

LAND – COASTAL OCEAN INTERACTIONS IN THE TROPICS AND SUBTROPICS:



HAWAI‘I AS AN EXAMPLE



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Summary

The culture, subsistence, and welfare of tropical and subtropical Pacific Island Nation people are all in some way tied to the interactions between the land and the adjacent and surrounding coastal waters. Land use plays an important role in the relative chemical species distribution and concentrations of particulate and dissolved nutrients that reach coastal waters by riverine, groundwater, and atmosphere. Some key human activities on land that affect coastal waters through land-sea connections and interactions are: (1) the application of nitrogenous and phosphorus-bearing fertilizers and biocides to the landscape and subsequent leaching of significant proportions of these materials into water courses, (2) the release of sewage into aquatic systems, including directly into coastal ocean waters, (3) the diversion of water flows through channelized structures and dams resulting in changes in retention times of water, nutrients and sediments and also in riparian communities on land and hence changes in water, nutrient and suspended sediment fluxes to the coastal ocean, (4) deforestation and/or conversion of land type from, for example, agricultural use to urban housing, (5) the fallout of nitrogen from the atmosphere derived from combustion sources on land and its ultimate transport into aquatic systems, (6) CO₂ emissions from fossil fuel and land-use activities (e.g., deforestation) and absorption of some of this CO₂ by coastal and open ocean waters, and (7) atmospheric nitrogen emissions from combustion sources on land that ultimately fall directly on the ocean surface, and especially that of the coastal ocean.

The first step in setting up a viable coastal ocean management plan is recognizing, monitoring, and managing these diverse and often nonpoint sources of land-derived materials. For example, nutrient inputs into receiving waters because of fertilizer application to farmlands can be reduced by conversion of older nutrient application practices to one of drip irrigation. Biocide and fertilizer use on golf courses and home lawns should be reduced to use of biocides that have the least effect on the biosphere. Sewage plants must be designed to prevent overflows during storm conditions, and sewage and storm pipes maintained to prevent breakage and leakage into soil and groundwater. Conversion of land from one use to another should be done with full recognition of what effects this conversion will have on any nearby aquatic systems and coastal ocean environments. Construction of holding tanks for soil disturbed during construction of homes and other buildings needs to continue to be part of any permit to build. Such management would greatly lessen negative impacts on coastal ocean ecosystems.

In addition, in order to manage coastal systems efficiently in terms of sustainability, it may be necessary to have routine continuously monitoring instrumented systems in place in several coastal areas and continuous synoptic studies of important water quality parameters. This will enable managers to assess whether or not a certain modification of the land has had any significant effects on the receiving coastal ocean ecosystem. In conjunction with the water quality programs, at some viable time scale, there should be monitoring of benthic organisms and fish in certain key coastal areas to not only discern if land-use fluxes are impacting the biota but also evaluate how temperature changes and ocean acidification are affecting the biological community on reefs and in other coastal ecosystems.

Aside from this, there are human activities that occur directly in coastal waters and require management through regulation, for example, of reef dynamiting to increase benthic fish catch, dumping of various types of waste directly into coastal zone waters, inadvertent destruction of reefs by boat traffic and people walking on them, conversion of wetlands to urban centers and other uses, and discharges by ships or oil wells at sea.

Hawai‘i as an Example

I. Introduction

In this case study volume, we investigate the interaction between the global coastal ocean in subtropical and tropical regions and the adjacent land via stream and overland runoff, atmospheric transport, and groundwater flow. Coastal zone management issues are discussed in the context of the science presented. The case study uses to a significant extent the data accumulated from many years of work done, for example, in Kāne‘ohe Bay and its watersheds on O‘ahu, Hawai‘i, USA, regarding biogeochemical processes and dynamics related to carbon (C) and its associated driver nutrients of nitrogen (N) and phosphorus (P), and to a lesser extent silicon (Si) and suspended solids. The case study provides insights into how natural and human activities on land and resulting inputs (fluxes) to the coastal ocean affect the biogeochemical cycles of C, N, P, and Si in the nearshore environment. In particular, because of the current interests in rising atmospheric CO₂ concentrations and ocean acidification, the study focuses on the C cycle of the bay and influences of fluvial inputs on the cycle. It is anticipated that the principles and conclusions outlined in this case study might be extended to other subtropical/tropical regions and should at least provide the reader with an understanding of the nature of land-coastal ocean linkages in one important type of coastal ocean setting.

In general, interfaces between the Earth’s larger material reservoirs (i.e., the land, atmosphere, ocean, and sediments) are important in the control of the biogeochemical dynamics and cycling of the major bioessential elements, including C, N, P, sulfur (S), and Si, found in organic matter and the inorganic skeletons, shells and tests of benthic and pelagic marine organisms, because these interfaces act as relatively rapid modifiers of storage, transport, and perturbation processes at geologically short time scales. The continental margin constitutes an important interface between the land and open ocean. It includes the region between the land and the open ocean dominated by processes resulting from land-ocean margin and ocean margin-open ocean boundary interactions. The continental margin includes the environments of the *proximal* estuaries, bays, lagoons,

and banks, and the *distal* continental and island shelves, oceanic slopes and adjacent marginal seas.

The surface area of the global continental margin is roughly equivalent to 21% of the total ocean, if one includes the continental shelf, slope and rise in the estimate (75.3 x 10⁶ km²). The area of the margin to the shelf-slope break is only about 24 to 29 x 10⁶ km² or about 7 to 8% of the surface area of the ocean. However, despite its smaller area compared to the open ocean, the continental margin is an important interface between the land and open ocean, and it is also in direct exchange with the atmosphere. Although the estimates are still debated, continental margin environments may account for 20 to 30% of total marine productivity and a significantly higher amount of organic matter export production, perhaps as much as 50% of the biological pump transfer of organic carbon to the deep ocean, and a minimum of 15% of the net air-to-sea CO₂ flux. In addition, at least 80% of the mass of terrigenous materials reaching the ocean is deposited in continental margin environments and 65% of total carbonate and more than 90% of total organic carbon accumulation in the ocean occurs in continental margin sediment environments.

Large river drainage basins connect the vast interiors of continents with the continental margin through river and groundwater discharges. The ocean surface links the margin to the atmosphere via gas exchange at the air-sea interface, production of sea aerosols, and atmospheric deposition on the sea surface; substances released at the air-sea interface of the continental margin may be subsequently transported through the atmosphere and deposited on land as wet and dry depositions; conversely, emissions from land to the atmosphere are in part deposited on the margin. Additionally, physical exchange processes at continental margin borders, involving, for example, coastal upwelling and onwelling and net advective transport of water, dissolved solids, and particles from the continental margin offshore connect the margin with the surface, intermediate and deep depths of the open ocean. Some materials biologically and inorganically produced *in-situ* or delivered to the continental margin via river and groundwater discharges, upwelling, and atmospheric deposition

may eventually accumulate in continental margin sediments. The processes of settling, deposition, resuspension, remineralization of organic matter, dissolution and precipitation of mineral phases, and accumulation of materials connect the water column and the sediments of the continental margin.

During the past several centuries, the activities of humankind have significantly modified the exchange of materials between the land, atmosphere, continental margins, and the open ocean on a global scale. Humans have become agents of environmental change. For example, the oceans, which were a source of CO₂ to the atmosphere in late pre-industrial time, are now a sink, although the global proximal continental margin, strongly influenced by the high specific-area CO₂ exchange fluxes of estuaries, still appears to be a source. This will change in the near future as atmospheric CO₂ levels continue to rise and global margin environments take up additional CO₂. During the 21st century, atmospheric CO₂ levels have been rising faster than during the later decades of the 20th century because of the worldwide increase in economic activity until 2007. Owing to global warming, increased stratification of the oceans might be anticipated with poorly known effects on upwelling of deep water onto the continental margins. In addition, burning of fossil fuels and release of nitrogen and sulfur to the atmosphere and their fallout onto primarily continental margin surface waters are leading to acidification of these waters along with the acidification of the ocean as a whole due to the absorption of anthropogenic CO₂. In point of fact, the ocean in late pre-industrial time was a source of sulfur (as marine-produced sulfate aerosols) via atmospheric transport to the land but it is now a net sink due to the deposition of sulfur derived from the burning of fossil fuels. The flux of nitrogen through the Earth's surface environment has doubled due to human activities. The acidification of the oceans will have a considerable effect on skeletal and inorganic production and dissolution of calcium carbonate and on marine ecosystems, in general, from the lower trophic level of bacteria to fishes. Despite the relatively small size of the global continental margin, its environments, like coral reefs, account for a disproportionately large amount of this production.

Rapid population growth has occurred in coastal regions, with about 40% of the world population

living within 100 km of the shoreline. The increasing population density in the areas of the major river drainage basins and close to oceanic coastlines, socio-economic development, and changes in land-use practices in past centuries have led to enhanced discharges of industrial, agricultural, and municipal wastes into continental margin waters via river and groundwater discharges and atmospheric transport, including C, N, and P loadings. Due to changes in global precipitation and evaporation patterns and dam construction, material fluxes to the coastal ocean have been dramatically modified and will continue to be in the future as the climate changes and land-use changes, such as deforestation, continue to occur. This will have significant effects on the budgets and behavior of C, N, P, Si, and suspended solids in continental margin environments.

Land-use activities have contributed to increased soil degradation and erosion, eutrophication of river and continental margin waters through additions of nitrogenous- and phosphorus-bearing fertilizers to agricultural land and sewage discharges, degradation of water quality, and alteration of the coastal marine food web and community structure. It is estimated that only about 20% of the world's drainage basins has pristine water quality at present. In addition, rising sea level will lead to flooding of low-lying coastal areas, like Bangladesh and Pacific atoll nations, movement of seawater inland up estuaries, and intrusion of seawater into groundwater reservoirs. It is thus understandable why the continental margin is regarded as both a filter and a trap for natural as well as anthropogenic materials transported from the continents to the open ocean. Estuarine and coastal regions showing much human-induced change are located, for example, along the coasts of the North Sea, the Baltic Sea, the Adriatic Sea, the East China Sea, and the east and south coasts of North America.

As demonstrated above, the continental margin is not only the oceanic region that is most susceptible to changes in water quality, organic productivity, and biodiversity, but it also has been perturbed disproportionately more by human activities than the much larger area of the open ocean. However and importantly to date, it has received far less attention and study in the context of the Earth's surface environmental biogeochemical system compared to the open ocean. In addition, biogeochemical

processes occurring in tropical and subtropical coastal margin environments and their link to land activities are even less understood because most scientific research to date has been focused on temperate margin environments. Furthermore, the high and low-lying islands of the world's oceans and the linkages between the land and coastal ocean in

these regions have not been studied in much detail. Thus the management schemes for land inputs into coastal environments are not always on a firm basis. One outstanding exception to our lack of knowledge, especially of subtropical coastal environments, is Kāneʻohe Bay, Oʻahu, Hawaiʻi.

II. An Introduction to the Global Coastal Ocean

The coastal ocean, excluding the outer reaches of continental slopes and rises, is the environment of continental and insular shelves to 200 m depth, including bays, lagoons, estuaries, and near-shore banks that occupy 7% to 8% of the surface area of the ocean (estimates range from 24×10^6 to 29×10^6 km²). The mean depth of coastal ocean water is approximately 130 m. The occurrence and extent of continental shelves are shown on the world map in Figure 1 and on the hypsometric curve in Figure 2. Estuaries are the main points of input from land to the coastal zone and their total area is estimated at about 1×10^6 km² or less than 5% of the shelf area.

The continental shelves average 75 km in width, with a bottom slope of 1.7 m/km, and they can be divided

into the interior or proximal shelf, and the exterior or distal shelf. The mean depth of the global continental shelf is usually taken as the depth of the break between the continental shelf and slope at approximately 200 m, although this depth varies throughout the world oceans. In the Atlantic, the median depth of the shelf-slope break is at 120 m, ranging from 80 m to 180 m. The depths of the continental shelf are near 200 m in the European section of the Atlantic, but they are close to 100 m on the African and North American coasts. The sea-level stand at the Last Glacial Maximum (LGM: 18,000 years ago) was about 120 m below the present level (Figure 3), making the shelf water area 40% or less of its present area.

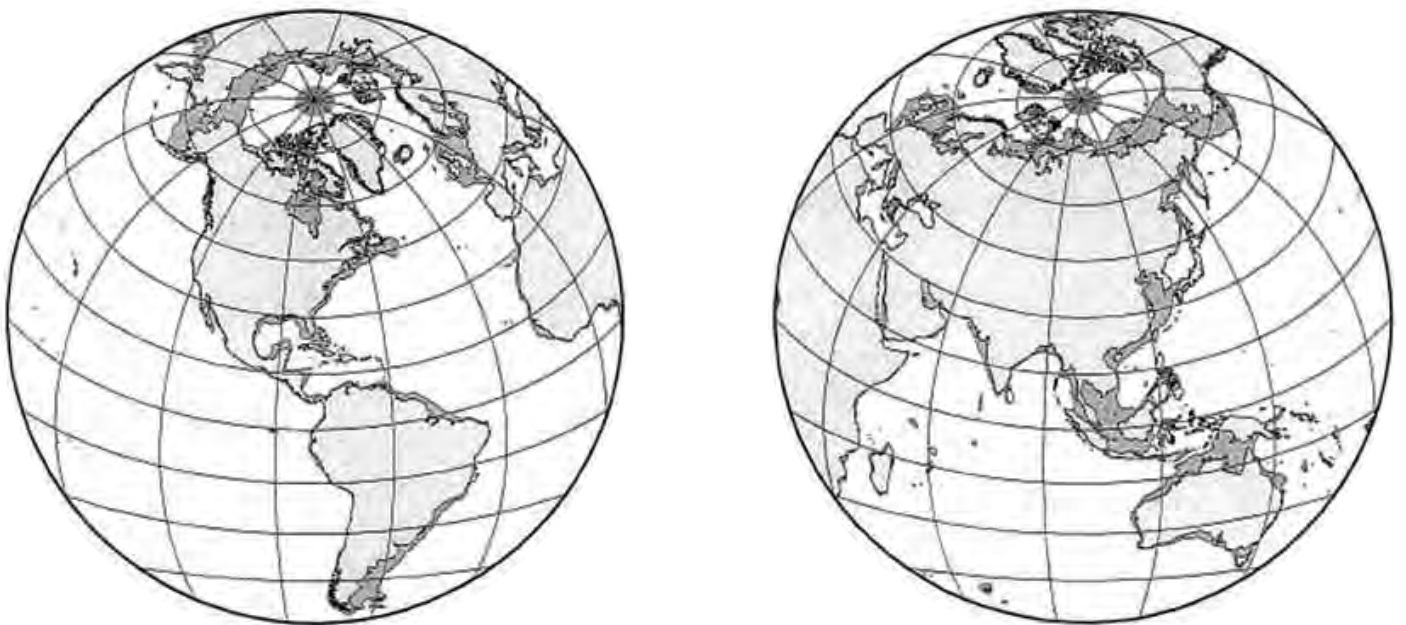


Figure 1. Global coastal zone of 0 to -200 m depth (shaded areas). Lambert azimuthal projection, from ETOPO5 data. The parallels are 15° apart and the meridians 30° apart.¹

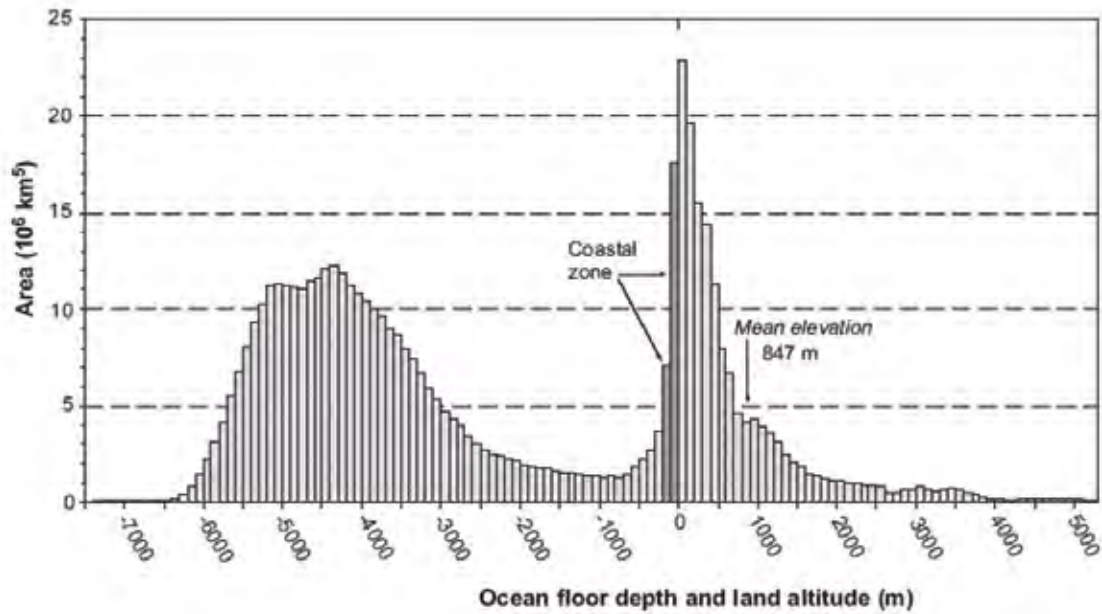
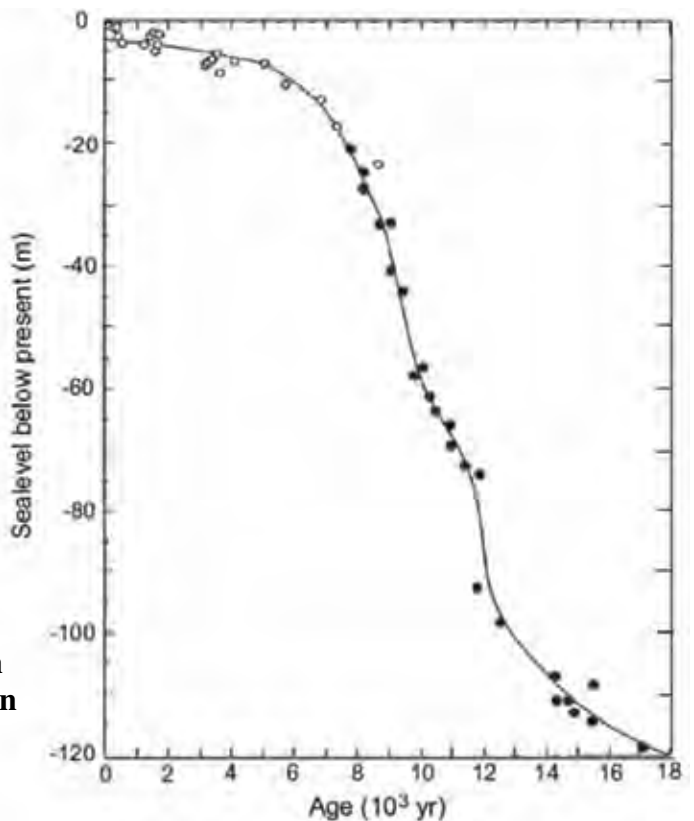


Figure 2. Global hypsometric curve showing the surface areas of the ocean floor and land surface in 100 m intervals. Areas deeper than -7000 m and higher than $+5500$ m are too small to be seen in the graph. Total global surface area is 510×10^6 km². Coastal zone area between 0 and -200 m (darker shaded two bars) is 24.6×10^6 km².²

Notice in Figure 3 the relatively rapid rise in sea level of approximately 95 cm per century between 18,000 and 7000 years ago and the slowing down of sea level rise to between 12 to 20 cm per century since 1900. The flooding of continental shelves during the late Pleistocene and Holocene has been responsible for major changes in land-sea exchange of materials, including organic carbon and nutrients, and has increased the ocean area of air-sea exchange of atmospheric CO₂.

Figure 3. Rise in sea level since the Last Glacial Maximum, based on corrected radiocarbon ages (years before present, counted from year 1950 as zero) of corals on Barbados (filled circles) and other Caribbean locations (blank circles), and corrected for mean land uplift of 34 cm per 1000 years.³



This concept of the coastal ocean includes essentially all of the continental shelves and the points of input from land. Yet it differs from some other definitions of the coastal zone that extends from some elevation on land above mean sea level to some depth on the continental shelf: for example, the international program on Land-Ocean Interactions in the Coastal Zone (LOICZ) defines the coastal zone as extending from +200 m elevation on land to about -200 m on the continental shelves. Global continental shelves have a very uneven distribution around the continents, as the map in Figure 1 shows.

The main drainage basins of the rivers are important areas of input of water, solids and nutrients from the continents to the coastal ocean (Figure 4). Some of the larger river outflows occur on relatively narrow or poorly developed continental shelves (northeast coast of South America, east and west coasts of Africa). This physiographic feature shows that the bigger and wider continental shelves are not merely physical links on the path between river mouths or deltas and the open ocean, but they play a broader role in the global transport and transformation of materials in the land-atmosphere-ocean system.

Estimated amounts of particulate matter transported from land by rivers at present are 13 to 20 × 10⁹

tonnes yr⁻¹ [In this case study, mention of the unit ton refers to a metric ton (1000 kilograms) unless otherwise denoted]. Riverine input of particulate organic carbon to the oceans increased from about 0.19 × 10⁹ tonnes C yr⁻¹ in late pre-industrial time to about 0.24 × 10⁹ ton C yr⁻¹ in the early 21st century, and this carbon is likely to be significantly derived from soil humus of an average C:N:P atomic ratio of 268:17:1. Thus the particulate organic carbon flux accounts for a fraction of 1 to 2% of the total particulate matter input by rivers to the oceans.

In the Northern Hemisphere, above latitude 60° N, the shelves make up a relatively large fraction of the total surface area, about 20%. This is also a region of major inputs of materials by some of the rivers in North America and Siberia (Figure 5). The shelves in the Northern Hemisphere occupy a much larger area than in the Southern Hemisphere. The climatic differences between the latitudinal zones affect primary production and biological calcification. Carbonate production on the continental and island shelves by corals, calcareous algae, mollusks, and foraminifera is greater in the warmer latitudes, but large accumulations of carbonate (cold-water carbonates) are also found at colder, higher latitudes.

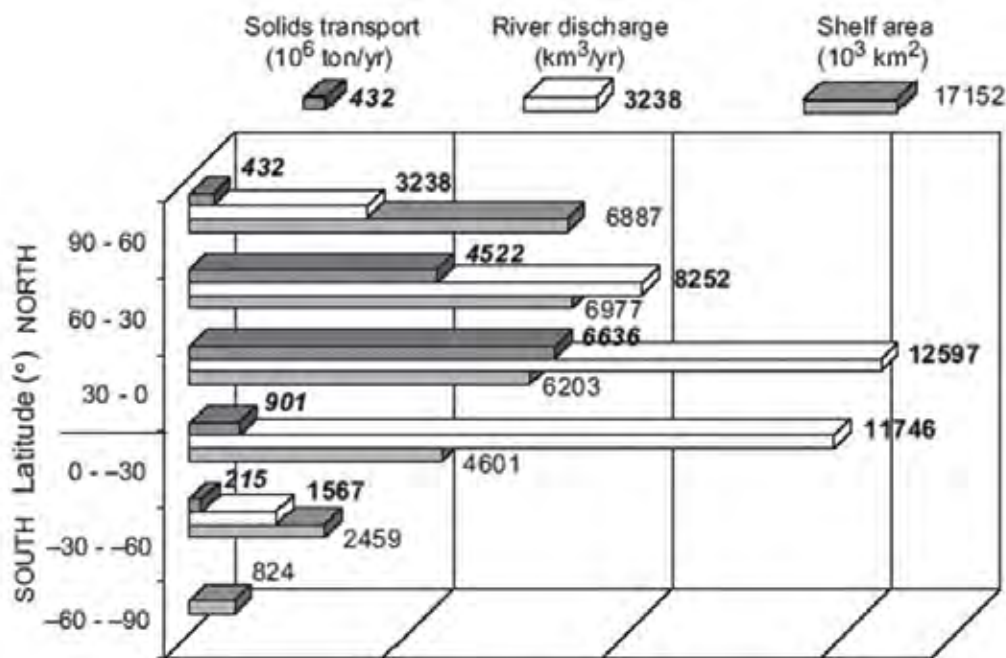


Figure 4. Continental shelf area (0 to -200 m depth), river water discharge, and delivery of suspended solids to the coastal ocean in 30°-latitudinal zones. No data for Antarctica. Note how discharge is greater in the Northern Hemisphere.⁴

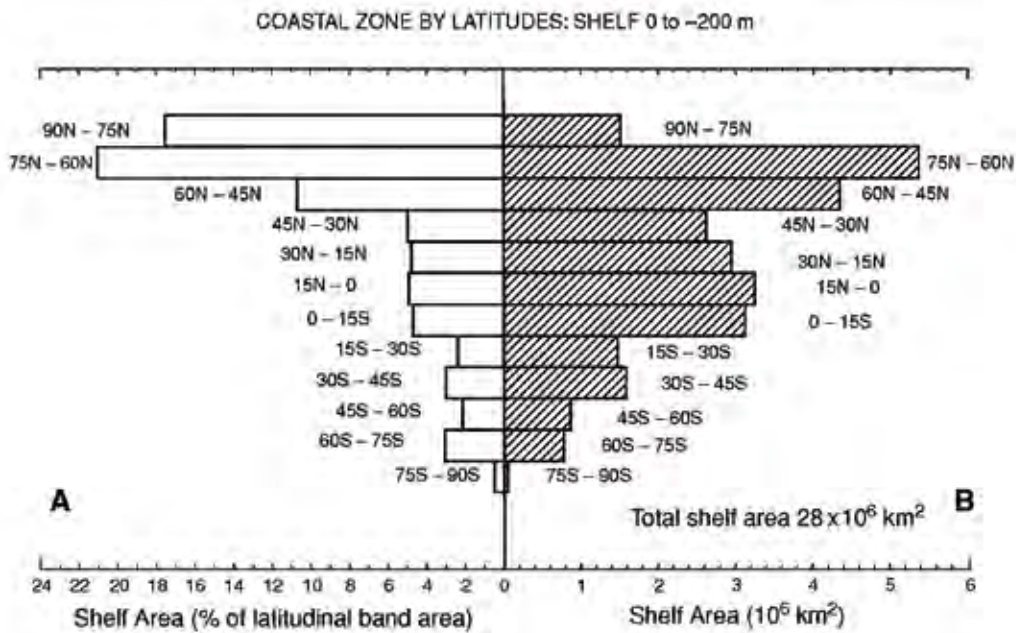


Figure 5. Distribution of the coastal zone in 15°-latitudinal bands. Panel A: Shelf area as a fraction of the total area of each latitudinal band. Note that the coastal zone in the northern latitudes occupies relatively large parts of the total surface area. Panel B: Shelf areas of the latitudinal bands showing the greater prominence of the shelves in the Northern Hemisphere.⁵

III. Global Land-Coastal Ocean Temporal Patterns of Change

Riverine fluvial transport is the most important linkage between the land and coastal ocean of dissolved and solid materials, followed by groundwater discharge of mainly dissolved constituents, and lastly atmospheric transport of particles and gases subsequently deposited on or absorbed by coastal ocean waters. During the past recent centuries, there has been a net overall loss of organic carbon from the terrestrial biota and soil humus reservoirs mainly via riverine inputs, and to a lesser extent, groundwater and atmospheric fluxes to the coastal ocean. The pattern of loss of N and P from these reservoirs is similar to that for organic carbon shown in Figure 6. From 1850 to about 1950, organic C, as well as N and P, were generally lost from both living phytomass and soils in the terrestrial realm. Between 1850 and 1950, the terrestrial biota sustained net annual losses averaging about 1.5×10^6 tonnes N (10^6 tonnes = 1 megaton = Mt) and 1 Mt P. These amounts are equivalent to approximately 220 Mt C yr^{-1} . In Figure 6, notice the sharp reversal in the carbon mass of the land phytomass reservoir near the middle of the 20th century (before 1950).

This reversal is also seen less dramatically in the biotic reservoirs of N and P. From 1950 to 2000, the terrestrial biota gained about 300 Mt C yr^{-1} , which is equivalent to 3 Mt N yr^{-1} and 2 Mt P yr^{-1} . This time of reversal appears to be the start of the enhanced storage of the elements C, N, and P on land due to the combined feedback effects on atmospheric CO_2 of the fertilization of the terrestrial biosphere by rising atmospheric CO_2 , release of N and P from the humus and chemical fertilizers on land and deposition of atmospheric N over land, and the re-growth of forests in previous disturbed areas. The temperature rise of approximately $0.8 \text{ }^\circ\text{C}$ over the past 150 years and potentially slight changes in global precipitation may also have played a role in the enhanced growth of the forests and consequent increased storage of C, N, and P in terrestrial ecosystems. The humus reservoir, except for a slight reversal in C between 1950 and 1980, also shows sustained net losses of C, N, and P masses throughout much of the entire period from 1850 to 2000, averaging about 170 Mt C yr^{-1} , 15 Mt N yr^{-1} , and 4 Mt P yr^{-1} during the 150 years since the Industrial Revolution.

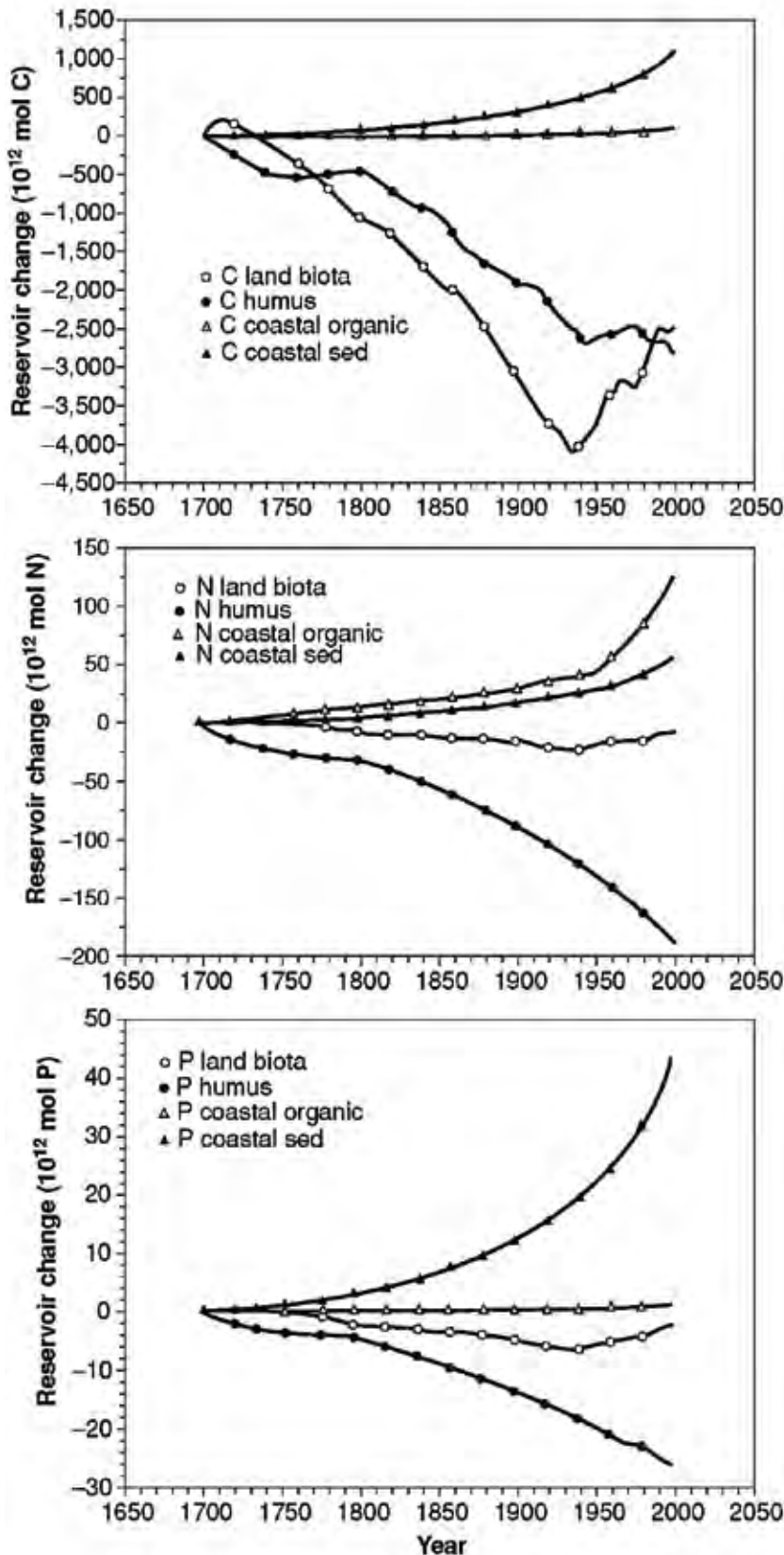


Figure 6. Changes in the carbon, nitrogen, and phosphorus masses of land plants, humus, coastal organic matter, and coastal sediments computed for the period 1700 to 2000, normalized to 0 in 1700. Notice in particular the decline of all three elements in the terrestrial phytomass and humus from 1800 to the mid-20th century and the reversal thereafter, perhaps due to the fertilization of the land plants by rising CO_2 , excess nutrient application to the landscape and some re-growth of temperate forests. Also note that the coastal ocean organic pool and sediments are major reservoirs for the loss of materials from the land, as well as the ocean waters for the loss of carbon from changing land-use activities (1 mol C = 12 g; 1 mol N = 14 g; 1 mol P = 31 g).⁶

This redistribution of carbon constitutes a sink for atmospheric CO_2 and must be accounted for in any budget of the carbon cycle. The magnitude of the sink is still controversial but, in recent decades, may be on the order of 1 Gt C yr^{-1} ($\text{Gt} = \text{Gigaton} = 10^9$ tonnes). Nevertheless, a significant portion of the remineralized N and P was transported to the coastal ocean and other aquatic environments via river and groundwater discharges, stimulating new production and leading to enhanced burial of organic matter (Figure 7). The enhanced burial of organic matter from new production in aquatic environments also constitutes a sink, albeit small, for anthropogenic CO_2 , on the order of 0.1 to 0.2 Gt C yr^{-1} , only a few percent of the fossil fuel flux in 2010.

