STABLE ISOTOPIC VARIATION IN PARTICULATE ORGANIC MATTER AND DISSOLVED INORGANIC COMPOUNDS IN A NORTHERN FJORD: IMPLICATIONS FOR PRESENT AND PAST ENVIRONMENTS

NATHANIEL E. OSTROM, B.Sc., M.Sc.

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© Nathaniel E. Ostrom, B.Sc, M.Sc.

A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Earth Sciences
Memorial University of Newfoundland
April, 1992

St. John's Newfoundland

ISBN 0-315-73331-4

Abstract

The principle objectives of this study were (1) to gain a detailed understanding of processes resulting in isotopic variation in water column organic matter and (2) to establish a relationship between the isotopic composition of water column material to that of underlying sediments. To facilitate this task nutrient and elemental abundance data and the stable isotopic composition of seston, sinking POM, sediments and inorganic compounds (DIC, NO_3^- and NH_4^+) was determined on a seasonal and spatial basis in a northern fjord, Conception Bay, Newfoundland.

The concentration and isotopic composition of inorganic nitrogen in deep and pore waters provided insight into sources and cycling of these compounds. Ammonium in the porewaters obtained from the surface 20cm of sediment cores ranged in concentration from 34.7μM to 239.9μM. The nitrogen isotopic composition of porewater ammonium averaged 7.0‰ and was depleted in ^{15}N by 2‰ relative to sediments. This difference indicates a small fractionation effect during the remineralization of ammonium from organic matter in sediments. Nitrate in water column samples had a very wide range in $\delta^{15}N$ values of -6.2‰ to 7.9‰ and an average of 0.2 ± 3.6‰. The low $\delta^{15}N$ of nitrate relative to pore water ammonium indicates that there is a large fractionation effect associated with nitrification (β = 1.0193) and that this reaction does not

proceed to completion at the cold temperatures (<0°C) present in the deep waters of this fjord. The presence of ammonium in deep waters and as a measurable flux from sediments confirms that this substrate is not completely consumed during nitrification.

The $\delta^{15}N$ of suspended POM varied from 5.2‰ to 20.2‰, with the highest values occurring in the spring at the base of the euphotic zone. High $\delta^{15}N$ values may be a consequence of fractionation during peptide bond cleavage or deamination of proteins during partial degradation. Suspended POM $\delta^{13}C$ values were narrower in range than $\delta^{15}N$ and were between -26.7‰ and -21.9‰. Enrichments in ^{13}C were frequently associated with the chlorophyll maximum during periods of high productivity. Concomitant decreases in the concentration of dissolved inorganic carbon and increases in seston $\delta^{13}C$ values confirmed results of earlier research which found a inverse correlation between pCO_2 and the $\delta^{13}C$ of phytoplankton. The carbon isotopic composition of DIC ranged from -4.1‰ to 1.6‰. Low $\delta^{13}C$-DIC values may be related to brief periods of enhanced respiration as a result of increased substrate concentration during the spring bloom. The higher $\delta^{13}C$-DIC values are typical for DIC equilibrated with atmospheric CO_2. Sediment trap $\delta^{15}N$ and $\delta^{13}C$ values were similar in range to suspended POM. The isotope values predicted by a model, which uses the isotopic composition of particulates and flux measurements, are similar to the average $\delta^{15}N$ and $\delta^{13}C$ determined for

sediments in Conception Bay, 8.6‰ and -21.4‰, respectively. These results indicate that sediments are most similar in $\delta^{15}N$ and $\delta^{13}C$ to phytoplankton during periods of high primary production.

Acknowledgements

The cooperation and assistance of many people were essential to the completion of this dissertation. To all who helped, in even minor ways, I extend my thanks and appreciation.

This project would not have been possible without the foresight, efforts, and collaboration of the founders and participants in COPE (Cold Oceans Productivity Experiment). In particular, I am indebted to Drs. Don Deibel and Ray Thompson for providing field support, enthusiasm, and an understanding of the biological aspects of COPE. Much inspiration and knowledge was gained through extensive conversations with Drs. Larry Pomeroy and Bill Wiebe. Additional support, assistance, and insight was given by other COPE participants, including, Anna Redden, Rick Dittman, Sabina Schiebe, Juanita Urban and Drs. Gil Rowe, Peter Schwinghammer, and Cindy McKenzie. A perspective on the physical oceanography of Conception Bay was achieved through conversations with Drs. Brad DeYoung and Brian Sanderson. To Mike Riehl I owe a special heartfelt thanks. Mike's assistance in sample collection and data handling greatly facilitated completion of this project. I also extend my appreciation to the Ocean Science Centre's divers, for operating the Karl and Jackie II and the Elsie G, and the officers and crew of the CSS Baffin.

A portion of the data processing and dissertation writing

occurred while I was not in residence in Newfoundland. I greatly value the courtesy and assistance that was extended to me by Dr. Brian Eadie and Margaret Lansing of the NOAA Great Lakes Environmental Research Laboratory in Ann Arbor, Michigan. During the writing stages, support and assistance was provided by the faculty and staff of the Department of Geological Sciences at Michigan State University and the Geosciences Branch, Chemical Technology Division of Argonne National Laboratory. Assistance with computing and printing was provided by Dr. Alice Tse of Loyola University.

Throughout my career at Memorial the cooperation and aid provided by faculty and staff in the Department of Earth Sciences was greatly appreciated. In particular, the efforts of Pat Browne and Maureen Moore have been most helpful. The School of Graduate Studies at Memorial was not only responsible for handling the dissertation but also provided financial support while completing this project. I am indebted to my committee members Drs. John Welhan, Mark Wilson, and Christopher P.G. Pereira for advice and assistance. The criticism, comments and counsel extended by my internal and external examiners, Drs. Juanita Gearing, David Velinsky, and T. Jun Abrajano, were appreciated. To my supervisor, Dr. Stephen A. Macko, I extend my deepest gratitudes. Steve has always provided direction, counsel and the freedom to pursue my own research initiatives. I thank my wife, Peggy, for her invaluable companionship, insight, and patience throughout this entire process. Many smiles were

generated from my friends Zoee, Shido, Beaker, Tuxedo, Oscar, Rocky, Casmerian, Pouncer and other assorted companions at the Brookfield Zoo.

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1.0 Introduction

1.1 General Statement

The carbon and nitrogen stable isotopic composition of sedimentary organic matter has often been used to evaluate past changes in productivity and climate (Sackett, 1964; Gearing et al., 1977; Rau et al., 1987; Macko, 1989; Macko and Pereira, 1990). This approach requires that isotopic abundances are not altered during diagenesis and are a reflection of overlying productivity at the time of deposition. Whereas, alteration of isotope values within sediments is generally thought to be restricted to highly organic rich deposits (Behrens and Frishman, 1971; Macko, 1981; Ostrom and Macko, 1991), differences between the $\delta^{15}N$ and $\delta^{13}C$ of sedimentary and water column organic matter have been observed in several studies (Entzeroth, 1982; Tan and Strain, 1983; Wada et al., 1987; Libes and Deuser, 1988). The $\delta^{15}N$ and $\delta^{13}C$ values of water column samples may not accurately reflect those of the sediments owing to size discrimination during collection, degradation in the water column, and seasonal variability (Entzeroth, 1982; Mariotti et al., 1984; Gearing et al., 1984; Altabet and Deuser, 1985; Saino and Hattori, 1987; Altabet, 1988; Cifuentes et al., 1988).

The primary objective of this study was to establish a firm understanding of the relationship between the isotopic

composition of phytoplankton and that of underlying sediments. To accomplish this task, this research (1) identified processes resulting in variations in $\delta^{13}C$ and $\delta^{15}N$ of water column organic matter and (2) developed a model relating the flux and isotopic composition of water column organic matter to sediment isotope values.

An understanding of the causes of isotopic variation in newly produced organic material such as phytoplankton[1] requires a knowledge of the cycling of carbon and nitrogen in the marine environment. The $\delta^{15}N$ and $\delta^{13}C$ of this material is dependent on the isotopic composition of the source of inorganic carbon and nitrogen and the degree of fractionation (shift in $\delta^{13}C$ or $\delta^{15}N$) that occurs during uptake and metabolism. Once produced, water column organic matter is subjected to a multitude of degradation processes such as microbial and zooplankton consumption that have the potential to alter isotope values. As a consequence of fractionation during transformations of organic matter within the water column, the isotopic composition of the sediments may not reflect that of newly produced organic matter at the time of deposition. The following sections (sections 1.2 to 1.5) presents a description of the carbon

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[1] Material collected on seston filters or in sediment traps is commonly referred to as phytoplankton if contributions of organic matter from other sources can be considered or are assumed to be negligible. The term "phytoplankton" is used in this study to describe phytoplankton derived material.

and nitrogen cycle in a manner that will provide a foundation for understanding the use of $\delta^{13}C$ and $\delta^{15}N$ to identify sources and transformations of organic matter in the sea.

1.2 Production and cycling of organic matter in the sea

Levels of primary production in the ocean vary from as little as 10gC/m^2/yr for polar seas to as high as 1000-2000gC/m^2/yr in certain areas of intense upwelling, such as off the coast of Peru (Walsh, 1988; Berger et al., 1989). The vast areas of oceanic central gyres are on the low end of this range and average 25-60gC/m^2/yr. Continental shelf productivity is significantly greater than the deep ocean and has been estimated to average 215gC/m^2/yr (Walsh, 1988). Continental shelves comprise 25% of total oceanic production while occupying only 10% of the ocean's land area (Walsh, 1988; Table 1).

Only a small portion of the organic matter produced in the marine environment escapes utilization and is preserved in sediments. Of the total organic carbon fixed in the open ocean only 10% survives grazing in the upper 100m (Walsh et al., 1981a). In addition, only 1% of oceanic productivity escapes degradation during a descent of 4,000m to 5,000m and only a fraction of this is preserved in sediments (Honjo, 1980). Estimates of annual carbon budgets for a variety of

shelf environments indicate that 50% of primary production is not consumed or degraded (Walsh, 1981). In that most shelf sediments have low organic carbon contents (less than 0.5%), the shelves themselves do not appear to be an area of storage for the undegraded material produced in overlying waters. However, sediments of the continental slope typically have greater organic contents (greater than 1%) than either the shelf or adjacent deep seafloor and may be an area of storage for material produced further inshore (Table 1; Walsh et al., 1981a).

Organic matter in aquatic environments can be characterized by analysis of particulate organic matter (POM). Two classes of POM (seston and sinking POM) are recognized on the basis of their residence time, size and method of collection. Although seston and sinking POM are often considered separately it should be recognized that both collect particles within the same size range but in differing proportions. Suspended POM or seston consists primarily of small particles which have residence times on the order of several hundred years (McCave, 1975; Sackett, 1978). Seston is arbitrarily defined as all the material retained on a filter with a pore size of approximately 0.45μm to 1μm (Riley, 1970; Parsons, 1975). The larger less abundant fraction of this material, sinking POM, remains within the water column from days to weeks and consists mainly of fecal pellets and phytoplankton tests (McCave,

1975). Sinking POM is collected primarily by moored or drifting sediment traps.

Studies of the size distributions of seston reveal that most of biogenic particles are less than 3μm fraction (Herbland and LeBouteiller, 1981). Stokes Law predicts that settling velocities of particles less than 2μm would be 6.2m/yr (Walsh, 1988). At this rate seston would, effectively, remain within the euphotic zone. If they are to reach the seafloor, particles of this size must, therefore, increase their density and/or size. Aggregation as phytoplankton or fecal pellets serves as a mechanism for this process (Anderson and Sweeney, 1978; Shanks and Trent, 1980; Knauer et al., 1982). The rate of vertical transport of POM in many types of oceanic environments range between 100-200m/day (Shanks and Trent, 1980; Davies and Payne, 1984; Honjo, 1984; Bodungen et al., 1986). This observation emphasizes the importance of aggregation of POM in transporting organic matter to the seafloor. In that aggregation has a large influence on the type and amount of material reaching the ocean floor, an understanding of isotopic segregation during this process is essential to interpreting the geochemistry of sediments.

Dissolved organic matter (DOM) represents another large and important carbon reservoir. This material is generally defined as the fraction which passes through a filter used to collect seston. Recent studies emphasize the importance

of DOM in terms of the size and lability of this reservoir (Suzuki et al., 1985; Sugimura and Suzuki, 1988). The understanding of the influence of DOM on carbon and nitrogen cycling is limited owing to the difficulty in measuring the isotopic composition and concentration of this fraction (Toggweiler, 1989; Sharp, 1991).

1.3 The marine nitrogen cycle

Primary production occurring in the euphotic zone has traditionally been considered to draw on two sources on nitrogen compounds: new and regenerated (Dugdale and Goering, 1967). New sources are those which are not produced within the euphotic zone and must be conveyed from either the atmosphere or deep ocean. These consist predominantly of upwardly advecting nitrate from the oxidation of ammonium (nitrification) in oxic waters or sediments and to a lesser extent atmospheric N_2 via nitrogen fixation (Howarth et al., 1988). Nitrogen compounds from precipitation are generally not considered significant but may be the cause of slightly higher productivity estimates for oligotrophic oceans receiving atmospheric pollution (Knap et al., 1986; Galloway and Whelpdale, 1987; Fanning, 1989).

At least 90% of the nitrogen that is utilized by oceanic phytoplankton is derived from regeneration, as

opposed to 50% on continental shelves (MacIsaac and Dugdale, 1972; Conway and Whiteledge, 1979; Eppley and Peterson, 1979; Eppley et al., 1979). Higher productivity on shelves in comparison to the deep ocean is related to a large supply of new nutrients to the shelf from rivers and coastal upwelling (Walsh et al., 1981b). Coastal upwelling and other mixing processes transfer approximately 10 to 100 times more nutrients to surface waters than can be expected by diffusion, the principal transport mechanism in the oceanic environment (Walsh, 1976). As a consequence of this nutrient-rich environment, within a few weeks or months, coastal spring blooms may produce as much as 50% of the annual production (Walsh, 1976; 1981; Yentsch et al., 1977; Walsh et al., 1981a, 1981b).

New nitrogen consists almost exclusively of nitrate that is generated through the process of nitrification. Nitrification requires a supply of ammonium, high concentrations of dissolved oxygen and low light intensities (Olson, 1981; Ward et al., 1984). Recent studies have demonstrated that nitrification occurring in the lower euphotic zone can be a significant source of nitrate for productivity (Ward, 1987; Ward et al., 1989). However, the rate of nitrification in this zone is probably not sufficient to be a significant nitrogen source during peak productivity periods.

Within sediments, nitrate is produced from dissolved

ammonium by bacteria capable of nitrification (Fig. 1). The porewater ammonium supplying nitrification is derived from the mineralization of sedimentary organic matter (Fig. 1). Inorganic nitrogen may diffuse out of sediments into the water column and serve as a nutrient source for phytoplankton or bacteria. Within Conception Bay fluxes of nitrate, nitrite and ammonium into the water column from sediments were observed (Fig. 1).

Nitrate may be lost to the water column and sediment pore waters by reduction to N_2 gas via denitrification (Fig. 1). The processes of nitrogen fixation and denitrification must balance each other and ultimately control the amount of nitrogen available for productivity. Much less than 1% of the nitrogen input to oceanic surface waters results from nitrogen fixation (Howarth et al., 1988). Denitrification in estuarine systems may remove up to 50% of the total nitrogen input (Seitzinger, 1988). The low contribution of nitrogen fixation and high loss of nitrogen by denitrification has been suggested to be the cause for nitrogen limitation in marine systems and a heavy reliance on regeneration (Howarth et al., 1988; Seitzinger, 1988).

Regenerated nitrogen used in primary productivity consists mainly of ammonium. Of lesser importance are amino acids, urea and other dissolved organic nitrogenous compounds (Eppley and Peterson, 1979). Ammonium is generated by heterotrophic excretion and may supply as much

as 95% of the total nitrogen utilized by phytoplankton in oligotrophic oceans (King, 1987; Ward et al., 1989). Assuming that the nitrogen balance in the euphotic zone is at steady-state, regeneration can only sustain productivity. For productivity to be maintained or increased, inputs of new nitrogen must equal or exceed losses due to sinking of particles (Eppley and Peterson, 1979). In this way the vertical flux of nitrate into the euphotic zone controls productivity and the export of sinking organic matter to the deep sea (Eppley and Peterson, 1979; Lewis et al., 1986).

1.4 Isotopic tracing of carbon in the sea.

The use of $\delta^{15}N$ and $\delta^{13}C$ for determining the origins of organic matter in marine systems is well-established (Sackett and Thompson, 1963; Hunt, 1970; Tan and Strain, 1979b; Peters et al., 1978; Macko, 1983). Water column organic matter in the deep ocean is often assumed to be derived primarily from phytoplankton, however, nearshore systems may be influenced by detritus from other sources such as land plants and macroalgae. The successful distinction of sources or endmembers is dependant on two basic premises: (1) sources must have dissimilar isotopic compositions and (2) geochemical characteristics should not be altered during the transport, deposition and preservation of organic matter.

The geochemically distinct isotope signatures of marine and terrestrial endmembers are a consequence of differences in both metabolism and sources of inorganic nutrients in primary productivity. Isotopic segregation or fractionation during CO_2 assimilation by marine and terrestrial C_3 plants occurs primarily during carboxylation by ribulose 1,5-bisphosphate carboxylase (RuBP) and to a lesser extent during CO_2 diffusion into the cell. Aquatic and marine plants are more commonly diffusion limited than terrestrial plants and this process effectively reduces the observed enzymatic fractionation (O'Leary, 1981). The end result is a distinction between marine and terrestrial endmembers with typical values in temperate systems of -20‰ and -26‰, respectively (Sackett and Thompson, 1963; Schultz and Calder, 1976; Macko, 1983; Gearing, 1988).

The $\delta^{13}C$ of phytoplankton varies considerably with both time and location. Variation in the $\delta^{13}C$ of phytoplankton has been explained by a plethora of mechanisms including changes in temperature, differences among water masses, the concentration of CO_2 (pCO_2), and species composition (Sackett, 1964; Sackett et al., 1965; Fontugne and Duplessy, 1978, 1981; Wong and Sackett, 1978; Gearing et al., 1984; Fogel et al., 1988; Rau et al., 1989; Descolas-Gros and Fontugne, 1990). Among these mechanisms variations in atmospheric pCO_2 is, perhaps, the most important determinant in controlling the $\delta^{13}C$ of phytoplankton. Experimental

evidence has shown an inverse relationship between pCO_2 and the $\delta^{13}C$ of marine phytoplankton (Degens et al., 1968; Calder and Parker, 1973; Pardue et al., 1976; Fry and Wainright, 1991). The difference between the $\delta^{13}C$ of inorganic carbon and that of plants ranges between 0‰ at pCO_2 of less than 5% and 28‰ at CO_2 concentrations of 5% (Mizutani and Wada, 1982; Kerby and Raven, 1985). Marked decreases in both pCO_2 and the concentration of dissolved inorganic carbon (DIC) have been observed during spring blooms in northern oceans (Codispotti et al., 1982; Watson et al., 1991). Therefore, an increase in $\delta^{13}C$ of marine phytoplankton during periods of high productivity may be related to a reduction in the availability of dissolved CO_2 gas (Deuser and Degens, 1967; Degens, 1969; Deuser, 1970; Fogel et al., 1988). In southern oceans latitudinal trends in phytoplankton $\delta^{13}C$ have been observed that recently have been related to temperature induced changes in pCO_2 (Rau et al., 1989). Owing to an inverse correlation between pCO_2 and phytoplankton $\delta^{13}C$, marine sediments have the potential to preserve a record of changes in atmospheric CO_2 levels (Dean et al., 1986; Arthur et al., 1988; Rau et al., 1991). To fully evaluate this possibility, the relationship between the $\delta^{13}C$ of phytoplankton and sediments needs to be understood.

The isotopic composition of newly produced organic matter derived from phytoplankton can be altered prior to reaching the sediment (Tan and Strain, 1983; Libes and

Deuser, 1988; Altabet, 1988). Consequently, the assumption that the $\delta^{13}C$ of organic matter preserved in sediments is a reflection of the $\delta^{13}C$ of productivity in the overlying water column may be incorrect. An understanding of the magnitude and direction of the shift in $\delta^{13}C$ that occurs in the water column is essential for interpreting the sedimentary isotope record.

In general, the $\delta^{13}C$ of sediments are most similar to that of sinking POM (Entzeroth, 1982; Tan and Strain, 1983). Within the water column sinking POM experiences less degradation than seston (Cho and Azam, 1988; Caron et al., 1989). Owing to density stratification, seston may be trapped at the thermocline and subjected to extensive biological utilization and associated depletions in ^{13}C (Eadie and Jeffrey, 1973; Eadie et al., 1978; Jeffrey et al., 1983). Further isotope shifts at greater depths can result from aggregation of DOM, disaggregation of sinking POM, and oxic degradation (Jeffrey et al., 1983). The $\delta^{13}C$ of near-bottom seston can be influenced by sediment resuspension (Tan and Strain, 1979a).

The carbon isotopic composition of DIC can be used as an indicator of the extent to which biological respiration influences the degradation of POM. Increases in water column DIC below the euphotic zone can be a result of respiration or dissolution of carbonate. However, respiration and carbonate dissolution affect the $\delta^{13}C$ of DIC

in opposite ways (Fig. 2). Owing to differences in the $\delta^{13}C$ of these two reservoirs ($\delta^{13}C$ of dissolved carbonate and respired $CO_2 \approx 0$ and $<-20‰$, respectively) the relative contribution of respiratory CO_2 and dissolved carbonate has been distinguished using isotope mass balance equations (Kroopnick 1974a; 1974b; 1980). Periods of intense photosynthesis may result in a decrease in the concentration and an increase in the $\delta^{13}C$ of DIC (Smith and Kroopnick, 1981; Fig. 2). Decreases in the concentration of DIC during photosynthesis are counteracted by equilibration with atmospheric and dissolved CO_2 (Fig. 2).

1.5 Delineation of sources and cycling of nitrogen using $\delta^{15}N$

Differences between marine and terrestrial end members in $\delta^{15}N$ are primarily related to their sources of inorganic nitrogen. The ultimate nitrogen source for terrestrial productivity is derived from the atmosphere and is made available to plants through fixation by certain species of soil bacteria and blue-green algae. Fractionation during nitrogen fixation have been shown to be small and therefore a $\delta^{15}N$ near that of atmospheric N_2 of $0‰$ is expected for the terrestrial biosphere (Table 2). The refractory component retained in soil is similar in $\delta^{15}N$ to atmospheric N_2 and is thought to be preserved during transport to the sea (Cheng et al., 1964; Sweeney et al., 1976; Peters et al., 1978).

The $\delta^{15}N$ of the terrestrial organic matter contributing to the marine environment has been characterized by values between 0 and 5‰ (Peters et al., 1978; Macko, 1983; Ostrom and Macko, 1992).

The primary source of nitrogen for marine algae is dissolved inorganic nitrogen in the form of ammonium or nitrate with $\delta^{15}N$ values commonly in the range of 6‰ to 10‰ (Table 3). Phytoplankton frequently have isotope values similar to their inorganic nitrogen source (Miyake and Wada, 1967; Wada, 1980). This results in a clear distinction between marine (≈ 6 to 10‰) and terrestrial (≈ 0‰) sources in $\delta^{15}N$, that in conjunction with $\delta^{13}C$, can be used to assess the relative contributions of these endmembers in coastal systems (Peters et al., 1978; Macko, 1983).

