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The purpose of this thesis is to provide a first look at the spatial and temporal distributions of dissolved organic material (DOM) off the Oregon coast of North America. While this paper is not a comprehensive examination of these distributions, several patterns are identified as promising candidates for continued research. Most of the data presented was acquired during a strong El Niño event. The DOM data is presented as dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) and is accompanied by temperature, salinity, nitrate plus nitrite (N+N), ammonium, silicate, chlorophyll, total organic carbon (TOC), particulate organic carbon (POC), total nitrogen (TN), total organic nitrogen (TON), and zooplankton biomass measurements. During July 1997, we examined the distribution of DOM in the surface waters off the Oregon and Southern Washington coasts. Eleven east-west transects were sampled from nearshore waters to 190km offshore. DOC concentrations as high as 180 μM were observed in the Columbia River plume. Patterns in the DOC distribution were also associated with upwelling regions, an offshore coastal jet, and an oligotrophic water mass in the northern portion of our study area. Beginning with the July 1997 study and continuing until July 1998, samples were collected on weekly and seasonal time scales at station NH-05, located 9km offshore from Newport, Oregon. Various problems have limited our seasonal comparisons, but we were able to collect high quality data depicting the changes in organic matter partitioning

during a phytoplankton bloom and its decline during a two month period from mid-July through mid-September in 1997. During the bloom, POC increased dramatically, but DOC decreased. Possible explanations for this decrease and for changes in the C/N ratio of the DOM during the bloom are explored. Suggestions for future research are presented in the final chapter.

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The Distribution and Partitioning of Dissolved Organic Matter off the Oregon Coast: A First Look

by

Jon K. Hill

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Jon K. Hill, Author

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DEDICATION

This thesis is dedicated to two special groups of people: to all the teachers I've learned from in my twenty-two (!) years of formal schooling and to all of my future students. Learning is a part of life we can't afford to ignore or leave to chance, and the best way to learn is to teach.

THE DISTRIBUTION AND PARTITIONING OF DISSOLVED ORGANIC MATTER OFF THE OREGON COAST: A FIRST LOOK

1 Overview

The purpose of this thesis is to present a description of the spatial and temporal distribution of dissolved organic matter (DOM) off the Oregon and southern Washington coasts. DOM has been measured in these waters before, but never on the scales presented here. The primary focus will be on dissolved organic carbon (DOC), but the distribution of dissolved organic nitrogen (DON) will also be described because of the value of examining variation in the C/N ratios within the regions studied. Distributions of particulate organic matter (POM) will also be discussed, along with accompanying chlorophyll, nutrient, and physical data.

The reasons for conducting this study are numerous. DOC is tightly linked to planktonic and bacterial processes and its distribution can provide insight into the ecology of a region. DOC comprises a large pool of carbon in the ocean, and so knowing its concentration can help modelers predict how a particular part of the ocean might exchange carbon with the atmosphere, important knowledge when considering the current global warming trends. The coastal waters off Oregon are well suited to studies of DOM for a few reasons. There have been fewer studies of DOM in temperate regions than in polar and equatorial regions. Upwelling occurs along the coast, so we can observe its effect on DOM distribution patterns. We also have nearby input of one of the largest rivers in North America, the Columbia. Rivers can drastically change DOM patterns, so we have the opportunity to observe this influence.

The following chapters will document studies of DOM off the Oregon and Washington coasts during 1997 and 1998. Chapter 2 will examine the history behind the project, looking at past studies of DOM and also details about the oceanography of our study region. Chapter 3 will focus on the spatial distribution of DOM in the surface waters of our study area during a two-

week period in July 1997. Chapter 4 will present the results of a one-year time series of data collected from a station off Newport, Oregon, focusing on a two month period in 1997 corresponding to a bloom and its eventual decline. And, finally, Chapter 5 will serve as a thesis summary and will present suggestions for future research.

2 Background Information

2.1 Past Studies of DOM

DOM is one of the largest reservoirs of reactive carbon in the ocean (Carlson and Ducklow, 1995, 1996, Chen et al., 1996). As such, it plays an important role in the carbon cycle, which involves biological, chemical, geological, and atmospheric aspects of oceanography. The study of DOM has been critical to understanding marine food web dynamics, especially in the new understanding of the role of bacteria that has come about in the last 20 years (Carlson and Ducklow, 1995, Williams, 1995, Thingstad et al., 1997). DOC abundance is linked to primary production, though the connection is often unclear (Carlson et al., 1994, Carlson and Ducklow, 1995).

The current interest in DOM has been brought on by new measuring techniques and an increased awareness of the role of DOM in ecosystems. In spite of many recent technological advances and renewed interest in DOM, and especially DOC, the factors controlling its abundance and distribution in time and space are not well understood (Williams, 1995). Intensive research in a variety of marine environments over various time scales accompanied by continued laboratory studies are required in order for the full importance of DOM in the marine environment to be realized.

2.1.1 Methods of Measuring Bulk DOC

DOC in the open ocean has been measured at levels below 40 μM (Carlson and Ducklow, 1995) and above 8,000 μM (references given in Carlson et al., 1998) though these high numbers are suspect. Typical high values are still well below 1,000 μM. Typical open ocean values are in the range of 35-80 μM. Typical coastal ocean values range from 50-500 μM.

Prior to the mid-1980s, DOC was measured by wet-chemical oxidation techniques (Menzel and Vaccaro, 1964) or by photo-oxidation with UV light (Armstrong and Tibbitts, 1968). These methods were time consuming and inaccurate, especially when the samples contained large biomolecules (Wangersky, 1993). In 1988, Japanese researchers, Sugimura and Suzuki, released data collected using a newly developed high temperature catalytic combustion (HTC) method for measuring DOC. Their measurements suggested that DOC was much more abundant in the marine environment than was previously thought. This generated considerable interest accompanied by controversy over the discrepancy between measurements by the two methods. Other researchers, quick to try the new HTC method, could not reproduce the high levels of DOC observed by Sugimura and Suzuki. It was determined that their methods were flawed, primarily in the area of blank preparation. Their blanks were too high and were not subtracted from their final measurements, resulting in overestimates. In spite of these mistakes, the Japanese researchers succeeded in getting the biological oceanography community to refocus its attention on the potential importance of DOC.

The HTC method has improved after much research and standardization, and refinement of the method is still in progress. HTC, while difficult to make precise, is conceptually a simple process. Organic carbon is combusted in the presence of a platinum catalyst at high temperature (600-800 °C), converting it to CO_2. This CO_2 is then measured using a nondispersive infrared detector. Careful execution of the new HTC methods has resulted in precision to 1-2% on a single instrument and 7% among different instruments. HTC is faster and more precise than previous methods used, i.e. wet-chemical analysis and UV-oxidation. Reevaluation of methods and revised methods for handling blanks have brought estimates of marine DOC back down to levels which agree with those obtained by the older wet-chemical and UV-oxidation methods.

In recent years, many researchers have been developing tools that allow the in situ measurement of DOM. Remote sensing devices, such as the SeaWIFS ocean color sensor currently in use by NASA, measure the reflected radiation from several wavelengths and through

a series of algorithms, arrive at an estimate of DOM in the surface water. Other instruments in use also make optical measurements, but are actually lowered into the water or towed from a ship. One such tool is the Spectral Fluorescence Instrument (SAFire™) package by WET Labs, Inc.™. This instrument measures the absorption by seawater at several wavelengths of light and estimates DOM based on these measurements. Both of these techniques are limited in their ability to measure bulk DOM for two important reasons. First, the methods only detect colored DOM, or CDOM. Not all DOM has color, so any colorless DOM remains undetected. Second, the amount of color among the various molecular forms of colored DOM is not directly related to the amount of carbon in the molecules. So a small molecule could generate a large colorimetric signature while a large molecule could generate almost none, giving a skewed estimate of actual carbon present. Nevertheless, these new techniques are promising, primarily because of the spatial scales which can be covered in a very short amount of time.

2.1.2 What We Know About DOC

Information about the characterization and distribution of DOC has expanded rapidly in the last decade as a direct result of the new measurement techniques becoming available.

2.1.2.1 Characterizing DOC

Dissolved organic carbon (DOC) is found in a seemingly infinite variety of organic molecules (Biddanda and Benner, 1997). These molecules include nitrogenous compounds such as amino acids, proteins, and polypeptides; sugars including mono-, oligo- and polysaccharides; organic acids including vitamins; lipids; and other various carbohydrate polymers. This variety of molecules makes characterization of DOC very difficult. It creates problems both in the measurement techniques for DOC and in understanding the role of DOC in the environment.

There is a huge range of molecule sizes in DOC (Biddanda and Benner, 1997). Most DOC is described as "low molecular weight", or LMW, and has a size range extending up to 1,000 Daltons. An estimated 20-30% of DOC is "high molecular weight" (HMW). This range of sizes poses particular difficulties when separating DOC from particulate organic carbon in seawater. HMW DOC can include "colloidal" DOC which will not settle like particles, but which will also not pass easily through filters.

The operational definition of DOC, as differentiated from particulate organic carbon (POC), is primarily based on size. DOM is whatever goes through a 0.2 (Libby and Wheeler, 1997), 0.45 (Wangersky, 1993), or 0.7 μm GFF filter (Williams, 1995). Colloids, or small particles held in suspension, pose a problem because they are so small and yet they are not fully solubilized. Their typical size is close to our filter pore size. While on the topic of filters, there has been recent discussion over whether the filter material makes a significant difference in the measurement obtained. Some have claimed that DOC will adsorb onto GFF filters, lowering the resulting DOC in the filtrate. Others also argue that the act of filtering itself alters the DOC measurement, claiming that filtering will cause fragile cells to lyse and release their internal DOC into the filtrate (Wangersky, 1993). The definition of DOC is still a topic of discussion.

The huge variation of molecules observed within the DOC pool is also manifest in the chemical reactivity of the molecules, and has major consequences regarding the bioavailability and turnover rate of DOC. Typically, DOC is divided into three separate pools based on turnover rate, though this is a somewhat arbitrary classification method since there is a continuum of turnover rates and the rates depend on factors other than the characteristics of the molecules themselves (such as bacteria abundance). The three pools are: 1) labile, 2) semi-labile, and 3) refractory. Until recently, it was thought that the labile portion of DOC is typically LMW. This has been shown to be incorrect. Typically, the molecules taken up the fastest are large molecules like polysaccharides, which are the least altered from their original "living" state (Amon and Benner, 1996). Labile DOC has a turnover rate of minutes to hours. The semi-labile component

of DOC exists on time scales measured in days to weeks. This portion of DOC often accumulates on a seasonal basis. An example of semi-labile DOC might be a complex carbohydrate. The refractory pool of DOC is fairly uniform throughout the water column, having had plenty of time to become thoroughly mixed without being significantly consumed. Refractory DOC has turnover times measured in years. Most of the refractory DOC is in the form of small molecules that are the unusable (by most bacteria) degradation products of larger biomolecules (Amon and Benner, 1996). Some of the refractory DOC in the ocean is thought to have a residence time in excess of 6,000 years (Bauer et al, 1992).

New techniques for determining the specific molecular structures present in DOM are being used more frequently. Specifically, nuclear magnetic resonance (NMR), High Pressure Liquid Chromatography (HPLC), and various forms of mass spectroscopy (MS) are currently in use. These techniques can be used to determine what kinds of products are being released by phytoplankton and give insight into the role that the DOM might play as it becomes available to bacteria.

2.1.2.2 DOC Distribution Patterns

The fact that DOC has been difficult to study in the past has resulted in more attention being paid to other pools of carbon in the ocean. The amount of attention given DOC has not been proportional to it importance and abundance in the ocean. In fact, the DOC pool is the second largest pool of carbon in the ocean. Figure 2.1 shows the dissolved organic pool of carbon in seawater as much smaller than the dissolved inorganic pool, but at 1,000 BMT (billion metric tons), still much larger than the particulate pools which total only 33 BMT.

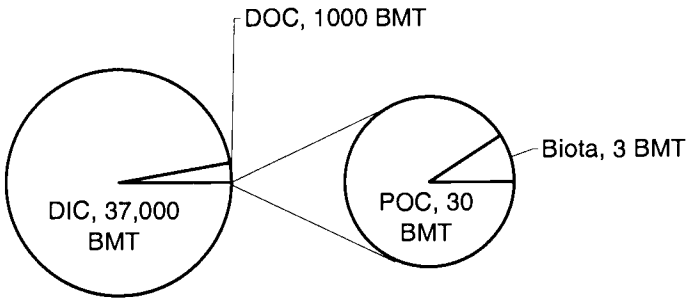

Figure 2.1 Relative sizes of marine carbon pools. (Data from Libes, 1992.)

Researchers have observed higher DOC than POC in nearly all ocean regions, both coastal (Williams, 1995) and oceanic (Carlson et al., 1994). It is a common assumption that DOM will account for 90% of all organic matter in oceanic waters (Wheeler et al., 1997). However, there are exceptions. A recent study of bloom dynamics in the Ross Sea revealed that POC was nearly an order of magnitude higher than DOC (Carlson et al., 1998). Also, studies in the Arctic Ocean (Wheeler et al., 1997) and Bering Sea (Agatova et al., 1995) have demonstrated situations where POM and DOM occurred in similar distributions.

DOC is typically highest in surface waters (Carlson and Ducklow, 1995, Williams, 1995). This is likely due to the fact that the sources of DOC, which are biological, are concentrated in the euphotic zone (Biddanda and Benner, 1997). As previously stated, the refractory component of DOC has a fairly uniform distribution in the ocean. The excess DOC in surface waters is therefore composed of the labile and semi-labile components of DOC.

DOC has been shown to be concentrated in the proximity of upwelling regions. Often the association is not perfect. DOC is commonly highest downstream from very intense upwelling zones (Carlson and Ducklow, 1995, Peltzer and Hayward, 1996). Typically the DOC concentration in deep water is low, around 40 or 50 μM. So the relationship between upwelling

and high DOC cannot be a direct one. There must be an indirect reason for the correlation and it seems assured that this is biological in nature. Phytoplankton blooms often occur following upwelling. As inorganic carbon is fixed, the potential for the release of organic carbon is increased (Carlson and Ducklow, 1995, Chen et al., 1995).

DOC concentrations are usually higher near coastlines. Rivers typically contain DOC at concentrations 1 to 2 orders of magnitude higher than in seawater, and so are important sources of DOC to coastal waters (Maybeck, 1982). The DOM in river water has been leached from the soil in the river's drainage basin or is the product of biological activity in the lakes and streams feeding the river (Spitzy and Leenheer, 1991). Studies in the Bothnian Sea have shown a significant correlation between river flow rates and the mean DOC concentration at nearshore study sites (Zweifel et al., 1995). Biological activity in estuaries, intertidal zones, and subtidal zones often contributes significantly to DOC as well. According to Raffaelli and Hawkins (1996), as much as 40% of macroalgal production is lost directly to DOC. DOC in seawater can be as high as 1000 to 10,000 μM near algal mats (Schramm, 1991).

There is large temporal variation in the distribution of DOC. Carlson et al. (1994), in their studies of the Sargasso Sea, observed a spring and summer increase in DOC followed by a decrease in the fall. Reasons for such increases and decreases can be either changes in biological activity or the result of hydrography that also follows distinct seasonal patterns in many parts of the ocean. Precipitation over land can also increase riverine input of DOC on a seasonal basis (Zweifel et al., 1995). This is especially important at high latitudes which experience larger seasonal changes in precipitation and runoff than lower latitudes.

As previously mentioned, biological processes in the ocean seem to influence DOC concentration. It has been estimated that "5-30% of marine primary production is directly released as DOM by phytoplankton" (Biddanda and Benner, 1997). This increase seems logical, but some evidence suggests that DOC might also be removed from seawater as phytoplankton abundance increases. DOC (especially the larger forms which are often classed as "colloids") is

"sticky" and tends to coagulate with solutes, colloids, and larger particles, both non-living and living. This coagulation process results in the formation of polymer gels, also known as "marine snow" in its larger forms (Honeyman and Santschi, 1992, Chin et al., 1998, Wells, 1998). As the number of phytoplankton in the water increases, so does the surface area to which DOC might adsorb. This idea has been used as an explanation in situations where DOC concentrations are lower than expected, relative to the amount of POC present (Agatova et al., 1995, Wheeler et al., 1997).

DOC tends to vary on time scales related to primary production (Carlson et al., 1994, Zweifel et al., 1995, Chen et al., 1996). The summer increase and fall decrease in surface DOC mimics a similar pattern in phytoplankton biomass. DOC also varies on shorter time scales which have been associated with specific bloom events (Carlson, 1994, Chen et al., 1995, Carlson et al., 1998).

High levels of DOC have been negatively correlated with availability of major nutrients (Zweifel et al., 1995, also references to Ittekkot et al., 1981 and Goldman, 1992 in Carlson et al., 1998, also Williams, 1995) but this is not always the case (Carlson et al., 1998). Zweifel showed strong negative correlation with inorganic phosphate. Carlson and others have hypothesized, in some cases, DOC will not decrease unless sufficient inorganic nutrients are present to sustain organisms that would make use of the DOC. Carlson et al. (1998) also observed in the Ross Sea that DOC was not reduced, in spite of high levels of nutrients, so clearly other factors can be more important than this negative association with inorganic nutrients.

Patterns are clearly evident which link DOC concentration to primary production. But the link is not a direct one. This quote is taken from a 1998 paper by Carlson et al., "Despite four to five fold greater P(rimary)P(roductivity) in the Ross Sea, almost an order of magnitude less DOC accumulated during the Ross Sea bloom compared to that in the Sargasso Sea." Different processes seem to have more or less control over DOC, depending on time and location in the sea. The differences could be due to biolability of DOC produced (less lability leads to

accumulation), uptake and growth characteristics of bacteria present, or differences in the relative importance of DOC sources (Carlson et al., 1998).

DOC is derived from several sources (Carlson and Ducklow, 1995). These sources include direct exudation by phytoplankton and macroalgae, zooplankton excretion, phytoplankton cell lysis after viral infection, sloppy feeding of zooplankton on phytoplankton, dissolution of fecal pellets, and egestion by microzooplankton. And, as previously mentioned, terrestrial runoff can significantly increase DOC in coastal regions. Recent studies are suggesting that the zooplankton involvement in DOC release is more important than previously believed. Strom (1997) showed in laboratory experiments that DOC production due to zooplankton activities should be 4-6 times higher than direct DOC release by phytoplankton, at least in areas where grazing is the primary phytoplankton loss process.

Decreases in DOC are also due to a variety of phenomena. Bacterial consumption, transformation, and remineralization of DOC can decrease the concentration and/or change the nature of the DOC in seawater (Kirchman, 1991). Adsorption of DOC onto particles and colloidal materials can also remove measurable DOC from seawater. Diffusion from and advection of DOC-rich water masses can dilute or move concentrated DOC away from an area being studied. Downward advection is especially important in areas known for downwelling and at times of the year when vertical mixing increases. Lateral advection is an important form of DOC transport, especially near upwelling regions. Past and current studies, such as JGOFS, aim to identify the major sinks for DOC in different ocean regions. Often, the sinks are the same but differ in terms of relative importance (Carlson 1994, Peltzer and Hayward, 1996, Carlson et al., 1998).

In the last twenty years or so, more attention has been paid to the role of bacteria in marine ecosystems. In particular, the "microbial loop" portion of food webs has received much attention. In the microbial loop (Figure 2.2), DOC from the various sources previously mentioned is consumed by bacteria and then these bacteria are consumed by protists and other

small heterotrophs. However, the effectiveness of the microbial community at reducing DOC is highly variable (Carlson et al., 1998, Thingstad et al., 1999).

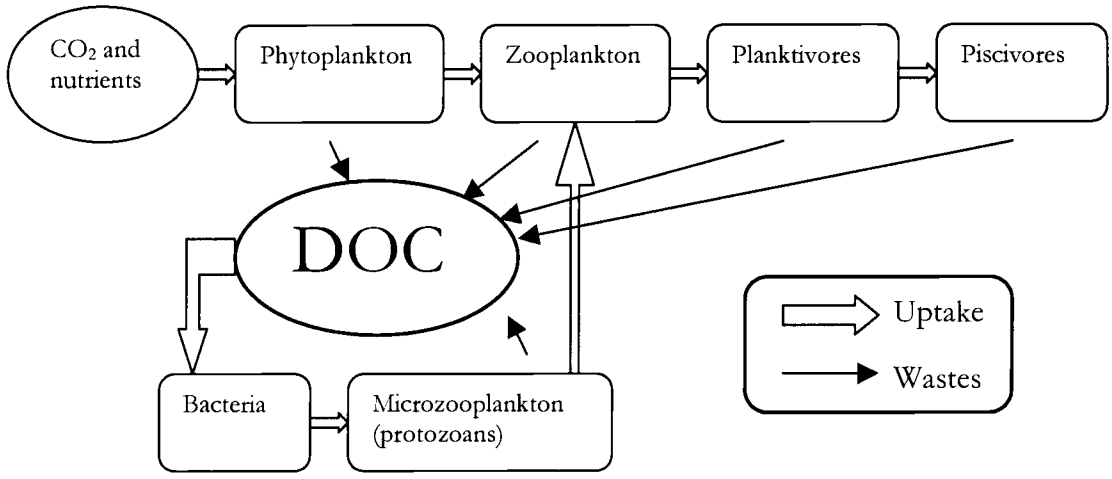

Figure 2.2 The microbial loop. Note the central importance of DOC.

Physical processes can also be effective in removing DOC from surface waters. The traditional carbon pump in the ocean involves particulate carbon sinking out of the euphotic zone. This sinking flux has often been thought to balance new production in surface waters. New consideration given to DOC dynamics could change that view. A very different pump could be present in some places in the ocean, one that does not rely on sinking particles but on downward advection of residual DOC (Carlson et al., 1994, Thingstad et al., 1997). This pump would be especially important in regions where there exists sustained downwelling.

Export of carbon from the surface waters is important to our understanding of the ocean's role in modifying the atmosphere. DOC, as a large pool of carbon, is an eventual reservoir for atmospheric CO_2. As such, a better understanding of DOC and its turnover rates could play a large role in modeling the ocean's ability to buffer changes in atmospheric carbon

(Kirchman, 1991). This ability is of great importance when one considers the climatic effects caused by elevated CO_2 in the atmosphere.

2.1.2.3 Relating DOC and DON

Measuring both DOC and DON can provide very useful information about the nature of the DOM being produced or consumed in an environment. DON is still commonly measured using wet-chemical techniques. Typically particulate organic matter (POM) has the standard Redfield C:N ratio of 6.6. Often the C:N ratio in DOM is higher, commonly ranging from 8 to 20 (Williams, 1995, Chen et al., 1996). Variation in this ratio could depend on the biolability of the DOM or it could depend on what types of DOM are being released. Biolability (or bioreactivity) refers to the rate at which a substance is utilized by bacteria. Amon and Benner (1996) have shown that HMW POM, especially those forms with high C:N ratios (like polysaccharides) are taken up more quickly than LMW DOM.

The C:N ratio is typically lower in LMW DOM than in HMW DOM. Biddanda and Benner (1997) report that in culture studies of four different phytoplankton species, LMW DOM had a C:N ratio ranging from 3-11. They also found a range of 19-25 for the C:N ratio in HMW DOM. This somewhat higher than the range of C:N ratios seen in HMW DOM in the ocean which is 15-22 (Benner et al., 1992).

Lab experiments have also shown large differences in the C:N ratio of DOM produced depending on the species of phytoplankton observed. For example, Biddanda and Benner(1997) found that the cyanobacteria *Synechococcus* produced DOM with a C:N ratio of 4.1 while a diatom in the genus *Skeletonema* produced DOM with a C:N ratio of 14.1.

Earlier in this chapter a negative correlation in the concentrations of DOC and inorganic nutrients was mentioned. Heterotrophic bacteria often will use DOC but rely on inorganic nutrients at the same time (Zweifel et al., 1995). This can result in an accumulation of carbon rich

DOC if nutrients are limiting. This will also cause C:N ratios to shift and provides a mechanism for the uncoupling of DOC and DON cycling (Williams, 1995, Biddanda and Benner, 1997).

2.2 Oregon Coastal Ocean Dynamics

The coastal ocean off Oregon and southern Washington is a complex region, oceanographically. It is dynamic and most patterns are transitory. Water in the surface layer can come from any of four sources: rain, horizontal advection, rivers, and upwelling. The last two are what make our study area different from other regions, and so, they will be the main focus of this summary.

2.2.1 Currents

The major current in the region is the southward-flowing, wind-driven California Current which exists at middle-depths and at the surface over the continental shelf. This current is also often referred to as the "coastal jet" (Figure 2.3). The California Current is highly seasonal and can stall or even reverse in the winter. During the summer, when the current is strongest, the southward flow can progress at a rate of 25 cm/sec at the core of the current. The maximum flow often occurs between 15 and 20 km from shore (Kundu and Allen, 1976, Huyer, 1983).

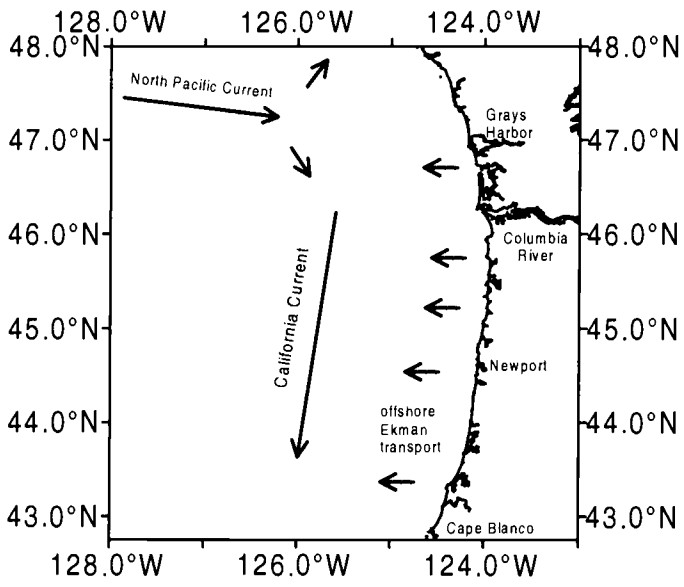

Figure 2.3 A depiction of the surface ocean currents off the Oregon coast in the upwelling season.

The North Pacific Current (or West Wind Drift) also contributes water to the region as it flows eastward across the north Pacific and splits to the north and south as it nears the North American continent. The water in this current is nutrient-poor, biologically unproductive, and of lower salinity than upwelled water along the coast. The current flows year-round being sustained by both summer and winter wind patterns over the Pacific. The effects of this current are most strongly felt outside of the coastal jet (Figure 2.3).

The third current worth mentioning, but which has little bearing on this study, is a poleward undercurrent, known as the Davidson Current (Figure 2.4). It is another current running parallel to the coast, but it lies beneath the California Current and flows northward. This current flows at around 5 cm/sec (Huyer, Pillsbury, and Smith, 1975a). This current strengthens enough in the winter to transport significant numbers of grazers of species typically seen off the California coast to Oregon waters (Peterson and Miller, 1975, Peterson, 1999).

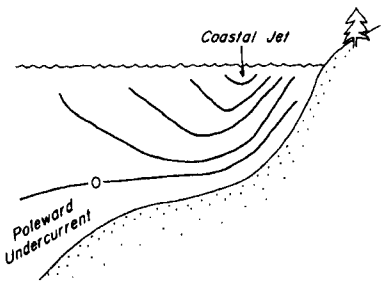

Figure 2.4 Cross sectional view of the alongshore currents off the Oregon coast during the upwelling season. The Coastal Jet flows southward. (Adapted from Huyer, 1983. Used with permission.)

2.2.2 *Upwelling*

Upwelling is vertical advection of deep water toward the surface. Along the Oregon coast, upwelling can occur at any time of year in response to upwelling-favorable winds. These winds are out of the north and create offshore transport of water in the upper 20 meters via Ekman transport. As surface waters move offshore, deep water is drawn upward to replace the water along the coast (Figure 2.5). The direct results are cooler sea surface temperatures, increased surface salinity, and increased nutrients in the photic zone. The indirect result is increased primary productivity.