Figure 7 shows the historical and projected future changes from 1850 to 2040 in the river fluxes of dissolved inorganic and organic carbon (DIC, DOC), nitrogen (DIN, DON), and phosphorus (DIP, DOP), and fluxes associated with the atmospheric deposition and denitrification of N, and accumulation of C in organic matter in coastal marine sediments. It is this transfer of C, N, and P from the land to the ocean, as well as C and N to the atmosphere, which accounts for much of the decline in the masses of these elements on land for most of post-Industrial Revolution time as seen in

It may be the case that globally a major fraction of the remobilized organic matter was not remineralized but was redistributed on land and sequestered in artificial water bodies such as agricultural ponds and dammed reservoirs and in natural lacustrine sediments and river floodplains.

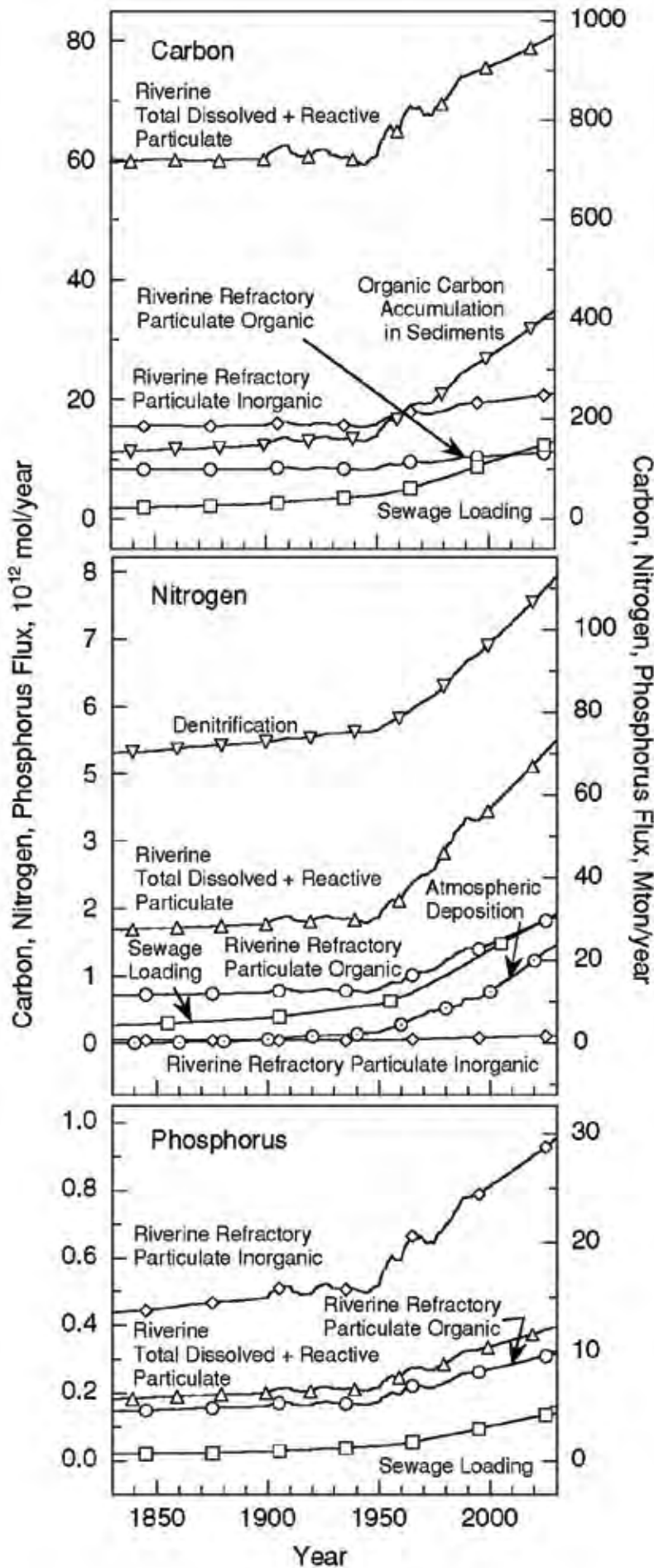


Figure 7. Past, present, and future projections for river carbon, nitrogen, and phosphorus fluxes from land to the sea in 10^{12} mol yr⁻¹ and Mt yr⁻¹. The accumulation fluxes of organic carbon in coastal marine sediments, atmospheric deposition of N on the coastal ocean sea surface and the changes in denitrification fluxes in the coastal ocean are also shown (1 mol C = 12 g; 1 mol N = 14 g; 1 mol P = 31 g).⁷

Figure 6. As a result of the human activities on land, the fluxes of materials to the coastal zone have changed during historical times. It can be seen in Figure 7 that the global river fluxes of C, N, and P all increase in the dissolved inorganic and organic phases from about 1850 projected to 2040. For example, for C, the total river flux (organic + inorganic) increases by about 35% during this period of time. The increased river fluxes are mainly due to changes in land use practices, including deforestation, conversion of forest to grassland, pastureland, and urban centers, and application of fertilizers to croplands and the subsequent transport of C, N, and P into aquatic systems.

Inputs of nutrient N and P to the coastal zone, which support new primary production, are from the land by river and groundwater flows, from the open ocean by coastal upwelling and onwelling, and to a lesser extent from atmospheric deposition of N species. New primary production depends on the availability of nutrients from these external inputs, without consideration of internal recycling of nutrients. Thus, any changes in the supply of nutrients to the coastal zone owing to changes in the magnitude of these source fluxes are likely to affect the cycling pathways and balances of C and the nutrient elements in the coastal ocean. In particular, input of nutrients globally from the open ocean by coastal upwelling is quantitatively greater than the combined inputs from land and the atmosphere. This makes it likely that there could be significant effects on coastal primary production not only because of increased loading of nutrients via river inputs, but because of changes in ocean circulation and stratification. For example, because of global warming, the

oceans could become more strongly stratified owing to freshening of polar oceanic waters and warming of the ocean in the tropical zone. This could lead to a reduction in the intensity of the oceanic thermohaline circulation (ocean circulation owing to differences in density of water masses, also popularly known as the “conveyor belt”) of the ocean and perhaps changes in the rate at which nutrient-rich waters upwell into coastal environments.

It is likely that the trends observed for the past 150 years will continue well into the 21st century, unless there are major, worldwide endeavors to regulate releases of C, N, and P to the environment. In general there is some attempt in the developed and industrialized world countries to control these emissions but only meager efforts are underway in the developing and under-developed countries. One can understand why. The developing world countries aim to improve their standard of living, striving towards that of the developed countries. To achieve this goal many of these countries are following the pathway of the developed world since the Industrial Revolution in 1850. The developing countries rely heavily on fossil fuels for an energy source, particularly oil, gas, and coal, are using increasing quantities of P and synthetic N-bearing fertilizers of urea and ammonium nitrate on croplands, are applying increasing quantities of synthetic organic chemicals to their croplands, are modifying land-use patterns especially in terms of conversion of forests to croplands, cattle ranges and urban centers, particularly in the tropical forests of Southeast Asia, Central Africa, and Brazil, and they are growing their transportation sectors, again using refined petroleum products to do so. Thus as the 21st century progresses, increasing per capita emissions of C, N, and P from the developing world countries are very likely. This along with continued emissions from the developed countries, despite the regulations and controls already in effect, will most likely lead to continued growth in anthropogenic emissions of C, N, and P to the aquatic environment during the 21st century. The rate of growth of these emissions will depend extensively on the rate of economic growth of the world and individual nations and their thirst for fossil fuel energy and other natural resources. An example is the reduced emissions of CO₂ to the atmosphere from fossil fuel combustion during the economic downturn associated with the oil embargo of the 1970s, at which time modern

energy conservation practices began in many of the developed world countries. Another is the decline in fertilizer use in the early- to mid-1990s following the demise of the economy of the former Soviet Union and the subsequent increase from the late 1990s into the 21st century as world economies improved. The global financial crisis of the first decade of the 21st century and subsequent global recession have also influenced emission fluxes.

To exemplify how anthropogenic fluxes of C, N, and P and their fate will change in the immediate future, the anthropogenic sources and their partitioning on land and into other reservoirs have been projected to the year 2040 assuming a business-as-usual (BAU) scenario. Total anthropogenic CO₂ emissions to the atmosphere by the year 2040 could be equivalent to 14.5 Gt C yr⁻¹, with changing land-use patterns and combustion of fossil fuels accounting for 2.5 Gt C yr⁻¹ and 12.0 Gt C yr⁻¹, respectively. This is an increase of approximately 45% relative to C emissions in 2000. The sinks for these emissions, mainly in the atmosphere, ocean, and uptake by terrestrial ecosystems will increase by about 50%, 50% and 33%, respectively, from the year 2000 to 2040. The change in net storage of C on land will depend significantly on changing land-use patterns and the CO₂ emissions resulting from these changing patterns and the future magnitude of the fertilization effect on land. The fluxes of CO₂ emissions associated with both changes in land use and the strength of the fertilization effect on land are not well known and their projections to the future can only be considered as tentative estimates. One potential problem is that as global temperatures continue to rise, respiration of organic matter on land may increase and override any effect from fertilization.

As C emissions grow through the 21st century so will those of N and P. The emissions of N and P from remobilization of organic matter on land, the application of fertilizers to croplands and the atmospheric emissions of N from transportation and fixed combustion sources are particularly important as are deposition of the fixed N on land and the subsequent leaching of some of the applied N and P to aquatic systems of soil, ground, and surface waters. The total N and P emission fluxes from these sources will grow by about 45% from 2000 to 2040. The sink of these fluxes on land will be in

humus accumulation, terrestrial biotic uptake, export of dissolved and particulate N and P to the coastal ocean and, in the case of N on land, denitrification. Denitrification removes N from the pool available for primary production and is strongest on land. In the year 2000, this process accounted for 73% of N removed from land by the combined processes of denitrification and riverine export of N to the coastal

ocean. As a result of all these changes on land, the fluxes of C, N, and P to the coastal ocean will grow in the future, accounting for changes in the rates of organic carbon burial in coastal marine sediments, denitrification rates in coastal waters and sediments, transport of atmospheric fixed N to the coastal ocean, and uptake of anthropogenic CO₂ in the coastal and open-ocean surface waters.

IV. The Global Scale of Coastal Impacts

The coastal ocean is a transitional zone between terrestrial and open ocean and serves to mediate and modulate the exchanges between those environments. Due to its location between terrestrial and open-ocean environments, coastal areas are home to unique ecosystems, which serve as habitats for species found nowhere else. Additionally, they also provide protection to juvenile forms of many open ocean and anadromous species (i.e., those species that ascend rivers from the sea to breed such as salmon). These unique coastal ecosystems, habitats, and areas characterized by high specific area primary production are directly influenced by nutrients that are transported (e.g., via rivers and groundwaters) from land reservoirs of nutrients to the ocean reservoirs of nutrients.

Because of the benefits derived from access to ocean navigation, human settlements are often more concentrated in the coastal zone and adjacent watersheds than elsewhere. As population density and economic activity in the coastal zone increase, pressures on coastal ecosystems increase. River transport is one of the principal ways nutrients are transported from land to the ocean. Streams

and rivers transport fresh water, sediments, and chemical products of natural and human-influenced terrestrial processes to coastal areas. Globally, half of the available river runoff from land to ocean is controlled by humans. The global river sediment discharge has at least doubled from pre-industrial levels (only 300 years ago) due to the increase in the human population and its activities. Some of the anthropogenic impacts on fluvial transport are:

- reduction of river and stream discharge due to the diversion and impounding of runoff;
- changes in water quality due to the direct addition of sewage and industrial effluents; and
- a variety of activities increasing non-point source pollutant loads.

Recognizing that the fluvial fluxes of water, nutrients and suspended matter on a global scale have been strongly influenced by human activities, we now explore some sources of this influence and how these fluxes affect coastal ocean nutrient subsidies, chemical and biological changes in the water column, air-sea exchange of CO₂ and acidification of the coastal ocean.

A. Sources of Influence from Human Activities

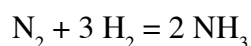
1. Fertilizer Use

Natural organic fertilizers have been used by farmers for centuries. People have recycled nutrients by applying animal dung and carcasses to croplands to obtain better crop yields. When the first settlers arrived on the American continent, the North American Indians showed them how to bury a fish with each maize seed planted. The decaying fish provided nutrients for the soil in which the maize

grew. In medieval times, European farmers applied dung to the soil and planted nitrogen-fixing legumes, such as clover, on agricultural land to increase the productivity of the soil. By the time of the Industrial Revolution, the use of organic fertilizers was a well-established practice. However, the reasons for the effectiveness of these chemical compounds in stimulating plant productivity were not well understood. In 1840, Justus von Liebig discovered that nutrients removed from the ground by crops

could be chemically replaced. This discovery eventually led to the development and expanded use of chemical fertilizers.

Prior to the Green Revolution of the 1950s, most increases in crop yield were due to expansion of areas of cultivated land. After 1950 crop-yield increases were mainly the result of chemical fertilization of the pre-existing agricultural lands. Nitrogen, phosphorus, and potassium are the three basic plant nutrients that are generally applied to the soils in the form of chemically processed fertilizers. These nutrients are essential constituents of organic matter. Most of the phosphorus and potassium used presently as fertilizer, however, is the mining product of ores of these elements, and the nitrogen, principally as ammonia, is usually derived from an industrial chemical process. In this process, known as the Haber-Bosch process, atmospheric nitrogen is reacted with hydrogen derived from natural gas. The reaction is:



The product is ammonia, which is then used as a fertilizer in liquefied form or as a salt. In 1950, about 14 million tons of chemical fertilizers were applied to the world's crops. By 1990, this figure had increased tenfold to 143 million tons. This value represents about 60 million tons of nitrogen in 1980, with an increase to about 80 million tons or about 5 grams of nitrogen per square meter of agricultural land in 1990. From 1990 to 1995, fertilizer use decreased to 122 million tons per year but rebounded to 141 million tons per year in 2000. Fertilizer use continues to grow into the 21st century and the increased growth is almost entirely due to the expanding use of nitrogen fertilizers. As a result of fertilizer application, crop yields have increased, as has the use of energy to mine, produce, and transport these fertilizers.

Between 1981 and 1995, the total area harvested for grain decreased about 9%. However, because of the growing world population, the area harvested per person fell by 48% between 1955 and 1995. To increase per capita food supplies during the last half of the 20th century, it was proven necessary to develop new high-yield varieties of crops and to use large amounts of fertilizer. The per capita use of fertilizer increased during the last half of the 20th century, although decreasing slightly in the early

1990s. In the mid-1980s, China surpassed the U.S. in both grain production and fertilizer use, and India in the year 2000 used as much fertilizer as the U.S. Other Asian countries are becoming major consumers of commercial fertilizers. Thus, it is very likely that commercial fertilizer production and use will continue to increase into the 21st century.

Excess nitrogen- and phosphorus-bearing fertilizers added to croplands may be leached and washed into aquatic systems. Rivers and groundwater transport organic matter and dissolved nutrients downstream to lakes or coastal marine areas, where the excess nutrients may cause phytoplankton blooms and accelerate eutrophication.

2. Pesticide Use

Agricultural pests such as fungi, insects, rodents, and weeds are responsible for reducing world food production by about 50%. As a result, the effort to keep pests at bay is given a high priority by farmers. Pesticide chemicals, which include insecticides (for insects), herbicides (for plants), and fungicides (for fungi), have been used extensively during the past century. Different measures to control pests, however, have been employed by people since the beginning of agriculture. In 1939, Paul Muller developed the synthetic organic pesticide DDT (dichlorodiphenyl-trichloroethane). This pesticide helped to prevent the destruction of food crops by pests and diseases carried by mosquitoes. DDT was the first of the synthetic organic pesticides.

Modern synthetic pesticides, especially the organophosphate insecticides, were developed from chemicals tested for use in the manufacture of nerve gas weapons during World War II. In the 1940s, industrialized countries began to use these substances for the control of agricultural pests. Subsequently, their use increased substantially, with more than 33,000 commercial pesticides in use today. In the interval from 2000 to 2001, 2.5 million tons of pesticides valued at about \$28 billion were consumed worldwide. This represents an increase in pesticide consumption of 238% since 1970.

Eighty percent of the world's pesticide production is consumed in North America, Western Europe, and the Far East. In the U.S. alone, 860 active-ingredient

pesticide chemicals are formulated into 21,000 commercial products, and about 450 thousand tons of pesticides are produced annually. On a global scale, most of the pesticides used in agriculture are applied to a small number of crops—corn, rice, cotton, soybeans, and wheat. Despite Rachel Carson’s warnings in her book *Silent Spring* (1962) concerning the adverse environmental effects of pesticides, most of the toxic pesticides she discussed are still in use. One important exception is DDT, which, because of its adverse effects, has been banned in most countries of the world. Synthetic organic pesticides applied to crops may enter the water cycle along with fertilizers and be carried far from their source of application where they can be incorporated into biological systems.

Organochlorine-based insecticides are relatively volatile and are transported through the atmosphere as well as by water. These chemicals have been found in tree bark collected from every continent, with relatively high concentrations in the U.S., Europe, the Middle East, and China. Low concentrations have been observed at high northern latitudes. Pesticides are an important contributor to water pollution in the U.S. and elsewhere. It has been estimated that 500,000 to two million pesticide poisonings occur worldwide each year. In the U.S., perhaps as many as 45,000 farm and chemical workers annually suffer from some form of pesticide poisoning.

3. Changes in Land Use and Irrigation Systems

Changes in land use dramatically affect the surface of the land. Forests are converted to grasslands and

grazing lands, urban sprawl covers once open ground with roads, buildings, etc. Vast quantities of soil and dirt are moved around during land use changes, often resulting (upon runoff) in increased suspended sediment loads for aquatic systems, including coastal ocean waters. Alternatively suspended sediment also may be trapped in reservoirs behind dams, depriving coastal waters of the reactive elements in the suspended sediment load of rivers that drive their productivity.

Irrigation systems have contributed greatly to the growth in crop production. Water diversions from rivers and dammed reservoirs and water withdrawal from groundwater systems have significantly enhanced the productivity of agricultural lands. Agriculture worldwide accounts for about 65% of the total annual demand for water (4430 km³) or about 2880 km³ of water. This represents a per capita withdrawal rate of 505 m³ per year.

Industry accounts for most of the remaining water use (22%) worldwide, with only 7% withdrawn for domestic use. In the U.S., nearly equivalent volumes of water are withdrawn annually for agricultural and industrial use. Domestic yearly use accounts for about 12% of total water withdrawal of 467 km³, or 216 m³ per person. Water use is rapidly lowering groundwater tables in some regions of the world, especially in sunny hot dry areas, as agriculture, industry, and domestic uses compete for limited water supplies.

B. Impacts on the Global Coastal Ocean

1. Overall Situation

The coastal zone is heavily impacted by the human activities discussed above and others because at least 40% of the global population lives within 100 kilometers of the coast. In addition, nearly a billion people live in coastal urban centers that are now experiencing unprecedented growth. Furthermore, coastal waters are affected by activities occurring far upstream in watercourses that drain into these areas. As the world population grows, such impacts will

increase because of the continual migration of people to urban centers located on or near the coast or within major river basins. Despite the obvious potential for damage to coastal aquatic systems, few countries have implemented effective plans to manage coastal zone environments and protect their ecosystems. Effective management is difficult to accomplish because it requires consideration of human activities that lead to point source and non-point source pollution both adjacent to and far upstream of the coastal environment.

According to the World Resources Institute, 34% of the world's coasts have a high potential risk of degradation (Table 1). Another 17% face moderate risks. Most of the coasts threatened by development are in northern equatorial or temperate regions. In Europe and Asia, 86% and 69% of their coasts, respectively, face moderate to high risk of degradation. Desert, subarctic, and arctic regions are the least threatened by degradation.

Wetlands, estuaries, and coastal coral reefs are under increasing pressure from population growth and from stream and river courses that deliver dissolved and solid materials of anthropogenic origin. Population growth causes increased discharges of waste, suspended sediments, fertilizers, synthetic and organic chemicals, and toxic metals to coastal marine systems, potentially degrading habitat and causing species loss. Nutrient pollution leading to eutrophication of coastal marine systems is especially important and widespread.

Some recent studies indicate that up to 70% of pollution owing to excess nitrogen and phosphorus nutrient inputs to coastal environments derive from sources upstream of coastal environments. Nitrogen and phosphorus from sewage, agricultural runoff, human enhanced erosion, and other land-based sources have increased the nutrient load of rivers entering the coastal zone by 50 to 200% over the pre-industrial fluxes. A correlation exists between the population of people living in watersheds upstream of these environments and the quantity of nutrients

entering coastal environments. As the population density of a watershed increases, the nitrate and soluble, biologically reactive phosphorus fluxes of the major rivers draining that watershed into the coastal environment increase. This relationship portends increased nutrient inputs into coastal environments and accelerated eutrophication in the future because of increasing population density unless steps are taken worldwide to reduce nutrient inputs from agricultural and other sources. The high probability of enhanced eutrophication, coupled with increased inputs of pathogenic bacteria and viruses, heavy metals, and synthetic organic compounds into the coastal zone, suggests increased degradation of coastal margin ecosystems and loss of habitat and species. Because major fishing and shellfish industries are located in coastal margin environments, coastal habitat destruction and consequent species loss can have severe economic and social repercussions.

Another product of human activities affecting the global ocean is marine litter. Floating litter is found throughout the world's oceans and is particularly abundant along coasts. Litter includes floating plastic, wood, and other natural or man-made materials that have been dumped from ships or blown or washed from land. Little is currently known about the effects of such materials on marine populations. Some marine organisms, however, have died after ingesting litter or becoming entangled in it. Litter also detracts from the intrinsic beauty of coastal areas. A study on Inaccessible Island, a remote island in the Tristan da Cunha group in the South Atlantic Ocean, showed that

Table 1. Percentage of coastline of various regions of the world threatened with potential degradation.⁸

Region	Threat		
	Low	Moderate	High
Africa	49	14	38
Asia	31	17	52
North and Central America	71	12	17
South America	50	24	26
Europe	14	16	70
Former Soviet Union	64	24	12
Oceania	56	20	24
World	49	17	34

litter washing up on the island increased dramatically from 1984 to 1990. The litter density in 1984 was 500 pieces per kilometer and in 1990, almost 2500 pieces per kilometer of shoreline. The “garbage patch,” consisting of mainly floating plastic debris of all sizes focused by currents in the North Pacific subtropical gyre, is another example of the result of extensive marine littering.

Because in the past their usefulness was not readily apparent, wetlands have often been filled in to develop agricultural land, garbage dumps, or for urban expansion. It has been estimated that wetlands in the U.S. once comprised approximately 70 million hectares. Less than one-third of this area remains today. In tropical countries, mangroves dominate many wetland areas. Where data exist, more than 50% of mangrove area alone has been lost since the pre-Green Revolution era. Table 2 shows the extent and percentage loss of mangrove ecosystems for some selected countries. Mangroves, like coral reefs, protect the shoreline from erosion and are important habitats for invertebrates and fish. These systems are particularly vulnerable to sea-level rise and flooding, a potential consequence of climatic change.

Nearshore coral reefs (fringing and barrier reefs) are particularly vulnerable ecosystems. Unfortunately in various regions, they are threatened by chemical pollutants, excess nitrogen and phosphorus inputs, and siltation from erosion in the drainage basins. The use of dynamite and poisons to obtain fish from reef environments and the mining of reef materials for construction purposes are other stresses. Finally rising temperatures and increased acidity of ocean waters present a potentially far reaching challenge to the integrity of reefs.

Elevated sea temperatures (especially during El Niño events) may induce bleaching in corals. Bleaching is a result of the loss of a coral’s symbiotic algae (zooxanthellae) that impart color to the coral. Zooxanthellae contribute to coral nutrition and without them the coral will eventually die. Bleaching events in recent years have been observed in Bermuda, the Caribbean, and the Pacific. The reasons for these events remain controversial and probably are due to a number of environmental stresses,

including warming of the waters in which the corals live. A predicted average temperature increase since late pre-industrial times of 3°C or more in the year 2100 owing to global warming and other stresses associated with an enhanced greenhouse effect (sea-level rise and lowering of the pH of surface seawater) increase the likelihood that coral ecosystems could be severely degraded in the future.

Southeast Asia has 30% of the coral reef area of the world. Some 60 to 70% of those reefs are in poor condition because of deforestation and enhanced sediment discharge to coastal waters, and also because of coral mining and fishing with dynamite. In the Indian Ocean, with 24% of the world’s coral reefs, 20% of the reefs have been lost through mining, fishing practices that use explosives, and chemical and nutrient pollution.

Caribbean reefs are threatened by deforestation and development along the coasts of the countries of this area. In particular, the reefs of countries with high rates of both population growth and poverty, like Haiti, Jamaica, and the Dominican Republic, are heavily stressed. Reefs of the Atlantic Ocean are also threatened by coastal development and tourism. Because of past fishing pressures and other stresses on the Bermuda reefs, much of the coral reef area of this North Atlantic island is now in a protected reserve.

Most Pacific Ocean reef systems, accounting for 25% of global reef area, and Middle East reefs, like those of the Red Sea, are the least threatened by human activities. Unfortunately ocean acidification and rising sea surface temperatures are a threat to all coral reef systems.

On a global scale to date, 5 to 10% of coral reef ecosystems have been lost and at current rates of destruction another 60% of these important ecosystems could be lost in the next several decades. Aside from their scenic beauty and intrinsic value, the loss of coral reefs as habitats for fish, as providers of calcareous sediment, and as barriers to beach erosion and damage from storm-generated waves will have serious economic and social implications.

Table 2. The areal extent and percentage of loss of area of mangrove ecosystems for some selected countries of the world.⁹

Region and country	Current extent (1000s of hectares)	Approximate percentage lost (%)	Period covered
Asia			
India	100 to 700	50	1963 to 1977
Peninsular Malaysia	98.3	17	1965 to 1985
Philippines	140+	70	1920s to circa 1990
Singapore	0.5 to 0.6	20 to 30	Preagricultural period to present
Thailand	196 to 269	25	1979 to 1987
Viet Nam	200	50	1943 to early 1990s
Latin America			
Puerto Rico	6.5	75	Precolonial to present
Ecuador	117+	30+	Preagricultural to present
Guatemala	16	30+	1965 to 1990
Africa			
Cameroon	306	40	Preagricultural to mid-1980s
Kenya	53 to 62	70	Preagricultural to mid-1980s
Guinea-Bissau	237	75+	Preagricultural to mid-1980s
Liberia	20	70	Preagricultural to mid-1980s

2. Long-term Prospects for the Global Coastal Ocean

In this section, we discuss briefly how the world's coastal zone functioned prior to major human impacts on the land–water system, how it looks today, and the potential future of this important global environment. Prior to extensive land use and fossil fuel burning activities of humankind, carbon, nutrient, and suspended sediment inputs via rivers to the coastal zone were steady and did not change greatly on a decade to centuries time scale. Riverine calcium and bicarbonate inputs were deposited on the seafloor in the skeletons of organisms like foraminifera, mollusks, corals, and echinoids. The suspended sediment flux of rivers was about 10 billion tonnes per year and on entering the ocean settled to the seafloor. The flux of organic carbon in organic matter was 400 million tonnes per year and fluxes of N and P were about 14 million and 1.4 million tonnes per year, respectively. The organic matter of terrestrial origin entering the coastal zone via rivers was sedimented and buried on the seafloor, was transported to the open ocean, or decayed or was respired and ultimately its carbon returned to the atmosphere as carbon dioxide gas. A geological quasi-steady state existed (Figure 8).

It is important to realize that the global ocean was once a source of CO₂ to the atmosphere. The open ocean is now a CO₂ sink because of the human activities of fossil fuel burning and land use changes (e.g., deforestation). At present the global continental shelf appears to be a sink of CO₂ but estuaries, reefs, and other nearshore (proximal) coastal environments on the global scale are still sources due to calcification and in some environments net heterotrophy (Gross Production – Total Respiration < 1). On the global scale, this situation will change in the near future due to rising atmospheric CO₂ concentrations and the global coastal ocean will probably become an overall sink.

The flux of suspended solids via rivers to the oceans has nearly doubled to 18 billion tons annually. Much of this suspended sediment comes from rivers draining Southeast Asia and Oceania, where about 30% of the coral reef cover of the world and a significant amount of the production of shallow-water calcareous sediments is found. The rate of sediment discharge is changing today because of competing practices of damming river courses that block water and sediment discharge to the coastal ocean and other practices, like deforestation, which increases

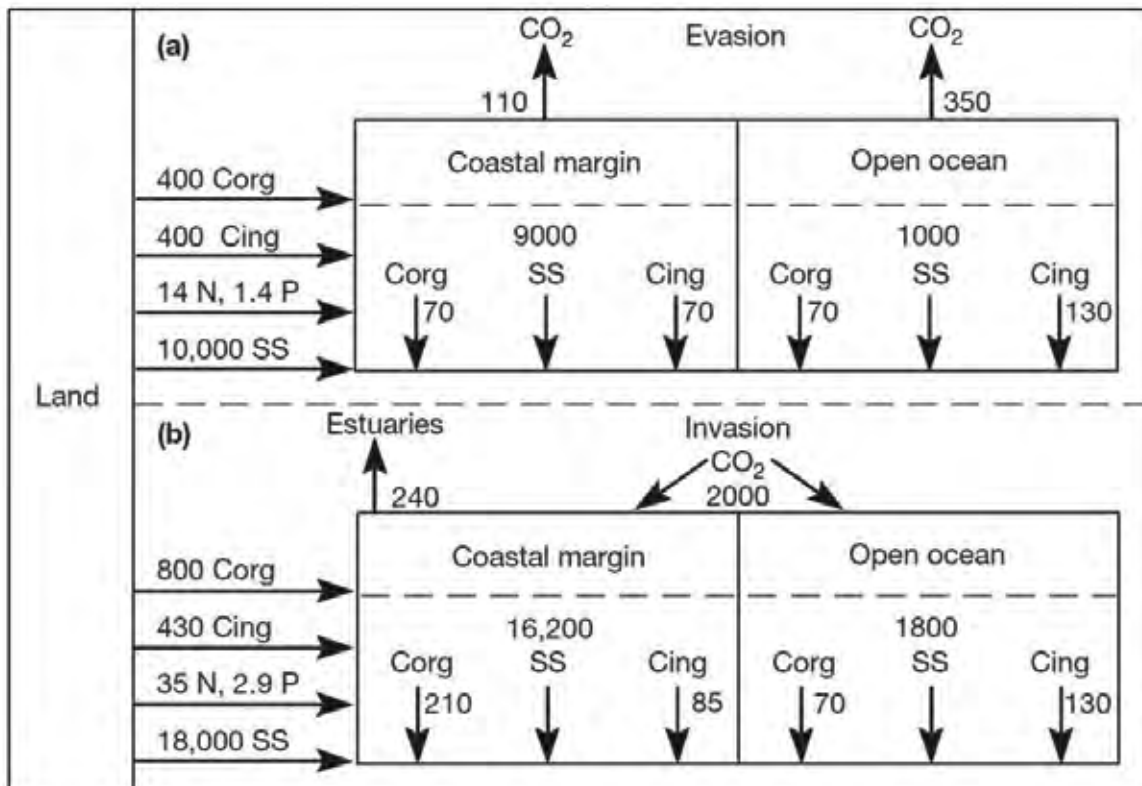


Figure 8. (a) The pre-industrial fluxes of C, N, P, and suspended solids to the ocean and their fate in the global coastal margin and open ocean and (b) the modern anthropogenic fluxes and fate of these materials.¹⁰

the discharge. Most of the sediment that reaches the ocean settles out in the nearshore coastal zone; only 10 to 20% is transported out to the shelf and open ocean. The enhanced sediment flux stemming from human activities is responsible for siltation of fresh water and marine water bodies and is contributing to ecosystem deterioration in many regions of the world.

Organic carbon, nitrogen, and phosphorus nutrient discharges via rivers to the coastal ocean have also doubled over their pristine values (Figure 8). This has led to enhanced productivity and cultural eutrophication of some coastal marine environments.

In these environments, it is likely that there has been a modification of the exchanges between the sea surface and the atmosphere of gases involved in biological activities, such as CO₂, nitrous oxide (N₂O) and dimethylsulfide (DMS). These gases are involved in climatic change; CO₂ and N₂O are greenhouse gases, and DMS and its conversion in the atmosphere to sulfate aerosol affect the radiative properties of the atmosphere and cool the

planet. Many estuarine systems of the world have suffered changes in fluxes of materials from rivers, groundwaters and via the atmosphere and in addition exhibit permanent or seasonal oxygen depletion in their waters. The Scheldt and Rhine estuaries of Western Europe, Mobile Bay, San Francisco Bay, Chesapeake Bay, Delaware Bay, Hudson Bay, Potomac Bay, Kāne‘ohe Bay of the U.S.A., and the Baia de Guanahara of Brazil are excellent examples of the worldwide problem of human modification of estuarine systems and (except for San Francisco Bay and Kāne‘ohe Bay) their eutrophication. The oxygen depletions in most of these systems were brought about by high inputs of organic matter, N and P and by inflows of wastes and suspended sediments.

