutrient loading (Furnas, 1992). Because nutrient processing increases with water residence time (Eyre and Twigg, 1997), maximum Chl *a* yields are probably a function of the residence time of runoff nutrients in surface waters. To investigate this possibility, a fraction of "residual" NO_3^- remaining in the bay surface waters after a 24-hour period was estimated for each event by dividing the NO_3^- concentrations at the bay sites measured on day 2 by the NO_3^- concentrations measured on day 1 (runoff day). Results are shown in Figure 4.38. The estimated fractions of residual NO_3^- range between 0.10 and 0.40 between the storm events. Assuming that during the first 24 hours removal of nutrients by phytoplankton uptake is minimal due to light limitation of productivity (see section 4.2.5 B), this indicates that advection and mixing of runoff nutrients are important processes. Interestingly, 40% of the initial runoff NO_3^- remained in surface waters after the first day of the October 2002 event whereas only 10% of the initial runoff NO_3^- was left in surface waters after the first day of the January 2002 event. The factors of increase in biomass appear to be proportional to the fractions of residual NO_3^- (Figure

4.38, R^2=0.61), suggesting that variability in advection and mixing rates of runoff nutrients were more likely to control the phytoplankton response rather than nutrient loading alone.

Smith et al. (1981) estimated an average water residence time of 13 days for the southern basin. Because flushing times are inversely proportional to stream flow (Kennish, 1986; McKee et al., 2000), the water residence time in southern Kaneohe Bay is presumably smaller than 13 days following significant runoff. In addition, because in general the surface flow (upper 3 meters) is greater than the water circulation below three meters in the bay (Bathen, 1968), the buoyant runoff waters are likely to be advected offshore more rapidly. A recovery time, or in other words the time period for baseline conditions to return in South Bay, was estimated for each event based on salinity, temperature and turbidity profiles at the bay sites. Results are shown in Figure 4.39. Recovery times ranged from three to eight days, indicating that freshwater water residence times in the southern basin were in fact less than 13 days for all storm events.

Interestingly, it took twice as long for South Bay waters to recover from storm perturbations following the smallest runoff event in October 2002 than to recover from the largest event in January 2002. The volume of water exchanged between the southern basin and the ocean is likely to vary with tidal range. Bathen (1968) demonstrated that the tidal exchange volume in the Bay during maximum tidal change (112 cm) increased by a factor of 1.4 relative to the mean diurnal tidal change (62.6 cm). Tidal ranges recorded on the first day of each event are presented in Table 4.5. Tidal amplitudes were above the mean for both the February and January events, while the ranges were below average for the remaining storms. Despite the small number of storm events samples during this study, the excellent correlation between tidal ranges and recovery times (R^2=0.995, Figure 4.40) suggests that tidal exchange strongly influences the retention times of runoff waters. Thus, variations in circulation patterns and tidal exchange rates could explain why the maximum phytoplankton biomass following a given runoff episode does not necessarily scale with the nutrient loading.

Table 4.5. Tidal ranges measured at Mokuoloe station for the first day of each event. Range is taken as the diurnal change from the lower-low to the higher-high tide.

Storm event	Tidal range (cm)
January 2002	107.6
May 2002	40.9
October 2002	49.6
February 2003	91.7

Kimmerer et al. (1981) demonstrated that the residence time of freshwater plumes in the southern basin is a function of the prevailing winds.

In addition, Bathen (1968) demonstrated that the surface flow in South Bay (upper three meters) is significantly increased under strong trade winds. Wind conditions for each storm event are shown in Figure 4.41. The light winds prevailing during the October 2002 event most likely contributed to retention of runoff waters for a longer time in the basin, while the strong trades associated with the February event probably accelerated flushing of the plume. Although changes in wind regime likely account for some of the variability observed in estuaries, the effects of wind on nutrient distribution and productivity are often neglected in studies of coastal water quality. Galliani et al. (1992) demonstrated that besides variations in nutrient supply from rivers, meteorological events such as variations in wind speed and directions are the most likely forcing factors responsible for the time series patterns observed at a coastal station in Italy.

A common feature of all storms is that the termination of the phytoplankton bloom is associated with depletion of dissolved inorganic N and P. While both nutrients are likely co-limiting the primary production in southern Kaneohe Bay (Smith et al., 1981; Laws and Allen, 1996), PO_4^{3-} appears to be the primary limiting nutrient following runoff. Evidences supporting this hypothesis are the high DIN:DIP ratio (27) in stream runoff and the exhaustion of surface PO_4^{3-} prior to DIN following a storm event. There is a growing volume of literature on P-limitation in coastal waters under freshwater influence (Doering et al., 1995; Yin et al., 2000; Labry et al., 2002). In addition, several studies in various coastal zones demonstrated evidence of a seasonal switch from N to P-limitation of phytoplankton growth (D'Elia et al., 1986; Fisher et al., 1992; Herrera-Silveira, 1998; Labry et al., 2001). Thus, the assumption of "permanent" N-limitation in Kaneohe Bay is questionable. Additional evidence for P-limitation such as short phosphate turnover times and high alkaline phosphatase enzymatic activity (Fisher et al., 1992) would help to validate the hypothesis of post-flood P-limitation of phytoplankton productivity in southern Kaneohe Bay.

Because particulate nitrogen to phosphorus ratios are not available for this study, cellular ratios cannot be used to support the hypothesis that P is the primary limiting nutrient following runoff. However, the fact that C:N ratios increase as the phytoplankton populations crash reflects nitrogen depletion in algal cells (Goldman, 1980). Relative growth rates (μ_r) correspond to the ratio of observed growth rates to the maximum reproductive rates (μ_{max}). Phytoplankton C:N ratios of about 5.7 or less are associated with a relative growth rate of 1.0 (DiTullio and Laws, 1983; DiTullio and Laws, 1986) . However, a phytoplankton C:N ratio of 8.2 is associated with a μ_r of about 0.55 (Taguchi and Laws, 1989). This indicates that declines in biomass are probably associated with a decrease in growth rates, further supporting the hypothesis that nutrient limitation plays an important role in the termination of a phytoplankton bloom in the southern basin.

Because of the limited HPLC analyses carried out for this study, it is difficult to infer with certainty which phytoplankton species are likely to dominate during a post-flood bloom. However, available data revealed different assemblages for two storm episodes, indicating that successful species may vary depending on the conditions. The abundance of dinoflagellates during the October 2002 event suggests that calm and low-turbidity conditions favor dinoflagellate species as reported by Smayda, (2002). However, the dominance of large diatoms during the February 2003 bloom indicates that this algal group does well during episodes of high turbulence, consistent with findings of Train and Rodrigues (1998). The fact that large diatoms are relatively resistant to grazing (Sommer, 1989) may also have contributed to their proliferation following the February 2003 event. Results from mesocosm bioassays to evaluate group-specific biomass responses of the phytoplankton community in the Neuse River Estuary suggest that phytoflagellates increased in abundance under static conditions (Pinckney et al., 1999). Moreover, these authors also demonstrated that mixed, turbid, and high nitrate conditions were favorable for diatoms and chlorophytes. Although additional data are needed, HPLC analyses from this study also suggest that environmental conditions may indeed have considerable effects on the community composition of the post-flood population. Unsurprisingly, Chl *a* size fractionation data revealed that larger cells are likely to dominate during post-flood blooms in the southern basin. The tendency for larger plankton to increase in importance during bloom events is a well-documented phenomenon (Malone, 1971; Hitchcock et al., 1987; Gervais et al., 2002). During the peak of the February 2003 bloom, picoplankton accounted for only 4% of the total Chl *a*, which is significantly lower than the average baseline value of 21%. However, the cell size of the bulk of the phytoplankton community decreased as nutrients were depleted. This observation is consistent with the "classical" models for resource competition, in which successional stages are often characterized by a progression from resource sufficiency to resource deficiency and competition (Kilham and Kilham, 1980; Tilman, 1982; Sommer, 1989).

Assessment of the role of zooplankton on the phytoplankton community was beyond the scope of this study. Hence, the possibility that grazing could be an important factor in the decline in the algal population cannot be ruled out. However, there are some indications that grazing was not necessarily the major control. Following the 1988 flood, almost no zooplankton could be found in southern Kaneohe Bay during the time of the bloom, most likely due to a stress caused by low-salinity bay waters (Jokiel et al., 1993). In addition, large diatoms such as those observed during the

February bloom are typically rather resistant to grazing, and mesoplankton grazers typically have generation times greater than 2-3 days (Sommer, 1989).

Interestingly, storms can have a number of impacts on the productivity of the bay. Results of this study suggest that significant reductions in light and nutrient availability (following a bloom) can inhibit production. However, productivity rates are greatly elevated above baseline rates during bloom periods. Consequently, the duration of each phase (decreased versus increased production) is likely the key factor in controlling the overall net bay productivity for a given storm episode. Daily gross productivity (GP) rates versus Chl *a* concentrations for all measurements carried out during this study are shown in Figure 4.42. Most of the time, rates of primary production in southern Kaneohe Bay appear to be correlated to phytoplankton biomass. However, during times of apparent light or nutrient limitation, the low productivity indices (productivity normalized to Chl *a*) suggest an uncoupling of production from population biomass. When the two data points with unusually low PI are removed (circled points on graph), there is a good correlation between GP and Chl *a* (Figure 4.42, R^2 = 0.91). The productivity dataset from this study, however, is not large enough to establish a robust functional relationship.

It might seem contradictory that one of the primary sources of dissolved nutrients to southern Kaneohe Bay is depleted in P relative to N and yet a primary limitation of N is observed during baseline conditions. During this study, emphasis was on the short-term impacts of runoff episodes. However, the effects of transient runoff events most likely operate on two timescales. On short timescales (hours-days), dissolved nutrients that are already biologically available are presumably the controlling factors on nutrient limitation and primary productivity. On longer timescales (weeks-months), processes associated with nutrient remineralization and benthic fluxes are more likely to govern the nutrient status in the bay. Many of the water-column and diagenetic processes in estuaries tend to drive the system towards nitrogen limitation. Because soluble nutrients excreted by zooplankton tend to be enriched in P relative to N (Lehman, 1984), recycling tends to be more rapid for P than for N. Benthic processes are particularly important in shallow-water systems (Corredor et al., 1999). Hence, processes occurring in the bay sediments are likely to have a major impact on the long-term baseline DIN:DIP in the shallow southern Kaneohe Bay. In many temperate estuaries, nutrient fluxes out of the sediments are often depleted in N relative to P (Rowe et al., 1975; Howarth, 1988; Heiskanen and Tallberg, 1999). For example, an average molar ratio of N to P of approximately 6 was measured during a study of benthic fluxes in Narragansett Bay (Nixon et al., 1980). A globally significant sink for marine N is denitrification occurring in coastal sediments (Mackenzie et al., 1993). Estimates of denitrification rates in estuaries commonly range between 0.44 and 2.19 moles N m^{-2} year $^{-1}$ (Seitzinger et al., 2002). No data are available on denitrification fluxes in Kaneohe Bay sediments. However, results of detailed nutrient budget calculations for Kaneohe Bay indicate that the southern basin is currently a net denitrifying system (Hoover, 2002). Sediments in the bay can serve as both a source and a sink for phosphorus. Highly weathered soils in windward Oahu are dominated by iron and aluminum hydroxides (Juvik and Juvik, 1998), for which PO_4^{3-} has a strong affinity. A small fraction of particle-bound P is probably rapidly desorbed from material entering the bay, but the bulk of it likely remains bound to minerals upon deposition (Froelich, 1988). A significant amount of P is probably released subsequently (timescales of months) from the sediments upon reductive dissolution of the iron host phases (Krom and Berner, 1981). Carbonate sands in Kaneohe Bay, however, are potentially an important sink for phosphorus. PO_4^{3-} can either be adsorbed onto carbonate phases (Short et al., 1985; Corredor et al., 1999), or be permanently sequestered during the formation of authigenic carbonate fluorapatite (Howarth et al., 1995). Based on scanning electron microscopy (SEM) analyses and porewater PO_4^{3-} concentrations profiles in sediments of Kaneohe Bay, (Ristvet, 1977) concluded that formation of authigenic apatite was a very minor process within the bay sediments. Additional benthic measurements are critical to ascertain the role of sediments in regulating water-column PO_4^{3-} concentrations. However, the low DIN:DIP ratios observed in the southern basin during baseline conditions suggest that the sediments are a greater sink for N than for P.

4.3.2 Comparison with Historical Events

Few water quality data exist for the May 1965 flood. The technical report following the event (Banner, 1968) consists mostly of qualitative observations, and the emphasis of the report was on the impacts of flooding on coral reefs. A strong upper level trough lingering above Oahu early in May 1965 produced intense precipitation on the windward side of Oahu (Table 4.6). The variable winds associated with this event were unusually light. On 3 May, the day following maximum precipitation rates, a very turbid and cold surface layer about 1.5 m thick was observed throughout the southern basin. The first measurements of salinity were carried out on 7 May. At this time, surface salinity at a station located near the position of D Buoy was 7.84 and surface salinities lower than 30 remained more than two weeks after flooding. A few days after the major rainfall of 2 May 1965, the southern basin developed a smell of decomposition (most likely from significant H_2S production), and oxygen measurements carried out on 12 May indicated a significant depression of oxygen levels. One week after the rainstorm, a visible bloom was first noticed beyond Coconut Island in the Sampan Channel, but no water samples were taken. Chl *a* determinations were only carried out on 20 May and concentrations of 4.78 µg/l were reported for a station located near the position of E Buoy. The increase in biomass corresponded roughly to a doubling of the average pre-flood concentrations of 2.40 µg/l reported for this station. Shallow water coral reef communities were extensively killed by runoff waters during the May 1965 flood.

Table 4.6. Five-day total rainfall and maximum instantaneous stream flow recorded for each storm event.

Storm event	**5-day total rainfall * (cm)**		**Maximum instantaneous stream flow ** (m^3/s)**
	Kaneohe Mauka	**Luluku**	
1965 flood	67.0		152.9
1988 flood	18.5		46.7
November 2001		13.68	4.5
January 2002		20.41	8.0
May 2002		27.13	21.5
October 2002		6.93	1.1
February 2003		13.49	13.4

* Rainfall data were not available at Luluku rain gage for the 1965 and 1988 events.

Kaneohe Mauka station was not operational after 1998.

** Peak in streamflow recorded at the USGS Kamooali site.

The greatest rainstorm in 23 years (Table 4.6) occurred on New Year's Eve 1987-1988 and resulted in a large flood. Calm winds (mean speed of about 5.7 km/h) were associated with this weather system. Daily rainfall, cumulative storm rainfall and maximum stream flow for the 1988 flood were considerably less than 50% of values measured in 1965. Nevertheless, a severe reef kill comparable to the 1965 episode occurred during the 1988 flood. Jokiel et al. (1993) reported that the 1988 storm was immediately preceded by heavy and prolonged rainfall during mid-December. Thus, soils in the watershed were saturated and stream flow recorded at Kaneohe stream was already elevated prior to the rainstorm of 31 December. Consequently, both the 1965 and 1988 events were similar in terms of total stream discharge into Kaneohe Bay over a period of 72 hours (Jokiel et al., 1993). A surface freshwater layer averaging 15 to depths of 1-2 meters was observed in the southern basin during the first day of the 1988 storm. Surface salinities remained below 20 until after 4 January. One week after the event, salinities exceeded 30 throughout the bay. Similarly to the 1965 flood, reduced light and decomposition of organisms killed by the storm led to depletion of dissolved oxygen. Due to elevated stream discharges, concentration levels of NO_3^- were already increased to 10 µM prior to the flood. Following the major storm, NO_3^- concentrations of 30 µM were recorded. Within two weeks of the storm, Chl *a* concentrations in the southern basin reached values as high as 40 µg/l. However, this bloom was probably not the direct result of the New Year's Eve flood. Because of elevated stream flow prior to the main flood event, a phytoplankton bloom had begun to develop by 22 December (Taguchi and Laws, 1989). The bloom consisted mostly of diatoms of the genus *Chaetocerous*. Subsequently, NO_3^- concentrations were drawn down to undetectable levels, leading to a rapid decline of the phytoplankton population. Unfortunately, there are no available data for phosphate and silicate concentrations. Water column parameters returned to pre-flood conditions within a month.

Meteorological and hydrological data for all storms events are summarized in Table 4.6. Five-day total rainfall was lower for the 1988 flood than the total precipitation recorded for two events during this study. Because of the lower elevation and windward location of the Kaneohe Mauka station (58 m) relative to the Luluku station (85 m), the amount of rain recorded at the Mauka site is likely to be less for a given rain storm. The difference in total rainfall between the Coconut Island (CI) station and the Mauka station was 4.3 cm for the 1988 flood. The change in elevation between Luluku and Mauka sites is less than half the elevation difference between CI and Mauka sites. Thus, an upper-limit of 4.3 cm for a correction factor seems reasonable to estimate the corresponding total rainfall at Luluku station. Nonetheless, the corrected total rainfall for the 1988 flood is not significantly different from the one recorded for the May 2002 event. However, the peak in stream flow measured during the 1988 flood was higher by more than a factor of two. This indicates that the prior wet conditions and existing soil saturation greatly contributed to runoff during the 1988 flood. In addition, available data on daily mean discharge for Kaneohe stream show that stream flow was already elevated prior to the major rains (Figure 4.43).

Extreme rates of freshwater discharge for the historical floods are likely to be responsible for the “reef kills” caused by low salinity. In addition, both the 1965 and 1988 floods occurred during spring tides. While the residence time of runoff waters is likely to decrease during maximum tidal range (see section 4.3.1), more reef area can be in close contact with the surface freshwater layer during extreme low tides. Throughout this study, only the January 2002 event occurred during spring tides. Salinities for the upper meter averaged 24.5 on the first day of this event. Given the estimates of 15 to 20 as the lower lethal salinity for corals (Coles and Jokiel, 1992), the January 2002 event probably did not cause any permanent damage to reef communities in the southern basin.

Because sampling was carried out only at weekly intervals during the 1988 flood, it is difficult to compare the nutrient data between the events. However, total nutrient loading to southern Kaneohe Bay can be estimated using the daily mean discharge for each event. Inorganic nutrient concentrations measured in the southern basin during the period of 1989-1992 (Laws and Allen, 1996) are comparable with those measured during this study. Therefore, it seems reasonable to assume that the average dissolved nutrient concentrations in storm runoff at the time of the 1988 flood are similar to those measured by Hoover (2002). Estimates of nutrient loading for each event (Table 4.7) can be made using average concentrations for NO_3^- and

PO_4^{3-} in stream runoff of 28 µM and 1.2 µM, respectively. Results indicate that the dissolved nutrient inputs due to runoff for the two largest events sampled during this study (January and May 2002) correspond roughly to 20% of the amount delivered to the southern basin during the 1988 flood. No discharge data were available for the 1965 storm, but Jokiel et al. (1993) reported that both 1965 and 1988 storms were similar in terms of 72-hour total stream discharge in Kaneohe Bay. However, in 1965 the Bay received municipal sewage discharge and bay waters were significantly eutrophic. Given the same amount of stream discharge, total nutrient inputs following runoff were presumably higher in 1965 than in 1988.

Table 4.7. Estimates of NO_3^- and PO_4^{3-} loading into southern Kaneohe Bay using the daily mean discharges for the five first days of each event. No data were available for the May 1965 flood.

Storm event	NO_3^--loading (moles)	PO_4^{3-} -loading (moles)	% relative to 1988 flood
1988 flood	94457	4048	
November 2001	6484	278	7
January 2002	18971	813	20
May 2002	20550	881	22
October 2002	2813	121	3
February 2003	11948	512	13

4.4 Summary and Conclusions

Nutrient and ecosystem behavior during post-flood recovery are similar for essentially all storm events considered in this study. Following runoff, dissolved oxygen levels are significantly reduced most likely due to a combination of the high BOD of organic materials in runoff waters and light-limitation of primary productivity in southern Kaneohe Bay. Periods of low dissolved oxygen following rainfall events have also been reported for other estuaries (Lapointe and Matzie, 1996; Eyre and Twigg, 1997). Because of decreased flushing times during floods, a large proportion of nutrients delivered to the bay are most likely discharged directly offshore. This possibility is supported by the quasi-exponentional decline of nutrient concentrations typically observed for the first few days after a storm. An increase in the algal biomass is generally observed, but the rapid depletion of dissolved inorganic nutrients promotes a relatively rapid recovery of the pre-flood planktonic communities. The intensity, the duration and the timing of the impacts previously mentioned obviously vary with the importance of the runoff event. Nonetheless, storm events sampled during this study are in many ways a representation of the historical episodes that occurred in southern Kaneohe Bay.

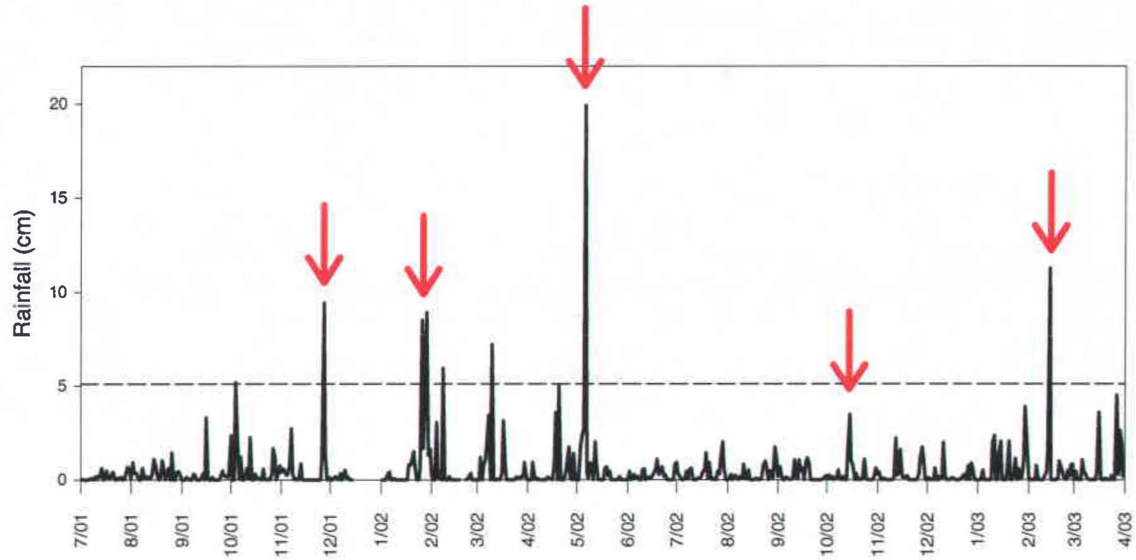


Figure 4.1. Daily rainfall at Luluku rain gage station from July 2001 to April 2003. Dashed line represents the arbitrary threshold of 5.1 cm of daily rainfall for storm sampling. Sampling was carried out for storm runoff events marked by a red arrow.

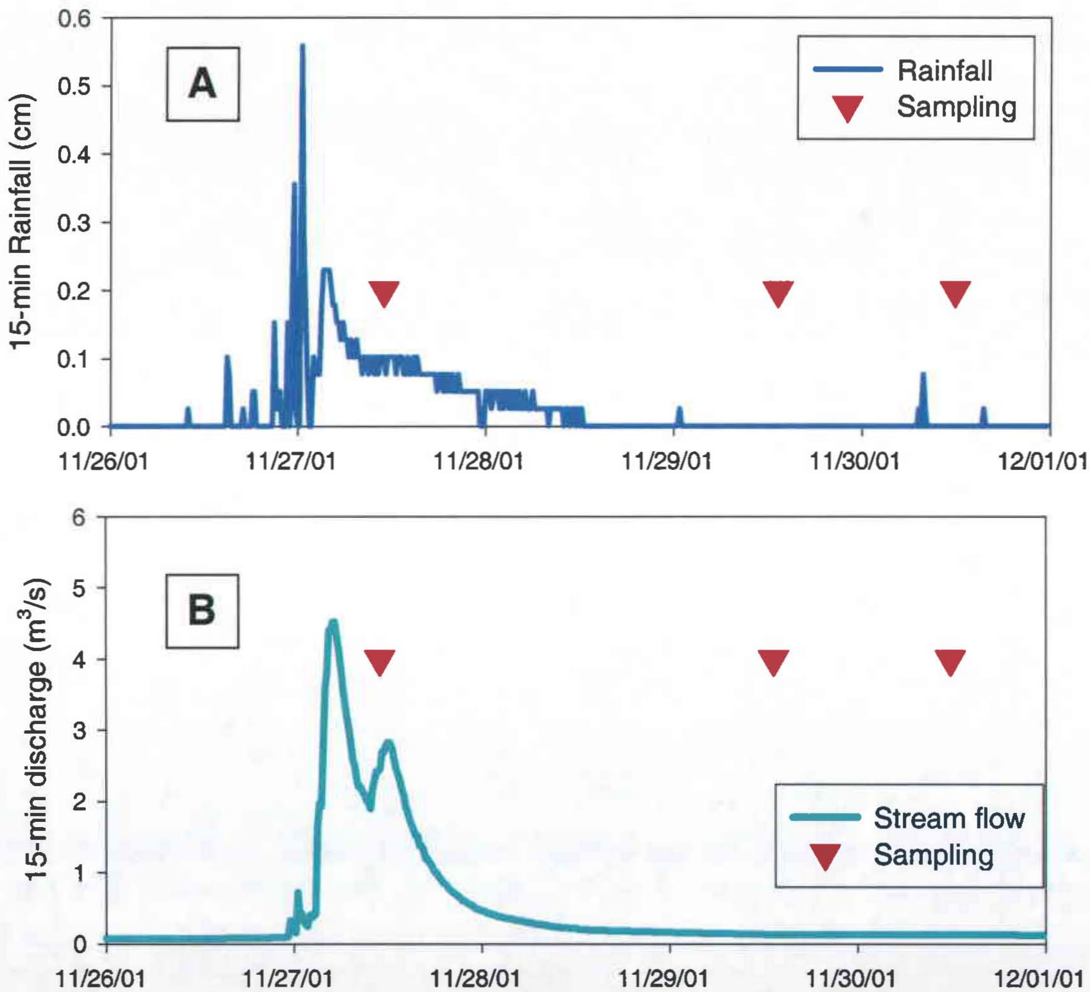


Figure 4.2. **(A)** Rainfall data recorded at 15-minute intervals at Luluku rain gage for the November 2001 storm event. **(B)** Kaneohe stream discharge recorded at 15-minute intervals at the USGS Kamooalii stream site below Luluku. Red triangles represent sampling times at D Buoy.