Within specific environments the natural abundance of ^{15}N of dissolved inorganic nitrogen and phytoplankton may vary as result of fractionation during metabolism and microbial cycling. The light isotope is favored in the product of nitrate and ammonium uptake by phytoplankton, ammonium remineralization, nitrification and denitrification (Table 2). For example, in oxygen-depleted waters of the Eastern Tropical North and South Pacific, denitrification results in large increases in the $\delta^{15}N$ of residual nitrate, with values as high as 19‰ (Cline and Kaplan, 1975; Liu et al., 1987; Liu and Kaplan, 1989). Enriched $\delta^{15}N$ values of phytoplankton off the coast of California are believed to be associated

with this isotopically distinct nitrate originating in the Eastern Tropical North Pacific (Peters et al., 1978; Sweeney et al., 1976; Sweeney and Kaplan, 1980a; 1980b; Liu and Kaplan, 1989).

The degree of fractionation during uptake is a function of the concentration of the nutrient source (Macko et al., 1987; Cifuentes et al., 1988; Velinsky et al., 1989b). Maximum fractionation during uptake has been associated with productivity occurring under high nutrient concentrations. As inorganic nitrogen concentrations decline, as is commonly observed with decreasing depth in the euphotic zone, the fractionation between phytoplankton and dissolved inorganic nitrogen decreases until it is not observed (Saino and Hattori, 1980; 1985; 1987; Altabet and McCarthy, 1985; Altabet 1988). This interdependence suggests that the concentration of inorganic nutrients and the $\delta^{15}N$ of phytoplankton and dissolved inorganic nitrogen is necessary for a complete understanding of nitrogen cycling.

The $\delta^{15}N$ of sediments could provide a record of variations in nutrient or productivity levels. Productivity may be directly related to carbon flux. In the Sargasso Sea, the $\delta^{15}N$ of sinking POM was inversely correlated with carbon flux (Altabet and Deuser, 1985). Seasonal advection of nutrient rich deep waters to the surface stimulated phytoplankton growth and associated vertical transport of carbon to the sediments. During this time low $\delta^{15}N$ values of

POM were a consequence of nutrient abundant conditions. This observation demonstrates that shifts in the nitrogen isotope values of POM can be a reflection of changes in productivity and supports studies suggesting that variations in $\delta^{15}N$ with depth in sediments may reflect variations in nutrient or productivity levels (Macko, 1989; Macko and Pereira, 1990; Ostrom and Macko, 1991).

Inconsistencies between the $\delta^{15}N$ of sediments and that of newly produced organic matter in the water column can result from a host of transformation processes. Degradation of seston in the lower euphotic zone has been shown to cause an enrichment in ^{15}N in the suspended load (Saino and Hattori, 1980; 1985; 1987). Increases in the $\delta^{15}N$ of suspended or sinking POM can also result from ^{15}N enriched zooplankton detritus (Checkley and Entzeroth, 1985; Altabet, 1988). Enrichment in the $\delta^{15}N$ of sinking relative to that of suspended POM has been suggested to result from a contribution of isotopically heavy fecal matter (Checkley and Entzeroth, 1985; Altabet, 1988). Increases in the $\delta^{15}N$ of seston can also result from dissolution of sinking POM, fractionation during deamination reactions and/or oxidative degradation in deeper waters.

1.6 Summary and objectives

The objectives of this study are to (1) identify

processes resulting in variations in $\delta^{13}C$ and $\delta^{15}N$ of water column organic matter and (2) develop a model relating the flux and isotopic composition of water column organic matter to sediment isotope values. The $\delta^{15}N$ of seston can vary as a consequence of changes in the $\delta^{15}N$ of inorganic nitrogen, nutrient availability, productivity levels, and degradation. Similarly, the carbon isotopic composition of seston is dependent on the $\delta^{13}C$ of inorganic carbon, decomposition, and pCO_2. A detailed elemental and isotopic study of carbon and nitrogen may reveal processes resulting in unique isotopic values for POM. Knowledge of isotopic variation in the present will provide a foundation for understanding environmental conditions in the past.

Conception Bay, Newfoundland was chosen as a study site owing to several characteristics that facilitated a detailed study of isotopic variation in POM. This bay is characterized by an oceanic environment where changes in primary production are dramatic (Table 4) owing to the short time period during which conditions are conducive to growth. Many of the factors causing in isotopic variation in phytoplankton, such as changes in nutrient availability or pCO_2, are associated with changes in productivity levels and may be exaggerated within this system. The nearshore location of Conception Bay allowed frequent sampling necessary to characterize isotopic variation in POM over short periods of time. In addition, the cooperation of

other investigators involved in COPE (Cold Ocean Productivity Experiment) facilitated access to sampling stations, contributed background on the physical and biological aspects of Conception Bay and provided access to data that was important in interpreting isotopic trends.

2.0 **Methods and experimental results**

2.1 Sample collection and preparation

Oceanographic sampling was accomplished using the Department of Fisheries and Oceans CSS Baffin, FRV Shamook and Memorial University's Karl and Jackie II, and Elsie G. Freshwater samples were collected from rivers in acid-cleaned PVC buckets (Fig. 3). Sampling was conducted from late March to early September, 1990. Niskin or Go-flow bottles were lowered to appropriate depths in the water column to obtain seawater samples. Prior to sampling, the water column was characterized by deployment of a Seabird CTD with a Sea Tech fluorometer. On occasion, when the Seabird malfunctioned, a Neil Brown CTD was used. Profiles of water column Chlorophyll a concentrations were determined using a Seatech fluorometer on the seabird CTD. Chlorophyll a concentrations were calculated, as recommended by Seatech, by multiplying fluorescence by 0.7. Five samples were then collected at each station at 5m, 20m above the chlorophyll maximum, the chlorophyll maximum, 20m below the chlorophyll maximum, and 40m above bottom. Most of the sampling was done at one station, BRLP5, located near the head of Conception Bay (Fig. 3). A series of four collections were made at US3.5, located approximately in the center of the Bay, and in early May collections were made along a transect from the head of the bay to outside the

mouth (Fig. 3; Appendix 1).

Water samples were brought aboard and aliquots for dissolved oxygen concentration and for DIC were taken and fixed to prevent further respiration. To obtain seston and nutrient samples seawater was filtered initially by gravity and then by low vacuum suction through preheated (450°C, 1hr) Whatman GF/C glass fiber filters (2.4cm diameter, 1.2μ poresize). Typically 10L of seawater was filtered to obtain sufficient amounts of material for analysis of seston. Approximately 2L of the gravitational filtrate was collected in acid-cleaned Nalgene bottles for analysis of $[NO_2]$, $[NO_3]$, $[NH_4]$, $\delta^{15}N\text{-}NH_4^+$ and $\delta^{15}N\text{-}NO_3^-$. On board ship seston and water samples were stored in ice or dry ice and upon returning to laboratory, placed in a freezer.

Sediment samples were collected by either box core or Van Veen grab at all stations in Conception Bay, with the exception of CC13, along a transect from head to mouth (Fig. 3). A portion of the surficial 1cm of sediment was taken and frozen for subsequent determination of $\delta^{15}N$, $\delta^{13}C$, %C and %N in the organic fraction. At two stations, box cores were subsampled by pushing a 7.5cm diameter acrylic tube into the mud. Cross sectional slices (approximately 3cm) were then taken from this smaller core for collection of porewaters and for isotopic and elemental abundances of sedimentary organic matter. Slices were placed in a modified Jahnke sediment squeezer to obtain porewaters (Jahnke, 1988).

Approximately 10 to 40mL of porewater was obtained from each sediment section.

Sediment traps were deployed at two stations during the 1990 season, BRLP5 and US3.5, and at only BRLP5 in 1988. Elemental concentrations and flux data were available for only the 1988 season. Four traps were suspended at each of two depths to provide replication. Replicates were used in elemental and flux determinations and once for isotopic analysis to assess variability (Table 5). In 1990, these depths were 80m and 40m above the seafloor. The seafloor at stations BRLP5 and US3.5 was at 250m and 220m, respectively. Traps were deployed at four depths in 1988: 40m, 80m, 150m, and 240m. Sediment traps were cylindrical in shape with a 6:1 aspect ratio and a 7.5cm outside diameter. In the field, the traps were attached to moorings fixed to the seafloor and raised approximately once every two weeks (see Appendix 2 for lengths of deployment). Excess water was removed and the trapped material concentrated to a small volume (approximately 100mL). Owing to the short deployment times and generally low microbial activity present in Conception Bay (Pomeroy et al., 1991) no preservatives were used within the traps. Use of poison within traps would have prevented losses of organic material to degradation but might also have increased collections of zooplankton.

2.2 Preparation and analysis of organic material for elemental and isotopic analysis

In the laboratory, sediment trap material was resuspended in a known quantity of filtered seawater and a measured aliquot removed to calculate the sinking flux. Organic carbon and nitrogen contents for the sediment trap material were determined on a CHN analyzer (in the laboratory of Dr. Ray Thompson, Ocean Science Centre, Memorial University). The remaining material was frozen for further analysis. Typically only one of the four trap samples collected at each depth was analyzed for the $\delta^{15}N$ and $\delta^{13}C$ of sinking POM. Each sample was thawed and inspected under low magnification (4X) for removal of large non-phytoplankton material. This typically consisted of zooplankton, zooplankton molts and rope fibers. Seston filters were similarly inspected and cleaned. The remaining material was then concentrated by filtering onto a precombusted glass fiber filter (Whatman GF/C).

Filters containing seston or sinking POM were rinsed with approximately 300mL distilled water to remove salts, acidified (approximately 0.5 mL of 30% HCl) and dried at 40°C. Once dry, seston filters were weighed and the surface layer of the filter containing POM was removed. In preparation for isotopic analysis the sediment, seston and sediment trap samples were dried (40°C), acidified using 30%

HCl, dried again and ground into a fine powder. Sediment samples were acidified using approximately 10mL of 30% HCl. Combustion of organic matter was performed using a modified Dumas method (Macko, 1981). The surficial layer of the glass filter containing POM or 100mg to 200mg of sediment was placed in an ashed quartz tube to which precombusted copper oxide (BDH Chemical; 400mg) and pure copper (Alpha Resources; 200mg) was added. Evacuated samples were heated to 850°C and allowed to cool gradually (approximately 30°C/hr) to prevent formation of carbon monoxide and nitrous oxides.

Carbon dioxide and nitrogen gas were separated cryogenically from the combustion products on a vacuum line. The quartz tube, containing the combusted sample, was broken within a flexible metal tubing (Cajon) allowing gases to enter a previously evacuated portion of a vacuum line. Water and CO_2 were frozen within a liquid nitrogen cooled U-trap for five minutes. Purified nitrogen gas was then collected onto a liquid nitrogen cooled 5A binderless molecular sieve (Aldrich Chemical) for an additional five minutes. Placement of a methanol/dry ice slush (-70°C) onto the U-trap liberated CO_2 gas while retaining the water. The CO_2 gas was collected in a liquid nitrogen cooled 6mm pyrex tube (5min) and sealed for later isotopic analysis.

Purified carbon dioxide and nitrogen isolates from samples were analyzed for their isotopic compositions on a

either a VG Prism or Finnigan-Mat 252 stable isotope ratio mass spectrometer. All samples were analyzed in comparison to internal laboratory tank standards that had been calibrated against NBS-22 and other international standards. Values for $\delta^{13}C$ and $\delta^{15}N$ are reported in per mil (‰) notation relative to PDB and atmospheric nitrogen, respectively.

Abundance measurements for gas samples of nitrogen were determined using a calibrated volume within the mass spectrometer, and for carbon on a calibrated manometer during cryogenic gas separation. The concentrations of carbon and nitrogen were used to calculate molar C/N. Reproducibility for isotope and abundance determinations are listed in Table 5.

2.3 Carbon isotope analysis of DIC

Extraction of DIC from water samples was performed by cryogenic purification on a vacuum line. A sample of 20mL was acidified with phosphoric acid to release carbon dioxide gas. Water vapor was isolated from the evolved carbon dioxide by two dry ice/methanol cooled traps in series. Purified carbon dioxide was then transferred using liquid nitrogen to a calibrated manometer for determination of DIC concentration and similarly condensed into a pyrex tube and sealed for storage. The precision of $\delta^{13}C$ and concentration of DIC determinations 0.1‰ and 0.03μmol/kg, respectively

(Table 5).

2.4 Measurements of dissolved oxygen, nitrate, nitrite and ammonium

To obtain oxygen concentrations a modified Winkler method was used. Excess manganous sulfate and alkaline iodide azide (Hach Chemical) was added to 300mL BOD bottles that had been filled with a minimum of aeration. Upon returning to the laboratory excess sulfamic acid was added and the resulting solution titrated against 0.0125N phenylarsine oxide (Hach Chemical) to a clear endpoint (Strickland and Parsons, 1968; Grasshoff et al., 1983). Concentrations of nitrate and nitrite were determined using standard procedures (Strickland and Parsons, 1968; Nydahl, 1976; Grasshoff et al., 1983). The reproducibility of dissolved oxygen and nutrient determinations are listed in Table 5. Owing to small amount of sample available, dissolved ammonium and nitrate concentrations in porewaters were determined by measuring the abundance of ammonium collected by the isotope distillation procedure described below.

Concentrations of ammonium were determined using a gas-sensing ammonia electrode (Orion). This technique has advantages relative to other techniques (Solarzano, 1969; Liddicoat et al., 1975; Koroleff, 1976) because of its low

cost, portability, minimal use of hazardous reagents and lack of salt-effects. The basic principle on which the electrode is based is that the electrical potential measured is related to the log of the ammonia concentration by the Nernst equation. Intrinsic to this measurement is a shift in the pH of the sample solution to greater than 10 thereby converting all dissolved ammonium (NH_4^+) to ammonia gas (NH_3). For 100mL seawater samples 1mL of 5N NaOH solution is more than sufficient to effect this change in pH.

During the development of the ammonia electrode method it was discovered that the potential deviated significantly from a predicted Nernstian slope at concentrations that are commonly found in estuaries and the ocean (Fig. 4). A pivotal concentration of 1.8μM (μmol/L) was identified below which potential was proportional not to the log of (as indicated by the Nernst equation), but directly to, the concentration. Nonetheless, when three standards each were run above and below 1.8μM a high degree of prediction was obtained (Fig. 5; $r^2 = 0.99$). A high degree of correlation was also obtained using a exponential equation that encompassed all standards (Fig. 4).

Prior to use, the inner body of the electrode was activated by soaking in electrode filling solution (obtained from Orion or substituted with 0.1M NH_4Cl) overnight. For samples with ammonium concentrations less the 20μM the electrode performed better when the internal filling

solution used for analysis was diluted 1:10 (0.01μM NH_4Cl). Analysis was initiated upon zeroing the electrode by placing it in pH 4 buffer solution and waiting a few minutes.

A blank solution was made by placing 100mL of ammonium-free water in a 125mL erlenmeyer flask and adding a small teflon-coated stir bar. To this solution 1mL of Orion Ionic Strength Adjuster (ISA; 5N NaOH in a 10% methanol solution with a pH indicator) was added to shift the pH to greater than 10. Gentle stirring was initiated and the electrode was allowed to equilibrate with the solution for 10min. Absorption of ammonia from the air was never observed during this 10min period. After 10min, the mV meter was set to zero. For analysis of samples, the electrode reading was brought below zero by immersing in pH 4 buffer, rinsed with distilled water and immersed in a 100mL sample or standard with 1mL ISA added. Samples were given precisely 5min to equilibrate with the electrode; timing initiated as the mV readings passed through the zero point. The precision and limit of detection for this technique are 0.1 and 0.2μM, respectively (Table 5).

2.5 Nitrogen isotope measurements of nitrate and ammonium

Extraction of nitrate and ammonium from water samples for isotopic analysis was done by a modification of steam distillation procedures (Bremner and Keeney, 1966; Velinsky

et al., 1989a; Horrigan et al., 1990). In summary, ammonia was distilled out of a sample, bound by ion-exchange onto a zeolite molecular sieve and combusted by the modified Dumas procedure described earlier. Devardas alloy (50 % Cu, 45 % Al, 5 % Zn) was added to the remaining ammonia-free sample to reduce nitrate to ammonia and a second distillation was commenced.

Approximately 500mL of sample was placed in a 1L round bottom flask. The pH of the solution was shifted to greater than 10 to convert ammonium to volatile ammonia gas. For seawater and freshwater samples 4mL and 1mL of 5N NaOH was added, respectively. A water cooled reverse Hopkins condenser was placed onto the joint of the flask (Fig. 6). Boiling was initiated and the collection rate adjusted to between 1.1-1.5mL/hr. Condensate was collected through silicon tubing to which was attached a glass pasteur pipet. The tip of the pipet was immersed in 20mL of 0.03N HCl, thereby trapping ammonia gas in solution as ammonium. Quantitative recovery of ammonium was obtained when 250mL have been transferred to the trap flask. This solution was then set aside for zeolite binding of the trapped dissolved ammonium.

A second trap flask was set up as before and the solution remaining in the round bottom flask was diluted back to 500mL with ammonia-free deionized water. Finely ground devardas alloy, 0.3g, was added to the round bottom

flask and the condenser quickly fitted to the flask. The alloy had been previously ground to obtain a powder with 100% passing through a 100mesh screen and 75% passing through a 200mesh screen (Kreitler, 1975) and baked at 150°C for 8hr. Boiling was initiated and the collection rate adjusted as before. Addition of the alloy reduced any nitrate to ammonia by the following reaction:

$$3\ NO_3^- + 8Al + 5OH^- + 2H_2O \rightarrow 8AlO_2^- + 3NH_3$$

Distillations have been shown to quantitatively recover nitrate and ammonium from standards in the range of 1-20μmols. Yields of ammonium and nitrate average 102.9 ± 4.5% and 106.4 ± 5.2% (Table 6), respectively, and are similar to steam distillation results (Velinsky et al., 1989a). During development of this technique it was discovered that there is a substantial background of ammonium generated during the distillation. Background contribution during the ammonium and nitrate distillations averaged 0.317μmols and 0.970μmols, respectively (Table 7). Correction for background yielded recoveries for ammonium and nitrate during distillation very close to 100% (Table 6).

The background found during the distillation was most likely derived from ammonia in the air and/or base and, in the case of nitrate, from the devardas alloy. To reduce the

ammonia content of the NaOH solution, the base was distilled as if it were a sample and diluted back to its original volume. To further minimize background contamination all glassware, with the exception of the condenser, was cleaned with a laboratory cleaner (Alcanox) and rinsed with generous amounts of ammonia-free water. Cleaning was followed by distillation of 500mL of ammonia-free water to which had been added 1mL of the NaOH solution. Distillation of ethanol, a procedure followed in a previous study, was not found to have any effect on the background ammonium levels (Velinsky et al., 1989a). Nonetheless, 300mL of ethanol was distilled in the apparatus every 3 or 4 samples as a precaution. Between samples round-bottom flasks were soaked in 6N HCl overnight to remove any devardas alloy that had adhered to the sides of the glassware during the distillation.

Because of the background nitrogen contribution analyzing samples with high concentrations was preferable. No attempt was made to analyze a sample with less than 3μmol nitrate or ammonium (Velinsky et al., 1989a). With some samples this threshold abundance was obtained by concentrating 1-2L to a volume of 500mL through slow distillation prior to a final distillation to obtain isotopic abundances.

Once ammonium was collected in the trap flask of the distillation apparatus it was bound by absorption onto a

zeolite molecular sieve (Union Carbide Ionsiv W-85). The molecular sieve was initially dried at 40°C under low vacuum and a slow stream of air. Initially, two different techniques were implemented to improve the binding efficiency of ammonium by the molecular sieve. In the first technique, 60mg of the dried sieve was stirred for 1hr in a solution containing 40μmol of NH_4Cl and 20mL of 0.003M HCl (Velinsky et al., 1989a). At the end of 1hr the sieve was vacuum filtered onto a precombusted Whatman GF/C glass fiber filter, dried at 40°C under vacuum, and prepared for combustion. Recovery of ammonia on zeolite by this method was similar to previous studies with a yield of 97.0 ± 0.1% (Table 8; Velinsky et al., 1989a). To improve binding efficiency a second technique was developed in response to experimental observations.

Experimentation demonstrated that the ammonium binding efficiency of the sieve varied dramatically as a function of pH (Table 9). The technique described above is expected to have varying binding efficiencies because pH varies as a function of ammonium concentration. The concentration of ammonium collected in the trap flask would not be constant because concentrations of ammonium or nitrate in different samples varies. Binding efficiency was optimized using 100mg of the molecular sieve and maintaining the pH between 4.8 and 5.2 while stirring (Table 9). The pH of the solution was monitored using an electrode and pH meter and

adjusted by additions of either 0.1M Na_2CO_3 or 0.4M HCl. No more than 1-2mL of either solution was required to maintain the pH within this range. Generally, the pH of the solution containing sieve and ammonium remained constant after 10min of stirring at which point the solution was covered and stirred for an additional 50min.

The sieve containing the bound ammonium was filtered onto a glass fiber filter as described above. This initial binding resulted in approximately 97% recovery of NH_4^+ by the sieve. To improve recovery, 100mg of sieve was added to the filtrate and a second binding was initiated. The binding procedure was repeated and the two filters were combined and prepared as one sample for combustion. Recoveries of NH_4^+ by this method were very close to 100% (Table 10). The nitrogen isotopic composition of ammonium recovered by the two methods differed by less than 0.1‰, however, the precision was better using the procedure involving two bindings (Tables 8 and 10). In both cases, the isotopic composition of the ammonium bound by the sieve was nearly identical to the $\delta^{15}N$ of the NH_4Cl standard used in the experiments of -0.03 ± 0.24‰ (n = 5). These results demonstrate that the zeolite molecular sieve is capable of quantitative recovery of dissolved ammonium without sacrificing isotopic fidelity.

Because of background contamination during the distillation process it was necessary to correct nitrate and

ammonium samples for this contribution to obtain indigenous isotope values. The isotopic composition and concentration of background nitrogen for both distillation of ammonium and nitrate is shown in Table 7. Samples were corrected for background by the following equation:

$$\delta^{15}N_{sam} = \frac{\delta^{15}N_{meas}\ (A_{sam} + A_{back}) - (\delta^{15}N_{back} * A_{back})}{A_{sam}} \qquad \text{(eq. 1)}$$

where: $\delta^{15}N_{sam}$ = the $\delta^{15}N$ of the sample.

$\delta^{15}N_{meas}$ = the $\delta^{15}N$ measured.

$\delta^{15}N_{back}$ = the $\delta^{15}N$ of the background (from Table 7).

A_{sam} = the abundance of nitrate or ammonium placed in the distillation apparatus (μmol-N).

A_{back} = the abundance of ammonium associated with background nitrate or ammonium (from Table 7).