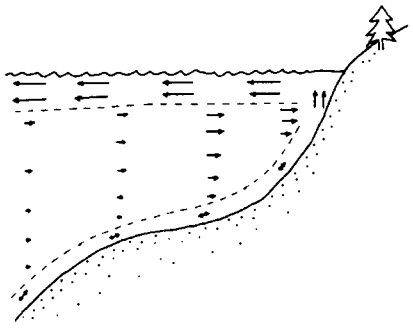

Figure 2.5 Diagram of the single-cell upwelling model for the Oregon coast.

Wind can blow out of the north at any time of the year along the Oregon coast. However, it is much more common during the months of April through October when a high-pressure cell is positioned over the northeast Pacific (Figure 2.6). This cell results in steady winds off California, but transitory winds off Washington and Oregon. As a consequence, California coastal waters have strong sustained upwelling through most of its upwelling season, but Oregon and Washington exhibit upwelling "events." In a typical year, 5 or 6 major upwelling events lasting on time scales measured in days to weeks will occur. These events are often followed by phytoplankton blooms initiated by increased nutrients in the euphotic layer.

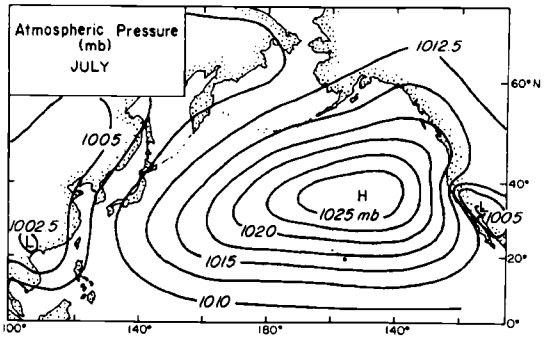

Figure 2.6 General pattern of atmospheric pressure over the north Pacific during the summer months. (Anonymous, 1961)

2.2.3 *Influence of Rivers*

Several small rivers empty into Oregon's coastal waters. Their influence on the hydrography is greatest in the nearshore zone during the winter and spring. This is for two reasons: 1) in winter, the net onshore-offshore circulation is toward the shore, so the fresh water is held there, and 2) runoff is increased due to increased precipitation in the winter and snowmelt in the spring. In summer, when net flow is offshore, the input of freshwater is insignificant and quickly mixed into obscurity.

Dwarfing the influence of all the small rivers combined is that of the Columbia River. Like the small rivers, in winter fresh water from the Columbia will "pile up" against the shore of northern Oregon and southern Washington. But even in summer, the flow of this river is enough to be clearly observed as a freshwater "plume" extending from the mouth southward and away from the shore. The direction of the plume is guided by two features already mentioned, the California current and offshore Ekman transport in the upper 20 meters of the water column over the shelf. Being fresh and less dense, the river water resists mixing and can be observed as a "lens" of relatively fresh water floating above the saltier sea water (Figure 2.7).

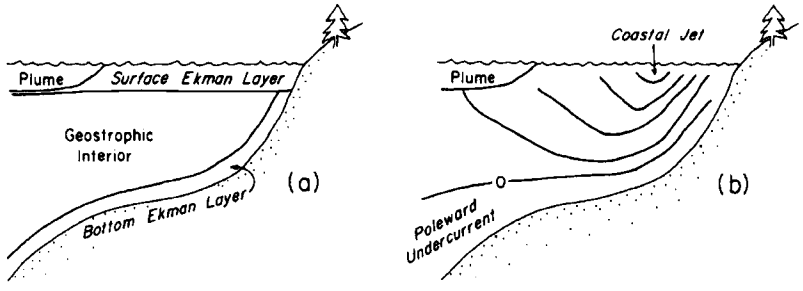

Figure 2.7 Diagram showing the position of the Columbia River water "lens" in relation to the a) surface Ekman layer and b) the southward-flowing coastal jet. (Adapted from Huyer, 1983. Used with permission.)

2.2.4 Effects of El Niño

Typically, the effects of an El Niño event would not need to be discussed in a thesis of this nature. However, it just so happens that nearly all of the data presented later in this work were collected during what could prove to be the strongest El Niño event on record. Certainly, the conditions were altered further from normal than they were even during the exceptionally strong 1982-83 El Niño event. Perhaps the most evident change was observed in the sea temperatures. During the summer of 1997, offshore sea surface temperatures were as much as 3°C higher than normal, and even mid-water temperatures over the shelf were >1°C higher than normal. High temperatures continued throughout the entire study period (Smith et al., 1998).

The 1997 upwelling season was especially weak, also a probable result of altered weather patterns in response to El Niño conditions. Upwelling was nearly non-existent during the period from May through mid-July in 1997 (Peterson, 1999), when it is often the strongest in normal years. Even in June of 1998, upwelling was weak. Isopleths sloped upwards toward the coast, but were not as steep as normal for that time of year (Smith et al., 1998).

It is likely that our measurements of biological and chemical parameters were significantly altered by the occurrence of the 1997-1998 El Niño event. This is both good and bad for the study. It is unfortunate that we cannot make many statements about the distribution of DOM under normal conditions. At the same time, it was very lucky that we timed our sampling to coincide with such a strong event. Future researchers will have the advantage of our data to make comparisons with their data collected under normal or weaker El Niño conditions.

3 The July 1997 Wide Spatial Survey of DOM Near the Sea Surface off Oregon and Washington

3.1 Purpose of the Wide Spatial Survey

The distribution of dissolved organic material in the waters off the Oregon coast has not received much attention prior to this study. Our goal was to describe this distribution in both space and time and to begin looking at possible correlation between DOM concentrations and other biological, chemical, physical, and geological properties and patterns. To accomplish this task, we decided to conduct our study in two parts. The first was a wide spatial study conducted over a period of around two weeks which focused on patterns in the surface waters off the coasts of southern Washington and Oregon. The second part of the study was a time series lasting one year that focused on seasonal changes in the depth profile of DOM at a site near Newport, Oregon. This chapter will describe the first part of the study. Chapter 4 will deal with the time series study.

3.2 Methods

Our initial study took place between the dates of July 9 and July 21, 1997. Samples were collected in conjunction with a National Marine Fisheries Service (NMFS) project led by Bob Emmett using the NMFS research vessel *Sea Otter*. Physical properties of the upper water column were measured by the NMFS researchers. Some of these data will be presented here. The NMFS team also collected zooplankton and chlorophyll samples. Most of the chlorophyll data presented in this chapter is from their work.

3.2.1 Where We Collected Samples

Samples were collected along eleven transects extending westward from the coast (Figure 3.1). The transects varied in length, most extending from the coast to approximately 190 kilometers offshore. The northernmost transect was near Grays Harbor, Washington and the southernmost transect was near Cape Blanco, Oregon, giving a north-south range of 450 km. We started collecting samples from the northernmost sites and proceeded south as each transect was completed. Samples were not collected at a specified time of day, but were collected as soon as we reached each site, regardless of the hour. Appendix A contains a log of station locations and indicates the date on which each station was visited.

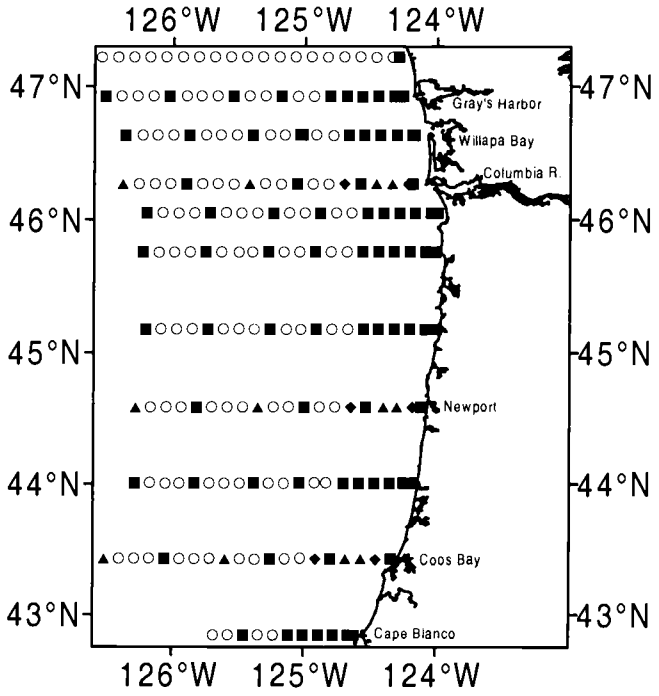

Figure 3.1 Sampling map for the July 1997 study. Depth profiles of seven or more samples were taken at sites marked with closed diamonds. Closed triangles denote sites where samples from only 3 or 4 depths were collected. At the closed squares, only 3 meter samples were collected. Open circles show where only CTD data are available (no chlorophyll, carbon, or nitrogen data).

3.2.2 Seawater Collection

Water samples were collected from 3 meters below the surface using a Niskin bottle. The water was immediately filtered through 335 μM Nitex screen to remove debris and zooplankton from the sample. The pre-filtered water was then stored in 1-liter polycarbonate bottles from which various subsamples were collected. All subsamples were processed and stored within 6 hours of collection. Most were processed within one hour. Samples waiting to be processed were kept cold in covered coolers. Subsamples from the pre-filtered water included chlorophyll, total organic carbon, particulate organic carbon/nitrogen, total nitrogen, and nutrients.

3.2.3 Chlorophyll

The chlorophyll data in this study are actually from two sources. All of the chlorophyll samples taken from 3 meters depth were collected and analyzed by the NMFS team. At a few stations (see Figure 3.1), chlorophyll samples were collected from between three and seven depths and were analyzed by the author.

For the 3 meter samples, one sample (no replicates) from each station was collected. 100 ml of seawater was filtered on pre-combusted 25mm Whatman™ GF/F filters using vacuum filtration. The filters were then stored in plastic centrifuge tubes and kept frozen, awaiting processing on shore following the cruise. On shore, pigments were extracted in 90% HPLC grade acetone in DIW for at least twelve hours in a dark freezer before measuring sample fluorescence. Chlorophyll-*a* was calculated from these fluorescence measurements.

The depth profile samples analyzed by the author were processed using a method very similar to that described above, with only two differences. First, duplicate samples were collected

instead of single samples. Second, the filters were stored in glass Vacutainers™ and were transferred to plastic centrifuge tubes just prior to the extraction step.

Fluorescence was measured using Turner Designs™ Model 10-AU fluorometers. The instruments were calibrated less than 2 months prior to our study using Sigma® chlorophyll-*a* powdered standard dissolved in HPLC grade acetone. The calibration was confirmed daily using a preparation of Sigma™ coproporphyrin in HPLC grade acetone and an acetone blank.

3.2.4 Particulates

Particulate material was also collected on 25mm GF/F filters using vacuum filtration. A volume of 500 ml seawater was filtered for each station. The filters were frozen immediately following filtration. After fuming with sulfuric acid (to remove calcium carbonate) and drying, the filters were analyzed using a Carlo Erba™ CNS analyzer to provide particulate organic carbon (POC) and particulate organic nitrogen (PON) concentrations.

3.2.5 Nutrients

Nutrient samples were filtered through 25mm GF/F filter using a syringe and filter holder. Duplicated samples of approximately 20 ml were stored in HDPE bottles and frozen. The samples were later analyzed for nitrate, nitrite, ammonium, silicate, and phosphate using an autoanalyzer (Atlas et al., 1971). Usually only one of the two samples was measured. The duplicate samples were reserved for confirmation of suspect values.

3.2.6 Total Nitrogen

Total nitrogen (TN) samples were collected and measured in triplicate. Ten milliliters of seawater were transferred by pipette into 60 ml HDPE bottles. These samples were frozen until

analysis. Organic nitrogen was converted to nitrate using a persulfate wet oxidation method (Libby and Wheeler, 1997). Total nitrogen was measured using a single channel autoanalyzer.

3.2.7 Total Organic Carbon

Triplicate total organic carbon (TOC) samples were collected in 8 ml borosilicate vials with Teflon cap liners. Each vial contained 5 ml seawater and was preserved by adding 50ml of 90% phosphoric acid. The samples were then stored at room temperature. Later the samples were analyzed using the High Temperature catalytic Combustion (HTC) method on a Shimadzu TOC-500 analyzer. Prior to analysis, the samples were sparged for 5 minutes using 0.1 grade (ultra-low CO_2) compressed air for the purpose of removing inorganic carbon.

The TOC analyzer was calibrated daily using a DIW blank and four concentrations of an acid potassium pthalate standard solution. A stock solution was kept refrigerated and diluted each day to make the working calibrations standards. After the initial calibration, a deep water sample of known TOC concentration was used to test the accuracy of the calibration. Three subsamples of 60 μL were taken from each of the samples and injected in sequence once the calibration was completed. Standards were injected after every six samples (18 subsample injections) to check for slope and baseline shifts. Using these calibration methods, we saw less than 1% variance among injections from the same sample vial and less than 5% variance among triplicate sample vials.

3.2.8 DON

Dissolved organic nitrogen (DON) was determined by subtracting our values for particulate organic nitrogen (PON) and inorganic nitrogen (nutrients) from our TN values, as expressed in Equation 3.1.

$$DON = TN - PON - Nutrients \quad (3.1)$$

3.2.9 DOC

The concentration of dissolved organic carbon (DOC) was determined by difference, using the TOC and POC measurements, as shown in Equation 3.2.

$$DOC = TOC - POC \quad (3.2)$$

Other researchers have taken a more direct approach to measuring DOC, filtering seawater to remove particulates and measuring the organic carbon in the filtrate. Recent experiments by Karl et al. (1998) have shown that this method can be confounded by adsorption of DOC onto GF/F filters. This is less of a problem if the volume filtered is very large because the filters become saturated with DOC and cease to adsorb DOC. The same problem can occur when measuring POC. DOC can accumulate on the filter and give erroneously high POC values. The solution is the same, i.e. minimize the relative error by filtering large volumes. Time and equipment constraints limited our ability to filter large volumes for both DOC and POC, so we opted to filter large volumes for POC (a necessity for the method we employed) and relied on a difference method for determining DOC.

3.2.10 Physical Oceanographic Data Collection

Physical data were collected using a pumped SeaBird Model 19 CTD. Collection and processing of the physical data was completed by the NMFS team. A subset of the physical data will be presented later in this chapter. Sea surface temperature data were also collected in situ using a standard mercury thermometer. An accident with the CTD during the transect at 44.6°N

caused all of the CTD data for that line to be lost. Another cruise, led by Dr. Jack Barth of OSU, collected CTD data from the same general area later in the month, July 28-30 (R/V Wecoma, cruise number W9707b, data unpublished). These data have been used in the place of the lost data from the first trip.

3.2.11 Data Processing

Data were most often entered directly into Microsoft Excel™ spreadsheets designed for each specific measurement and method. Once entered and screened for anomalous entries or results, the data was organized into summary sheets. These were then linked to other spreadsheets containing related data and/or sampling logs using Microsoft Access™. After linking, the data were exported as Excel™ files appropriate for graphing. The data are also presented at the end of this thesis in Appendix A.

3.2.12 Graphical Output

Because of the wide variety and large quantity of data involved in this project, finding suitable methods of graphical display was a critical step. Where scatter plots and line graphs sufficed, MS Excel™ was used. However, much of the data is best observed as 2-dimensional surface plots, similar in a ppearance to topographic maps. "Surfer™," by Golden Software™ possessed the features I needed and has proved to be a very user-friendly software package for oceanographic data. Any original plots of surfaces included in this thesis were created with Surfer™. The interpolation method used on all surface plots was "kriging".

3.3 Results and Discussion

The data set resulting from our wide area coverage has proven to be of good quality, indicating the presence of several interesting spatial features in the properties we measured. While the precision in some cases is not as high as could be wished for, especially in the case of our TOC measurements, the data is certainly of high enough quality to depict the large features discussed here. The combination of oceanic currents from the west, winds from the north, offshore flow of upwelled water along portions of the coast, and riverine inputs along the northern coast can make explanations for organic matter distributions complex and uncertain. Based on the data gathered in this study, explanations for POM distributions are fairly intuitive. The distributions of the DOM fractions are much more difficult to explain. The problem of explanation is further confounded with the fact that this study was conducted during a strong El Niño event. Hence, any explanation put forth, even if correct for July 1997, may not apply under more representative conditions.

3.3.1 Carbon Distributions and Related Measurements

Figure 3.2 shows the surface distribution of TOC. Three features should be pointed out. First, there is a large area of high TOC just offshore and to the south of the mouth of the Columbia River. The highest TOC concentration values in the center of this area are in excess of 200 μM. The second feature of interest is a large patch of relatively TOC-poor (70-100 μM) surface water in the northwest corner of the map. The third feature showing up in this map is a smaller patch of TOC-enriched (>140 μM) water near 43.5°N which is located offshore and is separated from the nearshore waters by an area with lower TOC concentration.

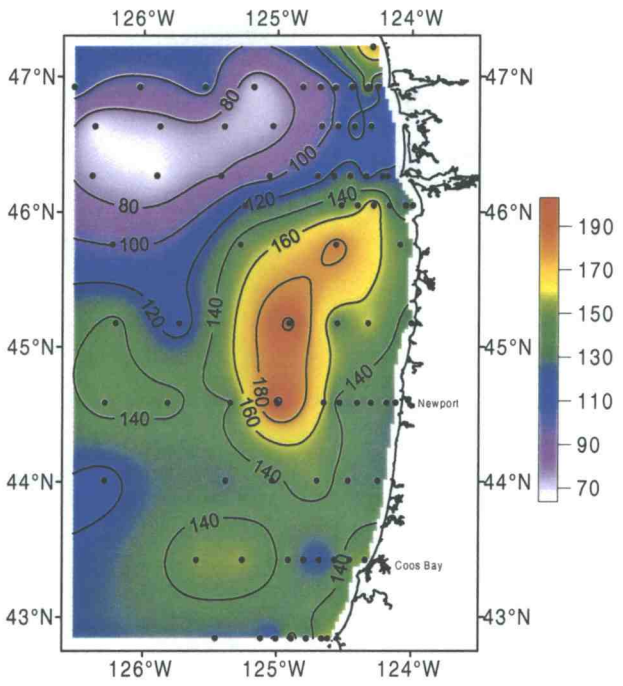

Figure 3.2 Distribution of total organic carbon in the surface waters off Oregon and southern Washington during July, 1997.

3.3.1.1 The Columbia River Plume

The patch of high TOC water off the Columbia River suggests that the source of TOC in this area might be related somehow to the freshwater input in the area. Figure 3.3 shows the corresponding salinity data. Salinity for the entire region is lower than expected by about 1 ppt. These results are, however, confirmed by measurements reported in Smith et al. (1998). Water from the river shows up as an area of even lower salinity and appears in generally the same area as the TOC patch. It would appear that the Columbia River "plume" is either a source of high organic carbon or that it modifies the ocean conditions in such a way that TOC increases rapidly in the region.

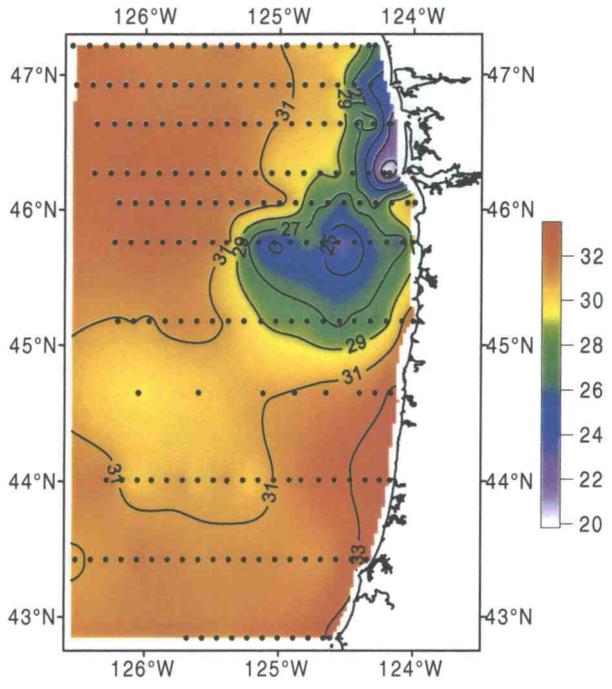

Figure 3.3 Salinity of the surface waters off Oregon and southern Washington during July, 1997.

It is interesting to note that the partitioning of POC and DOC in this plume changes with distance from the mouth of the river. Figure 3.4 shows the POC concentration. The highest POC concentration occurs just around 60 km from the mouth and is approximately 70 μM. POC is also elevated along the southern coast of Washington and in a large feature extending offshore and south at 44°N. This feature will be discussed later in the chapter. In general, POC concentrations were found to be high (30-70 μM) over the continental shelf and low (<30 μM) beyond the shelf break.

Figure 3.5 shows the DOC concentration. Here the highest concentration is further downstream, somewhere between 120 and 190 km from the mouth of the river. The highest DOC values approached 180 μM. In the northern part of the study area we observed significantly lower concentrations, ranging from 50 to 100 μM. Along the southern coast, the levels of DOC were also lower than in the surrounding waters. This area coincides well with newly upwelled

water. This water will be further characterized later in the chapter when nutrient and temperature results are presented.

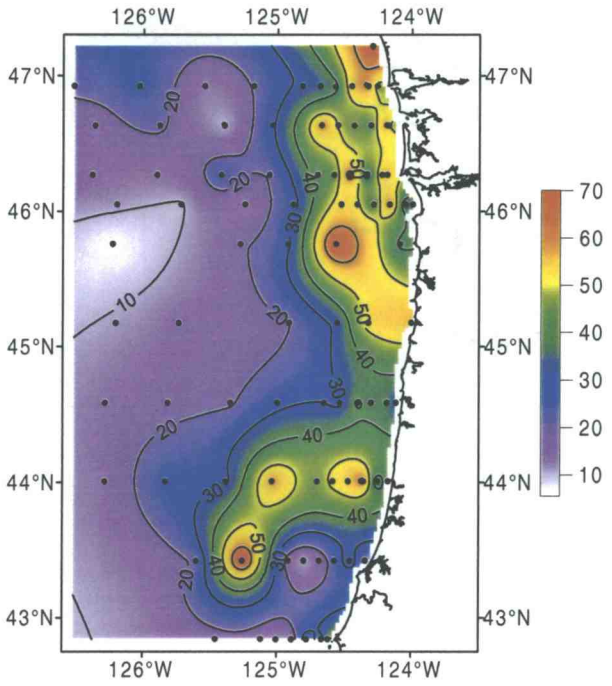

Figure 3.4 Distribution of particulate organic carbon in the surface waters off Oregon and southern Washington during July, 1997.

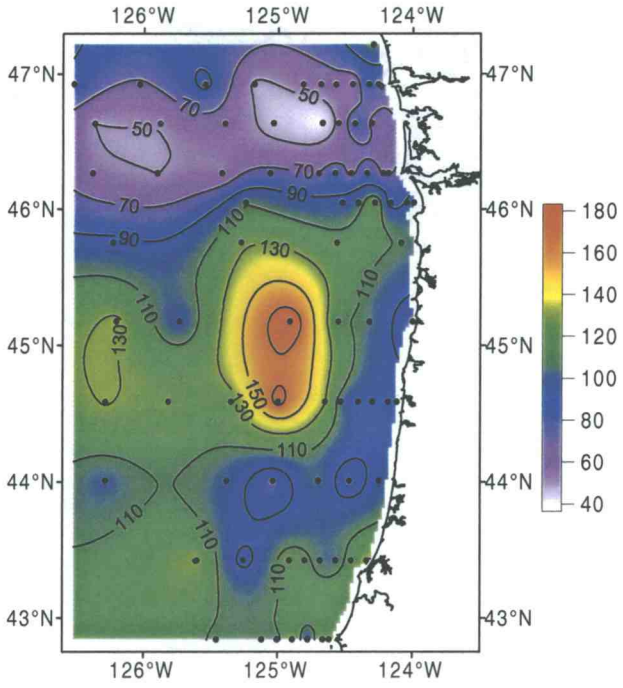

Figure 3.5 Distribution of dissolved organic carbon in the surface waters off Oregon and southern Washington during July, 1997.

3.3.1.2 The Oligotrophic NW Region

The second major feature of the TOC map is the patch of TOC-poor water in the northwest corner of the study area. Figure 2.3 shows the current patterns in this region. The West Wind Drift carries water across the northeast Pacific toward the North American continent where it splits. The large area of TOC-poor surface water is likely derived from this source of oceanic input. The salinity (Figure 3.3) and nutrient (Figure 3.6) maps support this conclusion.

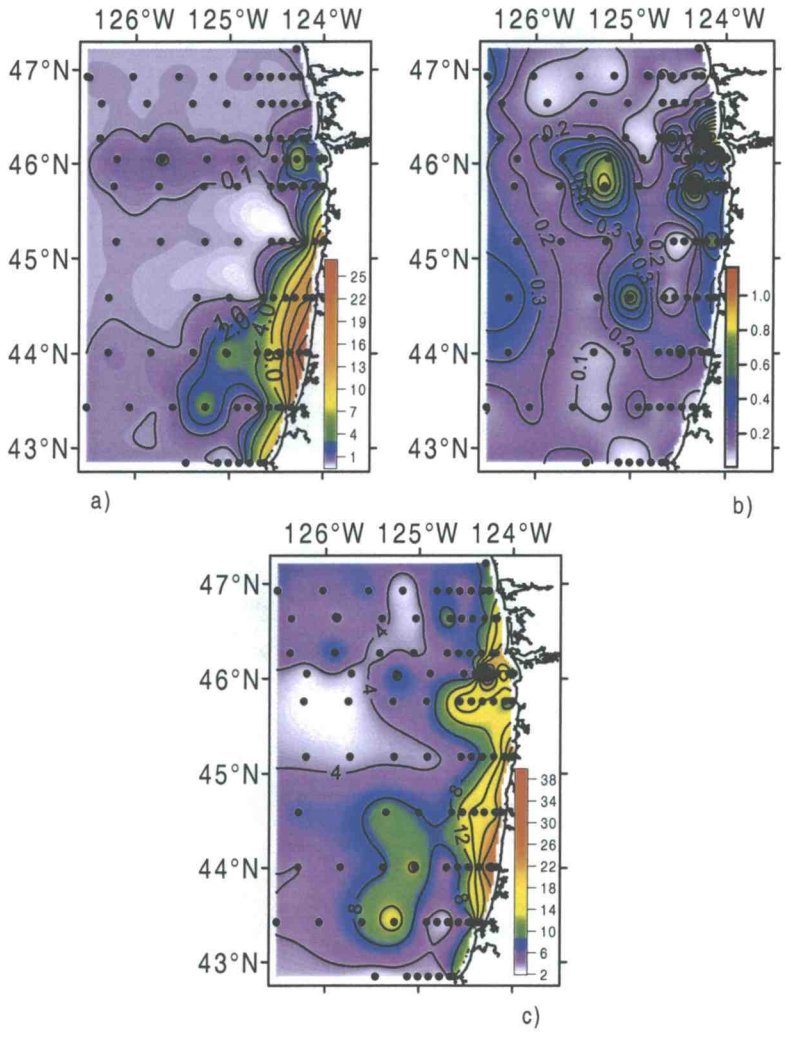

Figure 3.6 Distributions of a)nitrate + nitrite, b) ammonium, and c) silicate in the surface waters off Oregon and southern Washington during July, 1997. All concentrations are given in μM.

3.3.1.3 The Southern Coastal Jet Feature

The third feature of interest in the TOC map is the offshore patch of TOC-enriched water at 43.5°N. Careful inspection of the DOC (Figure 3.5) and POC (Figure 3.4) distributions show that this patch is high in POC but low in DOC. The POC distribution also suggests a

connection with another feature, possibly a deviation in the "coastal jet" originating near the coast around 44°N and extending offshore approximately 80 km before curving to the south. It is thought that this jet is a result of current patterns caused by a widening of the continental shelf in this area. This widening is known as Heceta Bank. Figure 3.7 shows the bathymetry of the study area. The high POC feature is located over Heceta Bank. This feature also shows up clearly in the DOC distribution (Figure 3.5), sea surface temperature (Figure 3.8), chlorophyll a (Figure 3.9), and nitrate + nitrite (Figure 3.6) distributions. The low sea surface temperatures and high nutrients along the coast indicate the presence of seasonal upwelling. From the increases in POC and chlorophyll, it is evident that a bloom is occurring within this jet. The low DOC in the jet is also consistent with water that has been upwelled. Deep water off the Oregon coast typically has DOC concentrations between 40 and 60 μM, significantly lower than what is observed in the waters surrounding the jet feature.