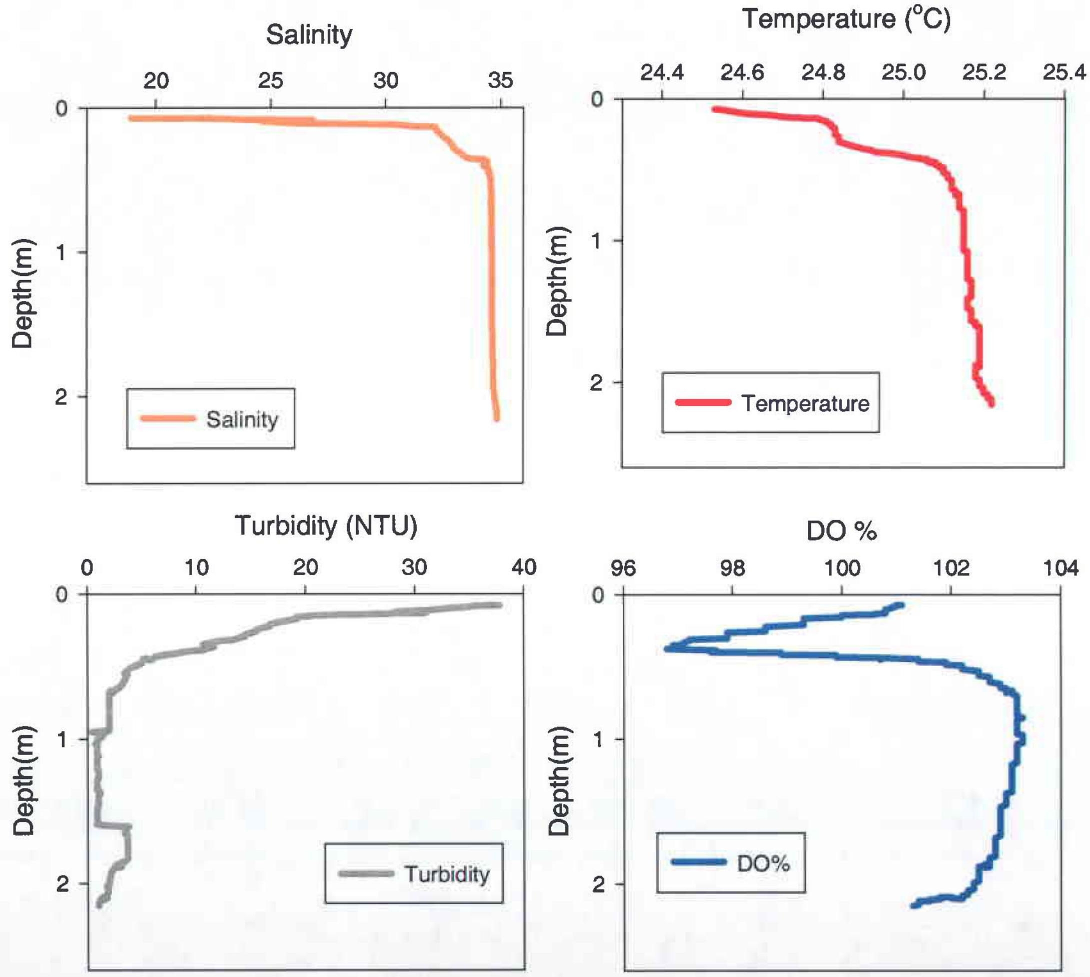


Figure 4.3 Vertical profiles of water temperature, salinity, dissolved oxygen and turbidity taken at mid-plume around 12:00 on 11/27/2001.

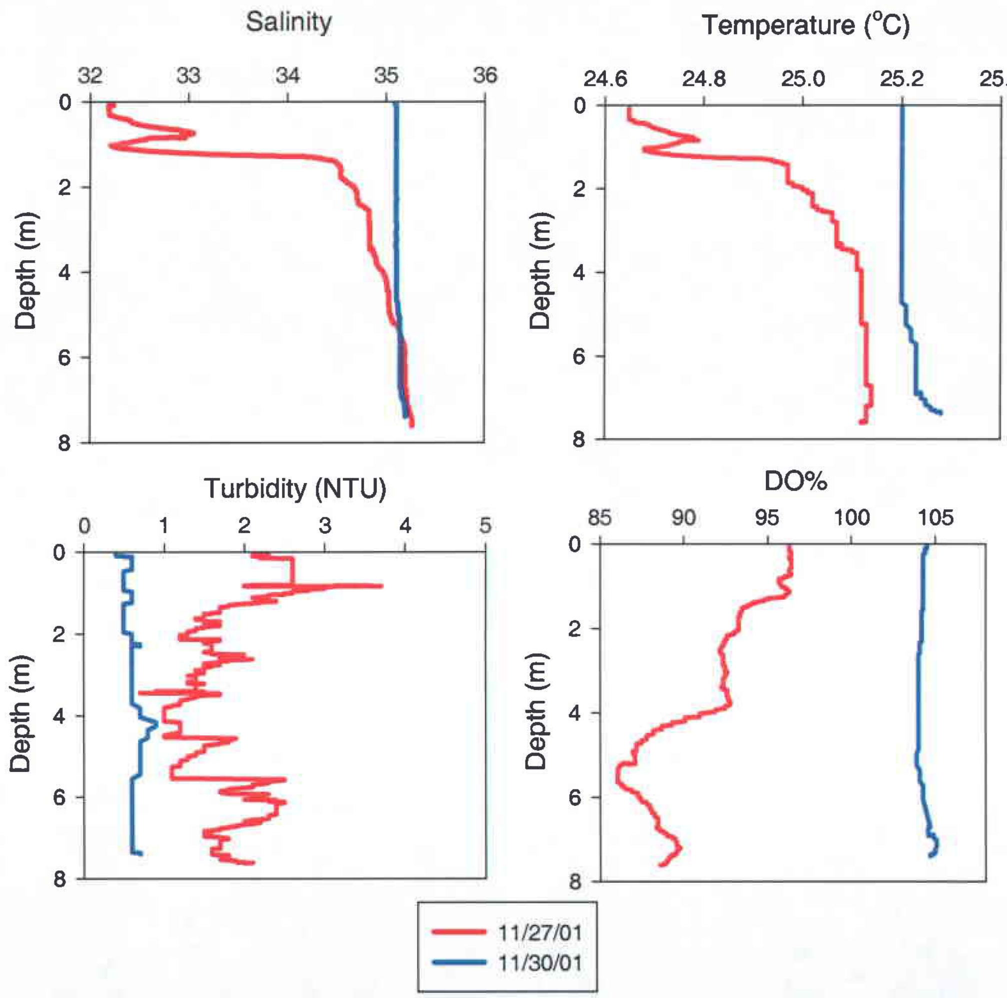


Figure 4.4. Vertical profiles of water temperature, salinity, pH, dissolved oxygen and turbidity taken at D Buoy on 11/27/01 and 11/30/01.

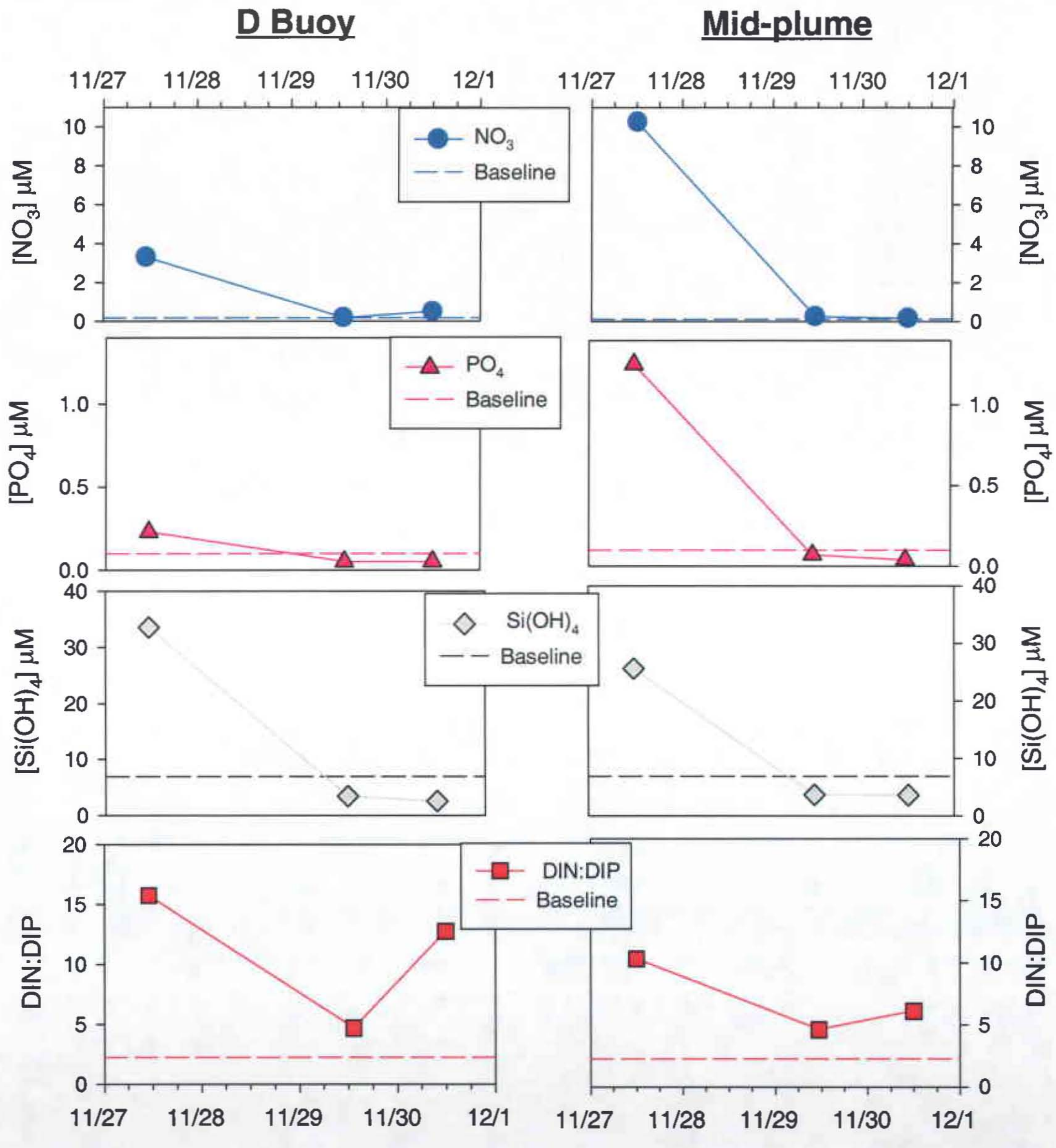


Figure 4.5. Surface dissolved nutrient concentrations at sites D Buoy and Mid-plume following the November 2001 runoff event. Dashed lines are the average baseline concentrations from Chapter 3.

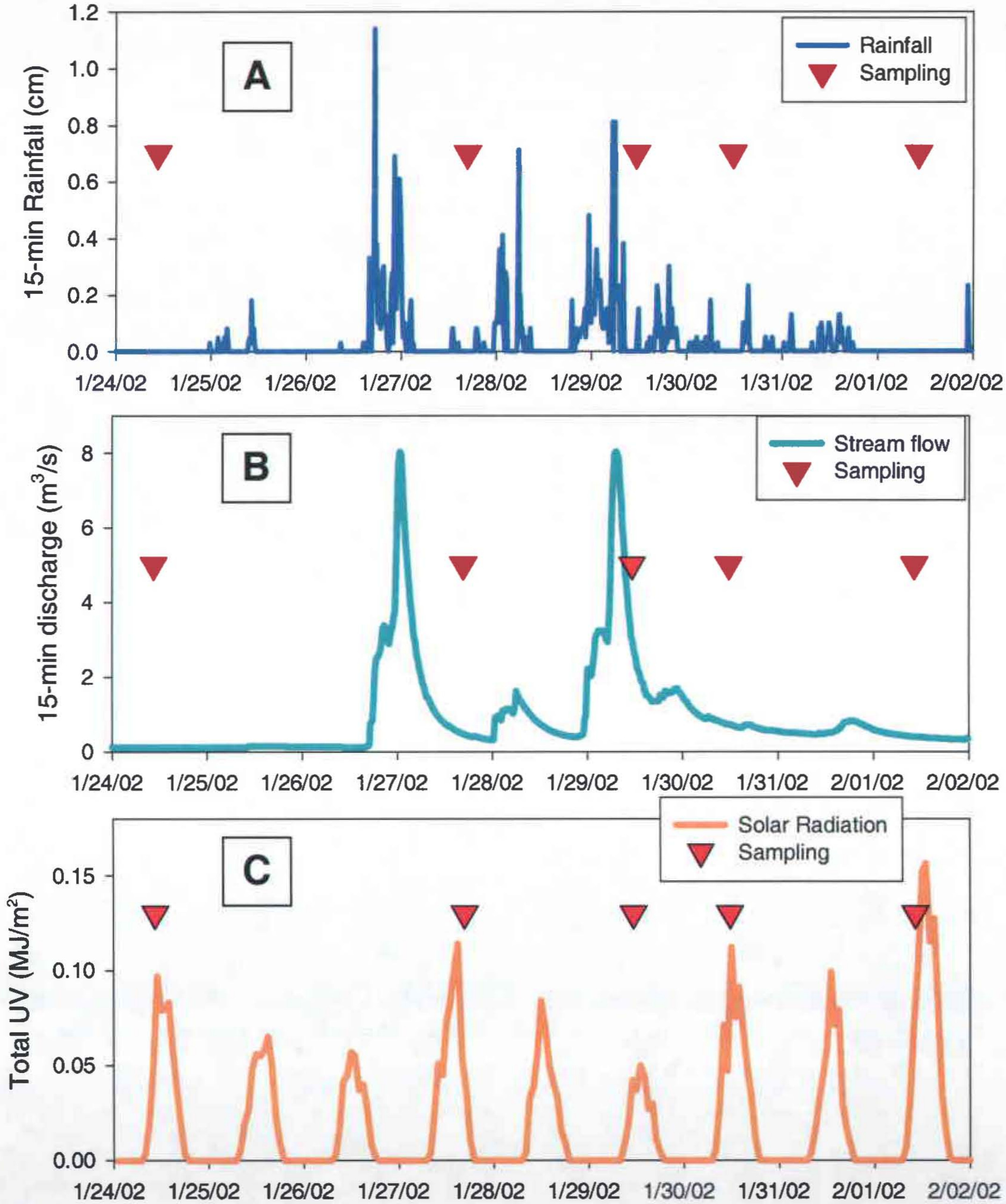


Figure 4.6. (A) Rainfall data recorded at 15-minute intervals at Luluku rain gage for the January 2002 storm event. **(B)** Kaneohe stream discharge recorded at 15-minute intervals at the USGS Kamooalii stream site below Luluku. **(C)** Solar radiation recorded at the HIMB meteorological station. Red triangles represent sampling times at D Buoy.

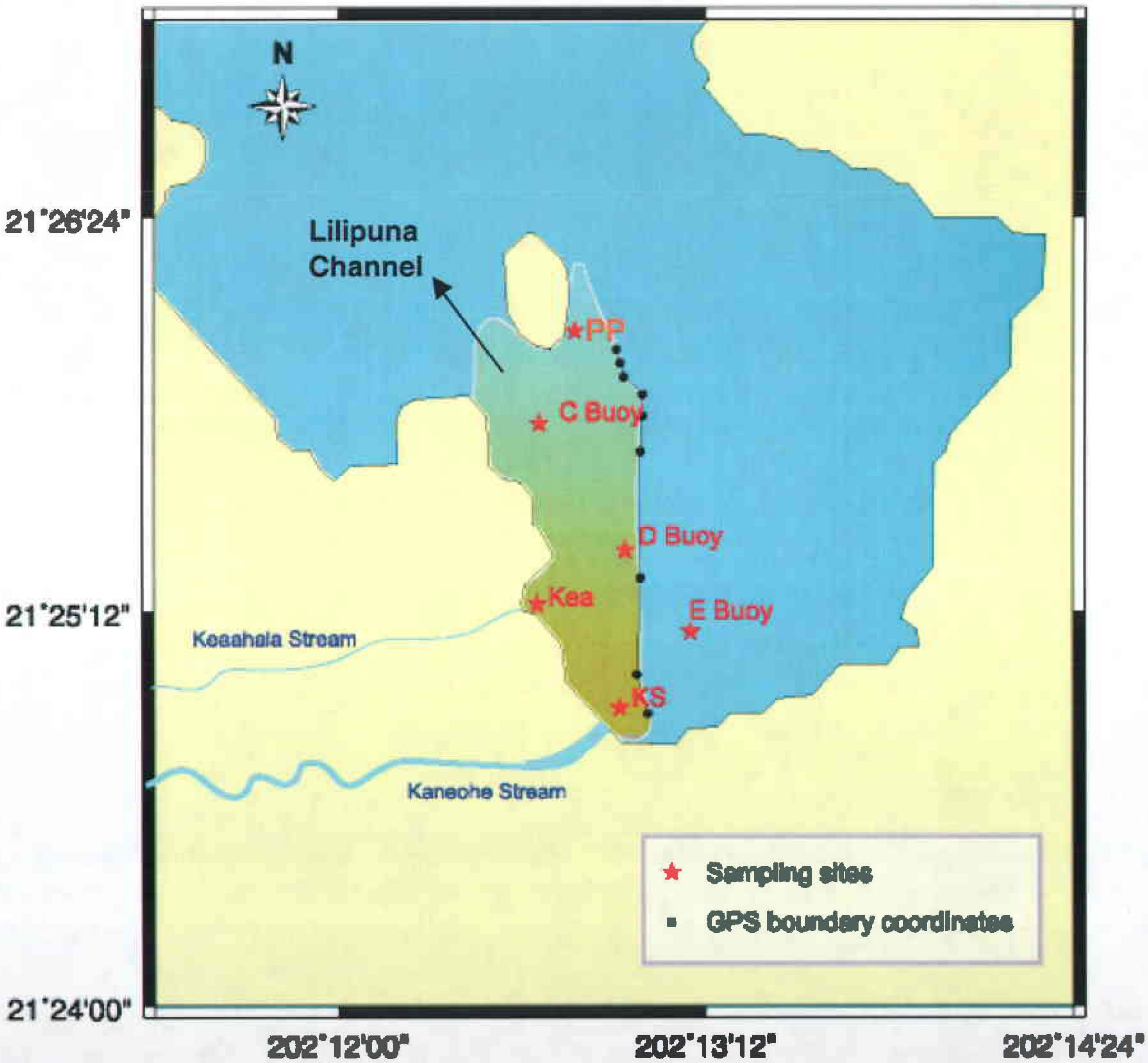


Figure 4.7. Runoff plume boundaries recorded in southern Kaneohe Bay on 29 January 2002 around 9h30.

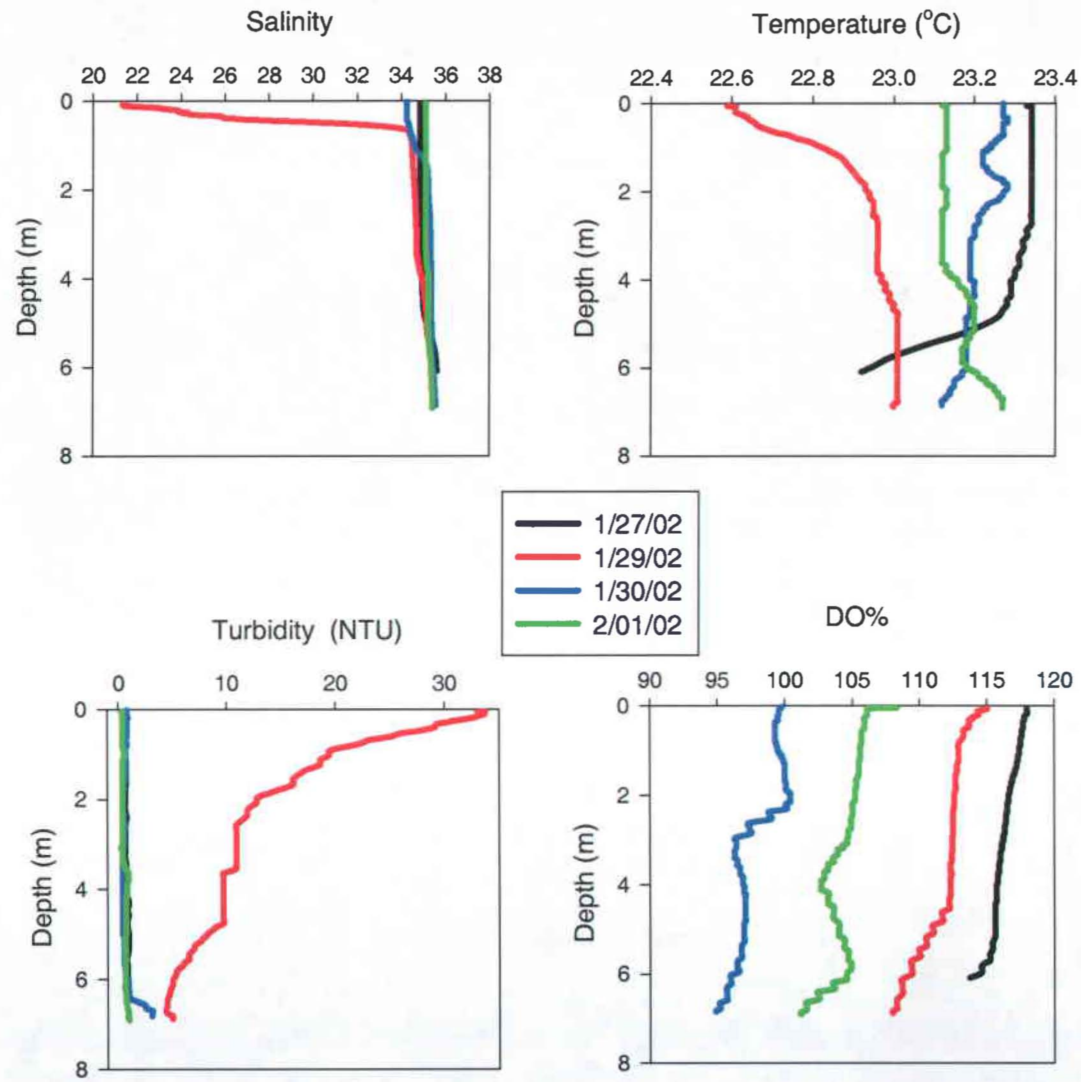


Figure 4.8. Vertical YSI profiles of salinity, temperature, turbidity and dissolved oxygen saturation (DO%) at D Buoy during the January 2002 storm event.