In light of the preceding global coastal ocean discussion, it is informative to look in more detail at a regional land–coastal environment, that of islands. One example is the state of Hawai‘i in the U.S.A., located in the subtropical gyre of the North Pacific Ocean and the Northeast Trade Wind belt. The southernmost high islands of the Hawaiian Chain (Big Island of Hawai‘i, Maui, Lāna‘i, Moloka‘i,

O'ahu, and Kaua'i) have the vast majority of the human population of Hawai'i of 1.29 million. The island of O'ahu has the highest coastal-zone population density of any coastal state in the United States. Figure 9 shows the flows of N through the state of Hawai'i in its pristine state before extensive modification of the landscape by both the indigenous Hawaiians and subsequent immigrant populations and the situation as of 1992. Notice how the number of sources of N has increased from the pristine state to the 1990s. These new sources are mainly the application of nitrogenous fertilizers to croplands, the combustion of fossil fuels, and the importation of feed for livestock and food. Notice also that there are new sources of N to the atmosphere and increased fluxes of N to coastal bays, estuaries, and shelf/open ocean environments by river and groundwater flows owing to human activities. The total throughput of N in the Hawaiian environment in the 1990s has doubled since pristine time because of these activities. This doubling of the N flux has a similar order of magnitude increase as that of the doubling of the global flux of N owing to human activities. Despite the fact that N flows to the coastal zone have increased substantially because of agricultural and fuel combustion activities in Hawai'i, there are few coastal ecosystems in Hawai'i that exhibit significant cultural eutrophication. This is mainly due to the fact that the residence time of excess N from human activities in most coastal waters of Hawai'i is relatively short. The excess N is rapidly diluted by low-nutrient shelf and open ocean waters and transported out of coastal ecosystems to the open ocean, which is only a short distance seaward. At least one coastal system in Hawai'i, Kāne'ohe Bay, however, with a relatively slow circulation, is a notable exception where nutrient subsidies have a much greater impact on the trophic status of the bay waters. This coastal system and others in Hawai'i will be examined in greater detail later in this case study.

Another problem affects estuaries particularly in semiarid and arid regions of the world, like the Nile river estuary in Egypt. In these climatic regions, the diversion of river water for agricultural use and the impoundment of sediment behind dams on rivers upstream of an estuary further complicate other human modifications of the estuary. Reduced water and sediment discharge into the estuarine system

results in decreased sediment deposition and nutrient inputs. This may give rise to flooding of wetlands by seawater and to decreased organic productivity.

What will the global coastal margins look like in the future? This is a difficult question to answer, because the answer requires knowledge of a number of future economic and social considerations, as well as environmental ones. However, it is clear that unless we change our agricultural and industrial practices worldwide to decrease discharges of potential pollutants, coastal margin ecosystems will continue to deteriorate. The continuous movement of populations to the coastal zone will also increase stresses on the coastal system. Nutrient loading of estuaries, bays, and other coastal environments will lead to increases in production of organic matter in these systems. Figure 10 shows that as gross primary productivity increases, coastal environments tend to become more heterotrophic and the gap between production and consumption of organic carbon widens. As a result, more carbon is released from coastal waters to the atmosphere as CO₂. Such a situation could lead to loss of dissolved oxygen via decay/respiration processes from an increasing number of coastal margin environments in the future and to an enhanced potential for eutrophication. Loading of these environments with other pollutants like trace metals, pesticides, and hydrocarbons, as well as organic matter from external sources, will tend to lead to even more rapid environmental deterioration of a system undergoing eutrophication.

Figure 9. Pristine nitrogen flows through Hawai'i (A) and nitrogen flows in the early 1990s (B). The total flux of nitrogen through the environment has at least doubled since contact with humans mainly because of application of nitrogenous fertilizers to the land surface and food and feed imports of nitrogen into the society.¹¹

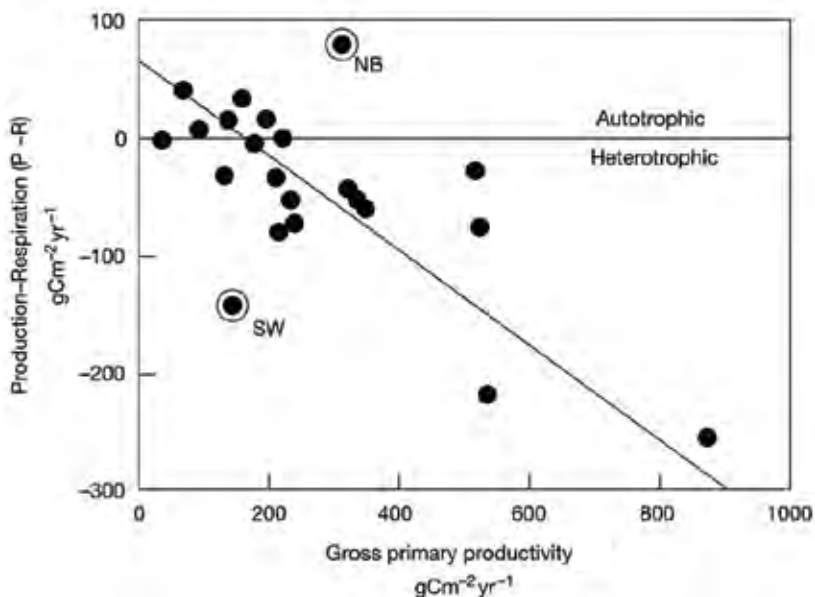
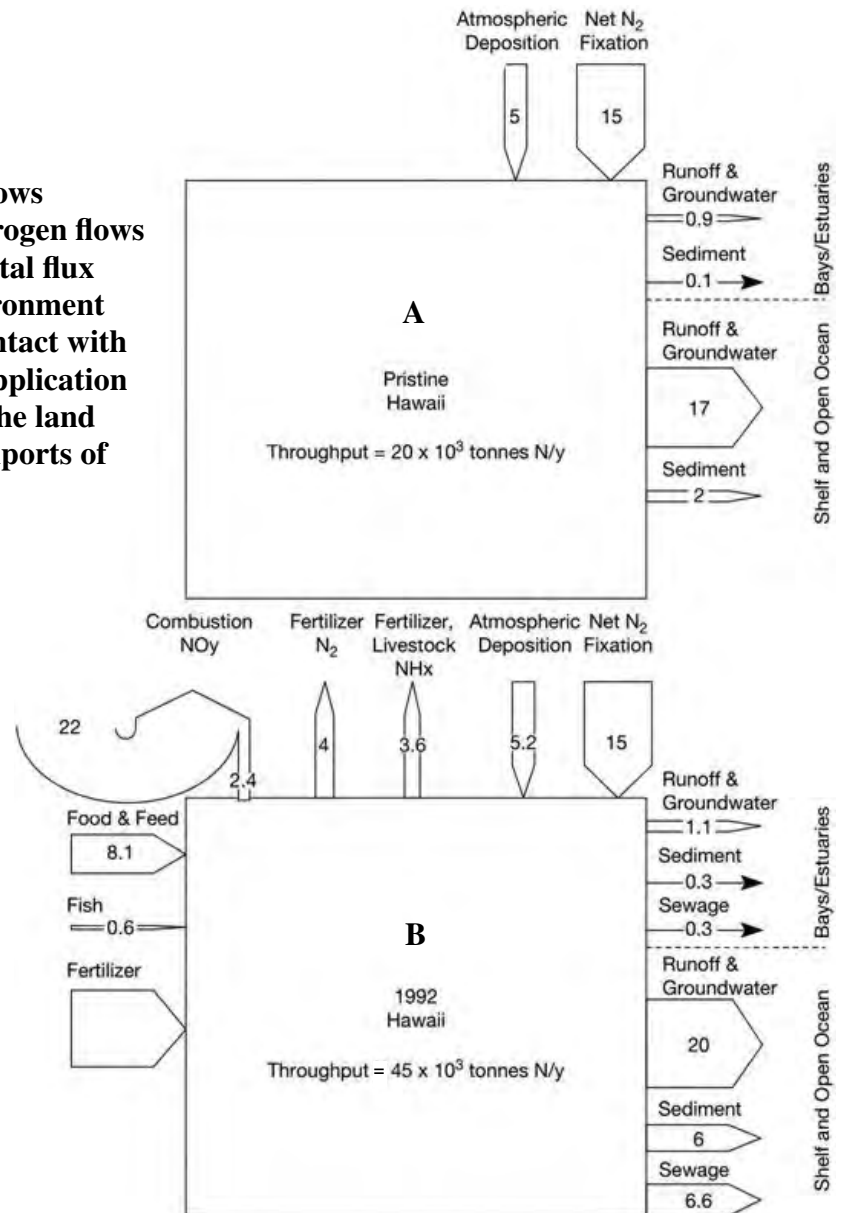


Figure 10. Gross primary production vs production minus respiration for a number of coastal environments. Notice in particular as Gross Primary Productivity (GPP) increases, there is a tendency for systems to become more heterotrophic (e.g., the balance between production and respiration becomes progressively more negative).¹²

a. Coastal Productivity – Water Column and Benthos

Nutrient pollution, principally related to N and P inputs, is widespread in populated coastal ecosystems. As mentioned previously, N and P from land-based sources, such as sewage, agricultural, and urban runoff, and atmospheric emissions of NO_x and subsequent deposition have increased the nutrient loading via rivers to the coastal ocean by 50 to 200% compared to their pre-industrial fluxes. Increased rainfall enhances terrestrial erosion and fluvial inputs of terrigenous materials to the coastal ocean. Normal base-flow conditions affect the coastal environment surrounding the stream and river mouths; storm events, however, impact a much larger area. Subtropical coastal environments such as bays are vibrant productive ecosystems with biological activity in both the water column and the benthic substrate. Large scale rain events, however, can significantly impact both water column and benthic productivity. The ecosystem-level trophic implications of storm runoff events are that a large component of the estuarine food web may be altered both in structure and function of the system. In addition, estuarine environments host fish nurseries and provide refuge habitats and storm runoff may cause stress or direct mortality of fisheries stocks. Anoxia and hypoxia also have direct impacts on biogeochemical reactions and processes in affected habitats.

During storm events, the large volume of runoff (compared to base-flow conditions) generates substantial (volumetrically and distance from source) plumes of fresh water that provide important nutrient subsidies to the coastal region. This nutrient loading from runoff can increase the primary productivity and phytoplankton biomass of the coastal water column. Under base-flow conditions, the primary production of many coastal regions, especially enclosed or semi-enclosed bays, is usually N limited. After storm events, there can be a depletion of P relative to dissolved inorganic nitrogen (DIN) in surface waters and the system switches to being P limited before returning to the baseline condition of N limitation (See Box 1: Nutrient Limitation, for general discussion). After initial storm pulses, a subsequent decrease in the concentrations of nutrients in the plumes is attributed to a combination of two effects: (1) dilution as the storm plume mixes into the water column and (2) uptake of nutrients by phytoplankton. Chlorophyll concentrations

peak a few days after the storm as particles settle and light levels increase in the water column allowing enhanced photosynthetic activity. In addition to the runoff pulse via streams and rivers, groundwater input to coastal waters containing elevated concentrations of nutrients such as nitrate (NO_3^-) and dissolved silica (SiO_2) has also been observed. It is therefore possible that groundwater seeps occasionally contribute significant amounts of both freshwater and nutrients to coastal environments. In tropical estuaries, flood events mostly occur sporadically during the wet season but they may account for up to 80% of the yearly loading of nutrients and sediments to these systems.

It is quite evident that storm events impact the chemistry of the water column in coastal environments, their productivity, and the ecosystem, but what about the benthic community? Benthic community production is impacted by dissolved and particulate nutrient availability along with the amount of light available. For example, high phytoplankton production in the water column following storms produces higher dissolved O_2 concentrations than observed during base-line conditions. In contrast, in bottom waters of the water-sediment interface, deposited phytoplankton and other organic matter may result in large-scale bottom water anoxia due to O_2 consumption by benthic microbial degradation and respiration of deposited organic matter. Long-term changes in the nutrient inputs to the benthic community can change the benthic productivity and community structure as has been observed with the onset or termination of sewage inputs. Shorter-term changes in the nutrient inputs, via storm-related runoff events, seem not to cause dramatic or permanent shifts in the benthic biomass and community structure.

As discussed above, phytoplankton productivity is controlled by the abundance of nutrients and by light. However, the phytoplankton biomass is controlled by both the nutrient input and the flushing of the coastal environment. On the other hand, the metabolism of the benthic community is controlled largely by nutrients derived from particulate loading. Benthic metabolism can also provide a major source of recycled nutrients after sewage diversion, for example, which may only decrease slowly with time.

Box 1 Nutrient Limitation

In the coastal and open ocean, primary producers (phytoplankton) need light and nutrients to grow. As long as light is penetrating the water column (i.e., not blocked by clouds or suspended materials in the water) and nutrients are present, phytoplankton will usually grow. In coastal areas, nutrients come from point and non-point sources, such as rivers and watershed agricultural areas, respectively, from in-situ regeneration of nutrients initially deposited in sediments, and via upwelling.

The Redfield ratio for marine phytoplankton is C:N:P 106:16:1 and can be used to determine the limitation of phytoplankton growth. The ratio of N to P is 16:1. This means that if the proportion of N to P is different from 16:1 then phytoplankton growth is '*nutrient limited*' by one or the other nutrient. If both nutrients are added in excess amounts, more than what can be used by phytoplankton; however, the system is considered as '*nutrient saturated*.'

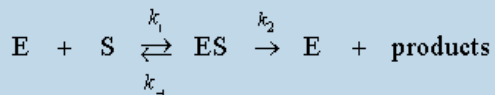
The system is considered:

- N limited when there is an excess of P (typical of marine ecosystems);
- P limited when there is an excess of N (typical of freshwater ecosystems); and
- Nutrient saturated when N and P are in excess amounts or under low light conditions.

Other elements that impact productivity such as silicon have to be considered for growth limitation for diatoms or iron for pelagic open ocean phytoplankton.

Measuring nutrient limitation is a tool for tracking temporal changes due to management efforts or changes in watershed use and inputs. N limitation can also be used to define future watershed management needs and priorities, and to help determine what management strategies are most likely to have the desired effects on controlling, for example, excess algal growth and associated adverse impacts on the ecosystem.

When dealing with nutrient uptake by organisms, the Michaelis-Menten equation is an important concept to understand. This equation describes the relationship between the rate of substrate conversion by an enzyme (E) to the concentration of the substrate (S):



The rate of conversion will depend on the capacity of the enzymes to process the substrate (or nutrient). This means that even if substrates are present in increasingly excess amounts, the reaction will not go faster. When all of the enzymes reach their maximum K_M (rate), then the rate of the reaction (use of substrate) reaches a plateau where:

$$v = \frac{V_{\max} [S]}{K_M + [S]}$$

where V_{\max} is the maximum growth rate.

This concept can be extended to an ecosystem. When the system has relatively low nutrient concentrations, then the rate of increase in growth rate (for phytoplankton first) increases rapidly with rising external nutrient concentrations (e.g., runoff events). When the system experiences higher dissolved nutrient concentration, however, further increases in nutrient concentrations will not necessarily translate into a further increase in growth rate (and increase in phytoplankton population) with rising external nutrient inputs from successive runoff events.

b. Coastal Productivity – Coral Reefs and CO₂ Exchange

The Intergovernmental Panel on Climate Change report of 2007 concluded that with a business-as-usual scenario of anthropogenic emissions, the atmospheric concentration of CO₂ could double by the year 2100. As the ocean absorbs CO₂ from the atmosphere, dissolved inorganic carbon (DIC) and CO₂ in surface ocean waters will increase resulting in acidification and consequent lowering of the calcium carbonate saturation state. Lowering of the carbonate saturation state may decrease the rate of calcification of skeletons and shells of marine calcifying organisms (i.e., corals, coralline algae, mollusks, and foraminifera) and also lead to dissolving of calcium carbonate (CaCO₃) substrates. A common outcome from the IPCC scenarios is that the continuous emissions of anthropogenic CO₂ to the atmosphere will decrease the future pH and the calcium carbonate saturation state of the ocean. Even with a future decrease in anthropogenic CO₂ emissions to the atmosphere, the oceans will continue to be a major sink of the CO₂ emissions stored in the atmosphere and, therefore, ocean acidification will continue to intensify.

In spite of abundant studies of air-sea exchange of atmospheric CO₂ and ocean acidification, the impacts associated with acidification on the marine carbon system in coastal waters remain incompletely understood. Although the concentration of atmospheric CO₂ continues to rise steadily, recent research shows that some coastal oceans are sources and others are sinks for atmospheric CO₂. These apparent contradictions are likely attributable to differences in regional geography, local climatic variability, biogeochemical cycling, and relative abundance of calcifying and non-calcifying organisms. Further investigation is required to understand the effects of rising atmospheric CO₂

on the open ocean and coastal environment marine ecosystems and also to quantify the behavior of the global coastal ocean with respect to atmosphere CO₂. The spatial and temporal scales of many studies have been restricted and need to be both extended and duplicated in numerous locations if we are to capture the dynamic nature of diverse coastal areas.

In addition to surface ocean acidification from atmospheric CO₂, there are other ways the surface ocean is acidified. From atmosphere and ocean models, the biogeochemical impacts of atmospheric inputs of HNO₃ (nitric acid), H₂SO₄ (sulfuric acid) and NH₃ (ammonia) from fossil fuel combustion and agriculture have been quantified. There is a direct acid flux (from HNO₃ and H₂SO₄) in the temperate Northern Hemisphere, but an alkaline flux exists in the tropics because of ammonia inputs. Excess ammonia is nitrified to NO₃⁻ (nitrate) in the upper ocean, hence the effective net atmospheric input is acidic almost everywhere. On a global scale, the effects of anthropogenic nitrogen and sulfur depositions on surface water chemistry are only a few percent of the total acidification and dissolved inorganic carbon increases due to the oceanic uptake of anthropogenic CO₂. In coastal waters, the atmospheric induced effects are also perturbed by nitrogen and phosphate fertilization leading to elevated primary production and biological DIC uptake that can locally reverse the change in pH and air-sea CO₂ flux. Reactive nitrogen and sulfur have relatively short lifetimes (one day to a week) in the atmosphere. Therefore, most of the acid deposition occurs relatively close to its source, on land, in the coastal ocean and in the open ocean downwind of the primary sources in North America, Europe and Asia. (See Box 2: Marine Carbon Chemistry, for chemical fundamentals behind the problem of ocean acidification).

Box 2 Marine Carbon Chemistry

The carbon dioxide-carbonic acid-carbonate system is one of the most studied of seawater chemical systems and is very important in terms of the modern environmental problems involving the carbon cycle on Earth. Dissolution of carbon dioxide in water is the first step that enables photosynthetic production of organic matter in aquatic systems, precipitation of carbonate minerals, and chemical weathering of the crust of the Earth. Carbon dioxide dissolves in water and reacts with water (H_2O) producing negatively charged bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. The electrical charges of these ions are balanced in pure water by the hydrogen ion (H^+) or in a natural solution like seawater by other metal cations and the hydrogen ion. Absorption of the gaseous species $\text{CO}_{2(\text{g})}$ into seawater is represented by the following reaction:

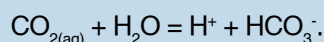


The aqueous uncharged CO_2 chemical species also includes the carbonic acid (H_2CO_3) species, which constitutes only a small fraction, about 1/400, of CO_2 in solution. To further describe relations in the CO_2 -carbonic-acid-carbonate system, it is necessary to introduce the concept of an equilibrium constant. When the forward rate of a chemical reaction equals the backward rate, the reaction is said to be at equilibrium and this equilibrium can be represented by an equilibrium constant. In seawater the usual type of equilibrium constant employed to describe chemical relationships is the apparent or stoichiometric constant, which is a function of temperature, pressure, and salinity. An apparent constant is defined as the product of the concentrations of the products, each product concentration raised to the power of its stoichiometric constant in the reaction, divided by a similar expression for the reactants in the reaction. For reaction (1) above, the apparent equilibrium constant for the reaction in seawater may be written as:

$$K'_0 = [\text{CO}_{2(\text{aq})}] / \text{PCO}_2$$

where K'_0 is the apparent constant of the reaction, the brackets denote concentration, and PCO_2 is the partial pressure of CO_2 gas in the atmosphere. The value of K'_0 at 25°C , an average seawater salinity (S) of 35 parts per thousand (ppt), and a total pressure of 1 bar (≈ 1 atmosphere) is 2.84×10^{-2} .

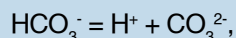
After absorption of the CO_2 gas, the aqueous CO_2 reacts with water



Under the environmental conditions specified above,

$$K'_1 = [\text{H}^+] [\text{HCO}_3^-] / [\text{CO}_{2(\text{aq})}] = 1.39 \times 10^{-6}$$

The HCO_3^- ion in reaction (2) then dissociates (“breaks down”)



and

$$K'_2 = [\text{H}^+] [\text{CO}_3^{2-}] / [\text{HCO}_3^-] = 1.19 \times 10^{-9}$$

Box 2

As mentioned previously, the values of the K' s vary with the salinity, temperature, and total pressure of the seawater environment.

Because of the formation of the aqueous ions HCO_3^- and CO_3^{2-} from CO_2 in solution, the total concentration of dissolved inorganic carbon (DIC) in seawater is the sum of the concentrations of all the inorganic carbon species, $\text{CO}_{2(\text{aq})}$, HCO_3^- , and CO_3^{2-} , and is defined as

$$\text{DIC} = [\text{CO}_{2(\text{aq})}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

The concentration unit for DIC is usually in moles of carbon per 1 kilogram of solution; in the case of seawater, the total moles of the DIC chemical species per kilogram of seawater.

For seawater the difference between the charges of the conservative cations and anions is equal to the algebraic sum of the charges of the H^+ -dependent ions, and this difference is called the *total alkalinity* of the solution, denoted $[\text{Alk}_T]$

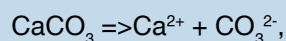
$$\begin{aligned} &2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] \\ &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] \end{aligned}$$

and

$$[\text{Alk}_T] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+].$$

The Alk_T is usually given in units of mol-equivalent/kg seawater. The determination of Alk_T and DIC in ocean waters is a powerful tool to trace water masses (Alk_T) in the ocean and to obtain estimates of primary productivity and the dissolution and precipitation of carbonate minerals (DIC and Alk_T). Also if you know the values of these two variables, you can calculate the pH and pCO_2 of seawater.

It is also possible to write reactions and equilibrium constants for the dissolution and precipitation of minerals in aqueous solutions. The carbonate minerals are especially important minerals found in the ocean as the skeletons and tests of marine organisms and as cements in marine sediments. Calcite (hexagonal CaCO_3), aragonite (orthorhombic CaCO_3), and dolomite [hexagonal $\text{CaMg}(\text{CO}_3)_2$] are important marine minerals. The latter mineral is not found in great abundance in the modern oceans but it is an important carbonate mineral found in ancient rocks deposited in the marine environment. The reaction representing both the dissolution of calcite and aragonite in seawater may be written



and at 25°C , salinity = 35 ppt, and 1 bar total pressure, the apparent equilibrium constants are

$$\begin{aligned} K'_{\text{cal}} &= [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 4.27 \times 10^{-7}, \text{ and} \\ K'_{\text{arag}} &= [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 6.48 \times 10^{-7}. \end{aligned}$$

Despite the two minerals having the same chemical composition, they differ in their atomic structure, and thus the K' values for the two minerals differ. These K' s basically represent the solubilities of the two minerals. The larger K' value for aragonite than that for calcite implies that aragonite is a more soluble mineral than calcite and is not stable relative to calcite under the environmental conditions specified above. However for these minerals to dissolve, the seawater in which the minerals are bathed must be undersaturated with respect to the two minerals. This implies that the product of the concentrations of

Box 2

Ca^{2+} and CO_3^{2-} (termed the ion concentration product, ICP) in the seawater must be smaller than the K' values for the minerals. The converse is true for the minerals to precipitate, where $\text{Ca}^{2+} + \text{CO}_3^{2-} \Rightarrow \text{CaCO}_3$.

Both calcite and aragonite contain other elements in minor or trace amounts and this affects their solubilities. Strontium (Sr) is especially important in aragonite and magnesium (Mg) in calcite. Indeed Mg can be so plentiful in biologically and inorganically produced calcite that a special term has been applied to the calcites containing more than about 4 weight % Mg, the *magnesian calcites*, which generally have greater solubilities than pure calcite, and for some magnesian calcite compositions, even aragonite.

The general relationships discussed above for the CO_2 -carbonic acid-carbonate system are true for all natural waters. The major difference is that for other water compositions, the K' 's have different values. These concepts involving this chemical system in seawater are especially important to the consideration of the problems of how rocks chemically weather and remove CO_2 from the atmosphere in the process and of rising atmospheric concentrations of CO_2 and the acidification of the world's oceans.

It is clear from the brief discussion above on ocean acidification and effect on calcification that the direction and magnitude of CO_2 air-sea exchange are important factors in any understanding of how the global coastal ocean reacts physically, chemically, and biologically to increasing atmospheric CO_2 , especially as the global atmospheric CO_2 concentration is projected to exceed 800 ppm by the year 2100. Currently the global mean atmospheric CO_2 concentration is 390 ppm and before the economic turn-down of 2007 was increasing at an average rate of 2.12 ppm per year. Roughly 40% of the anthropogenic CO_2 emissions released into the atmosphere since the start of the Industrial Revolution is still presently in the atmosphere.

Changing atmospheric CO_2 concentrations influences global temperature and this can result in changes in storm patterns (frequency, intensity, and locality) and alterations of the land-ocean heat exchange due to changes in ocean circulation patterns. This may also contribute to a global climate feedback mechanism, which changes surface ocean temperatures, the ocean circulation patterns and accelerates the changes in storm patterns. In addition to modifying the physical system, changes in atmospheric CO_2 concentration

also alter global coastal ocean water chemistry and consequently the coastal habitats of marine organisms.

How do changes in atmospheric CO_2 concentrations alter global coastal ocean water chemistry? If the partial pressure of atmospheric CO_2 is greater than the partial pressure of CO_2 in coastal waters, CO_2 moves from the atmosphere to the water. Therefore if the CO_2 concentration of the coastal ocean increases, due to increased atmospheric CO_2 concentration and invasion of CO_2 from the atmosphere to the ocean, the coastal ocean pH will subsequently decrease and the coastal ocean becomes more acidic. Increased acidification in turn decreases the saturation state of the water with respect to CaCO_3 minerals, inhibiting their precipitation and growth, as well as more readily dissolving the existing calcium carbonate structures of corals, coralline algae, and other calcifying organisms. Ocean acidification and decreasing calcium carbonate saturation states have already been observed in the open ocean in both Atlantic (Bermuda Atlantic Time Series or BATS) and Pacific Oceans (Hawaii Ocean Time-series or HOT) stations (Figures 11 & 12).



Figure 11. Locations of HOT and BATS. The Hawai'i Ocean Time-series station is shown by the red A balloon in the Pacific Ocean at 22° 45'N and 158° 00'W. The Bermuda Atlantic Time Series station is shown by the red B balloon in the North Atlantic Ocean at 31° 40'N and 64° 10'W.¹³

Before extensive fossil fuel emissions of CO₂ to the atmosphere, the global coastal ocean was considered to be a net source of CO₂ to the atmosphere over recent geologic time. The present *proximal* global coastal ocean is also estimated to be a net source of CO₂ to the atmosphere of 0.38 mol C m⁻² yr⁻¹ while the global shelf is a sink. When biological productivity is high in coastal waters, however, the production takes up dissolved CO₂ from coastal seawater leading to decreased dissolved CO₂ concentrations. This reduction in seawater dissolved CO₂ concentrations coupled with relatively elevated atmospheric CO₂ concentrations can result in air-to-sea transfer of CO₂ from atmosphere to ocean. Based on predictions of enhanced autotrophy in the coastal ocean due to increased riverine nutrient fluxes and continuously rising atmospheric CO₂ levels, numerical model simulations have shown that the global coastal ocean will soon switch from acting as a net source of, to a net sink for, atmospheric CO₂. Long-term monitoring of coastal zones is therefore critical for detecting and estimating when this shift may occur and its changing strength as a sink over time.

In summary, seawater CO₂ dynamics in coastal areas are affected by the proximity to land and human influences. Local forcing mechanisms, land-derived inputs and also complex coastal current patterns influenced by bathymetry and coastal boundaries, tidal exchange, upwelling, and variations in wind and precipitation due to local topography are all factors which variably influence the CO₂ carbonic acid system in coastal seawater. Biologically mediated carbon cycling in coastal systems reacts to these processes, impacting seawater CO₂ concentrations and hence air-sea CO₂ exchanges. In general terms, the processes that affect seawater CO₂ concentrations include production and respiration of organic matter, calcification and dissolution of CaCO₃, riverine and groundwater inputs, water advection to and from the open ocean, water column mixing, and ocean-atmosphere CO₂ exchange, heat, and water fluxes. Finally, in addition to those processes that can alter seawater CO₂ concentration, there are also other controls on general air-sea CO₂ gas exchange, or any other gas for that matter, including wind speed (which influences surface currents, atmospheric properties, and gas transfer velocities), bubble formation, organic surface films, rain, waves, temperature and salinity.

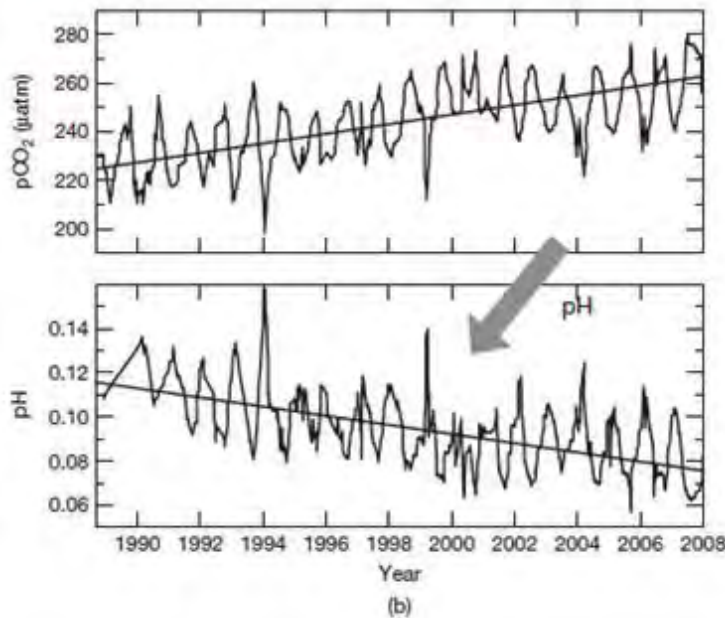
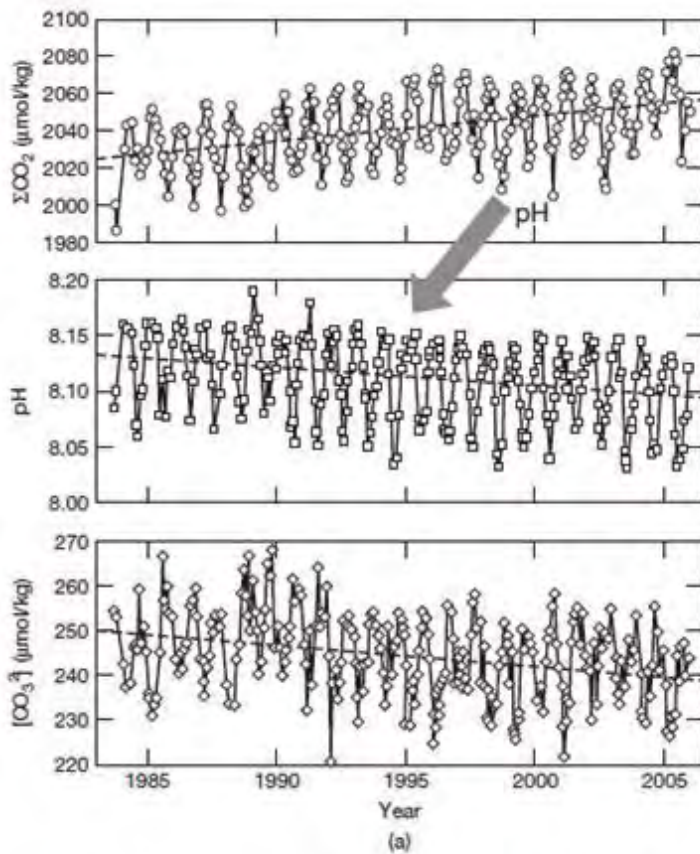


Figure 12. Time series of measurements of pH and dissolved inorganic carbon parameters for the surface waters of (a) Bermuda Atlantic Time-series (BATS) hydrostation in the North Atlantic and (b) Hawaii Ocean Time Series (HOT) hydrostation in the North Pacific. Notice the declining pH values, from past towards the present, at both stations.¹⁴ (Sources: <http://bats.bios.edu>; http://hahana.soest.hawaii.edu/hot/hot_jgofs.html.)

V. Hawai‘i as a Subtropical Coastal Ocean Example

To this point, we have reviewed how the global coastal ocean is reacting to anthropogenic forcings. It is evident that the global coastal ocean is important economically and as a sustainable resource for humans. We now narrow our focus to subtropical coastal systems by turning our attention to Hawai‘i as an example of such a system.

The lower latitude islands of Hawai‘i, as many other high oceanic islands, commonly experience intense storm events that lead to increased discharges of dissolved nutrients and suspended particulate matter into proximal (nearshore) coastal waters through small river, stream, and groundwater flows. These events deliver large amounts of materials usually in a period of a few hours to a few days and the effects on receiving waters can last several weeks. For example, a day-long large scale storm event occurred on the island of O‘ahu (November 29, 2003) delivering more than 12 inches of rain within a 24-hour period. In Hawai‘i, such storm runoff from steep watersheds leads to pulses of sediment and freshwater to coastal waters quickly impacting nearshore water quality.