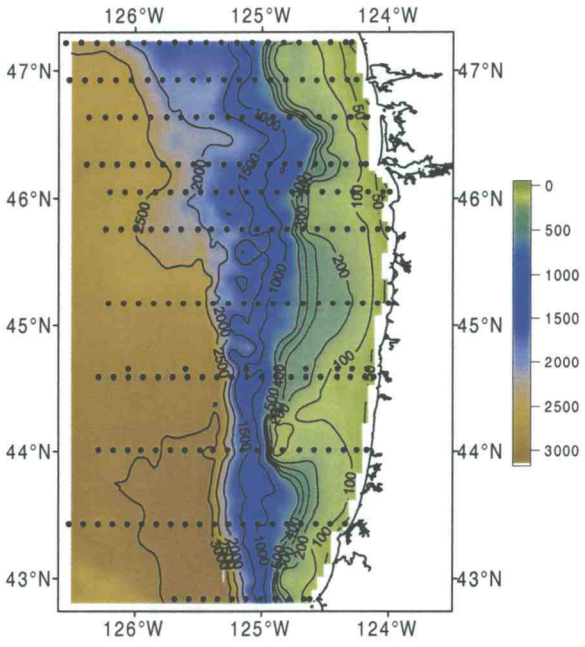

Figure 3.7 Bathymetry (measured in meters) of the July, 1997 study area. The closed circles indicate locations of surface sampling during the study. Data courtesy of Steve Pierce.

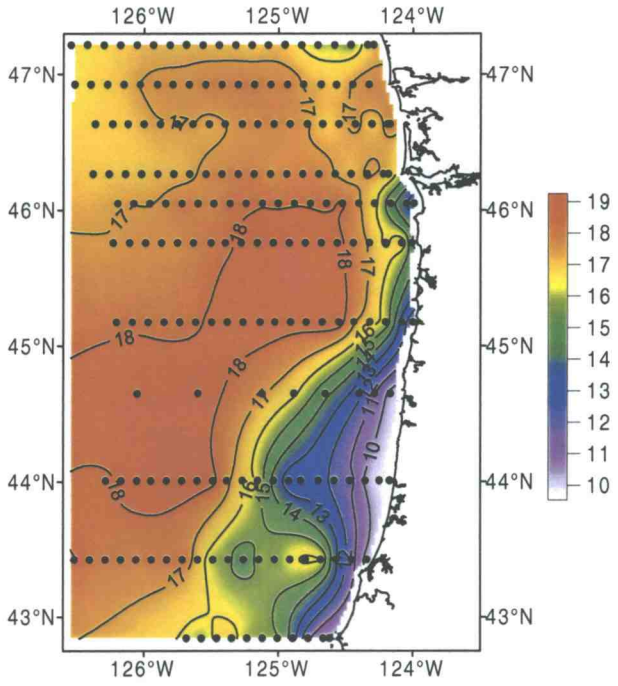

Figure 3.8 Sea surface temperature (°C) of the waters off Oregon and southern Washington during July, 1997.

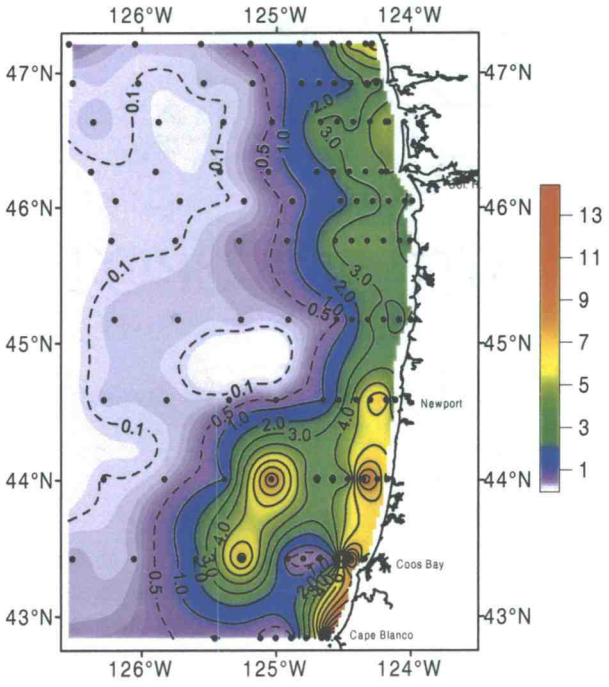

Figure 3.9 Distribution of chlorophyll *a* (μg/L) in the surface waters off Oregon and southern Washington during July, 1997.

One other feature in the POC distribution should be mentioned. The waters off Gray's Harbor and Willapa Bay in the northern part of the study area exhibited high POC levels. Based on the low nutrients and high sea surface temperatures in these waters, it does not appear that this high POC is due to a bloom occurring in response to upwelling. There is slightly elevated chlorophyll in the region, but not on the same level as seen over Heceta Bank. The spring of 1997 was unusually wet, even for the Pacific Northwest, and runoff during the summer was higher than normal. It is possible that this runoff was carrying high levels of terrestrial POC out of the large estuaries along the southern Washington coast. Another possibility also exists. The dominant phytoplankton species could be different along the northern coast compared to the southern coast. Such a difference could account for a different POC/Chl-a ratio. This idea is explored later in the chapter in more detail.

3.3.2 Nitrogen Distributions

Figure 3.10 shows the total nitrogen (TN) distribution for the study area. Nitrogen in the surface waters ranged from less than 4 μM in offshore areas to around 36 μM near the coast where upwelling was strongest, as indicated by sea surface temperature (Figure 3.8).

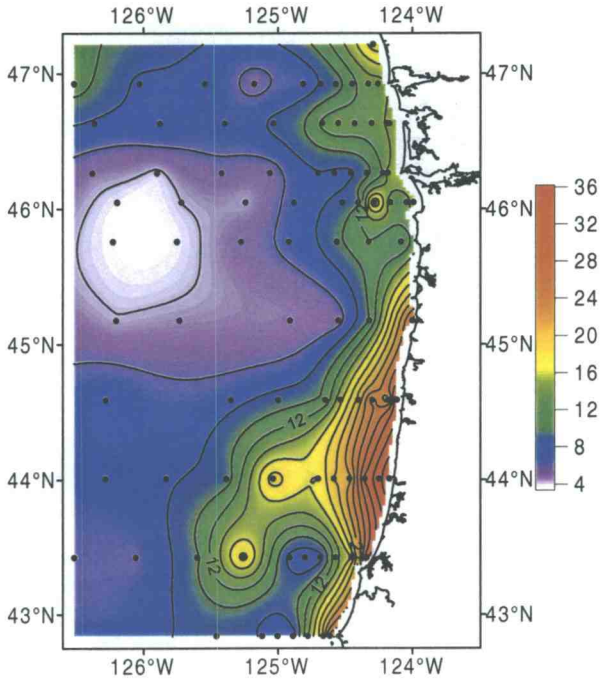

Figure 3.10 Distribution of total nitrogen (μM) in the surface waters off Oregon and southern Washington during July, 1997.

The distribution of nitrate plus nitrite (N+N) shows a pattern almost identical to that observed in the TN distribution. At the center of upwelling, approximately 70% of TN in the surface waters is represented as N+N, or about 26 μM. N+N is also elevated at a station just off of the mouth of the Columbia River. It would appear that these elevated nutrients are the result of a small upwelling center south of the Columbia River mouth. The temperature and salinity distributions support this idea. It is unlikely that the nitrate is from the Columbia River water.

Prahl (1998) shows that the nitrate concentration in the Columbia River during the summer of 1992 was only around 1μM.

Total organic nitrogen (TON) was elevated along the Washington coast and offshore of the upwelling centers along the Oregon coast (Figure 3.11). The fact that a gradient in TON concentration occurs at the major upwelling center reaffirms the idea that a bloom is in progress in the water moving offshore. TON concentrations ranged from less than 3 μM in offshore oceanic waters to more than 13 μM in areas where upwelling-induced blooms occurred. TON was also high off the Washington coast where upwelling did not appear to be happening.

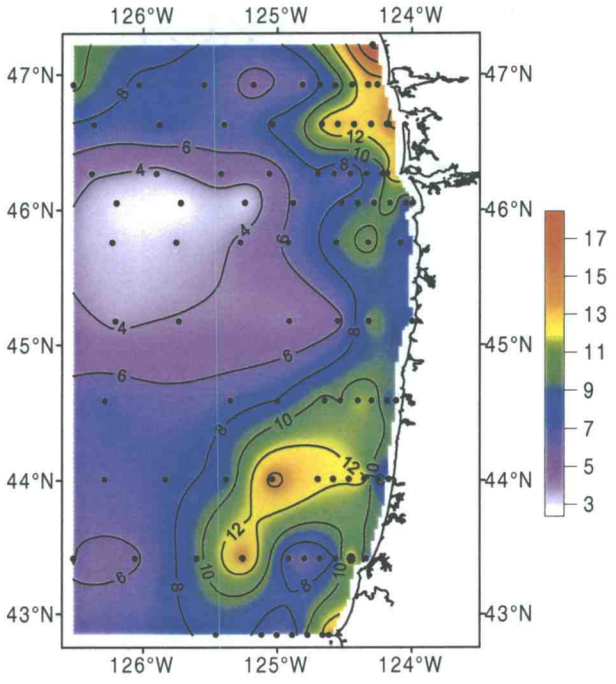

Figure 3.11 Distribution of total organic nitrogen (μM) in the surface waters off Oregon and southern Washington during July, 1997.

Particulate organic nitrogen (PON) exhibited a pattern very similar to that of TON (Figure 3.12). Concentration values ranged from less than 1 μM in offshore waters to more than 8 μM in a few places along the coast. A somewhat surprising feature was located at the coast near

45°N. PON was elevated at this location with but none of the other measured attributes showed a particular feature of any kind in the same location.

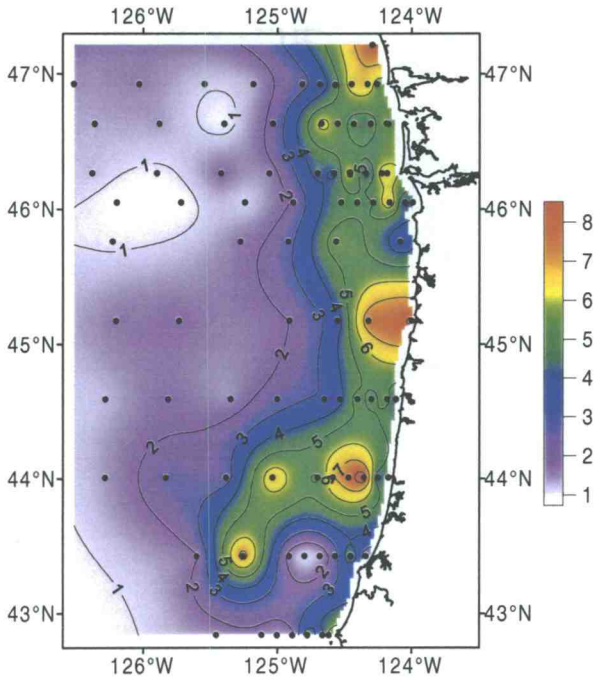

Figure 3.12 Distribution of particulate organic nitrogen (μM) in the surface waters off Oregon and southern Washington during July, 1997.

The distribution of dissolved organic nitrogen (DON) is shown in Figure 3.13. DON was high (>6 μM) along the Washington coast. It was also high (>6 μM) in most of the offshore waters south of 45°N. DON concentration was reduced (<5 μM) at the major upwelling center along the southern Oregon coast (near 44°N), but was high again near the coast at the southern extent of the study area (near 43°N). A large area, from 45°N to around 46.3°N, and from the coast to the offshore extent of the study area, showed low (<4 μM) DON concentrations.

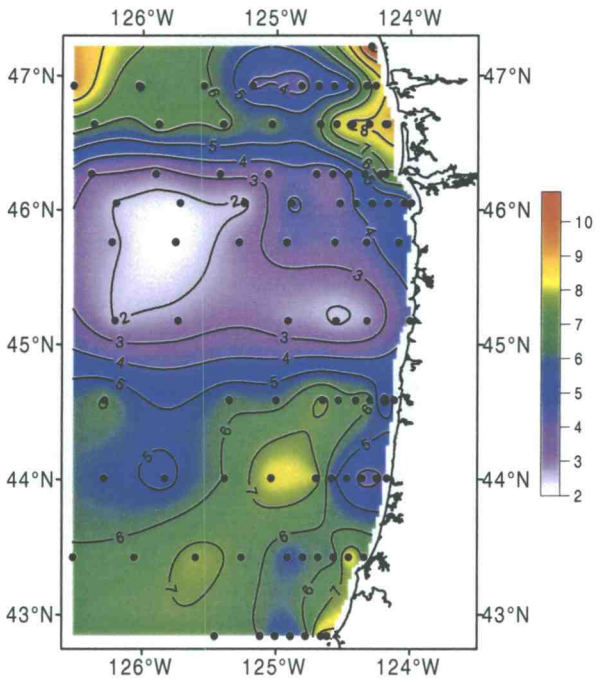

Figure 3.13 Distribution of dissolved organic nitrogen (μM) in the surface waters off Oregon and southern Washington during July, 1997.

3.3.3 Patterns in POM

Particulate organic matter (Figure 3.4 and Figure 3.12) closely follows the distribution of chlorophyll *a* (Figure 3.9), indicating that this particulate matter contains living phytoplankton. Figure 3.14 shows POC vs. Chl-a. The general positive trend is what one would expect in coastal regions where productivity is relatively high. Assuming that particulate samples with both low POC and low Chl-a are primarily detritus, the remaining phytoplankton-dominated samples can be divided into two groups based on their POC/Chl-a ratio. Chan (1980) demonstrated that two diatom species had low POC/Chl-a values (~32 to 35) and that two dinoflagellate species had much higher POC/Chl-a values (~90 to 120). Using 60 as an approximate midpoint between these groups, the samples represented in Figure 3.14 can be described as being dominated by

either diatoms or by flagellates. The living POC along the northern coast would then be mostly flagellates, while the POC along the southern coast, where the nutrients were highest, is likely to be mostly diatoms.

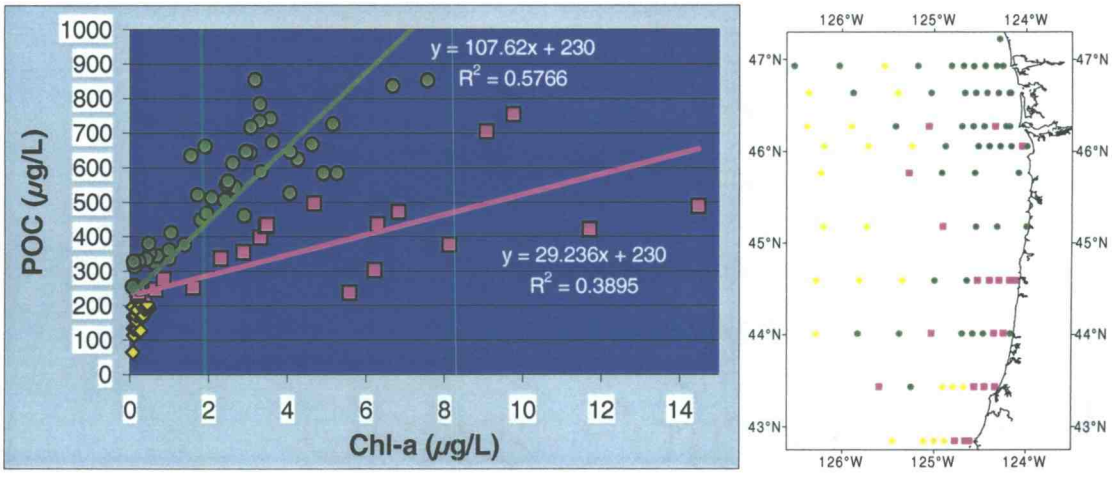

Figure 3.14 POC (µg/L) vs. Chl-a (µg/L). In a scatter plot of POC vs. Chl-a for the July 1997 study, none of the points below 230 µg/l POC (yellow diamonds) showed Chl-a levels above 1 µg/L, suggesting that this might be a natural cutoff for the average amount of detritus in these waters. The remaining points were divided into two groups based on the ratio of POC (minus detritus) to Chl-a. The green circles and fitted green line correspond to those samples with a ratio higher than 60. The pink squares and line correspond to samples having a ratio less than 60. Higher ratios suggest phytoplankton populations dominated by flagellates, while lower ratios suggest domination by diatoms.

The chlorophyll distribution mimics the N+N and temperature distributions (Figure 3.6, Figure 3.8) along the southern coast, indicating that a bloom was occurring in response to upwelling. Based on the data presented in Figure 3.14, it seems likely that this bloom was primarily diatoms. Kokkinakis and Wheeler (1987) demonstrated that netplankton, i.e. diatoms,

are the dominant phytoplankton species off the Oregon coast in regions where nutrients are high, further evidence that the phytoplankton along the south coast are mainly diatoms.

The northern coast poses more of a mystery. Chlorophyll is high, but nutrients are low. This could be the result of a flagellate-dominated system. Smaller phytoplankton species, such as flagellates, tend to fare better in nutrient depleted waters off the Oregon and Washington coasts (Kokkinakis and Wheeler, 1988). This idea is also supported by the POC/Chl-a data in Figure 3.14. There are other possible explanations for the high Chl-a, low nutrient condition along the north coast. The nutrients could have simply been used up by the phytoplankton. It is also possible that plant material has been flushed out of the large estuaries along the southern Washington coast. Such flushing is supported by the low salinity (Figure 3.3) and elevated sea surface temperatures (Figure 3.8) observed. However, without flow rates and organic matter measurements from within those estuaries, it is impossible to attribute the POM and chlorophyll to those sources with any certainty.

The offshore surface waters were almost uniformly low in concentration of POM, but more variability existed in the DOC than in the DON. This is evident in a map of the POC/PON ratio (Figure 3.15). Note that the POC/PON ratio approaches the Redfield C/N ratio of 6.6 near the coast, but also that it is much higher in the offshore regions, especially in the northern oligotrophic waters.

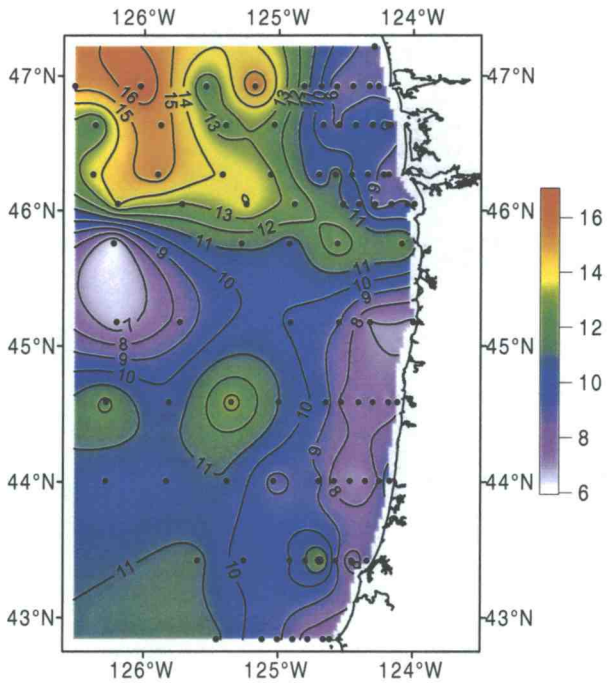

Figure 3.15 POC/PON ratio in the surface waters of the July, 1997 study.

An exception seems to occur at 126°W between 45°N and 46°N. Here the POC/PON ratio is at its lowest, unlike the surrounding waters. The anomaly coincides spatially with a minimum in the POC distribution. However, the exact reason for this minimum is unclear to the author. It is possible that the POC is present but was missed because it is located deeper in the water column. Depth profiles of Chl *a* and POC (Figure 3.16) show that the bulk of the living material in offshore waters is deeper than near the coast, probably due to the reduced nutrients in the surface waters when compared with inshore nutrient depth profiles (Figure 3.17). This might explain the low POC in the 3 meter sample, but it does not explain why the samples contain lower POC than those collected to the north or south of this area.

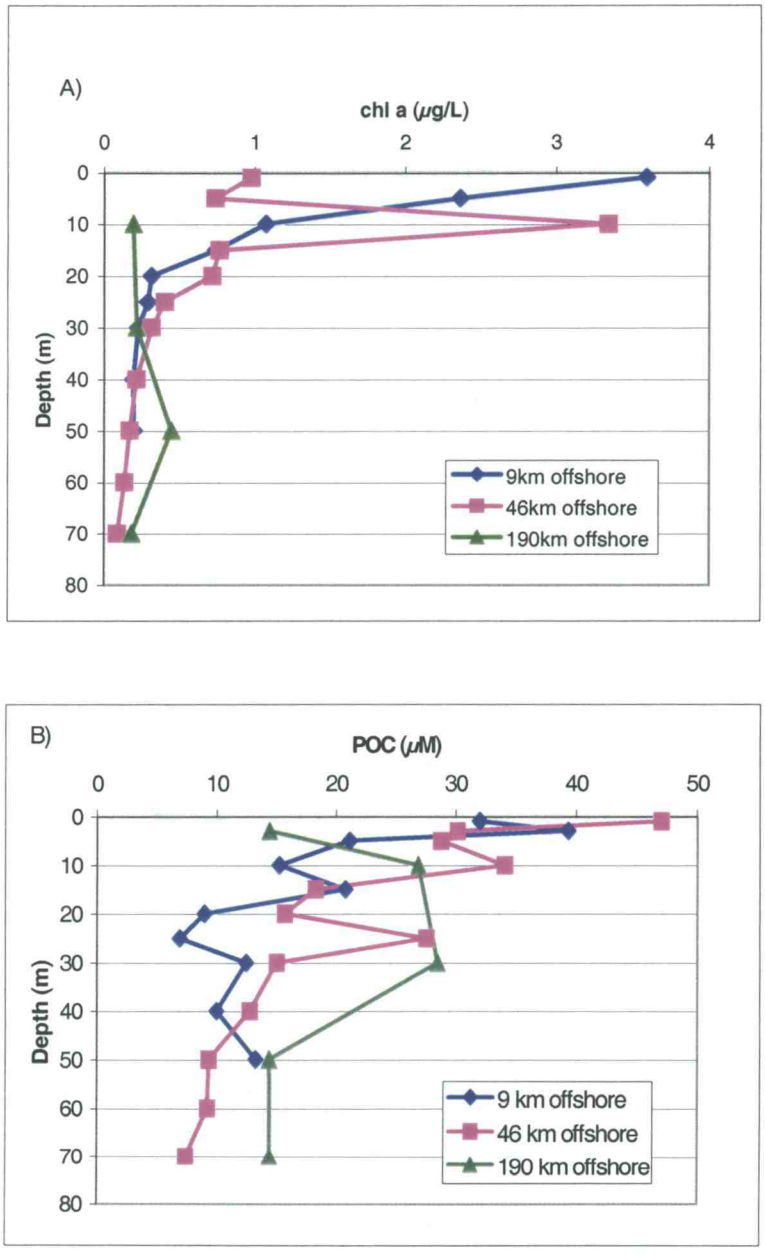

Figure 3.16 Depth profiles of A) chl a, and B) POC, at nearshore and offshore stations along the Newport (NH) transect.

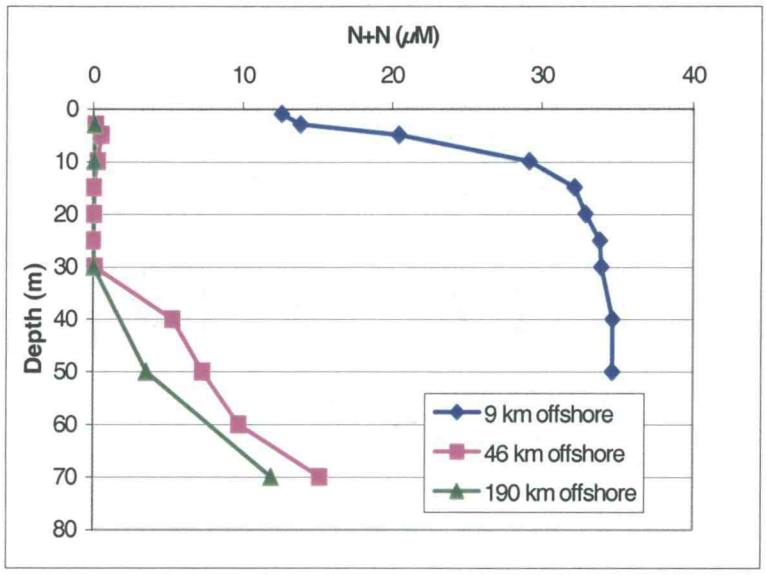

Figure 3.17 Depth profiles nitrate + nitrite (μM) at nearshore and offshore stations along the Newport (NH) transect.

3.3.4 Patterns in DOM

The distribution patterns of DOC and DON are quite different from one another (Figure 3.5 and Figure 3.13). DOC is highest, >180 μM, in the Columbia River plume. At the same location, the DON concentration is near the low end of the range observed, 2 to 4 μM. DOC is lowest, ranging from 40 to 90 μM, north of the Columbia River mouth. Here, DON is high relative to what is seen in the Columbia River plume, ranging from 4 to 8 μM. South of 45°N, both DOC and DON exhibit concentration values in the middle to upper end of their observed ranges. Yet comparison of the actual distribution patterns in this area show few similarities. Figure 3.18 shows DOC plotted against DON for the three regions just mentioned. There is little evidence in any of the regions for a positive or negative correlation between DOC and DON. A positive relationship might occur north of the Columbia River, but this a weak

correlation at best (r^2=0.38). A map of the DOC/DON ratio (Figure 3.19) indicates that the area in the middle of the study area, from around 45°N to 46°N, has a much higher DOC/DON ratio than the rest of the study area. This ratio can be as high as 80 and is higher than 30 throughout this region. Figure 3.18 shows that this is due primarily to low concentrations of DON rather than especially high DOC.

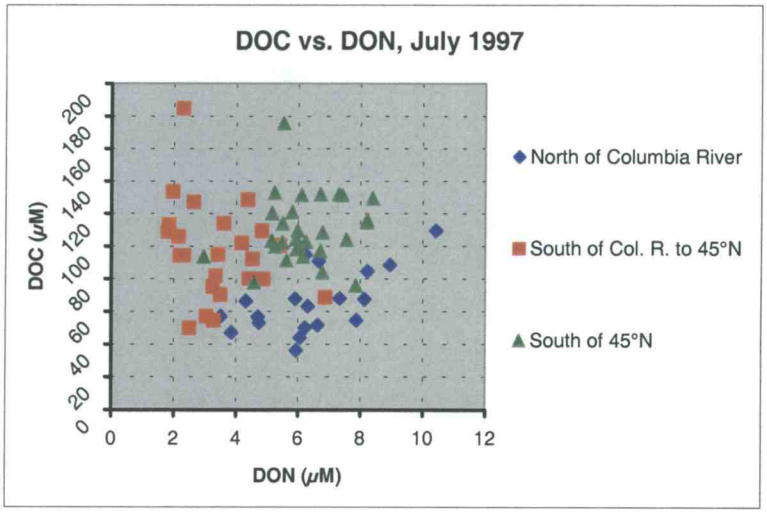

Figure 3.18 DOC vs. DON

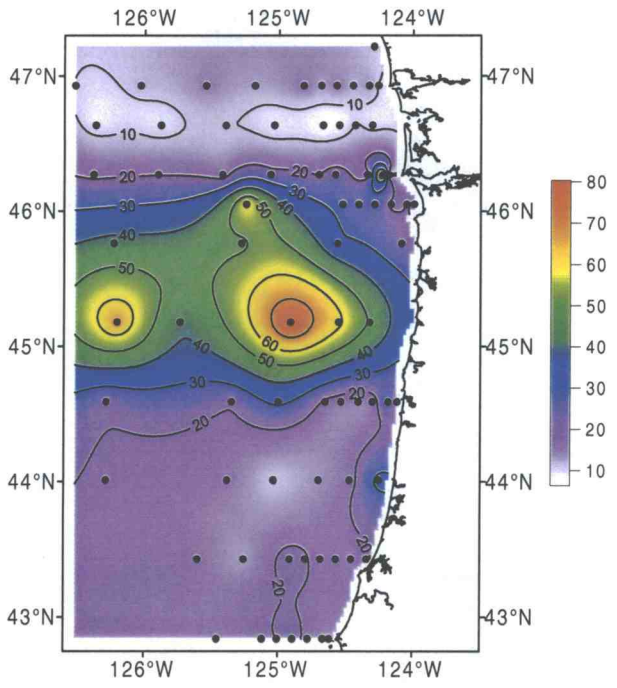

Figure 3.19 DOC/DON ratio in the surface waters of the July, 1997 study.