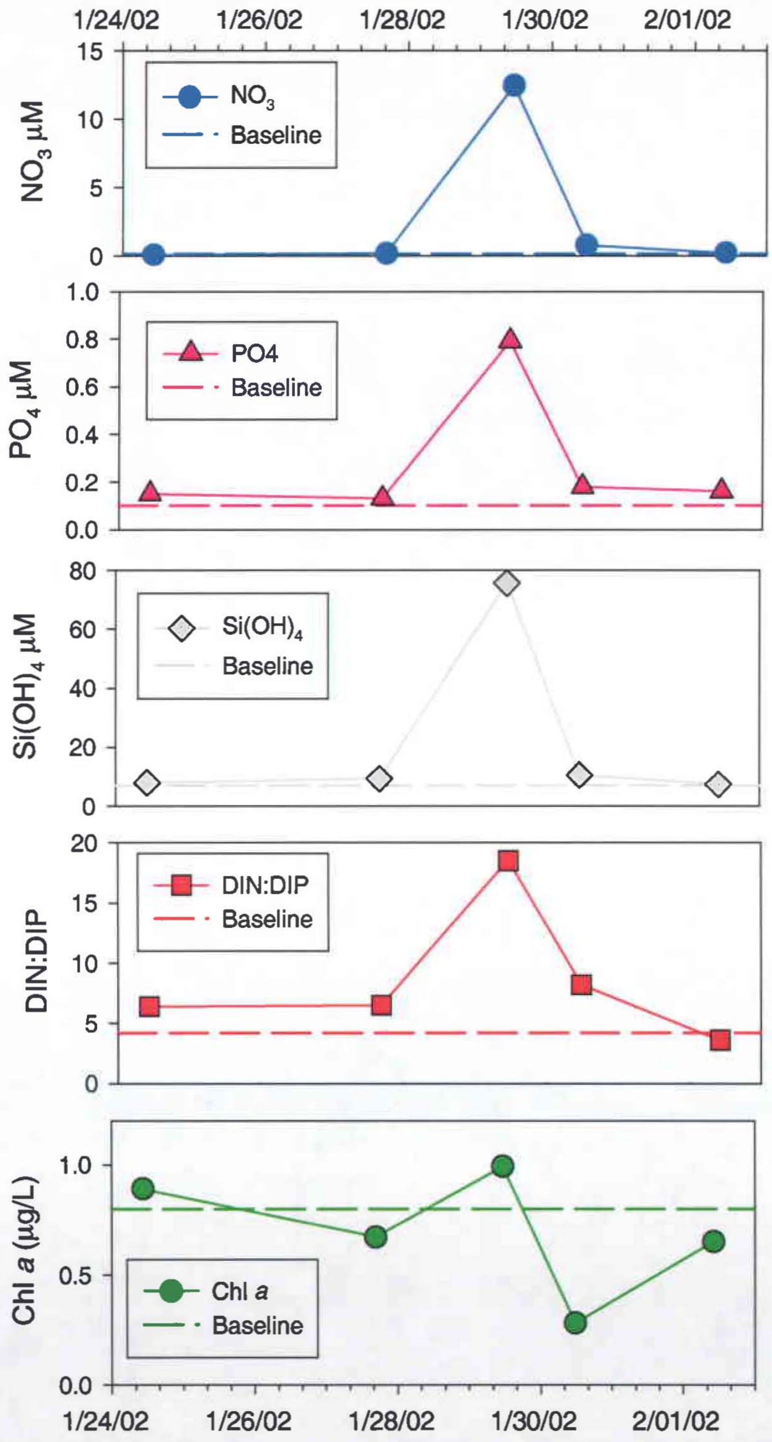


Figure 4.9. Surface dissolved nutrient and Chl *a* concentrations at D Buoy following the January 2002 runoff event. Dashed lines are the average baseline concentrations from Chapter 3.

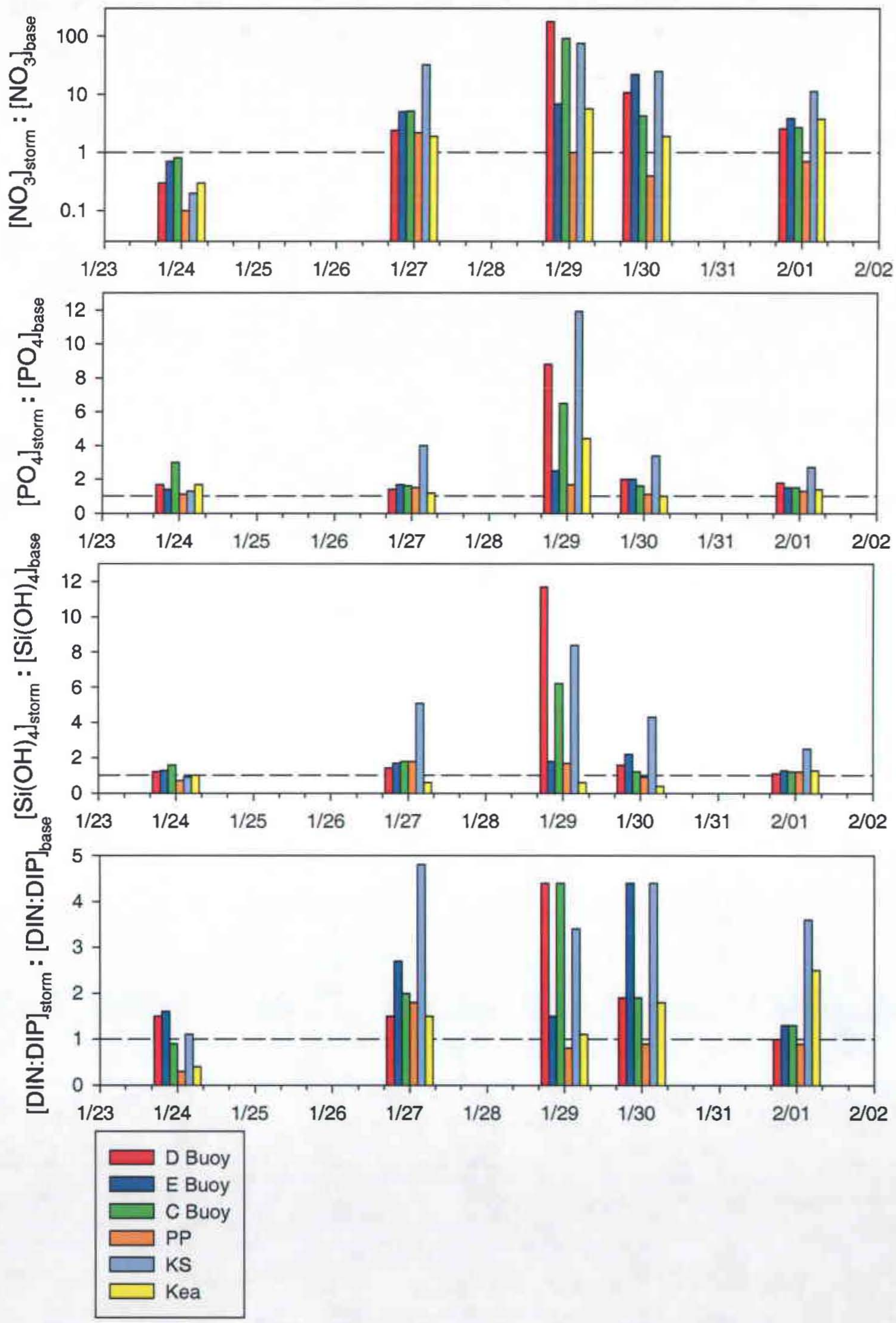


Figure 4.10. Surface dissolved inorganic nutrient concentrations for the January 2002 storm event relative to the baseline concentrations described in Chapter 3 for all sites in southern Kaneohe Bay. Note the log scale for NO_3^-. Dashed line represents a ratio of 1.

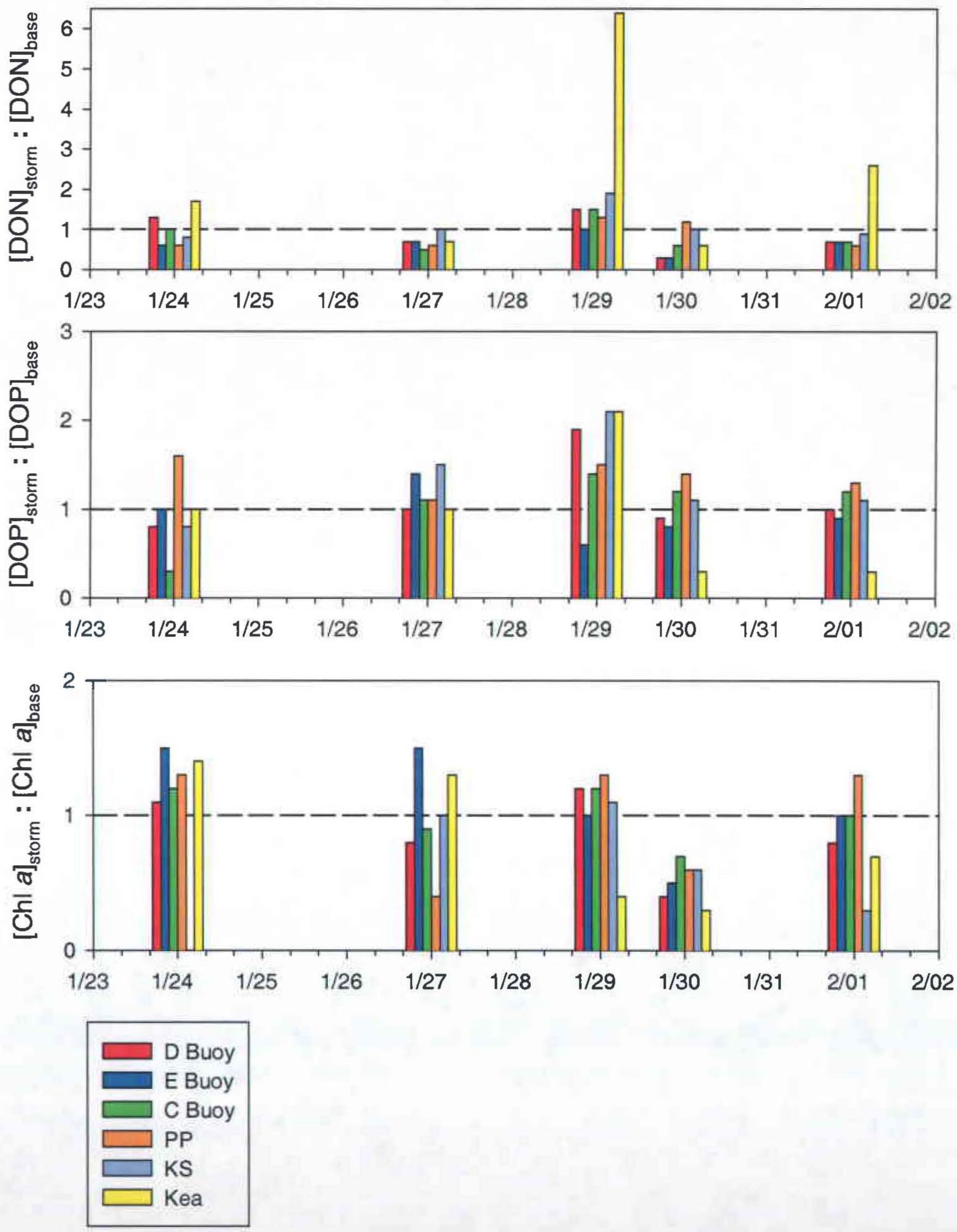


Figure 4.11. Surface dissolved organic nutrient and Chl *a* concentrations for the January 2002 storm event relative to the baseline concentrations described in Chapter 3 for all sites in southern Kaneohe Bay. Dashed line represents a ratio of 1.

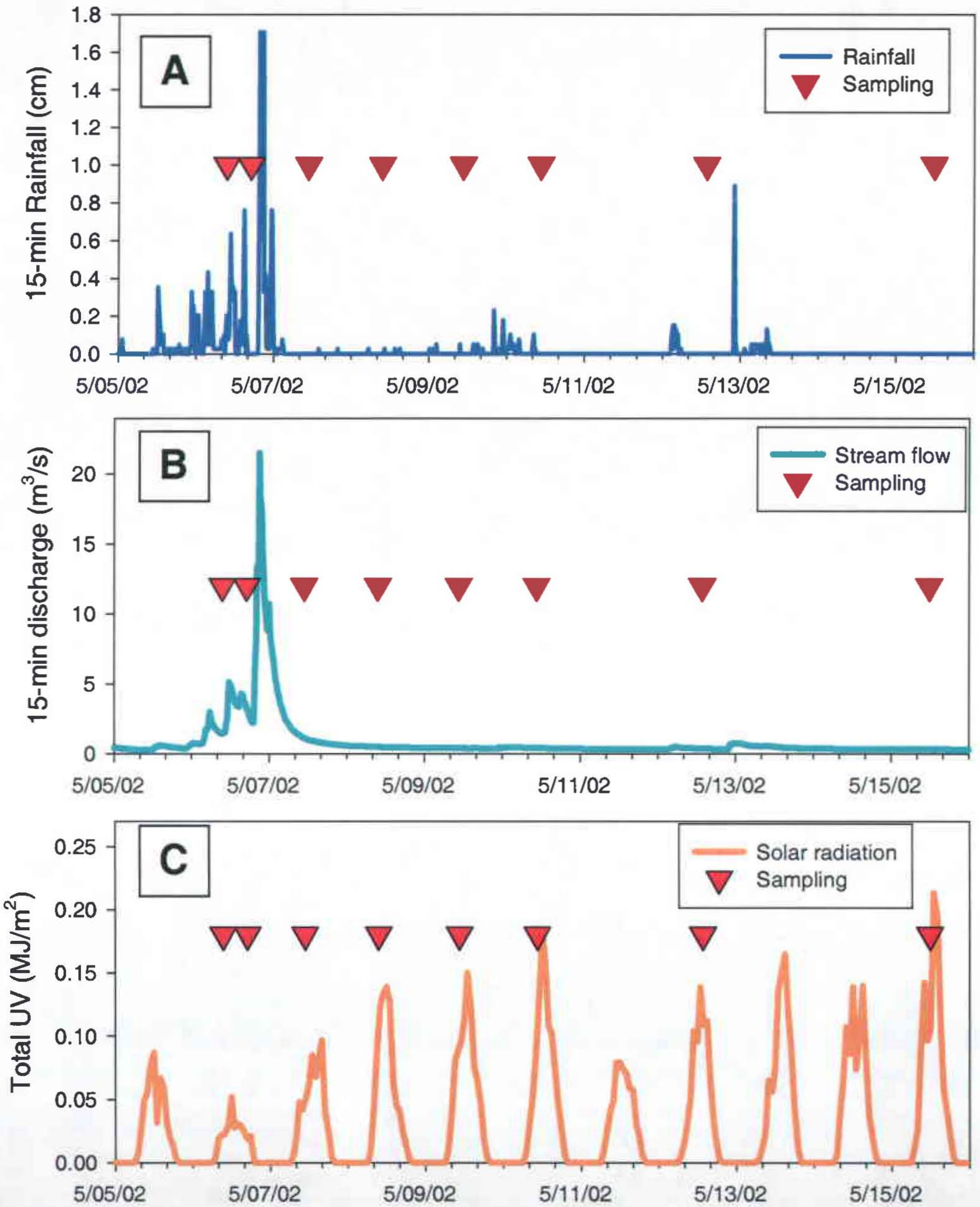


Figure 4.12 (A) Rainfall data recorded at 15-minute intervals at Luluku rain gage for the May 2002 storm event. **(B)** Kaneohe stream discharge recorded at 15-minute intervalsat the USGS Kamooalii stream site below Luluku. **(C)** Solar radiation recorded at the HIMB meteorological station. Red triangles represent sampling times at D Buoy.

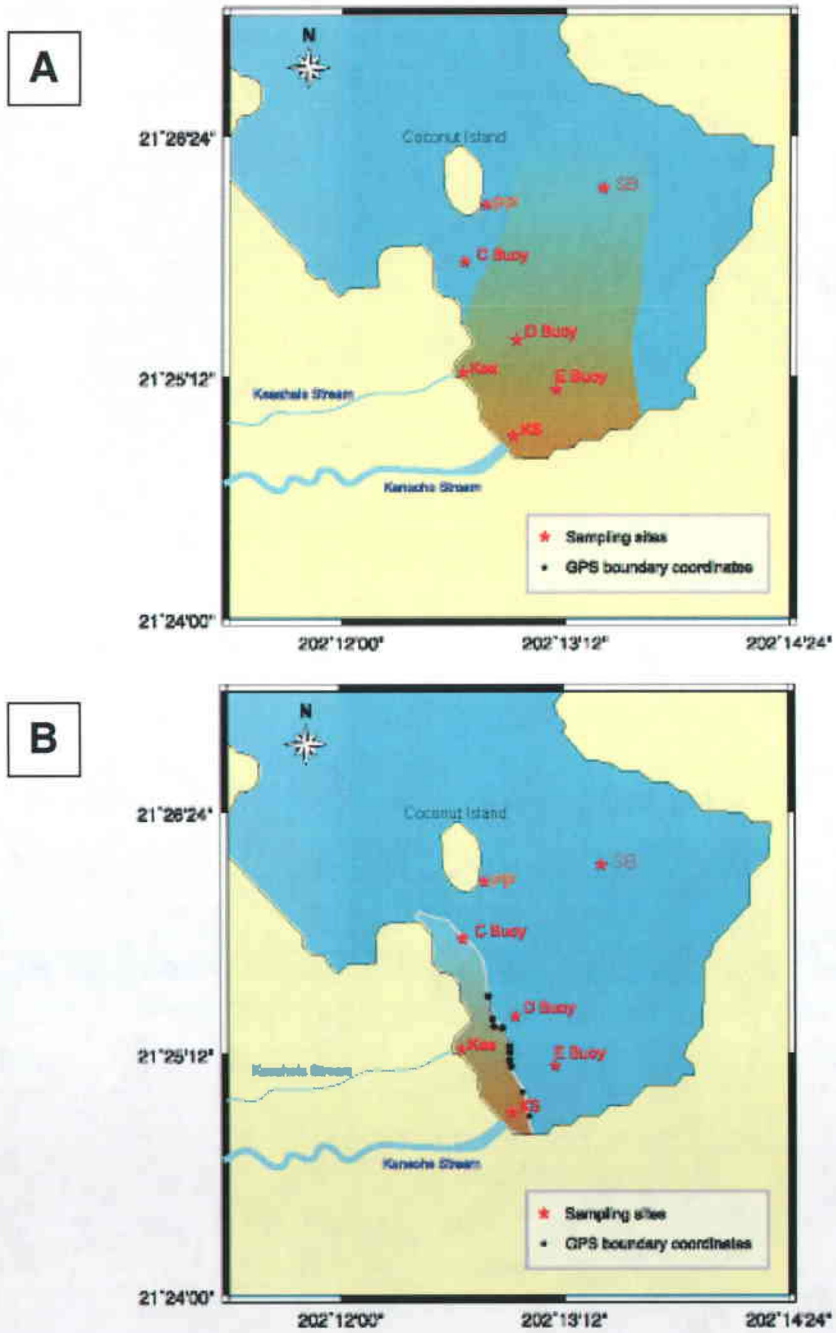


Figure 4.13. Freshwater plume boundaries recorded in southern Kaneohe Bay on 6 May 2002 around 16h30 **(A)** and on 7 May around 10h00 **(B)**.

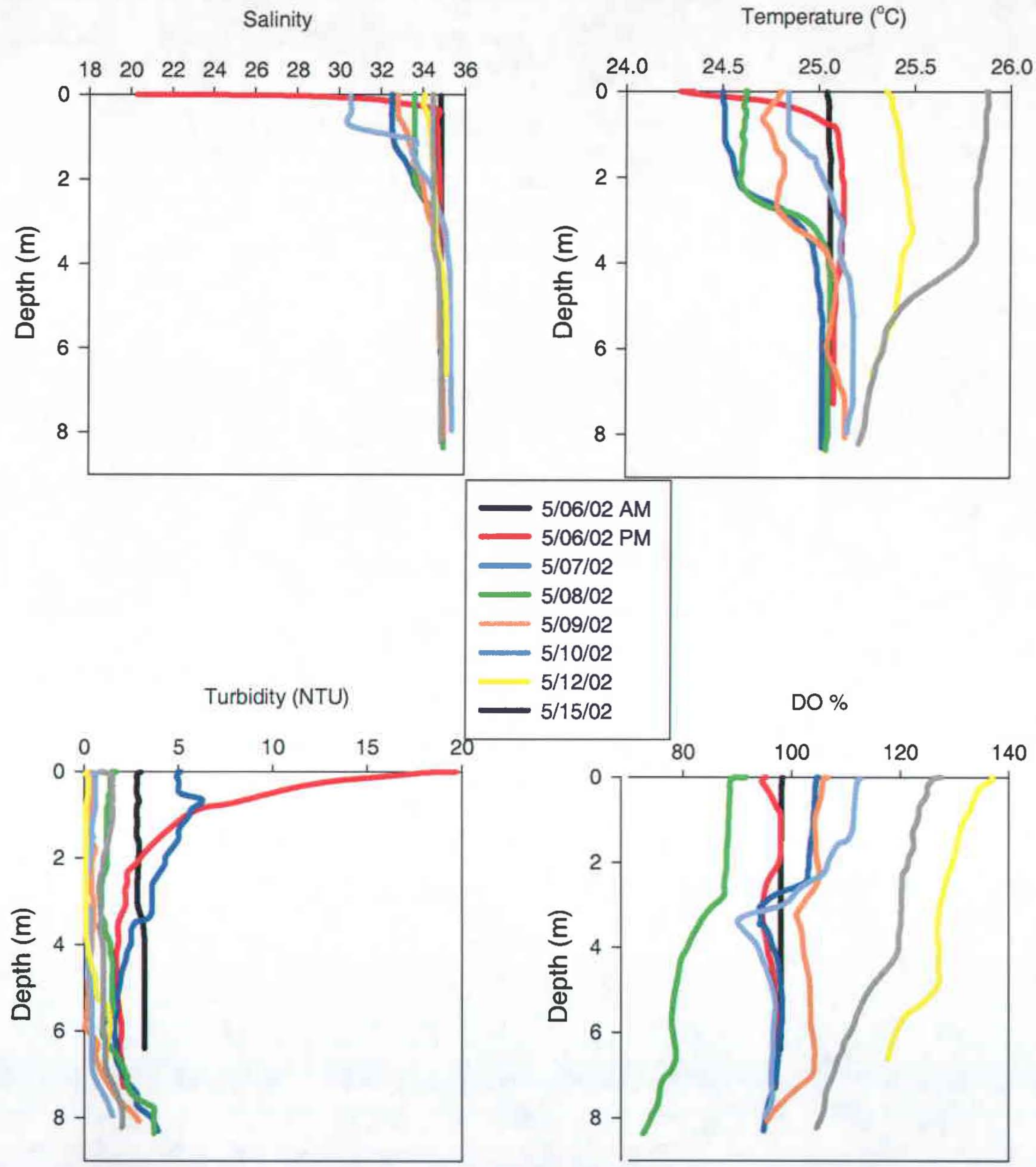


Figure 4.14. Vertical YSI profiles of salinity, temperature, turbidity and dissolved oxygen saturation (DO%) at D Buoy during the May 2002 storm event.

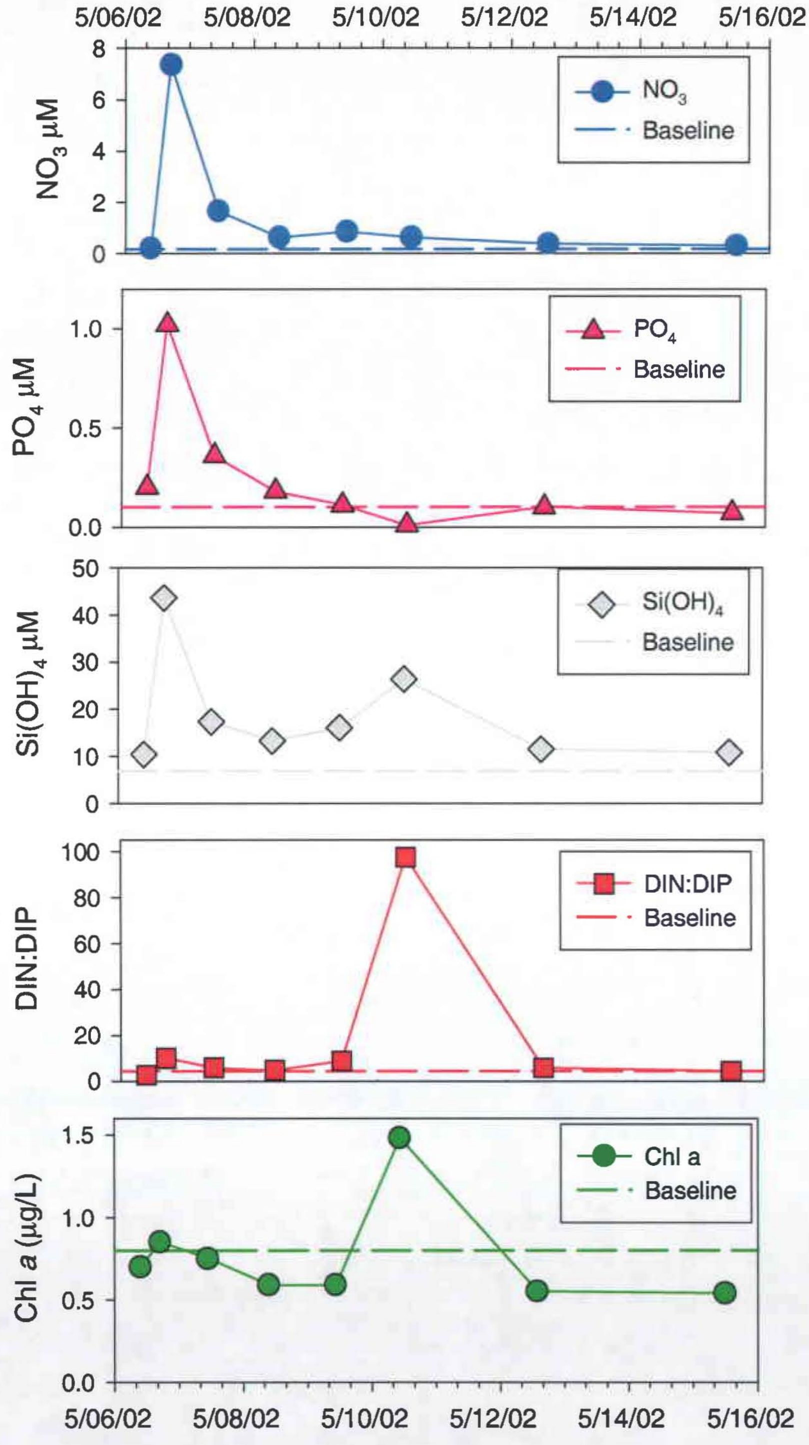


Figure 4.15. Surface dissolved nutrient and Chl a concentrations at D Buoy following the May 2002 runoff event. Dashed lines are the average baseline concentrations from Chapter 3.