Naturally, the magnitude of the background correction depends on the concentration and isotopic composition of both the background and sample. The concentration and isotopic composition of the background should, ideally, be constant. Therefore, the magnitude of the correction is primarily a function of sample size and the difference between the $\delta^{15}N$ of sample and background. However, the $\delta^{15}N$

of the background for nitrate and ammonium was quite variable and less confidence could be attached to small samples with a large difference in $\delta^{15}N$ between sample and background (Table 7). For example, using the above equation for a 5μmol nitrate sample with a $\delta^{15}N$ of 10‰ (9.01‰ greater than background) the background corrected value and confidence associated with the correction (using the standard deviation in Table 7) would be 11.75 ± 0.49‰. For a sample of 3μmol nitrate and similar $\delta^{15}N$ the corrected value and error would be 12.91 ± 0.81‰. To this must be added the analytical precision of the method, which as discussed below, is approximately 1‰. Fortunately, no samples were found to have an uncorrected $\delta^{15}N$ greater than 7‰ different from the background. Background correction is less of a concern for ammonium as the background contribution was substantially less than for nitrate (Table 7).

The ability of the distillation technique to accurately determine the $\delta^{15}N$ of nitrate in various solutions was tested with a KNO_3 standard previously characterized by direct combustion ($\delta^{15}N$ = 1.46 ± 0.16‰, n = 3; Table 11). An effort was made to analyze standards of the same composition and treated in the same manner as samples. For this reason nutrient-free surface water was collected after the spring bloom from Conception Bay and, for some treatments, subjected to freezing. The reproducibility of the technique

of better than 1‰ is similar to what has been reported for this method in other studies (Kreitler, 1975; Heaton and Collett, 1985; Velinsky et al., 1989a). Under the various experimental conditions shown in Table 11, the average $\delta^{15}N$ measured was within 1‰ of the standard. Analysis of enriched or depleted nitrate or ammonium standards was not conducted; however, a previous study found a small fractionation of -1‰ at high $\delta^{15}N$ values for the distillation of ammonium (≈ 20‰; Velinsky et al., 1989a).

A portion of the samples collected for dissolved inorganic nitrogen abundance and isotopic determinations were poisoned with $HgCl_2$ to prevent microbial alteration. It was later discovered that the presence of mercury in the sample interfered with the measurement of nitrate and ammonium. Nitrate concentrations for these collections (3/23 - 4/29) were provided from a collaborator (R. Thompson), however, sampling depths did not always coincide. Mercury in the sample also affected the reducing ability of devardas alloy during the distillation process. Mercury was removed from these samples by passing the sample through a 30cm x 1cm buret filled with copper metal turnings. The salt form of mercury was reduced to the metallic state which then formed an amalgam with the copper. The amalgam could then be removed from the copper by washing with dilute sulfuric acid (0.03M). Distillation of standards to which $HgCl_2$ was added and removed by this procedure yielded

quantitative recovery and isotopic fidelity (Tables 6 and 11). The reproducibility and limit of detection of the distillation and other techniques used in this study are shown in Table 5.

3.0 Results

3.1 Research approach

Many of the factors that may alter the $\delta^{15}N$ and $\delta^{13}C$ of POM vary markedly in Conception Bay as a function of depth in the water column and/or from spring to summer. One station in Conception Bay was sampled repeatedly from March to September, 1990, for collection of water column samples. Samples were analyzed for the concentration and isotopic composition of sinking POM, suspended POM, sediments, nitrate, ammonium, DIC and the concentration of O_2. During each sampling the water column was also characterized by vertical profiles of salinity, density, temperature, light transmittance and chlorophyll fluorescence. To assess spatial variation in water column geochemistry four stations were sampled, from late April to early May, along a transect from the head to offshore the mouth of Conception Bay.

3.2 Geochemical composition of sediments and porewaters

The carbon and nitrogen isotopic and elemental compositions of organic matter in surficial sediments in Conception Bay are similar to what has been previously reported for the inner continental shelf and Bays of Newfoundland (Ostrom and Macko, 1992). The ranges of

sediment $\delta^{15}N$ and $\delta^{13}C$ values along a nearshore to offshore transect are 7.8 to 9.0‰ and -21.7 to -21.1‰, respectively (Figs. 3 and 7). Ratios of carbon to nitrogen along this transect vary from 4.9 to 11.4. There is no discernable trend in isotope or C/N values with distance from the head of the bay (Fig. 7). The values of $\delta^{15}N$, $\delta^{13}C$, and C/N of sediments within Conception Bay are consistent with an origin consisting of phytoplankton or a mixture of phytoplankton and macroalga organic matter (Ostrom and Macko, 1992). These data suggest that contributions of terrestrial organic matter to Conception Bay may be restricted to shallow nearshore environments.

Elemental abundances of carbon and nitrogen range from 0.78% to 4.07% and 0.19% to 0.69%, respectively, and decrease toward the offshore (Fig. 7). Higher concentrations of organic matter in the inner part of Conception Bay may be related to bathymetric features. Samples inside the Bay were all taken in the deep central basin where calm waters provide a low energy environment that favors deposition (Fig. 3). Deposition at shallower depths, found at the sill and outside the bay, may be reduced by wave and/or current action. The inner basin of Conception Bay acts as a sediment trap, collecting inshore and offshore debris, in a similar manner as was previously found for basins on the continental shelf of Newfoundland (Scott et al., 1984).

At several stations, duplicate grabs or cores were obtained. The range in isotopic and elemental determinations for duplicate sediment samples at stations CC5 and CC7 is similar to that for replicate samples (Tables 5 and 12). However, C/N values and the $\delta^{15}N$ of duplicate sediment grabs can differ by as much as 3 and 1‰, respectively (Table 12). Although grabs were collected at different times of the year over several years no seasonal trends were apparent. The isotopic variation along the head to mouth transect is not any greater than what can be found within a single station. This observation suggests that the relative contribution of sources of organic matter is relatively constant throughout the sediments of Conception Bay.

The $\delta^{15}N$ and $\delta^{13}C$ of sediments from cores collected in 1990 is similar to that of surficial sediments from grabs (Figs. 8, 9, and 10; Tables 12 and 13). This suggests that the relative contribution of phytoplankton and macroalgae has not changed during the period these sediments were deposited and that diagenesis has not significantly affected these parameters. Based on sedimentation rates in nearby fjords of 0.5cm/yr, the deepest sample from these cores is approximately 400 years in age (Ostrom and Macko, 1991).

The concentration of porewater ammonium in boxcores ranges from 34.7μM to 239.9μM (Figs. 11, 12, and 13; Table 13) and increases with depth in the sediment (Figs. 11 and

12). This trend in ammonium data results from production of ammonium from remineralization and losses by nitrification and diffusion to the overlying water column. Nitrate and nitrite concentrations range between 3.1μM to 34.2μM and 0.0μM to 2.8μM, respectively. The presence of nitrate and nitrite within the porewaters of these cores indicates production of these compounds from ammonium by nitrification. Low concentrations of nitrate and nitrite in the deeper samples suggests that nitrification at these depths is inhibited by a lack of oxygen.

The $\delta^{15}N$ of porewater ammonium for all cores ranges from 4.5‰ to 9.2‰ (Table 13). The average $\delta^{15}N$ values for porewater ammonium in cores at BRLP5 and CC5, 7.7‰ and 6.4‰, respectively, are 2‰ less than the average sediment values for these cores. This difference in $\delta^{15}N$ is consistent with a kinetic fractionation effect during production of ammonium from mineralization. Enrichments in ^{15}N associated with the depth where nitrification occurs were not evident in Conception Bay and other coastal locations (Velinsky et al., 1991). Fractionation during nitrification has been shown to be large and results in an enrichment in ^{15}N in the remaining ammonium (Table 2). However, the lack of an isotope shift suggests that the ^{15}N enriched ammonium that is a byproduct of nitrification is probably not sufficient in quantity to alter the isotopic composition of ammonium produced during remineralization.

3.3 Water column organic matter and nutrient geochemistry

3.3.1 Station BRLP5

3.3.1.1 BRLP5 March 23, 1990

Sampling at BRLP5 on 3/23 occurred when water and air temperatures were quite cold (less than 0°C). Sea ice had just recently retreated, permitting sampling, but was still present at certain locations in the Bay. Water temperatures were less than -1°C throughout the water column and density stratification was weak in comparison to later samplings (Fig. 14; Table 14). The surface sample at 5m was supersaturated in dissolved oxygen by 24.55μM, in response to recent primary production or surface water mixing (Fig. 15)[2]. The $\delta^{13}C$ of DIC was nearly constant at all depths and equal to approximately 0.5‰ (Fig. 15). The isotopic composition of DIC is slightly lower than expected for equilibration with atmospheric CO_2 (Deuser and Hunt, 1969; Kroopnick et al., 1970; Kroopnick, 1980). The concentration of DIC in surface waters is markedly reduced compared to values deeper in the water column and values expected for atmospheric equilibration (Kroopnick, 1974b; 1980). Lowered concentrations of DIC of 1.7mmol/kg in surface waters may be

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[2] Dissolved oxygen concentrations in the figures and text are expressed in two ways. The more common and traditional unit for dissolved oxygen is mL/L at STP. Although not as common, μM oxygen above or below saturation concentration has had recent usage (Bender and Grande, 1987) and is more easily related to concentrations of DIC and nutrients.

the result of utilization of inorganic carbon during photosynthesis. Similar DIC concentrations have been reported for spring blooms in the North Atlantic and Bering Sea (Codispotti et al., 1982; Watson et al., 1991).

Chlorophyll-a fluorescence data was not available on this date, however, the decreased transmittance of light for waters above 35m suggests of the presence of a substantial phytoplankton population (Fig. 16). High concentrations of particulate organic carbon (POC), particulate organic nitrogen (PON) and total suspended material (TSM) for the upper two near surface samples confirm this observation and indicates that the spring phytoplankton bloom was in progress (Fig. 16). Reductions in transmittance and high concentrations of POC and PON, indicate that the majority of phytoplankton productivity was occurring at shallow depths, above the pycnocline.

Nitrate concentrations ranged from 0.9μM at 5m to 6.7μM at 100m (Fig. 17). At no time or place in Conception Bay were concentrations of nitrite in water column samples greater than 0.3μM. The presence of detectable quantities of nitrate within the chlorophyll maximum indicate that phytoplankton productivity was not limited by nitrogen at this time and suggest that the spring bloom had only been in progress for a short time. The $\delta^{15}N$ of nitrate was 6.3‰ at a depth of 210m and -1.6‰ at 80m (Fig. 17). Previous studies have suggested that the isotopic composition of nitrate

should increase towards the surface in the euphotic zone (Saino and Hattori, 1987; Altabet and McCarthy, 1985; 1986). This effect is a consequence of a preferential assimilation of ^{14}N enriched nitrate by phytoplankton that concentrates ^{15}N in the residual nitrate. Decreasing nitrate $\delta^{15}N$ values within the euphotic zone are opposite the trend that is commonly associated with fractionation during nutrient uptake.

The sample collected at 210m was characterized by the highest $\delta^{15}N$ value observed for nitrate in Conception Bay (Fig. 17). The $\delta^{15}N$ value for this sample, 6.3‰, is similar to the isotopic composition of dissolved ammonium in sediment porewaters (Table 13). Ammonium diffusing into the oxic layer of sediments or water column is oxidized to nitrate during nitrification. In the lower euphotic zone of certain marine environments nitrification has been shown to be an important source of nitrate (Ward, 1987; Ward et al., 1984; 1989), however, the low water column microbial respiration rates present at this time in Conception Bay (Table 4) suggest that this process occurs primarily in sediments. Ammonium concentrations might provide some evidence of water column nitrification, however, this data was not available between 3/23 and 5/2.

Nitrification involves a substantial fractionation whereby the product can become depleted in ^{15}N (Table 2). During unidirectional kinetic reactions the product will

have the same isotope value as the initial substrate if the reaction proceeds to completion. The ^{15}N enriched nitrate at 210m may be the product of nitrification that quantitatively oxidized the substrate, ammonium. The low $\delta^{15}N$ value for nitrate at 80m may be associated with nitrate derived during nitrification in which the substrate was not completely consumed. The wide range in $\delta^{15}N$ represented by these two samples may indicate that the extent of ammonium consumption during nitrification is variable.

Seston collected on 3/23 exhibited a very wide range of $\delta^{15}N$ values, from 6.5‰ to 22.1‰ (Fig. 17). Similar ranges in $\delta^{15}N$ have been reported for other oceanic environments. Seston from various locations in the Pacific Ocean has been reported to range between -3‰ to 23‰ (Saino and Hattori, 1987; Libes and Deuser, 1988). Slope water entrained in Gulf Stream meanders has been characterized by seston $\delta^{15}N$ values as high as 39.9‰ (Altabet and McCarthy, 1985). Variation in $\delta^{15}N$ within a single station may be in excess of 30‰ (Altabet and McCarthy, 1985). Low $\delta^{15}N$ values for seston are commonly attributed to phytoplankton using nitrogen fixation or fractionating during the assimilation of nitrate or ammonium (Minagawa and Wada, 1986; Altabet and McCarthy, 1985; 1986; Saino and Hattori, 1980; 1985; 1987; Ostrom and Macko, 1992). High $\delta^{15}N$ values have frequently been associated with oxidative degradation occurring below the euphotic zone (Altabet and McCarthy, 1985; 1986; Saino and

Hattori, 1980; 1985; 1987; Ostrom and Macko, 1992).

The C/N for phytoplankton and marine organisms is commonly less than 6 and may be as low as 3 (Banse, 1974; Walsh et al., 1981b). Preferential recycling of nitrogen relative to carbon may result in C/N values greater than 10 for detrital particles (Degens, 1970). Nitrogen limitation may also result in an increase in the C/N of phytoplankton (Walsh et al., 1981b). Thus, the low C/N values for seston on 3/23 of less than 4 are suggestive of relatively undegraded phytoplankton growing without nitrogen limitation (Fig. 17). The high C/N values, greater than 13, for the two deepest samples are indicative of a highly degraded material (Fig. 17). The $\delta^{15}N$ values for these samples, 12.5‰ and 13.7‰, are elevated with respect to the surface sample and consistent with fractionation during oxic degradation. Alternatively, an increase in the $\delta^{15}N$ of seston may result from preferential utilization of an organic fraction depleted in ^{15}N.

Although the sample at 60m is characterized by a very high $\delta^{15}N$ of 22.1‰ that is suggestive of degradation, this sample also has a low C/N of 3.6. Colonization of organic matter by bacteria can often enrich the substrate in nitrogen, thereby lowering the C/N during the degradation process (Tenore, 1983; Zieman et al., 1984). Incoporation of inorganic nitrogen with an isotopic signature unique from the substrate has been hypothesized to cause shifts in the

$\delta^{15}N$ of seston (Wada, 1980; Libes and Deuser, 1988). The high $\delta^{15}N$ and low C/N for the seston sample at 60m is consistent with degradation and bacterial incoroporation of ^{15}N enriched inorganic nitrogen.

The carbon isotopic composition of seston on 3/23 ranged from -25.0‰ to -22.6‰ (Fig. 17). The values for the deeper samples, less than -24‰, are within the range of phytoplankton growing at high latitudes (Sackett et al., 1965; Tan and Strain, 1979a; Rau et al., 1982; Ostrom and Macko, 1992). A recent study has correlated enrichments in ^{13}C in phytoplankton with decreases in pCO_2 (Rau et al., 1989). The occurrence of elevated seston $\delta^{13}C$ values and lowered DIC concentrations (Figs. 15 and 17) supports this correlation.

3.3.1.2 BRLP5 March 29, 1990

Sea ice was still present at station BRLP5 on 3/29 and water temperatures were primarily less than -1°C throughout the water column (Fig. 18). Although the pycnocline was present at a depth of approximately 40m, water column stratification remained weak (Table 14). Dissolved oxygen concentrations were supersaturated above the pycnocline and obtained a maximum concentration of 9.41mL/L, that was 0.38mL/L greater than the maximum value on 3/23 (Fig. 19; Table 15). The deepest sample was characterized by a very

low oxygen value of 6.79mL/L. Concentrations of DIC were low in surface waters and increased to a maximum of 2.42mmol/kg at 80m (Fig. 19). The DIC sample at 80m was also characterized by a very low $\delta^{13}C$ value of -3.9‰. Although microbial activity has been found to be generally quite low throughout Conception Bay there were brief moments of enhanced activity that may be related to increased availability of substrate during the spring bloom (Pomeroy et al., 1991). The low $\delta^{13}C$ and high concentration of DIC at 80m is similarly suggestive of enhanced episodic respiration (Smith and Kroopnick, 1981).

Chlorophyll-a concentrations were high above the pycnocline and reached a maximum of 9.0μg/L at 15m (Fig. 20; Table 14). Concentrations of POC, PON, and TSM were also very high at these depths which confirms that the spring bloom was in progress (Fig. 20). The percentage of light transmitted by the fluorometer on the CTD was low in the surface waters, owing to phytoplankton production, increased with depth and then abruptly decreased below 180m (Fig. 20). Within this deep layer the concentration of TSM increased relative to the sample above, however, POC and PON concentrations shifted only slightly. These trends are likely indicative of sediment resuspension. Sediments are relatively poor in organic matter in comparison to seston. Therefore, resuspension will affect transmittance and TSM dramatically while POC and PON concentrations are not

changed extensively.

Ratios of POC to chlorophyll have been shown to vary between about 20 to greater than 100 (Redalje and Laws, 1981; Kiefer, 1984; Geider et al., 1986; Sakshaug et al., 1989). Factors affecting the POC to chlorophyll ratio have been related to changes in nutrient supply, light regime, degradation and species composition (Laws et al., 1985; 1988; Geider and Platt, 1986; Sakshaug et al., 1989). In Conception Bay POC to chlorophyll a ratios varied between 6.5 and 262.4 (Table 16). Values less than 20 may not be realistic and reflect errors in the measurement of chlorophyll a or POC compounded by taking a ratio. This may be particularly true for the chlorophyll data since direct sampling is generally considered more accurate than in situ florescence profiles. Ratios less than 100 are generally considered to reflect healthy phytoplankton growing under light limited, nutrient abundant conditions (Goldman, 1980; Laws et al., 1983; 1988). Therefore, the POC to chlorophyll ratios less than 60 for the upper 50m of the water column on 3/29 indicate that the seston consists of primarily viable phytoplankton cells (Table 16). The high ratios, of greater than 130, for the lower water column suggest that this material is more degraded and does not consist of recently produced phytoplankton.

Concentrations of nitrate on 3/29 decrease from nearly 9μM at 210m to below detection limits in surface waters

(Fig. 21). Although concentrations of nitrate above the pycnocline are lower than on 3/23, the low C/N values of 5 or less in this layer suggest phytoplankton were not nitrogen limited and that little degradation had occurred (Walsh et al., 1981b; Fig. 21). The increase in the $\delta^{15}N$ of nitrate, from 0.2‰ at 210m to 2.9‰ at 80m, is suggestive of fractionation during nitrate utilization, but may also result from variation in fractionation during sediment nitrification (Fig. 21).

Seston $\delta^{15}N$ values of 7.2‰ to 9.6‰ for the surface three samples are similar to the upper water column samples on 3/23 (Figs. 17 and 21). The very high $\delta^{15}N$ for seston at 80m, 20.5‰, is similar to the value at 60m on 3/23. This sample differed by being characterized by a high C/N of 11.0. The high $\delta^{15}N$ and C/N values for the sample at 80m are consistent with the effects of oxic degradation. Seston at 210m was also characterized by a high $\delta^{15}N$, 16.1‰, and a low C/N. These values suggest the presence of oxic degradation coupled with nitrogen enrichment resulting from bacterial colonization.

Carbon isotope values for seston on 3/29 ranged from -25.8‰ to -22.9‰ (Fig. 21; Table 17). A maximum in $\delta^{13}C$ was found at 25m, which was with the layer of high chlorophyll- and low DIC concentrations. These trends were also present on 3/23 and are suggestive of decreased fractionation during carbon fixation associated with lowered pCO_2 (Rau et al.,

1989). On 3/29 the maximum in the $\delta^{13}C$ of seston is not concomitant with the minima in DIC concentration. This trend may be related to a resupply of DIC from atmospheric CO_2 or deeper waters.

3.3.1.3 BRLP5 April 4, 1990

Surface waters above 15m on 4/4 exhibited an increase in temperature from 3/29 of nearly 1°C (Table 14). Temperatures throughout the water column remained less than 0°C (Fig. 22). Density stratification was noticeable above 35m, but was not very distinct. Dissolved oxygen concentrations were quite high above the pycnocline and reached a maximum for the season of 74.83μmol/L in excess of saturation (Fig. 23; Table 15). DIC concentrations were low above the pycnocline, a trend similar to the two previous sampling days and consistent with utilization by phytoplankton (Fig. 23). The $\delta^{13}C$ of DIC remained fairly constant with depth, at approximately -0.5‰, indicative of CO_2 derived primarily from atmospheric equilibration (Kroopnick, 1974b; 1980). The low $\delta^{13}C$ value and concentration for DIC at the surface is suggestive of simultaneous photosynthesis and respiration.

Chlorophyll-a concentrations were very high in a narrow layer above the pycnocline between 15m and 35m (Fig. 24). The maximum chlorophyll concentration of 12.5μg/l is similar

to that found during the peak of a spring bloom in the Bering Sea (Codispotti et al., 1982; Table 14). Concentrations of TSM, PON, and POC were all very high at the chlorophyll maximum and either are or are close to the highest values for the sampling season (Fig. 24). Ratios of POC to chlorophyll at all depths were 100 or less and indicative of recently produced phytoplankton material (Table 16). A decrease in transmittance and increase in TSM below 180m is indicative of sediment resuspension, though not of the magnitude present on 3/29.

Nitrate was depleted from surface waters on 4/4, however, there was a very sharp gradient between the sample at 22m, where no nitrate was present, to the sample at 35m, where the concentration was 5.4μM (Fig. 25). Ratios of carbon and nitrogen within the upper 50m remained low and less than 7 suggesting that phytoplankton were not affected by nitrogen limitation or degradation (Fig. 25). Apparently weak stratification present at this time was not sufficient to completely inhibit transfer of nitrate into surface waters. The $\delta^{15}N$ of nitrate at 210m was similar to the values obtained on previous days (Fig. 25).

The range in $\delta^{15}N$ seston values on 4/4, 8.5‰ to 14.6‰, was narrower than found in March. Seston in deeper waters was characterized by higher $\delta^{15}N$ and C/N values than at the surface that suggested partial degradation. The slight decrease in C/N and $\delta^{15}N$ for deep water seston on this date

in comparison to 3/29 may be related to a greater contribution of recently produced phytoplankton material. Carbon isotope values for seston ranged from -25.2‰ to -22.0‰ (Table 17). The most ^{13}C enriched sample occurred concomitantly with maximum chlorophyll and low DIC concentrations (Figs. 23, 24, and 25). These trends also occurred on 3/23 and 3/29 and appear to be related to high productivity levels.

3.3.1.4 BRLP5 April 18, 1990

The pycnocline on 4/18 was not very distinct and density gradually increased from the surface to a depth of about 70m (Fig. 26; Table 14). Water temperatures decreased from a maximum at the surface of 0.7°C to a minimum of approximately -1.5°C near 70m. Surface waters above the pycnocline had oxygen concentrations in excess of 30μM above supersaturation (Fig. 27; Table 15). Concentrations of DIC, 2.2mmol/kg, were fairly constant with depth (Fig. 27). The trend of low DIC concentrations in surface relative to deep waters was not as distinct as previous days, perhaps owing to atmospheric equilibration. Evidence of increased respiration with depth was provided by DIC $\delta^{13}C$ values that decreased slightly with depth from 0.7‰ at the surface to -1.1‰ at 210m (Fig. 27; Table 15).