Storm runoff can occur throughout the year but is more frequent and intense during Hawai‘i’s late fall, winter, and early spring seasons. The “ho‘oilō,” the term for wet season in the Hawaiian language, runs from November to March. Peak flows during short-lived storm events occur quickly (e.g., in minutes) and the flows return to a lower base-flow level after a few hours. The recovery time (i.e., time required for the flow to return to baseline conditions), however, can be impacted by human modifications to stream channels. Land use and differences in watershed characteristics also impact runoff and particle transport. Overall, brief and sharp increases in the amount of water, suspended matter, and dissolved and particulate nutrients delivered via runoff are observed during storm events.

Differences in runoff between watersheds reflect variability in rainfall, which can be dramatic over short distances on mountainous tropical islands such as the Hawaiian Islands. As an illustration of such variability over short distances, the rainfall pattern for the Hawaiian Island of O‘ahu is shown in Figure 13. Because of the persistent and prevailing trade winds,

O‘ahu’s rainfall pattern is dominated by orographic rainfall along the windward side of its mountain ranges. The topography of the island is a result of the original structure and form of the two volcanoes that comprise O‘ahu, in conjunction with weathering, erosion, and slope failure, which have modified the original surfaces of the island and control the hydrologic setting. The result is a landscape of steep basaltic mountains and deep valleys and steep interfluvial ridges.

O‘ahu can be divided into two main physiographic zones, windward and leeward, which relate to the exposure of these areas to the prevailing northeasterly trade winds and orographic rainfall. During the dry season (Northern Hemisphere summer), a stable North Pacific anticyclone results in persistent northeasterly trade winds (80 to 95% of the time). During the rainy season (winter–spring), migratory weather systems often move past the Hawaiian Islands resulting in less persistent trade winds (50–80% of the time). Southerly to southwesterly (or Kona) winds associated with low-pressure systems can bring heavy rains to the island. The dry coastal leeward areas can receive much of their annual rainfall during these less common Kona storms. During heavy storms, 24-hour rainfall can exceed 250 mm over coastal areas and 500 mm over the mountainous interior of the Ko‘olau Range.

The windward area is characterized by smaller drainage basins, higher rainfall, hence more abundant perennial streams, than the leeward area, which generally has larger drainage basins, lower rainfall, and intermittent stream flow. The Honolulu area is highly urbanized in coastal areas and mostly undeveloped in the interior mountainous areas, and contains large U-shaped valleys. The saddle area of O‘ahu (Schofield Plateau) is becoming increasingly urbanized, although remnants of large-scale plantation agriculture pineapple and more recent diversified agriculture persist; this area contains the largest drainage basins on the island.

In certain situations, large freshwater inputs from storm events can decrease coastal water salinity for periods long enough to promote osmotic damage to marine organisms. As freshwater mixes with

saline coastal water, the resultant reduced salinity of coastal water can be harmful to marine organisms. In most coastal areas of Hawai'i, however, the adverse impacts of freshwater input are limited by the rapid mixing with seawater and short coastal ocean residence times of water and nutrients. The areas impacted by freshwater input are also generally restricted to the upper portion of the water column and to intertidal and shallow subtidal benthic habitats (e.g., areas that are very close to the freshwater input).

The relatively large amount of research done on Hawai'i coastal systems enables us to review the impacts of land-coastal interactions on subtropical

coastal ecosystems. Our focus includes the Big Island of Hawai'i (Hilo Bay and its inputs) and the island of O'ahu with Kāne'ohe Bay (the most studied body of coastal water in Hawai'i), Kailua Bay, Kawai Nui canal and marsh, Maunawili, and Enchanted Lakes environments. We cannot directly compare all these systems and their behaviors as the focus, scale, and detail of research on each vary. However, we will describe the systems to the degree warranted by the research conducted to date and draw some conclusions across ecosystems. We now proceed to a discussion regarding Hilo Bay on the Big Island of Hawai'i.

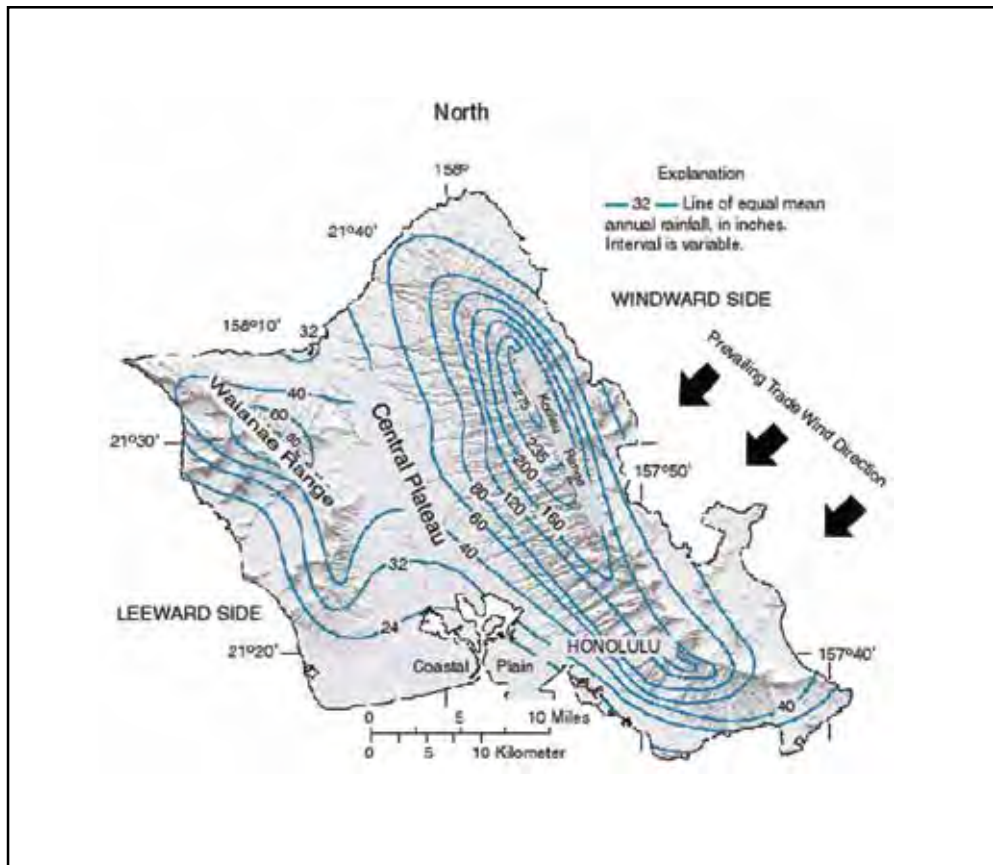


Figure 13. Median annual rainfall pattern of O'ahu, Hawai'i. Rainfall isopleths are in units of inches per year.¹⁵

A. Big Island of Hawai‘i: Hilo Bay and Inputs

1. Background

The dynamics of the CO₂ - carbonic acid system and CO₂ exchange across the air - water surface interface in tropical freshwater and coastal marine ecosystems have been investigated for the Big Island of Hawai‘i. An overall understanding of those dynamics is important because 60% of global freshwater inputs, more than 50% of total organic carbon burial, and 45% of total inorganic carbon burial occur at tropical and subtropical latitudes.

On the Big Island of Hawai‘i, Hilo Bay experiences large variations in current patterns, salinity, pH and total alkalinity (TA) due to the variability of weather, mainly the intensity of rainfall and freshwater discharge into the bay. Freshwater inputs into Hilo Bay derive from the nearby streams - Wailuku and Wailoa rivers - and from numerous spatially poorly known basal springs (Figure 14).

The Wailuku river is the longest river in the State of Hawai‘i with a drainage area of 590 km² that is covered by forest reserve (76%), pasture (20%), and a few urban areas downstream (4%). The Wailuku river forms the approximate boundary between lava flows

from the Mauna Kea volcano (North) and the Mauna Loa volcano (South) and biological and chemical data indicate it is a relatively pristine river. The river substrate consists mainly of basaltic bedrock and large basalt boulders. Soils consist of andisols, which are formed from the weathering of volcanic ash. Andisols contain high proportions of silica glass and amorphous colloidal materials that have a high-water retention capacity and the ability to sequester large quantities of phosphorus.

The Wailoa River lies to the east of Hilo and is largely associated with a highly urbanized area (Figure 15). The Wailoa River estuary system has moderate tidal mixing and is considered a brackish water aquatic system with salinity ranging between 0 and 10 ppt. The drainage basin area is 410 km² including the slopes of Mauna Loa. Several tributaries entering the pond, Waiākea-Kawili stream, ‘Alenaio stream and Palai creek, cross wooded areas, sugar cane fields or farmlands. The flow from Palai creek emerges from the subsurface as a spring in the lower part of the pond. These tributaries are channelized in the city, most of the time dry, poorly defined, and flow mainly during major heavy rain events.

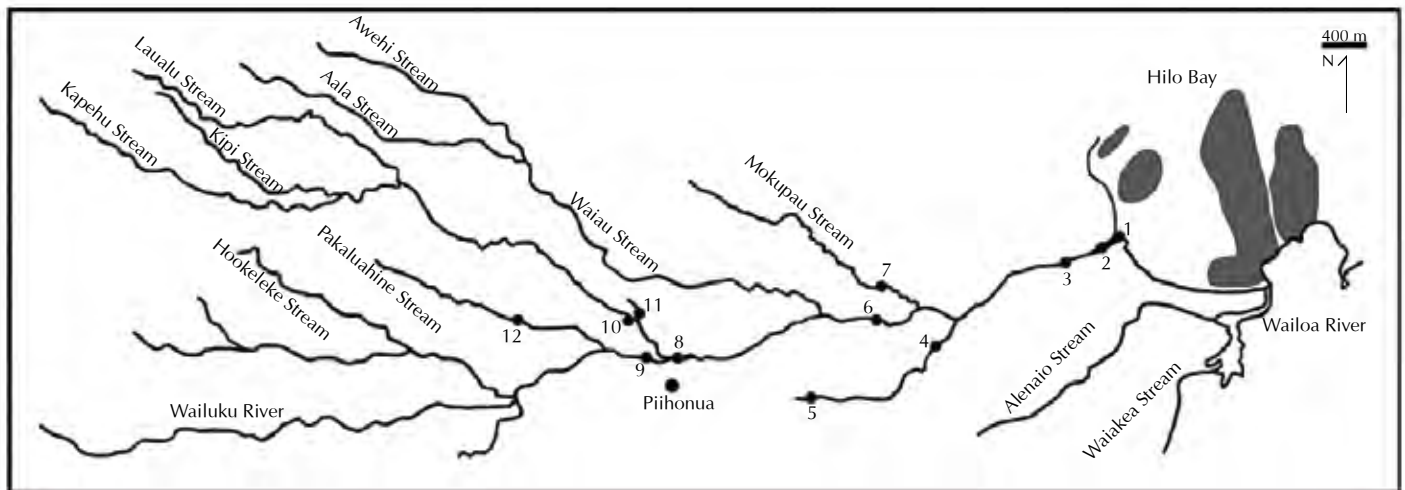


Figure 14. Map of Wailuku River (from bottom left) with its tributary streams and Wailoa River (bottom right) flowing into Hilo Bay (top right) on the Big Island of Hawai‘i. Grey areas are areas in Hilo Bay where freshwater springs emerge from the seafloor. Sampling stations on the Wailuku River are numbered.¹⁶

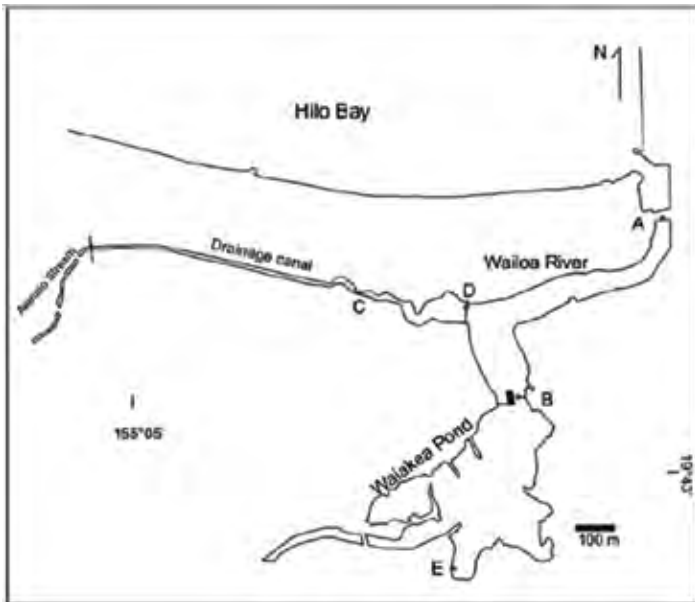


Figure 15. Close-up of Wailoia River and drainage area.¹⁷

Sampling of the riverine and estuarine system on Hawai‘i (Hilo) took place during the Hawaiian winter and spring, from November 2003 to May 2004, and included both dry and heavy rain conditions.

2. Observational Results

During baseline conditions (March 13 and May 1, 2004), similar TA values were observed for the Wailuku watershed waters on the two dates and were lower than those of estuarine waters (Figure 16). On average, freshwater stations on the Wailuku River showed TA values ranging from 0.190 to 0.793 mmol kg⁻¹ with a mean of 0.362 mmol kg⁻¹, and DIC values ranging from 0.206 to 0.837 mmol kg⁻¹ with a mean of about 0.4 mmol kg⁻¹. Mokupau stream exhibited

higher TA (0.792 mmol kg⁻¹) and DIC values (0.825 mmol kg⁻¹) than other freshwater stations. TA and DIC values were variable in the river and tributaries of the watershed. In the estuary, however, TA and DIC are conservative because of the very rapid mixing of freshwater and seawater during baseline conditions. The end-member values (river and in the bay) for TA and DIC fall along the mixing line with respect to the salinity of the two corresponding end member water masses. Variations in TA and DIC values are related to changing weather conditions. Increased TA values appear to be associated with the warmer periods of drought in the area leading to enhanced chemical weathering fluxes and longer soil and ground water residence times, during which time, TA, DIC, and pCO₂ increase in concentration in the subsurface systems. On the other hand, runoff is important during cooler periods of heavy rains with shorter residence times for subsurface water decreasing the chemical weathering rates and the alkalinity signal is diluted by the rapid water recharge. TA values in riverine water are lower following a heavy rain event, as dilution occurs. As another example, a negative relationship observed between DIC and discharge of the Kalamazoo River (southwest Michigan) was due to dilution during flood events. A similar relationship was also reported for the Mississippi River. Temporal variations of DIC, however, are probably very rapid in the Wailuku River, where freshwater discharge can change quickly from one day to another depending on the rainfall pattern and intensity.

The variations of HCO₃⁻ concentrations, which comprise the bulk of the TA, depend on chemical weathering intensity related to rainfall, rock age,

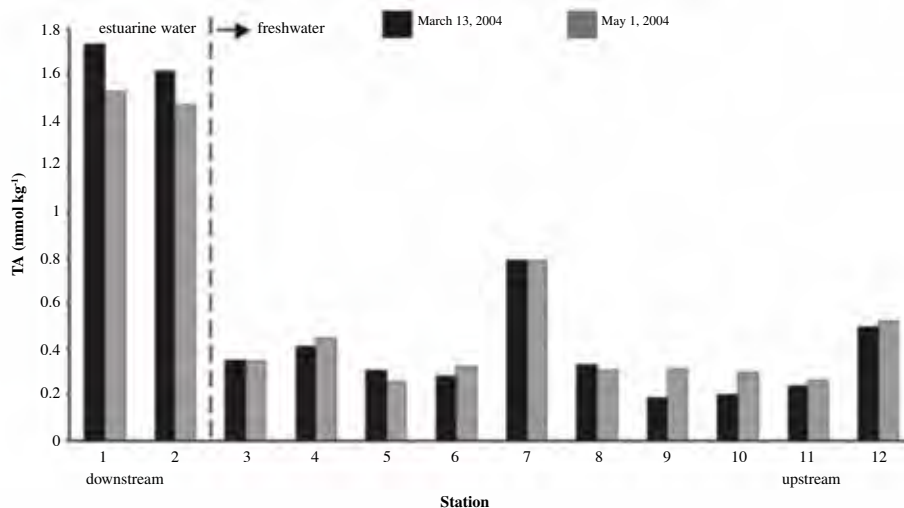


Figure 16. Longitudinal variations of TA during two surveys (March 13, 2004 and May 1, 2004) of baseline conditions in the Wailuku River. See Figure 14 for Wailuku station locations.¹⁸

topography, bedrock, soil thickness, temperature, and presence or absence of lichens. In the Wailuku watershed system, the highest concentration values found in the tributaries probably result from different local conditions such as the presence of more reactive rocks and soils and are less likely the result of anthropogenic inputs.

The $p\text{CO}_2$ values for baseline conditions of the Wailuku River (not shown) indicated oversaturation relative to atmospheric equilibrium. This oversaturation in river water is not unusual for worldwide rivers and freshwater lakes, but also suggests inputs of groundwater because of a low in-stream biotic metabolism. The average $p\text{CO}_2$ for Wailuku estuarine waters was close to or below saturation with respect to atmospheric CO_2 equilibrium (water average: 328 ppm; atmosphere: 375 ppm at Mauna Loa Observatory in 2003).

Following heavy rain events, the Wailuku River mouth showed a decrease in salinity, TA and DIC values. The $p\text{CO}_2$ values on the other hand increased up to 1,500 ppm, but 48 hours later baseline conditions returned (Figure 17). The high $p\text{CO}_2$ may reflect inputs of groundwater CO_2 flushed out of the soils and diverted to the river. Groundwater and soil $p\text{CO}_2$ values are high due to CO_2 production from microbial respiration of organic matter. In Kāneʻohe Stream, on Oʻahu, when sampling was performed in stream waters at appropriate times following the peak of a storm event, $p\text{CO}_2$ values were of the same order of magnitude as in the Wailuku River, with values up to 1,880 ppm.

Although relationships between $p\text{CO}_2$ and discharge are not always evident, in general an increased $p\text{CO}_2$ at the time of the highest stream discharge is due to the flushing out of high $p\text{CO}_2$ soil and groundwater (Figure 17). The dynamics of CO_2 in the Wailuku River are primarily controlled by variations in rainfall and the flushing of carbon and nutrients from soil and subsurface waters into rivers and less by seasonal variations in biological activity or temperature.

For the Wailuku River, the average flux of DIC into Hilo Bay is 19.35 g C d^{-1} during baseline conditions and reaches levels of $7,050 \text{ g C d}^{-1}$ during heavy rains. As with the Wailuku River, the salinity, TA and DIC in the Wailoa River estuary decreases

during heavy rains. DIC followed TA values, with TA higher than DIC. The $p\text{CO}_2$ values ranged from 1,515 ppm to 10,545 ppm during the flood event of March 2004. Salinity and $p\text{CO}_2$ were found not to be correlated in the pond at the mouth of the Wailoa River. There was a clear decrease in TA, DIC, $p\text{CO}_2$, and salinity of the Wailoa River estuary during the flood event. Net CO_2 oversaturation was observed at all Wailoa River stations with variations in $p\text{CO}_2$ values observed inside the pond. At one station $p\text{CO}_2$ decreased with the flooding, which could be due to two different reasons. First, a phytoplankton bloom may have drawn down the $p\text{CO}_2$, but no bloom was observed and other factors such as the turbidity and cloudiness were not conducive to a bloom. Alternatively, the low $p\text{CO}_2$ could be due to an input of lower TA freshwaters, although it was demonstrated that Hawaiʻi groundwaters are generally extremely high in $p\text{CO}_2$ (3,000 ppm) and have a pH value of about 6. The computation of the $p\text{CO}_2$ values at the stream temperature from the *in situ* salinity, TA and DIC values indicated no strong deviations from *in situ* $p\text{CO}_2$ values. The lower $p\text{CO}_2$ value of the Wailoa River at the time of the study appears to have been due to dilution because the drawdown of CO_2 in the river was not due to any phytoplankton bloom or groundwater inputs. After three days, the $p\text{CO}_2$ increased to a maximum of over 10,000 ppm due to excessive remineralization and respiration of the terrestrial suspended organic matter. The long residence time of the estuary water enhanced the $p\text{CO}_2$ build up.

The Wailuku River surface waters have a drainage basin dominated by tropical forests, barren lava rocks, and impermeable ash and are oversaturated in CO_2 . The $p\text{CO}_2$ values are within the range of values reported for other temperate and tropical river systems. The Wailuku River estuary, with a short water residence time, is undersaturated in CO_2 in contrast to the CO_2 oversaturation as observed in many other tidal estuaries. Waterfalls located on the Wailuku River allow the ventilation of river CO_2 to the atmosphere and the freshwater then mixes with seawater in the estuary. The result is water with CO_2 values near equilibrium with the atmosphere.

The smaller Wailoa River, located in a populated area with limited fresh water discharge, exhibits variable CO_2 oversaturation values. The difference between

the two river estuarine systems is likely due to their differences in physical characteristics; the Wailuku River is very turbulent, has a short residence time, and drains a relatively unpopulated region while the Wailoa River receives freshwater inputs from surface sources sporadically and is relatively calm, has a longer residence time, and drains mainly a populated area.

In Hilo Bay, the dynamics of DIC, TA and $p\text{CO}_2$ are largely dominated by the carbon inputs from the Wailuku River. The concentrations of DIC and TA

in the bay generally follow a conservative mixing line (i.e., the concentrations follow a straight line between the concentrations of the two mixing water masses), except during transient events following heavy rains. This conservative behavior likely implies that carbonate mineral formation through the process of calcification is not overly important in Hilo Bay waters (Figure 18) (reefs are not abundant in the bay). The Wailuku River plume has higher $p\text{CO}_2$ values than measured in the rest of the bay and also in the less extensive Wailoa River plume (Figure 19). The bay as a whole is slightly oversaturated with

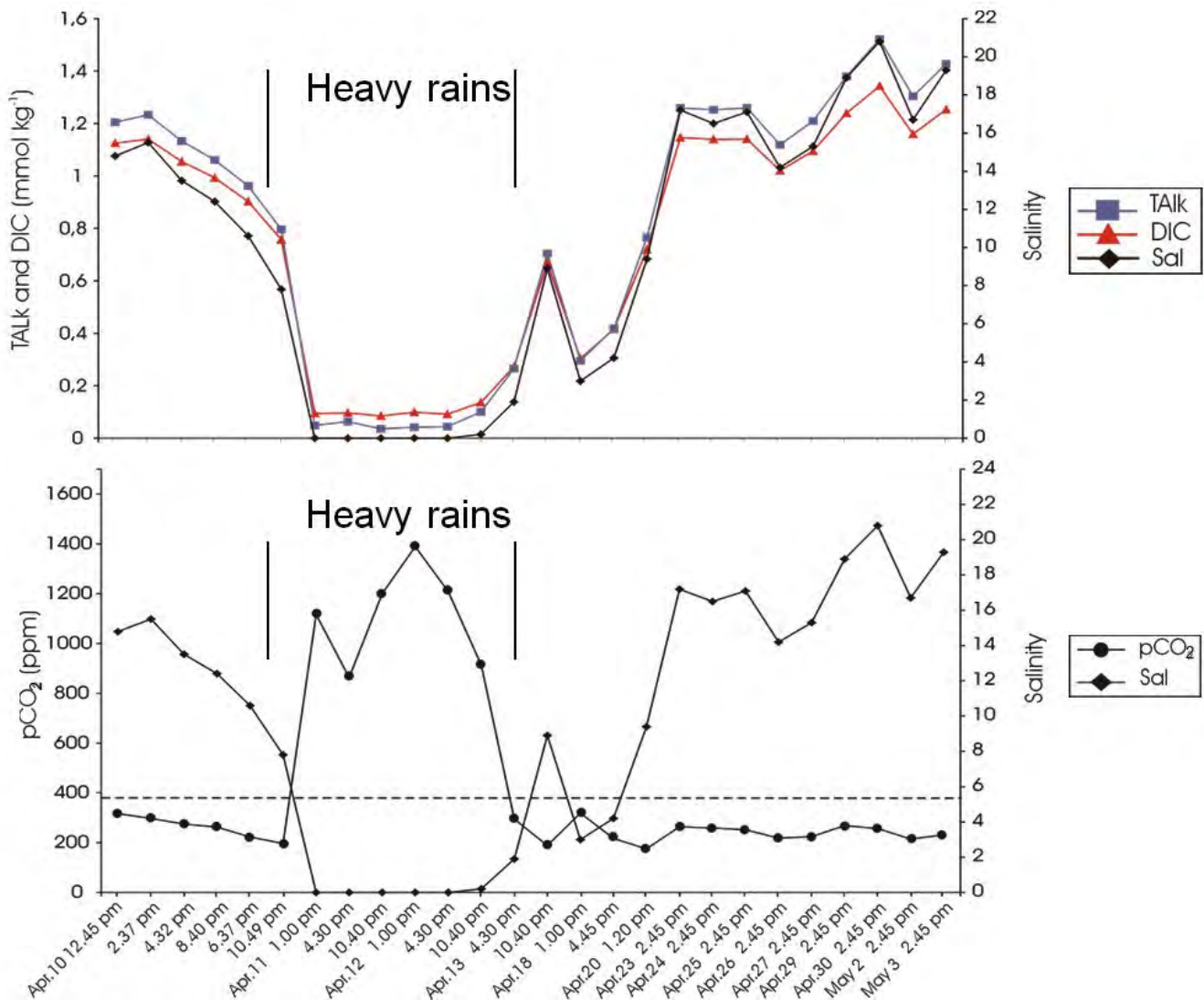


Figure 17. TA (mmol kg^{-1}), DIC (mmol kg^{-1}), salinity and $p\text{CO}_2$ (ppm) values of Wailuku River during two heavy rain events in April 2004. Atmospheric CO_2 equilibrium is represented by the dotted line at the bottom graph. There are drops of salinity, DIC and TA following the discharge of fresher water into the Wailuku River, and an increase in $p\text{CO}_2$ right after the first event (probably groundwater discharge).¹⁹

respect to CO_2 and thus vents CO_2 to the atmosphere. In the absence of significant calcification, the biogeochemical process maintaining pCO_2 values above atmospheric equilibrium is the imbalance between production and respiration of organic matter in the bay. The respiration of river derived and *in situ* total organic carbon exceeds gross primary production. This conclusion is supported by the dissolved oxygen data obtained from 21 cruises from 2001 to 2005 by the Marine Science Department of the University of Hawai'i at Hilo (<http://www.kmec.uhh.Hawaii.edu>). These data show that surface and subsurface waters of the bay and slightly outside the

bay are undersaturated with respect to oxygen. Hilo Bay is likely a net heterotrophic system.

The widespread groundwater springs in Hilo Bay containing relatively high pCO_2 did not appear to be significant inputs to the surface waters of the bay, since no anomalies were found during transects. The reasons could reside in the strong stratification of the water column due to the freshwater inputs from the Wailuku River and intrusion of open ocean waters on the bottom, combined with the short water residence time of Hilo Bay waters (on the order of a few days).

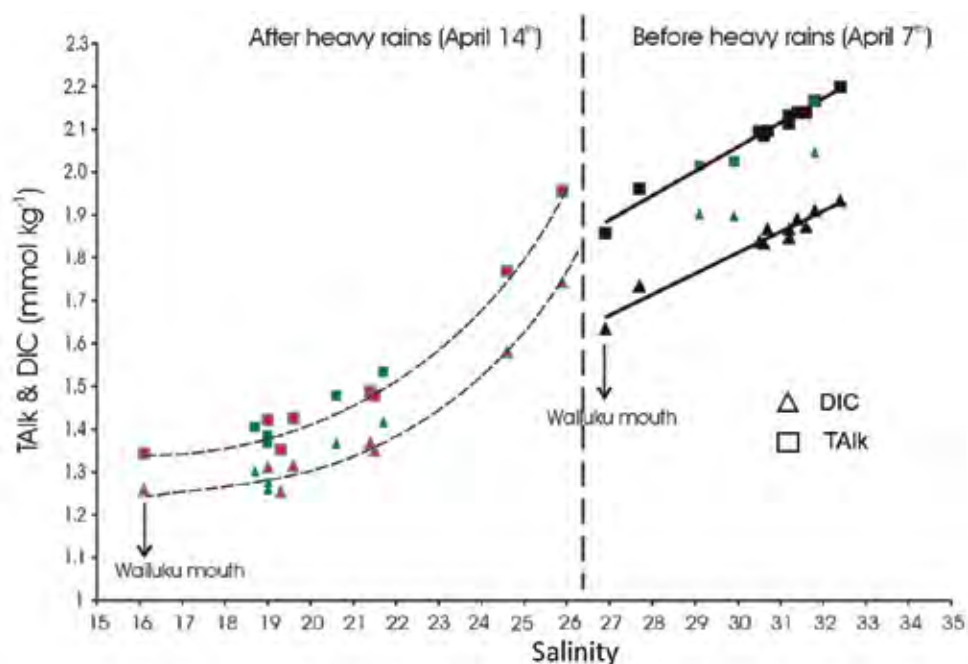


Figure 18. Changes of parameters TA and DIC (mmol kg^{-1}) in Hilo Bay along a transect from the Wailuku River mouth to the inner bay (break wall) before and after heavy rains of April 14th, 2004. Before the heavy rains (right), the end members fall on a conservative mixing line. After the heavy rains (left), the conservative behavior is gone.²⁰

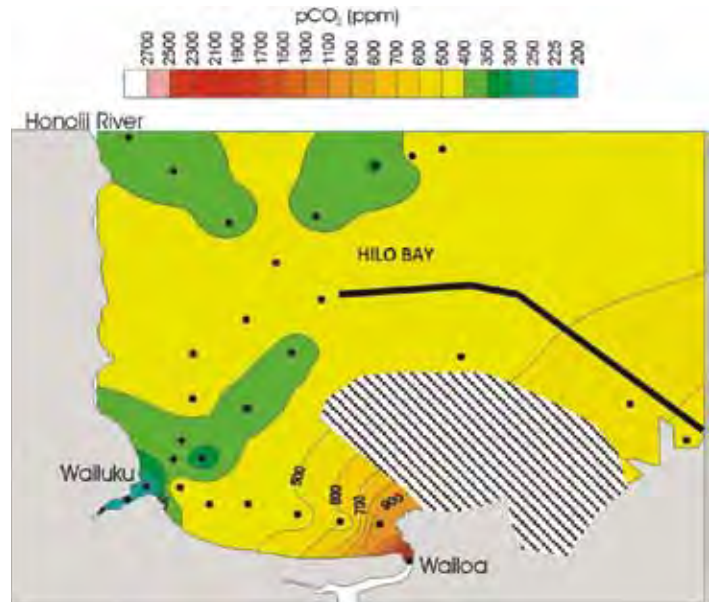
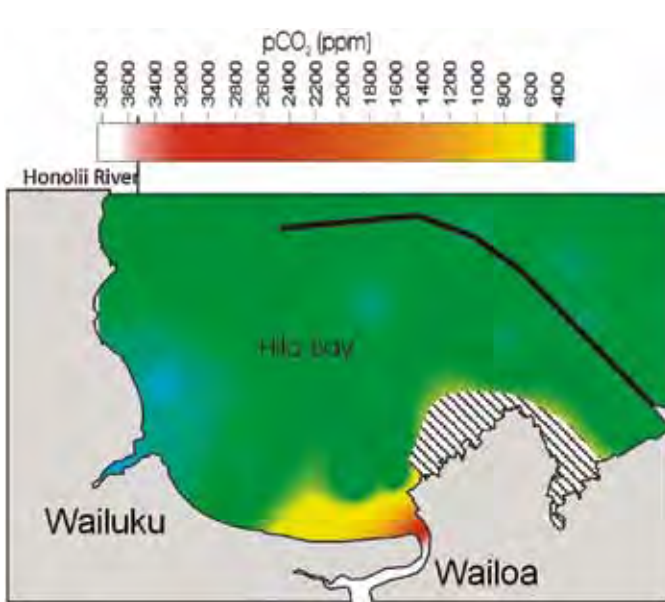


Figure 19. pCO₂ (ppm) in Hilo Bay on Jan. 21 (left) and Feb. 5, 2004 (right) before and after a heavy rain event, respectively. Note how the pCO₂ of the bay is higher after the heavy rain event.²¹

3. General Conclusions

- Hilo Bay acts as a source of CO₂ to the atmosphere, which is an observation similar to many other subtropical and tropical continental proximal coastal environments.
- Hilo Bay acts as a CO₂ source to the atmosphere due to net heterotrophy and not due to inputs of CO₂ from calcification.
- Hilo Bay DIC, TA, and pCO₂ are dominated by Wailuku river carbon inputs during storms.
- Wailuku river values of TA, DIC, and salinity fell during storm events due to dilution.
- In one storm event, river values of pCO₂ increased. This pCO₂ increase was likely due to flushing and subsequent groundwater input to the river of CO₂-charged groundwater (a result of soil microbial activity respiring organic matter).
- During heavy rains, the conservative mixing behavior of TA and DIC between the end members of Wailuku river water and inner bay water is lost.

B. Kāneʻohe Bay, Oʻahu

1. Background

We now turn our focus to Kāneʻohe Bay on the island of Oʻahu (Figure 20). The study of Kāneʻohe Bay represents one of the first high temporal resolution time series study of the CO₂ - carbonic acid and nutrient systems for a Hawaiian embayment as well as for a Pacific island coastal ecosystem. Kāneʻohe Bay is the largest sheltered body of water in the main Hawaiian Islands. The semi-enclosed southern basin of Kāneʻohe Bay has a mean depth of 9.5 meters and a mean water residence time of 6 to 13 days. The southern portion of the bay is relatively well mixed vertically and horizontally, except during periods of high stream input when density stratification

develops due to the density differences between freshwater runoff and seawater. The southern portion of the Kāneʻohe watershed is mainly characterized by urban development and some agricultural areas, making its adjacent coastal waters an excellent site to investigate the effects of urban runoff and nonpoint source nutrient pollution. Observations from Hawaiʻi are applicable to other subtropical and tropical Pacific Islands with similar drainage basins and hydrologic regimes.