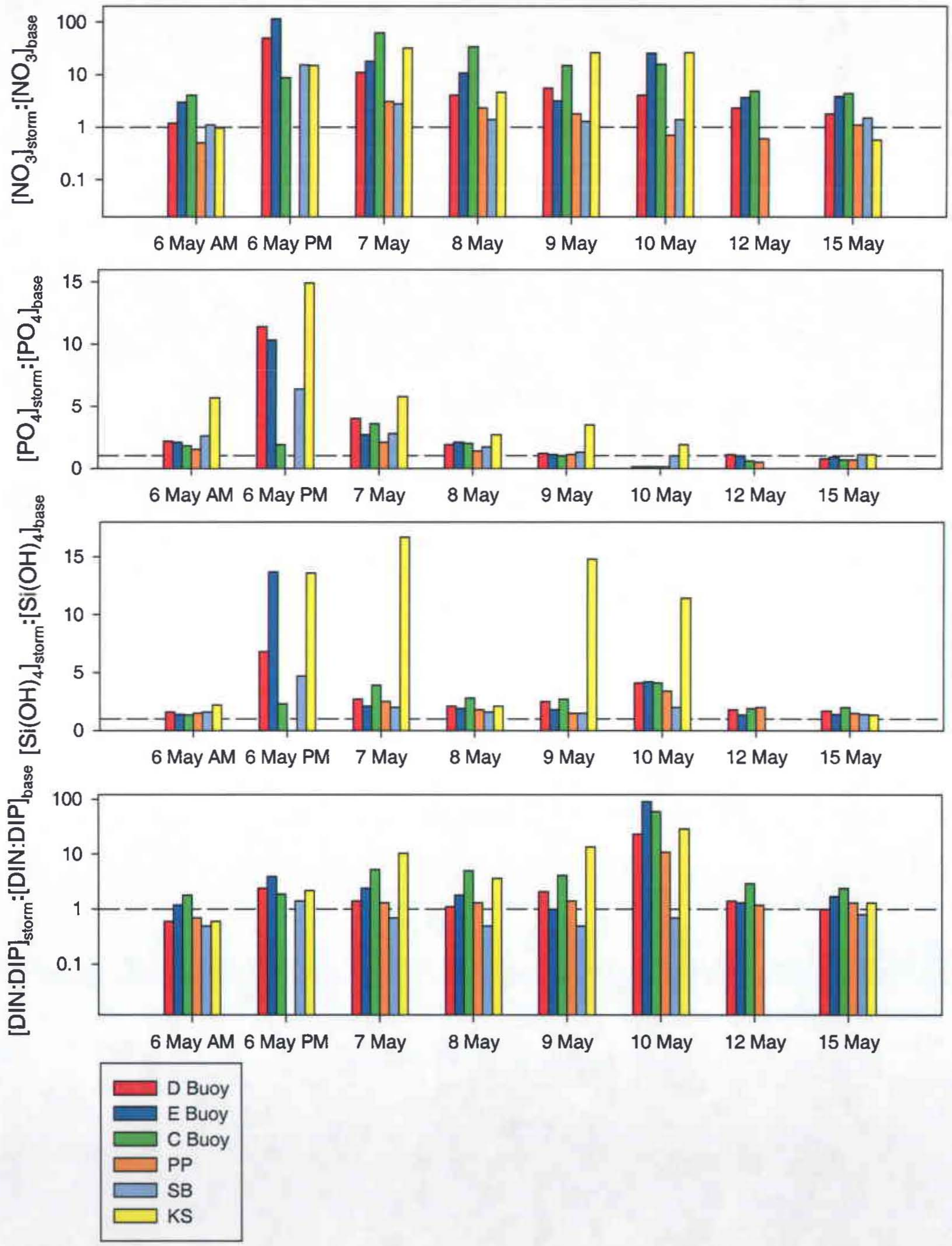


Figure 4.16. Surface dissolved inorganic nutrient concentrations for the May 2002 storm event relative to the baseline concentrations described in Chapter 3 for all sites in southern Kaneohe Bay. Note the log scale for NO_3^- and DIN:DIP. Dashed line represents a ratio of 1.

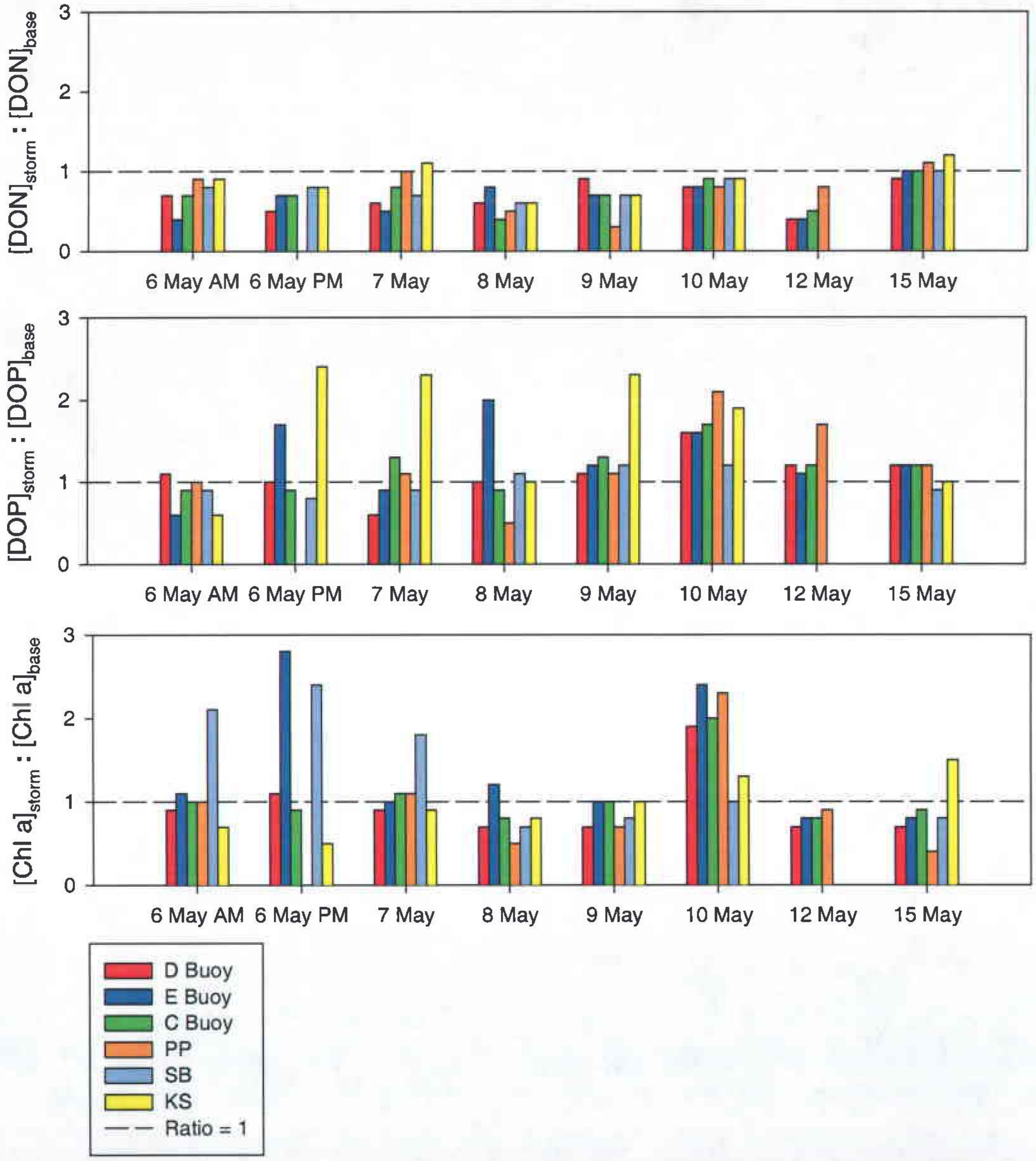


Figure 4.17. Surface dissolved organic nutrient and Chl *a* concentrations for the May 2002 storm event relative to the baseline concentrations described in Chapter 3 for all sites in southern Kaneohe Bay. Dashed line represents a ratio of 1.

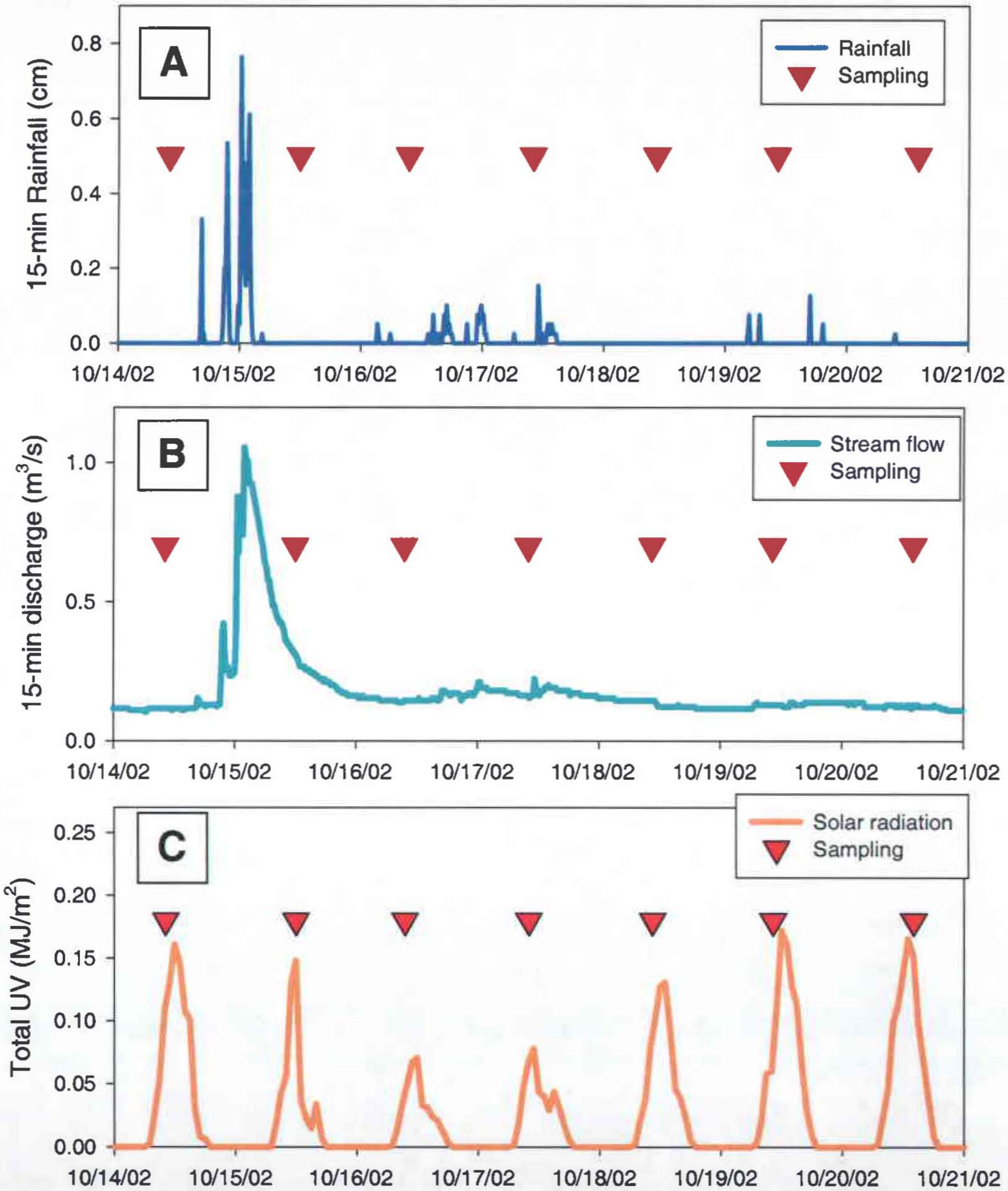


Figure 4.18. (A) Rainfall data recorded at 15-minute intervals at Luluku rain gage for the October 2002 storm event. **(B)** Kaneohe stream discharge recorded at 15-minute intervals at the USGS Kamooalii stream site below Luluku. **(C)** Solar radiation recorded at the HIMB meteorological station. Red triangles represent sampling times at D Buoy.

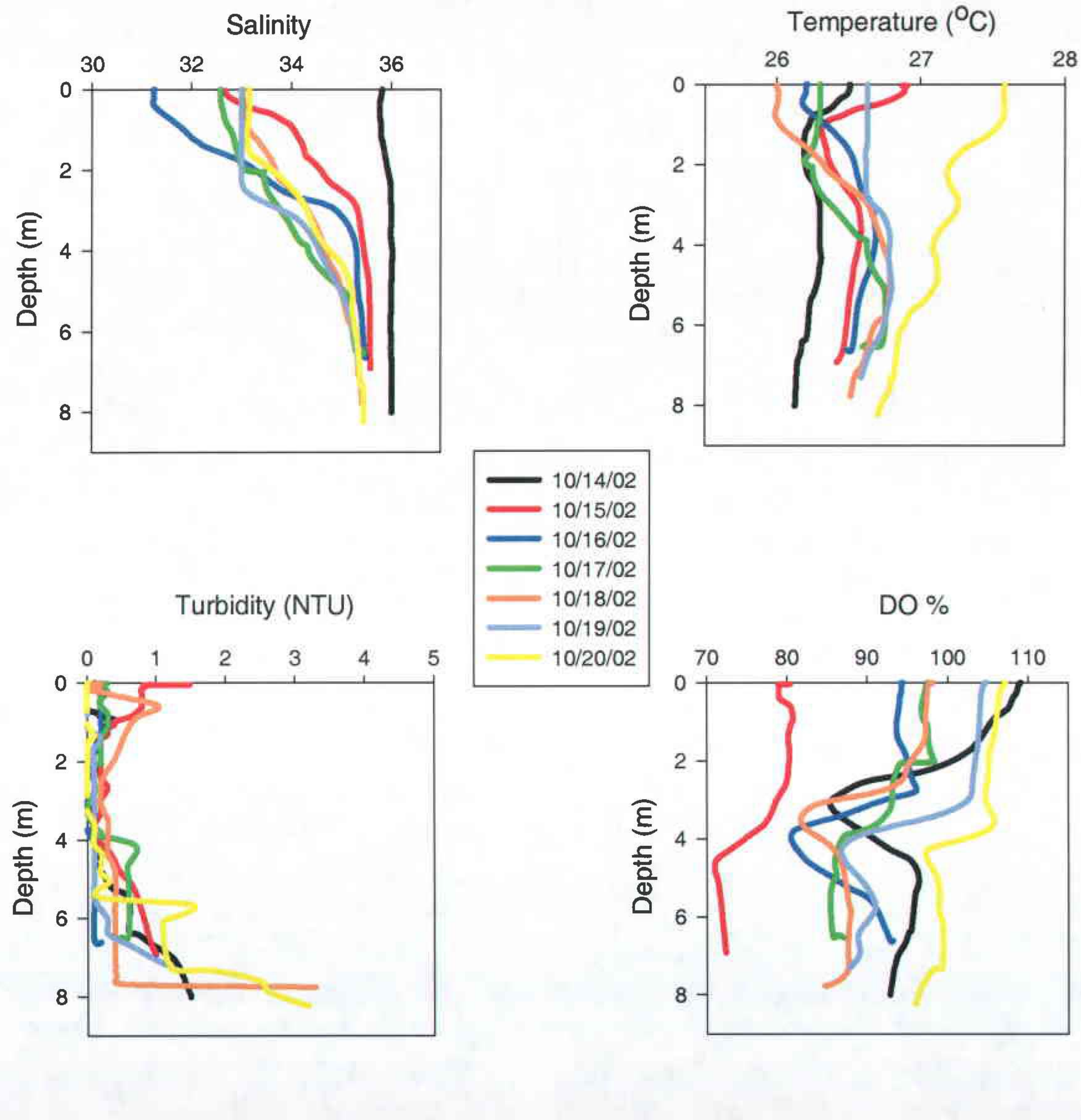


Figure 4.19. Vertical YSI profiles of salinity, temperature, turbidity and dissolved oxygen saturation (DO%) at D Buoy during the October 2002 storm event.

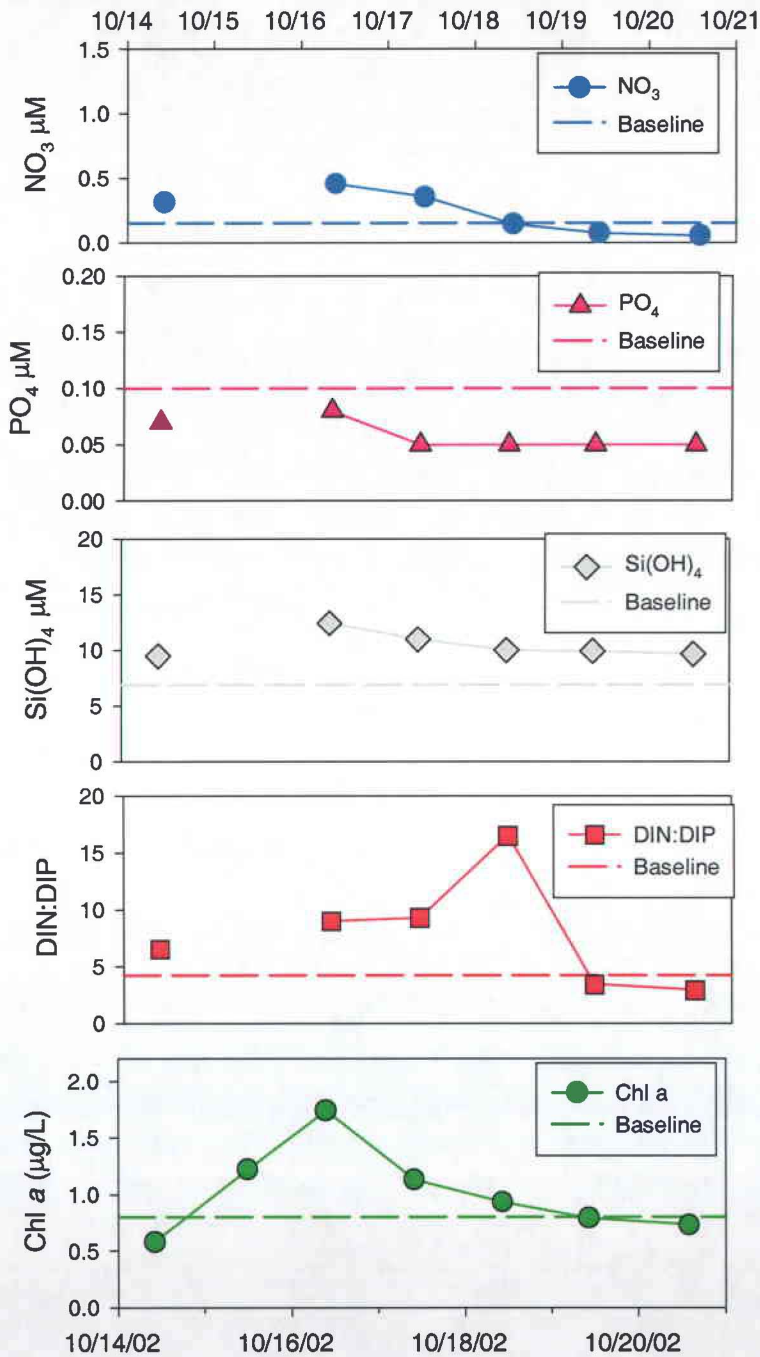


Figure 4.20. Surface dissolved nutrient and Chl *a* concentrations at D Buoy following the October 2002 runoff event. Dashed lines are the average baseline concentrations from Chapter 3.

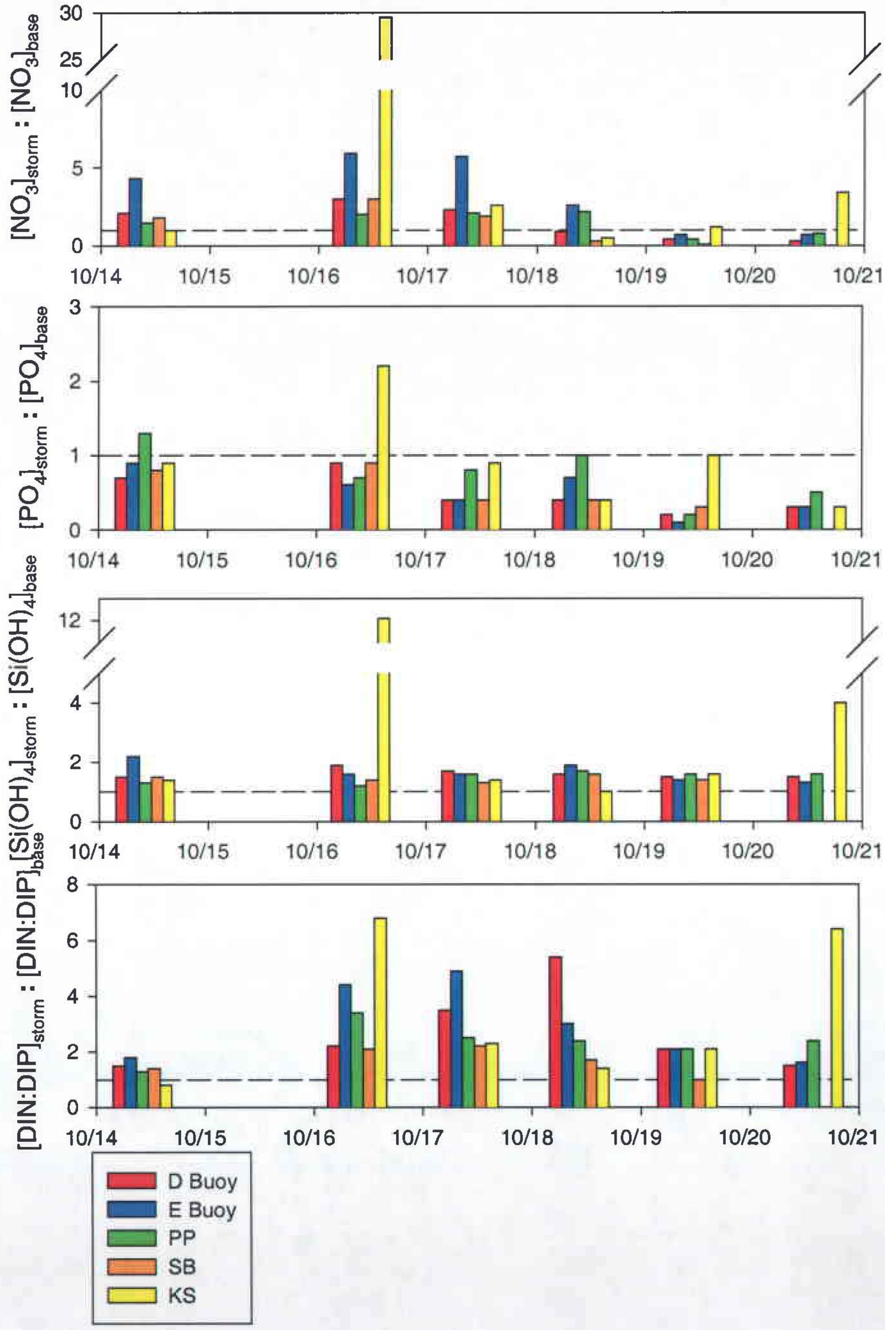


Figure 4.21. Surface dissolved inorganic nutrient concentrations for the October 2002 storm event relative to the baseline concentrations described in Chapter 3 for all sites in southern Kaneohe Bay. Dashed line represents a ratio of 1.