Chlorophyll-a concentrations on 4/18 were at a maximum at 15m and were detectable to the base of the pycnocline

(Fig. 28). The maximum concentration of chlorophyll, 12.4μg/L, was similar to that of 4/4, however, the horizontal width of the chlorophyll rich layer was greater (Fig. 28; Table 14). Concentrations of POC, PON, and TSM were not as high as on 4/4, but relatively high concentrations were present in a wider portion of the water column (Fig. 28). High values of chlorophyll, POC and PON indicate that the spring bloom was still in progress and phytoplankton were quite probably at the peak of their seasonal productivity. Ratios of POC to chlorophyll varied between 12.5 and 82.1 and are indicative of fresh phytoplankton material (Table 16). The reduction in transmittance and increase in TSM indicated the presence of resuspended sediments in the water column below 180m (Fig. 28).

Nitrate concentration were below detection in surface waters and 0.6μM at 45m (Fig. 29). Low ratios of carbon to nitrogen for seston above the pycnocline reaffirm earlier observations that productivity was essentially free from the effects of nitrogen limitation and degradation. The nitrogen isotopic composition of nitrate decreased from -1.4‰ at 210m to -4.7‰ at 80m (Fig. 29). This trend in the $\delta^{15}N$ of nitrate is opposite that expected for fractionation during assimilation. The low $\delta^{15}N$ value at 80m may indicate nitrate transported from another location or derived from mid-water column nitrification. Seston $\delta^{15}N$ values were

quite variable and ranged between 5.4‰ and 18.6‰ (Fig. 29; Table 17). Bacterial degradation and assimilation of inorganic nitrogen is suggested by the high $\delta^{15}N$ and low C/N, of 4.9, for the sample at 210m. Degradative processes resulting in enrichments in ^{15}N and nitrogen appear to be episodic and occur primarily in the deeper waters. Variation in the $\delta^{13}C$ of seston was not as wide as previous days, however, the trend of ^{13}C enriched values associated with the chlorophyll maximum was also observed at this time (Fig. 29).

3.3.1.5 BRLP5 April 29, 1990

Sampling on 4/29 followed a period of very strong winds that depressed the depth of the pycnocline to approximately 100m (Fig. 30). Water temperatures were not appreciably warmer than on 4/18 and remained less than 0.5°C throughout the water column (Fig. 30; Table 14). Dissolved oxygen exceeded saturation levels in samples taken at 100m or above (Fig. 31). As in previous collections, the concentration of DIC increased with depth from 2.11mmol/kg at the surface to 2.40mmol/kg at 100m (Fig. 31). The $\delta^{13}C$ of DIC was fairly constant with depth and ranged between 0.6‰ and 1.1‰ (Fig. 31; Table 15). Elevated oxygen and lowered DIC concentrations in surface waters is suggestive of active photosynthesis to a depth of 100m or more. The $\delta^{13}C$ values

for DIC are similar to those expected for equilibration with atmospheric CO_2.

Chlorophyll-a concentrations were generally greater than 3μg/L from 140m to the surface suggesting substantial primary production (Fig. 32). A maximum concentration of chlorophyll of approximately 10.6μg/L was found at a depth of 87m (Fig. 32; Table 14). The presence of chlorophyll at depths greater that 100m is surprising in that this is generally considered the maximum depth of the euphotic zone. Material collected at depths in excess of 100m may consist of recently produced phytoplankton material that was sinking to the seafloor or mixed downward by the high winds. This conclusion is supported by the observation of POC to chlorophyll ratios of less than 40 to a depth of 120m (Table 16). Transmittance was low within the euphotic zone and decreased slightly near the bottom (Fig. 32). Concentrations of POC, PON, and TSM were all high above 120m (Fig. 32). The concentration of TSM at 80m, 797μg/L, was the highest measured in the sampling season.

Nitrate concentrations were undetectable at the surface and at very low levels, 0.5μM, at a depth of 90m (Fig. 33). These observations contrast data on 4/18 when nitrate was measured at a depth of 45m (Fig. 29). The high winds resulted in a lowering of the pycnocline and apparently mixed phytoplankton to a depth of approximately 100m. Subsequent primary production then depleted nitrate from the

water column to the base of the euphotic zone. Low C/N values for seston at and above 100m suggest that phytoplankton were not nitrogen limited and little degradation had occurred (Fig. 33). The $\delta^{15}N$ of nitrate at 210m, -2.9‰, was lower than porewater ammonium values and indicative of fractionation during nitrification (Fig. 33; Table 13).

Nitrogen isotope values for seston collected on 4/29 ranged between 7.2‰ and 12.9‰ (Fig. 33; Table 17). High $\delta^{15}N$ values present in the early spring were not observed, possibly owing to mixing of surface and deep seston in response to the high winds. Similarly, $\delta^{13}C$ values, -23.8‰ to -22.7‰, were fairly constant with depth and showed no indication of a maximum associated with a peak in chlorophyll concentration (Fig. 33; Table 17).

3.3.1.6 BRLP5 May 2, 1990

Surface water temperatures increased from 0.3°C on 4/29 to 1.2°C on 5/2 (Fig. 34; Table 14). Two pycnoclines were present at this time, one at 10m and the second at approximately 65m (Fig. 34). Concentrations of dissolved oxygen above the pycnocline were similar to what was measured on 4/29, however, a lower portion of the water column was supersaturated (Fig. 35; Table 15). Dissolved inorganic carbon concentrations ranged between 2.14mmol/kg

and 2.27mmol/kg (Fig. 35; Table 15). The $\delta^{13}C$ of DIC exhibited lower values at depth than at the surface and had a minimum value of -1.5‰ at 210m (Fig. 35). Respiration in deep waters resulted in the observed low oxygen concentrations and $\delta^{13}C$ values for deep waters.

Concentrations of chlorophyll, POC, PON, and TSM at equivalent depths were all substantially lower on 5/2 than on 4/29 (Figs. 32 and 36). These reductions suggest that productivity during the spring bloom was beginning to decline. Photosynthetically active radiation was also measured by the Seabird CTD and was not detected below a depth of 100m. Therefore, the presence of substantial chlorophyll concentrations below this depth could not be due to active phytoplankton and suggests that phytoplankton material was sinking to the seafloor. Ratios of POC to chlorophyll are less than 100 for all samples indication recently produced material (Table 16). A decrease in transmittance and increase in TSM near the seafloor is indicative of sediment resuspension (Fig. 36).

Trace quantities of nitrate were detected in surface waters and a change in concentration was most marked between 30m and 90m (Fig. 37). Ratios of carbon to nitrogen increased from 120m to the surface and suggest nitrogen limitation (Fig. 37). The $\delta^{15}N$ of seston ranged between 9.1‰ and 15.5‰ (Fig. 37; Table 17). The sample with the highest $\delta^{15}N$ value was collected at 120m and is similar to previous

observations of a $\delta^{15}N$ maximum at the base of or below the chlorophyll maximum. The greatest $\delta^{13}C$ value occurred within the chlorophyll maximum layer. Carbon isotope values for the entire water column varied by only 1.3‰ (Fig. 37; Table 17).

3.3.1.7 BRLP5 May 6, 1990

Surface water temperatures on 5/6 were similar to those on 5/2 and approximately equal to 1.4°C (Fig. 38; Table 14). On both days two pycnoclines were present, however, the depth of the shallow pycnocline on 5/6, 25m, was deeper than on 5/2 (Figs. 34 and 38). Saturation levels for dissolved oxygen decreased from 22.23μM at 5m to -81.17μM at 245m (Fig. 39; Table 15). The value at 245m was one of the lowest measured during the sampling season in Conception Bay. Concentrations of DIC were virtually constant with depth at 2.2mmol/kg (Fig. 39; Table 15). Carbon isotope values for DIC progressively decreased with depth from 0.8‰ to -1.5‰ (Fig. 39; Table 15). Decreases in dissolved oxygen and the $\delta^{13}C$ of DIC with depth indicate increased respiration and reduction in oxygen diffusion downward from surface waters. Chlorophyll and transmittance data was not available on this date, nonetheless, low concentrations of POC and PON throughout the water column suggests that productivity was low. A decrease in transmittance and

increase in TSM to 0.87mg/L at 245m indicates sediment resuspension (Fig. 40).

Concentrations of nitrate on 5/6 increased with depth from detection limits to 9.3μM and the nitricline was present at the depth of the pycnocline (Fig. 41). Ammonium concentrations were 0.1μM or less at all depths (Fig. 41). The $\delta^{15}N$ of nitrate decreased from 4.9‰ at 245m to a minimum of -2.8‰ at 80m (Fig. 41). This trend is inconsistent with fractionation during uptake.

Low carbon to nitrogen ratios of less than 4 for seston in the upper water column suggest that productivity was not limited by nitrogen. Seston $\delta^{15}N$ values, 13.8‰ to 18.0‰, were generally high throughout the water column and indicative of partial degradation (Fig. 41; Table 17). The $\delta^{13}C$ of seston were between -24.8‰ and -22.3‰ and greater in deep waters than at the surface (Fig. 41; Table 17). The ^{13}C enriched values may be the result of productivity previously associated with the chlorophyll maximum that was sinking to the seafloor.

3.3.1.8 BRLP5 May 20, 1990

Water temperatures at the surface increased by 1°C from 5/6 to 2.4°C (Table 14). A distinct, but gradual, change in density was most marked between 40m to 120m (Fig. 42). Oxygen concentrations ranged between 20.04μM and -55.77μM

relative to saturation levels and were lower at the surface than previously measured (Fig. 43; Table 15). The concentration and isotopic composition of DIC was quite variable (Fig. 43). Low $\delta^{13}C$ DIC values were present at 40m and 120m and are suggestive of increased respiration. Release of CO_2 from respiration should result in an increase in DIC concentration. The lack of an elevated DIC concentration for the sample at 40m is probably the result of photosynthetic CO_2 utilization occurring simultaneous with respiration.

Concentrations of chlorophyll, POC, PON, and TSM were all quite low relative to earlier collections (Fig. 44). Concentrations of chlorophyll had a maximum value of 3.2μg/L at 60m and were generally less than 2μg/L throughout the water column (Fig. 44; Table 14). The very high POC to chlorophyll ratio at the surface of 262.4 indicated that seston at this depth was not composed of viable phytoplankton material and was most likely highly refractory (Table 16). Transmittance was greater than 85% except for the water column below 160m (Fig. 44). These observations indicate that the spring bloom was essentially over at this time.

Concentrations of dissolved nitrate ranged from 11.1μM at 210m to below detection at 40m and above (Fig. 45). Although nitrate was depleted in the surface waters trace quantities of ammonium, less than 1μM, persisted (Fig. 45).

The presence of ammonium indicates that the mineralization of organic matter was occurring in the water column. Primary production occurring at this time would subsist primarily on ammonium, as opposed to nitrate, because concentrations of ammonium as low as of 0.3μM may inhibit nitrate uptake (Wheeler and Kokkinakis, 1990). The $\delta^{15}N$ of nitrate increased from -4.2‰ at 210m to 0.3‰ at 80m (Fig. 45). This trend in the $\delta^{15}N$ of nitrate is consistent with fractionation during nitrate assimilation by phytoplankton. The evidence for and against nitrate utilization may be the result of nocturnal ammonium regeneration followed by uptake of nitrate as ammonium became depleted during the day. Diurnal variation in ammonium concentrations in polar waters has been explained by such a process (Wheeler et al., 1989).

Seston $\delta^{15}N$ values, 12.4‰ to 15.0‰, were considerably narrower in range than those was commonly observed earlier in the spring (Fig. 45; Table 17). Carbon isotope values for seston ranged between -25.2‰ and -22.3‰ (Fig. 45; Table 17). The trend of a $\delta^{13}C$ maximum associated with the chlorophyll maximum was not present at this time. The high $\delta^{13}C$ value present at 210m may be the result of earlier productivity sinking to deeper waters or to sediment resuspension. Ratios of carbon to nitrogen in surface waters were generally greater than those found earlier in the spring and suggest that degradation may have been more pronounced at this time (Fig. 45; Table 17). The sample

with the highest C/N also had the highest $\delta^{15}N$ value. This trend is indicative of degradation.

3.3.1.9 BRLP5 June 24, 1990

During the series of collections at BRLP5 from spring to late summer density stratification gradually became more distinct (Fig. 46; Table 14). On 6/24 density stratification was well developed. Surface temperatures increased from 2.4°C on 5/20 to 7.4°C (Table 14). The concentration of oxygen at 5m was lower than any time previously, however, because of the warmer temperatures oxygen was still supersaturated (Fig. 47). Concentrations of DIC were low in surface waters, which suggests utilization during photosynthesis (Fig. 47). The occurrence of low chlorophyll abundances at this time suggests that the low DIC concentrations for surface waters may be related to earlier productivity and a lack of subsequent atmospheric equilibration. High DIC concentrations were found in deeper waters that, in addition to low oxygen levels indicate that respiration was active. The $\delta^{13}C$ of DIC averaged 0.4‰ and was nearly constant with depth (Fig. 47). Apparently respiration in lower waters was not sufficient to markedly alter the isotopic composition of DIC.

Some of the lowest concentrations within surface waters of chlorophyll a, POC, PON, and TSM measured during the

sampling season were present at BRLP5 on 6/24 (Fig. 48). Chlorophyll concentrations reached a maximum value of 1.4μg/L at a depth of 32m (Table 14). Ratios of POC to chlorophyll remained less than 100 suggesting that most of the seston was composed of recently produced material (Table 16). Below 125m a gradual decrease in transmittance was noticeable with depth (Fig. 48). This trend was accompanied by a slight increase in POC and POM and a sharp increase in TSM. These data are indicative of sediment resuspension that could be the result of slumping or current scouring.

Nitrate concentrations decreased from 7.1μM at 210m to below detection at 40m and above. Ammonium was undetectable at 5m and increased with depth to a maximum of 2.1μM at 210m (Fig. 49). Ratios of carbon to nitrogen ranged from 4.3 to 6.8 and were slightly higher than values found in the early spring (Fig. 49; Table 17). The isotopic composition of nitrate varied markedly from 4.5‰ in the lowermost sample to -4.4‰ at 80m (Fig. 49). Seston $\delta^{15}N$ values varied between 9.2‰ and 18.7‰ (Table 17). The minimum in seston $\delta^{15}N$ occurred at a depth where the change in nitrate concentration was greatest. This trend has previously been interpreted as resulting from fractionation during nitrate uptake (Saino and Hattori, 1980). A decrease in the $\delta^{15}N$ of nitrate with decreasing depth is contradictive to this conclusion. The presence of ammonium at this transition suggests that ammonium was the preferred nitrogen source for

phytoplankton. Although ammonium isotopic data is not available it is conceivable that phytoplankton may have been drawing on ammonium with an isotopic signature distinct from nitrate. Carbon isotope values were low throughout the water column and varied from -25.3‰ to -24.0‰ (Table 17). No relationship between seston $\delta^{13}C$ and chlorophyll concentration was evident.

3.3.1.10 BRLP5 July 27, 1990

Density stratification on 7/27 continued to strengthen as surface water temperatures warmed to 12.3°C (Fig. 50; Table 14). Dissolved oxygen concentrations in surface waters were low and only the uppermost sample was supersaturated (Fig. 51). The isotopic composition and concentration of DIC ranged between 0.1‰ to 1.4‰, and 2.05mmol/kg to 2.36mmol/kg, respectively (Fig. 51; Table 15). Chlorophyll, POC, PON, and TSM concentrations all continued to remain low within the euphotic zone suggesting that primary production was quite low at this time (Fig. 52). Particulate carbon to chlorophyll ratios ranged between 36.4 and 70.4, indicating that seston was composed of recently produced material (Table 16). A mid-water column minimum in transmittance was suggestive of sediment resuspension elsewhere in the bay that was carried by currents to this station.

Dissolved inorganic nitrogen was present at all depths in the water column on 7/27. Nitrate concentrations decreased toward the surface from 8.9μM to undetectable levels. Ammonium concentrations similarly varied from 1.9μM at 210m to 0.2μM at 5m (Fig. 53). The nitrogen isotopic composition of both nitrate and ammonium was determined on lower water column samples (Fig. 53). Nitrate $\delta^{15}N$ values ranged from -3.2‰ to 2.5‰, with a sharp increase from 80m to 60m. The $\delta^{15}N$ of ammonium was nearly constant with depth and varied between 3.7‰ and 4.8‰. Seston $\delta^{15}N$ values continued to be distinct from dissolved inorganic nitrogen and ranged from 10.0‰ to 16.5‰ (Table 17). The $\delta^{13}C$ of seston, -25.1‰ to -24.3‰, was constant with depth (Fig. 53; Table 17). Ratios of carbon to nitrogen showed a general decrease with depth from 6.8 to 5.0 (Fig. 53; Table 17).

3.3.1.11 BRLP5 August 30, 1990

Density stratification on 8/30 was similar in magnitude and depth to 7/27 (Figs. 50 and 54; Table 14). Surface water temperatures increased to 13.3°C (Table 14). Although still above saturation values the oxygen concentration at 5m, 6.47mL/L, was the lowest measured in surface waters throughout the season (Fig. 55). Saturation of oxygen and a low DIC concentration of 1.77mmol/L, above 50m suggested that substantial primary production had recently occurred

(Fig. 55). Respiration in deeper waters was indicated by lowered oxygen concentrations and a decrease in the $\delta^{13}C$ of DIC (Fig. 55).

Chlorophyll concentrations reached a maximum of 2.0μg/L at 20m and were undetectable below 50m (Fig. 56; Table 14). Ratios of POC to chlorophyll continued to remain less than 100 suggesting that seston consisted of recently produced material (Table 16). Concentrations of POC, PON, and TSM were all elevated above 50m with respect to the lower water column, though not nearly as high as values measured in the early spring (Fig. 56). The data on oxygen, DIC, chlorophyll, POC, PON and TSM in surface waters suggested that there were low levels of primary production occurring at this time. These trends may be the result of a low-level late summer phytoplankton bloom. Decreases in transmittance and increases in TSM in the lower water column were similar to what was observed on 6/24 and 7/27 and may be related to a resuspension event within Conception Bay (Figs. 48, 52, and 56).

The concentration of nitrate was undetectable above 50m and increased below this depth to a maximum of 8.9μM at 210m (Fig. 57). Ammonium concentrations decreased from 2.3μM at 210m to 0.2μM at 5m. The presence of ammonium within the chlorophyll maximum layer suggests that nitrate uptake was probably inhibited (Probyn, 1988; Kristiansen and Lund, 1989; Wheeler and Kokkinakis, 1990). However, the depletion

of nitrate in surface waters indicates that nitrate was also being utilized. Diurnal studies have shown ammonium regeneration at night followed by consumption during the day (Wheeler et al., 1989). If all of the ammonium regenerated at night was consumed before sunset then phytoplankton would begin to utilize nitrate.

The $\delta^{15}N$ of nitrate varied markedly from -6.2‰ near the seafloor to 3.9‰ at 80m (Fig. 57). This increase is consistent with isotopic fractionation during nutrient uptake. Ammonium at 210m was characterized by a $\delta^{15}N$ of 6.3‰ that is similar to and suggests an origin in sediment porewater ammonium (Fig. 57).

The $\delta^{15}N$ of seston ranged between 11.9‰ and 15.7‰ (Table 17). A minimum in $\delta^{15}N$ was present at 80m which is the trend associated with fractionation during nitrate utilization. Ratios of carbon to nitrogen, 3.7 to 5.2, were low and did not indicate nitrogen limitation or extensive degradation (Table 17). Seston $\delta^{13}C$ values were between -24.4‰ and -23.2‰ (Table 17). A maximum in $\delta^{13}C$ occurred in conjunction with high chlorophyll and low DIC concentrations, a trend that prevailed during the spring bloom.

3.3.2 Station US3.5

3.3.2.1 US3.5 May 1, 1990

Station US3.5 was sampled 4 times between May and July.

On May 1 surface water temperatures were 0.4°C which is 1°C cooler than was found for station BRLP5 on 5/2 (Figs. 34 and 58; Table 14). Density stratification changed gradually between 70m and 140m (Fig. 58). The low pycnocline was probably related to high winds which influenced stratification at station BRLP5 on 4/29 and 5/2 (Figs. 30 and 34). A slight increase in temperature was evident in depths below 120m. Dissolved oxygen concentrations were high and supersaturated above 100m (Fig. 59; Table 15). Concentrations of DIC were virtually constant with depth at 2.2mmol/kg (Fig. 59). Respiration was indicated by $\delta^{13}C$ values of DIC that were less than zero and low oxygen concentrations in deep waters (Fig. 59). The very low saturation level for oxygen, -83.79μM, at 215m may be related to the proximity of this sample to the seafloor.

Concentrations of chlorophyll were generally greater than 3μg/L above 120m (Fig. 60). Several sharp peaks in chlorophyll were present within the euphotic zone and a maximum of 10.2μg/l was present at 65m (Fig. 60; Table 14). Chlorophyll concentrations greater than 1μg/L as deep as 130m and were present at depths well below the deepest penetration of photosynthetically active radiation of 80m. This observation suggests that the presence of chlorophyll below 80m could not be due to recent productivity and indicated that phytoplankton material was sinking out of the euphotic zone. Low POC to chlorophyll ratios 61 or less

support this contention (Table 16). Concentrations of POC, PON, and TSM were all high within the upper 120m, which in conjunction with the chlorophyll data indicates that the spring bloom was in progress at this station (Fig. 60). Low transmittance values within the euphotic zone and below 180m, were probably associated with productivity and resuspension, respectively (Fig. 60).

Concentrations of nitrate decreased from 10.8μM at 215m to 0.2 μM at the surface (Fig. 61). Ratios of carbon to nitrogen in seston ranged between 4.7 and 7.1 and did not suggest nitrogen limitation or considerable degradation (Table 17). Seston $\delta^{15}N$ values, 7.3‰ and 10.7‰, did not exhibit the marked ^{15}N enrichments that were often observed at BRLP5 (Table 17). The $\delta^{13}C$ of seston was nearly constant with depth at -24‰ and no relationship between $\delta^{13}C$ and chlorophyll concentration was noticeable (Fig. 61). Similar patterns in $\delta^{15}N$, $\delta^{13}C$ and chlorophyll data were present at BRLP5 on 4/29 and may be related to mixing of the upper water column in association with a high winds (Figs. 32 and 33).

3.3.2.2 US3.5 May 6, 1990

Surface water temperatures at US3.5, 0.8°C, continued to be approximately 1°C cooler than at BRLP5 on this date (Table 14). Density stratification was similar between the

stations with the development of two pycnoclines (Figs. 38 and 62). Oxygen concentrations continued to remain high at this station and supersaturated above 75m (Fig. 63). Concentrations of DIC were variable and showed low values at 5m and 60m (Fig. 63). The $\delta^{13}C$ of DIC decreased from 0.7‰ at 30m to -1.1‰ at 170m in response to respiration (Fig. 61; Table 15). Concentrations of chlorophyll, POC, PON, and TSM in the euphotic zone were generally all lower than those observed on 5/2 (Fig. 64). Evidently the spring bloom had begun to decline at this time. The presence of chlorophyll at depths greater than that of the euphotic zone and low POC to chlorophyll ratios suggest that phytoplankton material was raining down to deeper waters (Fig. 64; Table 16).