3.3.5 The C/N Ratio

The mean C/N ratio for surface water DOM for all measurements taken was 21.9. This is much higher than the Redfield value as is typical for DOM (Williams, 1995, Chen et al., 1996). A high C/N ratio was expected, but the ratio here is definitely on the high side compared with values collected by previous researchers (Williams, 1995, Chen et al., 1996). The molecular weight of the DOM we collected was not measured, but the C/N ratio we observed is typical of high molecular weight (HMW) DOM (Biddanda and Benner, 1997). The extremely low DON values in the middle of the study area could be the result of bacterial activity selectively removing biolabile N-rich DOM from the surface layer.

The three regions of particular interest to us (oligotrophic northeast corner, plume, south coast jet feature) each had statistically different C/N ratios in both the POM and DOM samples ($p<.05$, t-test). Figure 3.20 summarizes those values.

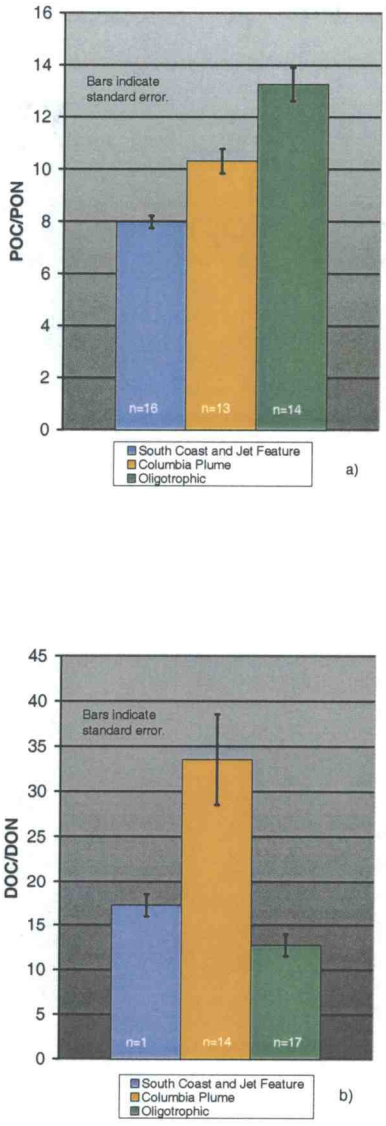

Figure 3.20 C/N ratios for a) POM and b) DOM samples in three regions examined during the July 1997 cruise.

3.3.6 *The Influence of Upwelling*

One of the primary purposes of this research was to identify which physical parameters influence the distribution of DOC off Oregon's coast. From the data presented here, it is clear that upwelling strongly influences the distribution of DOC, both directly and indirectly. Directly, upwelling reduces DOC in surface water near the shore. This is because deep water has low DOC values. This low DOC persists for a time as water is moved offshore.

Figure 3.5 shows DOC remaining low in the coastal jet of water extending offshore and south at 44°N. Indirectly, upwelling should eventually increase DOC concentrations. Upwelling bring nutrients to the surface which causes blooms to occur. As phytoplankton are moved offshore, they release DOC. This idea is supported by the generally high levels of DOC in the waters to the west of upwelling zones in our study area.

3.3.7 *The Influence of the Columbia River*

Riverine inputs were also expected to play a large role in the DOC distribution. The large plume of TOC extending from the Columbia River mouth, at first glance, might seem to indicate that the Columbia River is dumping a large amount of organic carbon into the coastal ocean. According to a study of the Columbia River by Dahm, Gregory, and Park (1981), typical TOC values in the river for the years 1973 and 1974 ranged from around 130 μM in the winter to somewhere between 200 and 300 μM in the summer, of which, around 200 μM was DOC. Let's assume maximum DOC output of 200 μM in river water with no salt. This is going to mix with ocean water with salinity around 31 PSU and a TOC value of perhaps 90 μM. If the two water types mix to give a salinity of 25 PSU (a value typical of surface water in the plume), then the DOC should be only around 111 μM by simple conservative mixing. This is quite close to values observed around 60 km downstream of the mouth of the river where salinity was indeed around

25 PSU. However, DOC increases dramatically further downstream where the salinity is higher. One would expect just the opposite. Calculating the expected DOC at 120 km where salinity is nearer to 28 PSU, the expected value is 101 μM, but the observed value is in excess of 180 μM! There is a large amount of DOC accumulating here from some other source.

Identifying the source of the high DOC patch is not a simple task. The chlorophyll levels in the area are not high enough to suggest that a bloom of phytoplankton is releasing the DOC directly at this location. However, it is important to recall the dynamic (features move) and transitory (features come and go) nature of patterns in these waters. The DOC *could* be a remnant of some event that occurred prior to our study. There is a large amount of POC upstream of the DOC patch that could have been converted to DOC, possibly by sloppy feeding and/or by release of waste materials by zooplankton. Figure 3.21 shows the estimated grazer biomass based on catches in vertical nets tows conducted by the NMFS team. Based on the patchiness of data along the four transect lines represented, it is safe to suppose that the distribution between transects is more variable than represented by the interpolation algorithm. Nevertheless, it is apparent that zooplankton biomass is highest over the continental shelf and especially high where the Columbia River plume crosses the shelf. It is possible that the high DOC to the south of this high concentration of grazers is due to their presence upstream. One could envision a bloom occurring off the mouth of the Columbia River in the days or weeks prior to our study. If this bloom were heavily grazed by the zooplankton in the area, a downstream patch of high DOC water could be the result. This is pure speculation, however, and further study is required to identify the actual source of the high DOC.

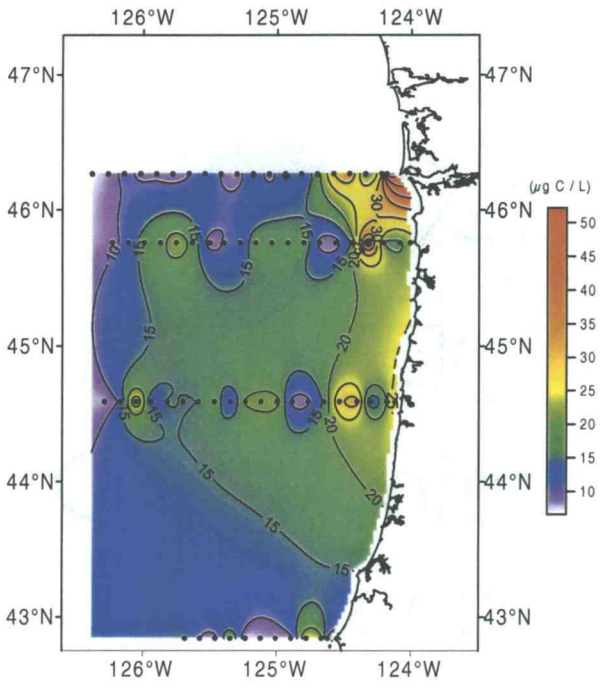

Figure 3.21 Zooplankton biomass (µg C / L) estimates based on catches in vertical net tows.

The whole picture of organic carbon mixing in the Columbia River plume is obscured by the complexity of the physical oceanography in the area. The ideal case for a linear TOC/Salinity relationship between TOC and salinity would involve the river pouring into an ocean with no circulation patterns and no upwelling. That is far from the case we observe off the Oregon Coast. A T-S diagram (Figure 3.22) shows that the area has three distinct water masses. With three water masses present and complex mixing occurring in the region, simple binary mixing is not expected or observed.

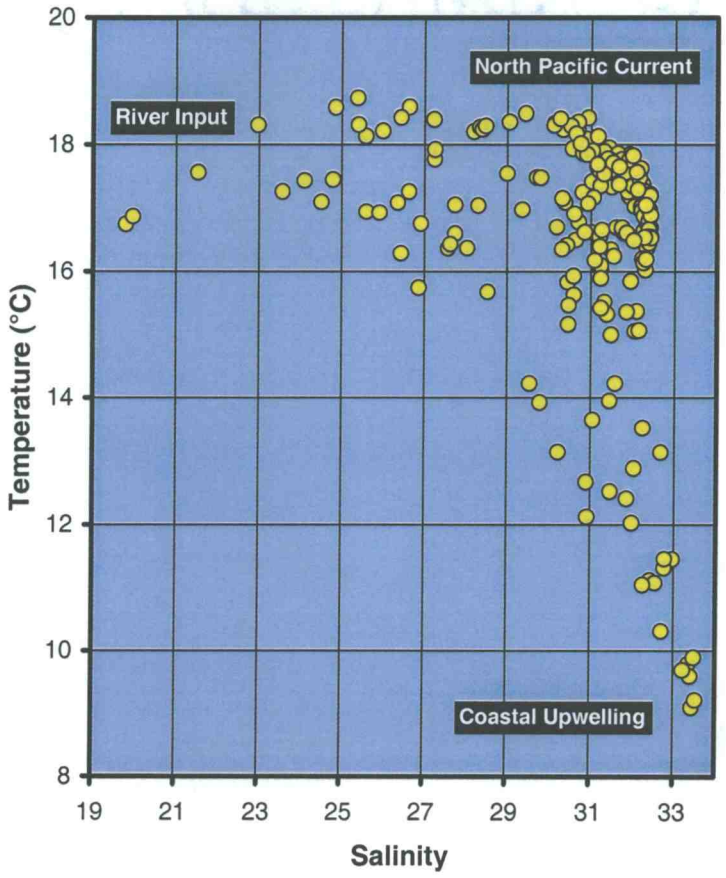

Figure 3.22 Temperature-Salinity diagram for the surface waters off Oregon and Southern Washington during July, 1997.

3.4 Summary of Major Patterns in DOC Distribution

In summary, the DOC concentration at any given point in the surface waters off Oregon is determined by four factors. First is the proximity to the Columbia River plume. The reasons for high DOC in the plume are not completely understood, but there is definitely an increase in DOC around 60 km downstream from the mouth of the river. Second is the proximity to newly

upwelled water. Water with the characteristics of being recently upwelled (low temperature, high salinity, and high nutrients) also contains little DOC. Third is the proximity to advected water originating in the oligotrophic central and northeast Pacific. This water is low in nutrients and supports relatively little productivity. DOC is not accumulated in great quantities within it. The fourth factor is recent biological activity. DOC does appear to increase in water that has moved offshore from upwelling areas. This water contains phytoplankton which are blooming or have bloomed recently in response to the increased nutrients introduced by upwelling. DOC may be released directly by the phytoplankton and/or be released during grazing by micro- and mesozooplankton.

4 A Year of Organic Matter Measurements off Newport, Oregon

4.1 The Purpose of the Time Series

We conducted a time series investigation in our study area in order to examine changes in organic matter concentration and partitioning related to upwelling events, phytoplankton blooms, and seasonal changes in the oceanic conditions off the Oregon coast. In an attempt to discover how these changing conditions affect organic matter concentrations, we collected samples from a station off Newport, Oregon from June 27, 1997, to July 6, 1998. Due to weather conditions, personal schedules, and lost samples, the data is not evenly distributed over the study period. However, we believe that we have enough high frequency data from a period of about two months to begin discussing changes in organic matter partitioning during and after a phytoplankton bloom. We also have enough data from each season to make general comparisons between the upwelling (summer) and non-upwelling (winter) seasons.

It is important to note at the outset of the chapter that our study period begins after the onset of a strong El Niño event that persisted into the early part of 1998. Since a portion of the information presented here is based on the first data of its kind collected in our geographical area, it is entirely possible that our findings will reflect patterns only observable under El Niño conditions.

4.2 Methods

Our study site for the time series was a station, designated NH-05, located 9 km from the shore off Newport, Oregon, at 44.65°N, 124.18°W. We visited this station using the R/V Sacajawea, a small vessel maintained by the Hatfield Marine Science Center in Newport, OR.

There were also four cruises aboard the R/V Wecoma and the cruise aboard the R/V Sea Otter in July of 1997, which is discussed in detail in Chapter 3. Table 4.1 lists the dates of our excursions. The depth at NH-05 is around 58 meters. We collected samples from just below the surface down to 50 meters using 1.8 liter Niskin bottles on a steel cable (in the cases of the Sacajawea trips) or 5-liter Niskins on a 12 bottle rosette (in the cases of the Wecoma cruises). Water samples were filtered through 335 μm Nitex and stored in 1-liter polycarbonate or HDPE bottles and kept in a dark box at ambient temperatures before being processes. Physical data was collected concurrently with water samples using a SeaBird Model 19 CTD.

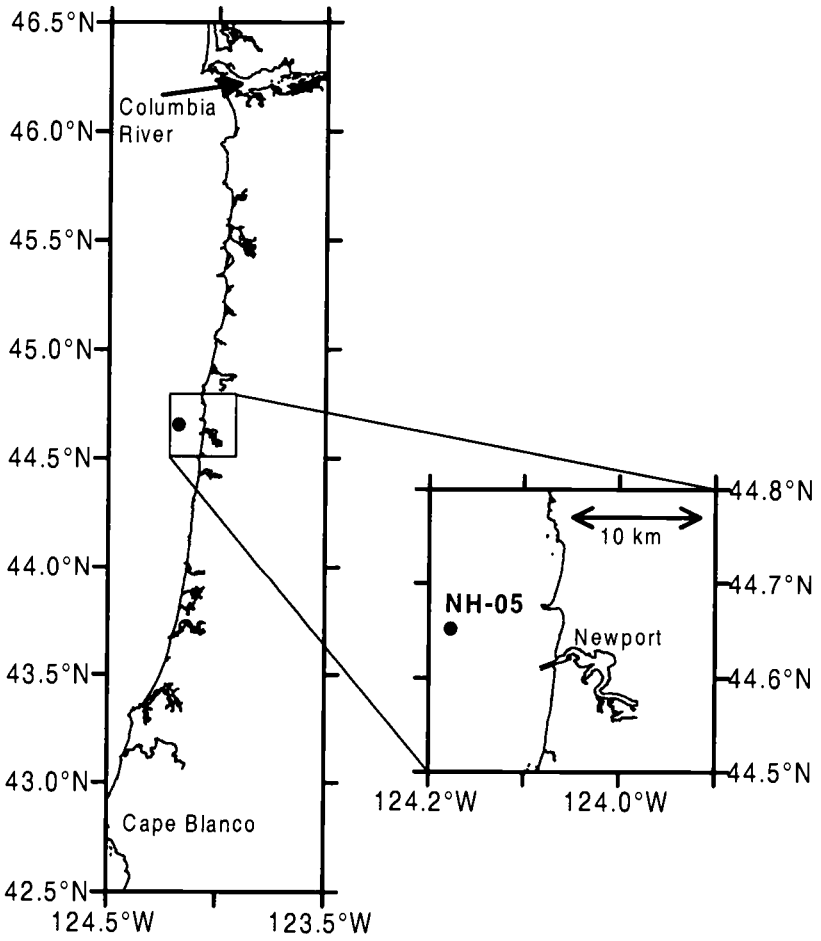

Figure 4.1 Map showing location of station NH-05 off Newport, Oregon.

Table 4.1 Sampling dates, ships used, and depths sampled for the NH-05 time series study.

Sampling Date	Ship Used	Depths Sampled (m)
6/27/97	Sacajawea	1,10,20,40
7/18/97	Sea Otter	1,3,5,10,15,20,25,30,40,50
8/6/97	Sacajawea	1,5,10,30,50
8/14/97	Sacajawea	1,5,10,20,30,50
8/21/97	Sacajawea	1,5,10,30,50
8/27/97	Sacajawea	1,5,10,30,50
8/28/97	Sacajawea	1,5,10,30,50
9/9/97	Sacajawea	1,10,20,30,50
9/19/97	Wecoma	1,5,10,15,20,25,35,40,45,50
10/15/97	Sacajawea	1,10
11/3/97	Sacajawea	1,5,10,30,50
11/15/97	Wecoma	1,5,10,15,20,23,25,30,40,50
12/12/97	Sacajawea	1,10,20,30,50
1/30/98	Wecoma	1,5,10,15,20,25,30,40,50
4/5/98	Wecoma	1,5,10,15,20,25,30,40,50
4/21/98	Sacajawea	1,10,20,30,50
6/2/98	Sacajawea	1,10,20,50
7/6/98	Sacajawea	1,10,20,30,50

For the trips using the R/V Sacajawea, we left port around 0700, local time. Samples were collected between the hours of 0800 and 1100. We returned to the labs around 1400 and immediately transferred the bottles to a refrigerator.

Subsamples were collected and processed using the water in the 1-liter bottles. We collected subsamples for the following measurements: total organic carbon, total nitrogen, particulate organic carbon, particulate organic nitrogen, inorganic nutrients, and chlorophyll. Please refer to the Methods section of Chapter 3 for more details on the analytical procedures used.

4.3 Results

Our results are presented here in three parts: ancillary data, organic carbon measurements, and nitrogen measurements. The data is also presented in Appendix B in table form.

4.3.1 Ancillary Data

The ancillary data, that not directly related to our estimates of DOM, consists of temperature, salinity, and chlorophyll measurements take over the course of the year-long study. The physical and biological ocean conditions provide important clues when interpreting the patterns in the organic matter records.

4.3.1.1 Temperature Records

Figure 4.2 shows the temperature record at station NH-05 for the entire time series. Physical data was collected on several days not mentioned in Table 4.1 by Bill Peterson, who was making more frequent trips to collect zooplankton throughout the year. Figure 4.3 shows a subset of the data, just the temperature record at 5 meters depth. According to Peterson (1999), the surface temperatures during the summer and fall of 1997 are some of the highest ever recorded, due to the El Niño event. Some of the values were in excess of 18 °C. Typical surface values for this time of year are typically several degrees less and as low as 10°C during upwelling events. Other than the extreme values, many of the basic patterns are what we would expect. In the late spring, summer, and early fall months, a distinct thermocline is evident as surface waters are heated by solar radiation and as cold deep oceanic water moves up onto the shelf at depth. In the winter, storms mix the water column and uniform temperatures are observed over the range

of depths. The deep water is warmer because weather patterns cause warmer surface water to pile up along the coast, resulting in downwelling (Huyer, 1983).

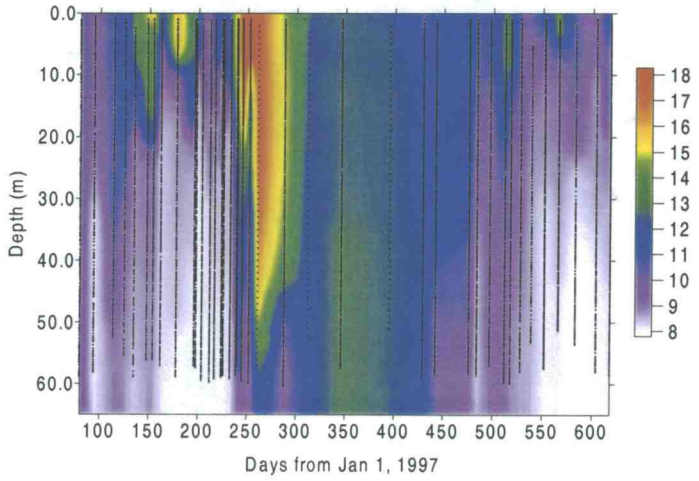

Figure 4.2 Graphical representation of all the temperature (°C) data collected at NH-05 during the one-year time series.

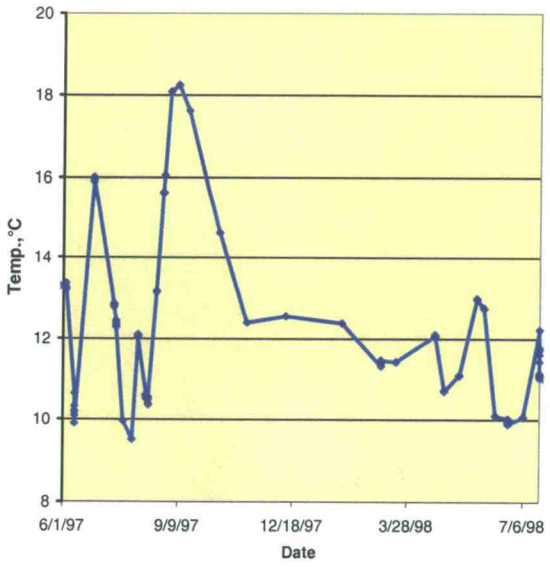

Figure 4.3 Temperature (°C) record for all measurements taken at 5 meters depth during the time series at NH-05.

Of special interest to us was the 2 month period starting around day 200 and extending until day 270 or so. Surface temperatures were low during the first month of this time period, indicating that upwelling events were taking place regularly enough to keep the temperature from increasing much above 12°C. However, around day 235 the temperatures warmed up significantly and remained warm for well over a month. Some of the biological implications of this drastic change in temperature will be discussed later in the chapter.

4.3.1.2 Salinity Profiles

The patterns in the salinity data (Figure 4.4) closely follow those in the temperature data. The water is either cold and salty, or warm and relatively fresh. On all dates, the water with the highest salinity was found near the bottom and was between 32 and 34 ppt. The highest salinity measurements were collected during the months when upwelling is more likely to occur. The surface waters showed much higher variability in salinity, ranging from just under 25 ppt to around 33 ppt. During the winter months, the water column was generally well-mixed. Stratification is evident in the summer and fall of 1997 and in the spring of 1998.

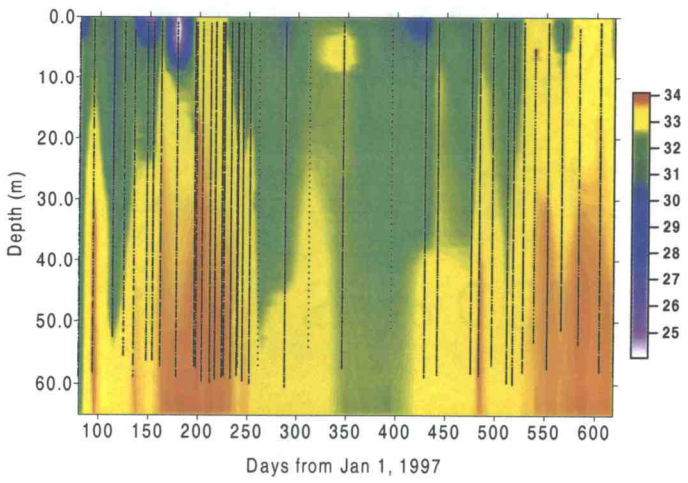

Figure 4.4 Graphical representation of all the salinity data collected at NH-05 during the one-year time series.

4.3.1.3 Chlorophyll

Total chlorophyll-a concentration (μg/l) is presented in Figure 4.5. There was an intense bloom (maximum [chl-a] = 15.3 μg/l) from day 200 to day 230 (mid-July to mid-August) which shows up nicely in the upper 30 meters of the water column. Chlorophyll levels remained low (generally around 1 μg/l) throughout the winter months and increased again at the start of the upwelling season in 1998. A bloom occurred in June and July of 1998 (seen on day 518 and day 552 in Figure 4.5), but did not appear to be as intense (maximum [chl-a] = 6.1 μg/l) near the sea surface as the bloom during July-August 1997.

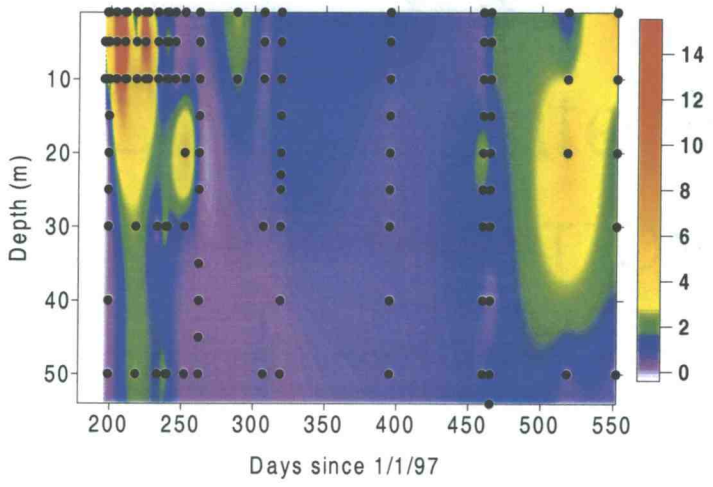

Figure 4.5 Chlorophyll-a (μg/L) record for July 1997 through July 1998 at station NH-05.

4.3.2 Organic Carbon Depth Profiles and Integrated Measurements

Organic carbon samples were collected during the entire year. However, the temporal resolution is poor in the second half of the study due to contamination problems in our TOC samples that were not discovered until the summer of 1998. We also lost several days worth of

particulate organic matter samples when a freezer was inadvertently left unplugged resulting in lost samples. Fortunately, our best resolution is during the months of July, August, and September when a major bloom occurred and eventually disappeared.

4.3.2.1 TOC

The total organic carbon measurements are summarized in Figure 4.6. TOC values varied over the year from around 50μM to over 190 μM. The highest values occurred just prior to the peak of the phytoplankton bloom in August. The lowest values (<95μM) occurred during the winter months, though low values were also observed on the last day of the study in July 1998. Based on the low temperatures observed on this day, it seems likely that low-TOC water was being upwelled at the site. The highest TOC concentrations were usually found in the upper 20 meters of the water column, though this was not always the case (see day 307).

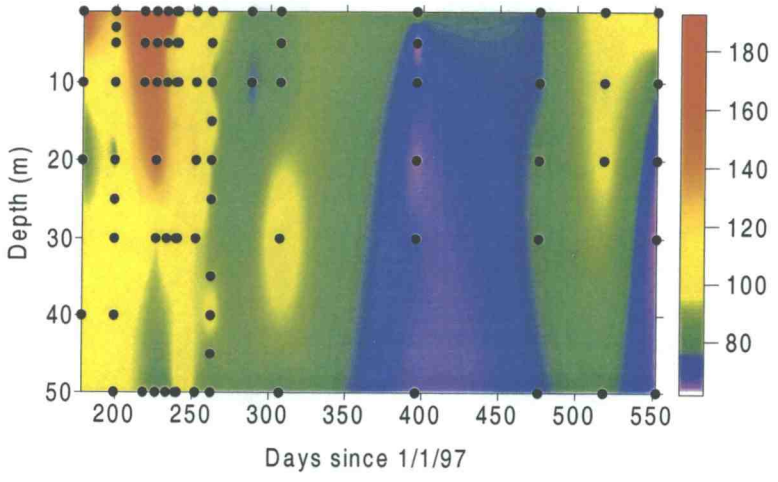

Figure 4.6 Total organic carbon (μM) record for June 1997 through July 1998 at station NH-05.

4.3.2.2 POC

The mean POC concentration for the year was 22.1±3.5 μM (n=100, 95% confidence). Assuming that the POC at NH-05 is predominantly living phytoplankton, a bloom event shows up extremely well around day 220 in Figure 4.7, reaching a maximum value of 127.4 μM on day 226 (August 14). It appears that summer upwelling tends to decrease POC at depth (see days 178, 199, 552). It seems likely that this is due to the fact that the upwelled water contains few organisms. The opposite may occur in the winter (see day 346) when detritus and organisms in the surface layer might be carried to depth by downwelling.