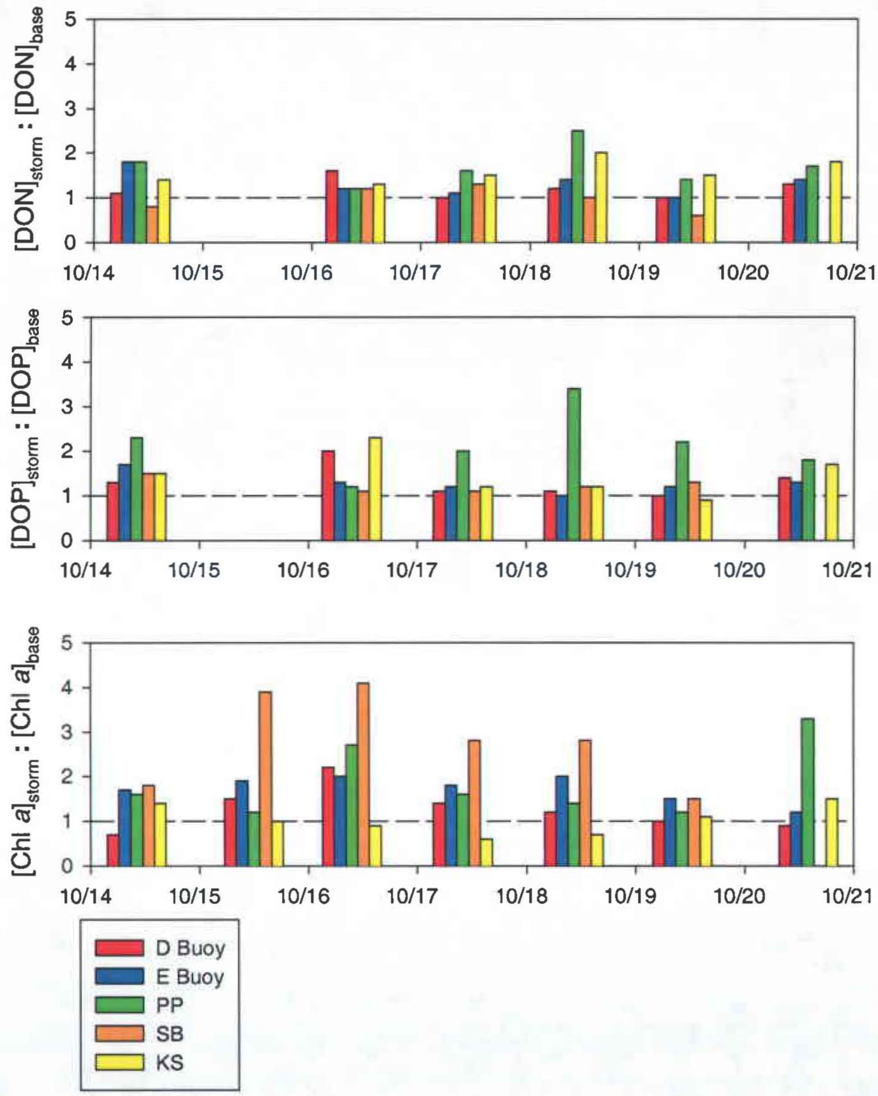


Figure 4.22. Surface dissolved organic nutrient and Chl *a* concentrations for the October 2002 storm event relative to the baseline concentrations described in Chapter 3 for all sites in southern Kaneohe Bay. Dashed line represents a ratio of 1.

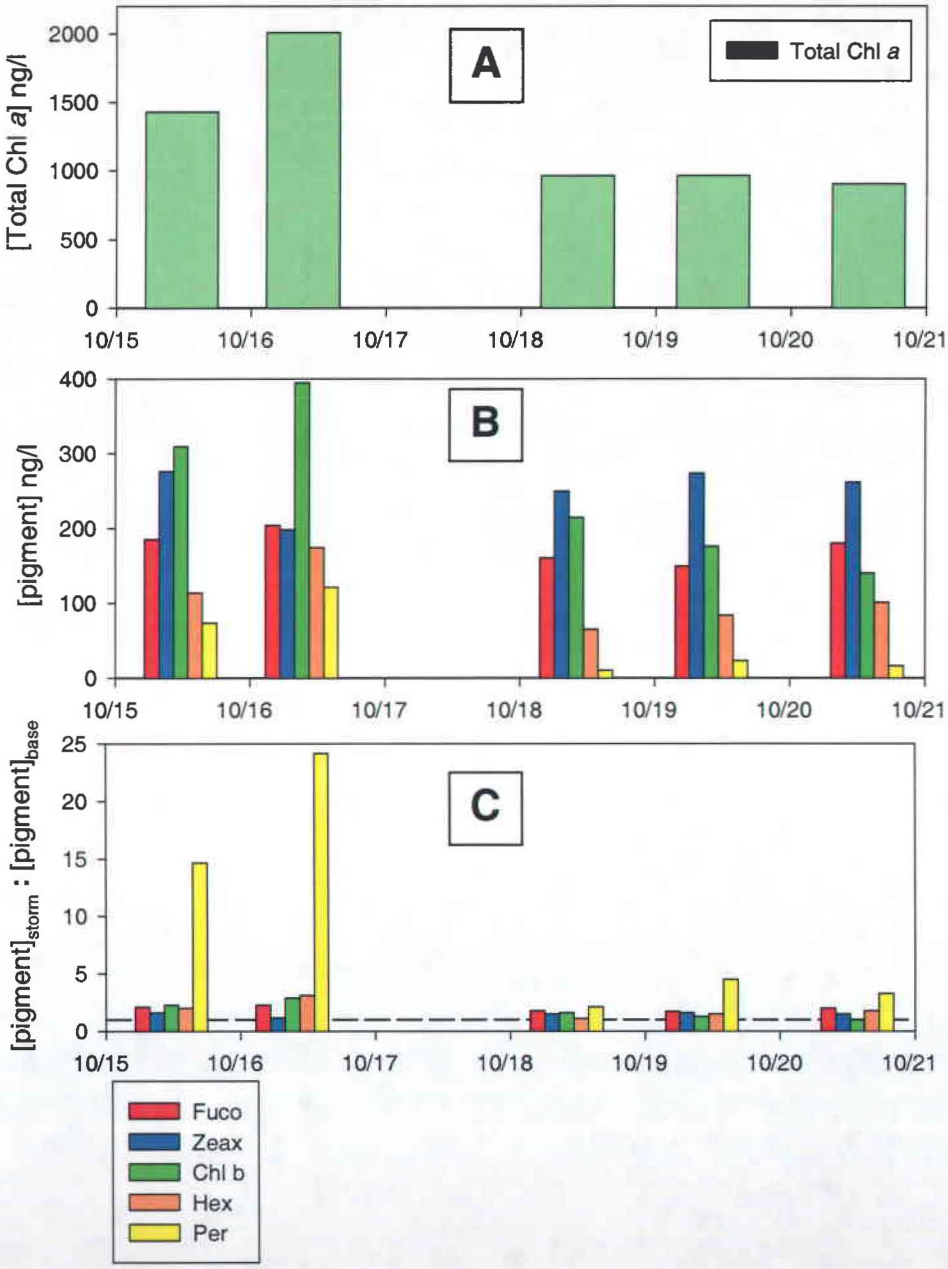


Figure 4.23. HPLC pigment data for surface water collected at D Buoy during the October 2002 event. **(A)** Total Chl *a* surface concentrations. **(B)** Diagnostic photopigment concentrations. **(C)** Ratios of storm pigment concentrations relative to baseline values described in Chapter 3. Fuco = Fucoxanthin, Zeax = Zeaxanthin, Chl b = chlorophyll b, Hex = 19'-hexanoyloxyfucoxanthin, Per = Peridinin.

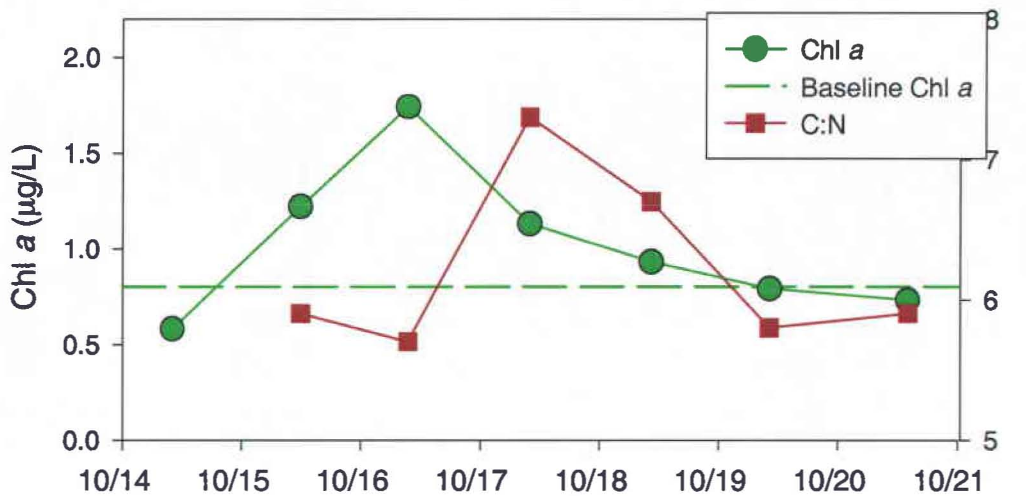


Figure 4.24. Chl *a* concentrations and particulate organic carbon to nitrogen ratios (C:N) at D Buoy following the October 2002 storm event. Dashed line is the average baseline Chl *a* concentration described in Chapter 3.

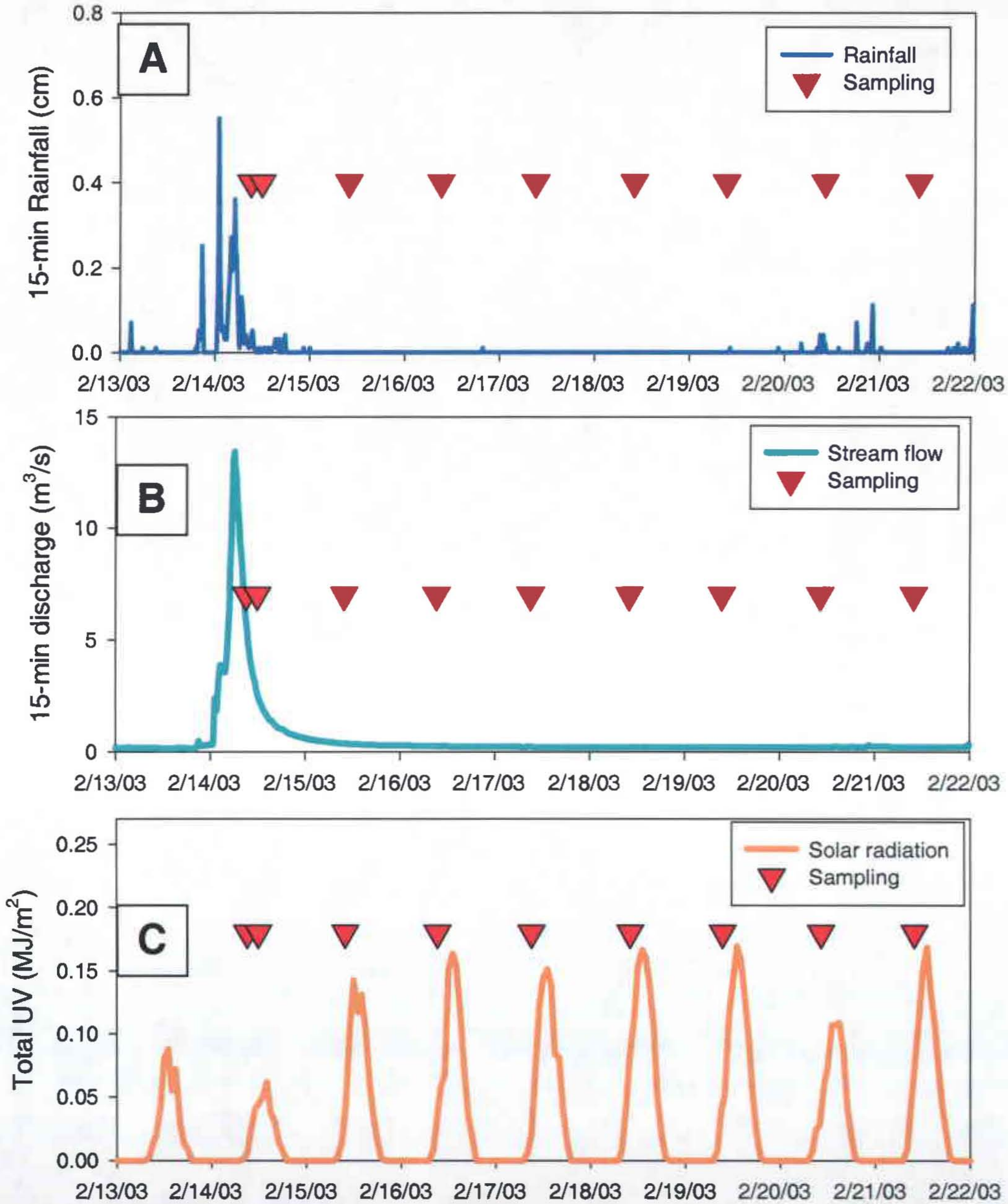


Figure 4.25. (A) Rainfall data recorded at 15-minute intervals at Luluku rain gage for the February 2003 storm event. **(B)** Kaneohe stream discharge recorded 15-minute intervals at the USGS Kamooalii stream site below Luluku. **(C)** Solar radiation recorded at the HIMB meteorological station. Red triangles represent sampling times at D Buoy.

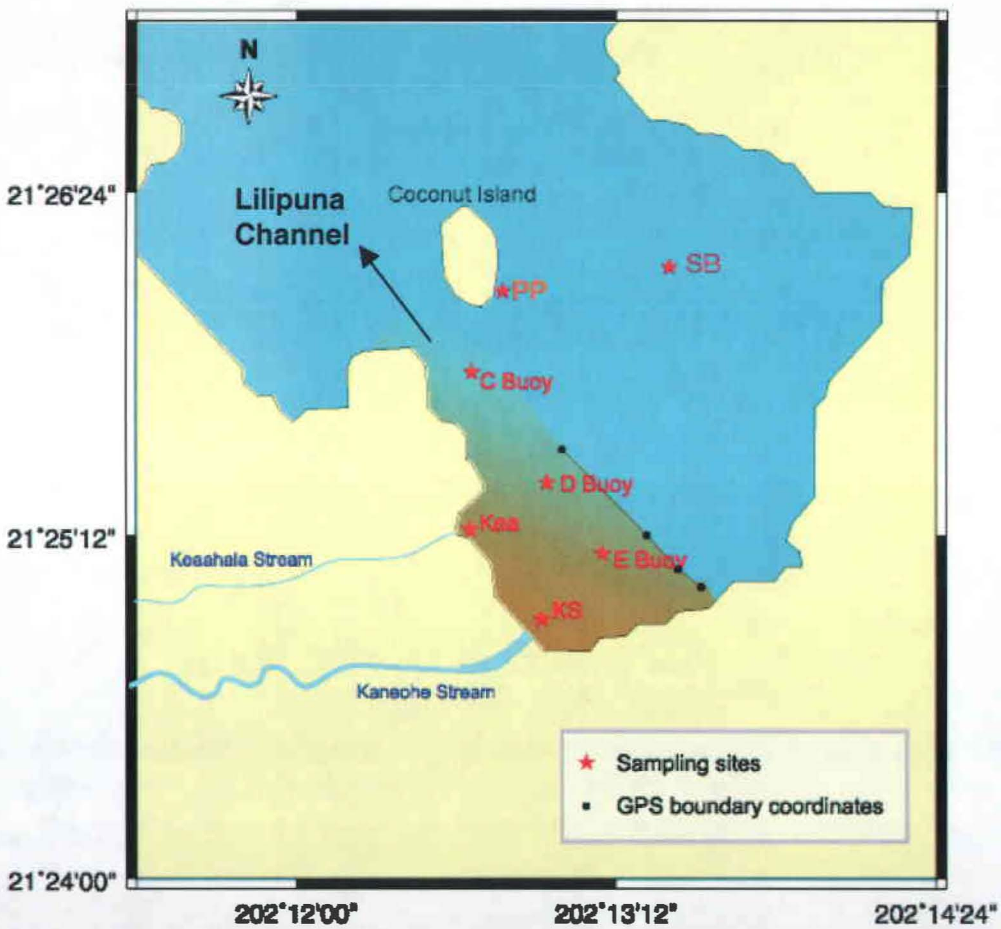


Figure 4.26. Runoff plume boundaries recorded in southern Kaneohe Bay on 14 February 2003 around 11h00.

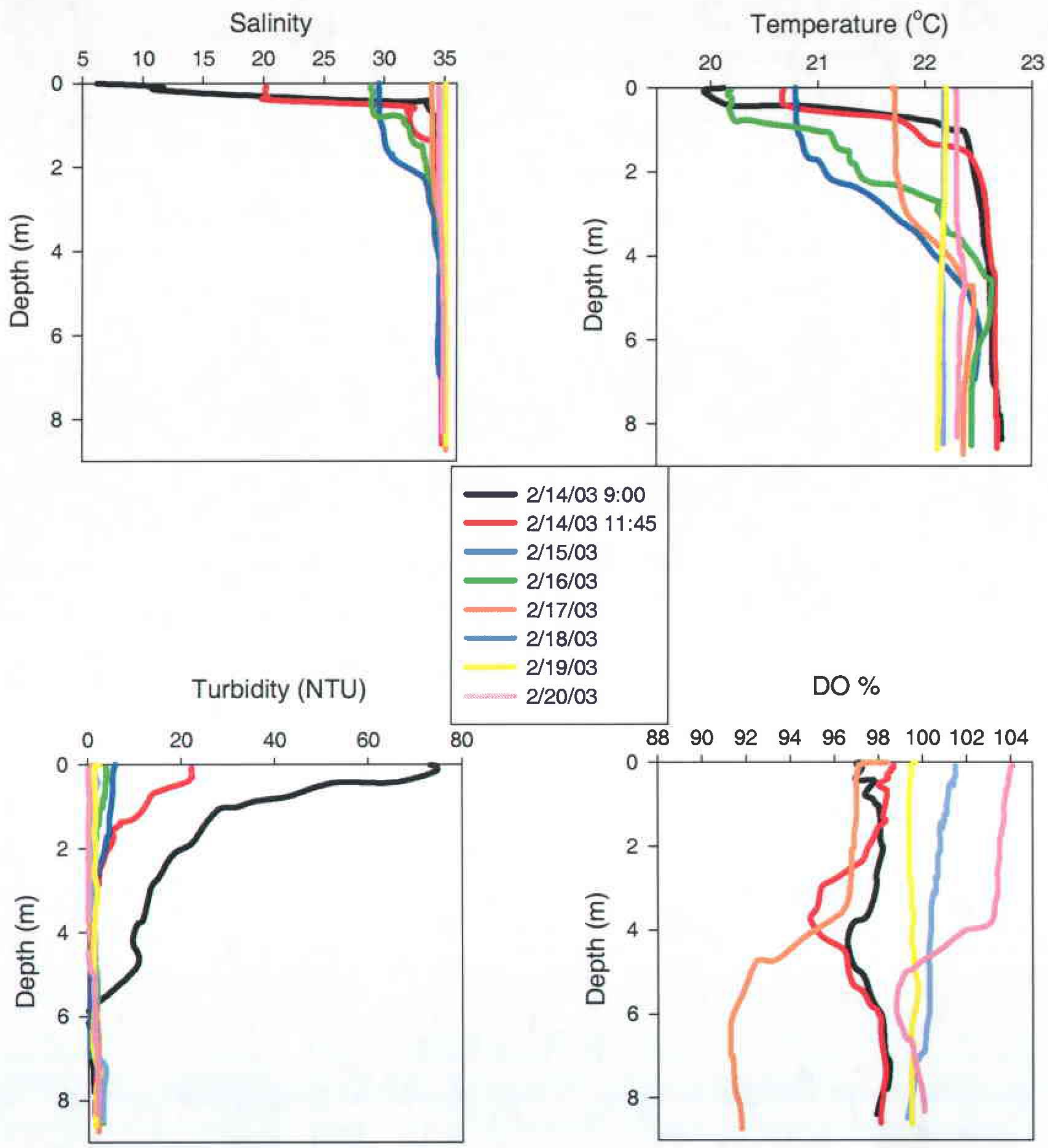


Figure 4.27. Vertical YSI profiles of salinity, temperature, turbidity and dissolved oxygen saturation (DO%) at D Buoy during the February 2003 storm event. Because of rough conditions, dissolved oxygen measurements taken on 2/15/03 and 2/16/03 are not reliable.

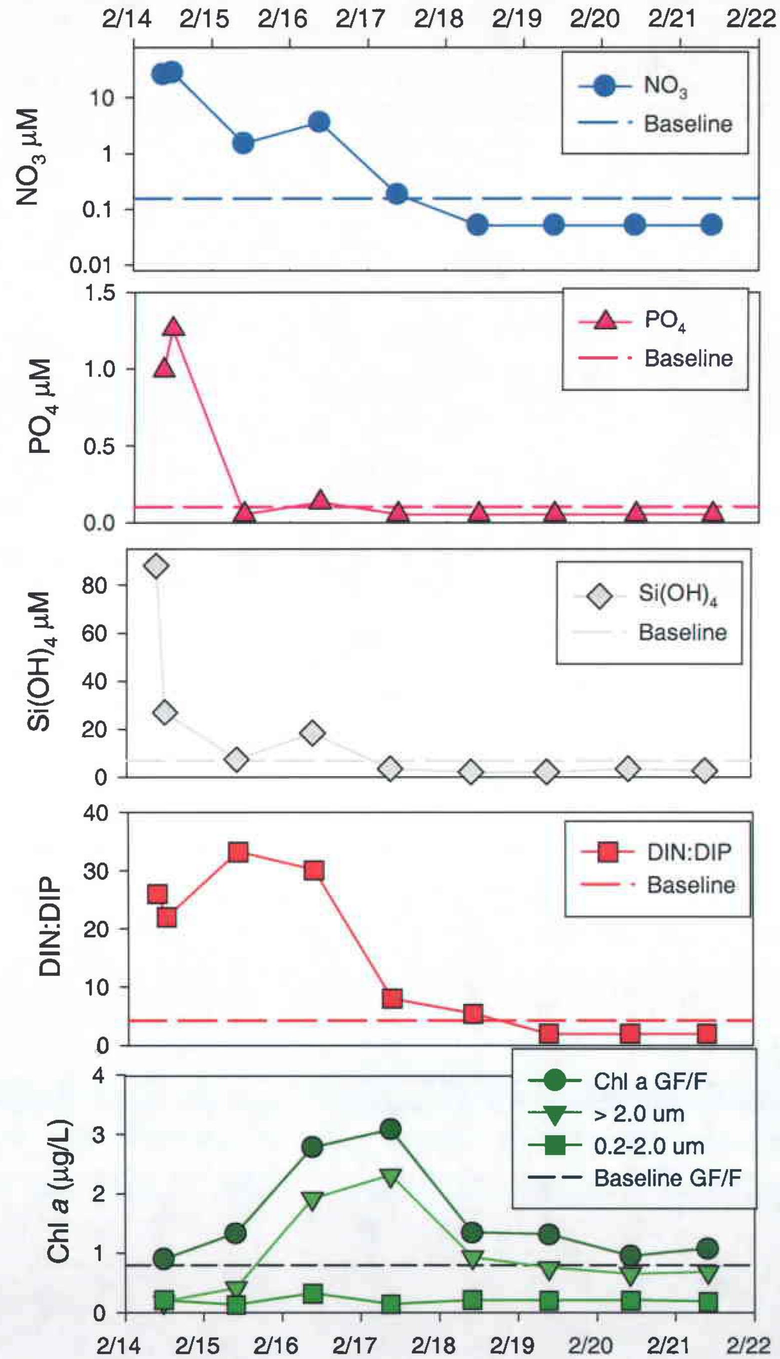


Figure 4.28. Surface dissolved nutrient and Chl a concentrations at D Buoy following the February 2003 runoff event. Dashed lines are the average baseline concentrations from Chapter 3. Note the log scale for NO_3^-. Each water sample for Chl *a* was filtered through different pore sizes.