Kāneʻohe Bay waters are normally oligotrophic (e.g., low dissolved nutrients and high dissolved oxygen content) and, especially in the southern basin, are strongly affected by land-derived nutrient inputs due



Figure 20. Satellite image of Kāneʻohe Bay, Oʻahu. MCBH is Marine Corp Base Hawaiʻi.²²

to regional geography, proximity to land, and land use changes. We know that storm events can enhance substantially land and river runoff and nutrient input to coastal waters. Associated with storm events can be large pulses of nutrient- and sediment-rich freshwater runoff, which induce phytoplankton blooms and therefore alter the coastal ocean carbon cycle and dynamics. The rapid freshwater input to estuarine ecosystems during storms can also lower coastal water salinity to levels that are threatening to coral reef organisms and deliver suspended sediment loads that can settle on to the coral reef thereby potentially affecting reef health.

Nutrient loading has been an especially important aspect of studies of southern Kāneʻohe Bay and the bay in general. The bay received increasing amounts

of sewage during the 1960s through the late 1970s. This increased sewage input resulted in eutrophication and noticeably impacted the water column, coral reefs, and soft-bottom benthic ecosystems. Currently, excess nutrients still enter Kāneʻohe Bay via stream and overland runoff and groundwater discharge. The primary production of the Kāneʻohe Bay coastal ocean ecosystem is mainly governed by changes in nutrient loading. Storm or heavy rain events lead to runoff and increased ground water discharge, which are the primary drivers of increased nutrient loading. The southern portion of Kāneʻohe Bay has a steady base-flow of freshwater input interrupted by intense surges in flow rates and nutrient loadings due to storm events. The main freshwater inputs into the southern portion of Kāneʻohe Bay are Kawa Stream, Keaʻahala stream and Kāneʻohe Stream (Figure 21). Kāneʻohe

Stream alone contributes nearly 75% of the total runoff into the bay. Also, there are fresh groundwater seeps into Kāneʻohe Bay along the predominantly basaltic coastline.

Based on a 25-yr record (1976 to 2000) of the United States Geological Survey (USGS) gauging station (# 16-972200) located in the Kamoʻoaliʻi upper branch of Kāneʻohe Stream, the mean stream flow is approximately 4,644 gal min⁻¹. For comparison, the highest mean stream flow in the state of Hawaiʻi is the Wailua River near Lihuʻe on the island of Kauaʻi with 54,208 gal min⁻¹. The state average stream flow is 8,559 gal min⁻¹. Discharge from other streams on Oʻahu can occasionally reach 7,925,161 gal min⁻¹ during Kona weather-generated storms and, under

such conditions, is highly enriched in sediments and nutrients. Because Hawaiian drainage basins are small and mountainous, streams respond rapidly to rainfall. Following an intense rain event, it takes only a few hours for the coastal streams to reach maximum flow delivering substantial amounts of sediments and nutrients to adjacent coastal waters. In the southern portion of Kāneʻohe Bay, storm discharge from the streams results in turbid plumes, which can cover approximately 1/3 of the south sector of the bay and typically travel northward along its western edge. These plumes are characteristically shallow (≥ 0.2 meters thick) with low salinity due to their fresh water stream source and carry suspended particles and nutrients.

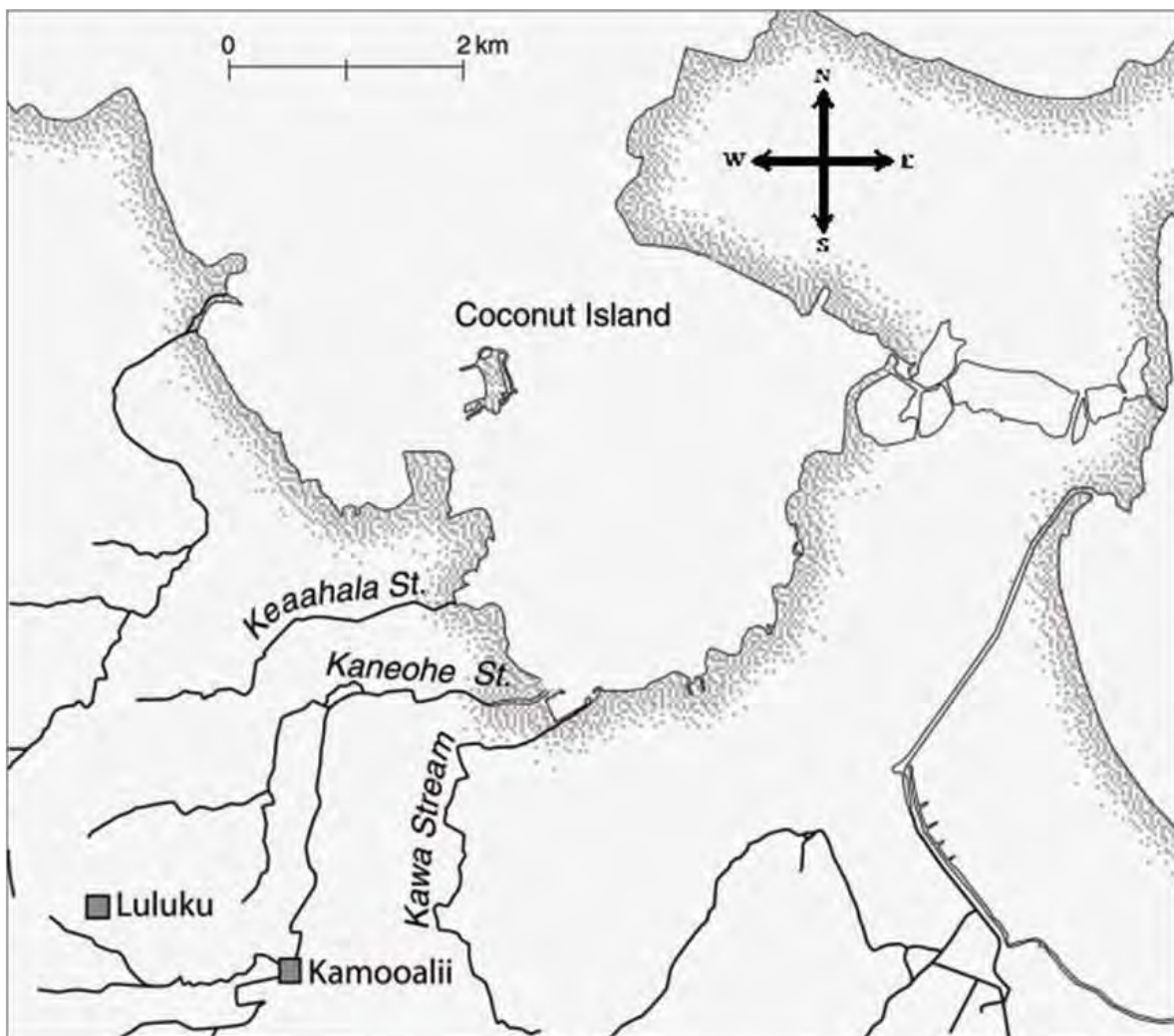


Figure 21. Map of the Kāneʻohe watershed with Keaʻahala, Kawa and Kāneʻohe streams. The gray boxes show the locations of Luluku and Kamoʻoaliʻi rain gauge stations.²³

With this brief introduction to the bay, we now discuss sequentially Kāneʻohe Bay studies from the following general time periods:

- a. 1997-2001: Study of stream inputs to Kāneʻohe Bay;
- b. 2001-2003: How nutrient inputs impact productivity in Kāneʻohe Bay;
- c. 2003: Storm runoff impact on Kāneʻohe Bay water quality and productivity;
- d. 2003-2004: Baseflow and storm event impacts on Kāneʻohe Bay air-sea CO₂ exchange;
- e. 2005-2007: Climate variability, interannual, and short-term event impacts on Kāneʻohe Bay air-sea CO₂ exchange; and
- f. 2005-2008: Comparing air-sea CO₂ exchange between Kāneʻohe Bay and two other Oʻahu locations.

Building on the classical work of Smith et al. (1981) on Kāneʻohe Bay, the following publications were used to compile this section of the case study on Kāneʻohe Bay: Fagan and Mackenzie, 2007; De Carlo et al., 2007; Ringuet and Mackenzie, 2005; Solomon, 2008; Hoover and Mackenzie, 2009; and Drupp et al., 2011. Our discussion of Kāneʻohe Bay is generally in the temporal order in which the studies were conducted. This is done for two reasons: (1) to illustrate how the studies build upon one another, and (2) to aid the reader in developing an understanding of how temporal variability in climate and stream water discharge coupled with different land uses within a watershed can influence nutrient delivery from land to the ocean, coastal ocean productivity and ecosystem community changes, and air-sea CO₂ fluxes.

The first study (a. 1997-2001) investigated how stream inputs to Kāneʻohe Bay varied over the span of four years, which happened to be during a strong extended El Niño event. Building on the conclusions of the first study, the second study (b. 2001-2003) explored how variations in nutrient inputs to the bay influence primary production and community succession in the bay. The purpose of the third study (c. 2003) was to look simultaneously at the evolution of a rainstorm-derived sediment and nutrient laden freshwater plume in Kāneʻohe Bay and its impact on water quality, productivity, and phytoplankton community structure, and how physical forcing impacts the recovery of the system from storm perturbations. It is a natural extension of

the work done in the second study (b. 2001-2003). The fourth study (d. 2003-2004), using the foundation formed by the previous two studies, investigated how changes in baseflow and storm event fluxes into the bay influenced air-sea CO₂ exchange between the bay and overlying atmosphere. This is an important current avenue of research as proximal coastal marine ecosystems are presently thought to be mainly sources of CO₂ to the atmosphere and CO₂ input into these ecosystems will result in acidification of the surface waters, which is harmful to calcifying organisms (e.g., coral reefs). The fifth study (e. 2005-2007) built upon the findings of the fourth study by investigating the effects of local climate variability on the air-sea CO₂ flux in a semi-enclosed coastal environment on interannual as well as shorter time scales of storm events to allow comparison with the results of the fourth study. The sixth study (f. 2005-2008) compares air-sea CO₂ data collected from two enclosed Oʻahu, Hawaiʻi coastal locations with the semi-enclosed environment of the Kāneʻohe Bay study. After reviewing the findings and conclusions of each study, we will summarize the general conclusions in terms of the overall picture of Kāneʻohe Bay regarding short- and long-term runoff inputs, productivity response of the bay to these inputs, how air-sea CO₂ exchange varies, impacts of land use, time of return of bay to normal, baseline conditions, and so forth.

2. Observational results and short conclusions

a. 1997-2001: Stream Inputs to Kāneʻohe Bay

Before examining the effects of short-term events, such as storms, on nutrient inputs to Kāneʻohe Bay and the subsequent impacts on coastal biological production, we first need to understand how the transfer of nutrients from land to the coastal ocean occurs during “baseflow” periods. Research from 1997-2001 examined the linkages between both stream storm runoff and stream baseflow to water, suspended particulate materials, and dissolved and particulate nutrient fluxes to Oʻahu coastal waters and the effects of land use (Table 3) on water and suspended particulate material, and associated nutrient fluxes. This study period occurred during an El Niño cycle and so there was characteristically less than average rainfall. Also during the study, few storm events occurred and the major ones were during the winter spanning 1999-2000.

Table 3. Watershed sites and percent land use type as defined in the 1997-2001 study.²⁴

Site	Conservation	Agriculture	Urban
Kahana	100	0	0
He'eia	100	0	0
Opaeula	56	44	0.2
Poamoho	17	82	1.0
Kāne'ohē	84	0	16
Kea'ahala	6	0	94

Normal base-flow conditions affect the environment surrounding the stream mouths; storm events, however, impact a much larger area. The runoff generates substantial plumes of fresh water that provide important nutrient subsidies to the bay. This nutrient loading from runoff increases the primary productivity and phytoplankton biomass of the water column. In the 1997-2001 study, stream flow volume rates were measured *in situ* by flowmeters and stream water samples were collected by automated water samplers. Storm runoff occurred during the study period, but was more frequent and intense during the winter months. Storm discharge maximums usually lasted only a few minutes and the flows returned to baseflow conditions within a few hours. Human modification of certain study areas and their stream channels caused storm flows to accumulate at or upstream of the modifications, thus resulting in a more gradual recession of storm flow than observed in the unaltered stream channels. Baseflow rates increased slightly following the storm-induced event flows and then declined gradually over a period of days to weeks. In populated areas, baseflow rates sometimes dropped and/or recovered more quickly likely due to upstream diversion (e.g., collection and diversion) by residents. Short-duration, punctuated storm events produced steep increases, more so than baseflow, in the total cumulative stream discharge volumes over time, although the relative contributions of baseflow and storm runoff varied considerably from year to year and between sites. Interestingly, storms were least important to the He'eia and Kāne'ohē Stream sites due to the steady, consistent, and elevated baseflow rates at those sites. The consistency is due to the prevailing tradewind-

induced orographic rain that regularly falls in the watersheds of these streams. A weighted average of all watersheds showed that over the period of the study, storms accounted for 8 to 77% (median 30%) of the total volume of yearly runoff.

Both baseflow and storm flow events carry suspended and dissolved nutrient loads. Suspended particulate matter concentrations increased exponentially with flow rates at all study sites, but exhibited a great deal of variability. Variable storm contributions caused annual suspended particulate matter loads to differ dramatically between years. In other words, the annual load variability was dependent mainly upon the frequency and relative strength of storm events and therefore baseflow was a minor contributor to annual yield. The one exception was Kāne'ohē Stream, where baseflow suspended particulate matter was 33% of the annual load due to two factors: (1) relatively high suspended particulate matter concentrations during baseflow conditions, and (2) relatively low storm yields. However for the island of O'ahu, even when keeping in mind the Kāne'ohē watershed, storms produced at least two-thirds of the total yearly yield in suspended particulate matter for each watershed over the course of the study. A weighted average of all watersheds showed that during the period of the study, storms accounted for 57 to 99% (median 93%) of the total suspended particulate matter flux.

Nutrients, suspended and dissolved, are also important components of coastal inputs from land. Dissolved nutrients analyzed in the 1997-2001 study included inorganic nitrogen (nitrate and nitrite, although nitrite is negligible in most samples), ammonium (hereafter referred to as ammonia), organic nitrogen, total nitrogen, inorganic phosphorus, and silica. Particulate nutrients analyzed in this study included inorganic phosphorus, organic phosphorus, and organic carbon. Concentrations of dissolved species exhibited considerable variability, particularly in intermediate and high-flow stream water samples, but many showed significant flow dependency. Flow dependency in nutrient concentrations was observed most frequently for nitrogen species. At the conservation watershed sites, all the nitrogen chemical species increased in storm runoff samples. Except for ammonia, similar but larger increases were observed at the urban sites, while trends at the agriculture sites

were weak or absent. For phosphorus, trends were weak or absent at the conservation and agricultural sites, but strongly positive trends were observed at urban sites. Interestingly, agriculture sites had statistically indistinguishable nitrogen concentrations when comparing baseflow to storm runoff samples.

Flow-dependent trends were generally more apparent in suspended particulate matter nutrient content compared to dissolved nutrient concentrations.

During low flow events, particulate organic nitrogen and carbon were generally higher in concentration compared to storm samples. Storm samples on the other hand exhibited lower concentrations of suspended particulate matter with increasing flow. Particulate organic phosphorus was the exception with little to no concentration variation with flow variation at all sites. As far as land use effects on concentrations, particulate organic C, N, and P concentrations were highest in high flow samples at conservation sites, had intermediate concentrations at urban sites, and were lowest at agriculture sites. Particulate inorganic P concentrations in high-flow samples were greatest at urban sites and lowest at conservation and agriculture sites. Overall, dissolved and particulate nutrient fluxes largely followed the interannual patterns established by water fluxes. In other words, during this relatively dry four-year period, the few storms that occurred were responsible for the majority of suspended particulate matter and particulate nutrient fluxes, and contributed significantly to water and dissolved nutrient fluxes at all sites studied. Nutrient budget analysis for the 1997-2001 study period demonstrated that suspended particulate matter could be a major source of new nutrients to southern Kāneʻohe Bay, and therefore factors that control suspended particulate matter (baseflow vs. storm, land-use, etc.) and also impact dissolved nutrient fluxes are important controls of overall nutrient input and thus primary production of Kāneʻohe Bay.

1997-2001 Conclusions

- Storm events were found to play a major role in water, suspended particulate material, and nutrient fluxes to Kāneʻohe Bay coastal waters despite unusually low storm frequency and intensity during the study period, indicating that storms probably play an even greater role during more typical (e.g., non-El Niño or La Niña) periods.

- Land-use played an important role in the relative distribution and concentrations of particulates and dissolved nutrients in streams.
- Runoff (baseflow and storm) from both urban and agricultural sources, was consistently elevated in concentrations of dissolved nutrients.
- Particulate organic matter fluxes were highest at conservation sites, similar or slightly lower at urban sites, and lowest at agriculture sites.

b. 2001-2003: How Nutrient Inputs Impact Productivity in Kāneʻohe Bay

After the stream water work conducted from 1997-2001, it was a natural progression to investigate how changes in nutrient inputs to Kāneʻohe Bay influence bay productivity. A common trend established in the 1997-2001 study (and subsequent studies) regarding nitrogen fluxes during storm events in the Kāneʻohe Bay watershed is that there is an initial major addition of dissolved NO_3^- and nitrite (NO_2^-) via runoff flux to the bay. Following the initial nitrate and nitrite additions, the concentration of ammonium (NH_4^+) increases within a few days in both surface and deep bay waters. The concentrations of nitrogen species and dissolved SiO_2 peak while salinity drops as freshwater plumes move away from the stream mouth and mix with seawater. Concentrations of N subsequently decline rapidly as phytoplankton take up the available nutrients. The Redfield ratio (See Box 1: Nutrient Limitation) is a useful tool to compare dissolved nutrient ratios and nutrient limitations to productivity in different parts of the bay. Except for the areas proximate to stream mouths, DIN to dissolved inorganic phosphorus (DIP) ratios (DIN:DIP) in southern Kāneʻohe Bay are well below the Redfield ratio of 16:1 required for phytoplankton growth. Assuming that N-fixation rates are negligible, this suggests that N is probably the primary limiting nutrient during normal baseline conditions. The DIN and DIP ratios in surface water from different bay sites during the first day of runoff events are generally substantially greater than the Redfield N:P ratio 16:1. This indicates that runoff nutrients are generally characterized by an excess of N relative to P (Figure 22). On the contrary, at the peak of the bloom events PO_4^{3-} is often exhausted while there is still sufficient DIN remaining in the surface waters to support production, suggesting a switch to P-limitation of bioproductivity.

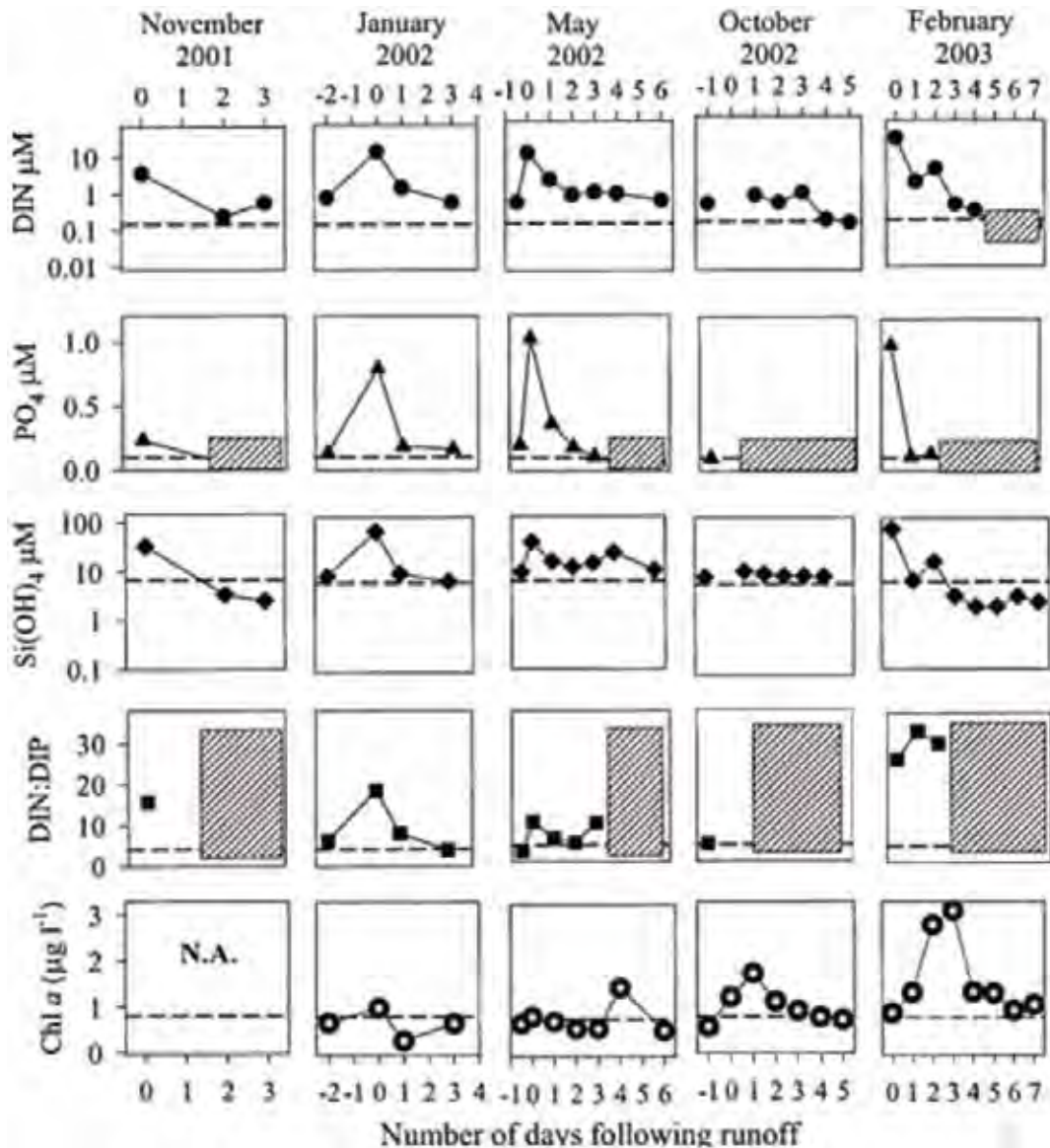


Figure 22. Evolution of DIN:PO₄³⁻ ratios, silicate, PO₄, DIN, and chlorophyll-*a* (Chl-*a*) concentrations in Kāneʻohe Bay during five storm events. For each event and property measurement, there is generally a change in value (either increase or decrease) after the first day of runoff, which is then followed in the next few days by a nutrient draw-down and a return to baseline values. The hatched boxes indicate concentrations below instrumental detection limits. Notice the excess N to P ratios (DIN:PO₄³⁻) after storms relative to the Redfield value of 16:1. Spikes in Chl-*a* correspond to increased primary productivity by phytoplankton.²⁵

One explanation for the sustained enhanced N concentrations in the Kāneʻohe Bay surface waters is the presence of lateritic soils in the suspended stream borne particle inputs to the bay. Lateritic soils (i.e., red soil characteristic of tropical rainforests containing a high percentage of aluminum (Al) and iron (Fe) hydroxides that may form an impermeable and infertile layer hindering plant growth) in Hawaiʻi contain high concentrations of Fe and Al oxyhydroxides and abundant clay minerals, and have a relatively high pH of zero net surface charge. This characteristic allows these soils to retain N (as NO_3^-) through electrostatic attractions with positive residual surface charges at typical Hawaiʻi soil pHs (as well as PO_4^{3-} through specific interactions). Over extended periods, some NO_3^- may penetrate the soils and enrich the shallow groundwater, especially if and when surface soils become water saturated. Surface soils eroded and carried into streams by storm runoff subsequently enter saline waters of higher pH and ionic strength. At this point, their surface charge reverses quickly leading to a rapid release of NO_3^- . Under these conditions, however, PO_4^{3-} release is much slower than NO_3^- . With consecutive storm events, freshwater runoff can have both different intensities and concentrations of nutrients. The differences are due to the duration of time between events, the origin of the suspended particles (urban, agricultural, fertilizers, or natural) and the amount of deeper-seated and older NO_3^- and SiO_2 enriched groundwater accumulated during dry summers.

2001-2003 Conclusions

- Under baseflow conditions, the primary production of the bay is N limited.
- After storm events, there can be a depletion of P relative to DIN in surface waters and the system switches to being P limited before returning to the baseline condition of N limitation.
- After initial storm pulses, a subsequent decrease in the concentrations of nutrients in the plumes is attributed to a combination of two effects: (1) dilution as the storm plume mixes into the water column, and (2) uptake of nutrients by phytoplankton.
- Chlorophyll concentrations peak a few days after a storm as particles settle and light levels increase in the water column allowing enhanced photosynthetic activity.

- Groundwater inputs containing elevated concentrations of nutrients such as nitrate (NO_3^-) and dissolved silica (SiO_2) along the windward coast of Oʻahu have also been observed. It is therefore possible that groundwater seeps occasionally contribute significant amounts of both freshwater and nutrients to the bay.

c. 2003: Storm Runoff Impact on Kāneʻohe Bay Water Quality and Productivity

The purpose of this 2003 research effort was to look simultaneously at the evolution of a rainstorm-derived sediment and nutrient laden freshwater plume in Kāneʻohe Bay and its impact on water quality, productivity, and phytoplankton community structure, and how physical forcing impacts the recovery of the system from storm perturbations. It is a natural extension of the work done in the b. 2001-2003 study. The impact of storms on the water quality properties in Kāneʻohe Bay was evaluated using the Coral Reef Instrumental Monitoring Platform or CRIMP to measure dissolved oxygen (DO), temperature, pH, chlorophyll-*a* (Chl-*a*), salinity, turbidity, solar radiation, and the particle abundance data collected during the storm events of November 29 and December 7, 2003 (Figures 23, 24, and 25). Normal diel (i.e., 24 hour period including a day and an adjoining night) fluctuations in water quality properties are strongly altered during storms. As an illustration, the water temperatures remained relatively constant near 25°C for several days after the December 2003 storm (Figure 23). A gradual return to diel cycles in temperature coincided with the re-establishment of the dominant trade wind pattern about one week after the storm. Dissolved oxygen values, which oscillated around saturation as expected for a well-mixed shallow water body, were depressed during and immediately following the storms (Figure 23). The depression in dissolved oxygen results from an initial decrease in primary productivity associated with low light levels and highly turbid surface waters in the bay immediately after a storm that delivers large amounts of suspended particles to the coastal environment. Similar to DO, a depression of pH is observed with the influx of freshwater (Figure 24). The diel fluctuations in measured chlorophyll-*a* correlate positively with solar radiation, temperature and other chemical parameters affected by photosynthetic activity such as dissolved oxygen and pH (Figures 23 and 24).

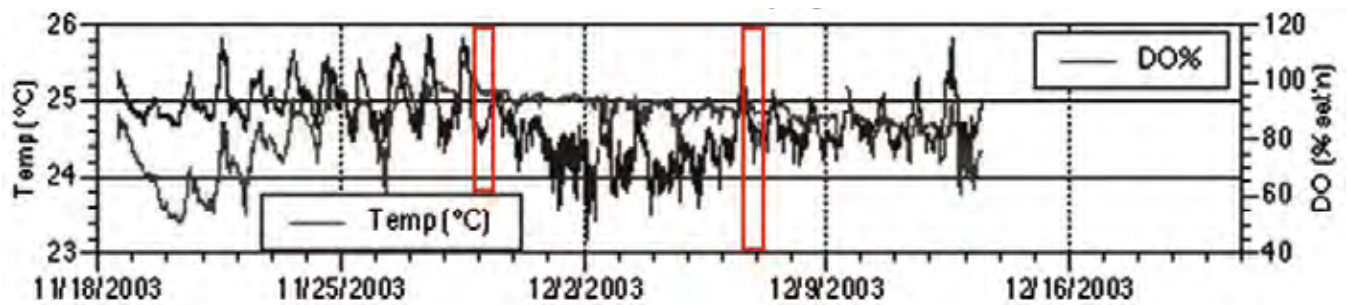


Figure 23. Temperature and dissolved oxygen data collected during the November 29th and December 7th, 2003 storms in Kāneʻohe Bay. Before the first storm, daily oscillations of both dissolved oxygen and temperature are readily apparent. After each storm, the temperature is dampened and the dissolved oxygen drops. The red boxes indicate the days of the storms.²⁶

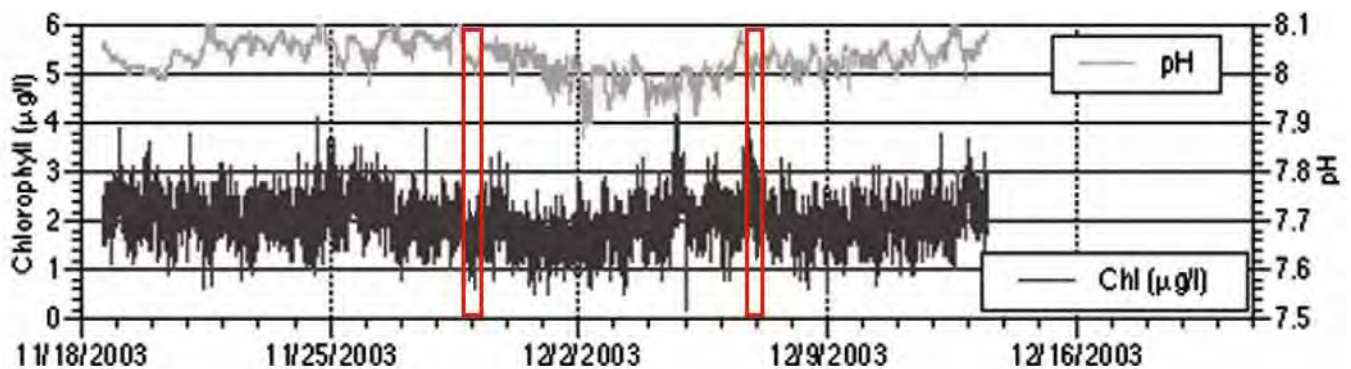


Figure 24. Chlorophyll-*a* and pH during two 2003 storms. The pH drops after both storm events, probably due to freshwater input with a lower pH compared to seawater. The concentrations of chlorophyll-*a* correlate with solar radiation and temperature patterns (not shown). The red boxes indicate the days of the November 29th and December 7th storms.²⁷

The salinity of bay waters at a depth of two meters is close to 35 ppt during non-storm periods. A drop of salinity at that depth observed during rain events is due to the input of freshwater from the land and the passage of the freshwater plume over the sampling site (Figure 25). It is not unusual for the subsurface salinity to remain near 34 ppt for about a week after a storm with some sharp, but short-duration, daily decreases. The sharp salinity decreases seen in Figure 25 coincide with low tides and are superimposed on a general trend of

increasing salinity as the freshwater plume is mixed into the high salinity water column. As seen in Figure 25, coastal areas experience an increased mass per unit volume of particulate matter in the water column after storm events. These particles increase water turbidity, which in turn reduces light penetration through the water column. The reduction in light penetration decreases both water column and benthic primary productivity. This is an important point to keep in mind in our further discussion of how the bay reacted to these two storm events.

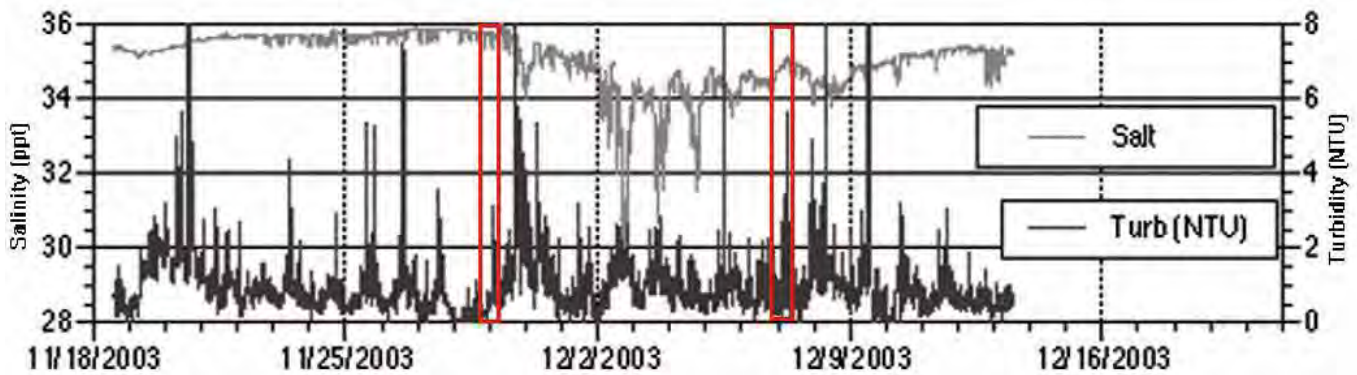


Figure 25. Salinity and turbidity in Kāne‘ohe Bay during the two storms in the winter of 2003. There is a sharp decrease in salinity after the first storm on November 29th. There is also a salinity decrease following the December 7th event. The turbidity data show increases after each storm indicating increased suspended particulate matter derived from runoff within the water column. The red boxes indicate the days of the storms.²⁸

Storm inputs of dissolved and particulate nutrients have significant effects on nearshore ecosystems. As mentioned previously, the storm inputs (e.g., via runoff waters) of dissolved reactive N and P have proportions close to or higher than the N:P ratio of marine phytoplankton. The C:N:P ratio of marine phytoplankton, also termed the “Redfield ratio”, is 106 C : 16 N : 1 P. Thus, if the N and P input is higher than the Redfield ratio, the nutrient inputs may support ‘new’ phytoplankton production. For new production to occur, two things must happen. First, the nutrients derived from the freshwater runoff must remain in the coastal water and not be quickly advected away before production can take place. Second, the mixed nutrient-rich freshwater and seawater must have a resulting salinity that is tolerable for marine organisms. With strong winds, waves and tidal forcing, however, the surface storm-water inputs are generally mixed rapidly and diluted and subsequently exported. Thus a large fraction of the dissolved nutrient load can leave the coastal environment before new production can occur.