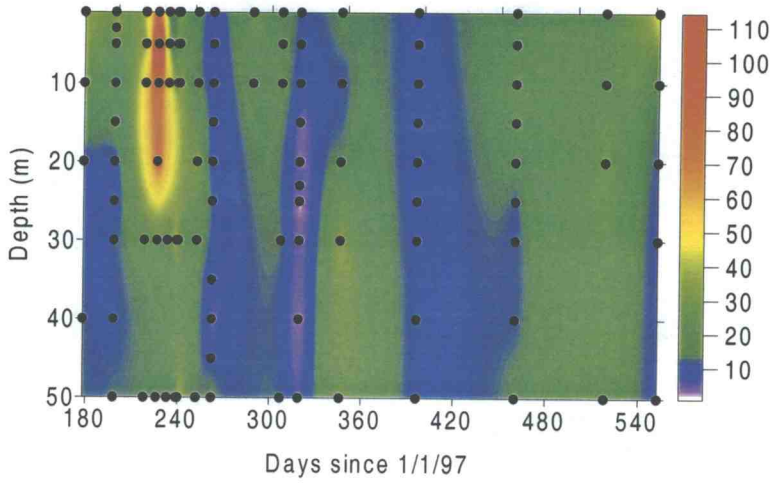

Figure 4.7 Particulate organic carbon (μM) record for June 1997 through July 1998 at station NH-05.

4.3.2.3 DOC

The dissolved organic carbon data is shown in Figure 4.8. Recall that DOC is calculated here as the difference in measured TOC and POC. Because of the combination of lost TOC or POC data on several sampling dates, the DOC record is even poorer in temporal resolution

during the second half of the time series than the other two organic carbon records. However, fairly good resolution in the DOC data remains for the early part of the study. The discussion later in the chapter will focus on this time period.

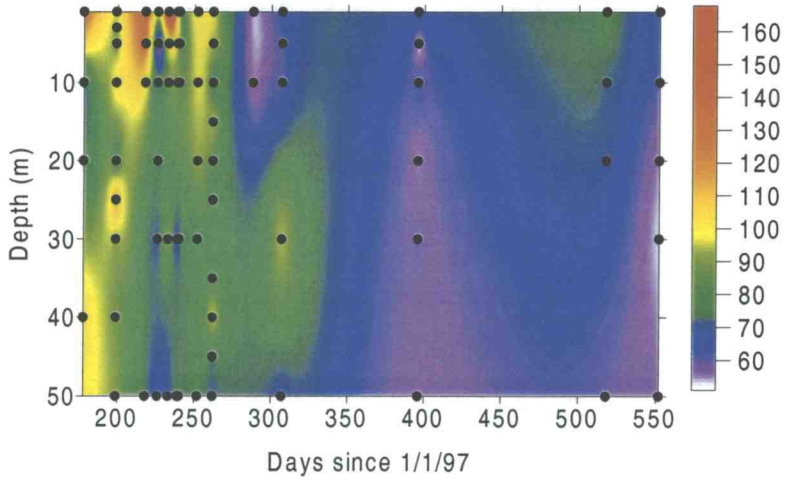

Figure 4.8 Dissolved organic carbon (μM) record for June 1997 through July 1998 at station NH-05.

The concentration of DOC was high (typically > 80 μM) during the summer and early fall of 1997, followed by low concentrations (< 80 μM) during the winter and spring months. It is interesting to note that there was a local minimum in DOC concentration at the peak of the bloom on August 14, 1997 (day 226). DOC levels were elevated prior to and following the peak of that bloom and they also appear to be elevated during the onset of the bloom the following spring, though this pattern is weak, with only sparse data supporting it.

4.3.2.4 Integrated Organic Carbon Measurements

Integrated organic carbon values have been calculated for those dates when both TOC and POC data are available. Discrete measurements from 1 to 50 meters depth (at varying intervals, see Appendix B) were used in Equation 4.1 to estimate the amounts of TOC, DOC, and

POC in units of mmol/m². D is the depth of a discrete measurement. C_D is the carbon concentration at depth D.

$$\sum_{D_n=D_1,D_2,D\ldots}\left[\frac{\left(C_{D_n}+C_{D_{n+1}}\right)}{2}\right]\bullet\left[\left(D_{n+1}\right)-D_n\right] \qquad \textbf{(4.1)}$$

Figure 4.9 shows the integrated organic carbon estimates for the time series. Clearly, DOC is the dominant form of organic carbon at NH-05, a result that is consistent with other researchers' findings at other geographic locations (Williams, 1995). DOC and POC are most alike in concentration on August 14, 1997 (day 226), at the peak of a bloom event. Of course POC would increase during a bloom, but the decrease in DOC is a bit of a surprise, a result that will receive more attention later in the chapter.

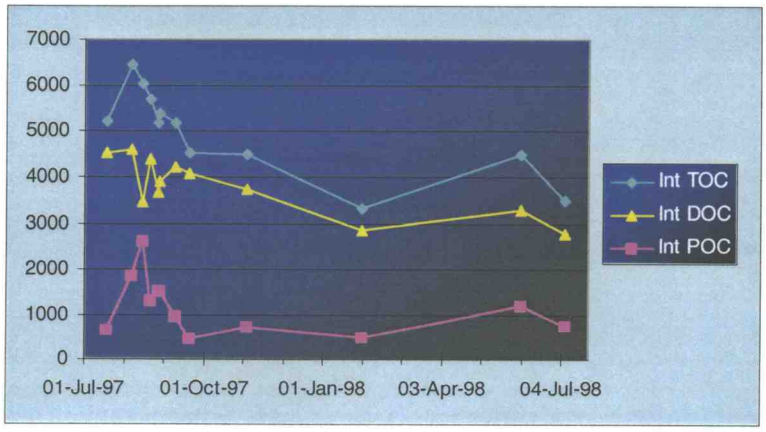

Figure 4.9 Integrated organic carbon estimates (mmol/m²) for dates when all three measurements were available.

4.3.3 Nitrogen Depth Profiles and Integrated Measurements

Nitrogen measurements often help explain the link between physical phenomena in the ocean and the resulting biological patterns. Inorganic nitrogen takes on the role of a limiting nutrient in much of the ocean. Even after being fixed into organic molecules, nitrogen plays an important role ecologically. For example, bacteria may utilize specific types of molecules in the DOM based on the nitrogen content of the molecules (Kirchman et al., 1989, Kirchman, 1990). This selection process provides a mechanism for the uncoupling of the nitrogen and carbon cycles.

4.3.3.1 TN

The distribution of nitrogen at NH-05 appears to be strongly influenced by upwelling. Figure 4.10 clearly shows elevated levels of nitrogen, as high as 45 μM, occurring in the summer and late spring periods, which are known for upwelling (Huyer, 1983). As will be seen in the following paragraphs, this distribution of total nitrogen is dominated by the distribution of inorganic nitrogenous nutrients. There can also be a very efficient transfer of inorganic nitrogenous nutrients to organic matter in the upper 20 meters of the water column.

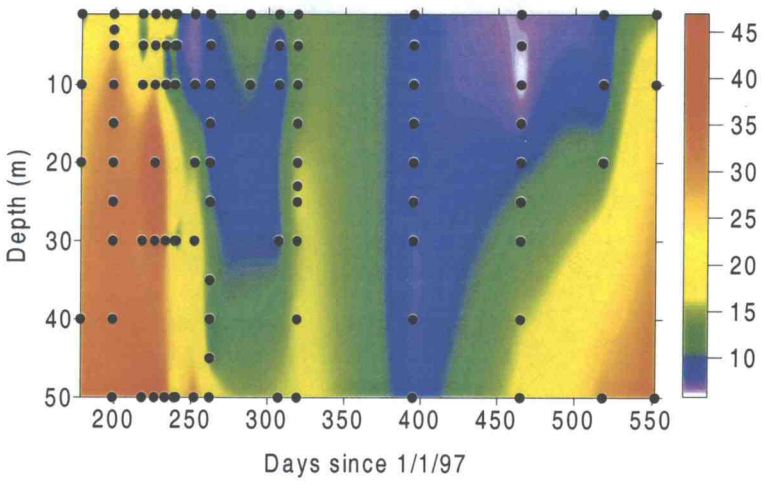

Figure 4.10 Total nitrogen (μM) record for June 1997 through July 1998 at station NH-05.

4.3.3.2 Nutrients

The levels of inorganic nitrogenous nutrients (Figure 4.11) closely follow the patterns seen in the temperature record. In the upper 5 meters, nitrate and nitrite (N+N) together range from less than 1 μM to around 20 μM. The high N+N values correspond closely with low temperatures. Figure 4.12 shows the relationship between N+N and temperature. It is interesting that anytime the temperature was below 9.8°C, high nutrient concentrations (8-30 μM) were observed. And anytime the temperature was above 12°C, very low nutrient levels (<4 μM) were observed.

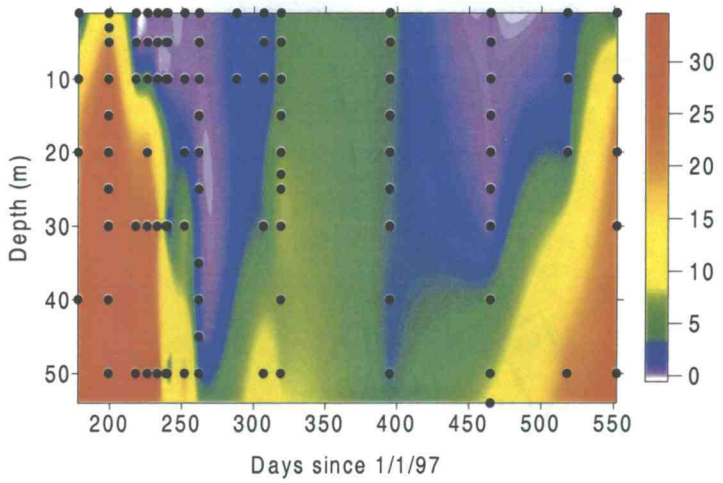

Figure 4.11 Nitrate + Nitrite (µM) for the 1997/1998 study period at station NH-05.

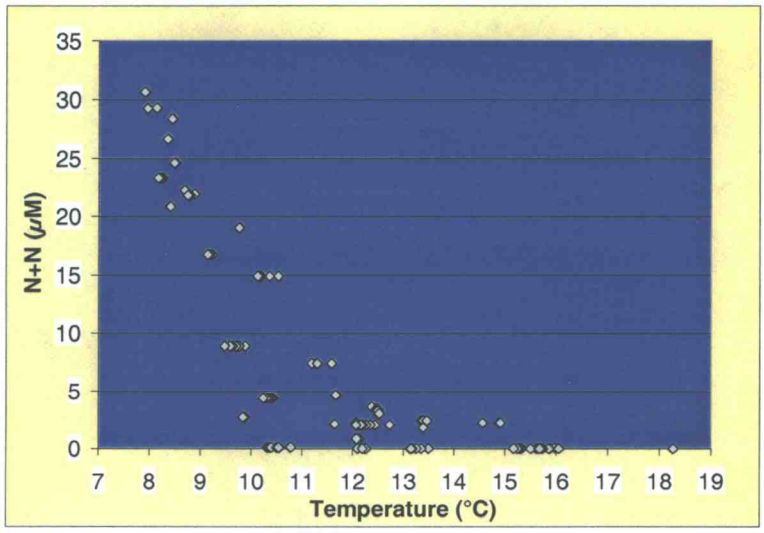

Figure 4.12 N+N vs. Temperature for the 1997/1998 study period at NH-05. Data are from all depths sampled.

4.3.3.3 TON

Figure 4.13 shows the record of total organic nitrogen at NH-05 for our study period. Total organic nitrogen is calculated as the difference in our total nitrogen and N+N measurements. It is interesting to note that the range of values here is almost identical to that of the N+N measurements. Also, the maxima of the N+N and TON records do not occur simultaneously. The TON maximum follows immediately after the N+N maximum in the summer of 1997, evidence that there was efficient uptake of nitrogen in the surface waters.

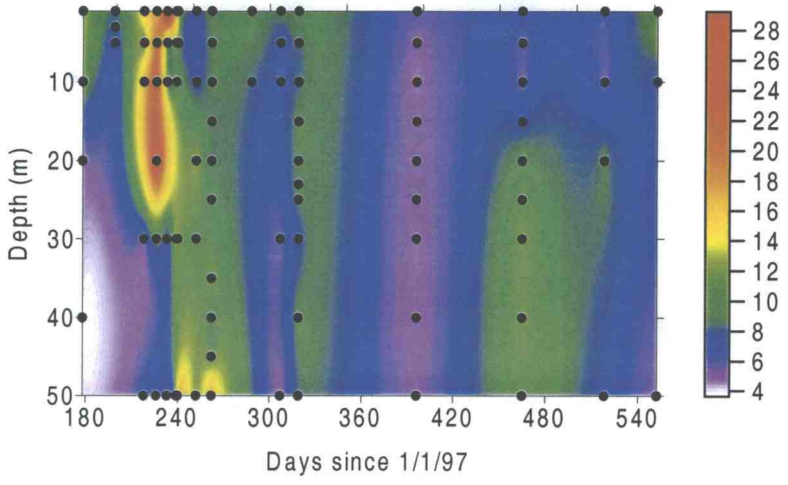

Figure 4.13 Total organic nitrogen (μM) record for June 1997 through July 1998 at station NH-05.

4.3.3.4 PON

Figure 4.14 shows the time-series record for all particulate organic nitrogen measurements. PON was measured directly using a Carlo-Erba CHN Analyzer. The PON maximum occurred on August 14, 1997, with maximum values occurring in the upper 20 meters and reaching concentrations of 10-15 μM. PON was generally highest in the surface waters,

though on one day in December 1997 the maximum was at 30 m. It is possible that this represented resuspended particles that were lifted off the bottom by intense winter mixing. PON increased concurrently with nutrient input during the spring of 1998.

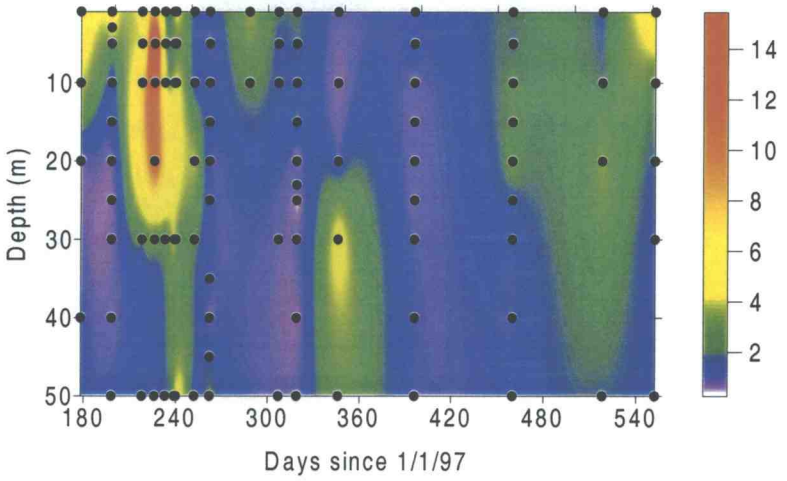

Figure 4.14 Particulate organic nitrogen (μM) record for June 1997 through July 1998 at station NH-05.

4.3.3.5 DON

Figure 4.15 shows the record of dissolved organic nitrogen measurements at NH-05. DON values ranged from near zero to >26 μM, near the same range as seen in N+N, however, the majority of observations fell in the 6 to 12 μM range. Unlike PON, DON was often higher at depth than at the surface, though the highest values were observed right at the surface soon after the peak in POM on August 14 (day 226). The fact that DON was often higher at depth could be due to degradation of detritus in the sediments or of resuspended particles near the sea floor. Or, it could be that DON is utilized in the surface waters more than at depth. The extremely low value of DON at 40 meters depth on day 178 is suspect for two reasons. First, they are much lower than any other measurements made throughout the year. And, second, the ratio of TN to

PON was so high that the resulting DON estimate could be seriously confounded by noise. Recall that DON is a calculated estimate based on TN, nitrogenous nutrients, and PON measurements. These low DON values will be considered again later in the chapter during a discussion of C/N ratios.

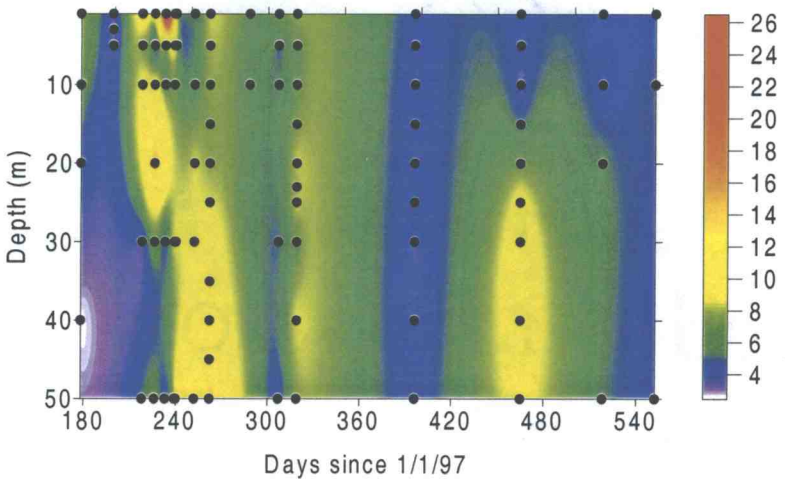

Figure 4.15 Dissolved organic nitrogen (μM) record for June 1997 through July 1998 at station NH-05.

4.3.3.6 Integrated Nitrogen Measurements

Integrating the various forms of nitrogen over the upper 50 meters of the water column at NH-05 is useful for showing the timing of the conversion of nitrogen from nitrate and nitrite (N+N) to PON to DON. Figure 4.16 shows this relationship. The general progression is evident during the months of July, August, and September of 1997. N+N is quite high on July 18, at >1500 mmol/m^2. As the N+N declines over a period of 2 months, PON peaks, followed by the peak in DON.

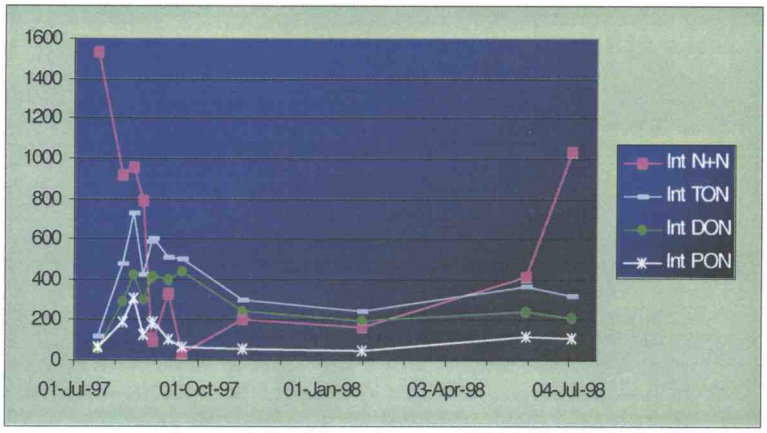

Figure 4.16 Comparison of integrated nitrogen (mmol/m^2) estimates.

4.4 Discussion

There are three main questions for this discussion. First, what seasonal differences in dissolved organic carbon concentration were evident at station NH-05? Second, what were the evident changes in organic matter partitioning during and after a phytoplankton bloom? And finally, what could the changes in C/N ratios on short and long time scales signify?

4.4.1 Relating the Patterns in DOC to Seasonal Ocean Dynamics on the Continental Shelf off Oregon

The coastal ocean off Oregon experiences two seasons, the endpoints of which are marked by indistinct events known as the "spring transition" and the "fall transition". The force driving these oceanographic seasons is wind direction. The winds during the months of November through April are typically from the south. Ekman transport causes surface water to move toward the coast, so sea temperatures are generally higher and salinity is lower over the shelf. Winter storms keep the water column over the continental shelf fairly well mixed. May

through October are characterized by winds blowing from the north. Ekman transport carries surface water offshore. The water is replaced by deep water that wells up, lowering sea surface temperatures while increasing salinity and nutrients. Increased solar radiation heats the surface waters and, in the absence of storms, the water column becomes stratified. This stratification often results in the concentration of organisms near the surface or at some middle depth where light and nutrients are optimal.

DOC concentrations at our study site were controlled by both physical and biological events. The recognizable biological events were the result of physical conditions, so it can be said that the winds off Oregon control the DOC distribution observed, directly and indirectly. Table 4.2 summarizes the DOC data from the time series, grouping the data by oceanographic season and by depth.

Table 4.2 A comparison of DOC concentrations at representative depths during the major oceanic seasons off the Oregon coast during the 1997-98 study.

Depth	May - October Values	November - April Values
1m	100-180 μM	60-80 μM
10m	80-100 μM	60-70 μM
50m	65-75 μM	55-60 μM
Integrated	3500-4600 mmol/m^2	2700-3700 mmol/m^2

During the May-October upwelling season, the water column is stratified and phytoplankton biomass is high, especially near the surface. DOC is also concentrated at the surface during this time of year, presumably because the organisms which produce DOC are also near the surface.. The range of DOC values at one meter depth was 100 to 180 μM during the upwelling season. At fifty meters depth, the DOC concentration was much lower, only 65-75

μM. If strong mixing were occurring, this wide difference in surface and deep values would not be present.

The depth distribution of DOC at NH-05 is very different during the November-April time period. The range of DOC concentrations for the entire water column was 55 to 80 μM. The highest values were still observed near the surface, but they were not much higher than the DOC values in rest of the water column. At all depths, the DOC concentration was less than during the May-October time period. Integrating DOC concentration over the upper fifty meters also shows that DOC is increased by around 900 mmol/m2 during the May-October upwelling season. This increase is due to increased biological activity, i.e. primary production, grazing, etc., during the months when the wind is from the north.

4.4.2 Organic Matter Partitioning During a Bloom and Its Decline

The temperature record for the time series shows an extended period of cooler sea temperatures in late July and early August of 1997. This is followed by an extended period of very warm temperatures lasting until the end of September. The biology in the coast region often correlates strongly with temperature, so we chose to look at the July-August period in detail. It was fortunate that we were able to collect data at much shorter intervals during this particular time period, because we have the resolution needed to examine an event occurring on a shorter time scale than the rest of our data allows.

Typically, cooler sea temperatures along the coast are caused by upwelling. Upwelling also carries nutrients to the surface. These nutrients often provide the stimulus for a phytoplankton bloom. So, we would expect that during the cooler period, there would be an increase in nutrients and phytoplankton. The phytoplankton increase is evident, both as increased particulate organic material, shown in Figure 4.17, and as increased chlorophyll, shown in Figure 4.18. Usually, increases in plankton biomass result in increased release of DOM.

However, DOC does not increase during the bloom, but rather it decreases as POC increases (see Figure 4.17).

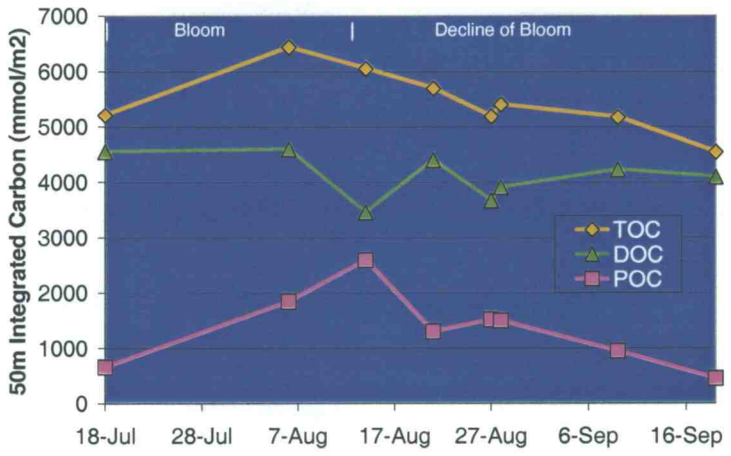

Figure 4.17 Changes in organic carbon partitioning at NH-05 during a phytoplankton bloom and its decline during the summer of 1997. Carbon measurements were integrated over the upper 50 meters of the water column.

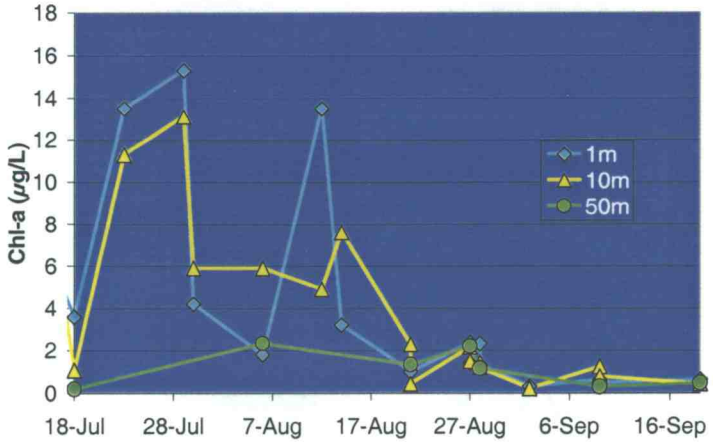

Figure 4.18 Chlorophyll measurements (µg/L) at representative depths during a phytoplankton bloom and its decline at NH-05 in 1997.

Several explanations for the decrease in DOC during the bloom are possible. The simplest explanation is based on simple physics. The deep water being upwelled during the bloom has lower DOC levels than the surface water. The surface water is either displaced or diluted by DOC-poor deep water. The dilution occurs at a higher rate than the production of DOC by the phytoplankton. As the water moves offshore, it is likely that the DOC will eventually show a net increase, but at NH-05, the phytoplankton haven't started releasing DOC at levels that can overcome the dilution factor.

Another possible explanation involves the "sticky" nature of DOC (Chin et al., 1998, Wells, 1998). DOC tends to coagulate with colloids and particles in the water, including phytoplankton, which often maintain their own "sticky" mucous layer. As the bloom progresses, a net decrease in DOC could result due to the presence of more particles in the water.

A third possible explanation for the decrease in DOC invokes the activities of the bacterioplankton. Something associated with the bloom, perhaps even the release of DOC by phytoplankton, might cause the bacteria to increase their activity and consume the DOC at a rate faster than it is produced. There is evidence in other systems that the presence of glucose can stimulate the uptake of other forms of DOM in heterotrophic bacteria (Kirchman, 1990, Carlson et al., 1999). Amon and Benner (1996) have shown that bacteria will rapidly consume HMW carbon-rich DOM if sufficient inorganic nutrients are also available, a condition that is consistent with the measurements we made.

Figure 4.17 indicates that integrated DOC was always higher than integrated POC at NH-05 during the bloom/decline event. The difference in DOC and POC abundance is minimized at the height of the bloom, but DOC remains higher than POC. Figure 4.19 tells a slightly different story. By comparing %POC measurements at various depths on three dates, we can see that POC actually accounts for about half of the TOC at shallow depths at the height of the bloom, which occurred on 14 August. At five meters depth, the POC concentration accounted for over 70% of the organic carbon present. Similar observations have been made at

high latitudes (Wheeler et al., 1997, Carlson et al., 1998) but have not been reported for temperate zones. High latitudes are known for very intense blooms and the bloom we studied could also fall under this description, so perhaps this is a common feature in situations where POC concentration is higher than DOC.

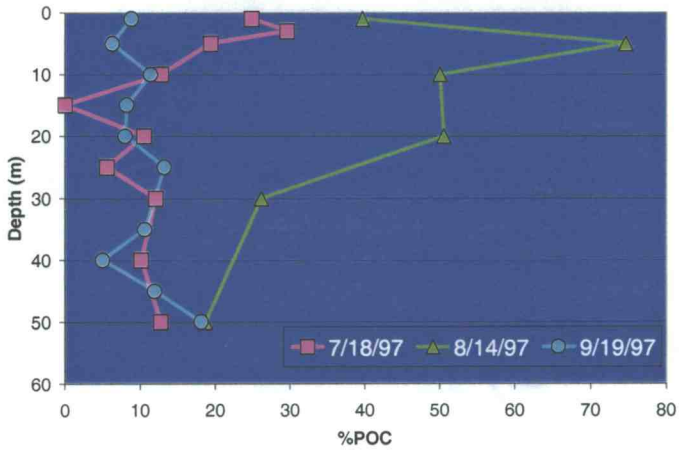

Figure 4.19 %POC at the start of the bloom (17 July), bloom maximum (14 August), and after the bloom has declined (September 19). %POC is defined as ([POC]/[TOC]) * 100.