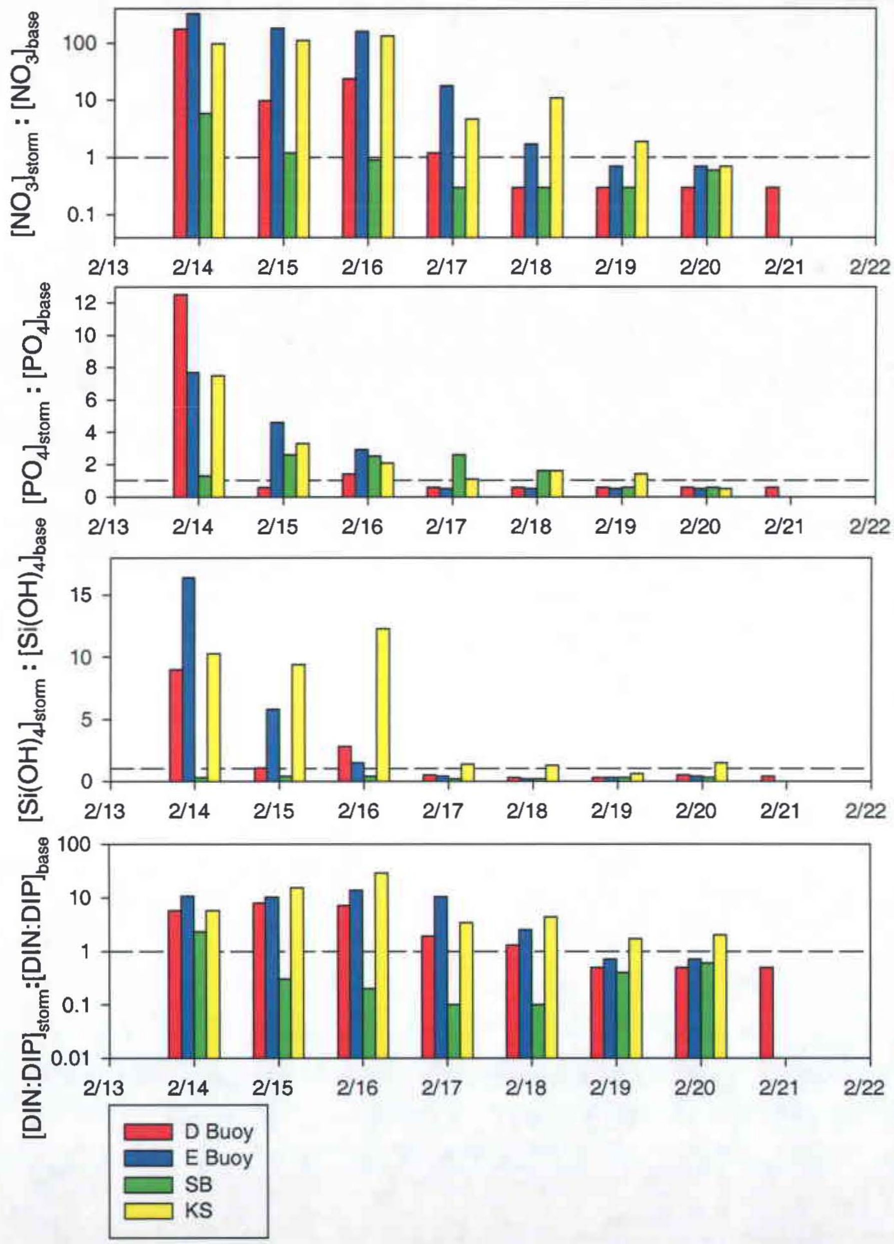


Figure 4.29. Surface dissolved inorganic nutrient concentrations for the February 2003 storm event relative to the baseline concentrations described in Chapter 3 for selected sites in southern Kaneohe Bay. Data were obtained only for D Buoy on 2/21/03. Note the log scale for NO_3^- and DIN:DIP. Dashed line represents a ratio of 1.

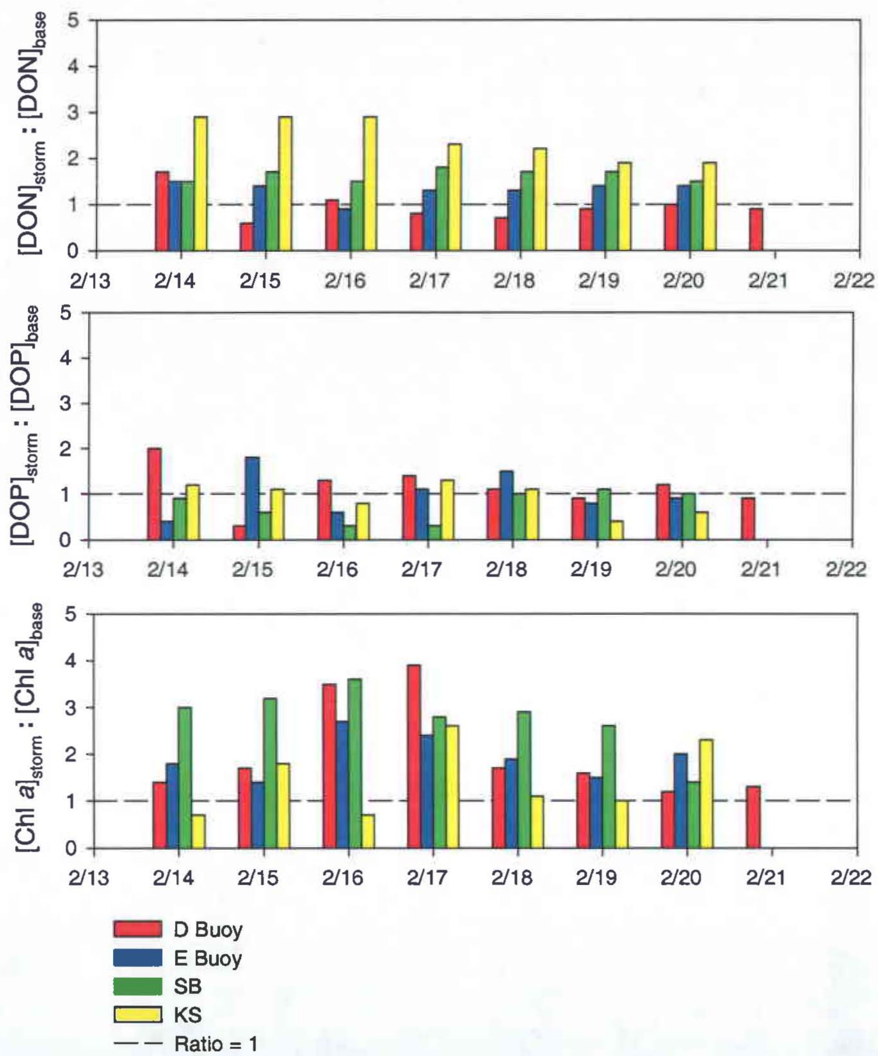


Figure 4.30. Surface dissolved organic nutrient and Chl *a* concentrations for the February 2003 storm event relative to the baseline concentrations described in Chapter 3 for all sites in southern Kaneohe Bay. Data were obtained only for D Buoy on 2/21/03. Dashed line represents a ratio of 1.

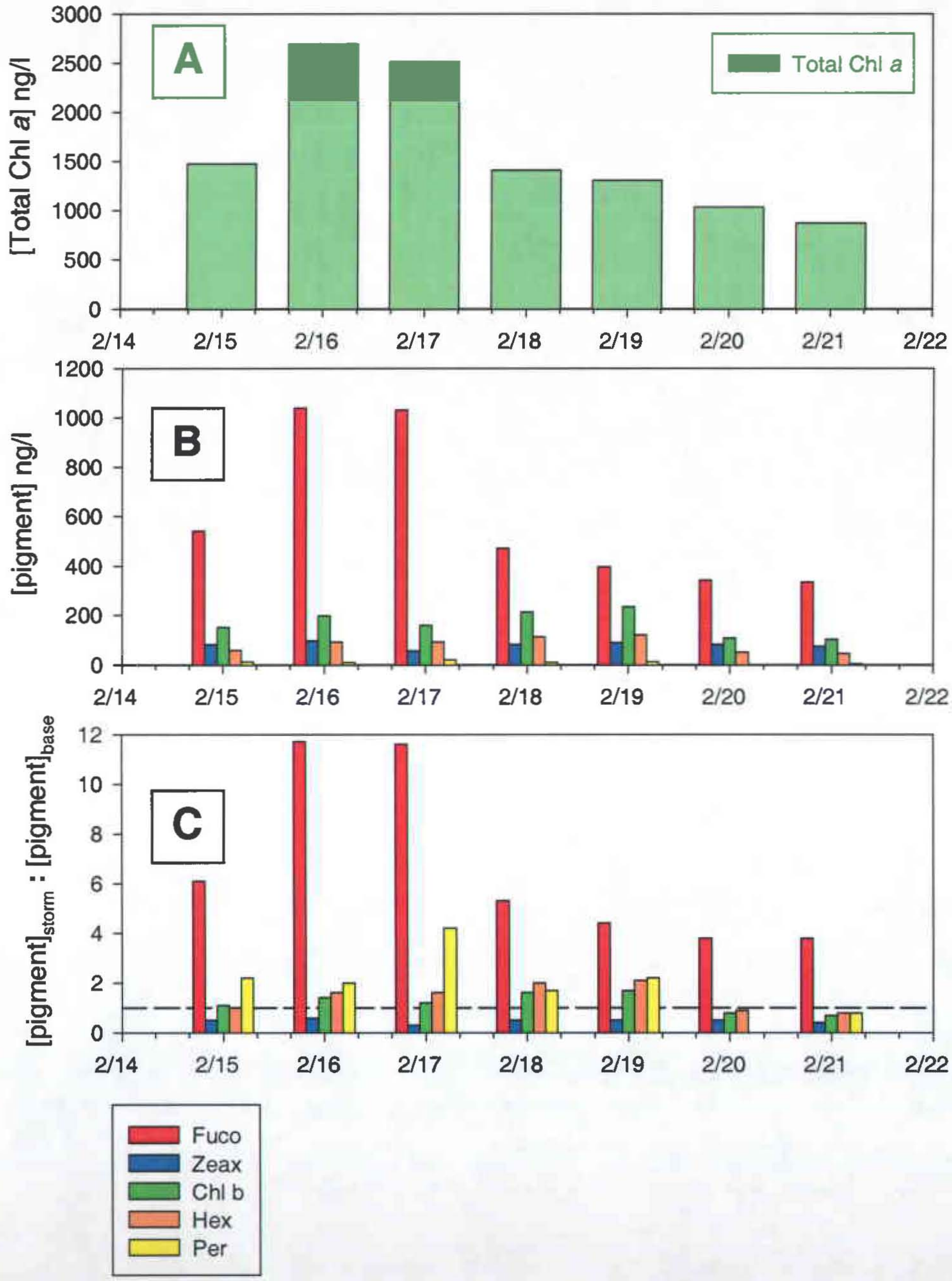


Figure 4.31. HPLC pigment data for surface water collected at D Buoy during the February 2003 event. **(A)** Total Chl *a* surface concentrations. **(B)** Diagnostic photopigment concentrations. **(C)** Ratios of storm pigment concentrations relative to baseline values described in Chapter 3. Fuco = Fucoxanthin, Zeax = Zeaxanthin, Chl b = chlorophyll b, Hex = 19'-hexanoyloxyfucoxanthin, Per = Peridinin.

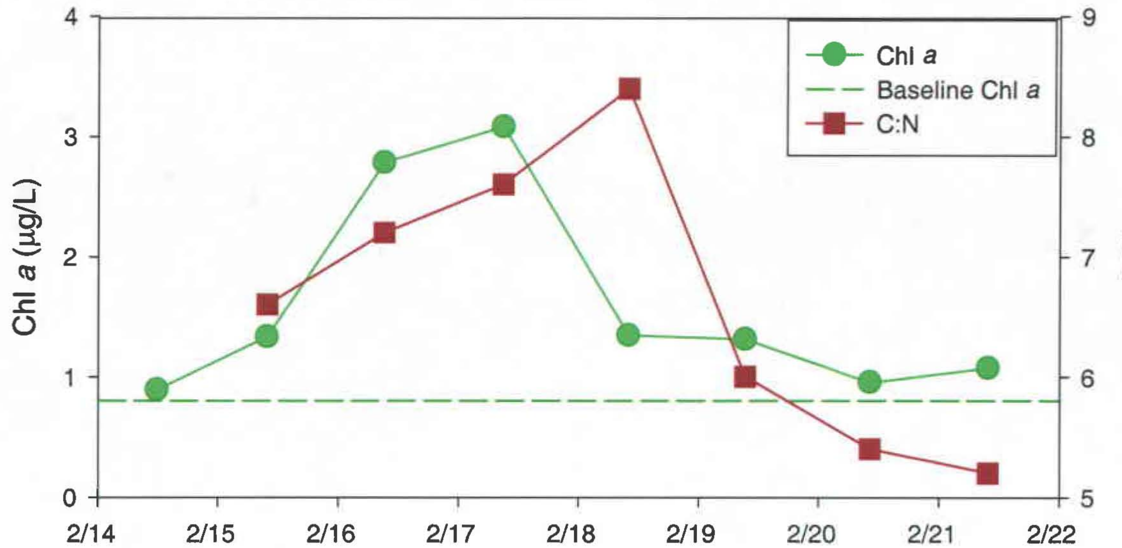


Figure 4.32. Chl *a* concentrations and particulate organic carbon to nitrogen ratios (C:N) at D Buoy following the February 2003 storm event. Dashed line is the average baseline Chl *a* concentration described in Chapter 3.

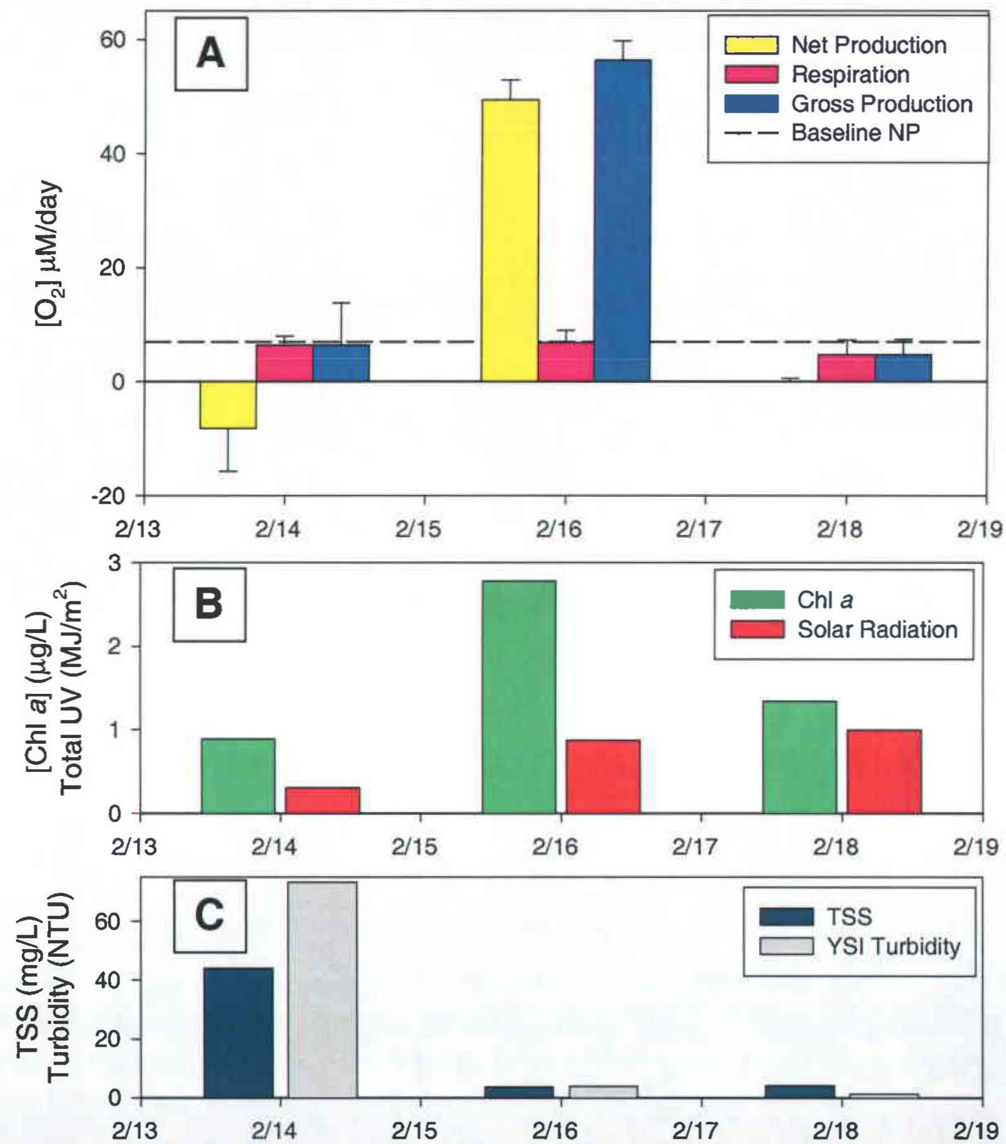


Figure 4.33. **(A)** Daily primary productivity rates measured at D Buoy during the February storm event. Number of replicates was no less than 4 for each set. The error bar corresponds to one standard deviation between the replicates. **(B)** Chl *a* concentrations at the start of the incubation and daily solar radiation for the corresponding dates. **(C)** Surface YSI turbidity and total suspended solid (TSS) concentrations at the start of the incubation.

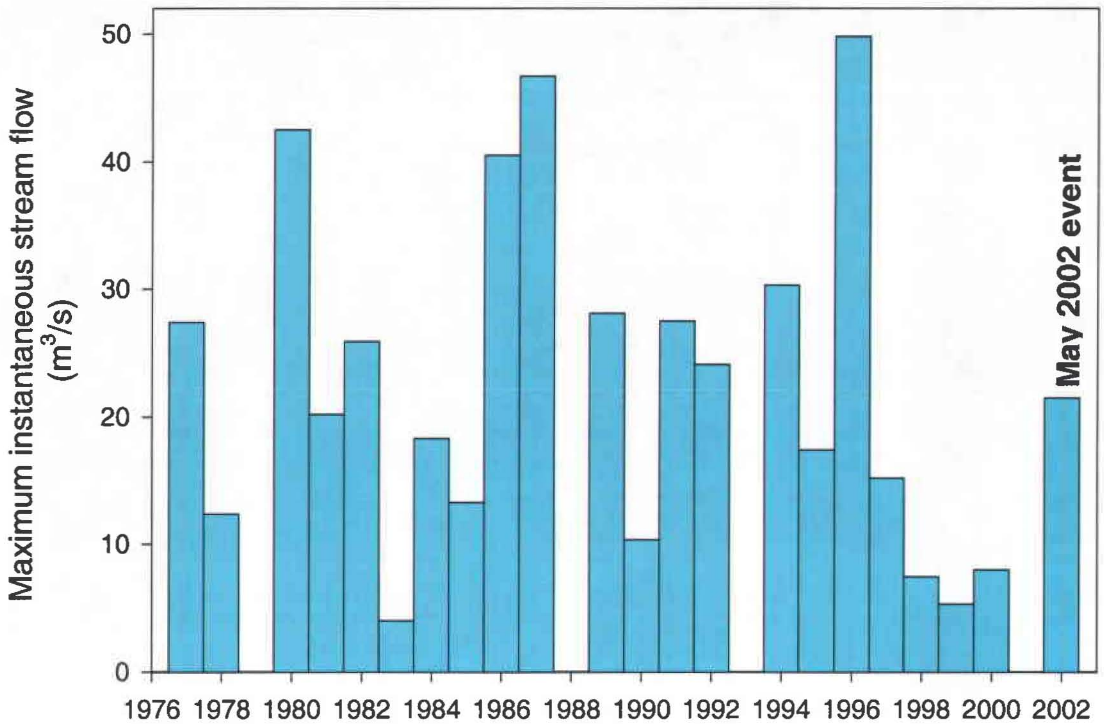


Figure 4.34. Maximum instantaneous stream flow recorded for Kaneohe stream at the USGS Kamooalii site each year for the period 1977-2002. No significant maximum stream flow was recorded for years with missing data.

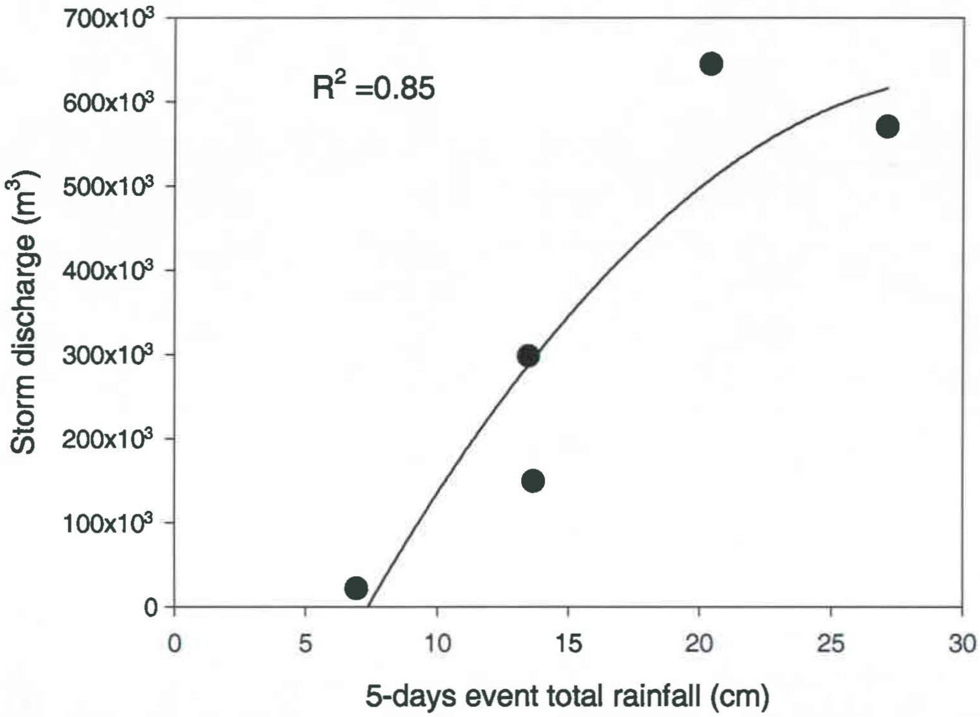


Figure 4.35. Relationship between five-days total rainfall and storm runoff discharge for the storm events sampled during this study. The smooth curve drawn through the data is a second-order polynomial fit by least squares obtained with the software SigmaPlot.

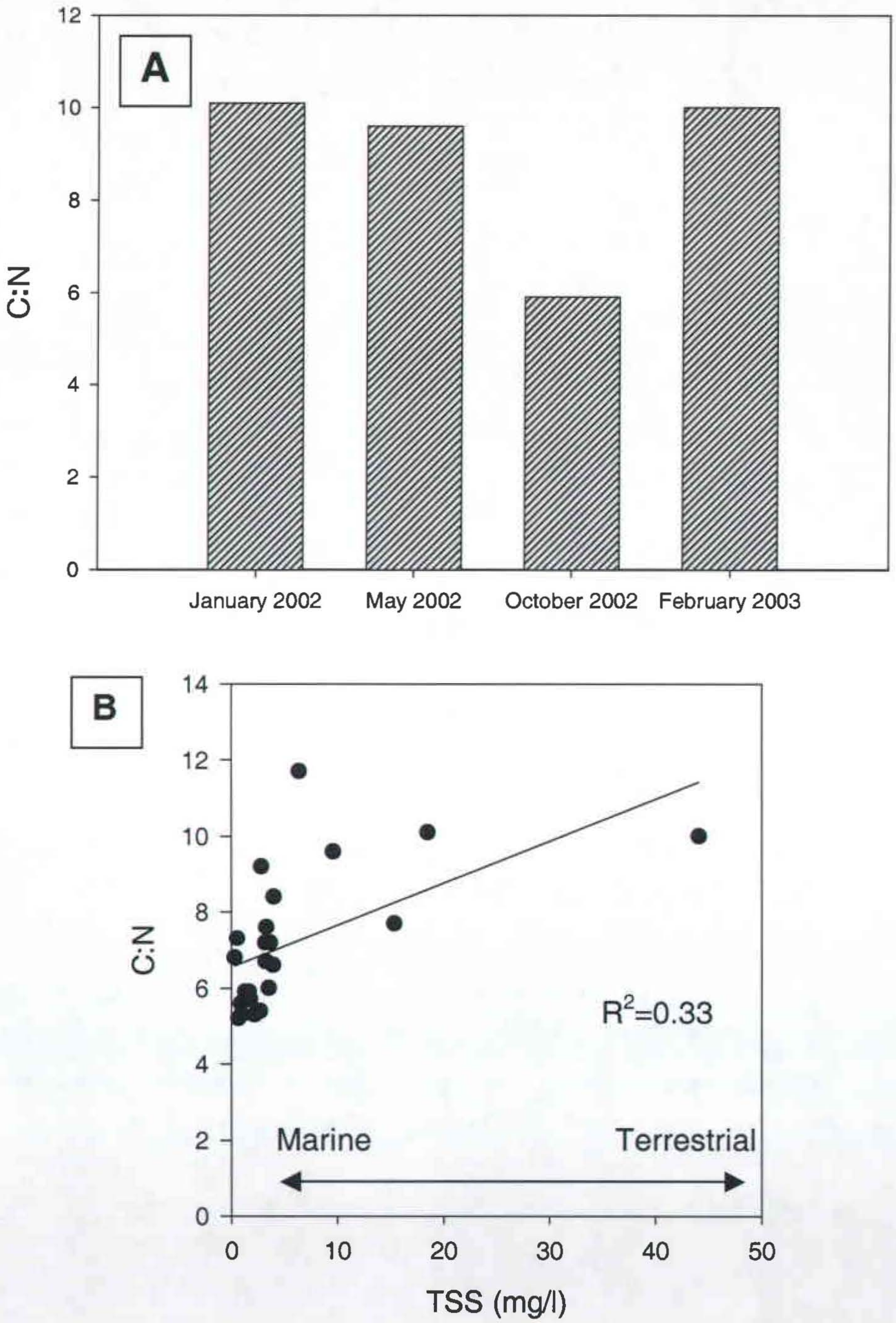


Figure 4.36 (A) Particulate carbon to nitrogen ratios (C:N) measured on the first day of each runoff event. **(B)** Relationship between total suspended solids (TSS) and C:N ratios. Linear regression was calculated with the software SigmaPlot.