Along with DO, temperature, pH, Chl-*a*, salinity, turbidity, solar radiation, and the particle abundance data previously mentioned (Figures 23, 24, and 25), the following parameters were measured during the 2003 storm events from three bay water sampling sites: silica, nitrate and nitrite, ammonium, and phosphate (Figure 26). The storm on November 29th delivered large amounts of freshwater with new nutrients to southern Kāne‘ohe Bay. Surface

bay water concentrations of nutrients subsequently increased. Interestingly, the concentrations did not increase as much in surface waters as those following the second storm on December 7th. Nitrogen was added as dissolved nitrate and nitrite. Concentrations of nitrate, nitrite, and silica peaked on December 4th when salinity was lowest. After which, nitrate and silica concentrations declined rapidly. Ammonium increased steadily after nitrate and silica began declining. Concentrations of soluble reactive phosphorus peaked two days, December 1st, after the first storm and declined sharply until a slight rebound during the period from December 5th to December 10th after which there was a slow decline. The previous discussion (section b. 2001-2003) found that the coastal system production was phosphorus limited during storm events due to the large amount of nitrogen input into the system. However, in the case of the later 2003 study, phosphorus never became the limiting nutrient because it is likely that phosphorus was being slowly released from storm-delivered soil particles suspended in the water column. This finding does not necessarily contradict the results of the previous study, but rather demonstrates how the duration between storm events is an important factor in determining the viability of a post-runoff phytoplankton bloom. In this case, the interval between storms was very short (~8 days) and from the nutrient and chlorophyll data (Figure 26), we observed that there was no large second phytoplankton bloom after the second storm event.

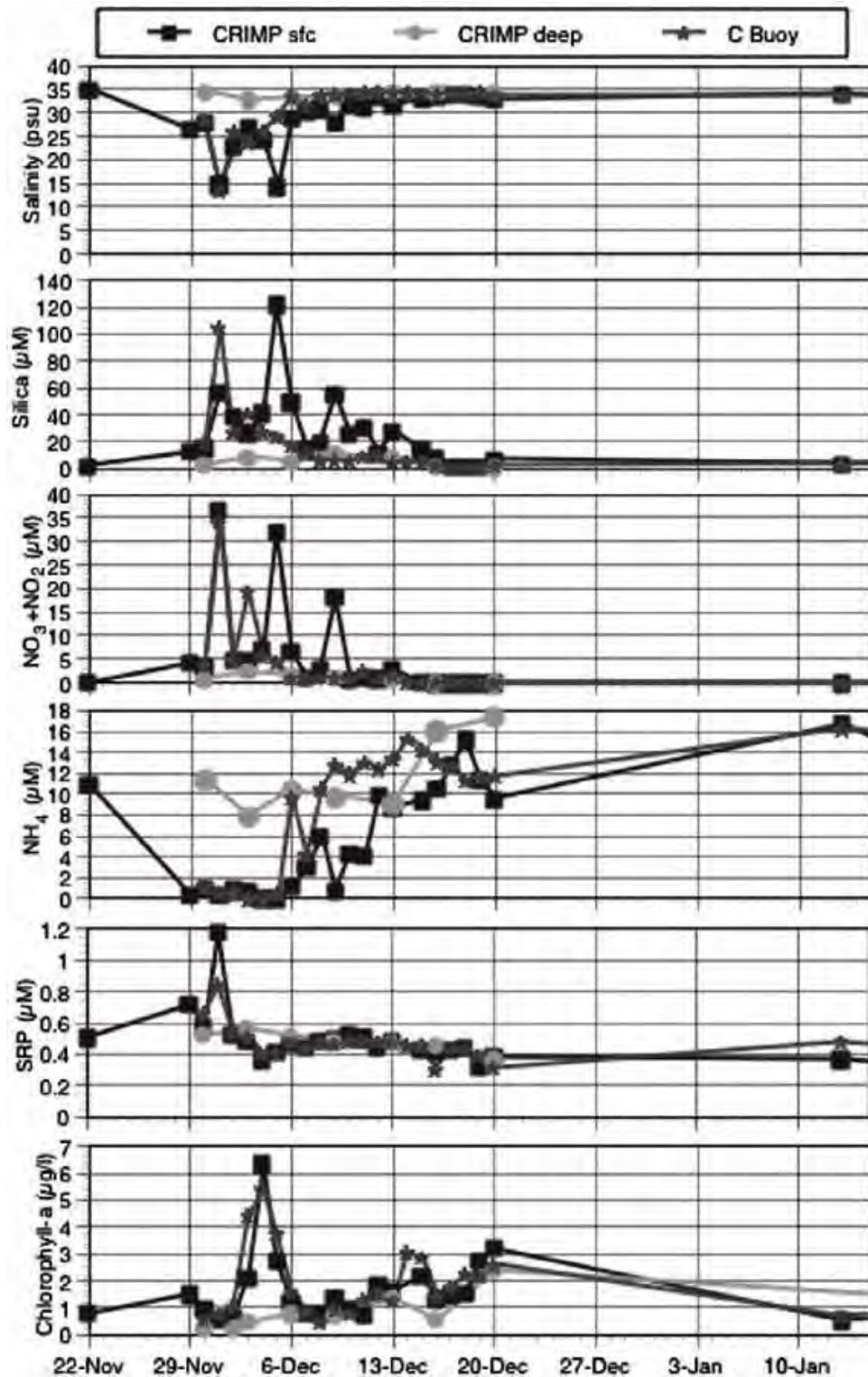


Figure 26. Concentrations of inorganic nutrients in synoptic samples collected manually during the 2003 study period. SRP is soluble reactive phosphorus assumed to be phosphate, PO_4^{3-} . NO_3^- is nitrate and NO_2^- is nitrite. NH_4^+ is ammonium. $\text{CRIMP}_{\text{srf}}$ and C_{bouy} are samples taken from a depth of 10cm. $\text{CRIMP}_{\text{deep}}$ are samples taken from 2m depth. Note no large second peak in chlorophyll-*a*.²⁹

The 2003 study also investigated both the phytoplankton and zooplankton community responses to the storm inputs. There was an observed succession in both phytoplankton and zooplankton communities in southern Kāneʻohe Bay in response to nutrient inputs from storm runoff. With respect to monitoring the evolution of the phytoplankton community response to the storm inputs, concentrations of pigments and chlorophyll were determined from analysis of collected surface water samples (Figure 27). A significant increase in chlorophyll-*a* concentrations was seen during the four days after the first storm. The chlorophyll-*a* concentration then declined rapidly over the following two days, but then there was a secondary peak between December 14 and 15th. Peridinin, an accessory pigment of dinoflagellates, exhibited a significant increase occurring on December 2nd indicating a rapid dinoflagellate response two days after the first storm. This increase in peridinin was followed by an increase in the pigment prasinoxanthin, the main pigment of prasinophytes, which occurred several days

later suggesting that small, autotrophic flagellates bloomed immediately after the dinoflagellates. The concentration of the pigment fucoxanthin, indicative of diatoms, increased steadily during the study period. Although zeaxanthin pigment concentrations, an indicator of photosynthetic bacteria, were low with little variability following the storm, the decreasing zeaxanthin concentrations at the end of the study period reflect a gradual decrease in photosynthetic bacteria. The abundant, sub-micron sized *Synechococcus* spp. in Kāneʻohe Bay, however, may be underrepresented in samples from the 2003 storms because of the relatively large pore size of the filters used for sampling. The steady increase in the relative concentrations of fucoxanthin suggests that diatoms dominated the phytoplankton community towards the end of the two-week study period. The primary zooplankton community response to that of the phytoplankton community was an initial, rapid (within 1 day) six-fold increase in the biomass of appendicularians. Appendicularians are capable of relatively high grazing rates and were primarily responsible (with minor contributions from various copepods) for the reduction and control of the initial, storm-induced phytoplankton community bloom. In response, increased predation on both appendicularians and copepods by other zooplankton (e.g., chaetognaths, hydromedusae, and meroplankton) relaxed zooplankton grazing pressure on the phytoplankton community enough to allow for a secondary peak in phytoplankton population. This phytoplankton community succession was similar in some respects to the February 2003 storm event from b. 2001-2003 study. The February 2003 storm event was dominated by a phytoplankton bloom of diatoms with a magnitude seven times higher than their baseline concentrations, but the cyanobacteria population showed a small decrease. Both the b. 2001-2003 and the c. 2003 studies exemplify the relatively rapid succession of phytoplankton to stimulation by the input of nutrients from runoff and how changing nitrogen and phosphorus ratios during storm events can cause shifts in the community structure.

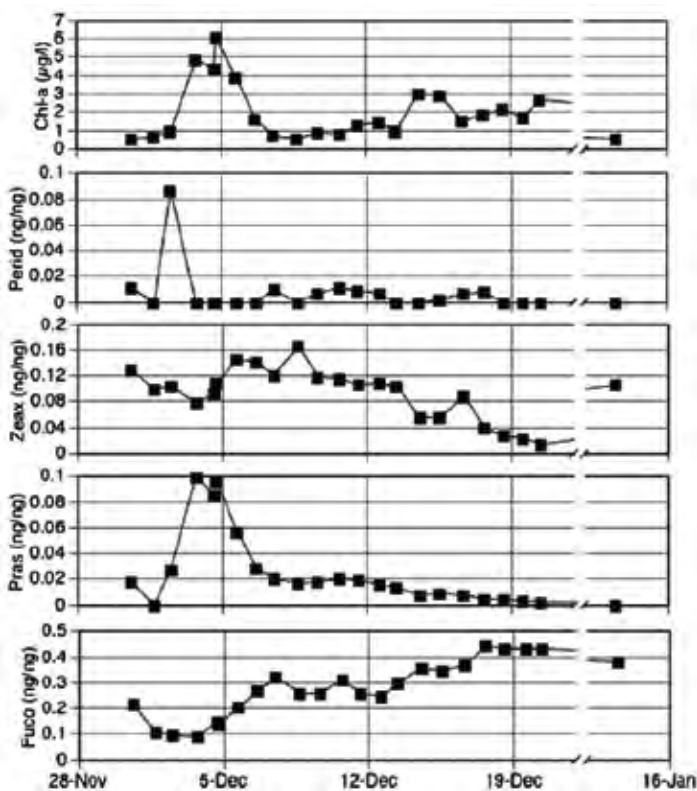


Figure 27. Concentrations of chlorophyll (Chl-*a*) and pigments (Fuco = fucoxanthin; Pras = prasinoxanthin; Perid = peridinin) from Kāneʻohe Bay water samples.³⁰

Before summarizing the conclusions of the 2003 study, a comment on the linkage between storm events and the residence time of water in Kāneʻohe Bay is relevant to our discussion. The flushing rate or residence time is the average time a parcel of water spends in the bay (residence time = total volume / input or output rate). The normal flushing rate or residence time of south Kāneʻohe Bay is between 13 to 18 days. With the increased runoff during storm events, however, the input rate increases and the flushing rate or residence time of the bay decreases to 3 to 8 days. In addition to storm events, the flushing rate is impacted by factors such as wind speed and direction, and tidal range. Although storm inputs can have significant short-term effects on the ecosystem and biogeochemistry of the bay, storm events tend to be short-lived, and various forcings can cause baseline conditions to return within a few days. Because in general the surface flow velocity during storm events is greater than the water circulation below 3 meters of depth in the bay, the buoyant freshwater runoff can be rapidly advected offshore. How long this process takes, however, depends on various factors.

In the case of the November and December 2003 storm events, conditions were relatively calm after the storm. This prevented thorough mixing of the turbid freshwater plume with bay water resulting in low light penetration throughout the water column. In addition, there was low insolation (light levels) since the days after the storm were cloudy. Light is a limiting factor to primary productivity and low light levels can temper the bloom response even if all other conditions are favorable. Finally, the second storm was in close temporal proximity to the first storm and it appears that the runoff nutrient load was also less compared to the successive storms of the b. 2001-2003 study. All of these factors probably resulted in the slightly different productivity bloom timing and behavior between the November and December 2003 storm events and the b. 2001-2003 study. In addition, other forcing factors, such as variations in wind speed and direction, have also been shown to be more important in affecting freshwater residence times and thus the productivity potential of storm water plumes in the southern portion of Kāneʻohe Bay.

2003 Conclusions

- The duration of intervals between storms impacts the nutrient load delivered to the bay.

- Despite high N loading, not all storm events result in phosphorus-limited bay production due to the *in-situ* release of phosphorus from storm-runoff generated particles suspended in the water column.
- Cloud cover and wind speed can strongly influence the productivity bloom response of the bay to storm events.
- Changes in nutrient ratios (nitrogen and phosphorus) can cause major shifts in the community structure.
- The November and December 2003 storm events have a similar behavior to the b. 2001-2003 events, but demonstrate some differences due to variability in the physical forcings (e.g., light cover, mixing times, wind speeds, etc.) on the bay.

d. 2003-2004: Baseflow and Storm Events Impact on Kāneʻohe Bay Air-Sea CO₂ Exchange

We now know that Kāneʻohe Bay is nitrogen limited during baseflow events and often phosphorus limited during storm events. We also know that there is variability between baseflow and storm dissolved and particulate nutrient loads and water inputs and that land-use in the watershed impacts all these variables. What are the implications of this knowledge for air-sea CO₂ exchange between the bay and overlying atmosphere?

Air-sea CO₂ exchange was first studied in Kāneʻohe Bay from September 2003 to September 2004. In order to calculate pCO₂ and air-sea CO₂ exchange, TA and DIC were measured in Kāneʻohe Stream and Kāneʻohe Bay waters. From the DIC and TA data, the dissolved CO₂ concentrations of the waters were calculated. For this period of time, atmospheric CO₂ concentrations were obtained from the measurement of air at Cape Kamakua, Hawaiʻi. Several wind speed parameterizations for gas transfer velocity were then used to calculate the air-sea exchange fluxes of CO₂. A total of about 500 surface water samples at 23 stations throughout Kāneʻohe Bay, within Kāneʻohe Stream, and outside the barrier reef were taken during baseflow and storm event periods. Storm events were defined as a period when the National Weather Service coastal Kāneʻohe rain gauges received at least 5.1 centimeters of rain within 24 hours.

From the weighted averages of parameters of these stations during baseflow conditions, it was shown that the northern, central, and southern bay surface

waters have similar salinities, total alkalinity, and dissolved inorganic carbon (Table 4). The $p\text{CO}_2$ at all locations was greater than atmospheric $p\text{CO}_2$ (average 378 μatm) at the time and the bay waters were oversaturated with respect to the carbonate minerals aragonite and calcite. Stream water was characterized by relatively low values of salinity, total alkalinity, dissolved inorganic carbon, and carbonate saturation state, and high $p\text{CO}_2$ concentrations. Kāneʻohe Stream $p\text{CO}_2$ was much higher than observed in Kāneʻohe Bay. This was likely due, in part, to soil and groundwater influence, as these waters have $p\text{CO}_2$ values that can exceed 3000 μatm in the main Hawaiian Islands. Depletion in $\delta^{13}\text{C}$ of the stream water, relative to seawater, was also observed as a result of respired terrestrial organic matter from soil and groundwater systems connected to Kāneʻohe Stream. High $p\text{CO}_2$ and negative $\delta^{13}\text{C}$ values, however, did not influence the bay water far beyond the stream mouth because the solubility of CO_2 decreases with increasing salinity and the “excess” CO_2 was flushed from the water during baseline conditions (e.g., at higher salinity). Despite all the similarities in the baseflow weighted averages, the inorganic carbon parameters for the bay and stream exhibited large variations over the time period of study. For example, the bay CO_2 concentrations ranged by over 600 μatm while stream water CO_2 ranged by almost 1800 μatm .

The bay surface water $p\text{CO}_2$ is in part a reflection of the balance of respiration/photosynthesis and

calcification/dissolution processes throughout the water column. In the absence of biogeochemical processes, there should be a linear mixing line between streamwater and seawater salinity and other conservative properties. In Kāneʻohe Bay, however, TA is depleted relative to the conservative mixing line because TA is consumed by calcification. This process occurs mostly at higher salinities because calcifying organisms prefer high salinity values closer to open ocean salinity values versus low freshwater salinity values. The TA depletion demonstrates active calcification throughout the year in Kāneʻohe.

Figure 28 shows the CO_2 flux from the three general bay physiographic areas: north, central, and south. Clearly over the study period, the bay is a net source of CO_2 to the atmosphere. There are, however, several short duration intervals where some or all bay sites were sinks for atmospheric CO_2 (i.e., December 2003, March and April 2004). In addition, the primary source of the CO_2 flux from bay waters to the atmosphere was determined to be from calcification. This is a similar air-sea CO_2 exchange behavior as Hilo Bay, which was also demonstrated to be a net source of CO_2 to the atmosphere, but for a different reason. The difference between Hilo and Kāneʻohe Bay is that in Kāneʻohe Bay the CO_2 flux is mainly due to calcification and in Hilo Bay it is mainly due to remineralization of organic matter brought in by the rivers. Following storm events during this study, $p\text{CO}_2$ in bay waters was reduced due to the use of this carbon by phytoplankton blooms stimulated by the

Table 4. Weighted averages of inorganic carbon parameters in Kāneʻohe Bay and stream water during baseflow conditions. Salinity is given in parts per thousand (ppt), total alkalinity (TA) and dissolved inorganic carbon (DIC) in $\mu\text{mol kg}^{-1}$, $p\text{CO}_2$ in μatm , and aragonite (Arag) and calcite (Calc) saturation states as omega values. Note similarities in all parameter values between all three bay locations and differences between those three locations and the stream, stream mouth, and stream perimeter.³¹

Location	Salinity (ppt)	TA ($\mu\text{mol kg}^{-1}$)	DIC ($\mu\text{mol kg}^{-1}$)	$p\text{CO}_2$ (μatm)	Arag (Ω)	Calc (Ω)
Northern Bay	34.3	2170	1920	500	2.8	4.2
Central Bay	34.3	2180	1920	460	2.9	4.4
Southern Bay	34.4	2160	1900	460	2.9	4.4
Outside Reef	34.6	2230	1950	420	3.2	4.9
Stream	3.5	1410	1400	800	0.6	1.0
Stream mouth	20.8	1950	1700	600	1.9	2.9
Stream perimeter	31.6	2110	1860	430	2.8	4.2

excess nutrients delivered by storm runoff. Looking at Figure 28, we can also see that Kāneʻohe Bay is a stronger CO₂ source during what are traditionally drier summer and fall months and a weaker source during wetter winter and spring months. To expand this result with any certainty to the longer-term intervals of drier (El Niño) versus wetter (La Niña) periods for Kāneʻohe Bay requires multiple years of data.

2003-2004 Conclusions

- pCO₂ values for Kāneʻohe Stream (600 to 1300 µatm) and the bay (400 to 500 µatm) during baseline conditions were higher than the mean atmosphere value for the period of study (average 378 µatm).
- During some storm events, the bay became a transient sink for atmospheric CO₂.
- As opposed to Hilo Bay, the flux of CO₂ from Kāneʻohe Bay to the atmosphere was mainly driven by calcification and not *in-situ* organic matter remineralization.
- Elevated pCO₂ values of Kāneʻohe Stream water (compared to the atmosphere) were mainly driven by the input of CO₂-charged soil and groundwaters into streams and the bay from organic matter remineralization on land.
- Overall, Kāneʻohe Bay appears to be a stronger CO₂ source to the atmosphere during summer and

fall months (drier) and a weaker source during winter and spring months (wetter). To extrapolate this conclusion to longer-term rainfall and climate variations [e.g., El Niño (dry) vs. La Niña (wet)] periods requires multiple years of interannual data.

e. 2005-2007: Climate Variability, Interannual, and Short-term Event Impacts on Kāneʻohe Bay Air-Sea CO₂ Exchange

In conjunction with the two previously mentioned studies dealing with nutrient impacts on Kāneʻohe Bay productivity, measurements made during a La Niña event (2005-2006) were used to examine the ecosystem's air-sea CO₂ exchange response. La Niña events have the potential to increase precipitation by 50 to 200 mm and decrease SST in Hawaiian waters. Three major storm periods in December 2005, February-March 2006, and November 2006 were observed. The February-March 2006 storm period was especially noteworthy lasting 40 days. In March 2006, the total rainfall exceeded all historical monthly totals from the Kāneʻohe Mauka Station since 1950 (77 cm). The total annual rainfall from Dec. 2005 to Nov. 2006 was 149.8 cm at HIMB and 298.8 cm at Luluku station, which is much higher than the historical averages at either site (80.0 and 187.2 cm, respectively).

How did the increase of precipitation for these three storm event periods affect the bay biogeochemical

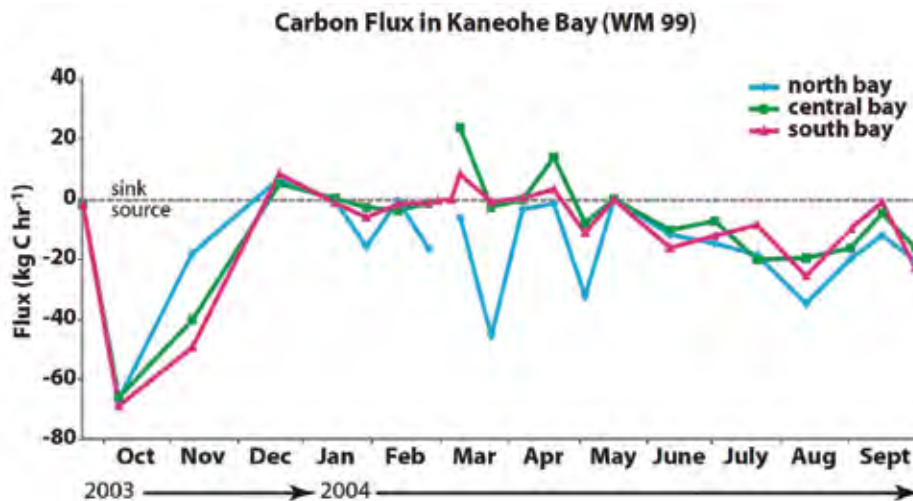


Figure 28. Flux of carbon dioxide (units of kg C hr⁻¹) in Kāneʻohe Bay from September 2003 through September 2004 for the northern (blue), central (green), and south (pink) bay sites. Positive flux values (above the dashed horizontal line) represent flux of carbon dioxide from the atmosphere to the water. Negative numbers (below the dashed horizontal line) represent flux of CO₂ from the water to the atmosphere.³²

and physical properties and ecosystem? High nutrient concentrations at the Kāne‘ohe Stream mouth during storm events reflect the large input of nutrients derived from elevated river discharge. Plankton blooms occurred after each of the three major storm events due to the increased delivery of nutrients. Low nutrient concentrations were measured at the CRIMP-CO₂ buoy in the southern portion of the bay indicating rapid uptake of storm runoff nutrients. Salinity stratification of near-surface water developed due to the fresh water plume created in Kāne‘ohe Bay by the storm runoff. In one particular case, the plume lowered salinity from 34 ppt (baseline value) to 17 ppt at the buoy location in the bay. Such low salinities can have direct effects on the biological community in the southern portion of the bay, possibly reducing metabolic rates.

Three large drawdowns of surface water pCO₂ occurred at the buoy following the onset of each of the three major storm events. In each case, the drawdown of seawater pCO₂ was such that the partial

pressure of CO₂ in seawater temporarily fell below that of the atmosphere and the air-sea CO₂ flux direction changed and made the southern sector of the bay act as a temporary sink for atmospheric CO₂ (Figures 29 and 30). During these storm events, the seawater temperature and also salinity decreased, which increased the solubility of CO₂ in seawater and facilitated the uptake and retention of CO₂ from the atmosphere (Figures 30 and 31).

A diel cycle of CO₂ gas concentration was observed at the buoy site with a median diel variability of 34.3 μatm. Seasonal variability in average (baseline) seawater pCO₂ was approximately 112 μatm, with the maximum seawater pCO₂ observed during September 2006 and the minimum during February 2006. During baseline conditions, surface seawater pCO₂ at the buoy site is high relative to air pCO₂, and its variations follow the seasonal temperature changes. In contrast, oxygen concentrations are in the opposite direction of the CO₂ concentrations.

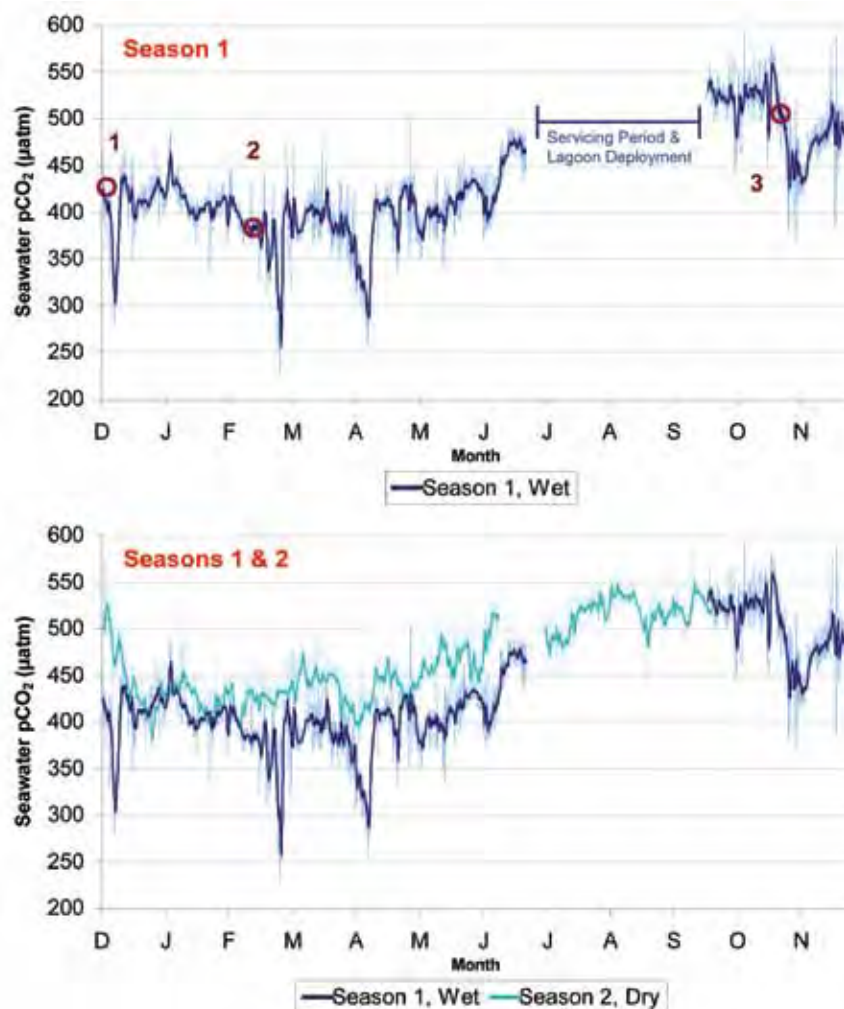


Figure 29. Seawater pCO₂ (μatm) at the CRIMP-CO₂ buoy during the winter of 2005-2006 with circles indicating the onset of each of the three major storm events (top); and during the winter of 2005-06 and 2006-07 (bottom). Note that all three major storms occurred during 2005-2006.³³

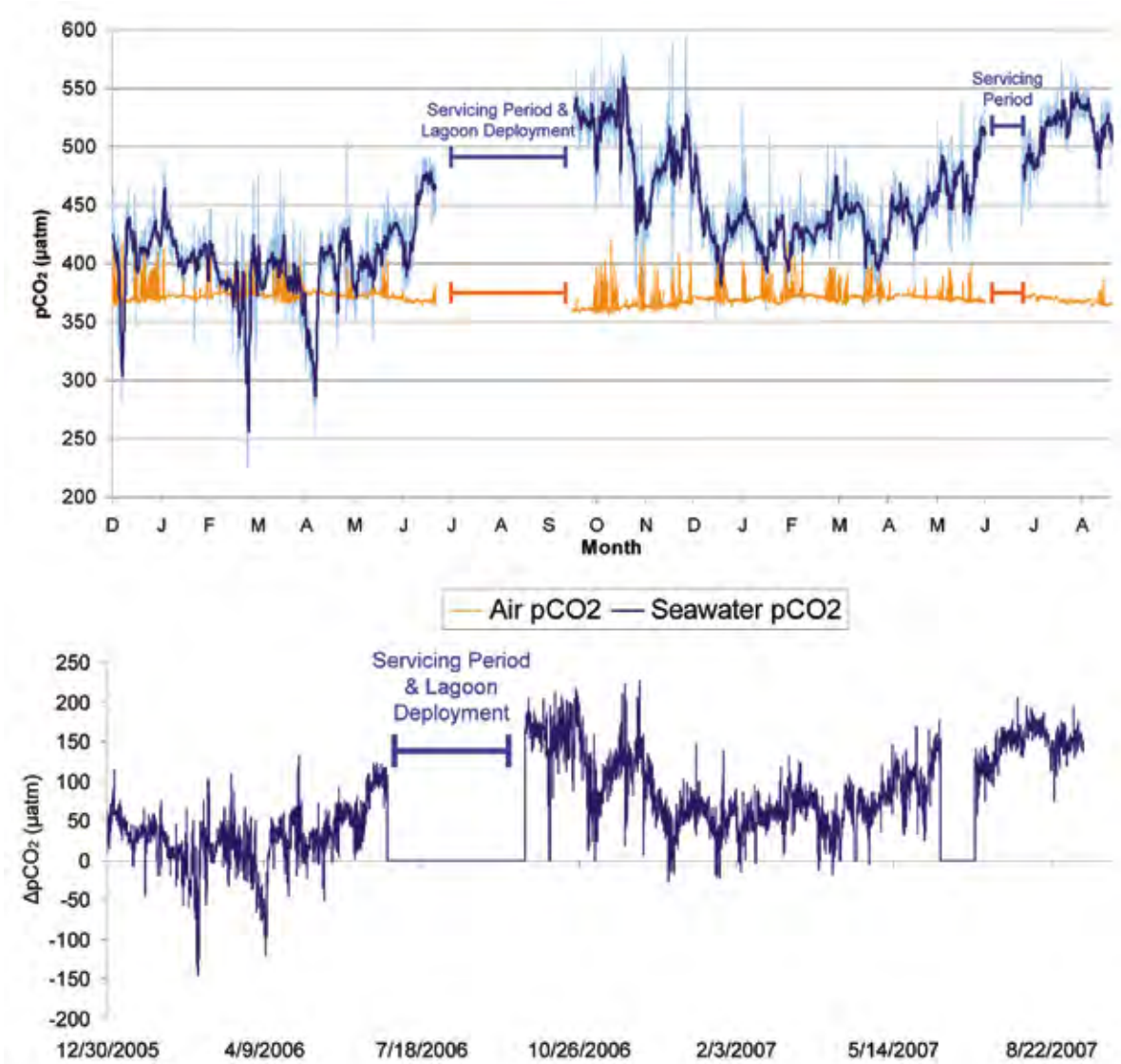


Figure 30. Time series (2005 to 2007) of air pCO₂ (µatm-orange) and seawater pCO₂ (µatm-blue) (top) and of ΔpCO₂ (µatm) throughout the study period. Positive values indicate that the bay is acting as a source of CO₂ to the atmosphere, while negative values indicate a sink behavior (bottom).³⁴

Storm events had important impacts on air and surface water pCO₂ and pO₂ concentrations. Average atmospheric pCO₂ during baseline conditions was 383.4 ± 6 µatm, with a range of 370.8 to 438.1 µatm. Wind speed and direction also influence the air-sea exchange as the atmospheric pCO₂ increased by 59.7 µatm with Kona winds that move over land, with a diel variability reaching 60.6 µatm. The data also showed that atmospheric pCO₂ was higher during slow southerly winds, which allowed accumulation of more forest-derived and anthropogenic CO₂ in the air moving over land than during higher velocity tradewinds. Below a wind speed of 2 m s⁻¹ the increase in air pCO₂ is approximately linear with

increasing wind speed. At higher wind speeds, air pCO₂ levels off near marine air averages.

As observed with dissolved CO₂, dissolved O₂ concentrations followed a diel cycle (Figure 32) with a median diel range of seawater pO₂ at the buoy site of 0.227 atm (26.7 µM). The range of baseline dissolved O₂ was 0.194 to 0.219 atm (199.2 to 230.8 µM) and tended to increase during storm periods (Figure 32). Seawater pO₂ variability is correlated with photosynthetically active radiation (PAR), as well as tidal height, depth averaged current, the EW current component, and seawater temperature.