4.4.3 Changes in the C/N Ratio: What Could They Signify?

Carbon to nitrogen ratios are not simple to explain. Redfield tells us that this ratio is 6.6 in the ocean. This applies to organisms and seawater. However, 6.6 is just some kind of average. It is not often that someone will report a C/N ratio of 6.6. Presumably, this is because the carbon and nitrogen cycles in the ocean are uncoupled as matter is transformed from one compound to another. Bacteria have C/N ratios of around 4-5 (Nagata, 1986, Kirchman et al., 1989). Phytoplankton have C/N ratios of 6-10 (Bishop et al., 1977, Benner, 1998) Bulk DOM has a wide range of C/N values from around 10 up to 20 (Benner, 1998). The processes that

move organic material between these pools must act selectively on the available molecules to create such differences in C/N ratios. But these processes are numerous and complex. Amon and Benner (1996) have concluded that bacteria will preferentially use DOM that is the least degraded from its "living" state. They also found that HMW, high C/N molecules, like non-structural polysaccharides, are the most bioreactive. Heterotrophic bacteria utilize DOM of this kind very rapidly and take up significant amounts of inorganic nutrients (ammonium or nitrate) at the same time. Kirchman (1990) reported that the presence of certain amino acids in seawater will inhibit ammonium uptake in favor of uptake of the amino acids. He found that other types of organic nitrogen did not have the same effect. So one can conclude that bacteria prefer HMW, high C/N DOM but only if there is enough inorganic nitrogen around and only if the concentration of free amino acids is low. High C/N ratios can indicate the presence of humic substances (Benner, 1998) or could be the result of direct exudation of polysaccharides by phytoplankton. It could also mean that bacteria are utilizing the low C/N fraction of the DOM pool. Low C/N ratios could indicate selective uptake of high C/N DOM by bacterioplankton, but might also indicate viral induced lysis of phytoplankton (Fuhrman and Suttle, 1993). These relationships are still poorly understood, but they demonstrate that these processes are not simple ones.

So what, if anything, can be said about the changes in C/N ratios observed at station NH-05 during this time series. Figure 4.20(a) shows the record of C/N ratios for TOC, DOC, and POC. The ratio was always higher in DOC than in POC, except for on one day when they were essentially equal. This day happened to correspond with the peak of the bloom event discussed in the previous section. On July 18, 1997, the DOM ratio was so high (~80) as to be suspect. This probably occurred because the inorganic nutrient measurements were so similar to our TN measurements, resulting in a DON estimate that was confounded by noise. Aside from this particular datum, our C/N ratios seem reasonable, based on the results of other investigators (Benner, 1998). During the winter month, the C/N ratio of DOC remained fairly high (>13).

This is probably because the number of organisms was reduced, so any DOM present would have been fairly refractory, high C/N molecules, such as humic substances from terrestrial runoff. The C/N ratios were much more variable during the upwelling season and mimic the shape in the POM C/N record, an indication that the DOM present is, at least in part, a direct product of the organisms present.

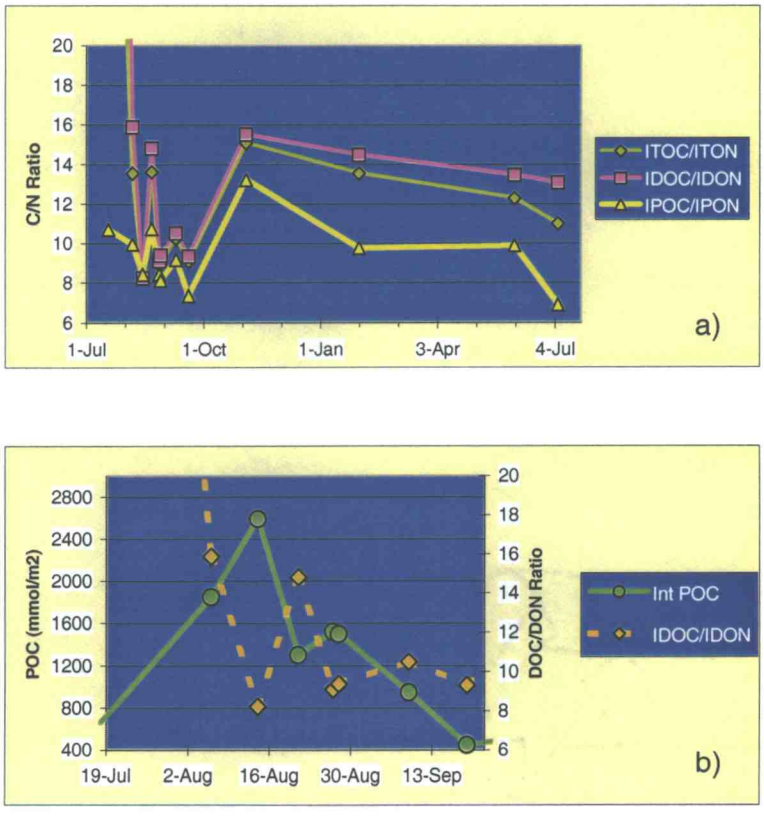

Figure 4.20 a) Changes in C/N ratios in the depth-integrated total, dissolved, and particulate pools of organic matter during the 1997-98 study. b) Changes in C/N ratio of depth-integrated DOM during bloom and decline of bloom during the summer of 1997. Depth integrated POC concentration shows progress of the bloom.

Is there an explanation of the patterns in C/N ratios observed during the July-September bloom/decline events? Figure 4.20(b) shows the changes in the C/N ratio of depth-integrated

DOM at NH-05 during the bloom and its decline. It is interesting to note that during this event, the C/N ratio was always changing in a manner opposite to the change in POC concentration, which we can assume was primarily phytoplankton biomass. The C/N ratio in DOM is affected either by, 1) the mixing of water masses with differing C/N ratios, 2) by changes in the DOM produced by phytoplankton (perhaps in response to nutrient input or growth phase), or 3) by selective decomposition of the DOM by bacteria.

The first possibility is the simplest answer. The decrease in C/N ratio at the onset of the bloom could simply be the result of mixing deep upwelled water with surface water. However, this would require the DOM in the deep water to have a low C/N ratio (below 8 to achieve the C/N ratios we observed), a characteristic that is not consistent with deep-water refractory DOM (Hansell et al., 1993). Simple mixing does not seem to be the answer.

Perhaps the change in C/N ratio of the DOM was due to a change in the physiological state of the phytoplankton as the bloom progressed. Williams (1995), Biddanda and Benner (1997), and Anderson and Williams (1998) have suggested that the seasonal increase in C/N ratio of DOC is due to storage and release of carbon-rich DOM by blooming phytoplankton. They also note that DOC peaks tend to lag behind chlorophyll peaks, a feature also present in our data set. This lag suggests that the age of the phytoplankton (and presumably their physiological state) is related to the amount of DOC released. Such changes might account for the changes in C/N ratio we observed as well.

The oscillatory and periodic nature of the changes in Figure 4.20(b) bring to mind the "boom and bust" plots showing population size of two organisms in a feeding relationship that are presented in every ecology text. If phytoplankton are not directly exuding DOM with the C/N ratio observed in the figure, then perhaps a bacterial response to the phytoplankton bloom is accounting for the changes in C/N ratio. No bacterial biomass estimates during the bloom and decline are available, so any explanation based on bacterial uptake will be hypothetical. Nevertheless, bacterial consumption of carbon-rich DOM during the phytoplankton bloom

seems a promising idea. Bacterioplankton are known to rapidly consume recently-produced, carbon-rich DOM (Amon and Benner, 1996, Carlson and Ducklow, 1996), but only when sufficient inorganic nitrogen (nitrate or ammonium) are present to support biosynthesis. Upwelling was occurring during the bloom in question, so it is likely that inorganic nutrients were in abundance and could support the needs of the bacteria. Amon and Benner (1996) showed that HMW DOC consumption was highest (22.5% of DOC per day) in lab experiments which simulated diatom blooms. While it is not possible to know how much DOC was actually produced by phytoplankton during the bloom, 22.5 % daily losses would be more than adequate to account for the observed net loss of DOC between July 18 and August 14, even with considerable DOC production occurring.

But what about the oscillations in Figure 4.20(b)? What would cause the C/N ratio to increase again after August 14? Two ideas come to mind. On August 14, DOC was at a minimum. Perhaps the bioreactive portion of the DOM was used up and the bacterioplankton population crashed, leading to another build-up of carbon-rich DOM. Eventually the bacteria population would respond and consume this accumulated carbon-rich DOM once again. The carbon-rich DOM and bacteria would oscillate in this manner opposite the DOC/DON ratio until finally the phytoplankton DOM production, the C/N ratio of the DOM, and the bacterioplankton population returned to some non-bloom equilibrium. Figure 4.21(a) shows how a bacterioplankton population *might* oscillate in such a scenario. There is a second possible explanation for the increase in the DOM C/N ratio following August 14. Suppose bacteriovores were increasing as the bacteria responded to the release of DOM by the phytoplankton. Grazing pressure might decimate the bacteria to a point where they couldn't keep up with the production of DOM by the phytoplankton. The crash of the bacteria population would lead to a crash of the bacteriovore population and the bacteria would increase and once again consume the carbon-rich DOM. Figure 4.21(b) shows how micrograzer and bacterioplankton populations might vary in such a scenario.

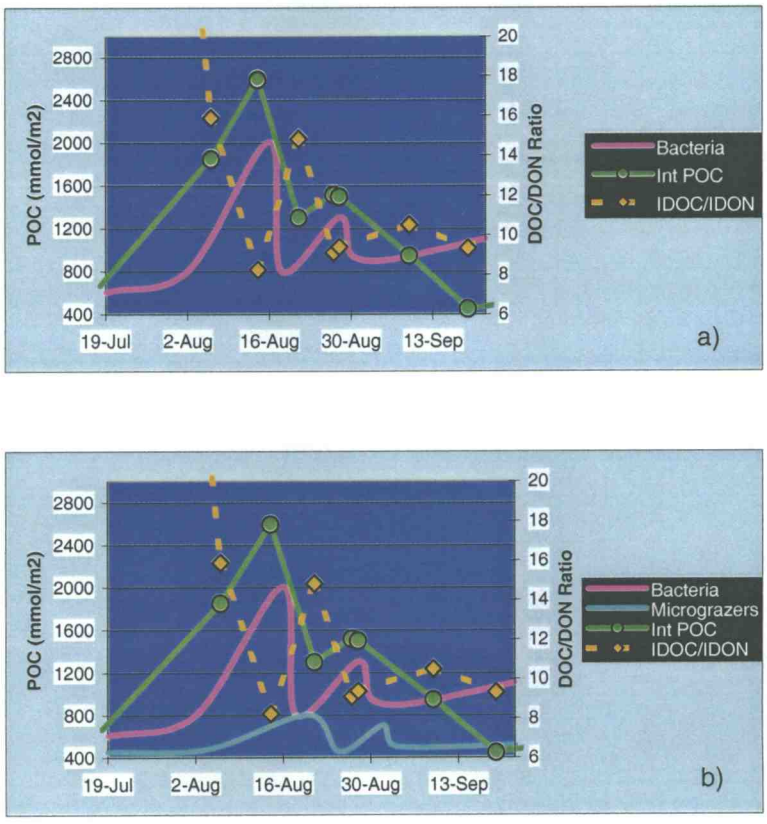

Figure 4.21 Charts of possible events producing observed C/N ratios in DOM during the bloom and decline of late summer, 1997. Note that the hypothetical data (bacterioplankton and micrograzer abundances) have not been calculated in any way and do not correspond to either y-axis.

The role of bacteria could be critical to our understanding of DOC distribution and composition during and following bloom events off the Oregon coast. Future time series studies of DOM in the area, especially on shorter time scales, should include measurements of bacterial and micrograzer abundance in order to test the hypotheses presented here. It would also be extremely helpful to size fractionate the DOM and to measure the C/N ratios of the different classes of DOM being produced. This could help to verify whether the bacteria are indeed

preferentially consuming the HMW DOM and whether such a preference might alter the C/N ratio of the DOM.

5 Conclusions and Suggestions for Further Study

The information presented in this thesis is not comprehensive, but rather it is intended to be directional. The goals of the projects described here were to examine and begin to quantify the organic carbon and nitrogen pools off the Oregon coast, to describe variation in those pools over time and space, and to find other parameters that seem to correlate with organic matter concentrations. As is typical in such situations, every new pattern brings up more questions. And so, each conclusion here will be accompanied by questions for future research. These conclusions are qualitative, primarily because it is uncertain how much our data were influenced by the El Niño conditions that persisted for most of the study period.

5.1 The DOC Patch in the Columbia River Plume

The Columbia River carries large amounts of DOC and POC. The Columbia River plume, extending south and offshore over the continental shelf, also exhibits high levels of DOC, but the highest levels are not nearest the mouth of the river. This is an indication of some biological or chemical process that merits investigation. Several questions should be asked. First of all, the pattern has only been observed once, so we should ask whether or not the pattern is a permanent, seasonal, intermittent, or one-time event? Is POC in the river water being converted to DOC? Is the DOC a product of some biological process or sequence of processes occurring on the shelf? What might those processes be?

Multiple hypotheses could be examined. Consider the following as an example. We know the river carries more water in the spring and summer due to snowmelt. Increased runoff in the mountains would increase the amount of weathering and raise the levels of silicate in the

river water entering the ocean. The increased silicate in the water could induce a bloom of small diatoms that are quickly consumed by zooplankton that feed sloppily and excrete large amount of DOC. Since the sequence of events in the ocean is likely to take time, the DOC patch would appear downstream of the mouth. Such a process is consistent with the data presented in this thesis, but further evidence is required to test this hypothesis. The scenario also shows the importance of examining the characteristics of the water in the Columbia River in conjunction with studies of processes in the Columbia River plume.

5.2 Upwelling and DOM

A quick comparison of the temperature and DOC distribution maps in Chapter 3 reveals the similarity in the patterns of these two parameters. Sea surface temperature along the Oregon coast is strongly influenced by upwelling. Upwelling brings nutrients to the surface and stimulates blooms of phytoplankton. Phytoplankton release DOC. We know that upwelled water contains less DOC than surface water. Put these facts together and it is clear that DOC distributions are directly and/or indirectly affected by upwelling. However, even with these logical connections, the questions remain: What is the effect of upwelling on DOC concentration over short and long time scales and what mechanisms are most important in relating upwelling to DOC concentration? We observed decreases in DOC in areas where upwelling was occurring and as a bloom progressed. Did this occur because of hydrography, because of colloidal adsorption, or because of bacterial uptake of DOM? These questions reveal the necessity of combining future studies of DOC off Oregon with continued hydrographic observations, better size-fractionation of DOC samples, and experiments examining bacterial growth and DOC uptake.

5.3 DOM Sources and Sinks

Chapter 2 describes the known sources and sinks of DOM. The main sources are phytoplankton and zooplankton. The primary sink is bacterioplankton. Advection can be a source or a sink. Of these four sources and sinks, only phytoplankton were measured with much accuracy in the present study. Zooplankton and advection were examined to a lesser extent and bacterioplankton were not measured at all. Future research should go beyond descriptions of distributions and focus on the processes that create those distributions. Such research might take any of three forms: continued in situ sampling, controlled experiments, and modeling. Sampling efforts will only be possible in the setting of interdisciplinary studies such as the GLOBEC project with several researchers or teams involved. There are simply too many variables to examine for any one person to collect the necessary simultaneous data. Continued sampling and observation will confirm or refute the patterns observed in this study, but it will not clearly demonstrate the precise role of the sources and sinks of DOM. Such roles will be best illuminated in controlled experiments. Such experiments have been conducted in other coastal and oceanic regions (Kirchman, 1990, Amon and Benner, 1996, Carlson and Ducklow, 1996, Carlson et al., 1998) and following the techniques used elsewhere will insure the ability to compare regional results. Modeling should also prove a useful technique where high resolution data of all parameters will not be easily collected. However, it would seem that modeling may not be very accurate until some of the key relationships are better understood. Among these relationships are colloidal adsorption, the DOC production during a bloom, and bacterial uptake of DOC and DON.

5.4 Other Suggestions Concerning Future Research

As a first look and as a graduate student project, this study was purposefully limited in its scope. The researchers that continue this work will undoubtedly take a more thorough and

comprehensive approach. The following sections make suggestions and predictions for future studies.

5.4.1 DOM Characterization

Measuring bulk DOM is useful only to a point. Because the term DOM encompasses such a diverse collection of compounds, it is difficult to link bulk DOM to specific mechanisms in the ocean. In the current study, we measured DOC and DON separately in an effort to begin characterizing the chemical nature of the DOM present off Oregon. However, we need more specific characterization of the various molecules comprising the DOM. We need to know the relative abundance of the various sizes, reactivities, and compositions of the DOM molecules at a given site and time. Only then we will begin to understand how the different types of DOM relate to the organisms that produce and consume them.

Characterization of DOM is now possible through a variety of techniques. $\delta^{13}C$ measurements of DOC can help to identify whether the DOC is of marine or terrestrial origin. Tangential-flow ultrafiltration is useful for fractionating DOM by molecular weight (Benner, 1991). Techniques involving the adsorption of DOM onto XAD resins are useful for fractionating DOM samples by chemical properties (Druffel et al., 1992, Benner, 1998). Nuclear magnetic resonance has been used to identify the structures of several forms of DOM, both humic substances and HMW forms (Benner et al., 1992, Hedges et al., 1992). Various other chemical methods involving colorimetry or chromatography are also being used to measure the concentration of specific types of DOM such as carbohydrates or aldoses (Benner, 1998).

5.4.2 *El Niño vs. non-El Niño*

The studies presented here were conducted during a strong El Niño event. As such, the results are most likely altered from those that would be obtained under "normal" conditions. The El Niño caused the ocean conditions near the Oregon coast to resemble conditions farther offshore. Water temperatures were elevated. Species of zooplankton commonly found far offshore occurred over the continental shelf. Tuna, which are commonly caught in excess of 30 km offshore were being caught within 10 km of the beach. Because of these changes in the hydrographic and biological conditions, it is safe to assume DOM distributions were affected as well. Increased upwelling would probably cause the DOM concentrations close to shore to drop. However, the increase in available nutrients would cause larger blooms of phytoplankton. These blooms would eventually result in large releases of DOM offshore. Based on these predictions, the gradient of low DOC at the coast to higher DOC at the shelf break (see Figure 3.5) would probably be even more pronounced. It is the opinion of this author that the general patterns described in this thesis would remain the same, but that the magnitude of those patterns would be altered under different oceanic conditions. Such a hypothesis could be easily tested in future research projects.

5.4.3 *Studies in Four Dimensions*

The present studies were conducted in only two dimensions. The spatial study attempted a snapshot of summer conditions using the dimensions of latitude and longitude. The temporal study measured changes with depth over time. All four dimensions were considered, but not simultaneously.

The spatial study was limited by its lack of a time component and can make few claims about the movements of water masses. For instance, we do not know if the patch of high-DOC

water in the plume is a semi-permanent feature in one location or if it is a feature that was moving southward with the California Current. We can make no claims about its history or future. Just monitoring the surface of the ocean is also inadequate. Suppose we did watch the DOC-patch for a period of a few weeks before it disappeared. After its disappearance it would be impossible to tell whether the patch had been consumed by bacterioplankton or whether it had merely been subducted under another water mass if only the surface waters were being observed.

Our temporal study was also limited by its lack of four dimensions. Water along the Oregon coast is always moving. Every time we took samples, we collected water from a different water mass. The changes we saw during the bloom and decline of the bloom may have had nothing to do with biological processes at all, and could have simply been the result of advection. Again, unless water masses are tracked in four dimensions, we have to make huge assumptions that might not be correct. In the time series study, we knew water was flowing north and south along the coast, so we had to assume that the same processes were in effect to the north and south of our site. Our own spatial study shows such an assumption to be faulty.

Conducting studies in four dimensions is difficult, but it is also getting easier. As real-time data collection becomes more common it will be possible to do more sampling with moorings and towed instrument packages. Remote sensing is also becoming critical to tracking the movement of water masses. Storing and analyzing four dimensional data is also a large concern, but one which is being addressed by advances in computer storage, processing power, and the current development of four-dimensional geographic information systems (GIS) (Mason et al., 1994, Wright and Bartlett, 1999). These advancements will revolutionize the way we examine ocean ecosystems in the future.

5.5 New Technology is the Key

It is evident that, while progress is being made in furthering our understanding of the role of DOM in the ocean, there is still much we do not understand about the factors controlling DOM concentration and the role DOM has in ecosystems. The technology for convenient measurement of DOC, i.e. HTC, is still relatively new, and the DOM distributions of many geographic regions remain unstudied. Advances in technology will result in DOM studies that are more thorough and of broader scope. Such studies will aid researchers in understanding this important pool of carbon and will allow better modeling of ecosystems and global trends such as climate shifts.

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APPENDICES

Appendix A: Three Meter Data from the July 1997 R/V Sea Otter Cruise

The following pages show all of the available data for the samples collected from three meters depth during the July 9-23, 1997 cruise aboard the R/V Sea Otter. Blanks in the tables indicate that no data is available. Either the samples were never collected, never analyzed, or they were analyzed but deemed unusable due to contamination.

Please note that the data from stations with names in the NH-XX format were not collected during our cruise, but about one week later by another group of researchers. This data was used to complement our data set in order to offset the hydrographic data that we lost due to damaged CTD equipment.

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	Date	Temperature (°C)	Salinity	Chl-a (μg/L)
A00	-124.26	46.93	7/11/97			2.50
A01	-124.33	46.93	7/11/97	17.45	24.79	3.29
A02	-124.45	46.92	7/11/97	17.09	26.36	1.91
A03	-124.57	46.92	7/10/97	16.50	30.63	1.80
A04	-124.68	46.92	7/10/97	16.78	30.70	1.04
A05	-124.81	46.92	7/10/97	16.91	30.61	1.39
A06	-124.93	46.93	7/10/97	17.66	31.15	
A07	-125.06	46.93	7/10/97	17.34	31.49	
A08	-125.18	46.93	7/10/97	17.67	31.39	0.23
A09	-125.30	46.92	7/10/97	17.61	31.48	
A10	-125.42	46.93	7/10/97	17.46	31.84	
A11	-125.54	46.92	7/10/97	17.45	31.87	0.17
A12	-125.67	46.92	7/10/97	17.16	31.99	
A13	-125.79	46.93	7/10/97	17.20	31.90	
A14	-125.90	46.93	7/10/97	17.18	31.92	
A15	-126.03	46.92	7/10/97	17.03	32.04	0.10
A16	-126.15	46.92	7/10/97	16.65	32.26	
A17	-126.27	46.92	7/10/97	16.50	32.37	
A18	-126.39	46.93	7/10/97	16.22	32.25	
A19	-126.52	46.93	7/10/97	16.02	32.30	0.11
B00	-124.17	46.63	7/11/97	17.56	21.53	4.91
B01	-124.19	46.63	7/11/97	17.26	23.57	5.14
B02	-124.30	46.63	7/11/97	16.37	28.03	4.06
B03	-124.43	46.63	7/11/97	17.26	26.63	2.45
B04	-124.55	46.63	7/11/97	16.70	30.18	3.33
B05	-124.67	46.63	7/11/97	16.41	30.43	3.07
B06	-124.78	46.63	7/11/97	17.09	30.38	
B07	-124.91	46.63	7/11/97	17.25	30.79	
B08	-125.03	46.63	7/11/97	17.42	31.02	0.50
B09	-125.15	46.63	7/11/97	17.36	31.22	
B10	-125.27	46.63	7/11/97	17.26	31.88	
B11	-125.40	46.63	7/11/97	16.98	32.23	0.11
B12	-125.52	46.63	7/12/97	16.77	32.32	
B13	-125.64	46.63	7/12/97	17.02	32.19	
B14	-125.75	46.63	7/12/97	16.96	32.19	
B15	-125.88	46.63	7/12/97	16.96	32.20	0.07
B16	-126.00	46.63	7/12/97	16.88	32.26	
B17	-126.12	46.63	7/12/97	16.49	32.35	
B18	-126.23	46.63	7/12/97	16.36	32.33	
B19	-126.36	46.63	7/12/97	16.45	32.38	0.19
C00	-124.18	46.27	7/13/97	16.74	19.79	4.07
C01	-124.22	46.27	7/13/97	16.87	19.96	3.62
C02	-124.34	46.27	7/12/97	17.10	24.51	3.44
C03	-124.46	46.27	7/12/97	16.60	27.74	3.30
C04	-124.58	46.27	7/12/97	16.98	29.36	2.08
C05	-124.70	46.27	7/12/97	17.55	29.00	1.72
C06	-124.82	46.27	7/12/97	17.49	29.71	
C07	-124.94	46.27	7/12/97	17.48	29.80	
C08	-125.06	46.27	7/12/97	17.16	30.32	0.65
C09	-125.18	46.27	7/12/97	17.65	31.32	
C10	-125.30	46.27	7/12/97	17.56	31.81	

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	Date	Temperature (°C)	Salinity	Chl-a (µg/L)
C11	-125.42	46.27	7/12/97	17.35	31.99	0.12
C12	-125.54	46.27	7/12/97	17.28	32.12	
C13	-125.66	46.27	7/12/97	16.80	32.37	
C14	-125.78	46.27	7/12/97	16.69	32.41	
C15	-125.90	46.27	7/12/97	16.66	32.37	0.10
C16	-126.02	46.27	7/12/97	16.55	32.35	
C17	-126.14	46.27	7/12/97	16.54	32.43	
C18	-126.26	46.27	7/12/97	16.53	32.43	
C19	-126.38	46.27	7/12/97	16.54	32.27	0.08
D00	-123.99	46.05	7/13/97	12.12	30.93	1.95
D01	-124.05	46.05	7/14/97	13.14	30.23	3.31
D02	-124.16	46.05	7/14/97	14.23	29.55	3.56
D03	-124.28	46.05	7/14/97	16.29	26.44	2.41
D04	-124.40	46.05	7/14/97	17.04	28.30	2.61
D05	-124.52	46.05	7/14/97	18.13	25.59	1.55
D06	-124.64	46.05	7/14/97	17.78	27.25	
D07	-124.76	46.05	7/14/97	17.92	27.26	
D08	-124.88	46.05	7/14/97	17.94	30.55	0.62
D09	-125.00	46.05	7/14/97	17.86	31.32	
D10	-125.12	46.05	7/14/97	17.95	31.42	
D11	-125.24	46.05	7/14/97	17.84	31.91	0.11
D12	-125.36	46.05	7/14/97	17.86	31.63	
D13	-125.48	46.05	7/14/97	17.38	32.23	
D14	-125.60	46.05	7/14/97	17.48	32.15	
D15	-125.72	46.05	7/15/97	17.63	32.18	0.10
D16	-125.84	46.05	7/15/97	17.17	32.38	
D17	-125.96	46.05	7/15/97	16.97	32.39	
D18	-126.08	46.05	7/15/97	17.00	32.35	
D19	-126.20	46.05	7/15/97	16.89	32.42	0.09
E00	-124.01	45.76	7/15/97	13.92	29.79	2.20
E01	-124.08	45.76	7/15/97	16.95	25.61	2.90
E02	-124.20	45.76	7/15/97	15.74	26.87	4.05
E03	-124.32	45.76	7/15/97	16.93	25.92	3.71
E04	-124.44	45.76	7/15/97	17.44	24.10	3.95
E05	-124.56	45.76	7/15/97	18.31	22.98	3.17
E06	-124.68	45.76	7/15/97	18.21	26.00	
E07	-124.80	45.76	7/15/97	18.59	26.64	
E08	-124.92	45.76	7/15/97	18.73	25.39	0.69
E09	-125.04	45.76	7/15/97	18.58	24.85	
E10	-125.16	45.76	7/15/97	18.31	25.41	
E11	-125.28	45.76	7/15/97	18.20	28.19	0.37
E12	-125.39	45.76	7/15/97	17.76	31.72	
E13	-125.50	45.76	7/15/97	17.76	31.90	
E14	-125.63	45.76	7/15/97	17.57	32.09	
E15	-125.75	45.76	7/15/97	17.27	32.28	0.09
E16	-125.87	45.76	7/15/97	17.21	32.41	
E17	-125.99	45.76	7/15/97	17.22	32.40	
E18	-126.11	45.76	7/15/97	17.20	32.41	
E19	-126.23	45.76	7/15/97	17.05	32.31	0.08
G00	-124.00	45.17	7/16/97	11.11	32.44	4.62
G01	-124.08	45.17	7/16/97	12.67	30.90	1.61