Nitrate was undetected from the water column above 100m (Fig. 65). Concentrations of ammonium, 0.5μM to 2.2μM, were low but detectable at all depths (Fig. 65). Carbon to nitrogen ratios remained low and ranged from 3.5 to 9.4 (Table 17). The $\delta^{15}N$ of nitrate decreased markedly from 7.9‰ at 170m to -1.3‰ at 100m (Fig. 65). This trend in $\delta^{15}N$ nitrate values is opposite that expected for fractionation associated with nitrate assimilation. Seston $\delta^{15}N$ values ranged between 7.9‰ and 18.2‰, and high values were present in the upper water column (Fig. 65; Table 17). Carbon isotope values for seston ranged from -24.9‰ to -23.4‰ (Table 17). High $\delta^{13}C$ values for seston in conjunction with the chlorophyll maximum was not clearly evident.

3.3.2.3 US3.5 May 21, 1990

Water temperatures in the upper 40m of US3.5 on 5/21 were 1.4°C. These values are 1°C lower than on the previous day at BRLP5 (Fig. 66; Table 14). Density stratification at the two stations was at similar depths (Table 14). Oxygen concentrations were between 7.37mL/L and 8.05mL/L (Fig. 67). The sample at 5m, 9.91μM, was the lowest oxygen saturation level measured during the season for this depth. Both the concentration and isotopic composition of DIC was variable (Fig. 67). Low DIC $\delta^{13}C$ values present at 60m and 80m, less than -1‰, are indicative of respiration, however, the low concentration at 60m, 1.87mmol/kg, and presence of a chlorophyll maximum near this depth suggests that DIC must have been consumed by photosynthesis as well.

Low concentrations of chlorophyll, POC, PON, and TSM all suggest that the spring bloom at both US3.5 and BRLP5 was waning at this time (Figs. 44 and 68). The high POC to chlorophyll ratio for the sample at 5m indicated that seston at this depth was not largely composed of viable phytoplankton (Table 16). Nitrate was undetectable from depths of 60m and above. Trace quantities of ammonium, 0.2μM to 0.7μM, were present at all depths (Fig. 69). The nitrogen isotopic composition of nitrate ranged from -2.8‰ to 4.9‰ and the maximum value was at a depth of 100m (Fig. 69). Seston $\delta^{15}N$ values were between 11.1‰ and 18.5‰ (Table

17). The greatest $\delta^{15}N$ value was associated with a low $\delta^{13}C$ value of -26.5‰. Carbon isotope values for all seston samples were less than -24‰ (Fig. 69). Seston C/N values generally increased with depth and ranged from 4.2 to 6.7 (Fig. 69; Table 17).

3.3.2.4 US3.5 June 24, 1990

Density stratification was well developed on 6/24 and present at a depth of approximately 30m (Fig. 70; Table 14). Temperatures at the surface increased from 5/21 to 6°C and were 1.5°C cooler than at BRLP5 on this date (Table 14). Dissolved oxygen was only supersaturated in the sample collected at 5m (Fig. 71). The concentration and $\delta^{13}C$ of DIC were variable and did not exhibit any noticeable trend with depth (Fig. 71). Concentrations of chlorophyll, POC, PON, and TSM were at some of the lowest levels determined for any station throughout the sampling season (Fig. 72). Only a slight increase in chlorophyll above background levels was measured within the euphotic zone. These data indicate that the spring bloom had ended and that there was very little primary production occurring at this time. Nonetheless, POC to chlorophyll ratios remained low and indicative of fresh phytoplankton material (Table 16). A decrease in transmittance and increase in TSM near the seafloor could be the result of resuspension (Fig. 72).

Nitrate concentrations decreased from 9.4μM near the seafloor to 0μM at 25m and above (Fig. 73). Ammonium was present at all depths and increased from 0.1μM at the surface to 1.7μM at 210m (Fig 73). The $\delta^{15}N$ of nitrate decreased from 4.0‰ at 210m to -4.3‰ at 80m (Fig. 73). Seston $\delta^{15}N$ values generally decreased with depth and ranged from 17.7‰ to 9.2‰ (Fig. 73). The $\delta^{13}C$ of seston was fairly constant with the exception of a relatively ^{13}C enriched sample at 25 m (Fig. 73). Carbon to nitrogen ratios generally increased in depth and ranged between 5.6 and 8.2 (Table 17).

3.3.3 Additional stations

3.3.3.1 CTR23 April 30, 1990

Station CTR23 is located approximately 5km northwest of BRLP5 (Fig. 3). This station was sampled on 4/30 to assess spatial variability in physical and geochemical parameters. Surface water temperatures and density stratification was similar to those measured at BRLP5 on 4/29 (Figs. 30 and 74; Table 14). Concentrations of dissolved oxygen in the upper water column were generally lower than was present at BRLP5 on 4/29 and US3.5 on 5/1 (Figs. 31, 59, and 75; Table 15). Concentrations of DIC were variable at CTR23 and ranged from 2.17mmol/kg and 2.41mmol/kg (Fig. 75; Table 15). DIC $\delta^{13}C$ values sampled at CTR23 ranged between 0.2‰ and 1.7‰ (Table

15). Concentrations of chlorophyll a were similar among stations CTR23, BRLP5, and US3.5 sampled between 4/29 and 5/1 (Figs. 32, 60, and 76). Ratios of POC to chlorophyll at CTR23 less than 30 for the upper 120m indicating recent nutrient abundant productivity (Table 16). All stations had chlorophyll concentrations above 100m that were generally greater than 4μg/L and narrow depth intervals that neared or exceeded 8μg/L (Table 14). Concentrations of POC, PON, and TSM were high and similar among these stations (Figs. 32, 60, and 76).

Nitrate concentrations ranged between 4.8μM and 5.2μM but were not determined for samples above 100m at CTR23 (Fig. 77). The $\delta^{15}N$ of nitrate varied from -2.2‰ to 5.3‰ and increased in the vicinity of the pycnocline (Fig. 77). Seston $\delta^{15}N$ values for stations CTR23, BRLP5 and US3.5 from 4/29 to 5/1 were at a minimum at 60m or 80m (Figs. 33, 61, and 77). At station CTR23 $\delta^{15}N$ values increased with depth from 8.5‰ at 80m to 20.6‰ at 210m (Table 17). Seston $\delta^{13}C$ values for all of these stations were fairly constant with depth, however, at CTR23 had the most ^{13}C enriched values of any station in the season (Figs. 33, 61, and 77; Table 17). Elevated $\delta^{13}C$ values were associated with the chlorophyll maximum at CTR23. Carbon to nitrogen ratios of seston decreased with depth from 11.41 to 3.6 (Fig. 77; Table 17).

3.3.3.2 CC13 May 4, 1990

Station CC13 is located outside of the mouth of Conception Bay and is dominated by Labrador Current water (Fig. 3). Density stratification was not distinct at this station although thermoclines at 25m and 100m were present (Fig. 78; Table 14). Water temperatures at the surface decreased along a transect from 1.3°C at BRLP5 on 5/6, through US3.5 on 5/6 to -0.2°C at CC13 (Table 14). Dissolved oxygen at CC13 was supersaturated in samples above 100m and reached a maximum saturation level of 29.57μM at 5m (Fig. 79). A distinct minima in the concentration of DIC of 1.82mmol/kg was measured at 40m (Fig. 79). The $\delta^{13}C$ of DIC at this station ranged between -0.3‰ and 1.2‰ (Table 15).

Variation in chlorophyll concentrations at CC13 very closely followed changes in temperature and density (Figs. 78 and 80). Chlorophyll reached a maximum concentration of 12.3μg/L at 13m and fluctuated around 7μg/l between 25 and 90m (Fig. 80; Table 14). These values were substantially greater than the maximum concentrations obtained at BRLP5 on 5/2 and US3.5 on 5/6 of approximately 5μg/L (Table 14). Apparently, while the spring bloom was waning inside Conception Bay, it was in full production outside the Bay. Remarkably low POC to Chlorophyll ratios were present at CC13 as a result of high nutrient replete productivity (Table 16).

Nitrate was detected within the chlorophyll rich layer and decreased with depth from 0.4μM to 6.8μM (Fig. 81). Carbon to nitrogen ratios for seston were low, 3.7 to 5.2, indicating a lack of nitrogen limitation (Table 17). The $\delta^{15}N$ of nitrate in deep waters ranged from -2.0‰ to -1.1‰ (Fig. 81). Seston $\delta^{15}N$ values ranged from 11.7‰ to 15.7‰, with a minima at 80m (Fig. 81; Table 17). The $\delta^{13}C$ of seston was at a maximum of -23.2‰, within the zone characterized by high chlorophyll and low DIC concentrations (Figs. 79, 80, and 81). Similar trends were observed at other stations during the spring bloom.

3.3.4 Seston mass averaged $\delta^{15}N$ and $\delta^{13}C$

Seasonal variation in $\delta^{15}N$ and $\delta^{13}C$ values at stations BRLP5 and US3.5 can be compared by the following mass balance relationship:

$$\delta_m = \frac{\sum_{i=1}^{n} \delta_i * C_i}{\sum_{i=1}^{n} C_i} \qquad \text{(eq. 2)}$$

where δ_m = the mass weighted carbon or nitrogen isotopic composition of seston at a station on a specific date

δ_i = the $\delta^{13}C$ of $\delta^{15}N$ of an individual

seston sample

C_i = the concentration of seston organic carbon or nitrogen

n = the number of seston samples at a station on a particular date.

The results of the mass balance seston model are shown in Figure 82 in comparison to the chlorophyll a concentration integrated over the water column during each sampling. The integrated chlorophyll concentrations are primarily a reflection of chlorophyll production and a proxy for primary productivity. There is a marked increase in $\delta^{15}N$ of 6.4‰ at BRLP5 and 4.3‰ at US3.5 between 4/29 and 5/6 (Fig. 82). This trend in $\delta^{15}N$ occurs concomitantly with a dramatic decrease in the chlorophyll concentration that represents the end of the spring bloom in 1990. Furthermore, there is an increase in weighted $\delta^{15}N$ from values less than 11‰ before the chlorophyll decrease to values greater than 12‰ afterwards.

Increases in $\delta^{15}N$ similar to those in Conception Bay were noticed within a North Atlantic warm core ring as density stratification strengthened (Altabet and McCarthy, 1985). Density stratification would inhibit the supply of nitrate from deeper waters and phytoplankton would rely to a greater extent on regenerated ammonium. An increase in density stratification is noticeable between early spring and summer (Table 14). Therefore, the increase in seston

$\delta^{15}N$ during the termination of the bloom and high $\delta^{15}N$ values throughout summer may be related to utilization of regenerated ammonium. In addition, high surface water temperatures in the summer may favor degradation and associated increases in $\delta^{15}N$.

Mass weighted carbon isotope values for seston vary by only 2‰ at both BRLP5 and US3.5 throughout the season (Fig. 82). Nonetheless, $\delta^{13}C$ values at BRLP5 are at a maximum (> -23.5‰ during much of the high chlorophyll productivity period. Following the decline in chlorophyll concentrations $\delta^{13}C$ values at BRLP5 remain less than this value. Given the few determinations it is not possible to determine if this trend is followed at US3.5. The predominance of higher $\delta^{13}C$ values during the high productivity period at BRLP5 may be related to a reduction in pCO_2 as discussed previously.

3.4 Sediment trap data

3.4.1 BRLP5 40m, 1988

Most of the sediment trap data presented was collected in 1988. Only isotope data was available for the 1990 sediment traps. In 1988 sediment traps were deployed at 4 depths at station BRLP5: 40m, 80m, 150m, and 240m. Ten samples were collected at each depth from early April to early June. These samples spanned the spring bloom. The trap at 40m is located approximately at the mid-euphotic

zone depth. Material collected within this trap was exposed to the least amount of degradation during transport to the seafloor. Measurements of the flux of organic carbon from the 40m trap increased from 23.9mgC/m^2/d on 4/6 to a maximum value of 725.0mgC/m^2/d on 5/13 (Fig. 83). The time of maximum flux may not necessarily represent the peak of the spring bloom, but indicates the time when aggregation and sinking of POM was increased. Abundances of carbon increased from 2.45% on 4/6 to 16.93% on 5/11. This trend is similar to the increase observed for carbon flux and indicates that material richest in organic matter was collected during the peak in organic flux (Fig. 83). The ratio of carbon to nitrogen also increased during this period from 5.7 to 14.0 during the period of the greatest organic matter flux (Fig. 83). Similar increases in the C/N of sediment trap material over a spring bloom was observed in the Southwest Baltic Sea (Smetacek et al., 1978). These changes in C/N may be related to an increase in the detrital composition of sedimenting material as spring bloom productivity declines or a result of nitrogen limitation (Walsh et al., 1981b).

The $\delta^{15}N$ of sediment trap material varied dramatically from 5.9‰ to 18.3‰ (Fig. 83). Highly ^{15}N enriched material, greater than 14‰, was collected on 4/6 and 4/28 and occurred when the organic flux was at a minimum. During the period of the greatest organic matter flux $\delta^{15}N$ values were

approximately 8‰ to 9‰. Carbon isotope values for sinking POM varied from -25.2‰ to -22.0‰ and obtained maximum values near the peak flux period (Fig. 83).

3.4.2 BRLP5 80m, 1988

The trap at 80m was placed at the maximum depth normally obtained by the pycnocline. Thus, this trap collected the majority of organic matter raining out of surface waters with a minimal amount of alteration in the water column. The organic carbon flux increased in a similar manner as the 40m trap from a low of 26.6mgC/m^2/d on 4/6 to a high of 720.1mgC/m^2/d on 5/11 (Fig. 84). Abundances of carbon and nitrogen also increased from 2.27% to 16.18% and 0.49% to 1.58%, respectively, during this period (Fig. 84). Ratios of carbon to nitrogen increased, in a manner similar to those for the 40m trap, from 5.4 on 4/6 to 11.7 on 5/11 (Fig. 84). The maximum C/N value in the 80m trap was less than that for the 40m trap suggesting that nitrogen limitation may not be as severe for phytoplankton in the lower euphotic zone as it is above. Nitrogen isotope values varied from 6.5‰ to 15.9‰ and maximum values occurred on 4/6 and 5/19 (Fig. 84). Sediment trap $\delta^{13}C$ values exhibited a general increase with time and varied from -24.8‰ to -22.1‰ (Fig. 84).

3.4.3 BRLP5 150m, 1988

Compared with the trap samples from 80m, the 150m samples had lower maximum organic carbon fluxes (545.6 versus 720.1mgC/m^2/d) that peaked slightly later in the year (5/26 versus 5/11). The nitrogen fluxes were not markedly different (71.2 versus 78.49mgN/m^2/d), but also reached maximum values on the same dates as the carbon fluxes (Figs. 84 and 85). Loss of organic matter through remineralization or consumption by zooplankton was suggested by the decrease in maximum flux values between the 80m and 150m traps. Abundances of carbon and nitrogen were also lower than the two upper water column traps, and obtained maximum values of 10.83% and 1.21%, respectively (Fig. 85). A reduction in carbon and nitrogen of over 6 and 0.6%, respectively, occurred between the 40m and 150m traps (Figs. 83 and 85). Ratios of carbon to nitrogen were low and ranged from 6.2 to 10.6 (Fig. 85). Nitrogen isotope values ranged from 6.6 to 19.1‰. Highly ^{15}N enriched sinking POM was collected on the same dates for both the 80m and 150m traps (Figs. 84 and 85). Sediment trap $\delta^{13}C$ values had the same general trend of increasing with time that was evident in the 40m and 80m traps and varied from -24.1‰ to -21.9‰ (Figs. 83, 84, and 85).

3.4.4 BRLP5 240m, 1988

The maximum carbon flux for the 240m trap occurred on 5/26 and was 577.3mgC/m^2/d (Fig. 86). This was the same day the maximum flux was obtained for the 150m trap but was shifted by 15 days relative to the trap at 80m (Figs. 84 and 85). If the shift in maximum flux measurements between the 80m and 240m was simply due to the time it takes for organic matter to sink between the traps then the rate of vertical transport would be 10.7m/d. This sinking rate is substantially less than the rate cited as common for oceanic environments of 50-100m/d (Shanks and Trent, 1980; Billet et al., 1983; Lampitt, 1985). It is interesting to note that ^{15}N enriched material (greater than 12‰) was collected in all traps on 4/6 and the lower three traps on 5/19 (Figs. 83, 84, 85, and 86). This finding suggests that the sinking of organic matter was very rapid and similar to other oceanic environments. Resuspension of sediments might be a factor resulting in the shift in the timing of the maximum flux between deep and surface sediment traps.

Abundance measurements of carbon and nitrogen for the 240m trap were nearly constant with time and ranged from 4.13% to 6.57% and 0.54% to 0.82%, respectively (Fig. 86). Similarly, C/N values, 7.3 to 10.3, did not vary with time (Fig. 86). These trends as well as the shift in the timing of maximum flux can be explained by a sediment resuspension

event in late May. Sediments are characterized by a lower organic matter content than sediment trap material (Fig. 7) and thus resuspension would result in a lowering of the percentage of organic matter in the traps. The lower trap would be affected to a greater extent than those above due to its proximity to sediments. Although lower in organic content than the trap materials, sediments contain sufficient organic matter such that resuspension would cause an apparent increase in the flux of organic matter to the seafloor. Thus sediment resuspension may explain the shift in the timing of the maximum flux between the surface and deep traps (Figs. 83-86). A contribution of sediment material would result in a shift in $\delta^{15}N$, $\delta^{13}C$, and C/N of sediment trap material toward sediment values. These trends are evident in late May and early June in the 150m and 240m traps (Figs. 85 and 86). Resuspension would also increase the total bulk weight material collected in the traps and affect the deepest trap to a greater extent than those at shallower traps. Total sedimented material increases dramatically after 5/13 for the 240m trap and to a lesser extent for the 150m trap. During the same time interval decreases are evident for the shallower traps (Fig. 87). Therefore, the differences in the geochemistry of sediment trap material between the deep and surface traps in late May are most likely in response to a sediment resuspension event.

3.4.5 BRLP5 and US3.5, 1990

Elemental composition and flux data for sediment trap material for 1990 was not available. Sediment trap material was collected between late April and September from two stations and two depths per station. Nitrogen isotope values for sinking POM at station BRLP5 at 80m ranged between 3.7‰ and 8.9‰ (Fig. 88). A slightly wider range was found for samples collected at 210m: 4.6‰ to 11.3‰ (Fig. 89). Nitrogen isotope values for sediment trap material collected at station US3.5 at 80m and 180m varied between 3.7‰ and 8.4‰ (Fig. 89).

Highly ^{15}N enriched values, greater than 15‰, such as those observed in seston in 1990 and sinking POM in 1988 were not evident in the trap collections. Seston with high $\delta^{15}N$ values did not commonly occur in conjunction with high organic concentrations. Similarly, in 1988 ^{15}N enriched sediment trap values did not usually occur during periods of high organic flux. Therefore, the lack of high $\delta^{15}N$ values in the 1990 sediment trap samples may be due to long deployment times, that allowed brief periods of ^{15}N enriched productivity to be overprinted by more prevalent organic matter with lower $\delta^{15}N$ values.

Low $\delta^{15}N$ values, less than 5‰, were present in both the 80m and 210m trap samples on 6/21 at BRLP5 and in the 180m trap on 7/5 at US3.5. The $\delta^{15}N$ for the 80m sample at US3.5

on this date was not determined. This time coincided with very low chlorophyll concentrations in the water column (Fig. 89). These low $\delta^{15}N$ values are typical of low productivity in cold polar waters (Wada et al., 1987; Biggs et al., 1988). During the late-summer to fall period there may be occurrences of phytoplankton blooms that are less productive than in the spring (C. McKenzie, personal communication). Nutrient limitation, during these events, may result in an increase in nitrogen isotope values for seston.

Considerable differences in $\delta^{15}N$ between trap samples and weighted seston values in 1990 are evident at both BRLP5 and US3.5 (Figs. 82 and 88). Nitrogen isotope values for these organic fractions are most similar during the peak of chlorophyll productivity (Figs. 82 and 88). Following the productivity seston is enriched in ^{15}N by 4 to 12‰ relative to sediment trap material. Similar results were found in the North Atlantic where the $\delta^{15}N$ of seston was similar to and greater than sinking POM during periods of high and low productivity, respectively (Altabet et al., 1991). These results indicate that during low productivity periods sinking POM either loses a fraction enriched in ^{15}N (such as proteins) or gains a fraction depleted in ^{15}N (Altabet et al., 1991).

Carbon isotope values for both the upper and lower traps at BRLP5 and US3.5 ranged from -27.2‰ to -21.6‰ and

-27.6‰ to -22.8‰, respectively (Fig. 89). Both traps at BRLP5 had ^{13}C enriched material in the very early spring when productivity was high and low $\delta^{13}C$ values on 6/21 when the spring bloom was over. The spring enrichments in ^{13}C may represent primary production associated with low pCO_2 levels. Depletions in ^{13}C may be associated with low productivity when pCO_2 levels returned to normal. Enrichments in the ^{13}C content of sinking POM observed in the early spring at BRLP5 were not present at US3.5. The longer deployment time of traps at US3.5 (27 days) at this time may have permitted subsequent ^{13}C depleted productivity to overprint early spring isotope values. Carbon isotope values for the deep traps at both stations were more enriched in ^{13}C than the surface traps. This trend may be related to degradation during sinking (Fig. 89).

Variation in $\delta^{13}C$ in sediment trap samples is considerable more that was found for the mass weighted seston. Seston tended to be more enriched in ^{13}C than sediment trap material in May and June and in ^{12}C July and August (Figs. 82 and 89). Seston was most similar in $\delta^{13}C$ to the deeper sediment trap at both stations. The differences in $\delta^{15}N$ and $\delta^{13}C$ between seston and sediment trap material indicates that transformations affecting sinking POM are distinct or of a different magnitude than those affecting the more abundant suspended fraction.

3.5 Freshwater organic matter and nutrient data

The carbon and nitrogen isotopic composition of seston collected from rivers or streams entering Conception Bay ranged from -28.1‰ to -24.5‰, and 6.4‰ to 17.8‰, respectively (Table 18). These $\delta^{13}C$ values are similar to ranges reported for other freshwater environments (Cai et al., 1988; Lucotte, 1989; Mariotti et al., 1991). Ratios of carbon to nitrogen, 7.7 to 18.8, are within ranges reported as common for terrestrial organic matter (Table 18; Goodell, 1972; Muller, 1977). Nitrogen isotope values are generally more enriched in ^{15}N than previously found for soils and seston in Newfoundland rivers (Feigin et al., 1974; Rennie et al., 1976; Aly et al., 1982; Ostrom and Macko, 1992). High $\delta^{15}N$ values may result from the oxic degradation of organic matter. Apparently processes that result in increases in the $\delta^{15}N$ of seston in the marine environment are similar to those that operate in Newfoundland freshwater streams. Although the range of carbon and nitrogen for freshwater seston is similar to marine seston a terrestrial contribution to the waters of Conception Bay would not be expected given the high salinities that prevailed throughout the year. Therefore, terrestrial inputs to this bay are most likely restricted to the nearshore environment.