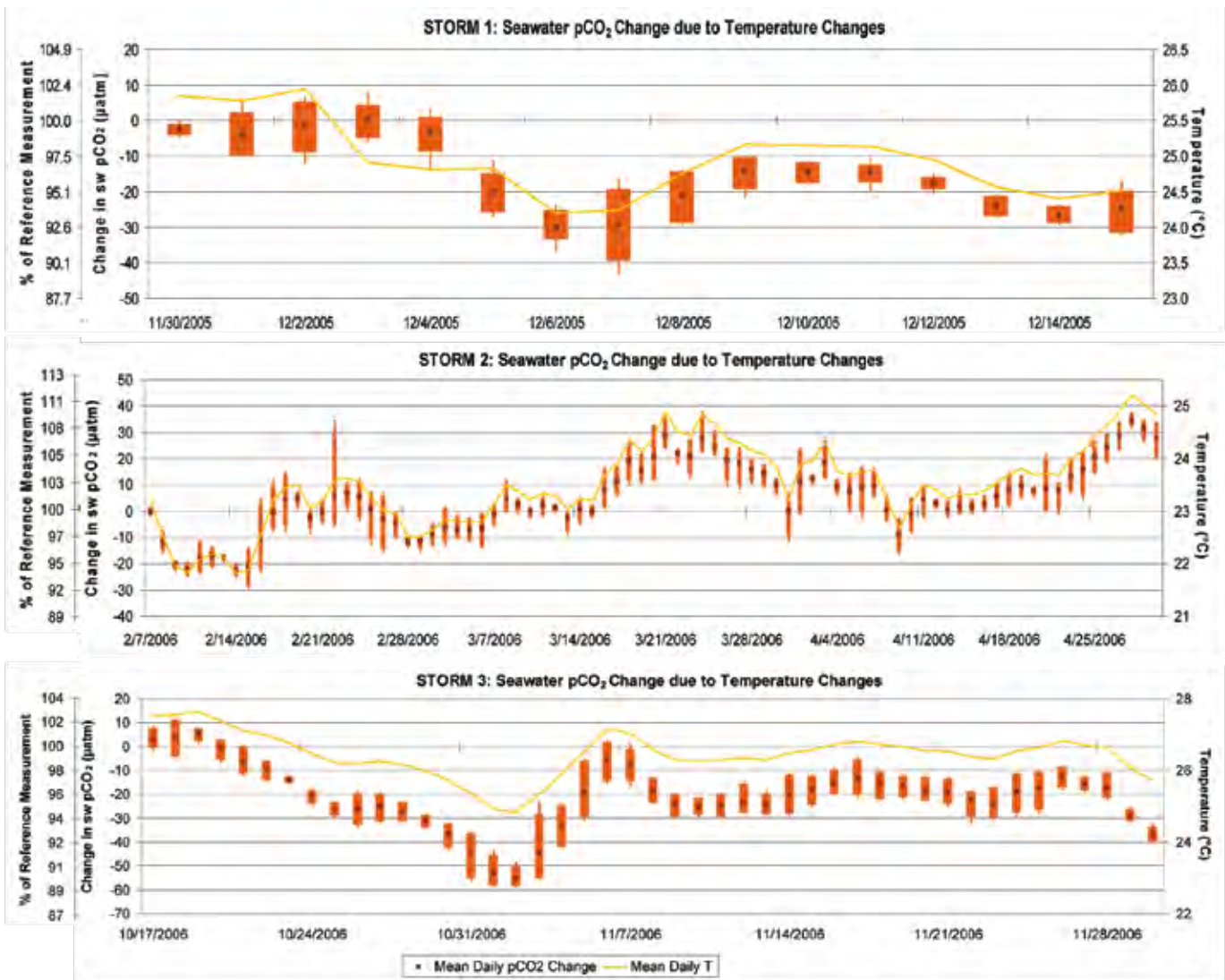


Figure 31. The relative effects of temperature variability on seawater pCO₂ (µatm) in the bay before, during, and after storm periods 1 (top panel), 2 (middle panel) and 3 (bottom panel) in µatm from the reference measurement and in % of reference pCO₂. Orange bars indicate the daily range of values, the darker orange squares indicate the daily median value, and the error bars represent the daily standard deviation from the mean.³⁵

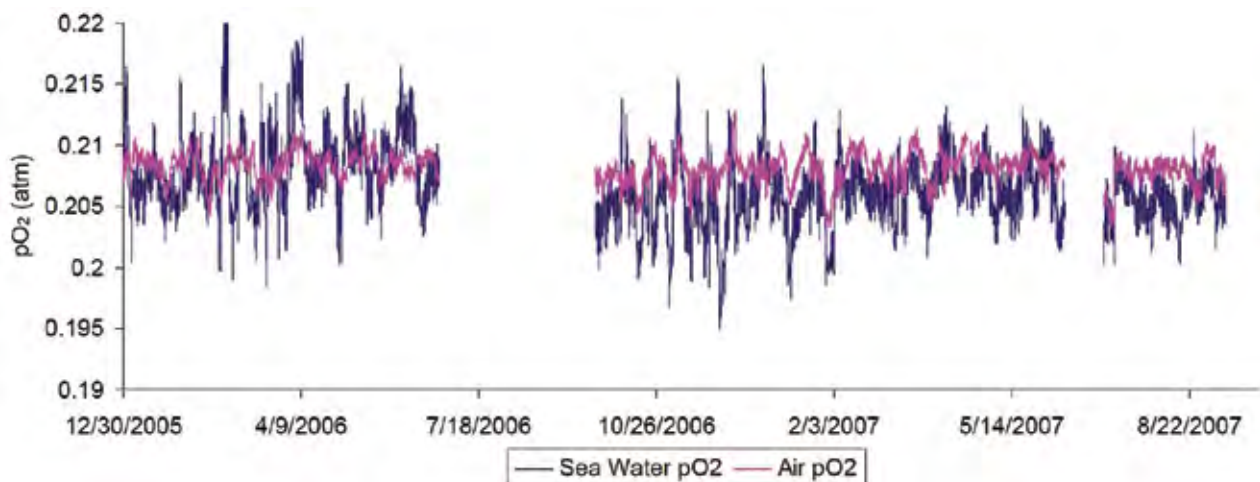


Figure 32. Time series of air and seawater pO₂ (µatm) throughout the three storm time periods.³⁶

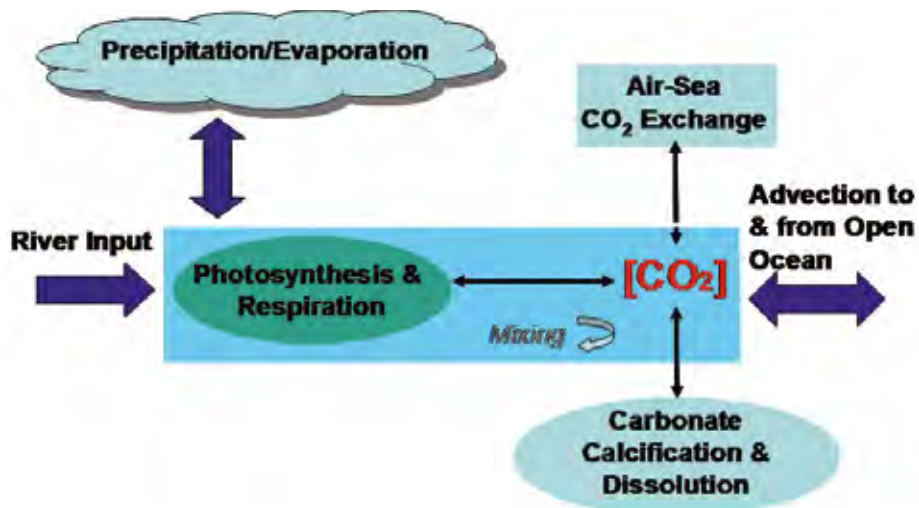


Figure 33. Conceptual diagram of processes affecting seawater CO_2 concentrations in Kāneʻohe Bay.³⁷

In addition, the processes that affect seawater pCO_2 also include the advection and diffusion of water masses of varying CO_2 concentrations, precipitation and dissolution of calcium carbonate, either by biological or abiotic processes, photosynthesis and respiration of organic matter, isochemical temperature changes, expansion, and contraction of CO_2 in seawater, evaporation and precipitation (i.e., loss or gain of water) and air-sea CO_2 exchange. The latter also includes the effects of temperature and salinity changes on CO_2 solubility (Figure 33).

During the three storm periods, the area-specific net annual air-sea CO_2 flux was inversely correlated with annual rainfall totals at both the Hawaiʻi Institute for Marine Biology (HIMB), located on Coconut Island in Kāneʻohe Bay, and the Lulukū (watershed) rain gauge locations. Because these relationships are based on only three years of data (three data points), they are insufficient to estimate the relative magnitudes of net annual flux as a function of rainfall. The existence of such a relationship nonetheless demonstrates that storm events (frequency, duration, and/or intensity, all of which affect annual rainfall totals) can influence net annual air-sea CO_2 flux in nearshore areas. The inverse correlation indicates that rainfall decreases the CO_2 source strength of the bay (i.e., net annual flux of CO_2 from bay water to atmosphere is less). This rainfall effect occurs through storm enhanced river and land runoff into the bay, causing nutrient loading and stimulating production.

On seasonal timescales, temperature variability is the primary factor controlling the intermediate time scale

variability of seawater pCO_2 . Calcification, however, may be the dominant process that maintains the high CO_2 content of surface waters in the southern portion of Kāneʻohe Bay, and hence drives the net annual flux of CO_2 to the atmosphere. On shorter timescales (i.e., days to weeks), local climatic variability (including variations in rainfall, winds, and river discharge) causes changes in bay water properties, which alter the major controls on seawater pCO_2 and consequently the air-sea flux of this gas.

Increased precipitation (rain) dilutes total alkalinity and dissolved inorganic carbon in surface waters decreasing pCO_2 . Rainfall also enhances land and river runoff which, in turn, depends on the season in which the rain occurs, the prior saturation of the soils, and the location of the rainfall. Rapid increases of sediment and nutrient inputs to bay waters observed during heavy precipitation are correlated with enhanced turbidity and subsequently cause increases in chlorophyll concentrations. The last important effect of increased precipitation is to cause turbulence and bubbles on surface waters, mediating air-sea CO_2 transfer. Results indicate that of these effects, the most important processes controlling surface water pCO_2 during storm periods are biological productivity and mixing.

Rainfall can have differing effects on coastal seawater depending on location. The first is when rain falls over land and results in increased runoff with nutrients, suspended sediments, and low salinity water input into coastal seawater. The second is when precipitation occurs directly over the seawater surface. The effect of this localized precipitation (and evaporation) is to

dilute (or concentrate) surface water total alkalinity and dissolved inorganic carbon. Peak changes in mean daily seawater $p\text{CO}_2$ due to water flux were $<23 \mu\text{atm}$ for all three major storm periods.

Instantaneous rain-mediated air-sea CO_2 flux at the buoy was found to vary between -0.27 and $0.08 \text{ mmol C m}^{-2} \text{ hr}^{-1}$. Net annual air-sea CO_2 flux due directly to rainfall was found to be $-0.039 \text{ mol C m}^{-2} \text{ yr}^{-1}$ for the wet winter of 2005-2006 and $-0.074 \text{ mol C m}^{-2} \text{ yr}^{-1}$ for the relatively dry winter of 2006-2007. This represents 3.12 and 3.27% of the net annual flux estimates for the two winter seasons, respectively, based on wind speed parameterizations. During rainfall, however, the direct short-term effect of rain hitting the sea surface can account for up to more than 120 times (mean of 2.5 times) the air-sea CO_2 exchange rate calculated using wind speed parameterizations. Hence, during storm events with moderate winds, the rain-mediated air-sea CO_2 flux can be relatively large.

In summary, the major processes that affect seawater $p\text{CO}_2$ in Kāneʻohe Bay include the advection and diffusion of water masses of varying CO_2 concentrations, precipitation and dissolution of calcium carbonate, either by biological or abiotic processes, photosynthesis and respiration of organic

matter, isochemical temperature changes, expansion and contraction of CO_2 in seawater, evaporation and precipitation (i.e., loss or gain of water) and air-sea CO_2 exchange. The latter also includes the effects of temperature and salinity changes on CO_2 solubility (Figure 33).

Finally, using CO_2 -carbonic acid system parameters gathered during this study, it was determined that the bay surface water was oversaturated with respect to the carbonate minerals aragonite and calcite. In contrast, saturation state calculations for metastable carbonate mineral phases indicated that surface waters were undersaturated with respect to some high magnesian-calcite compositions. This is important as many calcifying organisms (e.g., coralline algae, echinoids, benthic forams) produce biostructures that contain a relatively high concentration of magnesium (e.g., 10 to 30% mol MgCO_3). Ocean acidification will likely increase the dissolution rates of these high magnesian-calcites (See Box 3 for a review of an experimental and observation study done on the effects of CO_2 and ocean acidification on Kāneʻohe Bay calcifying organisms). Kāneʻohe Bay, at some time in the future, is expected to act as a net annual sink for atmospheric CO_2 , as atmospheric CO_2 continuously increases, possibly doubling within this century.

Box 3

Box 3 Effects of CO_2 on calcifying organisms in Kāneʻohe Bay

We can ask how the rise in atmospheric CO_2 will impact Kāneʻohe Bay calcifying organisms. To begin answering this question, researchers at the University of Hawaiʻi's Hawaiʻi Institute of Marine Biology (HIMB) and School of Ocean and Earth Science and Technology (SOEST) studied the consequences of lowering the carbonate saturation state on calcifying organisms in Kāneʻohe Bay by looking at the recruitment rate and growth of crustose coralline algae in elevated CO_2 mesocosms. In order to simulate natural diurnal cycles in solar radiation, temperature and seawater chemistry of a tropical reef flat, flow-through outdoor mesocosms were designed. The recruitment rate and percentage cover of crustose coralline algae in cylinders of elevated $p\text{CO}_2$ ($765 \mu\text{atm}$) mesocosms were significantly lower than those in control mesocosms with present day $p\text{CO}_2$ ($387 \mu\text{atm}$). In other words, the crustose coralline algae struggled under elevated $p\text{CO}_2$ conditions. Furthermore, mean percentage cover by non-calcifying algae (a mixed assemblage of macroalgae, diatoms and small filamentous algae) was statistically higher on cylinders with elevated $p\text{CO}_2$ compared with control mesocosms (Figure 34). Under elevated $p\text{CO}_2$ conditions, the recruitment rate of crustose coralline algae and percentage cover decreased by 78% and 92%, respectively, whereas non-calcifying algae increased by 52% relative to controls. These results indicate that elevated $p\text{CO}_2$ aided growth of non-calcifying algae, but inhibited both recruitment and growth of crustose coralline algae.

A decrease in the rate of crustose coralline growth must reflect either inhibition of the growth or the calcification processes. However, the cellular and molecular mechanisms of calcification in these organisms

Box 3

remain poorly understood. Under tropical and subtropical seawater conditions, the calcification process for coralline algae involves depositing magnesium (Mg)-calcite minerals that contain a significant amount of MgCO_3 (magnesium carbonate) usually expressed in terms of mol % MgCO_3 . In this study there was no significant difference in the composition of the crustose coralline algae (i.e., 13.6 ± 0.4 mol% MgCO_3 in both control and treatment mesocosms tanks) growing in elevated pCO_2 and the control samples, but in an earlier study such a difference was noted. These observations with calcifying algae may be extended to other marine calcifying species. With rising atmospheric CO_2 and thus increasing dissolved CO_2 in the ocean, calcifying species will likely display lower recruitment and growth rates, which will then allow non-calcifying species to proliferate.



Figure 34. Photograph of encrusting algal communities on experimental cylinders from a control (left) and a treatment (right) mesocosm. Note how non-calcifying organisms (green color) in the treatment mesocosms have overwhelmed the previously abundant calcifying crustose coralline algae (pinkish color) which still dominate the control cylinder on the left.³⁸

2005-2007 Conclusions

- Kāneʻohe Bay is a net annual source of CO_2 to the atmosphere ($-0.046 \text{ Gmol C yr}^{-1}$ or $-0.55 \text{ G grams C yr}^{-1}$) just as Hilo Bay is a source.
- The high pCO_2 values in bay waters are mainly due to calcification within the bay and respiration of terrestrial organic matter. This is in contrast to Hilo Bay which is primarily heterotrophic due to respiration of terrestrial organic matter.
- Kāneʻohe Bay typically acts as a strong source of CO_2 to the atmosphere during summer and fall (dry periods) and is a weaker source (wet periods) in winter and spring with wetter and drier years amplifying these seasonal effects.
- Runoff inputs to the bay depend on the season in which the rain occurs, the prior saturation of the soils, and the location of the rainfall.
- On seasonal time scales, temperature variability is the primary factor controlling the intermediate time scale variability of seawater pCO_2 in southern Kāneʻohe Bay.
- Calcification is the dominant process that maintains the high CO_2 content of surface waters in the southern portion of Kāneʻohe Bay, and hence drives the net annual flux of CO_2 from surface waters to the atmosphere.

f. 2005-2008. Comparing Air-Sea CO₂ Exchange Between Kāneʻohe Bay and Two Other Oʻahu Locations

Automated monitoring of surface water pCO₂ has been expanded to other locations. The CRIMP-CO₂ buoy deployed in Kāneʻohe Bay on November 2005 between Lilipuna Pier and Coconut Island was relocated two miles to the north adjacent to the barrier reef of central Kāneʻohe Bay in June 2008. In addition, two other buoys have been added to the network and were deployed on the south shore of Oʻahu in June 2008. The first buoy was placed at the Kilo Nalu site, which is exposed to open ocean water. The second buoy was deployed offshore of the Ala Wai channel and is exposed to open ocean water and diluted riverine runoff (Figure 35). Compared to southern Kāneʻohe Bay, the south shore of Oʻahu is directly exposed to strong physical forcings from waves, wind and tides. The adjacent watershed does, on average, not receive as much rainfall as the Kāneʻohe Bay watershed. The Ala Wai canal, however, is an important source of freshwater, suspended sediment, organic matter, and nutrients to nearshore coastal waters. The sites on the south shore are also adjacent to the highly urbanized city of Honolulu (approximately 400,000 people) on the island of Oʻahu (> 940,000 people) and therefore receive more anthropogenic runoff.

A range of pCO₂ is observed at the various Oʻahu coastal sites. pCO₂ ranges from 350 to 440 μatm at the Kilo Nalu site and from 360 to 470 μatm at the Ala Wai site. A much wider range of 300 to 1000 μatm is observed at the Kāneʻohe Bay site close to the reef. The annualized CO₂ fluxes for each site are -0.048, -0.055 and -1.487 mol C m⁻² yr⁻¹ for Ala Wai, Kilo Nalu, and the barrier reef of Kāneʻohe Bay, respectively. The water column and benthic productivity at the three sites was evaluated with DO, Chl-*a* and pCO₂ and is greater at the Kāneʻohe Bay site than on the south shore. Even with discharge of water containing higher nutrients and organic matter loads at the Ala Wai site, this site and the Kilo Nalu site have more similar ranges of pCO₂ than either the barrier reef site in Kāneʻohe or the southern Kāneʻohe site (Table 5).

From the data available, it is apparent that all buoy sites show rapid short-term variations in DO, Chl-*a* and pCO₂ values driven by biological cycles and that there is a need for higher frequency sampling. Furthermore, the wide variability in CO₂ fluxes at the different reef settings requires further examination if we hope to characterize tropical regions and be able to model the contributions of the tropical coastal ocean to global CO₂ exchange between the air and the sea surface.



Figure 35. Locations of Kilo Nalu and Ala Wai sites on the south shore of Oʻahu, and CRIMP-CO₂ #2 on the north shore in Kāneʻohe Bay close to the barrier reef.³⁹

2005-2008 Conclusions

- Seawater pCO₂ and air-sea CO₂ flux values vary between different coastal sites on O‘ahu.
- Compared to more open coastal environments, semi-enclosed locations (Kāne‘ohe Bay) displayed a much greater range in pCO₂ and larger air-sea CO₂ flux values.

Table 5. pCO₂ values and CO₂ fluxes for the CRIMP-2 buoy location in Kāne‘ohe Bay and the two south shore buoys (Ala Wai and Kilo Nalu). Negative CO₂ flux values indicate surface water to atmosphere flux of CO₂. Note the wider pCO₂ range of values at the Kāne‘ohe Bay buoy site and the much higher annual CO₂ flux to the atmosphere from Kāne‘ohe Bay.⁴⁰

	Ala Wai	Kilo Nalu	CRIMP-2 Kāne‘ohe Bay
pCO ₂ (µatm)	360 to 470	350 to 440	300 to 1000
CO ₂ fluxes (Mol C m ² yr ⁻¹)	-0.048	-0.055	-1.49

C. Enchanted Lake-Ka‘elepulu Estuary, O‘ahu

1. Background

Due to the large urban population (60,000), high residential density, and a large portion of impervious surface area (e.g., road surfacing), water quality is an issue for the Kailua watershed. The Kailua watershed is 95.3 km² and in terms of land use, it is classified as 50% conservation, 40% urban, and 10% agriculture. In the watershed, the Kawai Nui and Ka‘elepulu are the two main tributary systems for Kailua Bay (Figure 36). Kawai Nui and Ka‘elepulu were once

lagoons and part of Kailua Bay and before settlement the entire area was covered by forest. After 500 A.D. and human settlement, these areas were filled in with eroded sediment from upland agriculture activities. The native Hawaiians subsequently used these areas for taro cultivation from the fourteenth through seventeenth centuries. Highly permeable sand and limestone underlie the entire Kailua coastal plain, but low permeable rock underlies the Kawai Nui and Ka‘elepulu wetland areas.

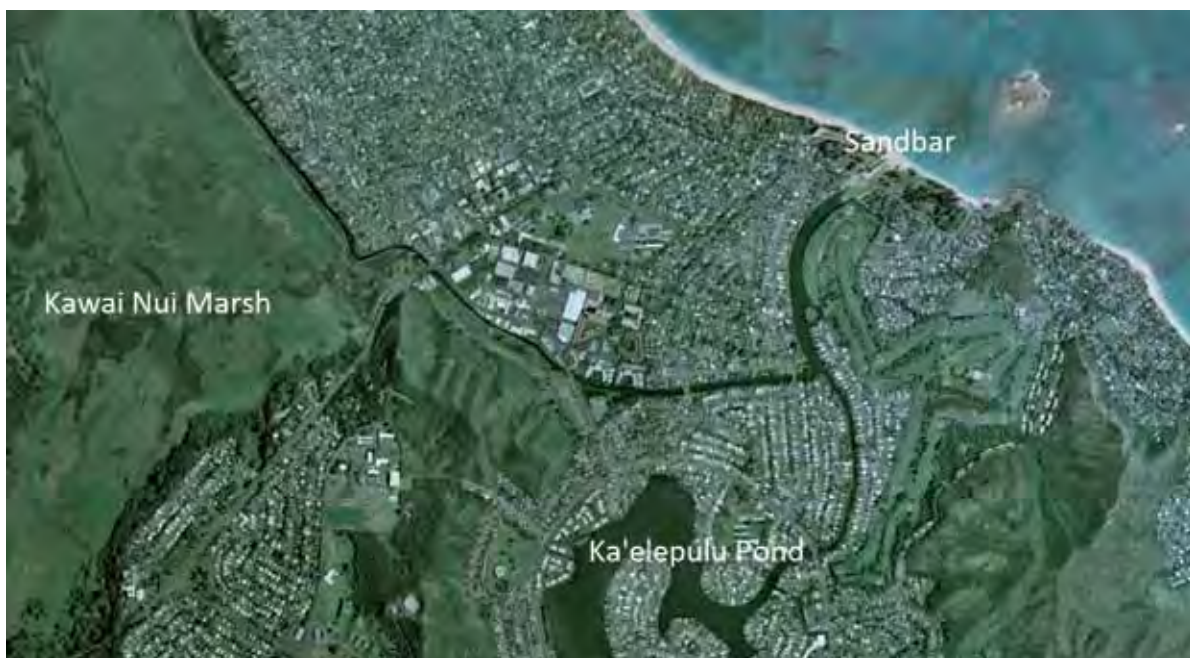


Figure 36. Kailua, O‘ahu watershed with Kawai Nui and the Ka‘elepulu marsh or pond which is also known as Enchanted Lake. Note the location of the sandbar at the land-ocean boundary. The focus in this study is primarily on the region between Ka‘elepulu and the sandbar.

Two important physical features of the Enchanted Lake-Ka'elepulu estuarine system are the sandbar located at the estuary-ocean interface and the sill forming the ocean-side perimeter of Enchanted Lake (Figure 37). These two physical features exert considerable influence on the physical, chemical, and biological properties of the system. Generally, the sandbar at the estuary mouth leading to Kailua Bay effectively isolates the estuary from regular ocean water tidal intrusion. Exceptions include occasions when the sandbar is breached either by storm runoff or human intervention (i.e., dredging) allowing for seawater intrusion into the estuary. When the sandbar is breached, the sill, which is the second important physical feature, provides another physical barrier to advection of seawater inland of the sill. No major perennial streams flow into Enchanted Lake, so there is very little fresh water input during baseline conditions. During storms, runoff generates transient, short-lived freshwater inputs to the lake.

The physical and biogeochemical properties of the Enchanted Lake-Ka'elepulu estuary system were investigated to understand more fully the relationship between watershed and water quality issues in the Hawaiian Islands. One question addressed was how storm runoff impacts nutrient inputs to the estuary system and whether or not the system is at times a source of CO₂ to the atmosphere. Baseline and storm event water samples were collected for determination of total alkalinity, pCO₂, chlorophyll-*a*, temperature, salinity, turbidity, dissolved oxygen, suspended sediment, silica, nitrate, and δ¹³C and δ¹⁵N of suspended sediment. We will look at salinity, pCO₂, and nutrient values to address how does storm runoff of nutrients impact the estuary system and whether or not the system is a sink or source of CO₂.

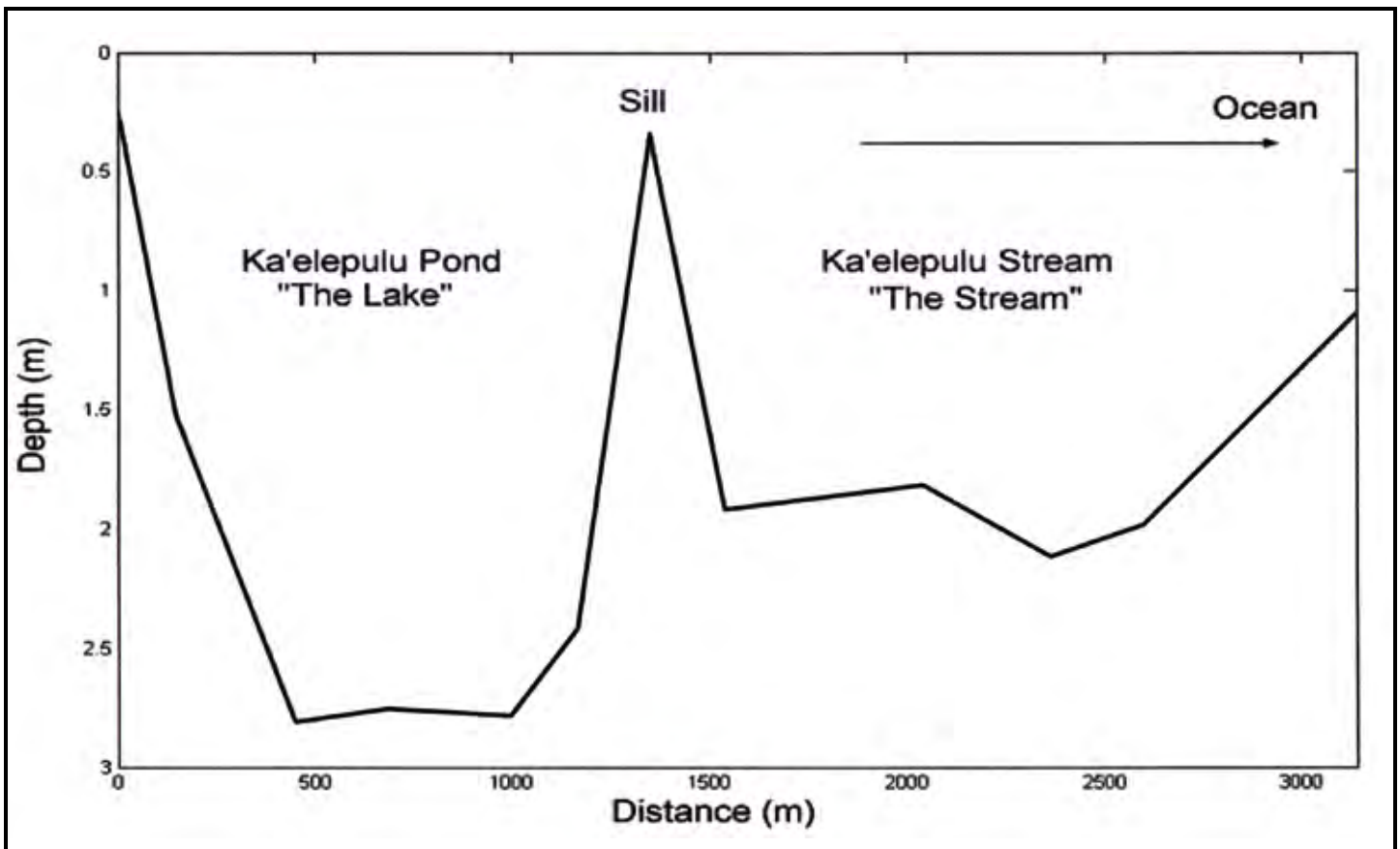


Figure 37. Cross section of study area. Note the sill feature within the lake that comes within 0.3 meters of the surface. Also note that during baseline and storm conditions, runoff water flows from left to right or from the lake towards the ocean.⁴¹

2. Observational Results

Waters are well mixed during the dry periods and partially mixed at times of tidal flow or high precipitation in the Enchanted Lake-Ka‘elepulu estuarine system. During the driest periods or months, salinity is virtually uniform vertically in the estuary reflecting the lack of significant input of groundwater and stream water (Figure 38). Additionally, the salinity within the lake (21 to 22 ppt) is less saline than ocean water (> 31 ppt) suggesting minimal intrusion of seawater. The vertical salinity uniformity combined with lower than seawater salinity values suggests that dry period nutrient inputs to the lake-estuary system are generally storm-related, and not from consistent, regular ground or stream water inputs. During baseline periods (i.e., dry), the sandbar and sill prohibit tidal effects on estuarine mixing and circulation. At these times, the primary influences on mixing and circulation are any surface water runoff (e.g., small ephemeral tributaries) and wind stress on the water surface. If storm runoff flow or human intervention ruptures the sandbar then tidal intrusion can occur in the estuary creating vertical stratification of salinity in the water column.

Storm runoff delivers excess dissolved nitrate, silica, and suspended particles into the estuary. Baseline nutrient profiles and storm event nutrient profiles demonstrate how different the lake and estuary nutrient profiles are between these two periods (Figure 39). Nutrient concentrations were much higher after the February 14, 2003 storm event for both nitrate and silicate in the lake.

To ascertain the impacts of the February 14, 2003 storm on nutrient inputs and subsequent effects on biological production, the estuary was sampled two weeks later, February 28, 2003, for nitrate and silicate (Figure 40). Since sampling took place two weeks after the storm event, it is likely that only the end of the storm runoff nutrient induced production bloom was measured. Nevertheless, it appears that nutrient loading by the storm ultimately led to nutrient draw down below storm and baseline nutrient concentration levels via phytoplankton blooms and rapid consumption of nutrients. Concentrations of both nitrate and silicate are 5 to 10 times lower after the storm compared to the storm runoff values.