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	Date	Temperature (°C)	Salinity	Chl-a (µg/L)
G02	-124.20	45.18	7/16/97	15.68	28.53	3.57
G03	-124.32	45.18	7/16/97	16.37	27.57	2.94
G04	-124.44	45.18	7/16/97	17.05	27.74	1.25
G05	-124.55	45.17	7/16/97	18.43	26.43	0.48
G06	-124.67	45.18	7/16/97	18.39	27.23	
G07	-124.79	45.18	7/16/97	18.27	28.34	
G08	-124.91	45.17	7/16/97	18.24	28.40	0.22
G09	-125.03	45.17	7/16/97	18.29	28.48	
G10	-125.14	45.18	7/16/97	18.35	29.05	
G11	-125.26	45.18	7/17/97	18.33	30.13	0.20
G12	-125.38	45.18	7/17/97	18.09	30.89	
G13	-125.50	45.17	7/17/97	18.13	31.16	
G14	-125.62	45.18	7/17/97	17.89	31.30	
G15	-125.73	45.17	7/17/97	17.76	31.44	0.21
G16	-125.85	45.17	7/17/97	17.77	31.39	
G17	-125.97	45.18	7/17/97	17.87	30.81	
G18	-126.09	45.17	7/17/97	17.90	31.03	
G19	-126.20	45.18	7/17/97	17.85	30.91	0.18
I00	-124.12	44.59	7/18/97			2.88
I01	-124.18	44.59	7/18/97			6.83
I02	-124.30	44.59	7/18/97			6.29
I03	-124.40	44.59	7/18/97			4.67
I04	-124.53	44.59	7/18/97			2.31
I05	-124.65	44.59	7/18/97			1.00
I06	-124.77	44.59	7/18/97			
I07	-124.88	44.59	7/18/97			
I08	-125.00	44.59	7/18/97	16.62	31.01	0.42
I09	-125.12	44.59	7/18/97			
I10	-125.23	44.59	7/17/97			
I11	-125.35	44.59	7/17/97			0.18
I12	-125.47	44.59	7/17/97			
I13	-125.58	44.59	7/17/97			
I14	-125.70	44.59	7/17/97			
I15	-125.82	44.59	7/17/97			0.20
I16	-125.93	44.59	7/17/97			
I17	-126.05	44.59	7/17/97			
I18	-126.17	44.59	7/17/97			
I19	-126.28	44.59	7/17/97			0.16
K00	-124.17	44.01	7/19/97	9.10	33.44	5.26
K01	-124.25	44.01	7/19/97	9.22	33.53	8.13
K02	-124.35	44.01	7/19/97	9.79	33.36	9.76
K03	-124.47	44.01	7/19/97	11.45	32.97	3.05
K04	-124.58	44.01	7/19/97	11.31	32.77	4.26
K05	-124.70	44.01	7/19/97	13.14	32.68	2.68
K06	-124.83	44.01	7/19/97	12.03	32.00	
K07	-124.92	44.01	7/19/97	12.52	31.47	
K08	-125.04	44.01	7/19/97	13.65	31.05	9.07
K09	-125.15	44.01	7/19/97	15.83	30.45	
K10	-125.27	44.01	7/19/97	16.35	30.31	
K11	-125.38	44.01	7/19/97	17.17	31.06	1.00
K12	-125.49	44.01	7/19/97	18.23	30.69	

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	Date	Temperature (°C)	Salinity	Chl-a (µg/L)
K13	-125.60	44.01	7/19/97	18.24	30.33	
K14	-125.72	44.01	7/19/97	18.42	30.93	
K15	-125.83	44.01	7/19/97	18.35	30.69	0.22
K16	-125.95	44.01	7/20/97	18.29	30.52	
K17	-126.05	44.01	7/20/97	18.30	30.11	
K18	-126.17	44.01	7/20/97	18.17	30.64	
K19	-126.28	44.01	7/20/97	17.83	31.99	0.11
M00	-124.34	43.43	7/21/97	9.60	33.41	5.58
M01	-124.45	43.42	7/21/97	11.45	32.78	11.70
M02	-124.57	43.43	7/21/97	12.89	32.04	0.85
M03	-124.68	43.43	7/20/97	16.04	31.24	0.37
M04	-124.80	43.42	7/20/97	16.09	31.23	0.27
M05	-124.91	43.42	7/20/97	15.89	31.24	0.49
M06	-125.03	43.43	7/20/97	15.00	31.49	
M07	-125.14	43.42	7/20/97	15.52	31.32	
M08	-125.26	43.43	7/20/97	13.95	31.45	7.56
M09	-125.37	43.42	7/20/97	15.32	31.38	
M10	-125.49	43.42	7/20/97	15.42	31.24	
M11	-125.60	43.42	7/20/97	16.55	31.21	1.60
M12	-125.71	43.42	7/20/97	17.71	31.52	
M13	-125.83	43.43	7/20/97	17.38	31.66	
M14	-125.94	43.42	7/20/97	17.65	31.67	
M15	-126.06	43.43	7/20/97	17.29	32.11	0.23
M16	-126.17	43.43	7/20/97	17.59	31.20	
M17	-126.29	43.43	7/20/97	17.54	31.30	
M18	-126.40	43.43	7/20/97	17.69	31.15	
M19	-126.52	43.43	7/20/97	18.02	30.75	0.25
O00	-124.62	42.84	7/21/97	9.89	33.50	14.47
O01	-124.66	42.84	7/21/97	10.31	32.71	6.21
O02	-124.78	42.84	7/21/97	11.07	32.56	3.48
O03	-124.89	42.84	7/21/97	13.52	32.25	0.31
O04	-125.00	42.84	7/21/97	15.06	32.05	0.34
O05	-125.12	42.84	7/21/97	15.07	32.15	0.44
O06	-125.23	42.84	7/21/97	15.37	32.09	
O07	-125.34	42.84	7/21/97	16.34	31.47	
O08	-125.46	42.84	7/21/97	16.24	31.54	0.44
O09	-125.57	42.84	7/21/97	15.36	31.85	
O10	-125.68	42.84	7/21/97	15.84	31.95	
Z00	-124.29	47.22	7/9/97	16.75	26.91	6.67
Z01	-124.34	47.22	7/9/97	16.43	27.62	5.41
Z02	-124.46	47.22	7/9/97	15.16	30.46	5.53
Z03	-124.58	47.22	7/9/97	15.63	30.59	2.51
Z04	-124.71	47.22	7/9/97	15.47	30.47	1.97
Z05	-124.83	47.22	7/9/97	15.93	30.59	1.80
Z06	-124.95	47.22	7/9/97	16.62	30.85	
Z07	-125.07	47.22	7/9/97	16.66	31.26	
Z08	-125.20	47.22	7/9/97	16.39	31.21	0.68
Z09	-125.32	47.22	7/9/97	16.61	31.79	
Z10	-125.44	47.22	7/9/97	16.58	31.89	
Z11	-125.56	47.22	7/10/97	16.70	31.61	0.20
Z12	-125.69	47.22	7/10/97	16.66	31.73	

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	Date	Temperature (°C)	Salinity	Chl-a (µg/L)
Z13	-125.81	47.22	7/10/97	16.63	31.76	
Z14	-125.93	47.22	7/10/97	16.69	31.74	
Z15	-126.05	47.22	7/10/97	16.61	31.85	0.17
Z16	-126.18	47.22	7/10/97	16.48	32.02	
Z17	-126.30	47.22	7/10/97	16.20	32.22	
Z18	-126.42	47.22	7/10/97	16.14	32.25	
Z19	-126.54	47.22	7/10/97	16.19	32.31	0.39
B200	-124.17	46.63	7/23/97			
B201	-124.19	46.63	7/23/97			
B202	-124.30	46.63	7/23/97			
B203	-124.43	46.63	7/23/97			
B204	-124.55	46.63	7/23/97			
B205	-124.67	46.63	7/23/97			
B206	-124.78	46.63	7/23/97			
B207	-124.91	46.63	7/23/97			
B208	-125.02	46.63	7/23/97			
B209	-125.15	46.63	7/23/97			
B210	-125.27	46.63	7/23/97			
NH-65	-125.60	44.65	7/28/97	18.41	30.26	
NH-85	-126.05	44.65	7/28/97	18.48	29.43	
NH-45	-125.12	44.65	7/28/97	17.07	30.93	
NH-35	-124.88	44.65	7/28/97	16.17	31.09	
NH-25	-124.65	44.65	7/28/97	14.23	31.59	
NH-15	-124.40	44.65	7/28/97	12.41	31.87	
NH-10	-124.28	44.65	7/28/97	11.04	32.26	
NH-05	-124.17	44.65	7/28/97	9.69	33.23	

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	TOC (μM)	POC (uM)	DOC (μM)	TN (μM)	PON (uM)	DON (μM)
A00	-124.26	46.93	114.64	46.68	67.97	12.78	5.40	7.33
A01	-124.33	46.93	151.87	61.07	90.80	13.63	6.87	6.66
A02	-124.45	46.92	108.12	55.18	52.94	11.33	6.51	4.73
A03	-124.57	46.92	103.64	37.36	66.28	8.99	4.53	4.31
A04	-124.68	46.92	90.86	34.25	56.61	8.17	3.43	4.70
A05	-124.81	46.92	88.32	31.31	57.01	6.53	2.72	3.50
A06	-124.93	46.93						
A07	-125.06	46.93						
A08	-125.18	46.93	67.89	20.82	47.08	5.17	1.30	3.85
A09	-125.30	46.92						
A10	-125.42	46.93						
A11	-125.54	46.92	107.84	13.00	94.84	7.45	1.07	6.23
A12	-125.67	46.92						
A13	-125.79	46.93						
A14	-125.90	46.93						
A15	-126.03	46.92	94.96	27.24	67.72	7.57	1.59	5.90
A16	-126.15	46.92						
A17	-126.27	46.92						
A18	-126.39	46.93						
A19	-126.52	46.93	110.17	21.60	88.57	10.95	1.41	8.94
B00	-124.17	46.63		48.68			5.30	
B01	-124.19	46.63		60.56			5.86	
B02	-124.30	46.63	111.29	43.85	67.44	12.92	4.54	8.13
B03	-124.43	46.63	130.68	45.96	84.72	12.90	4.60	8.22
B04	-124.55	46.63	103.59	49.01	54.58	13.47	5.51	7.86
B05	-124.67	46.63	95.83	59.76	36.07	12.41	6.42	5.93
B06	-124.78	46.63						
B07	-124.91	46.63						
B08	-125.03	46.63	73.35	29.27	44.08	8.55	2.34	6.05
B09	-125.15	46.63						
B10	-125.27	46.63						
B11	-125.40	46.63	72.60	9.54	63.06	7.21	0.77	6.30
B12	-125.52	46.63						
B13	-125.64	46.63						
B14	-125.75	46.63						
B15	-125.88	46.63	72.85	21.23	51.62	8.00	1.37	6.62
B16	-126.00	46.63						
B17	-126.12	46.63						
B18	-126.23	46.63						
B19	-126.36	46.63	65.74	15.69	50.05	7.70	1.31	6.21
C00	-124.18	46.27	122.50	53.88	68.62	15.00	6.32	6.86
C01	-124.22	46.27	124.22	56.21	68.01	11.78	6.63	
C02	-124.34	46.27	115.58	35.90	79.68	9.44	3.67	4.88
C03	-124.46	46.27	131.58	65.29	66.30	7.64	6.63	
C04	-124.58	46.27	124.25	42.77	81.48	7.71	3.69	3.34
C05	-124.70	46.27	113.43	43.49	69.94	7.92	4.36	3.49
C06	-124.82	46.27						
C07	-124.94	46.27						
C08	-125.06	46.27	95.76	20.63	75.13	4.92	1.57	3.24
C09	-125.18	46.27						
C10	-125.30	46.27						

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	TOC (μM)	POC (uM)	DOC (μM)	TN (μM)	PON (uM)	DON (μM)
C11	-125.42	46.27	80.51	26.14	54.37	5.44	1.87	3.28
C12	-125.54	46.27						
C13	-125.66	46.27						
C14	-125.78	46.27						
C15	-125.90	46.27	63.74	13.94	49.80	3.67	0.90	2.50
C16	-126.02	46.27						
C17	-126.14	46.27						
C18	-126.26	46.27						
C19	-126.38	46.27	73.37	16.39	56.98	4.55	1.19	3.04
D00	-123.99	46.05	139.39	38.91	100.48	16.38	4.53	5.39
D01	-124.05	46.05	125.14	33.15	91.99	12.16	3.60	4.53
D02	-124.16	46.05	141.75	61.77	79.98	12.82	6.89	4.40
D03	-124.28	46.05	170.61	42.19	128.42	20.23	4.95	4.37
D04	-124.40	46.05	152.85	51.06	101.79	9.20	4.89	4.17
D05	-124.52	46.05	147.67	52.93	94.74	8.77	4.80	3.41
D06	-124.64	46.05						
D07	-124.76	46.05						
D08	-124.88	46.05		27.07			2.10	
D09	-125.00	46.05						
D10	-125.12	46.05						
D11	-125.24	46.05	122.81	13.82	109.00	4.09	0.98	1.80
D12	-125.36	46.05						
D13	-125.48	46.05						
D14	-125.60	46.05						
D15	-125.72	46.05		9.43			0.73	
D16	-125.84	46.05						
D17	-125.96	46.05						
D18	-126.08	46.05						
D19	-126.20	46.05		11.16			0.79	
E00	-124.01	45.76						
E01	-124.08	45.76	147.66	38.40	109.26	9.89	3.18	4.82
E02	-124.20	45.76						
E03	-124.32	45.76						
E04	-124.44	45.76						
E05	-124.56	45.76	184.94	71.11	113.83	9.61	5.60	3.59
E06	-124.68	45.76						
E07	-124.80	45.76						
E08	-124.92	45.76		28.72			2.74	
E09	-125.04	45.76						
E10	-125.16	45.76						
E11	-125.28	45.76	146.32	19.34	126.98	5.28	1.72	2.63
E12	-125.39	45.76						
E13	-125.50	45.76						
E14	-125.63	45.76						
E15	-125.75	45.76						
E16	-125.87	45.76						
E17	-125.99	45.76						
E18	-126.11	45.76						
E19	-126.23	45.76	99.58	5.37	94.22	3.51	0.91	2.19
G00	-124.00	45.17	131.60	55.65	75.95	26.72	8.13	
G01	-124.08	45.17						

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	TOC (μM)	POC (uM)	DOC (μM)	TN (μM)	PON (uM)	DON (μM)
G02	-124.20	45.18						
G03	-124.32	45.18	159.51	53.80	105.71	10.00	7.73	2.15
G04	-124.44	45.18						
G05	-124.55	45.17	144.76	31.64	113.12	5.34	3.48	1.84
G06	-124.67	45.18						
G07	-124.79	45.18						
G08	-124.91	45.17	204.54	19.91	184.63	4.67	2.02	2.29
G09	-125.03	45.17						
G10	-125.14	45.18						
G11	-125.26	45.18						
G12	-125.38	45.18						
G13	-125.50	45.17						
G14	-125.62	45.18						
G15	-125.73	45.17	109.41	15.18	94.22	4.41	1.83	2.33
G16	-125.85	45.17						
G17	-125.97	45.18						
G18	-126.09	45.17						
G19	-126.20	45.18	144.47	10.98	133.49	4.10	1.71	1.97
I00	-124.12	44.59	127.78	29.62	98.16	33.22	3.65	5.94
I01	-124.18	44.59	132.89	39.33	93.56	22.74	5.64	2.95
I02	-124.30	44.59	133.37	36.31	97.06	26.84	4.54	6.70
I03	-124.40	44.59	134.89	41.44	93.45	20.60	5.52	6.15
I04	-124.53	44.59	130.99	28.12	102.87	15.59	3.63	6.24
I05	-124.65	44.59	161.95	30.11	131.83	10.64	3.13	7.30
I06	-124.77	44.59						
I07	-124.88	44.59						
I08	-125.00	44.59	203.37	27.90	175.47	8.91	2.54	5.51
I09	-125.12	44.59						
I10	-125.23	44.59						
I11	-125.35	44.59	139.72	18.96	120.75	7.33	1.41	5.80
I12	-125.47	44.59						
I13	-125.58	44.59						
I14	-125.70	44.59						
I15	-125.82	44.59		17.79			1.74	
I16	-125.93	44.59						
I17	-126.05	44.59						
I18	-126.17	44.59						
I19	-126.28	44.59	145.66	14.39	131.27	7.86	1.17	6.10
K00	-124.17	44.01		48.68			4.71	
K01	-124.25	44.01	130.23	31.45	98.78	32.92	3.91	
K02	-124.35	44.01		62.92			8.81	
K03	-124.47	44.01	131.33	53.71	77.62	20.94	7.51	4.58
K04	-124.58	44.01		52.03			6.97	
K05	-124.70	44.01	149.19	45.25	103.93	15.99	4.83	7.54
K06	-124.83	44.01						
K07	-124.92	44.01						
K08	-125.04	44.01	134.81	58.79	76.02	19.14	6.80	7.84
K09	-125.15	44.01						
K10	-125.27	44.01						
K11	-125.38	44.01	127.53	28.06	99.47	8.93	2.57	6.04
K12	-125.49	44.01						

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	TOC (μM)	POC (uM)	DOC (μM)	TN (μM)	PON (uM)	DON (μM)
K13	-125.60	44.01						
K14	-125.72	44.01						
K15	-125.83	44.01		27.33			2.68	
K16	-125.95	44.01						
K17	-126.05	44.01						
K18	-126.17	44.01						
K19	-126.28	44.01	114.14	14.33	99.82	7.27	1.41	5.24
M00	-124.34	43.43	151.45	19.86	131.59	29.62	2.31	6.71
M01	-124.45	43.42	150.91	35.10	115.81	15.97	4.87	8.21
M02	-124.57	43.43	125.62	23.15	102.47	13.49	2.54	5.48
M03	-124.68	43.43	120.49	15.93	104.56	7.32	1.27	5.93
M04	-124.80	43.42	124.58	10.64	113.94	6.87	0.98	5.49
M05	-124.91	43.42	136.17	15.96	120.21	7.30	1.61	5.15
M06	-125.03	43.43						
M07	-125.14	43.42						
M08	-125.26	43.43	154.85	70.98	83.87	18.84	7.54	6.77
M09	-125.37	43.42						
M10	-125.49	43.42						
M11	-125.60	43.42	152.27	21.13	131.15	9.65	1.87	7.41
M12	-125.71	43.42						
M13	-125.83	43.43						
M14	-125.94	43.42						
M15	-126.06	43.43						
M16	-126.17	43.43						
M17	-126.29	43.43						
M18	-126.40	43.43						
M19	-126.52	43.43						
O00	-124.62	42.84	155.28	40.70	114.58	27.38	5.73	8.18
O01	-124.66	42.84	154.58	25.33	129.24	19.69	3.25	8.38
O02	-124.78	42.84	127.45	36.16	91.29	14.18	4.86	5.61
O03	-124.89	42.84	146.30	13.73	132.57	6.86	1.60	5.23
O04	-125.00	42.84	117.79	14.36	103.43	6.70	1.57	5.13
O05	-125.12	42.84	125.93	16.26	109.67	7.83	1.78	5.97
O06	-125.23	42.84						
O07	-125.34	42.84						
O08	-125.46	42.84	125.49	17.14	108.35	8.67	1.53	6.77
O09	-125.57	42.84						
O10	-125.68	42.84						
Z00	-124.29	47.22	179.33	69.74	109.59	19.02	8.13	10.41
Z01	-124.34	47.22						
Z02	-124.46	47.22						
Z03	-124.58	47.22						
Z04	-124.71	47.22						
Z05	-124.83	47.22						
Z06	-124.95	47.22						
Z07	-125.07	47.22						
Z08	-125.20	47.22						
Z09	-125.32	47.22						
Z10	-125.44	47.22						
Z11	-125.56	47.22						
Z12	-125.69	47.22						

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	TOC (μM)	POC (uM)	DOC (μM)	TN (μM)	PON (uM)	DON (μM)
Z13	-125.81	47.22						
Z14	-125.93	47.22						
Z15	-126.05	47.22						
Z16	-126.18	47.22						
Z17	-126.30	47.22						
Z18	-126.42	47.22						
Z19	-126.54	47.22						
B200	-124.17	46.63						
B201	-124.19	46.63						
B202	-124.30	46.63						
B203	-124.43	46.63						
B204	-124.55	46.63						
B205	-124.67	46.63						
B206	-124.78	46.63						
B207	-124.91	46.63						
B208	-125.02	46.63						
B209	-125.15	46.63						
B210	-125.27	46.63						
NH-65	-125.60	44.65						
NH-85	-126.05	44.65						
NH-45	-125.12	44.65						
NH-35	-124.88	44.65						
NH-25	-124.65	44.65						
NH-15	-124.40	44.65						
NH-10	-124.28	44.65						
NH-05	-124.17	44.65						

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	NO3- (μM)	NO2- (μM)	NH4+ (μM)	Si(OH)4 (μM)
A00	-124.26	46.93	0.01	0.00	0.05	8.69
A01	-124.33	46.93	0.02	0.00	0.09	9.61
A02	-124.45	46.92	0.00	0.00	0.09	4.85
A03	-124.57	46.92	0.00	0.00	0.14	5.08
A04	-124.68	46.92	0.00	0.00	0.04	7.11
A05	-124.81	46.92	0.08	0.00	0.23	7.79
A06	-124.93	46.93				
A07	-125.06	46.93				
A08	-125.18	46.93	0.01	0.00	0.02	1.70
A09	-125.30	46.92				
A10	-125.42	46.93				
A11	-125.54	46.92	0.06	0.00	0.10	6.98
A12	-125.67	46.92				
A13	-125.79	46.93				
A14	-125.90	46.93				
A15	-126.03	46.92	0.00	0.00	0.07	5.21
A16	-126.15	46.92				
A17	-126.27	46.92				
A18	-126.39	46.93				
A19	-126.52	46.93	0.12	0.00	0.48	6.32
B00	-124.17	46.63	0.00	0.00	0.23	17.07
B01	-124.19	46.63	0.00	0.00	0.27	16.46
B02	-124.30	46.63	0.04	0.00	0.21	6.15
B03	-124.43	46.63	0.00	0.01	0.08	8.26
B04	-124.55	46.63	0.00	0.03	0.08	4.38
B05	-124.67	46.63	0.00	0.00	0.07	10.57
B06	-124.78	46.63				
B07	-124.91	46.63				
B08	-125.03	46.63	0.00	0.01	0.15	2.54
B09	-125.15	46.63				
B10	-125.27	46.63				
B11	-125.40	46.63	0.00	0.02	0.14	4.81
B12	-125.52	46.63				
B13	-125.64	46.63				
B14	-125.75	46.63				
B15	-125.88	46.63	0.00	0.00	0.01	3.65
B16	-126.00	46.63				
B17	-126.12	46.63				
B18	-126.23	46.63				
B19	-126.36	46.63	0.01	0.00	0.18	4.23
C00	-124.18	46.27	0.66	0.04	1.11	21.16
C01	-124.22	46.27	2.79	0.08	1.19	18.25
C02	-124.34	46.27	0.86	0.00	0.12	7.89
C03	-124.46	46.27	0.91	0.00	0.24	6.79
C04	-124.58	46.27	0.09	0.00	0.65	7.63
C05	-124.70	46.27			0.07	4.71
C06	-124.82	46.27				
C07	-124.94	46.27				
C08	-125.06	46.27			0.08	3.65
C09	-125.18	46.27				
C10	-125.30	46.27				

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	NO3- (μM)	NO2- (μM)	NH4+ (μM)	Si(OH)4 (μM)
C11	-125.42	46.27			0.27	3.01
C12	-125.54	46.27				
C13	-125.66	46.27				
C14	-125.78	46.27				
C15	-125.90	46.27			0.25	8.68
C16	-126.02	46.27				
C17	-126.14	46.27				
C18	-126.26	46.27				
C19	-126.38	46.27	0.00	0.01	0.31	5.61
D00	-123.99	46.05	5.22	0.24	1.00	30.06
D01	-124.05	46.05	3.35	0.18	0.50	14.74
D02	-124.16	46.05	1.37	0.05	0.10	15.11
D03	-124.28	46.05	10.03	0.24	0.63	42.73
D04	-124.40	46.05	0.21	0.00	0.00	4.89
D05	-124.52	46.05	0.34	0.00	0.29	5.55
D06	-124.64	46.05				
D07	-124.76	46.05				
D08	-124.88	46.05	0.59	0.00	0.06	5.30
D09	-125.00	46.05				
D10	-125.12	46.05				
D11	-125.24	46.05	0.30	0.24	0.77	8.81
D12	-125.36	46.05				
D13	-125.48	46.05				
D14	-125.60	46.05				
D15	-125.72	46.05	1.14	0.09	0.43	2.59
D16	-125.84	46.05				
D17	-125.96	46.05				
D18	-126.08	46.05				
D19	-126.20	46.05	0.76	0.00	0.14	2.10
E00	-124.01	45.76	2.96	0.10	0.17	10.63
E01	-124.08	45.76	1.04	0.02	0.83	11.34
E02	-124.20	45.76	1.89	0.05	0.12	14.47
E03	-124.32	45.76	0.03	0.03	1.23	15.63
E04	-124.44	45.76	1.59	0.03	0.50	18.53
E05	-124.56	45.76	0.18	0.00	0.32	18.78
E06	-124.68	45.76				
E07	-124.80	45.76				
E08	-124.92	45.76	0.00	0.00	0.20	5.61
E09	-125.04	45.76				
E10	-125.16	45.76				
E11	-125.28	45.76	0.06	0.00	0.90	6.09
E12	-125.39	45.76				
E13	-125.50	45.76				
E14	-125.63	45.76				
E15	-125.75	45.76	0.20	0.00	0.10	2.04
E16	-125.87	45.76				
E17	-125.99	45.76				
E18	-126.11	45.76				
E19	-126.23	45.76	0.18	0.00	0.25	2.05
G00	-124.00	45.17	18.00	0.54	0.20	29.93
G01	-124.08	45.17	11.37	0.44	0.57	19.01

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	NO3- (μM)	NO2- (μM)	NH4+ (μM)	Si(OH)4 (μM)
G02	-124.20	45.18	0.14	0.11	0.60	10.65
G03	-124.32	45.18	0.00	0.00	0.13	8.81
G04	-124.44	45.18	0.03	0.00	0.02	6.48
G05	-124.55	45.17	0.05	0.00	0.02	4.53
G06	-124.67	45.18				
G07	-124.79	45.18				
G08	-124.91	45.17	0.06	0.00	0.32	3.30
G09	-125.03	45.17				
G10	-125.14	45.18				
G11	-125.26	45.18	0.12	0.00	0.16	3.42
G12	-125.38	45.18				
G13	-125.50	45.17				
G14	-125.62	45.18				
G15	-125.73	45.17	0.10	0.00	0.17	2.58
G16	-125.85	45.17				
G17	-125.97	45.18				
G18	-126.09	45.17				
G19	-126.20	45.18	0.12	0.00	0.32	3.25
I00	-124.12	44.59	22.80	0.29	0.54	29.17
I01	-124.18	44.59	13.59	0.25	0.31	15.12
I02	-124.30	44.59	14.91	0.32	0.37	17.81
I03	-124.40	44.59	8.45	0.28	0.20	16.93
I04	-124.53	44.59	5.45	0.18	0.09	14.88
I05	-124.65	44.59	0.17	0.00	0.06	7.47
I06	-124.77	44.59				
I07	-124.88	44.59				
I08	-125.00	44.59	0.11	0.03	0.72	8.11
I09	-125.12	44.59				
I10	-125.23	44.59				
I11	-125.35	44.59	0.00	0.03	0.11	10.32
I12	-125.47	44.59				
I13	-125.58	44.59				
I14	-125.70	44.59				
I15	-125.82	44.59				
I16	-125.93	44.59				
I17	-126.05	44.59				
I18	-126.17	44.59				
I19	-126.28	44.59	0.11	0.00	0.50	6.83
K00	-124.17	44.01	26.81	0.40	0.30	27.01
K01	-124.25	44.01	25.63	0.20	0.16	29.85
K02	-124.35	44.01	17.92	0.25	0.18	21.10
K03	-124.47	44.01	8.31	0.19	0.36	7.67
K04	-124.58	44.01	7.69	0.14	0.23	9.09
K05	-124.70	44.01	3.22	0.10	0.30	3.12
K06	-124.83	44.01				
K07	-124.92	44.01				
K08	-125.04	44.01	4.20	0.17	0.13	13.05
K09	-125.15	44.01				
K10	-125.27	44.01				
K11	-125.38	44.01	0.25	0.00	0.06	7.26
K12	-125.49	44.01				