Concentrations of nitrate and ammonium in freshwaters varied from 4.0μM to 22.8μM and 0.9μM to 5.1μM, respectively

(Table 19). At no time was the concentration of nitrite in excess of 0.3μM. The $\delta^{15}N$ of nitrate ranged from -2.9‰ to 4.3‰ (Table 19). These values are consistent with an origin for nitrate from natural soils or fertilizers (Kreitler, 1975; Kreitler and Jones, 1975; Heaton, 1986). The presence of ammonium indicates that nitrification did not completely utilize this substrate and therefore low $\delta^{15}N$ values for nitrate may also be the result of fractionation during this reaction.

The concentration of DIC in freshwaters, 0.13 ± 0.10mmol/kg, was considerably less than that for samples in Conception Bay, 2.16 ± 0.15mmol/kg (Tables 16 and 20). Similarly the $\delta^{13}C$ of freshwater DIC, -11.7 ± 5.4‰, was lower than that of marine DIC, -0.1 ± 1.0‰. The isotopic composition of freshwater DIC ranged from -23.2‰ to -8.5‰, and was similar to values reported for DIC from other freshwater environments (Sackett and Moore, 1966; Mook, 1970; and Hitchon and Krouse, 1972). The ^{13}C depleted values for DIC collected from Conway Brook and St. Phillips River on 4/24 followed a period of heavy rain. These low values may be the result of increased leaching of ^{13}C depleted soil derived CO_2 into the rivers following rain. A predominance of rocky substrate in the Manuels River may have reduced the leaching of ^{13}C depleted soil DIC to this river during the rain event. The highest concentrations of TSM, POC, and PON within each river were observed on this date and are indicative of extensive runoff (Table 18).

4.0 Discussion

4.1 Preamble

The primary objective of this study was to establish a firm understanding of the relationship between the isotopic composition of phytoplankton and that of underlying sediments. This was accomplished by (1) identifying processes resulting in variations in the $\delta^{13}C$ and $\delta^{15}N$ of water column organic matter and (2) developing a model relating the flux and isotopic composition of water column organic matter to sediment isotope values. To facilitate the primary objective, multiple geochemical parameters were measured and extensive spatial and temporal sampling was conducted. As demonstrated in sections 3.3.3.1 and 3.3.3.2 of the Results, trends in many geochemical variables, including the isotopic composition and concentration of seston and concentrations of nitrate, oxygen, and DIC, were similar among stations (Tables 15, 16, 17, and 18). Consequently, variations in physical and chemical data, $\delta^{13}C$ and $\delta^{15}N$ of POM and differences between the isotopic composition of POM and that of sediments will be discussed primarily in terms of temporal changes.

4.2 Inorganic nitrogen

Ammonium in the porewaters of sediments is generated

from the mineralization of organic matter. Porewater ammonium in Conception Bay cores ranged in concentration from 34.7 to 238.8μM (Table 13). The average $\delta^{15}N$ of porewater ammonium in this study, 7.1 ± 01.3‰, was 1.7‰ less than the average $\delta^{15}N$ of sediments in the same cores, 8.7 ± 0.6‰. These results are consistent with the results of previous studies that have shown a small or negligible difference between the $\delta^{15}N$ of porewater ammonium and that of sediments (Pang and Nriagu, 1976; Sweeney et al., 1980; Velinsky et al., 1991). Lower $\delta^{15}N$ values for ammonium relative to sediments in Conception Bay suggests that there may be a small fractionation effect associated with remineralization.

Nitrate in the water column of oceanic environments may be derived from porewater ammonium upon nitrification and diffusion out of sediments. Nitrification in Conception Bay is expected to occur primarily in sediments since microbial respiration rates for sediments are much greater than those for the water column (Table 4). The presence of ammonium in the surficial layer of boxcores indicates than sedimentary nitrification did not completely consume the substrate (Table 13). Furthermore, in-situ sediment incubation experiments in Conception Bay indicate that there is a measurable flux of ammonium out of sediments into the water column (Table 4). These data indicate that nitrification in sediments did not entirely utilize the substrate ammonium.

The observation of substantial ammonium concentrations in deep waters at BRLP5 and US3.5 indicate that ammonium was not quantitatively consumed during water column nitrification (Figs. 45, 49, 53, 57, 65, 69, and 73).

The average $\delta^{15}N$ of nitrate in the water column, 0.2 ± 3.6‰, differed substantially from the isotopic composition of porewater ammonium in Conception Bay. The difference between the $\delta^{15}N$ of water column nitrate and that of porewater ammonium could result from an alternate source of nitrate or fractionation during nitrification. The most probable alternate sources of nitrate would be from offshore, rain or rivers. A freshwater influence in Conception Bay would not be expected given the presence of high salinities. Porewaters are the most likely source of water column nitrate. Nitrate originating from offshore would also be derived from porewaters. The large shifts in $\delta^{15}N$ between porewater ammonium and water column nitrate (approximately 7‰) indicates that there must be substantial isotopic segregation occurring as ammonium advects out of sediments and is nitrified.

Fractionation during nitrification can be quite large and the product, nitrate, is depleted in ^{15}N relative to the substrate, ammonium (Table 2). The difference between the isotopic composition of the reactant and that of the product is reduced to zero as the reaction proceeds to completion; ie. when the substrate is completely consumed. Nitrate in

the water column of Conception Bay had an average $\delta^{15}N$ of 0.2‰ and ranged between -6.2‰ to 7.9‰ (Appendix 3). These values are less than or approximately equal to the $\delta^{15}N$ of porewater ammonium (average equals 7.1‰) from which water column nitrate may be primarily derived (Table 13). Low $\delta^{15}N$ values are consistent with fractionation during nitrification. High $\delta^{15}N$ values are similar to porewater ammonium values and may be the result of nitrification that nearly or completely consumed the substrate, ammonium. The wide range in $\delta^{15}N$ values for nitrate suggests that the degree to which nitrification proceeds to completion is variable.

Fractionation occurring during nitrification should result in an increase in the $\delta^{15}N$ of the residual substrate, ammonium. Increases in the $\delta^{15}N$ of porewater ammonium as a consequence of nitrification were not apparent (Table 13). Furthermore, $\delta^{15}N$ values for ammonium in the water column, 3.7 to 6.3‰ (n = 4), were within the range of those of nitrate (Figs. 53 and 57). In porewaters, the lack of an isotope shift suggests the quantity of ^{15}N enriched ammonium that is a byproduct of nitrification is probably insignificant in comparison to the amount of ammonium produced during remineralization. Therefore, the $\delta^{15}N$ of porewater ammonium is primarily a reflection of the mineralization process. The similarity in $\delta^{15}N$ between ammonium in porewaters and the water column suggests that

ammonium diffusing out of sediments into the water column retains the isotope signatures produced by mineralization. Nitrification occurring in the water column should, with time, result in an enrichment in ^{15}N of the remaining ammonium. The fact that ^{15}N enriched ammonium in the water column was not detected may simply be due to the few number of measurements (n = 4).

The magnitude of isotopic segregation during a kinetic reaction can be expressed in terms of the fractionation factor, β. This factor is defined as the ratio of the reaction rates of the light and heavy isotopes ($\beta = k^{14}N/k^{15}N$). Fractionation factors for a unidirectional reaction may be calculated by use of a modified Rayleigh equation (Hoering, 1957; Mariotti et al., 1981; Macko et al., 1986):

$$\delta_p = \frac{(1-(1-f)^{1/\beta})}{f} * [1000+\delta_{so}]-1000 \qquad \text{(eq. 3)}$$

where f is the fraction of the initial substrate converted to product and δ_p and δ_{so} are the $\delta^{15}N$ values for the product and the initial substrate, respectively.

Calculation of β for nitrification at the sediment-water interface in Conception Bay was performed from data on the $\delta^{15}N$ and concentration of porewater ammonium and water column nitrate. The average $\delta^{15}N$ for porewater ammonium, 7.1‰, and near bottom nitrate, 0.8‰, were used for δ_{so} and δ_p, respectively. The fraction of reactant converted to

product was calculated based on a ratio of the concentration of ammonium to that of total inorganic nitrogen in the near bottom waters as:

$$f = 1 - \frac{[NH_4]}{[NH_4] + [NO_3] + [NO_2]} \qquad \text{(eq. 4)}$$

The solution to eq.4 yields a value for β of 1.0193. This value is within the range of reported fractionation factors for this process (Table 2) and is the first estimate of fractionation during sedimentary nitrification in a natural setting.

Use of the Rayleigh equation requires that the system be closed to outside influences. Conception Bay receives offshore surface water throughout the year and deep water episodically and is therefore not an isolated system (Leggett et al., 1984; Aggett et al., 1987; Taggart and Leggett, 1987). However, as nitrification occurs under similar conditions outside of Conception Bay it may be valid to consider the system to consist of the entire Labrador Sea. More work needs to be done to verify this presumption.

Nitrate in Conception Bay was characterized by some of the lowest $\delta^{15}N$ values ever reported for an oceanic environment (Table 3). Denitrification in anoxic waters of the eastern tropical Pacific Ocean has been shown to cause dramatic increases in the ^{15}N content of nitrate (Cline and

Kaplan, 1975; Liu et al., 1987; Liu and Kaplan, 1989). High $\delta^{15}N$ values for nitrate, in response to denitrification, have been cited as the primary factor resulting higher $\delta^{15}N$ values of phytoplankton on the west coast relative to those on the east coast of the U.S. (Sweeney et al., 1976; Liu and Kaplan, 1989). The highly oxygenated waters of Conception Bay inhibit water column denitrification. In contrast, Conception Bay and probably the northwest North Atlantic and Arctic Oceans are dominated by nitrification. Nitrification favors an enrichment in ^{14}N in nitrate. The generally low $\delta^{15}N$ values for nitrate relative to seston indicates that there must be additional processes enriching Conception Bay seston in ^{15}N.

Within the euphotic zone, the $\delta^{15}N$ of nitrate or ammonium may be altered during assimilation by phytoplankton. The light isotope of nitrogen is preferentially utilized during uptake of nitrate or ammonium by bacteria and phytoplankton (Table 2). The remaining nitrate or ammonium will become increasingly enriched in ^{15}N as assimilation proceeds (Mariotti et al., 1984). Increases in the $\delta^{15}N$ of euphotic zone nitrate relative to deep water nitrate was observed at only five water column collections (Figs. 21, 45, 53, 57, and 77). Most collections were characterized by nitrate $\delta^{15}N$ values that increased with depth in the euphotic zone (Figs. 17, 29, 41, 49, 65, 69, 73). This trend is contradictory to fractionation during

assimilation. Assessment of fractionation during nutrient uptake was inhibited by an inability to measure the $\delta^{15}N$ of nitrate or ammonium at the low concentrations prevalent within the euphotic zone.

Changes in nitrate $\delta^{15}N$ values that appear contradictory to fractionation during assimilation may be related to mid-water column nitrification or an influence of offshore water in Conception Bay. Nitrification in the water column was not considered likely given the low microbial respiration rates that were found during the spring in Conception Bay (Pomeroy and Deibel, 1986; Pomeroy et al., 1991). As surface water temperatures increase in the mid to late summer mid-water column nitrification may have been more important. Without measuring rates of nitrification it is difficult to assess the importance of this process.

In addition to nitrification, an offshore supply of inorganic nitrogen also has the potential to alter the $\delta^{15}N$ of nitrate in Conception Bay. A layer of cold Labrador Current water (less than -1°C) enters Conception Bay above the sill depth of 170m (Leggett et al., 1984; Taggart and Leggett, 1987). Labrador Current water enters along the northern coast of Conception Bay and exits along the southeastern shore at a normal maximum velocity of 8-10cm/sec (B. De Young, personal communication, 1990). This introduction of offshore water could act as a replenishible source of nitrate for primary production in

Conception Bay. Presumably, nitrification occurring in the Labrador Sea would also produce nitrate depleted in ^{15}N. This assumption is supported by the observation of low $\delta^{15}N$ values for nitrate at station CC13 located outside of Conception Bay. Therefore, the nitrate carried into Conception Bay by the Labrador current would be characterized by low $\delta^{15}N$ values.

An offshore source of nitrate in Conception Bay is suggested by respiration and primary production data. A rate of 164mgC/m^2/d (60gC/m^2/yr) has been estimated for all respiratory processes in the water column and sediments of Conception Bay (Pomeroy et al., 1991). The flux of organic matter from the 80m sediment trap over three months of deployment equated to 74gC/m^2/yr. Annual primary productivity in Conception Bay probably exceeds this value since this measurement does not account for respiratory losses and productivity during the remaining nine months of the year. Nitrogen regenerated from all microbial processes within Conception Bay is insufficient to meet the needs of primary production. Therefore, dissolved inorganic nitrogen must be supplied from outside Conception Bay to sustain this level of primary production. Dissolved inorganic nitrogen associated with the presence of an offshore water mass within the Bay is the most reasonable source. Nitrate in Labrador Current water would not be removed by primary production prior to entering the Bay because the spring

bloom off eastern Newfoundland tends to occur initially within nearshore bays and later offshore (Prasad et al., 1991).

A supply of nitrate from the offshore indicates that it is not appropriate to consider nutrient movement in only the vertical plane. Nutrients in the euphotic zone are supplied from the horizontal (offshore derived) as well as the vertical (sediment derived) directions. Therefore, differences in the $\delta^{15}N$ of nitrate in deep and euphotic zone waters may be related to a distinction in the source of nitrate.

4.3 Dissolved inorganic carbon data

The $\delta^{13}C$ of DIC in ocean waters may be influenced by a number of processes that include photosynthesis, respiration, atmospheric equilibration, organic matter decomposition, and carbonate dissolution (Kroopnick, 1974a; 1974b; Tan, 1989). Dissolution of carbonate is probably not a significant process in the shallow waters of Conception Bay. Respiration and organic matter degradation have a similar and indistinguishable effect of shifting the $\delta^{13}C$ of DIC in the direction of the isotopic composition of organic carbon (Fig. 2). The $\delta^{13}C$ of DIC of all samples collected in Conception Bay ranged between -4.0‰ and 1.7‰ (Table 15). High $\delta^{13}C$ values of 1.4‰ to 1.7‰ are typical for high

latitude DIC in equilibration with atmospheric CO_2 (Kroopnick et al., 1977; Kroopnick, 1980). Lower values indicate a contribution of CO_2 from the oxidation of organic matter or respiration (Craig, 1970; Kroopnick 1974a; 1974b).

During photosynthesis ^{12}C is preferentially utilized by phytoplankton and the remaining DIC is expected to become enriched in ^{13}C (Smith and Kroopnick, 1981). Despite high levels of productivity in the spring, $\delta^{13}C$ values were never observed to increase beyond the range expected for DIC in equilibrium with the atmosphere. This result indicates that when photosynthesis was active, respiration and atmospheric equilibration were also influencing the isotopic composition of DIC.

DIC at BRLP5 on 3/29 (80m) and 5/20 (40m) was characterized by markedly low $\delta^{13}C$ values of less than -3‰ (Figs. 19 and 43). With one exception, all other DIC $\delta^{13}C$ values were greater than -2‰ (Appendix 4). Despite occasional brief periods of increased respiration that appeared to be related to high substrate concentrations, microbial respiration rates in Conception Bay were found to be low in comparison to other marine environments (Pomeroy et al., 1991). Enhanced respiration was indicated by low $\delta^{13}C$ values and high concentrations for DIC at BRLP5 at 80m on 3/29 and at 120m on 5/20. In contrast, the near surface sample on 5/20 characterized by a low $\delta^{13}C$ value and a low concentration of DIC (2.10mmol/kg) indicates that other near

surface processes such as photosynthesis, diffusion, and atmospheric exchange are operative.

4.4 The isotopic and elemental composition of seston

In oceanic environments, a subsurface minimum in the $\delta^{15}N$ of seston has been observed to occur concomitant with a maximum in the concentration of PON, a minimum in C/N and a pronounced decrease in nitrate concentration (Altabet and McCarthy 1985; 1986; Montoya et al., 1990). These trends in $\delta^{15}N$, C/N, nitrate and PON at the surface of station BRLP5 on 3/23 and in subsurface waters on 3/29, 4/4, 4/18, 4/29 and 5/6 were most distinct during the spring bloom and occurred progressively deeper in the water column with time. (Figs. 16, 17, 20, 21, 24, 25, 28, 29, 32, 33, 40, and 41). The minimum in seston $\delta^{15}N$ may be the result of fractionation during nutrient assimilation by phytoplankton when growth is not limited by the availability of nitrate or ammonium. The presence of nitrate in the euphotic zone on 3/23 suggests that this may have been the case (Fig. 17). However, if fractionation was expressed then the isotopic composition of phytoplankton should be less than that of nitrate because the light isotope is preferentially assimilated in this process. Seston with $\delta^{15}N$ values less than that of nitrate was rarely observed and the average $\delta^{15}N$ of nitrate, 0.2‰, is considerably less than the weighted average of suspended

POM, 11.7‰ (Table 20).

The high $\delta^{15}N$ values for seston relative to nitrate could be explained by assimilation by phytoplankton of a source of nitrogen that is isotopically distinct from nitrate, degradation of seston, or fractionation during nutrient uptake at low concentrations. Concentrations of ammonium in excess of 0.3μM have been shown to inhibit nitrate uptake by phytoplankton. Therefore, the presence of ammonium in surface waters in summer suggests that this compound was an important source of nitrogen at this time (Figs. 45, 49, 53, 57, 65, 69, and 73; Probyn, 1988; Kristiansen and Lund, 1989; Wheeler and Kokkinakis, 1990). When in sufficient quantities to be determined, the nitrogen isotopic composition of ammonium in deep waters, 3.7‰ to 6.3‰, was too low to explain the higher $\delta^{15}N$ values for seston (Figs. 53 and 57). Fractionation during the uptake of dissolved nitrate or ammonium at concentrations less than 2μM could not be evaluated owing to experimental limitations. Higher $\delta^{15}N$ values were observed for seston in the summer than in the spring (Fig. 82). This result may be related to an increased utilization by phytoplankton of regenerated ammonium as stratification strengthened and inhibited the supply of nitrate from deeper waters. Thus, regenerated ammonium might be the cause of high $\delta^{15}N$ values for seston. Degradation has also been associated with high $\delta^{15}N$ values for POM in many oceanic environments and may be

an additional cause of a greater enrichments in ^{15}N in seston, relative to nitrate, in Conception Bay (Saino and Hattori, 1980; 1987; Altabet and McCarthy, 1985; 1986).

Dramatic enrichments in the ^{15}N content of seston were observed in many collections throughout the season. Nitrogen isotope values in excess of 20‰ were observed at BRLP5 on 3/23 (60m), 3/29 (80m), and CTR23 on 4/30 (210m; Figs. 17, 21, and 77). Nearly all collections at each station had at least one seston $\delta^{15}N$ value greater than 15‰. Fractionation during the hydrolysis of peptide bonds or deamination of proteins is consistent with the direction of this observed isotopic segregation (Saino and Hattori, 1980; 1987; Altabet and McCarthy, 1985; 1986; Silfer et al., 1990). Microbial respiratory rates in Conception Bay are quite low relative to other marine environments (Pomeroy and Deibel, 1986; Pomeroy et al., 1991). In the early bloom as little as 7% of the primary production is consumed by microbes and 68% during the late bloom. This indicates that the observed fractionation of seston nitrogen resulting from degradative processes must occur with low substrate losses.

Given a knowledge of the change in isotopic composition and concentration of seston resulting from degradation a fractionation factor for this process could be calculated[3].

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[3] The calculation of β for degradation was based on eq. 3. However, the isotopic composition of the product, δ_p, had to be determined first. This was done through the following equation that relates the $\delta^{15}N$ of the original substrate, δ_{so}, to that of the

In that phytoplankton production and decomposition occur simultaneously, an increase in the $\delta^{15}N$ of seston associated with degradation was not commonly accompanied by a decrease in concentration. For this reason a quantitative assessment of fractionation during degradation of POM in Conception Bay could not be calculated. However, by using the rates of microbial respiration from Pomeroy et al. (1991) as the extent of degradation occurring, a qualitative assessment of the magnitude of fractionation required to explain the observed changes in $\delta^{15}N$ could be made. For example, if an f of 0.07 is used, as indicated from the microbial respiration data, a β of 1.073 would be required to cause a shift in the $\delta^{15}N$ of seston on 3/23 from 6.5‰, at 5m, to 11.5‰, at 35m (Fig. 17). This value for β is exceptionally high in comparison to fractionation factors for other reactions involving nitrogenous compounds (Table 2). In summer, when microbial respiration consumes a greater portion of phytoplankton productivity than in the spring, a much smaller fractionation factor is needed to explain shifts in seston $\delta^{15}N$. On 7/27 a change in the $\delta^{15}N$ of seston from 10.0‰ to 16.5‰ (Fig. 53) can be explained by a β of 1.006 using an f of 0.68.

The fractionation factor for degradation calculated

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product and that of the residual substrate, δ_s, and the fraction of initial reactant converted to product, f (Macko et al., 1986):

$$\delta_\infty = f\delta_p + (1-f)\delta_s$$

from isotope and microbial respiration data in the spring is unrealistically high. A more reasonable estimate for β would be obtained if the fraction of substrate converted to product during degradation was greater. In addition to microbial respiration, other factors are responsible for the degradation of POM. Such non-microbial processes include leaching of dissolved organic matter and hydrolysis of peptide bonds. The estimated fractionation factor, β, during peptide bond hydrolysis is 1.006 (Silfer et al., 1990). While fractionation during this process could explain the observed isotopic variation in the $\delta^{15}N$ of seston in the summer, it cannot explain the large changes characteristic in the spring. Fractionation resulting from other degradative processes, such as cell leaching of DOM and deamination may have contributed to these results.

Seston characterized by high $\delta^{15}N$ values, greater than 20‰, were more common in the early spring than at other times and tended to occur at a depth just below the chlorophyll maximum. Such high $\delta^{15}N$ values were clearly evident at BRLP5 on 3/23, and 3/29, and at CTR23 on 4/30 (Figs. 16, 17, 20, 21, 76 and 77). High $\delta^{15}N$ values close to the chlorophyll maximum were also observed at BRLP5 on 4/4, 6/24 and 7/27 and at US3.5 on 5/21, though $\delta^{15}N$ values and chlorophyll concentrations were not as high as they were in the early spring (Figs. 24, 25, 48, 49, 52, 53, 68, and 69). Apparently, the degradative processes resulting in increases

in the $\delta^{15}N$ of seston may be enhanced by high substrate concentrations. Respiration was undoubtedly enhanced within the chlorophyll maximum as well, but, isotope effects associated with photosynthesis were probably masked by the high concentrations of fresh phytoplankton biomass with lower $\delta^{15}N$ values.

A maximum in the $\delta^{13}C$ of seston was frequently associated with the chlorophyll maximum and low DIC concentrations. These trends were most marked during the spring bloom when the chlorophyll maximum layer was narrow in depth and were clearly evident at BRLP5 on 3/23, 3/29, 4/4 and 4/18 and at CC13 on 5/4 (Figs. 15-17, 19-21, 23-25, 27-29, and 79-81). Seston in late spring and summer was not characterized by these trends. High winds at the end of April mixed the upper 100m of the water column and, as a result, changes in the geochemistry of seston in the euphotic zone were not distinct. Primary productivity, as suggested by chlorophyll data, in mid-summer was low and a relationship between $\delta^{13}C$ and chlorophyll was not apparent. On 8/30, a $\delta^{13}C$ maximum within the chlorophyll maximum and DIC minima was again evident (Figs. 55-57).