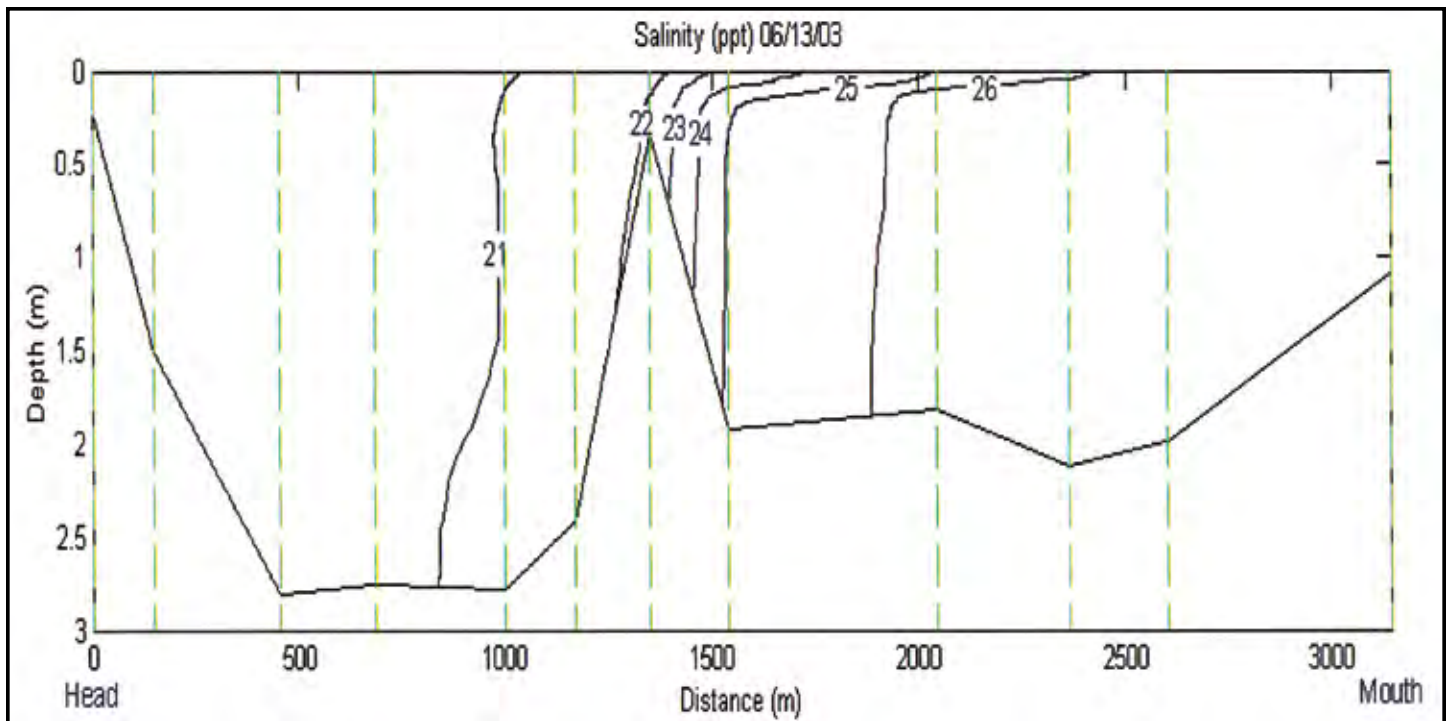


Figure 38. Baseline salinity profile for the Ka‘elepulu Pond from June 13, 2003. Note how salinity is nearly vertically uniform suggesting little, if any, groundwater or stream water inputs. The intrusion of seawater into Ka‘elepulu Stream is well demonstrated by the increase in salinity toward the ocean.⁴²

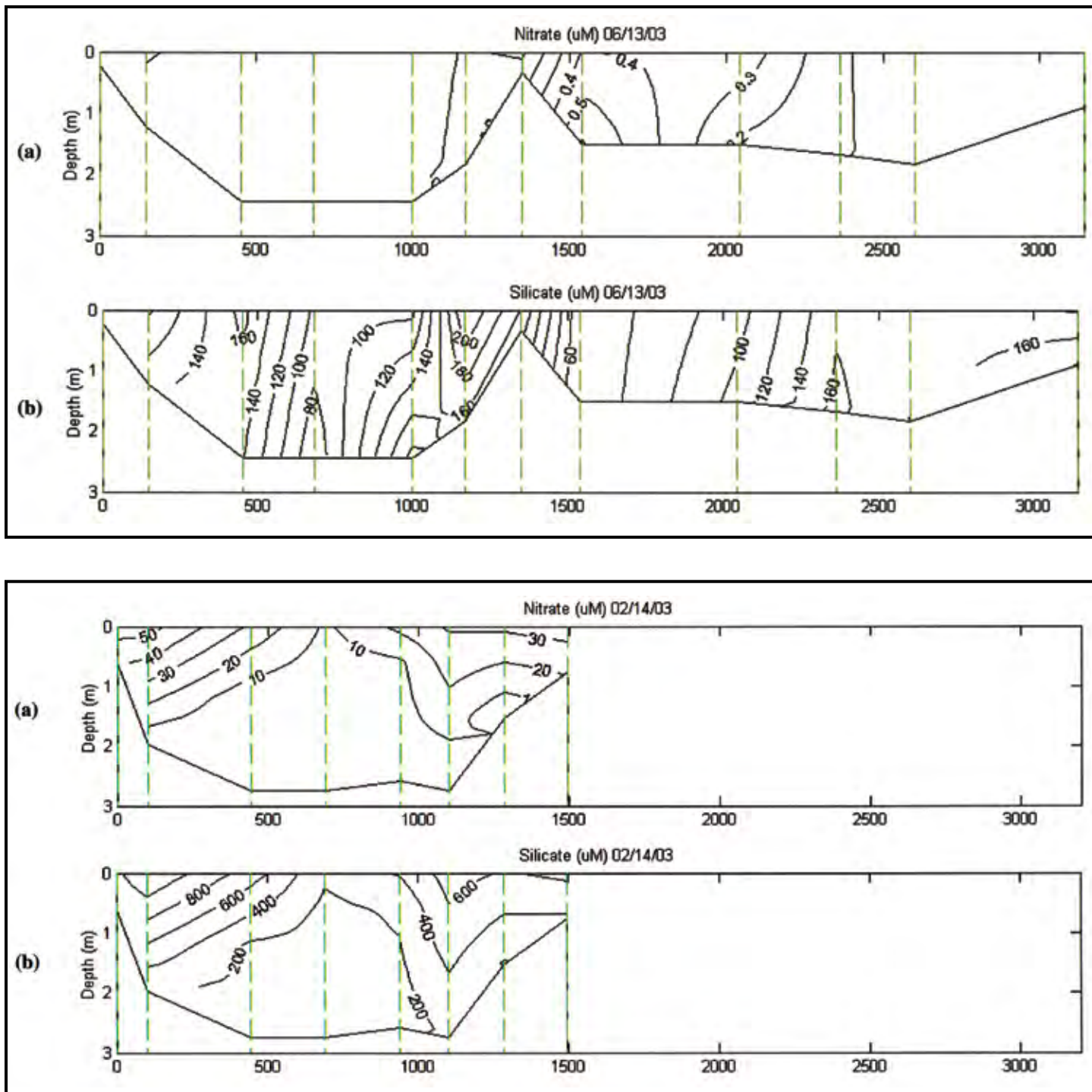


Figure 39. Baseline (top) and the February 14, 2003 storm event (bottom) nutrient profiles of dissolved nitrate (a) and silicate (b). Note that during the storm event, sampling was only possible from the lake. Also note the elevated nitrate and silicate values of the lake due to storm freshwater inputs, compared to the baseline lake values.⁴³

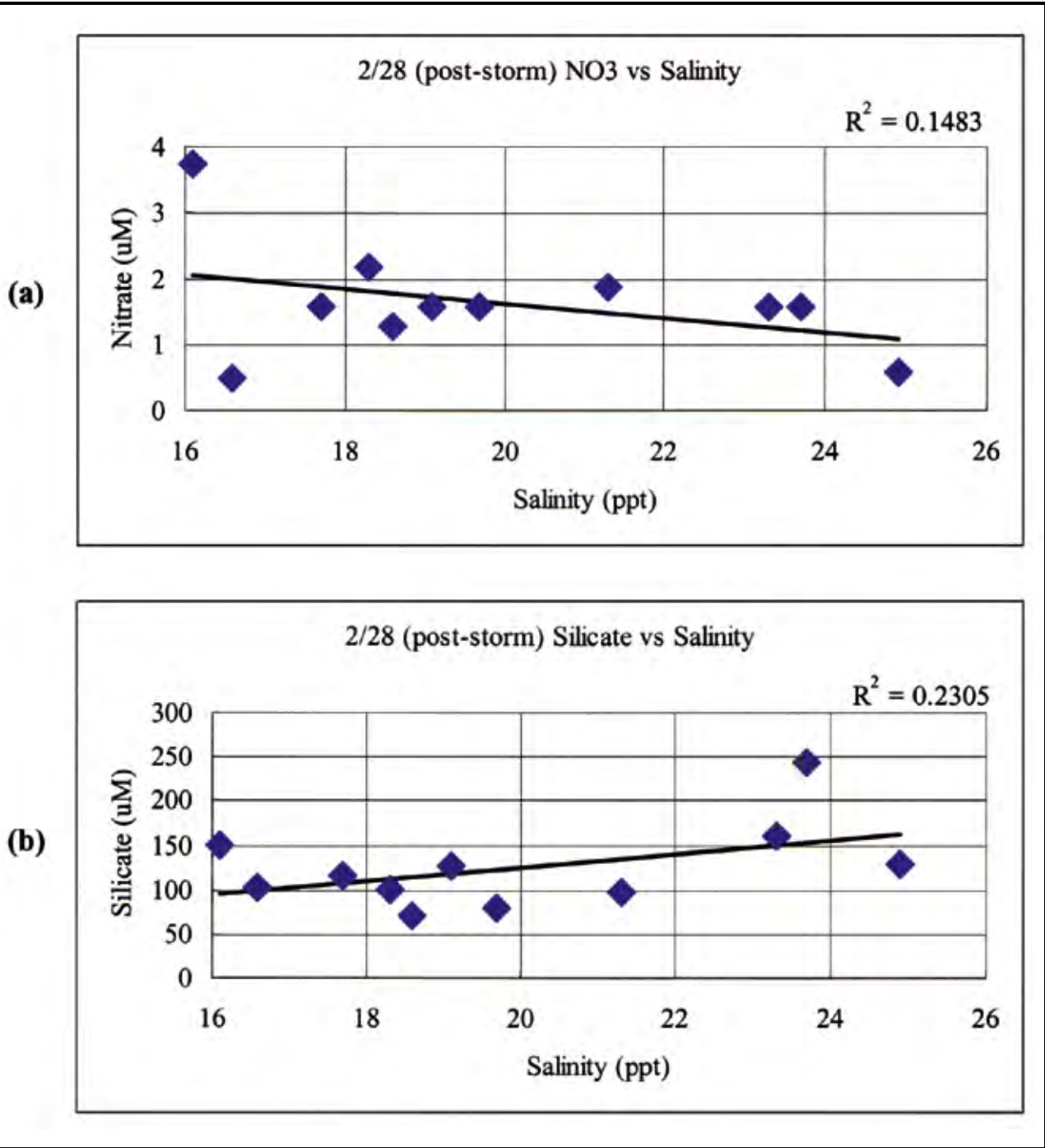


Figure 40. Post-storm nitrate versus salinity (top) and silicate versus salinity (bottom) values. Note how both the nitrate and silicate concentrations are less compared to the storm runoff nitrate and silicate values of Figure 39.⁴⁴

Many estuaries are heterotrophic ecosystems meaning they respire and produce more CO₂ than they consume via primary production. Lake-estuary pCO₂ values were calculated using pH and alkalinity data obtained from surface waters of the lake (Figure 41). The Enchanted Lake-Ka‘elepulu estuarine system is generally oversaturated with CO₂, at least during the sampling period, compared to the atmosphere suggesting the lake-estuary system is a source of CO₂ to the atmosphere. Since there is no evidence of calcification in the estuary system, it is the respiration of organic matter produced *in-situ* and also derived from runoff that creates elevated estuarine pCO₂

values. Like Hilo and Kāne‘ohe Bay, the Enchanted Lake-Ka‘elepulu estuarine system is a source of CO₂ to the atmosphere.

3. General Conclusions

- The Enchanted Lake-Ka‘elepulu estuarine system is strongly influenced by storm runoff derived nutrients and is a source of CO₂ to the atmosphere. There is little to no groundwater input into the system.
- The sill and sandbar physical features play important roles in the physical, chemical and biological dynamics of the system.

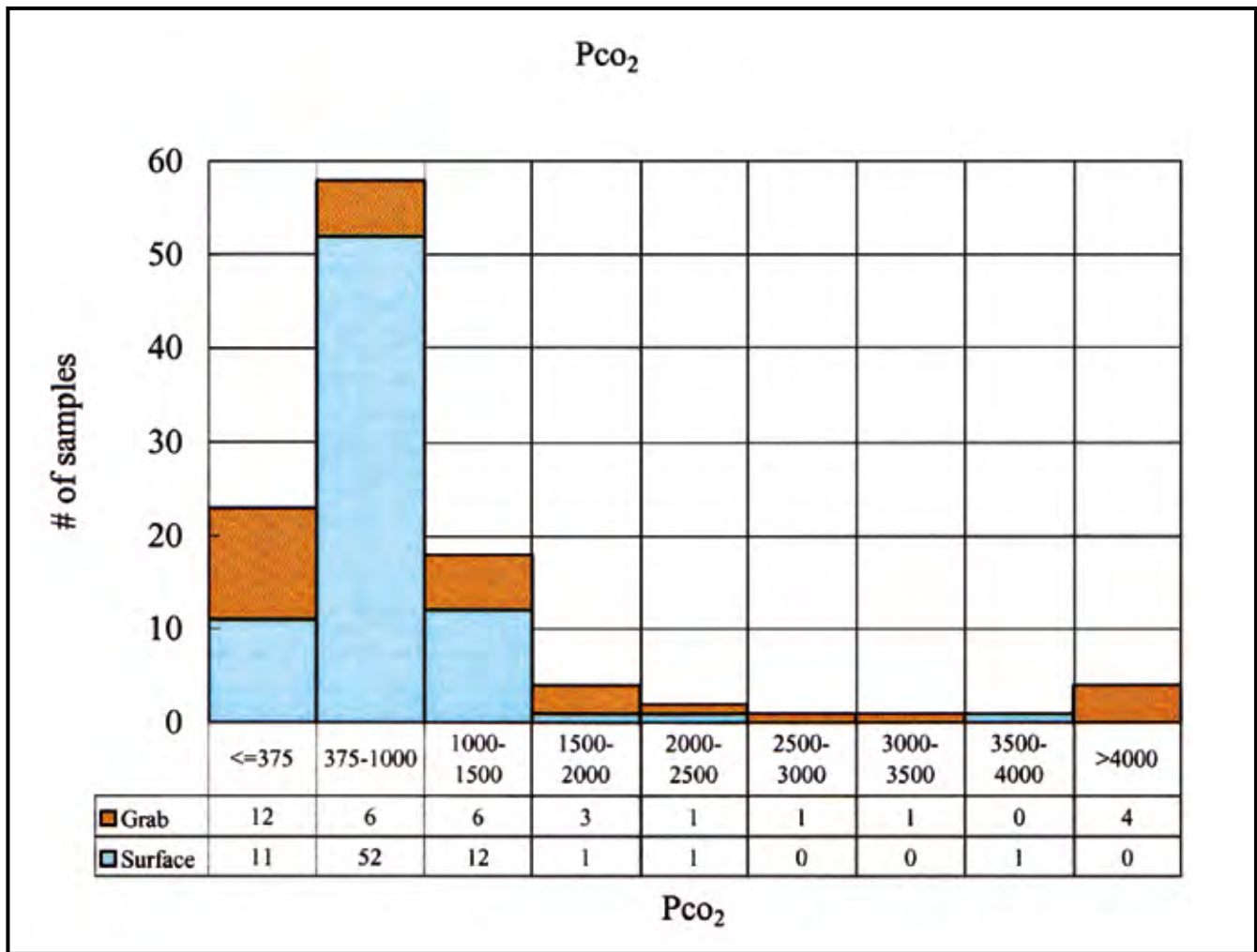


Figure 41. Lake-estuary pCO₂ values calculated using surface water pH and alkalinity data. The y-axis is the number of samples and the x-axis is the calculated pCO₂ values. Note that only the most left hand column (pCO₂ ≤ 375 μatm) water samples had pCO₂ values less than atmosphere. All other samples have CO₂ values greater than the average 2003 atmospheric CO₂ value of ~ 375 μatm.⁴⁵

D. Maunawili Watershed, Marsh, and the Kailua Coastal Zone, O'ahu

1. Background

In the previous sections, we looked at the air-sea exchange of CO₂ from bays with extended watersheds and drainage basins consisting of a mix of all or some of the following: tropical forests, lava rock beds,

farmlands and urbanized areas. In this section, we will discuss the influence of another type of drainage basin on air-water CO₂ exchange: marsh land from the watershed of Maunawili into the Kawai Nui marsh and canal and towards Kailua Bay (Figure 42).

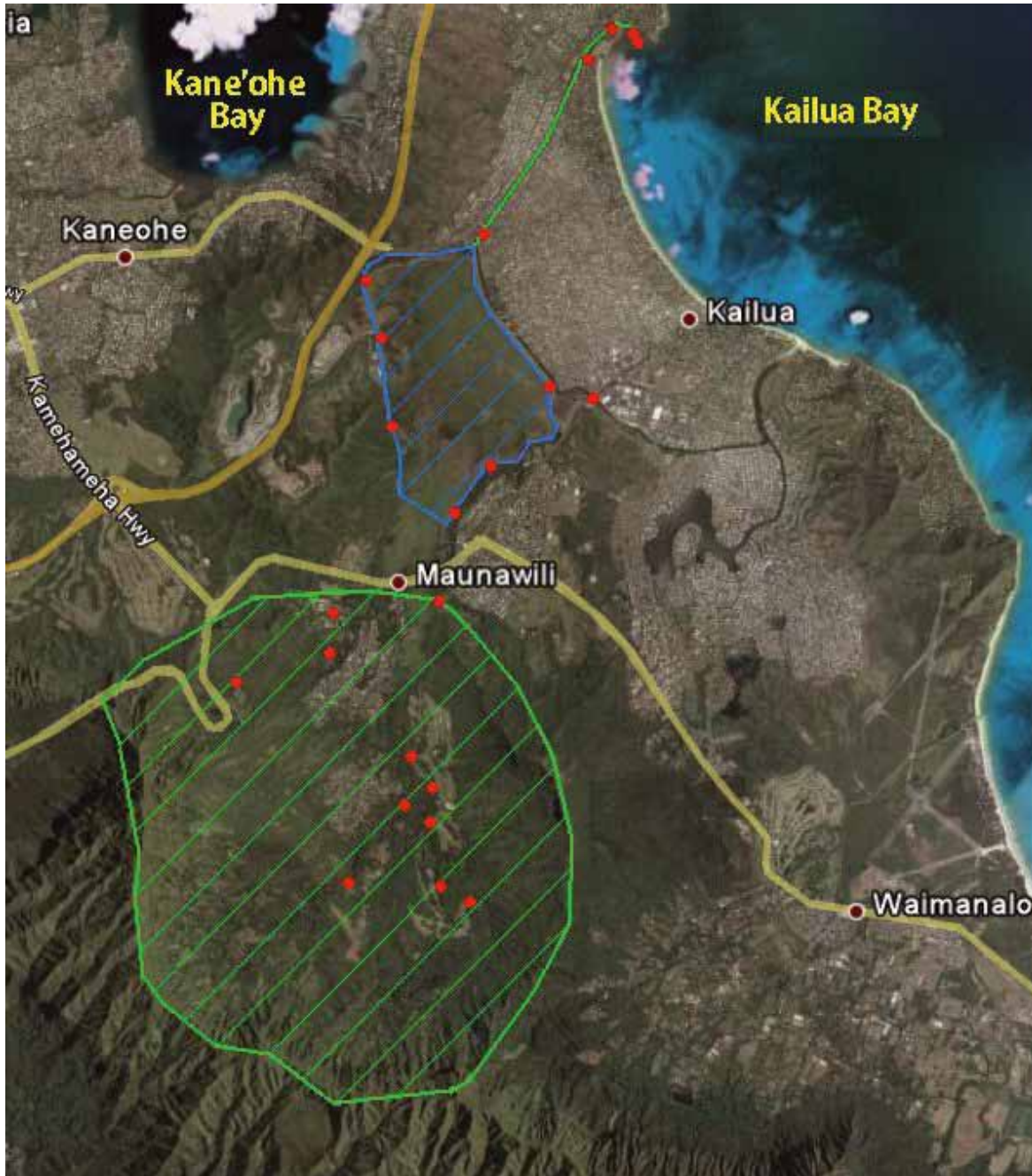
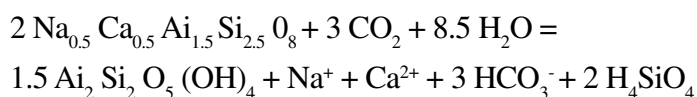


Figure 42. Map showing site locations for study of the watershed of Maunawili, the Kawai Nui marsh and canal, and Kailua Bay. The green striped area represents Maunawili watershed, the blue striped area represents Kawai Nui marsh and the yellow line is the Kawai Nui canal. The red dots are the 23 sampling locations of the study.

2. Observational Results

The pH and total alkalinity of water samples were determined analytically and the $p\text{CO}_2$ values calculated from the watershed to the bay of this land/sea ecosystem at different times of the year and during different rain regimes. In the Maunawili watershed, fresh water pH values varied between 6.90 and 8.49 with a mean of 7.7. Alkalinity fluctuated from 685 to 1,373 $\mu\text{mol kg}^{-1}$ with a mean of 1,052 $\mu\text{mol kg}^{-1}$. The waters were undersaturated with respect to both calcite and aragonite. $p\text{CO}_2$ values also had a wide range of concentrations from 165 to 8404 μatm with a mean of 1900 μatm . pH variations are, in part, linked to the environmental conditions at the sampling locations. For example, if the water flow is channelized with concrete walls, the pH and alkalinity of the water goes up as the cement dissolves releasing Ca^{2+} and CO_3^{2-} into the water. An increase in pH is also observed during rain events as well as a decrease of $p\text{CO}_2$. The weathering of the bedrock (mainly basalt in the watershed) by CO_2 produced by respiration of organic matter in the soil is linked to the production of alkalinity, dissolved silica, and consumption of $p\text{CO}_2$. The pH decrease in the rain percolating through the soils is due to excess respiration of organic matter. For example, the chemical weathering of basalt in the Maunawili watershed is represented by:



Generally, $p\text{CO}_2$ increased downstream and the watershed appears to be a source of CO_2 to the atmosphere.

The Kawai Nui Marsh exhibits pH values ranging from 6.8 to 7.6. The marsh alkalinity is higher than oceanic alkalinity. One unusually high value of 14,266 $\mu\text{mol kg}^{-1}$ was observed in the marsh. The mean marsh water alkalinity is 5740 $\mu\text{mol kg}^{-1}$ and is dominated by high bicarbonate and carbonic acid concentrations (5,632 and 549 $\mu\text{mol kg}^{-1}$, respectively). Also, there is a difference in alkalinity between the western side (up to 9,320 $\mu\text{mol kg}^{-1}$) and the eastern side of the swamp (3,000 $\mu\text{mol kg}^{-1}$ average). The $p\text{CO}_2$ values have no seasonal pattern, but are different on the western (32,000 μatm) and eastern side (3,000 μatm). The reasons for the differences have not been thoroughly investigated, but

differences in the organic matter content of the marsh soil and bedrock type (amount of marine limestone) between the two sides of the marsh may provide some explanation. The weathering of the limestone and the decomposition and/or respiration of organic matter will release CO_3^{2-} and CO_2 , respectively, into the water, as well as change the pH and DIC of the water. The differences in bedrock and amount of organic matter between the western and eastern sides of the marsh can translate into differences in alkalinity, pH and $p\text{CO}_2$.

The Kawai Nui canal and Kailua Bay have a salinity gradient increasing toward the bay from 3.5 to 36.2 ppt. The pH varies from 7.8 to 8.2 from inside the canal to the bay. The alkalinity (2,450 to 2,100 $\mu\text{mol kg}^{-1}$) was found to be influenced by the mixing of saltwater and freshwater in the canal and in the bay. The $p\text{CO}_2$ values are influenced by saltwater mixing and by the tides. The small estuarine system was found to be dominated by respiration. The $p\text{CO}_2$ varied from 2,293 μatm in the canal to 140 μatm in Kailua Bay.

The $p\text{CO}_2$ values of the fresh and estuarine waters were calculated in the mountain streams, marsh and the estuarine zone of Kailua (O'ahu) from salinity, temperature, pH and total alkalinity data during baseline and storm conditions. The $p\text{CO}_2$ of the mountain streams and the marsh waters were lower during storm events (702 and 4890 μatm , respectively) compared to the baseline conditions (1727 and 6160 μatm , respectively). On the other hand, $p\text{CO}_2$ in the estuarine waters was higher during storm events compared to baseline conditions. The estuarine baseline $p\text{CO}_2$ was around 1790 μatm and increased to an average of 2831 μatm during a storm event (Table 6). The marsh showed the highest $p\text{CO}_2$, which is attributed to the high rates of organic matter respiration and remineralization in the marsh. The estuary, however, reacted differently to inputs from the streams and marsh under storm conditions partly because of the "salting out effect." The solubility of CO_2 and other gases decreases with increased salinity and hence the mixing of high CO_2 freshwater with seawater. The decrease of $p\text{CO}_2$ was also due to the higher flow and increasing water turbulence during storms resulting in a higher degassing rate and a shorter accumulation time. Overall the Kailua system did not become a stronger source of atmospheric CO_2 during the storm, but it did not become a sink either.

Table 6. Comparison of pCO₂ values from mountain streams, marsh and estuary of Kailua basin during baseline conditions and after a storm event.⁴⁶

	Baseline	Storm event
	pCO ₂ (µatm)	
Mountain streams	1727	702
Marsh	6160	4890
Estuary	1790	2831

3. General Conclusions

- Kawai Nui Marsh has both elevated alkalinity (likely due to chemical weathering and dissolution of the underlying carbonate bedrock) and pCO₂ (due to high organic matter respiration).
- The estuary reacted differently from the bay under storm conditions due to the “salting out effect.”
- The Kailua watershed system is a source of CO₂ to the atmosphere.

E. Conclusions of the Hawai‘i-based Studies and Relevance to Other Tropical-Subtropical Land-Coastal Ocean Systems.

From the aforementioned Hilo, Kāne‘ohe, and Kailua Bay land-coastal interaction studies, we can draw some general conclusions regarding land-coastal interactions in tropical and subtropical high mountain island environments. First, land-use plays an important role in the relative chemical species distribution and concentrations of particulate and dissolved nutrients. Runoff, baseflow, and storm flow from both urban and agriculture sites were consistently elevated in concentrations of dissolved nutrients in the Hawai‘i studies. Particulate organic matter fluxes were highest at conservation sites, similar or slightly lower at urban sites, and lowest at agriculture sites. Thus, land use in other subtropical-tropical mountainous watershed-coastal ocean environments is likely an important controlling factor to consider regarding nutrient fluxes. Second, groundwater input containing elevated concentrations of nutrients, such as nitrate and dissolved silica, can be important along the windward coast of the island of O‘ahu. It is therefore likely that groundwater seeps contribute significant amounts of both freshwater and nutrients to other tropical-subtropical coastal environments.

Storm events were found to play a major role in water, suspended particulate material, and nutrient fluxes despite low storm frequency and intensity during many of the study periods considered in this case study. The duration of the interval between storms impacts the nutrient load delivered to coastal environments. Not all storm events may create phosphorus-limitation to production in proximal coastal systems due to *in-situ* release of phosphorus

from storm-runoff generated particles suspended in the water column. Production resulting from storm-derived runoff nutrient inputs is also dependent on many other factors. Cloud cover and wind speed can strongly influence the productivity bloom response of a coastal system to storm events. Furthermore, changes in nutrient ratios (N and P) can cause shifts in the community structure. During some storm events, proximal coastal environments can become temporary sinks for atmospheric CO₂ due to the depletion of coastal water CO₂ by primary production.

The pCO₂ values for Hawai‘i stream and coastal environments during baseline conditions are generally higher than those of the atmosphere. Elevated stream pCO₂ values were due to remineralization processes involving organic matter in the soil and groundwater source waters of the streams. For example, elevated pCO₂ values of Kāne‘ohe Stream water (compared to the atmosphere) were mainly driven by the input of CO₂-charged soil and groundwaters from organic matter remineralization. This observation is likely true for other stream watersheds. The high pCO₂ values in coastal waters can be due to one or both processes of calcification and respiration of terrestrial organic matter, as shown in this case study and also observed in other coastal environments.

All Hawai‘i coastal environments studied appeared to be sources of CO₂ to the atmosphere and the degree to which they are sources can have strong seasonal dependence. Some locations were strong CO₂ emitters during summer and fall (dry periods) and weaker emitters in winter and spring (wet

periods). Furthermore, year-to-year changes in overall precipitation (wetter versus drier years) amplified these seasonal effects. To expand this conclusion over longer-term rainfall and climate variations [e.g., El Niño (dry)

vs. La Niña (wet) periods] requires multiple years of interannual data and further study. These conclusions probably hold to one degree or the other for many subtropical/tropical land coastal sea environments.

VI. Management Implications

It should be evident in reading this case study that land-use practices of humankind affect coastal zones; thus, management of the anthropogenic land-based activities must be considered in any management plans designed to prevent degradation of coastal ocean environments. Some key human activities on land that affect coastal waters through land-sea connections and interactions are: (1) the application of nitrogenous and phosphorus-bearing fertilizers and biocides to the landscape and subsequent leaching of significant proportions of these materials into water courses, (2) the release of sewage into aquatic systems, including directly into coastal ocean waters, (3) the diversion of water flows through channelized structures and dams resulting in changes in retention times of water, nutrients and sediments and also in riparian communities on land and hence changes in water, nutrient and suspended sediment fluxes to the coastal ocean, (4) deforestation and/or conversion of land type from, for example, agricultural use to urban housing, (5) the fallout of nitrogen from the atmosphere derived from combustion sources on land and its ultimate transport into aquatic systems, (6) CO₂ emissions from fossil fuel and land-use activities (e.g., deforestation) and absorption of some of this CO₂ by coastal and open ocean waters, (7) atmospheric nitrogen emissions from combustion sources on land that ultimately fall directly on the ocean surface, and especially that of the coastal ocean, and (8) the global mean temperature rise of nearly 1°C for the past 150 years – which is likely to continue into the future – that affects organic decomposition and weathering rates on land and hence riverine transports to the coastal zone. The first step in setting up a viable coastal ocean management plan is recognizing these diverse and often nonpoint sources of land-sourced materials for the coastal ocean. Aside from this, there are human activities that occur directly in coastal waters and require management through regulation, for example, of reef dynamiting to increase benthic fish catch, dumping of various types of waste directly into coastal zone waters, inadvertent destruction of reefs by boat traffic

and people walking on them, conversion of wetlands to urban centers and other uses, and discharges by ships or oil wells at sea. In the following, we highlight aspects of this case study that have implications for the management of coastal ocean ecosystems in Hawai‘i and subtropical/tropical coastal zones in general.

1. There is ample evidence of nonpoint source pollution from urbanized areas in the southern Kāne‘ohe watershed. Among the pollutants, runoff nutrients likely have significant impacts on the bay’s ecosystem and biochemistry. Yet even after significant storm events, the recovery time of the bay is relatively short. This suggests that the natural conditions characteristic of Hawaiian coastal waters act as a buffer to anthropogenic inputs and their impacts and effects, although, this does not mean that Hawaiian coastal waters are not vulnerable to runoff inputs. Consecutive rainstorm events documented in Kāne‘ohe Bay show synergistic effects on bay waters. Perturbations attributable to sediment loading can be significant on longer time scales, particularly for coral reef communities because sediment-laden runoff can block sunlight and change water column pH, salinity, and temperature. It is important to establish complementary time series stations to monitor nutrient and suspended sediment loads for coupled river-coastal marine ecosystems during both baseline and storm conditions. This approach has been shown to be necessary to assess the effects of episodic storm runoff events on coastal marine waters, especially with regard to calculation of the fluxes of sediments and nutrients and quantifying the subsequent impacts on the coastal marine ecosystem.
2. Long-term studies have already demonstrated the utility of combining real time observations of biogeochemically relevant parameters with periodic synoptic sampling over a broader

geographic area to assess the response of receiving waters to land-derived inputs of nutrients. For example, the response of southern Kāneʻohe Bay to nutrient inputs associated with storm runoff is typically rapid, generally occurring within a day of inputs, but is also influenced by physical forcing mechanisms. Storm inputs to the bay from streams and groundwater provide large quantities of dissolved and particulate nutrients, which quickly drive phytoplankton productivity. Changing N:P ratios, however, can potentially cause shifts in the limiting nutrient responsible for biological productivity and in community structure that ultimately affect the overall phytoplankton response. In addition, the remineralization of terrestrial particulate organic matter deposited in the bay during storms appears to provide continued benthic nutrient inputs to the bay for periods extending from weeks to months after the original storm delivery. There are also other sources of nutrients to Kāneʻohe Bay that must be considered when investigating coastal response to nutrient inputs and their management. In addition to the storm/runoff water delivered by streams, groundwater inputs that are not currently well understood may be quite important.

3. Shallow water reefs are already under substantial stress as evidenced by recent bleaching events. The bleaching is a natural response of the corals to sharp environmental variations. Loss of the symbiotic zooxanthellae and/or the reduction of the abundance of photosynthetic pigments are what coral bleaching represents. Without the symbionts, which produce sugar subsequently used for energy by the corals, the corals begin to starve and may, in turn, die. Although most corals recover from single bleaching events, bleaching events have increased in frequency and extent in the past 20 years. Bleaching occurs in association with sharp temperature increase, changes in solar irradiance, excessive sedimentation, or freshwater dilution and, in some cases, inorganic nutrient inputs, and often increases in turbidity. High sediment and nutrient loading are observed in coastal areas

during and after storm events. Sedimentation adversely impacts corals by covering them and blocking sunlight from reaching the photosynthetic symbionts. Normally, many corals are capable of “cleaning” themselves, but with repeated and increased sediment loads delivered to the coastal areas via runoff, the cumulative effect of sediments results in stress for both zooxanthellae and corals. In addition to the temperature stress on corals, the past and predicted increase in anthropogenic CO₂ in the atmosphere and consequent transfer of CO₂ into the surface waters will cause the carbonic acid system balance to change, decreasing the seawater pH (ocean acidification). As surface waters become more acidic, the carbonate mineral saturation state is lowered potentially reducing the growth rate of calcifying species such as corals and also resulting in the dissolution of carbonate edifices. On a local level, the behavior of Hawaiʻi’s coastal waters with respect to air-sea CO₂ exchange, under conditions of rising atmospheric CO₂, will affect the local tourism economy due to increased water acidity and possible harm to coral reefs, impacting carbonate production and supply of carbonate sands to beaches, storm surge impacts, and coastal aesthetics. Since the temperature and ocean acidification effects are both global and regional in nature and caused by rising fossil fuel and land-use emissions of CO₂ to the atmosphere, the management of this problem in terms of reducing impact on the coastal ocean requires worldwide consensus among nations on reducing or capturing CO₂ emissions, not an easy task!

In summary, much of the problem involving degradation of coastal ocean environments in Hawaiʻi and elsewhere stems from land-use activities of humankind and hence these must be managed to the greatest degree possible to prevent coastal environmental degradation. For example, nutrient inputs into receiving waters because of fertilizer application to farmlands can be reduced by conversion of older nutrient application practices to one of drip irrigation. Biocide and fertilizer use on golf courses and home lawns should be reduced and only biocides with the least negative impacts on the biosphere employed. Sewage plants must be designed to prevent

overflows during storm conditions, and sewage and storm pipes maintained to prevent breakage and leakage into soil and groundwater. Conversion of land from one use to another should be done with full recognition of the effects this conversion will have on any nearby aquatic systems and coastal ocean environments. Construction of holding tanks for soil disturbed during construction of homes and other buildings needs to be part of any permit to build. Such management practices would greatly lessen negative impacts on coastal ocean ecosystems. In addition, in order to manage coastal systems efficiently in terms of sustainability, it may be necessary to have continuously monitoring instrumented systems (e.g.,

CRIMP-CO₂) in place in several coastal areas and continuous synoptic studies of important water quality parameters. This will enable managers to assess whether or not a certain modification of the land has had any significant effects on the receiving coastal ocean ecosystem. In conjunction with the water quality programs, at some viable time scale, there should be monitoring of benthic organisms and fish in certain key coastal areas to not only discern if land-use fluxes are impacting the biota but also evaluate how temperature changes and ocean acidification are affecting the biological community on reefs and in other coastal ecosystems.

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