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	NO3- (μM)	NO2- (μM)	NH4+ (μM)	Si(OH)4 (μM)
K13	-125.60	44.01				
K14	-125.72	44.01				
K15	-125.83	44.01	0.26	0.00	0.20	5.36
K16	-125.95	44.01				
K17	-126.05	44.01				
K18	-126.17	44.01				
K19	-126.28	44.01	0.25	0.04	0.34	3.94
M00	-124.34	43.43	20.37	0.23	0.00	22.56
M01	-124.45	43.42	2.75	0.04	0.11	1.73
M02	-124.57	43.43	5.14	0.10	0.23	7.61
M03	-124.68	43.43	0.05	0.00	0.09	2.06
M04	-124.80	43.42	0.28	0.00	0.13	3.30
M05	-124.91	43.42	0.24	0.02	0.29	3.68
M06	-125.03	43.43				
M07	-125.14	43.42				
M08	-125.26	43.43	4.35	0.10	0.07	14.68
M09	-125.37	43.42				
M10	-125.49	43.42				
M11	-125.60	43.42	0.26	0.00	0.11	9.11
M12	-125.71	43.42				
M13	-125.83	43.43				
M14	-125.94	43.42				
M15	-126.06	43.43	0.26	0.00	0.23	4.73
M16	-126.17	43.43				
M17	-126.29	43.43				
M18	-126.40	43.43				
M19	-126.52	43.43	0.21	0.00	0.09	4.29
O00	-124.62	42.84	13.05	0.17	0.25	12.44
O01	-124.66	42.84	7.82	0.11	0.14	4.50
O02	-124.78	42.84	3.49	0.09	0.12	2.61
O03	-124.89	42.84	0.01	0.00	0.03	3.88
O04	-125.00	42.84	0.00	0.00	0.01	3.11
O05	-125.12	42.84	0.07	0.00	0.03	3.07
O06	-125.23	42.84				
O07	-125.34	42.84				
O08	-125.46	42.84	0.13	0.00	0.24	2.28
O09	-125.57	42.84				
O10	-125.68	42.84				
Z00	-124.29	47.22	0.27	0.00	0.21	9.03
Z01	-124.34	47.22				
Z02	-124.46	47.22				
Z03	-124.58	47.22				
Z04	-124.71	47.22				
Z05	-124.83	47.22				
Z06	-124.95	47.22				
Z07	-125.07	47.22				
Z08	-125.20	47.22				
Z09	-125.32	47.22				
Z10	-125.44	47.22				
Z11	-125.56	47.22				
Z12	-125.69	47.22				

Appendix A - July 1997 Data (continued)

Station	Longitude	Latitude	NO3- (μM)	NO2- (μM)	NH4+ (μM)	Si(OH)4 (μM)
Z13	-125.81	47.22				
Z14	-125.93	47.22				
Z15	-126.05	47.22				
Z16	-126.18	47.22				
Z17	-126.30	47.22				
Z18	-126.42	47.22				
Z19	-126.54	47.22				
B200	-124.17	46.63				
B201	-124.19	46.63				
B202	-124.30	46.63				
B203	-124.43	46.63				
B204	-124.55	46.63				
B205	-124.67	46.63				
B206	-124.78	46.63				
B207	-124.91	46.63				
B208	-125.02	46.63				
B209	-125.15	46.63				
B210	-125.27	46.63				
NH-65	-125.60	44.65				
NH-85	-126.05	44.65				
NH-45	-125.12	44.65				
NH-35	-124.88	44.65				
NH-25	-124.65	44.65				
NH-15	-124.40	44.65				
NH-10	-124.28	44.65				
NH-05	-124.17	44.65				

Appendix B: Data from the NH-05 Time Series, July 1997 to July 1998

The following pages include the data used in the time series analyses in Chapter 4. All data was collected from Station NH-05, located at 44.65°N, 124.17°W. The dates of sample collection are listed in both formats used in the text, "Days from 1/1/97" and "month/day/year". Blanks in the tables indicate that no data is available. Either the samples were never collected, never analyzed, or they were analyzed but deemed unusable due to contamination.

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	Temp. (°C)	Salinity	Chl-a (µg/L)
178	6/27/97	1	15.87	23.88	
178	6/27/97	10	10.36	32.15	
178	6/27/97	20	8.69	33.13	
178	6/27/97	40	8.43	33.60	
196	7/15/97	5	12.81	32.52	2.2
196	7/15/97	10	12.22	32.60	1.6
198	7/17/97	1	12.82	32.84	3.6
198	7/17/97	3	12.78	32.76	
198	7/17/97	5	12.32	32.87	2.4
198	7/17/97	10	8.65	33.32	1.1
198	7/17/97	15	8.24	33.72	0.7
198	7/17/97	20	8.03	33.84	0.3
198	7/17/97	25	7.93	33.88	0.3
198	7/17/97	30	7.83	33.93	0.2
198	7/17/97	40	7.81	33.93	0.2
198	7/17/97	50	7.80	33.93	0.2
204	7/23/97	1	10.03	33.19	13.5
204	7/23/97	5	9.97	33.09	13.1
204	7/23/97	10	9.89	33.10	11.3
211	7/30/97	10	9.32	33.45	5.9
217	8/6/97	1	12.68	33.35	1.8
217	8/6/97	5	12.09	33.27	2.3
217	8/6/97	10	10.43	33.08	5.9
217	8/6/97	30	8.33	33.51	2.5
217	8/6/97	50	7.98	33.82	2.3
224	8/12/97	1	11.01	33.15	13.5
224	8/12/97	5	10.60	32.92	16.2
224	8/12/97	10	9.26	32.81	4.9
226	8/14/97	1	10.77	32.73	3.2
226	8/14/97	5	10.40	32.92	
226	8/14/97	10	10.35	33.06	7.6
226	8/14/97	20	8.40	33.35	
226	8/14/97	30	8.35	33.53	
226	8/14/97	50	7.90	33.81	
233	8/21/97	1	13.49		1.0
233	8/21/97	1	13.49		1.0
233	8/21/97	5	13.14		1.3
233	8/21/97	10	12.25		2.3
233	8/21/97	10	12.25		0.5
233	8/21/97	30	8.48	33.47	0.4
233	8/21/97	50	8.13	33.75	1.3
239	8/27/97	1	15.65	31.58	2.4
239	8/27/97	1	15.65	31.58	1.4
239	8/27/97	5	15.63	31.66	2.1
239	8/27/97	5	15.63	31.66	2.0
239	8/27/97	10	15.50	31.89	2.2
239	8/27/97	10	15.50	31.89	1.5
239	8/27/97	30	12.08	33.32	2.8
239	8/27/97	50	9.58	33.32	2.2
240	8/28/97	1	15.97	31.99	1.3
240	8/28/97	1	15.97	31.99	2.3
240	8/28/97	5	16.04	32.10	2.0
240	8/28/97	10	15.24	32.44	1.4
240	8/28/97	10	15.24	32.44	1.2
240	8/28/97	30	12.08	33.48	1.0

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	Temp. (°C)	Salinity	Chl-a (μg/L)
240	8/28/97	50	11.69	33.51	1.2
245	9/2/97	1	18.09	31.90	0.3
245	9/2/97	5	18.08	31.89	0.2
245	9/2/97	10	17.50	32.05	0.2
252	9/9/97	1	18.26	32.15	0.5
252	9/9/97	1	18.26	32.15	0.6
252	9/9/97	10	15.73	31.76	1.2
252	9/9/97	10	15.73	31.76	0.8
252	9/9/97	20	13.39	32.90	6.2
252	9/9/97	30	11.28	32.31	0.8
252	9/9/97	50	9.76	33.59	0.3
262	9/19/97	1	17.58	31.64	0.6
262	9/19/97	5	17.52	31.82	0.5
262	9/19/97	10	17.38	31.92	0.4
262	9/19/97	15	17.32	31.92	0.2
262	9/19/97	20	17.16	32.07	0.3
262	9/19/97	25	16.92	32.14	0.3
262	9/19/97	35	15.86	32.37	0.4
262	9/19/97	40	15.67	32.43	0.4
262	9/19/97	45	15.09	32.51	0.4
262	9/19/97	50	14.30	32.66	0.5
288	10/15/97	1	14.56	30.66	2.7
288	10/15/97	10	14.89	31.77	1.8
307	11/3/97	1	13.39	32.12	0.8
319	11/15/97	1	12.38	32.47	1.3
319	11/15/97	5	12.38	32.47	1.2
319	11/15/97	10	12.38	32.47	1.3
319	11/15/97	15	12.37	32.48	1.3
319	11/15/97	20	12.00	32.64	1.3
319	11/15/97	23	12.08	32.75	1.1
319	11/15/97	25	12.08	32.83	0.9
319	11/15/97	30	12.08	32.87	0.6
319	11/15/97	40	11.98	33.02	0.5
319	11/15/97	50	11.90	33.10	0.4
346	12/12/97	1	12.63	32.53	
346	12/12/97	10	12.60	32.63	
346	12/12/97	20	12.61	32.56	
346	12/12/97	30	12.70	32.49	
346	12/12/97	50	12.92	32.59	
395	1/30/98	5	12.38	31.22	1.0
395	1/30/98	10	12.46	31.60	0.9
395	1/30/98	15	12.49	31.76	0.8
395	1/30/98	20	12.50	31.79	0.7
395	1/30/98	25	12.51	31.87	0.5
395	1/30/98	30	12.50	31.92	0.7
395	1/30/98	40	12.51	32.22	0.7
395	1/30/98	50	12.53	32.46	0.7
460	4/5/98	1	11.82	31.89	0.7
460	4/5/98	5	11.83	31.90	0.7
460	4/5/98	10	11.80	31.93	0.7
460	4/5/98	15	11.54	32.16	0.9
460	4/5/98	20	11.06	32.43	2.7
460	4/5/98	25	10.98	32.62	1.5
460	4/5/98	30	10.88	32.68	1.1
460	4/5/98	40	10.69	32.93	0.9

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	Temp. (°C)	Salinity	Chl-a (μg/L)
460	4/5/98	50	10.49	33.01	0.9
465	4/10/98	1	11.71	32.04	1.6
465	4/10/98	5	11.71	32.04	1.6
465	4/10/98	10	11.70	32.04	1.6
465	4/10/98	15	11.74	32.11	1.2
465	4/10/98	20	11.72	32.10	1.3
465	4/10/98	25	11.72	32.13	1.2
465	4/10/98	30	11.47	32.42	1.3
465	4/10/98	40	11.11	32.63	0.5
465	4/10/98	50	10.82	32.82	1.1
465	4/10/98	54	10.76	32.85	1.5
518	6/2/98	1	12.73	31.55	1.0
518	6/2/98	10	12.11	31.77	2.6
518	6/2/98	20	9.85	32.51	5.8
518	6/2/98	50	8.87	33.37	0.7
552	7/6/98	1	11.64	32.93	6.1
552	7/6/98	10	9.17	32.98	3.1
552	7/6/98	20	8.78	33.22	1.8
552	7/6/98	30	8.23	33.63	2.2
552	7/6/98	50	7.95	33.75	0.7

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	TOC (μM)	POC(uM)	DOC (μM)	TN (μM)	PON (μM)	DON (μM)
178	6/27/97	1	173.1	40.2	132.9	13.2	5.4	7.7
178	6/27/97	10	98.3	27.4	70.9	24.7	4.0	5.7
178	6/27/97	20	86.4	9.9	76.5	27.3	0.7	4.3
178	6/27/97	40	116.1	12.1	104.0	32.3	1.2	2.4
196	7/15/97	5						
196	7/15/97	10						
198	7/17/97	1	128.8	32.0	96.8	20.8	4.1	3.7
198	7/17/97	3	132.9	39.3	93.6	22.7	5.6	3.0
198	7/17/97	5	109.0	21.1	87.9	27.1	2.5	4.1
198	7/17/97	10	119.0	15.2	103.8	32.6	1.4	2.1
198	7/17/97	15		20.8		34.6	1.5	0.8
198	7/17/97	20	85.2	9.0	76.2	33.9	0.7	0.3
198	7/17/97	25	123.8	6.9	116.9	35.2	0.6	0.6
198	7/17/97	30	103.1	12.5	90.6	34.9	0.7	0.2
198	7/17/97	40	98.4	10.0	88.4	36.5	0.8	1.0
198	7/17/97	50	104.2	13.3	90.9	36.1	1.2	0.3
204	7/23/97	1						
204	7/23/97	5						
204	7/23/97	10						
211	7/30/97	10						
217	8/6/97	1	180.7	45.3	135.4	16.2	5.5	10.6
217	8/6/97	5	168.5	36.9	131.6	11.3	4.0	7.2
217	8/6/97	10	156.4	57.2	99.2	21.0	7.9	9.5
217	8/6/97	30		19.9		33.1	2.0	3.3
217	8/6/97	50	89.9	15.2	74.7	38.6	1.7	5.1
224	8/12/97	1						
224	8/12/97	5						
224	8/12/97	10						
226	8/14/97	1	170.1	67.5	102.6	17.5	7.4	10.0
226	8/14/97	5	170.7	127.4	43.3	21.1	17.1	3.9
226	8/14/97	10	158.2	79.1	79.0	26.6	6.5	9.5
226	8/14/97	20	151.7	76.7	75.0	48.7	11.7	14.8
226	8/14/97	30	94.5	24.7	69.8	36.4	2.4	6.7
226	8/14/97	50	81.9	15.3	66.6	38.9	1.5	6.2
233	8/21/97	1	196.3	20.9	175.3	31.0	2.3	28.4
233	8/21/97	1	196.3	20.9	175.3	31.0	2.3	28.4
233	8/21/97	5	126.3	24.0	102.3	9.2	2.1	7.1
233	8/21/97	10	135.0	46.0	89.1	10.0	3.4	6.5
233	8/21/97	10	135.0	46.0	89.1	10.0	3.4	6.5
233	8/21/97	30	110.1	20.9	89.2	32.2	2.3	4.2
233	8/21/97	50	84.5	15.9	68.6	36.6	1.8	4.3
239	8/27/97	1	135.4	33.0	102.4	18.2	4.2	13.2
239	8/27/97	1	135.4	33.0	102.4	18.2	4.2	13.2
239	8/27/97	5	119.6	30.6	89.0	12.2	3.2	9.0
239	8/27/97	5	119.6	30.6	89.0	12.2	3.2	9.0
239	8/27/97	10	119.6	32.0	87.6	11.5	4.1	7.1
239	8/27/97	10	119.6	32.0	87.6	11.5	4.1	7.1
239	8/27/97	30	97.3	36.9	60.3	14.5	4.3	9.0
239	8/27/97	50	93.5	17.5	76.1	19.4	2.0	6.7
240	8/28/97	1	117.7	34.2	83.5	10.5	4.5	5.9
240	8/28/97	1	117.7	34.2	83.5	10.5	4.5	5.9
240	8/28/97	5	111.3	24.4	86.9	9.0	2.6	6.4
240	8/28/97	10	122.1	35.4	86.7		4.4	
240	8/28/97	10	122.1	35.4	86.7		4.4	
240	8/28/97	30	99.5	23.6	75.9	14.8	2.8	8.5

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	TOC (μM)	POC(uM)	DOC (μM)	TN (μM)	PON (μM)	DON (μM)
240	8/28/97	50	114.9	40.5	74.5	23.7	5.4	12.1
245	9/2/97	1						
245	9/2/97	5						
245	9/2/97	10						
252	9/9/97	1	117.8	16.2	101.6	7.0	1.5	5.5
252	9/9/97	1	117.8	16.2	101.6	7.0	1.5	5.5
252	9/9/97	10	113.0	14.4	98.5	7.5	1.4	6.1
252	9/9/97	10	113.0	14.4	98.5	7.5	1.4	6.1
252	9/9/97	20	124.7	33.3	91.5	15.1	3.9	8.5
252	9/9/97	30	94.4	17.6	76.8	19.3	2.1	8.5
252	9/9/97	50	90.0	14.1	75.9	31.0	1.3	10.7
262	9/19/97	1	105.8	9.3	96.4	10.2	1.4	8.6
262	9/19/97	5	99.4	6.2	93.1	9.0	0.9	8.0
262	9/19/97	10	86.9	9.9	77.0	9.2	1.4	7.7
262	9/19/97	15	102.2	8.4	93.8	8.8	1.4	7.3
262	9/19/97	20	89.7	7.2	82.5	9.1	1.0	7.8
262	9/19/97	25	89.1	11.8	77.3	10.4	1.2	8.5
262	9/19/97	35	89.5	9.5	80.0	13.4	1.2	10.6
262	9/19/97	40	101.2	5.1	96.1	11.5	0.8	8.8
262	9/19/97	45	84.1	10.0	74.1	13.2	1.6	9.2
262	9/19/97	50	86.5	15.7	70.8	20.5	2.0	15.1
288	10/15/97	1	82.3	29.6	52.7	12.5	3.7	6.5
288	10/15/97	10	74.2	18.9	55.3	10.4	2.2	6.0
307	11/3/97	1	85.9	20.4	65.5	11.7	2.1	7.6
319	11/15/97	1		11.6		14.0	2.0	8.0
319	11/15/97	5		9.8		12.2	1.8	6.4
319	11/15/97	10		10.3		12.1	1.3	6.8
319	11/15/97	15		4.5		13.3	2.0	7.3
319	11/15/97	20				15.4		
319	11/15/97	23				16.0		
319	11/15/97	25				16.3		
319	11/15/97	30				15.0		
319	11/15/97	40				16.4		
319	11/15/97	50				16.2		
346	12/12/97	1		17.0			0.8	
346	12/12/97	10		10.5			0.6	
346	12/12/97	20		14.7			1.0	
346	12/12/97	30		34.4			4.9	
346	12/12/97	50		25.4			2.7	
395	1/30/98	5	61.3	10.6	50.7	8.8	1.3	3.8
395	1/30/98	10	72.5	8.0	64.4	8.0	0.8	3.7
395	1/30/98	15				8.6		
395	1/30/98	20	63.7	8.8	54.9	8.5	0.9	4.3
395	1/30/98	25				8.7		
395	1/30/98	30	69.5	10.2	59.3	7.8	1.0	3.6
395	1/30/98	40				7.9		
395	1/30/98	50	66.3	10.3	56.1	8.2	1.0	4.1
460	4/5/98	1		22.0			2.1	
460	4/5/98	5		20.5			1.8	
460	4/5/98	10		26.1			2.3	
460	4/5/98	15		24.1			2.1	
460	4/5/98	20		17.5			2.6	
460	4/5/98	25		11.5			1.5	
460	4/5/98	30		11.7			1.2	
460	4/5/98	40		11.4			1.0	

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	TOC (μM)	POC(uM)	DOC (μM)	TN (μM)	PON (μM)	DON (μM)
460	4/5/98	50		15.2			1.4	
465	4/10/98	1		22.0		6.6		
465	4/10/98	5				6.0		
465	4/10/98	10		26.1		5.7		
465	4/10/98	15				7.3		
465	4/10/98	20				9.5		
465	4/10/98	25				11.0		
465	4/10/98	30				12.1		
465	4/10/98	40				15.5		
465	4/10/98	50				17.1		
465	4/10/98	54						
518	6/2/98	1	100.2	22.0	78.2	8.8	1.8	4.5
518	6/2/98	10	93.9	22.9	71.0	8.1	1.9	3.7
518	6/2/98	20	98.3	28.3	70.0	12.3	3.3	5.5
518	6/2/98	50	79.0	20.3	58.8	29.6	1.8	5.3
552	7/6/98	1	111.5	49.2	62.4	13.2	6.6	4.1
552	7/6/98	10	76.2	14.0	62.2	24.3	2.3	4.9
552	7/6/98	20	67.1	12.1	54.9		1.8	
552	7/6/98	30	62.7	10.5	52.2		1.5	
552	7/6/98	50	67.1	10.5	56.6	34.6	1.6	3.6

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	N+N (µM)	NH4+ (µM)	SiO4 (µM)	PO4 (µM)
178	6/27/97	1	0.0	0.1	21.2	0.1
178	6/27/97	10	14.9	0.1	20.9	1.5
178	6/27/97	20	22.2	0.1	28.8	2.1
178	6/27/97	40	28.4	0.2	37.2	3.2
196	7/15/97	5				
196	7/15/97	10				
198	7/17/97	1	12.6	0.4	16.4	
198	7/17/97	3	13.8	0.3	15.1	
198	7/17/97	5	20.4	0.1	16.9	
198	7/17/97	10	29.2	0.0	20.9	
198	7/17/97	15	32.2	0.1	28.5	
198	7/17/97	20	32.9	0.0	23.1	
198	7/17/97	25	33.8	0.1	20.2	
198	7/17/97	30	33.9	0.1	20.4	
198	7/17/97	40	34.7	0.0	39.1	
198	7/17/97	50	34.7	0.0	35.3	
204	7/23/97	1				
204	7/23/97	5				
204	7/23/97	10				
211	7/30/97	10				
217	8/6/97	1	0.0	0.1	0.6	0.5
217	8/6/97	5	0.0	0.1	0.9	0.4
217	8/6/97	10	3.5	0.1	5.1	1.0
217	8/6/97	30	27.6	0.1	33.2	2.3
217	8/6/97	50	31.4	0.4	46.1	2.8
224	8/12/97	1				
224	8/12/97	5				
224	8/12/97	10				
226	8/14/97	1	0.1	0.0	0.6	0.5
226	8/14/97	5	0.1	0.0	1.7	0.6
226	8/14/97	10	4.4	0.1	9.0	1.0
226	8/14/97	20	20.9	1.4	28.9	2.2
226	8/14/97	30	26.7	0.6	30.2	2.4
226	8/14/97	50	30.7	0.6	43.0	2.9
233	8/21/97	1	0.0	0.2	0.3	0.3
233	8/21/97	1	0.0	0.2	0.3	0.3
233	8/21/97	5	0.0	0.0	0.1	0.4
233	8/21/97	10	0.0	0.0	0.9	0.6
233	8/21/97	10	0.0	0.0	0.9	0.6
233	8/21/97	30	24.6	1.0	27.9	2.5
233	8/21/97	50	29.3	1.2	45.6	2.8
239	8/27/97	1	0.0	0.8	0.5	1.0
239	8/27/97	1	0.0	0.8	0.5	1.0
239	8/27/97	5	0.0	0.0	0.3	0.2
239	8/27/97	5	0.0	0.0	0.3	0.2
239	8/27/97	10	0.0	0.3	0.4	0.2
239	8/27/97	10	0.0	0.3	0.4	0.2
239	8/27/97	30	0.8	0.5	1.9	0.6
239	8/27/97	50	8.9	1.8	9.7	1.5
240	8/28/97	1	0.1	0.0	0.3	0.4
240	8/28/97	1	0.1	0.0	0.3	0.4
240	8/28/97	5	0.0	0.0	0.0	0.2
240	8/28/97	10	0.0	0.1	0.0	0.3
240	8/28/97	10	0.0	0.1	0.0	0.3
240	8/28/97	30	2.3	1.3	3.6	1.0

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	N+N (μM)	NH4+ (μM)	SiO4 (μM)	PO4 (μM)
240	8/28/97	50	4.7	1.6	6.1	1.3
245	9/2/97	1				
245	9/2/97	5				
245	9/2/97	10				
252	9/9/97	1	0.0	0.0	0.1	0.3
252	9/9/97	1	0.0	0.0	0.1	0.3
252	9/9/97	10	0.0	0.0	0.3	0.3
252	9/9/97	10	0.0	0.0	0.3	0.3
252	9/9/97	20	2.4	0.2	1.1	0.6
252	9/9/97	30	7.4	1.4	10.9	1.3
252	9/9/97	50	19.0		23.0	2.2
262	9/19/97	1	0.2	0.1	2.4	0.3
262	9/19/97	5	0.1	0.1	1.9	0.3
262	9/19/97	10	0.0	0.1	2.6	0.5
262	9/19/97	15	0.0	0.2	1.8	0.5
262	9/19/97	20	0.1	0.2	1.8	0.4
262	9/19/97	25	0.3	0.3	2.2	0.5
262	9/19/97	35	1.0	0.6	4.9	0.6
262	9/19/97	40	1.3	0.6	5.8	0.6
262	9/19/97	45	1.8	0.6	6.5	
262	9/19/97	50	2.7	0.7	9.4	0.6
288	10/15/97	1	2.2	0.0	11.2	0.4
288	10/15/97	10	2.2	0.0	11.7	0.4
307	11/3/97	1	1.8	0.2	5.2	0.5
319	11/15/97	1	3.9	0.1	8.5	0.8
319	11/15/97	5	4.0	0.0	8.3	0.7
319	11/15/97	10	3.9	0.0	8.5	0.7
319	11/15/97	15	4.0	0.0	8.3	0.7
319	11/15/97	20	6.4	0.1	11.2	0.8
319	11/15/97	23	7.0	0.1	11.5	0.9
319	11/15/97	25	7.5	0.0	10.6	1.0
319	11/15/97	30	7.4	0.1	10.7	0.9
319	11/15/97	40	6.8	0.2	10.1	0.9
319	11/15/97	50	7.8	0.2	10.4	0.9
346	12/12/97	1				
346	12/12/97	10				
346	12/12/97	20				
346	12/12/97	30				
346	12/12/97	50				
395	1/30/98	5	3.6	0.0	15.1	1.1
395	1/30/98	10	3.4	0.0	13.2	1.1
395	1/30/98	15	3.4	0.0	12.6	1.1
395	1/30/98	20	3.4	0.0	12.4	1.1
395	1/30/98	25	3.3	0.0	11.4	1.1
395	1/30/98	30	3.3	0.0	11.5	1.1
395	1/30/98	40	3.0	0.0	10.2	1.1
395	1/30/98	50	3.0	0.0	9.0	1.1
460	4/5/98	1				
460	4/5/98	5				
460	4/5/98	10				
460	4/5/98	15				
460	4/5/98	20				
460	4/5/98	25				
460	4/5/98	30				
460	4/5/98	40				

Appendix B - Time Series Data (continued)

Days since 1/1/97	Date	Depth (m)	N+N (μM)	NH4+ (μM)	SiO4 (μM)	PO4 (μM)
460	4/5/98	50				
465	4/10/98	1	0.1	0.0	0.3	0.5
465	4/10/98	5	0.1	0.0	2.1	0.5
465	4/10/98	10	0.0	0.0	2.4	0.5
465	4/10/98	15	0.1	0.0	1.6	0.5
465	4/10/98	20	0.1	0.0	2.0	0.4
465	4/10/98	25	0.2	0.0	2.1	0.5
465	4/10/98	30	0.7	0.0	3.1	0.7
465	4/10/98	40	4.1	0.1	6.9	1.0
465	4/10/98	50	7.2	0.0	13.6	1.4
465	4/10/98	54	9.1	0.0	17.4	1.5
518	6/2/98	1	2.0	0.5	0.5	0.2
518	6/2/98	10	2.0	0.4	0.8	0.3
518	6/2/98	20	2.7	0.8	1.0	0.6
518	6/2/98	50	21.9	0.6	30.6	2.0
552	7/6/98	1	2.1	0.4	3.8	0.3
552	7/6/98	10	16.7	0.4	20.5	1.5
552	7/6/98	20	21.8	0.2	28.3	1.9
552	7/6/98	30	23.3	0.0	32.2	1.9
552	7/6/98	50	29.3	0.1	40.7	2.3