Variation in the $\delta^{13}C$ of phytoplankton has been associated with changes in species, water mass, pCO_2, and temperature (Sackett et al., 1965; Fontugne and Duplessy, 1978; 1981; Gearing et al., 1984; Rau et al., 1989; Fry and Wainright, 1991). Temperature changes were small during the

spring bloom and were almost always between -1°C and 0.5°C within the euphotic zone and therefore, could not account for isotopic variability in phytoplankton. Changes in water mass are unlikely to result $\delta^{13}C$ variability in seston owing to a dominance of the Labrador Current in this bay. However, variations in non-conservative properties, such as pCO_2, within a water mass could result in changes in the $\delta^{13}C$ of phytoplankton. Phytoplankton were dominated by diatoms in the spring and species composition varied little with depth (McKenzie and Deibel, 1991). A maximum in the $\delta^{13}C$ of seston associated with a minima in DIC concentration within the chlorophyll maximum was not dependent on season or species (Figs. 54-57; C. McKenzie, personal communication regarding species composition, June, 1991). Therefore, changes in temperature, water mass or phytoplankton species do not appear to be the primary cause of seston $\delta^{13}C$ variability in Conception Bay.

The most likely cause of increases in the $\delta^{13}C$ of seston associated with decreases in the concentration of DIC is a reduction in pCO_2. Direct measurements of pCO_2 were not performed, however low concentrations of DIC suggest that concentrations of CO_2 would be low. Significant inverse relationships between the $\delta^{13}C$ of seston and the concentration of DIC were found at BRLP5 on 3/23 ($r^2 = 0.66$; $F_{1,2} = 3.85$, $P < 0.25$), 5/6 ($r^2 = 0.86$; $F_{1,2} = 12.39$, $P < 0.01$), 6/24 ($r^2 = 0.96$; $F_{1,2} = 45.62$, $P < 0.025$), and CC13 on

5/4 (r^2 = 0.61; $F_{1,2}$ = 3.12, P < 0.25). A lack of significant relationships on other dates may be related to the addition of DIC from respiration and/or atmospheric equilibration. The relationship between pCO_2 and phytoplankton $\delta^{13}C$ may be a function of decreased fractionation during CO_2 fixation by RuBP carboxylase as CO_2 availability is reduced (Fogel et al., 1988). Alternatively, an increased importance on active transport of isotopically enriched $HCO3^-$ across cell membranes as CO_2 levels decrease may be involved (Fogel et al., 1988).

Assimilation of CO_2 during periods of high primary production has been shown to lower DIC concentrations in surface waters (Smith and Kroopnick, 1981; Codispotti et al., 1982; Watson et al., 1991). The low DIC concentrations associated with the chlorophyll maximum in Conception Bay are probably associated with high productivity during the spring bloom. Similarly, along latitudinal transects in the southern hemisphere, pCO_2 was inversely correlated with the $\delta^{13}C$ of phytoplankton (Rau et al., 1989). In contrast to low latitudes in the southern hemisphere where pCO_2 varies in response to water temperature, fluctuations of pCO_2 in Conception Bay (as indicated by shifts in DIC concentration) are a consequence of changes in productivity. Significant relationships between seston $\delta^{13}C$ and chlorophyll (a proxy for primary production) at BRLP5 were found when productivity was high in the spring on 3/29 (r^2 = 0.96; $F_{1,2}$ =

48.0, $P < 0.025$), 4/4 ($r^2 = 0.81$; $F_{1,2} = 8.53$, $P < 0.25$), and 5/2 ($r^2 = 0.87$; $F_{1,2} = 13.38$, $P < 0.01$). A lack of a correlation in late April may be related to mixing of the upper water column by high winds. A significant relationship was again evident on 8/30 ($r^2 = 0.92$; $F_{1,2} = 23.97$, $P < 0.05$). Further evidence for the relationship between POM $\delta^{13}C$ and productivity is provided by the correlations between sediment trap $\delta^{13}C$ and carbon flux for the traps in 1988 at 40m ($r^2 = 0.50$; $F_{1,8} = 7.94$, $P < 0.25$), 80m ($r^2 = 0.94$; $F_{1,8} = 125.3$, $P < 0.001$), 150m ($r^2 = 0.59$; $F_{1,9} = 12.95$, $P < 0.01$), and 240m ($r^2 = 0.60$; $F_{1,8} = 12.00$, $P < 0.01$).

4.5 Relationships between the isotopic composition of POM and that of sediments

Sinking POM is derived from seston through aggregation and fecal pellet production. Consequently, processes that affect the isotopic composition of seston may also influence sinking POM. For example, enrichments in ^{13}C of both seston and sinking POM were associated with periods of high productivity as evidenced by high chlorophyll concentrations and high carbon flux (Figs. 16, 17, 83, 84, 85, and 86). Degradation processes that were attributed to $\delta^{15}N$ variability of seston (see discussion in section 4.2.3) probably affect the nitrogen isotopic composition of sinking

POM.

The origin of organic matter in marine sediments is generally assumed to be from productivity in the overlying waters. Differences in the isotopic composition of water column and sedimentary organic matter were evident in this and other studies (Entzeroth, 1982; Tan and Strain, 1983; Libes and Deuser, 1988; Wada et al., 1987; Ostrom and Macko, 1992). Seston and sinking POM were characterized by a very wide range of $\delta^{13}C$ and $\delta^{15}N$ values. Nonetheless, the range in both $\delta^{13}C$ and $\delta^{15}N$ of sediments in Conception Bay was less than 1.5‰ (Fig. 7). If terrestrial contributions are negligible, the isotopic composition of the sedimentary record should most closely resemble the $\delta^{15}N$ and $\delta^{13}C$ of phytoplankton during the period of highest primary production. This would be particularly in many high latitudes environments where much of the annual primary production occurs within a few months in the spring (Yentsch et al., 1977; Walsh, 1981; 1989).

A prediction of the isotope values of material reaching the seafloor during a period of a year can be expressed quantitatively as:

$$\delta_p = \frac{\sum_{i=1}^{n} \delta_i * F_i}{\sum_{i=1}^{n} F_i} \qquad \text{(eq. 5)}$$

where δ_p = flux or mass weighted carbon or nitrogen isotopic of seston or sinking POM

δ_i = the $\delta^{13}C$ of $\delta^{15}N$ of an individual sediment trap or seston sample.

F_i = the amount in grams of organic carbon or nitrogen collected for each deployment of a sediment trap or the concentration of POC or PON for a seston sample.

The results of this flux weighted average (eq. 5), with one exception, for seston or sinking POM from each sediment trap is depleted in ^{15}N and enriched in ^{13}C relative to the average isotope values for these samples (Table 20). The $\delta^{15}N$ value calculated from equation 5 for the 80m trap is approximately the same as the average for this trap. Estimates of the isotope values of material reaching the seafloor derived from the flux weighted relationship are more similar to the average $\delta^{15}N$ and $\delta^{13}C$ of surface sediments than are the average isotope values of the actual POM. Therefore, the results of the mass balance relation provide a better predictor of sediment isotope values than the mean $\delta^{15}N$ and $\delta^{13}C$ of seston or trap samples taken at a particular depth. The mass balance relationship demonstrates that the isotopic composition of sediments is more closely related to the $\delta^{15}N$ and $\delta^{13}C$ of phytoplankton during periods of high

primary production than average POM values.

The isotope values for seston were distinct from those for sediment trap material. On the basis of the mass weighted relationship, seston was more depleted in ^{13}C and enriched in ^{15}N by at least 0.93‰ and 1.29‰, respectively, relative to those of the predicted estimates of sinking POM (Table 20). The difference in $\delta^{15}N$ between these two fractions of POM is contrary to previous results in which sinking POM was found to be 3‰ greater than seston owing to a tropic-level fractionation effect (Altabet, 1988) and similar to results from the North Atlantic (Altabet et al., 1991). The enrichment in ^{15}N and depletion in ^{13}C of seston, relative to sinking POM, in this study is consistent with a greater degree of degradation in this fraction than in sinking POM (Macko, 1981; Saino and Hattori, 1987; Ostrom and Macko, 1991). This result substantiates earlier findings indicating that seston is more highly degraded than sinking POM (Cho and Azam, 1988; Caron et al., 1989).

Seston $\delta^{15}N$ and $\delta^{13}C$ values within the chlorophyll maximum during the peak of the spring bloom were more similar to sinking POM than at other depths and times of the year (Figs. 17, 21, 25, 29, 33, and 76; Table 20). This observation suggests that seston generated under conditions of high productivity may dominate the biomass that is aggregated to form sinking POM. However, it is difficult to ascertain if the difference in isotope values between

sinking and suspended POM is a function of fractionation during aggregation and/or diagenesis

A small shift of 1 to 2‰ in $\delta^{15}N$ and 1‰ in $\delta^{13}C$ was observed between sinking POM, as predicted by eq. 5, and sediments. Previously, macroalgae was considered to be an important source of organic matter in Newfoundland fjords (Ostrom and Macko, 1991; 1992). A small contribution of macroalgal detritus, approximately 20%, would be sufficient to shift isotope values for sediment trap material in the direction of that of sediments. Other mechanisms that result in differences in $\delta^{15}N$ and $\delta^{13}C$ between sinking POM and sediments includes diagenesis at the sediment-water interface and geochemical changes associated with decomposition and zooplankton grazing of trap material during lengthy deployments (Behrens and Frishman, 1971; Macko, 1981; Libes and Deuser, 1988; Ostrom and Macko, 1991). The greater period of deployment in 1990 (average of 16 days) relative to 1988 (average of 6 days) could compromise the ability to make interpretations based on geochemical analysis of trap material collected in 1990.

The ability to accurately determine the origin of sedimentary organic matter based on water column geochemistry is strongly dependent on sampling regime. Sedimentation rates in basins within northern Newfoundland bays of 0.01cm/yr to 0.5cm/yr may be predicted based on data from Ostrom and Macko (1991). Given a sampling interval of

1cm of sediment and the above sedimentation rates, a minimum of two years of data would provide the best prediction of the origins of sedimentary organic matter. The data set used in equation 5 consisted of only the few months of the year in 1988 when productivity was at a maximum. A more accurate delineation of the relationship between sinking POM and sediments may be derived from several years data collected over the entire annual cycle.

5.0 Summary and Conclusions

The primary objective of this study was to establish a firm understanding of the relationship between the isotopic composition of phytoplankton and that of underlying sediments. The approach was to evaluate processes controlling the $\delta^{13}C$ and $\delta^{15}N$ of POM through analysis of multiple geochemical parameters and extensive spacial and temporal sampling. The isotopic composition of phytoplankton is a function of the $\delta^{15}N$ of $\delta^{13}C$ of the inorganic nutrient source and fractionation during uptake and subsequent transformation pathways.

As has been observed in other studies, the $\delta^{13}C$ and concentration of DIC and as well as the abundance of dissolved oxygen in Conception Bay is controlled by the processes of photosynthesis, respiration, and diffusion (Kroopnick, 1974a; 1974b; Platt, 1984). Extremely low $\delta^{13}C$

values of DIC in Conception Bay appear to be related to brief periods of intensive respiration.

Nitrate was the primary source of nitrogen utilized by phytoplankton in Conception Bay. The isotopic composition of nitrate in Conception Bay was primarily controlled by fractionation during sedimentary nitrification. A fractionation factor, of 1.0193, was calculated for this reaction. A preferential incorporation of ^{14}N in nitrate resulted from isotopic shifts during this reaction and resulted in lower $\delta^{15}N$ values than have been found for other oceanic environments. The wide range of nitrate $\delta^{15}N$ values in Conception Bay indicates variation in the extent to which the substrate is utilized during nitrification. Although low microbial respiration rates suggested otherwise, mid-water column nitrification could not be eliminated as a possible source of ^{15}N depleted nitrate. Mass balance comparisons of the organic matter flux and microbial respiration rates suggest that much of the inorganic nitrogen utilized by primary production in Conception Bay may be derived from offshore Labrador Current water.

The ranges of $\delta^{15}N$ values for seston and sinking POM, 5.4‰ to 22.1‰ and 3.7‰ to 19.1‰, respectively, in Conception Bay was large. A dramatic increase in the weighted seston $\delta^{15}N$ values between spring and summer may have been the result of an increased reliance on regenerated ammonium as stratification became more pronounced. Oxidative

degradation was inferred to be an additional cause of the dramatic enrichments in the ^{15}N content of seston and sinking POM. Other degradative processes, including leaching of DOM, hydrolysis of peptide bonds and deamination, could also have resulted in variability in the $\delta^{15}N$ of POM.

Variation in the $\delta^{13}C$ of seston and sinking POM did not appear to be related to changes in temperature, water mass or phytoplankton species but were associated with changes in productivity. Changes in productivity probably resulted in shifts in the $\delta^{13}C$ of phytoplankton through variations in the concentration of DIC and the expression of fractionation during carbon fixation. Sediment carbon isotope values have been used to infer past levels of pCO_2 (Arthur et al., 1988; Rau et al., 1991). The results of this study indicate that the carbon isotope signature in some environments may reflect low pCO_2 levels as a consequence of high primary production and not the concentration of CO_2 in the atmosphere. The $\delta^{13}C$ record of sediment cores, preserving Late Wisconsinan to present sedimentation on the continental shelf of Newfoundland, do not vary in a manner consistent with changes in pCO_2 from ice core data (Barnola et al., 1987; Ostrom and Macko, 1991). This suggests that is some cases productivity levels have a greater impact on the $\delta^{13}C$ of sediments over geological time than CO_2 levels.

A mass weighted average was used to relate the isotopic composition and mass of POM to the $\delta^{15}N$ and $\delta^{13}C$ of sediments.

This weighted average appears to be a better predictor of isotope values for material reaching the seafloor than are the average isotope values of the actual POM. Interpretations of data generated from the model suggested that the isotopic composition of sediments is more closely related to the $\delta^{15}N$ and $\delta^{13}C$ of phytoplankton during periods of high primary productivity. Nonetheless, small differences between sinking POM and sediments were observed that may best be resolved by analysis of sediment trap material over many years.

This study is the first of its nature in a cold ocean, continental shelf environment. Many of the results of this study may be unique to these environments and may be used to gain insight into processes occurring in other cold ocean and Arctic environments. For example, the well oxygenated waters and cold temperatures caused the isotopic composition of nitrate to be influenced primarily by nitrification as opposed to denitrification prevalent in warmer areas. Furthermore, the prevalence of a predominant spring bloom produces and $\delta^{13}C$ value for POM and sediments that is not in equilibrium with atmospheric CO_2. The results of this study provide insight into carbon and nitrogen cycling in cold oceans and climate change in the past.

Table 1. A comparison of photosynthesis and nitrogen fixation with losses as sedimentary organic matter storage and denitrification in different aquatic environments (from Walsh, 1988).

Region	Area (km^2) ($x10^5$)	Net primary production ($x10^9$ tonsC/yr)	Nitrogen fixation ($x10^7$ tonsN_2/yr)	Sediment organic C ($x10^9$ tonsC/yr)	Denitrification loss ($x10^7$ tonsN_2/yr)
Open Ocean	3100	18.60	0.43	0.20	0
Continental Shelf	260	5.20	0.27	0	2.97
Continental Slope	320	2.24	0.06	0.50	5.50
Coral reefs	1.1	0.30	0.28	0.01	0
Seaweed beds	0.2	0.03	0	0	0
Estuaries/ Deltas	14	0.92	0.06	0.20	1.04
Salt Marshes	3.5	0.49	0.48	0.05	1.40
Freshwater Marshes	16	1.51	2.21	0.15	6.40
Rivers/Lakes	20	0.40	1.88	0.13	0.26
Totals	3734	29.7	5.7	1.2	17.6

Table 2. Isotope effects during specific reactions within the nitrogen cycle.

Fractionation Factor Value[4]	Substrate concentration	Species/ Sample	Reference
Nitrogen fixation			
β	0.9963 to 1.0022	Azotobacter sp.	Hoering and Ford, 1960
β	1.0039	Azotobacter vinelandii	Delwiche and Steyn, 1970
ϵ	-0.9	Rhizobium-legume plant pair	Amarger et al., 1977
β	1.004	Rhizobium-legume plant pair	Bardin et al., 1977
β	1.0012 to 1.0016	Soybeans (four varieties)	Amarger et al., 1979
β	0.99902	Soybean (Glycine max)	Kohl and Shearer, 1980
β	0.99812	Red clover (Trifolium pratense)	Kohl and Shearer, 1980

[4] Fractionation factors are expressed and defined in different ways depending on the author(s). The majority of these studies define fractionation factors in the following ways.

$\beta = R_s/R_p$ where $R = {}^{15}N/{}^{14}N$, s denotes substrate and p product.

$\Delta = \delta^{15}N$ of the product - $\delta^{15}N$ of the substrate

$\epsilon = (1/\beta - 1) * 1000$

Δ and ϵ are expressed in ‰ notation and are approximately equal at high substrate concentrations.

Table 2. Continued.

Fractionation Factor Value	Substrate concentration	Species/ Sample	Reference
Nitrogen fixation			
β	1.00063	Rhizobium-legume plant pair	Mariotti et al., 1980
β	1.001	Anabaena cylindrica	Minigawa and Wada, 1986
Δ	-2.35	Anabaena sp.	Macko et al., 1987
Ammonium assimilation			
β	1.0011 to 1.0148	18.7mM	Azotobacter vinelandii and soil yeasts	Delwiche and Steyn, 1970
Δ	-9.6 to 7.3		Chaetoceras sp.	Wada et al., 1975
β	0.9903 to 0.9947	0.18mM	Chaetoceras sp.	Wada and Hattori, 1978
β	1.000 to 1.010		Dunaliella tertiolecta and Cricosphaera carterae	Wada, 1980
Δ	-10.6	1mM	Freshwater algae	Estep and Vigg, 1985
Δ	-13.6	18mM	Anabaena sp.	Macko et al., 1987
ϵ	-20	50-70μM	mixed seawater species	Sharp et al., 1987
ϵ	-19.4	3-100μM	Skeletonema costalum	Pennock et al., 1988
ϵ	-9.1	0-75μM	mostly Skeletonema costalum	Cifuentes et al., 1989

Table 2. Continued.

Fractionation Factor	Value	Substrate concentration	Species/ Sample	Reference
Ammonium assimilation				
ϵ	-15	5 and 20mM	Vibrio harveii	Hoch et al., 1989
ϵ	-22	0.5mM	Vibrio harveii	Hoch et al., 1989
ϵ	-3.7	0-90μM	Chemosynthetic bacteria, Black Sea	Velinsky et al., 1989b
Nitrate assimilation				
Δ	-0.9 to -18.5		Phaeodactylum sp.	Wada et al., 1975
ϵ	-1.1		Rhizobium-plant pair	Amarger et al., 1977
β	1.0007	1mM	Phaeodactylum tricornutum stagnant culture	Wada and Hattori, 1978
β	1.0037	10mM	Phaeodactylum tricornutum stagnant culture	Wada and Hattori, 1978
β	1.0230	100mM	Phaeodactylum tricornutum stagnant culture	Wada and Hattori, 1978
β	1.0076 to 1.016	10mM	Phaeodactylum tricornutum shaking culture	Wada and Hattori, 1978
β	1.0009 to 1.0045	2.5mM	Chaetoceras sp. shaking culture	Wada and Hattori, 1978
β	1.0045 to 1.0049	7.5mM	Soybean, Ryegrass and Marigold	Kohl and Shearer, 1980

Table 2. Continued.

Fractionation Factor Value	Substrate concentration	Species/ Sample	Reference
Nitrate assimilation			
β	1.000 to 1.0025	Chaetoceras sp.	Wada, 1980
β	1.005	Natural seawater phytoplankton	Wada, 1980
Δ	-11.4	59mM	Anabaena sp.	Macko et al., 1987
Δ	-13.3	24mM	Anabaena sp.	Macko et al., 1987
β	1.0070	0-58μM	Natural Chesapeake Bay phytoplankton	Horrigan et al., 1980
Nitrite assimilation			
Δ	-1.4 to -4.0	Tricornutum sp.	Wada et al., 1975
β	1.0007	0.5mM	Phaeodactylum tricornutum	Wada and Hattori, 1978
Nitrification			
β	1.026	Nitrosomonas europaea	Delwiche and Steyn, 1970
β	1.015 to 1.026	1.4mM	Marine nitrifier	Miyake and Wada, 1971
β	1.01691	4mg-N/100g soil	loess soil	Fryer and Aly, 1975
Δ	-5.4 to -21.1		Marine nitrifier, Maizuru Bay, Japan	Wada et al., 1975

Table 2. Continued.

Fractionation Factor Value	Substrate concentration	Species/ Sample	Reference
Nitrification			
ϵ -34.7	5-25mM	Nitrosomonas europaea	Mariotti et al., 1981
$NH_4^+ \rightarrow NO_2^-$			
β 1.0246 to 1.0320	38mM	Nitrosomonas europaea	Yoshida, 1988
β 1.0120 to 1.0167	11.3-21.7μM	Natural Chesapeake Bay bacteria	Horrigan et al., 1990
$NH_4^+ \rightarrow N_2O$			
β 1.0604 to 1.0684	38mM	Nitrosomonas europaea	Yoshida, 1988 (measured)
β 1.0349 to 1.0362	38mM	Nitrosomonas europaea	Yoshida, 1988 (with NO_2^- as an assumed intermediate)
Denitrification			
β 1.020	10-30mM	Psuedomonas stutzeri	Wellman et al., 1968
β 1.0173		Psuedomonas dentirificans	Delwiche and Steyn, 1970
β 1.020	0.46mM	Marine denitrifier	Miyake and Wada, 1971
β 1.020	10-30mM	Psuedomonas stutzeri and Bacillus sp.	Cook et al., 1973
β 1.030 to 1.040	0-40μM	Denitrifier, eastern tropical S. Pacific	Cline and Kaplan, 1975

Table 2. Continued.

Fractionation Factor	Value	Substrate concentration	Species/ Sample	Reference
Denitrification				
Δ	-14.4 to -20.7		Denitrifier, Maizuru Bay, Japan	Wada et al., 1975
Δ	-1.9 to -12.3		Denitrifier, Lake Hamana, Japan	Wada et al., 1975
β	1.014 to 1.023	120mM	Iowa soil	Blackmer and Bremner, 1977
β	1.0142	120mM	Iowa soil	Bremner, 1977
β	1.0065 to 1.0191	14mM	Illinois soil	Chien et al., 1977
β	1.039	100mM	Serratia marinoruba	Miyazaki et al., 1980
β	1.002 to 1.012		Marine denitrifier	Wada, 1980
ε	-30±6	0.06-1.61mM	Groundwater, western Kalihari	Vogel et al., 1981
ε	-24.6 to -29.4	140mM	Natural soil	Mariotti et al., 1981
ε	-11 to -33	140mM	Natural soil	Mariotti et al., 1982
Δ	-20.7 to -32.3	3.2mM	Desulfovibrio, Lake Hamana, Japan	McCready et al., 1983
ε	-13 to -15		Denitrifier, eastern Pacific	Liu et al., 1987

Table 2. Continued.