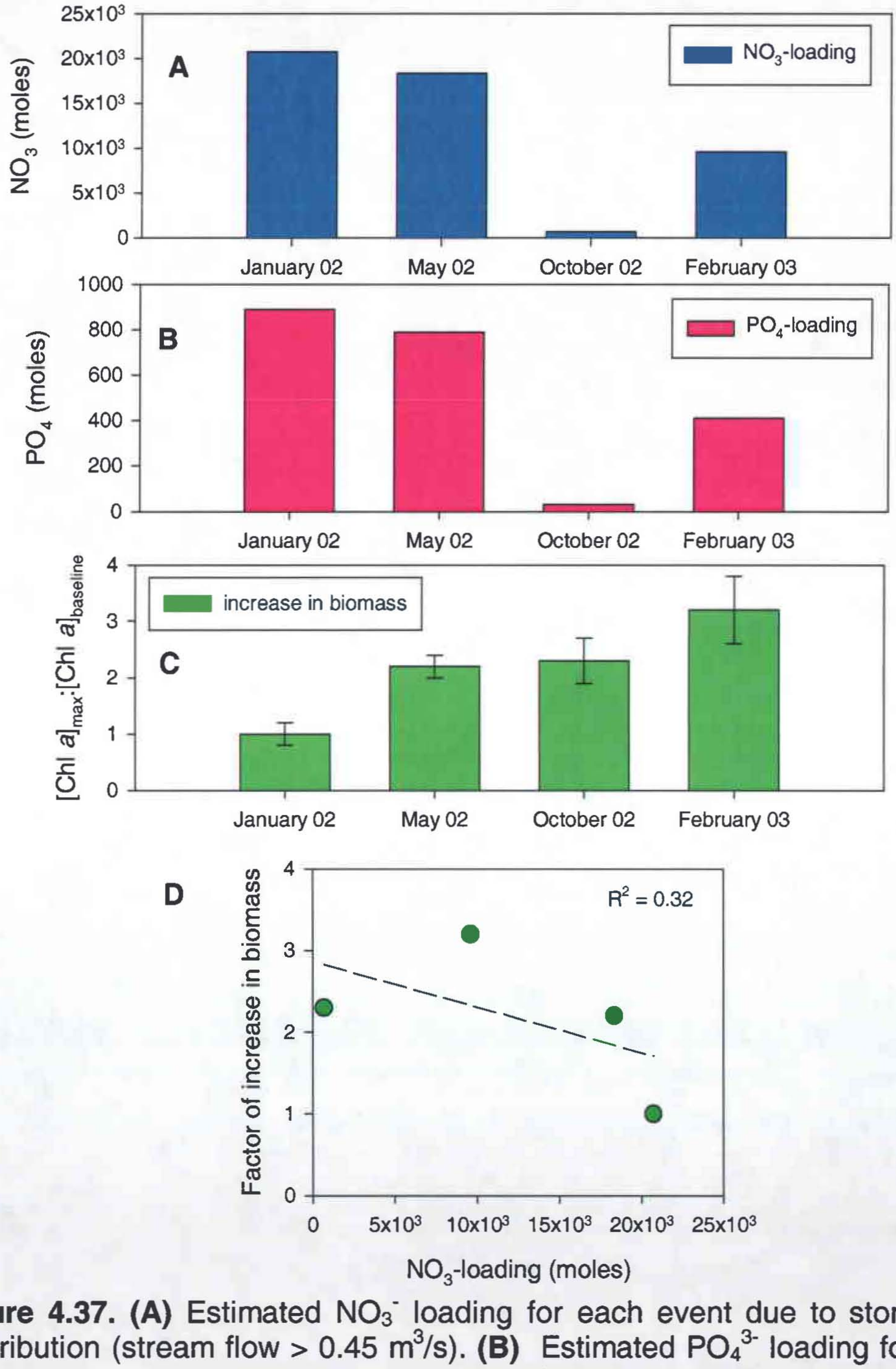


Figure 4.37. (A) Estimated NO_3^- loading for each event due to storm flow contribution (stream flow > 0.45 m^3/s). **(B)** Estimated PO_4^{3-} loading for each event due to storm flow contribution. **(C)** Average factor of increase in phytoplankton biomass in South Bay following each event. Error bars correspond to one standard deviation between the "bay" sites. **(D)** Relationship between factor of increase in biomass and NO_3^- loading.

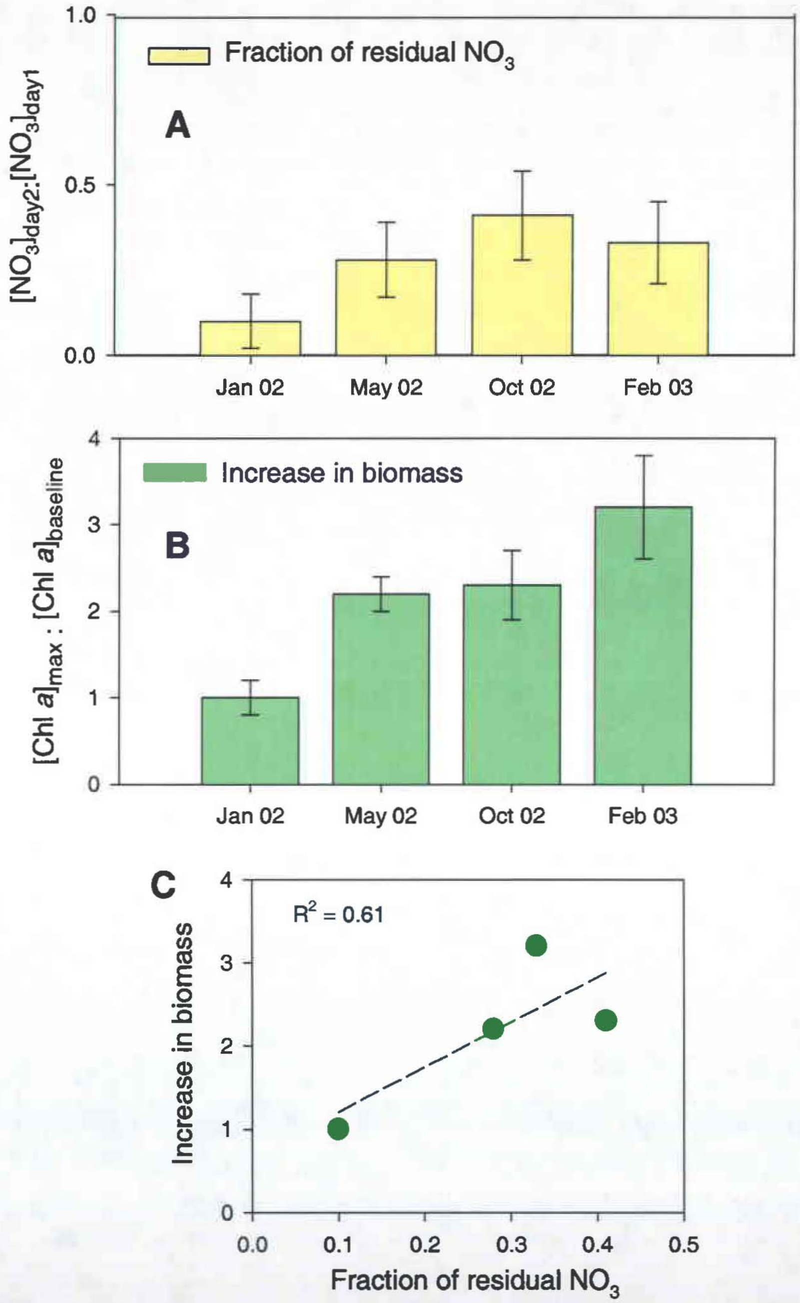


Figure 4.38. (A) Fraction of residual NO_3^- in Bay surface waters following the first day of each event. Error bars correspond to one standard deviation between the "bay" sites. **(B)** Average factor of increase in phytoplankton biomass in South Bay following each event. Error bars correspond to one standard deviation between the "bay" sites. **(C)** Relationship between factor of increase in biomass and fraction of residual NO_3^-.

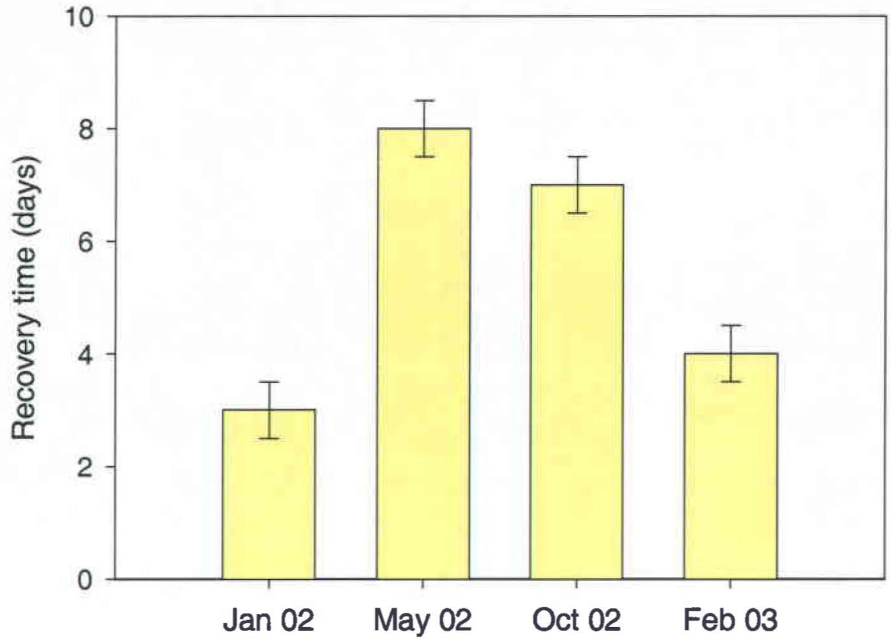


Figure 4.39. Recovery time estimates in South Bay following each storm event based on salinity, temperature and turbidity profiles at the "bay" sites. Error bars correspond to an uncertainty of one day.

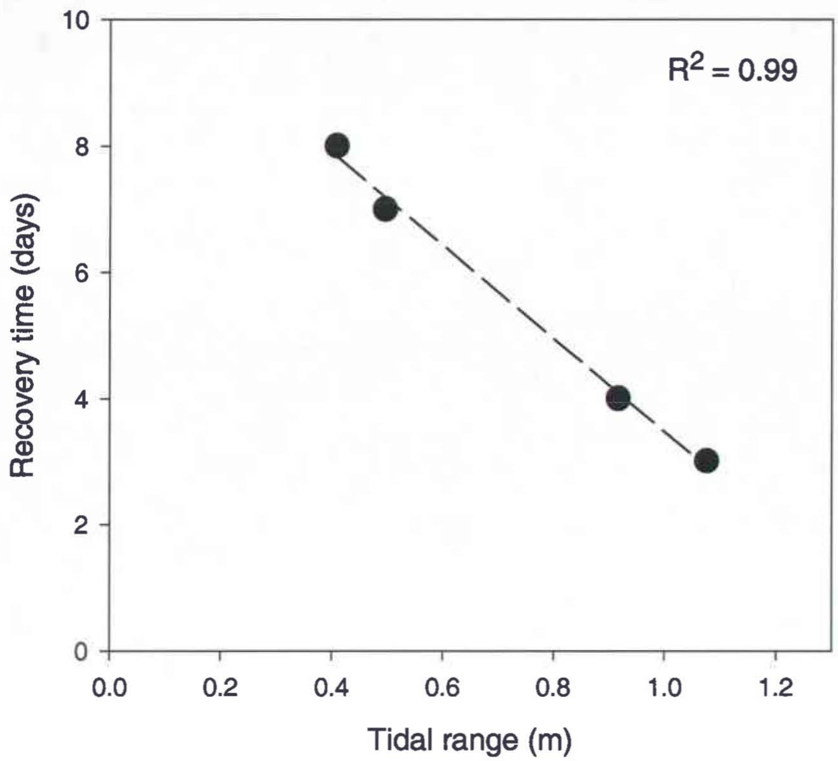


Figure 4.40. Relationship between recovery times and tidal ranges measured at the Mokuoloe station in Kaneohe Bay. Linear regression was calculated with the software SigmaPlot.

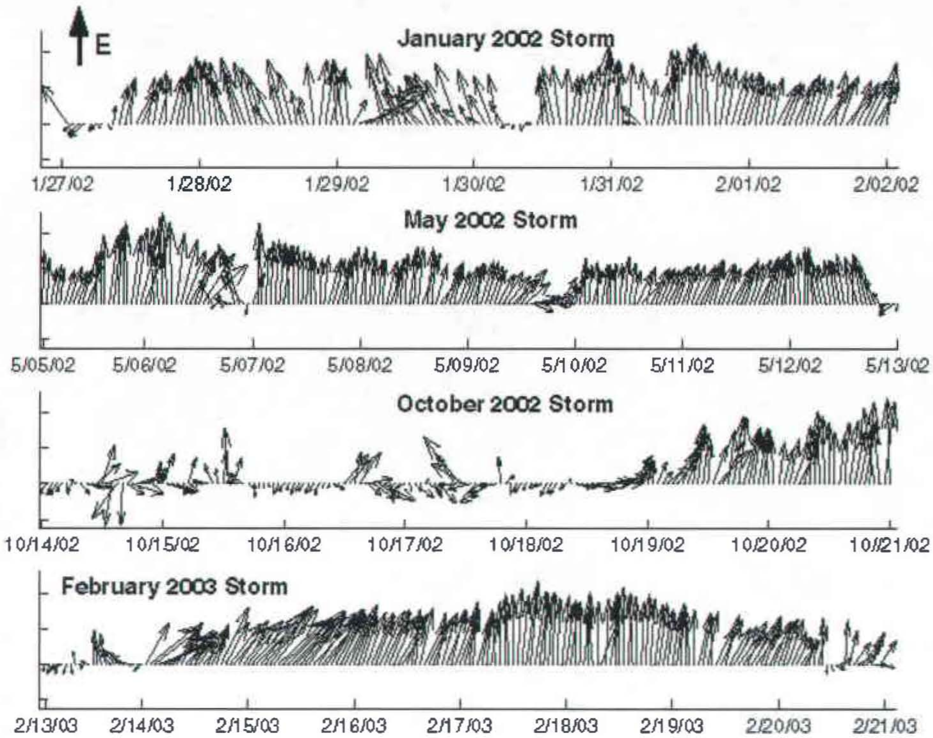


Figure 4.41. Vector plots of hourly wind measurements from the meteorological station located at HIMB for each storm event. Black arrow points East.

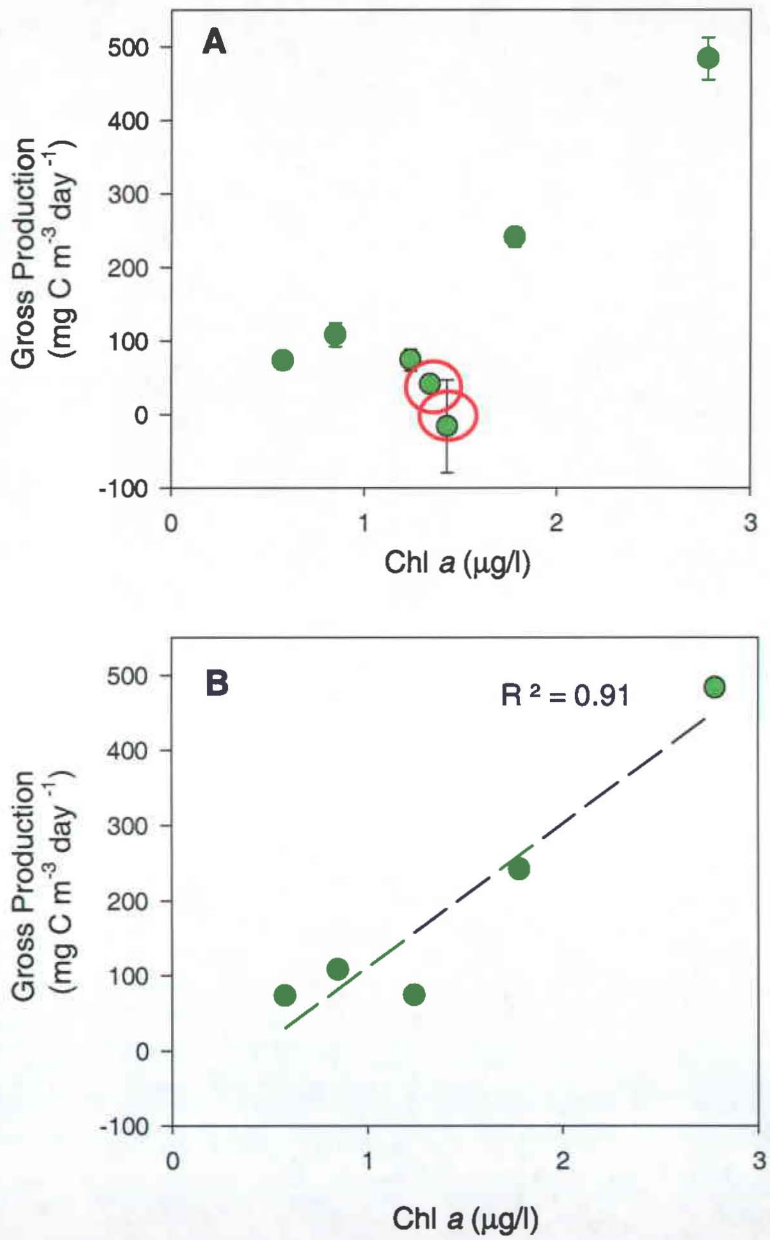


Figure 4.42. **(A)** Daily gross productivity rates versus Chl *a* concentrations for all measurements carried out at D Buoy during this study. Data points circled in red correspond to times of apparent light and nutrient limitation. **(B)** Relationship between gross productivity and Chl *a* obtained when excluding the circled data points in A. Linear regression was calculated with the software SigmaPlot.

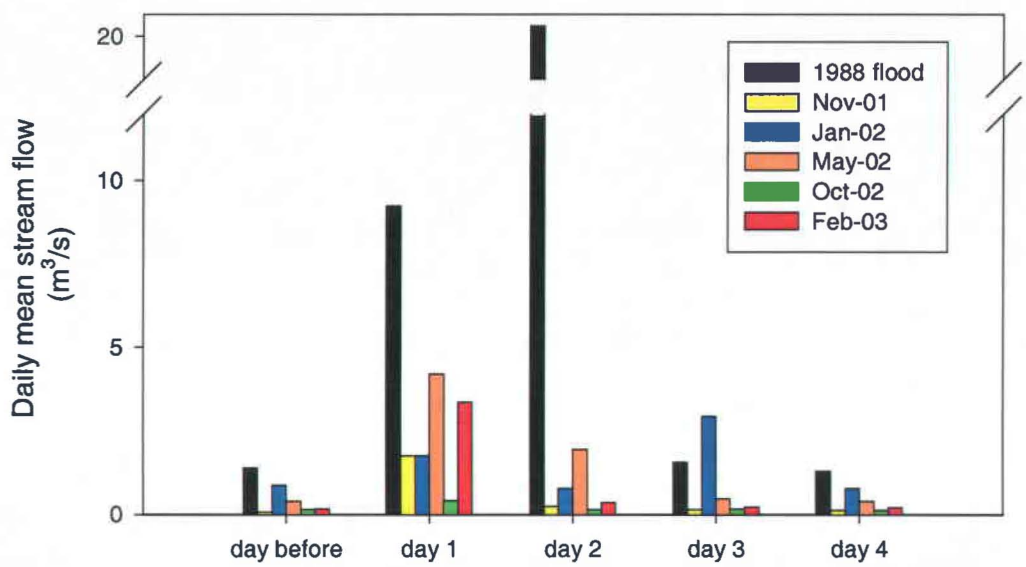


Figure 4.43. Daily mean stream flow recorded at the USGS Kamooalii site for each event. "Day before" corresponds to the day prior to the rainstorm and "day 1" corresponds to the first day of the event. No data were available for the 1965 flood.

CHAPTER 5 : SUMMARY AND CONCLUSIONS

The monitoring work discussed in this thesis was undertaken to assess the short-term impacts of runoff events on water quality in southern Kaneohe Bay. Data presented in Chapter 4 were used to address the four hypotheses outlined in the introduction:

(1) Storm perturbations of conservative water quality parameters such as salinity, temperature and turbidity are short-lived, and the duration of perturbations is determined by the amount of runoff discharged into southern Kaneohe Bay.

(2) Dissolved inorganic nutrient behavior during post-flood recovery in southern Kaneohe Bay is regulated by both physical processes (advection, mixing and dilution) and non-conservative processes (biological uptake).

(3) Moderate storm runoff events significantly enhance phytoplankton growth and productivity in southern Kaneohe Bay, and the magnitude of the ecosystem response is a function of nutrient loading.

(4) Post-flood phytoplankton blooms in southern Kaneohe Bay are primarily regulated by nitrogen availability.

Time-series of post-flood YSI salinity, turbidity and temperature profiles in southern Kaneohe Bay support part of Hypothesis 1: the narrow range of total days for baseline conditions to reestablish after a runoff episode observed in this study (3-8 days) indicates that the storm perturbations are transient events. However, no significant correlation was observed between the recovery time and the amount of discharge for the runoff episodes considered in this study. Changes in flushing times caused by variations in tidal ranges and wind conditions appear to be key factors in determining the duration of the storm perturbations.

Data presented in Chapter 4 revealed that nutrient dynamics are mostly regulated by physical processes such as advection and mixing during the first stages of a storm event. However, the observed fluctuations in nutrient ratios (such as DIN to DIP ratios) during the recovery period imply that non-conservative processes also affect post-flood nutrient behavior. Combined with the observation that an increase in algal population was usually detected following a runoff episode, results obtained in this study support Hypothesis 2.

Except for one storm event, all runoff episodes resulted in an increase in phytoplankton standing crops. Moreover, the productivity measurements carried out during the February storm event indicate that primary productivity rates can be greatly increased following runoff. However, because of variability in export and mixing rates of runoff nutrients, the ecosystem response does not seem to be proportional to the amount of nutrient loading. Thus, results partially support Hypothesis 3 and suggest that moderate runoff events generally enhance algal growth in southern Kaneohe Bay, but that the magnitude of the phytoplankton response is not solely a function of nutrient inputs.

Data presented in this thesis indicate that the termination of post-flood phytoplankton blooms is associated with depletion of both DIN and DIP. However, nitrogen was surprisingly not the primary limiting nutrient during the recovery period; in essentially all storm events considered in this study, NO_3^- was still in excess when PO_4^{3-} was depleted. Thus, although N availability undoubtedly plays an important role in biological processes following runoff events, results do not support Hypothesis 4 and suggest that post-flood blooms are primarily controlled by P availability.

Results of this study have important implications for management of southern Kaneohe Bay and other Hawaiian coastal waters. Because of evidences of non-point source pollution from urbanized areas of the southern portion of the Kaneohe watershed, it seemed reasonable to assume that runoff nutrients would have considerable impacts on the bay ecosystem. Although runoff episodes unquestionably affected bay waters, the recovery time of the ecosystem was short, even for significant and noteworthy storm episodes. This indicates that high flushing rates characteristic of Hawaiian coastal waters act as a natural buffer to anthropogenic impacts. However, it does not imply that Hawaiian coastal waters are not vulnerable to runoff inputs. As evidenced by historical events, consecutive rainstorms can have synergetic impacts. In addition, perturbations attributable to sediment loading are probably significant on longer timescales, particularly for coral reef communities (Gilmour, 1999).

Another important conclusion relates to the concept of nutrient limitation. There is strong evidence that the nutrient limitation status in Kaneohe Bay is subject to change on short timescales. As a result, generalizations concerning nutrient limitation of Hawaiian coastal waters should be viewed with caution. For example, prolonged wet conditions in the Kaneohe watershed could result in a long-lasting conversion from N to P limitation of bay productivity.

Meteorological and hydrological conditions and their effects on water residence time undoubtedly account for some of the observed variability in the timing and magnitude of the ecosystem response. Impacts of runoff nutrient loading are too often approximated as a simple linear "cause-to-effect" phenomenon, particularly for modeling considerations. As a result, model simulations of ecosystem dynamics do not always corroborate the observations, particularly with regard to timescales of processes. For example, the response patterns of the KECOM model (Kaneohe Bay ECOsystem Model, Tanaka 2002) to a typical storm perturbation generally agree with observations presented in this study. Almost immediately after the storm perturbation (nutrient loading via increased runoff), KECOM simulated an increase in phytoplankton biomass, which was followed by a decline of the pelagic algal population due to nitrogen depletion and increased grazing pressure. KECOM predicted an increase of the phytoplankton biomass of about 10 % above the pre-storm levels. Subsequently, the model simulated a second bloom of pelagic autotrophs in response to an increase in the respiratory release of ammonium by heterotrophs. The second phytoplankton bloom was much larger and was observed approximately one month after the storm perturbation in the model simulation. All reservoir masses returned to their original sizes after exhibiting oscillations for a period corresponding to roughly six months in the model simulation. While the directions of changes in the model simulation agree for the most part with field data, the magnitude and timing of ecosystem processes differ substantially. Results from this study demonstrate a greater initial response of pelagic autotrophs than the one predicted by KECOM. As pointed out by Tanaka, the discrepancy most likely results from the uncertainties in biological uptake kinetics. Observational data suggest that nutrient uptake rates were faster than those used in the model simulation. In contrast to KECOM simulations, no secondary algal blooms were observed during this study. Because Tanaka used a fixed value of 13 days for water residence time, the nutrient retention time in the model was also likely over-estimated. Data obtained during this study indicate that post-storm flushing times vary between 3 and 8 days. Thus, results from this study suggest that comprehensive models of tropical ecosystems, such as Kaneohe Bay, subject to episodic events should also incorporate factors influencing nutrient retention capacity such as variations in flushing times, wind regimes and tidal ranges.

REFERENCES

Antoniou, P., J. Hamilton, B. Koopman, R. Jain, B. Holloway, G. Lyberatos and S. A. Svoronos (1990). Effect of temperature and pH on the effective maximum specific growth rate of nitrifying bacteria. *Water Research* **24**: 97-110.

Arhonditsis, G., G. Tsirtsis, M. O. Angelidis and M. Karydis (2000). Quantification of the effects of nonpoint nutrient sources to coastal marine eutrophication: applications to a semi-enclosed gulf in the Mediterranean Sea. *Ecological Modelling* **129**(2-3): 209-227.

Banner, A. H. (1968). A freshwater "kill" on the coral reefs of Hawaii. Hawaii Institute of Marine Biology,Honolulu, 29.

Bathen, K. H. (1968). A descriptive study of the physical oceanography of Kaneohe Bay, Oahu, Hawaii. Hawaii Institute of Marine Biology,Honolulu, 353.

Bender, M., K. Grande, K. Johnson, J. Marra, P. J. L. Williams, J. Sieburth, M. Pilson, C. Langdon, G. Hitchcock, J. Orchardo, C. Hunt, P. Donaghay and K. Heinemann (1987). A comparison of four methods for determining planktonic community production. *Limnology and Oceanography* **32**(5): 1085-1098.

Bender, M., J. Orchado, M.-L. Dickson, R. T. Barber and S. Lindley (1999). In vitro O_2 fluxes compared with ^{14}C production and other rate terms during teh JGOFS Equatorial Pacific experiment. *Deep-Sea Research* **46**: 637-654.

Berner, R. A. and J.-L. Rao (1994). Phosphorus in sediments of the Amazon River and estuary: Implications for the global flux of phosphorus to the sea. *Geochimica et Cosmochimica Acta* **58**(10): 2333-2339.

Bolin, B., P. J. Crutzen, P. M. Vitousek, R. G. Woodmansee, E. D. Goldberg and R. B. Cook (1983). Interactions of Biogeochemical Cycles. The Major Biogeochemical Cycles and Their Interactions. B. Bolin and R. B. Cook. **SCOPE 21**.

Bostater, C. and R. Biggs (1985). River input as a principal cause of nutrient distribution in the Patuxent Estuary. *Estuaries* **8**(2B).

Brown, V. A., J. J. McDonnell, D. A. Burns and C. Kendall (1999). The role of event water, a rapid shallow flow component, and catchment size in summer stormflow. *Journal of Hydrology* **217**(3-4): 171-190.

Burr, S. (2003). Kaneohe Stream Bioassessment. Hawaii Department of Health,Honolulu, 21.

Caperon, J., S. A. Cattell and G. Krasnick (1971). Phytoplankton kinetics in a subtropical estuary: eutrophication. *Limnology and Oceanography* **16**: 599-607.

Caperon, J., D. Schell, J. Hirota and E. Laws (1979). Ammonia excretion rates in Kaneohe Bay, Hawaii, measured by a SUP-15 N isotope dilution technique. *Marine biology* **54**(1): 33-40.

Carpenter, J. H. (1965). The Chesapeake Bay Institute Technique for the Winkler dissolved oxygen method. *Limnology and Oceanography* **10**(1): 141-143.

Chanton, J. and F. G. Lewis (2002). Examination of coupling between primary and secondary production in a river-dominated estuary: Apalachicola Bay, Florida, U.S.A. *Limnology and Oceanography* **47**(3): 683-687.

Coles, S. L. and P. L. Jokiel (1992). Effects of salinity on coral reefs. Pollution in Tropical Aquatic Systems. D. W. Connell and D. W. Hawker. London, CRC Press: 147-166.

Corredor, J. E., R. W. Howarth, R. R. Twilley and J. M. Morell (1999). Nitrogen cycling and anthropogenic impact in the tropical interamerican seas. *Biogeochemistry* **46**(1): 163-178.

Correll, D. L., T. E. Jordan and D. E. Weller (1992). Nutrient flux in a landscape: Effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. *Estuaries* **15**: 431-442.

D'Elia, C. F., J. G. Sanders and W. R. Boynton (1986). Nutrient enrichment studies in a coastal plain estuary: Phytoplankton growth in large-scale, continuous cultures.

DiTullio, G. R. and E. A. Laws (1983). Estimates of phytoplankton N uptake based on super(14)CO sub(2) incorporation into protein. *Limnology and Oceanography* **28**(1): 177-185.

DiTullio, G. R. and E. A. Laws (1986). Diel periodicity of nitrogen and carbon assimilation in five species of marine phytoplankton: Accuracy of methodology for predicting N-assimilation rates and N/C composition ratios. *Marine ecology progress series* **32**(2-3): 123-132.

Doering, P. H., C. A. Oviatt, B. L. Nowicki, E. C. Klos and L. W. Reed (1995). Phosphorus and nitrogen limitation of primary production in a simulated estuarine gradient. *Marine ecology progress series* **124**(1-3): 271-287.

Dykes, A. P. and J. B. Thornes (2000). Hillslope hydrology in tropical rainforest steeplands in Brunei. *Hydrological Processes* **14**(2): 215-235.

Eyre, B. and P. Balls (1999). A Comparative Study of Nutrient Behavior along the Salinity Gradient of Tropical and Temperate Estuaries. *Estuaries* **22**(2A): 313-326.

Eyre, B. and C. Twigg (1997). Nutrient behaviour during post-flood recovery of the Richmond River Estuary northern NSW, Australia. *Estuarine, Coastal and Shelf Science* **44**(3): 311-326.

Eyre, B. D. (1995). A fisrt-order nutrient budget for the tropical Moresby Estuary and catchment North Queensland, Australia. *Journal of Coastal Research* **11**: 717-732.

Falkowski, P. G. and J. A. Raven (1997). Aquatic Photosynthesis. Malden, Blackwell Science 375.

Falkowski, P. G., A. Sukenik and R. Herzig (1989). Nitrogen limitation in Isochrysis galbana (Haptophyceae). 2. Relative abundance of chloroplast proteins. *Journal of Phycology* **25**(3): 471-478.

Ferrier-Pages, C., J. P. Gattuso, G. Cauwet, J. Jaubert and D. Allemand (1998). Release of dissolved organic carbon and nitrogen by the zooxanthellate coral Galaxea fascicularis. *Marine Ecology Progress Series* **172**: 265-274.

Fisher, T. R., J. M. Melack, G. J.U. and H. R.W. (1995). Nutrient Limitation of Phytoplankton and Eutrophication of Inland, Estuarine, and Marine Waters. Phosphorus in the Global Environment. H. Tiessen. Chichester, John Wiley & Sons: 301-322.

Fisher, T. R., E. R. Peele, J. W. Ammerman and L. W. Harding, Jr. (1992). Nutrient limitation of phytoplankton in Chesapeake Bay.

Froelich, P. N. (1988). Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnology and Oceanography* **33**(4): 649-668.

Furnas, M. J. (1992). The Behavior of Nutrients in Tropical Aquatic Ecosystems. Pollution in Tropical Aquatic Systems. D. W. Connell and D. W. Hawker. London, CRC Press: 29-65.

Galliani, G., F. Filippini, G. Montanari, A. Rinaldi and R. A. Vollenweider (1992). Time series analysis of oceanological parameters measured at a fixed station. *Science of the Total Environment* **Marine Eutrophication Suppl.**: 171-186.

Gervais, F., U. Riebesell and M. Y. Gorbunov (2002). Changes in primary productivity and chlorophyll a in response to iron fertilization in the Southern Polar Frontal Zone. *Limnology and Oceanography* **47**(5): 1324-1335.

Gilmour, J. (1999). Experimental investigation into the effects of suspended sediment on fertilisation, larval survival and settlement in a scleractinian coral. *Marine Biology* **3**: 451-452.

Goldman, J. C. (1980). Physiological processes, nutrient availibility and the concept of relative growth rate in marine phytoplankton ecology. Primary Productivity in the Sea. P. G. Falkowski. New York, Plenum: 179-194.

Goldman, N. C., J. J. McCarthy and D. G. Peavey (1979). Growth rate influence on the chemical composition of phytoplankton in oceanic waters. *Nature* **279**(5710): 210-215.

Grande, K. D., P. J. L. Williams, J. Marra, D. A. Purdie, K. Heinemann, R. W. Eppley and M. L. Bender (1989). Primary production in the North Pacific gyre: A comparison of rates determined by the ^{14}C, O_2 concentration and ^{18}O methods.

Harris, G. P. (1984). Phytoplankton productivity and growth measurements: Past, present and future. *Journal of Plankton Research [J. Plankton Res.].* **6**(2): 219-237.

Harvey, W. A. and J. Caperon (1976). The rate of utilization of urea, ammonium, and nitrate by natural populations of marine phytoplankton in a eutrophic environment. *Pacific Science* **30**(4): 329-340.

Hatcher, B. G., R. E. Johannes and A. I. Robertson (1989). Review of research relevant to the conservation of shallow tropical marine ecosystems. *Oceanography and Marine Biology Annual Reviews* **27**: 337-414.

Hecky, R. E. and P. Kilham (1988). Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment. *Limnology and Oceanography* **33**(4): 796-822.

Heiskanen, A. S. and P. Tallberg (1999). Sedimentation and particulate nutrient dynamics along a coastal gradient from a fjord-like bay to the open sea. *Hydrobiologia* **393**(1-3): 127-140.

Herrera-Silveira, J. A. (1998). Nutrient-phytoplankton production relationships in a groundwater-influenced tropical coastal lagoon. *Aquatic Ecosystem Health & Management* **1**(3-4): 373-385.

HIDOH (1998). Hawaii's water Quality-Limited Waters: The 1997 Assessment and 1998 CWA 303(d) List of Water Quality-Limited Segments. Hawaii Department of Health,Honolulu, 54.

Hill, B. R. (1996). Streamflow and suspended-sediment loads before and during highway construction, North Halawa, Haiku, and Kamooalii drainage basins, Oahu, hawaii, 1983-91. U.S. Geological Survey,Honolulu, 34.

Hitchcock, G. L., C. Langdon and T. J. Smayda (1987). Short-term changes in the biology of a Gulf Stream warm-core ring: Phytoplankton biomass and productivity. *Limnology and Oceanography* **32**(4): 919-928.

Hoover, D. J. (2002). Fluvial Nitrogen and Phosphorus in Hawaii: Storm Runoff, Land Use, and Impacts on Coastal Waters. Ph.D. Dissertation, Oceanography, University of Hawaii, 437.

Howarth, R. W. (1988). Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology and Systematics* **19**(89-110).

Howarth, R. W., H. S. Jensen, R. Marino and H. Postma (1995). Transport to and processing of P in nearshore and oceanic waters. Phosphorus in the Global Environment. H. Tiessen, John Wiley & Sons. **SCOPE 54:** 323-346.

Hubertz, E. D. and L. B. Cahoon (1999). Short-term Variability of Water Quality Parameters in Two Shallow Estuaries of North Carolina. *Estuaries* **22**(3B): 814-823.

Jokiel, P. L. and E. F. Cox (1999). Impact of pulsed streamflow on the delivery of land-derived materials from an urbanized watershed to the nearshore marine environments of Kaneohe Bay, Hawaii. Hawaii Institute of Marine Biology,Honolulu, 16.

Jokiel, P. L., C. L. Hunter, S. Taguchi and i. L. Watara (1993). Ecological impact of a fresh water "reef kill" in Kaneohe Bay, Oahu, Hawaii. *Coral Reefs* **12**: 177-184.

Jones, B. H. and L. Washburn (1998). Storm water runoff into Santa Monica Bay: Identification, impact and dispersion. *Taking a Look at California's Ocean Resources: An Agenda for the Future* **2**: 888-899.

Juvik, S. P. and J. O. Juvik (1998). Atlas of Hawaii. Honolulu, University of Hawaii Press.

Kennish, M. J. (1986). Ecology of Estuaries. Boca Raton, CRC Press 320.

Kilham, P. and S. S. Kilham (1980). The evolutionary ecology of phytoplankton. The Physiological Ecology of Phytoplankton. I. Morris. Oxford, Blackwell. **571-592**.

Kimmerer, W. J., T. W. Walsh and J. Hirota (1981). The effects of sewage discharge into a wind-induced plume front. Estuaries and Nutrients. B. J. Neilson and L. E. Cronin. Cliffton, New Jersey: 531-548.

Krom, M. D. and R. A. Berner (1981). The diagenetis of phosphate in anoxic sediments. *Geochimica et Cosmochimica Acta* **45**: 207-216.

Labry, C., D. Delmas, A. Herbland and P. Laborde (2001). Phosphorus limitation of winter/spring phytoplankton blooms within the Gironde plume in the bay of Biscay.

Labry, C., A. Herbland and D. Delmas (2002). The role of phosphorus on planktonic production of the Gironde plume waters in the Bay of Biscay. *Journal of Plankton Research [J. Plankton Res.].* **24**(2): 97-117.

Labry, C., A. Herbland, D. Delmas, P. Laborde, P. Lazure and J. M. Froidefond (2001). Winter phytoplankton blooms within the Gironde plume waters in the bay of Biscay.

Lapointe, B. E. and W. R. Matzie (1996). Effects of stormwater nutrient discharges on eutrophication processes in nearshore waters of the Florida Keys. *Estuaries* **19**(2B): 422-435.

Laws, E. A. (1991). Photosynthetic quotients, new production and net community production in the open ocean. *Deep-Sea Research* **38**(1A): 143-167.

Laws, E. A. and D. G. Redalje (1979). Effect of sewage enrichment on the phytoplankton population of a subtropical estuary. *Pacific Science* **33**(2): 129-1

Laws, E. A. and D. G. Redalje (1982). Sewage Diversion Effects on the Water Column of a Subtropical Estuary. *Marine environmental research* **6**(4): 265-279.

Laws, E. A., J. Hiraoka, M. Mura, B. Punu, T. Rust, S. Vink and C. Yamamura (1994). Impact of land runoff on water quality in an Hawaiian estuary. *Marine environmental research* **38**(3): 225-241.

Laws, E. A. and C. B. Allen (1996). Water quality in a subtropical embayment more than a decade after diversion of sewage discharges. *Pacific Science* **50**(2): 194-210.

Laws, E. A., M. R. Landry, R. T. Barber, L. Campbell, M. L. Dickson and J. Marra (2000). Carbon cycling in primary production bottle incubations: inferences from grazing experiments and photosynthetic studies using super(14)C and super(18)O in the Arabian Sea. *Deep-Sea Research* **Part II, Topical Studies in Oceanography**(7-8): 1339-1352.

Lehman, J. T. (1984). Grazing, nutrient release, and their impacts on the structure of the phytoplankton commmunities. <u>Trophic Interactions Within Aquatic Ecosystems</u>. D. G. Meyers and J. R. Strictland. Boulder, Westview.

Letelier, R. M., R. R. Bidigare, D. V. Hebel, M. Ondrusek, C. D. Winn and D. M. Karl (1993). Temporal variability of phytoplankton community structure based on pigment analysis. *Limnology and Oceanography* **38**(7): 1420-1437.

Lindell, D., E. Padan and A. F. Post (1999). Effect of ammonium on nitrate/nitrite uptake and ntcA expression in Synecococcus sp. Strain WH 7803. *Bull. Inst. Oceanogr. Monaco* **Marine Cyanobacteria. Vol. Suppl.**: 273-278.

Mackenzie, F. T. (2003). Our Changing Planet. Upper Saddle River, Pearson Education 580.

Mackenzie, F. T., L. M. Ver, C. Sabine and M. Lane (1993). C, N, P, S Global biogeochemical cycles and modeling of global change. Interactions of C, N, P and S Biogeochemical Cycles and Global Change. R. Wollast, F. T. Mackenzie and L. Chou, NATO ASI Series, Springer-Verlag. **4:** 1-62.

Maguer, J., S. L'Helguen and P. Le corre (2000). Nitrogen Uptake by Phytoplankton in a Shallow Water Tidal Front. *Estuarine, Coastal and Shelf Science* **51**(3): 349-357.

Malone, T. C. (1971). The relative importance of nannoplankton and netplankton as primary producers in tropical oceanic and neritic phytoplankton communities. *Limnology and Oceanography* **16**(4): 633-639.

Martin, J. H. (1990). Glacial-interglacial CO_2 change : The iron hypothesis. *Paleoceanography* **5**: 1-13.

McKee, L. J., B. D. Eyre and S. Hossain (2000). Transport and retention of nitrogen and phosphorus in the sub-tropical Richmond River estuary, Australia - A budget approach. *Biogeochemistry* **50**(3): 241-278.

Meybeck, M. H. (2001). Global alteration of riverine geochemistry under human pressure. Understanding the Earth System: Compartments, Processes and Interactions. E. E. Kraft, Springer**:** 97-113.

Milliman, J. D. and J. P. M. Syvitski (1992). Geomorphic/tectonic control of sediment discharge to the ocean: The importance of small mountainous rivers. *Journal of Geology* **100**(5): 525-544.

Murrell, M. C., R. S. Stanley, E. M. Lores, G. T. DiDonato, L. M. Smith and D. A. Flemer (2002). Evidence that phosphorus limits phytoplankton growth in a Gulf of Mexico estuary: Pensacola Bay, Florida, USA. *Bulletin of Marine Science* **70**(1): 155-167.

Nixon, S. W., J. R. Kelly, B. N. Furnas, C. A. Oviatt and S. S. Hale (1980). Phosphorus regeneration and the metabolism of coastal mariine bottom communities,. Marine Benthic Dynamics. K. R. Tenore and B. C. Coull. Columbia, University SC Press: 219-242.

Nixon, S. W. and M. E. Pilson (1983). Nitrogen in Estuarine and Coastal Ecosystems. Nitrogen in the Marine Environment. E. J. Carpenter and D. G. Capone. New York, Academy Press: 565-648.

Pinckney, J. L., H. W. Paerl and M. B. Harrington (1999). Responses of the phytoplankton community growth rate to nutrient pulses in variable estuarine environments. *Journal of Phycology* **35**(6): 1455-1463.

Puig, P. and A. Palanques (1998). Temporal variability and composition of settling particle fluxes on the Barcelona continental margin (Northwestern Mediterranean). *Journal of Marine Research* **56**(3): 639-654.

Redfield, A. C., B. H. Ketchum and F. A. Richards (1963). The influence of organisms on the composition of seawater. The Sea. M. N. Hill. New York, Wiley. **2:** 26-77.

Ricker, W. E. (1973). Linear regressions in fishery research. *Journal of Fisheries Research Board of Canada* **30**: 409-434.

Ristvet, B. L. (1977). Reverse weathering reactions within recent nearshore sediments, Kaneohe Bay, Oahu. Northwestern University,Illinois, 311.

Rowe, G. T., C. H. Clifford, K. L. Smith, Jr. and P. L. Hamilton (1975). Benthic nutrient regeneration and its coupling to primary productivity in coastal waters. *Nature* **255**(5505): 215-217.

Saenger, P. J. and N. Holmes (1992). Physiological temperature tolerance, and behavioural differences between trpical and temperate organisms. Pollution in Tropical Aquatic Systems. D. W. Connel and D. W. Hawker. London, CRC Press: 69-95.

Seitzinger, S. P., R. W. Sanders and R. Styles (2002). Bioavailability of DON from natural and anthropogenic sources to estuarine plankton.

Short, F. T., M. W. Davis, R. A. Gibson and C. F. Zimmermann (1985). Evidence for phosphorus limitation in carbonate sediments of the seagrass Syringodium filiforme. *Estuarine, Coastal and Shelf Science* **20**(4): 419-430.

Six, J., C. Feller, K. Denef, S. M. Ogle, J. C. Moraes and A. Albrecht (2002). Soil organic matter, biota and aggregation in temperate and tropical soils: Effects of no-tillage. *Agronomie* **22**: 755-775.

Smayda, T. J. (2002). Turbulence, watermass stratification and harmful algal blooms: an alternative view and frontal zones as 'pelagic seed banks'. *Harmful Algae* **1**(1): 95-112.

Smith, S. V. (1981). Physical, chemical and biological mass balances in estuaries.

Smith, S. V. and M. J. Atkinson (1984). Phosphorus limitation of net production in a confined aquatic ecosystem.

Smith, S. V., W. J. Kimmerer, E. A. Laws, R. E. Brock and T. W. Walsh (1981). Kaneohe Bay sewage diversion experiment: Perspectives on ecosystem responses to nutritional perturbation.

Smith, W. O., Jr., J. Marra, M. R. Hiscock and R. T. Barber (2000). The seasonal cycle of phytoplankton biomass and primary productivity in the Ross Sea, Antarctica.

Sommer, U. (1989). The role of competition for resources in phytoplankton succession. Plankton Ecology. U. Sommer. New York, Springer-Verlag: 57-106.

Staver, L. W., K. W. Staver and J. C. Stevenson (1996). Nutrient inputs to the Choptank River estuary: Implications for watershed management. *Estuaries* **19**(2B): 342-358.

Stockner, J. G. (1988). Phototrophic picoplankton: An overview from marine and freshwater ecosystems. *Limnology and Oceanography* **33**(4): 765-775.

Strickland, J. D. H. and T. R. Parsons (1972). A practical handbook of seawater analysis. Ottawa, Fisheries Research Board of Canada 310.

Sundareshwar, P. V., J. T. Morris, E. K. Koepfler and B. Fornwalt (2003). Phosphorus Limitation of Coastal Ecosystem Processes. *Science* **299**(5606): 563-565.

Taguchi, S. and E. A. Laws (1989). Biomass and compositional characteristics of Kaneohe Bay, Oahu, Hawaii, phytoplankton inferred from regression analysis. *Pacific Science* **43**(4): 316-331.

Tanaka, K. (2002). Statistical and Stability Analyses of Ecosystem Dynamics in Southern Kaneohe Bay. M.Sc., Oceanography, University of Hawaii, 324.

Tilman, D. (1982). Resource Competition and Community Structure. Princeton, Princeton University Press 296.

Train, S. and L. C. Rodrigues (1998). Temporal fluctuations of the phytoplankton community of the Baia River, in the upper Parana River floodplain, Mato Grosso do Sul, Brazil. *Hydrobiologia* **361**(1-3): 125-134.

U.S. Commission on Marine Science, Engineering, and Resources (1969). Our Nation and the Sea: A Plan for National Action. U.S. Govt. Print. Off,Washington, DC, 305.

Uthicke, S. (2001). Nutrient regeneration by abundant coral reef holothurians. *Journal of Experimental Marine Biology and Ecology* **265**(2): 153-170.

Van Dijk, P. M. and F. Kwaad (1996). Runoff generation and soil erosion in small agricultural catchments with loess-derived soils. *Hydrological Processes* **10**(8): 1049-1059.

Varela, D. E. and P. J. Harrison (1999). Effect of ammonium on nitrate utilization by Emiliania huxleyi, a coccolithophore from the oceanic northeastern Pacific. *Marine Ecology Progress Series* **186**: 67-74.

Yin, K., P.-Y. Qian, J. C. Chen, D. P. H. Hsieh and P. J. Hirrison (2000). Dynamics of nutrients and phytoplankton biomass in the Pearl River estuary and adjacent waters of Hong Kong during summer: Preliminary evidence for phosphorus and silicon limitation. *Marine Ecology Progress Series* **194**: 295-305.

Zhang, J. (2000). Evidence of trace metal limited photosynthesis in eutrophic estuarine and coastal waters. *Limnology and Oceanography* **45**(8): 1871-1878.