Fractionation Factor Value	Substrate concentration	Species/ Sample	Reference
Denitrification			
β 1.007 to 1.032		Denitrifier, eastern Pacific	Liu and Kaplan, 1988
ϵ -15.9	0.03-2.55mM	Groundwater, Fuhrberger Feld catchment, FRG	Böttcher et al., 1990
NO_2^- reduction			
β 1.0036 to 1.0158	100mM	Psuedomonas stutzeri	Bryan et al., 1983
N_2O reduction			
β 1.027		Psuedomonas denitrificans	Yoshida et al., 1984
β 1.039		Azotobacter vinelandii	Yamazaki et al., 1987
N_2O fixation			
β 1.034		Azotobacter vinelandii	Yamazaki et al., 1987
Organic N to NO_3^-			
β 1.001		Seawater	Miyake and Wada, 1967
Organic N to NH_4^+			
Δ 2.6 to 5.0		Santa Barbara Basin sediment	Sweeney and Kaplan, 1980
Δ -0.2± 0.8		Framvaren Fjord sediment	Velinsky et al., 1991
Δ -2.8 to -0.4		Chesapeake Bay sediment	Velinsky et al., 1991

Table 2. Continued.

Fractionation Factor Value	Substrate concentration	Species/ Sample	Reference
Organic N to NH_4^+			
Δ	-0.8± 0.6	Great Marsh, Delaware sediment	Velinsky et al., 1991
Soil epidiagenesis			
β	0.9942	Soil in rice paddies	Wada et al., 1984
NH_4^+ exchange			
β	0.99909 to 0.99941	Dowex 50	Delwiche and Steyn, 1970
β	0.99866 to 0.99939	Ione clay	Delwiche and Steyn, 1970
β	1.003 to 1.011	Clay colloids	Karamanos and Rennie, 1978
NO_3^- exchange			
β	1.00158 to 1.00283	Dowex 1	Delwiche and Steyn, 1970
Δ	5.5	Natural soil	Black and Waring, 1977
Δ	2.2	Oxisol subsoil	Black and Waring, 1977

Table 3. Range of reported $\delta^{15}N$ values for dissolved inorganic nitrogen (DIN) in ocean waters.

$\delta^{15}N$ (‰)	Number of samples	Location	Reference[5]
Nitrate			
5.1 - 7.5	9	Western North Pacific	1
5.8 ± 1.6	18	Western North Pacific	2
6 - 10	6	Western North Pacific	3
6 - 10	8	Western North Pacific	4
8 - 16	16	E. Tropical South Pacific	5
4.8 - 18.8	17	Northeast of Hawaii	6
5 - 19	35	E. Tropical North Pacific	6
3.1 - 16.2	95	Santa Barbara Basin	5
2.9 - 4.5	6	North Atlantic warm core ring	7
4 - 7	22	Northern North Atlantic	5
4.5 - 12.5	12	Tropical North Atlantic	5
3.5	?	Sargasso Sea	8
4.2 - 9.8	4	Black Sea	9
Ammonium			
-3.5 - 7.5	3	Western North Pacific	1
1.5 - 9.0	10	Black Sea	9

[5] 1 = Miyake and Wada, 1967; 2 = Wada et al., 1975; 3 = Wada, 1980; 4 = Yoshida et al., 1989; 5 = Liu and Kaplan, 1989; 6 = Cline and Kaplan, 1975; 7 = Altabet and McCarthy, 1985; 8 = Altabet, 1988; 9 = Velinsky et al., 1989b

Table 4. Data on microbial respiration, primary production and benthic nutrient fluxes in Conception Bay (from Pomeroy et al., 1991).

Process	Rate
Primary production	
Early spring bloom	5.2 $gCm-^{2}day^{-1}$
Late spring bloom	0.51 $gCm^{-2}day^{-1}$
Water column heterotrophic production and respiration	0.046 $gCm^{-2}day^{-1}$
Benthic aerobic respiration	0.107 $gCm^{-2}day^{-1}$
Benthic denitrification	0.011 $gCm^{-2}day^{-1}$
Benthic nutrient fluxes	
Ammonium	46 $\mu Mm^{-2}hr^{-1}$
Nitrate	5.3 $\mu Mm^{-2}hr^{-1}$
Nitrite	0.4 $\mu Mm^{-2}hr^{-1}$
Urea	1.6 $\mu Mm^{-2}hr^{-1}$
Phosphate	5.6 $\mu Mm^{-2}hr^{-1}$
Silicate	173 $\mu Mm^{-2}hr^{-1}$

Table 5. Reproducibility and limit of detection of the various techniques used in this study based on replicate standards or samples.

Technique[6]	Precision	Number of samples	Sample or standard	Limit of Detection[7]
$[NO_2^-]$	0.1μM	4	sam.	0.2μM
$[NO_3^-]$	0.1μM	4	sam.	0.2μM
$[NH_4^+]$	0.1μM	4	sam.	0.2μM
$[O_2]$	0.07mL/L	3 sets of 4	sam.	0.2mL/L
δ^{15}N-SOM	0.15‰	4	sam.	N.A.
δ^{13}C-SOM	0.1‰	4	sam.	N.A.
%C-SOM	0.15%	6	sam.	0.05%
%N-SOM	0.03%	6	sam.	0.01%
δ^{15}N-POM	0.2‰	2 sets of 3	sam.	N.A.
δ^{13}C-POM	0.4‰	2 sets of 3	sam.	N.A.
δ^{15}N-NO_3^-	0.9‰	21	std.	N.A.
δ^{15}N-NH_4^+	0.7‰	4	std.	N.A.
δ^{13}C-DIC	0.1‰	4	sam.	N.A.
[DIC]	0.03μmol/kg	4	sam.	0.6mmol/kg

[6] SOM = sedimentary organic matter; POM = particulate organic matter; DIC = dissolved inorganic carbon

[7] N.A. = not applicable

Table 6. Recovery of ammonium and nitrate by distillation.

Sample	Solution	μmol N	Recovery (%)	Recovery corrected for background (%)
NH_4 1	Deionized water	15.71	96.2	94.2
NH_4 2	Deionized water	15.71	101.8	99.7
NH_4 3	Deionized water	15.71	105.1	103.1
NH_4 4	Deionized water	15.71	108.3	106.2
		Avg.	102.9	100.8 ± 4.5
NO_3 1	Deionized water	15.71	99.8	93.6
NO_3 2	Deionized water	15.71	96.3	90.1
NO_3 3	Deionized water	15.71	107.5	101.3
NO_3 4	Deionized water	15.71	100.4	94.2
NO_3 5	Deionized water	20.0	113.2	108.3
NO_3 6	Deionized water	20.0	101.2	96.3
NO_3 7	Deionized water	20.0	105.1	100.3
NO_3 8	Deionized water	20.0	111.0	106.2
NO_3 9	Seawater nutrient-free	20.0	107.8	102.9
NO_3 10	Seawater nutrient-free	20.0	98.1	93.2
NO_3 11	Seawater nutrient-free	20.0	104.5	99.6
NO_3 12	Seawater nutrient-free	20.0	106.4	101.5
NO_3 13	Seawater nutrient-free Hg added and removed	10.0	113.2	103.5
NO_3 14	As above	10.0	116.0	106.0
NO_3 15	As above	10.0	116.0	106.0
		Avg. =	106.4	100.2 ± 5.4

Table 7. Abundance and isotopic composition of background nitrate and ammonium associated with the distillation technique.

Sample		μmols N	$\delta^{15}N$ (‰)
NH_4 Blank 1		0.383	15.09
NH_4 Blank 2		0.288	12.57
NH_4 Blank 3		0.279	11.03
	Avg	0.317 ± 0.057	12.90 ± 1.67
NO_3 Blank 1		0.968	-4.25
NO_3 Blank 2		1.024	1.60
NO_3 Blank 3		0.917	1.01
NO_3 Blank 4		nd	-1.08
NO_3 Blank 5		nd	4.04
NO_3 Blank 6		nd	1.37
NO_3 Blank 7		nd	-1.99
	Avg	0.970 ± 0.053	0.10 ± 2.53

Table 8. Recovery and isotopic composition of 40umol NH_4^+ in 300mL deionized water by 100mg zeolite ion sieve.

Sample	Recovery (%)	$\delta^{15}N$ (‰)
Z1	96.92	0.40
Z2	97.01	-0.16
Z3	96.99	-0.49
Z4	97.01	-0.16
Avg.	96.98 ± 0.04	-0.16 ± 0.35

Table 9. Recovery of 20μmol NH_4^+ in 300mL deionized water using 60mg zeolite with varying pH.

pH	Recovery (%)
7.0	76.59
7.0	77.28
6.5	85.20
6.5	85.38
6.0	89.02
5.5	94.16
5.0	94.98
5.0	95.56
4.5	94.72
4.0	88.69
3.5	63.18
3.0	0.00

Table 10. Recovery and isotopic composition of 40umol NH_4^+ in 300mL deionized water using two subsequent additions of 100mg zeolite ionsieve while maintaining the pH between 4.8 and 5.2.

Sample		Recovery (%)	$\delta^{15}N$ (‰)
Z5		99.39	-0.29
Z6		99.75	-0.15
Z7		99.92	0.22
Z8		99.88	-0.16
	Avg.	99.74 ± 0.21	-0.10 ± 0.22

Table 11. Isotopic composition of KNO_3 standard ($\delta^{15}N$ = 1.46‰) analyzed by distillation of 500mL of various solutions.

Sample	Solution	μmol NO_3	$\delta^{15}N$ (‰)
D1	Deionized water	20	1.30
D2	Deionized water	20	1.05
D3	Deionized water	20	2.02
D4	Deionized water	20	1.33
D5	Deionized water	20	-0.21
D6	Deionized water	20	1.56
D7	Deionized water	20	0.28
D8	Deionized water	20	2.88
			Avg. = 1.28 ± 0.90
D9	Inorganic nitrogen-free Conception Bay surface water	20	2.17
D10	As above	20	-0.61
D11	As above	20	0.81
D12	As above	20	0.07
			Avg. = 0.61 ± 1.03
D13	As in D9 and frozen 1 week	20	1.69
D14	As above	20	0.65
D15	As above	20	0.48
D16	As above	20	0.78
			Avg. = 0.90 ± 0.47
D17	As in D9 + 250mg $HgCl_2$ Hg removed through cleaning procedure (see text)	10	1.94
D18	As above	10	1.27
D19	As above	10	0.63
D20	As above	10	2.22
D21	As above	10	1.73
			Avg. = 1.56 ± 0.56
			Grand mean = 1.14 ± 0.86

Table 12. Carbon and nitrogen isotopic and elemental data for surficial sediment samples collected in Conception Bay. Samples collected in 1987 are from Ostrom (1989).

Station	Date	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	% N	% C	C/N
CC1	8/18/87	8.0	-21.5	0.60	3.28	6.4
BRLP5	4/29/90	9.1	-21.5	0.41	3.17	8.9
CC2	5/2/90	8.9	-21.6	0.40	3.17	9.3
CTR23	8/18/87	7.8	-21.2	0.56	3.55	7.4
CC5	5/4/90	8.7	-21.7	0.50	3.64	8.6
CC5	5/7/90	8.7	-21.5	0.38	3.74	11.4
CC5	5/7/90	9.0	-21.4	0.36	2.83	9.1
CC5.5	8/18/87	8.7	-21.2	0.69	4.07	6.9
CC7-1	5/5/90	8.4	-21.4	0.43	3.88	10.4
CC7-2	5/5/90	8.8	-21.7	0.42	3.23	8.9
US3.5	9/11/90	8.2	-21.5	0.34	2.03	7.0
CC8	8/17/87	8.3	-21.4	0.28	1.64	6.9
CC9-1	5/6/90	8.0	-21.6	0.26	1.74	7.8
CC9	5/6/90	9.0	-21.4	0.24	2.03	9.9
CC10.5	8/17/87	9.0	-21.1	0.19	0.78	4.9

Table 13. Carbon and nitrogen isotopic and elemental data on sedimentary organic matter (SOM), porewater dissolved inorganic nitrogen concentrations and the $\delta^{15}N$ of NH_4^+ from box cores collected in Conception Bay.

Stn./ Date/ Depth	$\delta^{15}N$ SOM (‰)	$\delta^{13}C$ SOM (‰)	%N	%C	C/N	[NH4]	[NO3]	[NO2]	$\delta^{15}N$-NH_4^+ (‰)
BRLP5 4/29									
0-5	9.1	-21.5	0.41	3.17	8.9	34.72	3.7	0.3	8.5
5-11	8.9	-21.4	0.42	3.99	11.1	133.84	16.1	0.2	6.1
11-15	9.1	-21.4	0.39	3.26	9.6	181.35	3.1	0.0	8.6
15-19	8.8	-20.8	0.40	3.52	10.1	233.59	8.7	0.0	7.7
CC5 5/4									
0-2	8.7	-21.7	0.50	3.64	8.6	98.19	20.9	2.8	5.4
2-5	7.9	-21.4	0.48	3.95	9.7	124.83	24.4	0.2	4.5
5-8	9.7	-21.3	0.45	3.35	8.6	177.71	11.4	0.0	7.0
8-11	9.7	-21.4	0.44	3.78	10.0	205.53	34.2	0.0	6.2
11-14	9.4	-21.4	0.43	2.93	7.9	197.14	16.0	0.0	8.0
14-17	8.4	-21.2	0.42	3.39	9.3	204.73	5.9	0.0	6.1
17-21	8.0	-21.4	0.41	4.42	12.7	239.92	8.6	0.0	7.4
CC5 5/7									
0-1	8.7	-21.5	0.38	3.74	11.4	44.63		0.5	8.9
1-3.5	8.3	-21.4	0.38	2.97	9.1			0.0	
3.5-5.	8.1	-21.4	0.38	2.91	9.0			1.5	
5.5-8	8.1	-21.4	0.33	3.05	10.8			0.0	
8-11	10.0	-21.2	0.39	2.52	7.5			0.0	
11-14	8.7	-21.1	0.30	2.79	10.8			0.0	
14-17	8.0	-21.4	0.34	3.47	11.7			0.0	
17-21	8.3	-21.2	0.38	2.79	8.5			0.0	
Avg.	8.7	-21.3	0.40	3.35	9.8	156.3	13.9	0.3	7.0
S.D.	0.6	0.2	0.05	0.48	1.3	66.2	9.2	0.7	1.3

Table 14. Surface temperature, change in density and maximum chlorophyll concentration for samples collected at stations in Conception Bay in 1990.

Station	Date	Surface Temp. (°C)	Δ Sigma-t[8]	Chlorophyll Max. (μg/L)
BRLP5	3/23	-1.07	0.677	n.d.
BRLP5	3/29	-0.99	0.611	9.03
BRLP5	4/4	-0.05	0.652	12.50
BRLP5	4/18	0.47	0.549	12.40
BRLP5	4/29	0.32	0.520	10.65
BRLP5	5/2	1.24	0.815	5.15
BRLP5	5/6	1.37	0.791	nd
BRLP5	5/20	2.43	0.797	3.20
BRLP5	6/24	7.38	1.674	1.42
BRLP5	7/27	12.29	2.554	1.17
BRLP5	8/30	13.28	2.582	1.98
US3.5	5/1	0.35	0.512	10.19
US3.5	5/6	0.91	0.683	4.94
US3.5	5/21	1.48	0.843	3.49
US3.5	6/24	5.91	1.397	0.63
CTR23	4/29	0.25	0.602	8.48
CC13	5/4	-0.22	0.351	12.34

[8] Δ Sigma-t is the maximum difference in density at a station.

Table 15. Range in dissolved oxygen saturation, and the concentration and $\delta^{13}C$ of DIC for samples collected at stations in Conception Bay in 1990.

Station	Date	O_2 (Sat.) Min.	O_2 (Sat.) Max.	$\delta^{13}C$-DIC (‰) Min.	$\delta^{13}C$-DIC (‰) Max.	[DIC] Min.	[DIC] Max.
BRLP5	3/23	-18.1	24.6	-0.6	0.5	1.70	2.19
BRLP5	3/29	-70.5	43.1	-3.9	0.2	1.97	2.42
BRLP5	4/4	-52.9	74.8	-0.7	-0.1	1.93	2.34
BRLP5	4/18	-60.7	50.5	-1.1	0.7	2.08	2.21
BRLP5	4/29	-54.6	30.3	0.6	1.1	2.11	2.40
BRLP5	5/2	-62.0	31.7	-1.5	0.5	2.14	2.27
BRLP5	5/6	-81.2	22.2	-1.5	0.8	2.15	2.20
BRLP5	5/20	-55.8	20.0	-4.0	0.3	2.04	2.35
BRLP5	6/24	-61.9	32.7	-0.1	0.6	1.98	2.27
BRLP5	7/27	-59.3	31.8	0.1	1.4	2.05	2.36
BRLP5	8/30	-71.8	33.6	-0.7	1.0	1.77	2.20
US3.5	5/1	-83.8	36.8	-1.1	1.2	2.17	2.26
US3.5	5/6	-47.3	36.6	-1.1	0.0	2.13	2.24
US3.5	5/21	-51.1	9.95	-1.8	1.0	1.87	2.29
US3.5	6/24	-70.5	39.0	-0.4	0.7	1.92	2.24
CTR23	4/29	-54.6	27.8	0.2	1.7	2.17	2.41
CC13	5/4	-39.3	29.6	-0.3	1.2	1.82	2.24

Table 16. Chlorophyll concentrations and carbon to chlorophyll ratios for stations in Conception Bay.

Station/Date/ Depth (m)	Chl a µg/L	C/chl	Station/Date	Chl a µg/L	C/chl
BRLP5 3/23 5	nd[9]		BRLP5 5/2 5	0.48	90.2
BRLP5 3/23 35	nd		BRLP5 5/2 40	2.24	28.6
BRLP5 3/23 60	nd		BRLP5 5/2 80	2.37	26.3
BRLP5 3/23 80	nd		BRLP5 5/2 120	1.86	27.1
BRLP5 3/23 210	nd		BRLP5 5/2 210	0.53	67.5
BRLP5 3/29 5	2.82	59.8	CC13 5/4 5	9.51	8.8
BRLP5 3/29 25	7.18	14.0	CC13 5/4 40	6.48	11.0
BRLP5 3/29 45	1.64	21.7	CC13 5/4 80	7.04	9.4
BRLP5 3/29 80	0.30	134.5	CC13 5/4 125	0.27	65.1
BRLP5 3/29 210	0.33	165.2	CC13 5/4 180	0.29	80.7
BRLP5 4/4 5	1.19	63.5	US3.5 5/6 5	0.53	77.3
BRLP5 4/4 22	10.18	16.2	US3.5 5/6 30	4.30	8.5
BRLP5 4/4 45	1.07	25.5	US3.5 5/6 60	2.66	14.0
BRLP5 4/4 80	0.32	91.0	US3.5 5/6 100	4.19	11.2
BRLP5 4/4 210	0.29	100.1	US3.5 5/6 170	0.34	76.2
BRLP5 4/18 5	2.63	36.7	BRLP5 5/6 5	nd	
BRLP5 4/18 20	11.60	12.5	BRLP5 5/6 50	nd	
BRLP5 4/18 45	4.80	19.3	BRLP5 5/6 80	nd	
BRLP5 4/18 80	0.45	82.1	BRLP5 5/6 150	nd	
BRLP5 4/18 210	0.34	80.9	BRLP5 5/6 245	nd	
BRLP5 4/29 5	3.83	21.0	BRLP5 5/20 5	0.39	262.4
BRLP5 4/29 80	4.05	39.9	BRLP5 5/20 40	0.69	71.6
BRLP5 4/29 100	6.17	11.4	BRLP5 5/20 80	2.27	21.2
BRLP5 4/29 120	2.18	21.7	BRLP5 5/20 120	0.42	103.6
BRLP5 4/29 210	0.41	72.7	BRLP5 5/20 210	0.56	64.7
CTR23 4/30 5	2.77	25.8	US3.5 5/21 5	0.27	132.7
CTR23 4/30 80	4.59	20.2	US3.5 5/21 60	0.99	55.2
CTR23 4/30 100	3.52	20.6	US3.5 5/21 80	1.46	30.6
CTR23 4/30 120	1.72	22.5	US3.5 5/21 100	0.87	31.2
CTR23 4/30 210	0.32	119.6	US3.5 5/21 170	0.82	38.5
US3.5 5/1 5	1.09	50.7	US3.5 6/24 5	0.30	80.1
US3.5 5/1 40	4.77	15.0	US3.5 6/24 25	0.56	38.6
US3.5 5/1 60	5.61	12.5	US3.5 6/24 50	0.57	24.4
US3.5 5/1 80	5.52	18.2	US3.5 6/24 80	0.32	38.5
US3.5 5/1 170	0.38	61.0	US3.5 6/24 210	0.43	60.7

[9] nd = not determined.

Table 16. Continued.

Station/Date	Chl a µg/L	C/chl
BRLP5 6/24 5	0.34	56.0
BRLP5 6/24 40	1.13	23.2
BRLP5 6/24 60	0.37	28.0
BRLP5 6/24 80	0.32	37.9
BRLP5 6/24 210	0.38	82.2
BRLP5 7/27 5	0.42	70.4
BRLP5 7/27 30	1.04	49.3
BRLP5 7/27 60	0.45	39.2
BRLP5 7/27 80	0.41	36.4
BRLP5 7/27 210	0.29	70.1
BRLP5 8/30 5	0.61	67.5
BRLP5 8/30 20	1.83	18.8
BRLP5 8/30 40	0.74	44.4
BRLP5 8/30 80	0.31	47.7
BRLP5 8/30 210	0.23	48.5

Table 17. Range in $\delta^{15}N$, $\delta^{13}C$, and C/N for seston collected at stations in Conception Bay in 1990.

Station	Date	$\delta^{15}N$ (‰) Min.	$\delta^{15}N$ (‰) Max.	$\delta^{13}C$ (‰) Min.	$\delta^{13}C$ (‰) Max.	C/N Min.	C/N Max.
BRLP5	3/23	6.5	22.1	-25.0	-22.6	3.1	18.5
BRLP5	3/29	7.2	20.5	-25.8	-22.9	3.4	11.0
BRLP5	4/4	8.5	14.6	-25.2	-22.0	3.3	14.4
BRLP5	4/18	5.4	18.6	-25.1	-22.6	3.3	12.1
BRLP5	4/29	7.2	12.9	-23.8	-23.0	2.8	6.2
BRLP5	5/2	9.1	15.5	-24.1	-22.7	2.9	15.5
BRLP5	5/6	13.8	17.3	-24.3	-22.3	3.0	6.3
BRLP5	5/20	12.4	15.0	-25.2	-22.6	8.5	11.2
BRLP5	6/24	9.2	18.7	-25.3	-24.0	4.3	6.8
BRLP5	7/27	10.0	16.5	-25.1	-24.3	5.1	6.8
BRLP5	8/30	11.9	15.7	-24.4	-23.2	3.7	5.2
US3.5	5/1	7.3	10.7	-24.4	-23.8	4.7	6.9
US3.5	5/6	7.9	18.2	-24.9	-23.4	3.5	9.4
US3.5	5/21	11.1	18.5	-26.4	-24.3	4.2	6.7
US3.5	6/24	9.2	17.7	-24.6	-23.4	5.6	8.2
CTR23	4/29	8.5	20.6	-22.8	-21.9	3.6	11.4
CC13	5/4	11.9	15.7	-24.4	-23.2	3.7	5.2

Table 18. Isotopic and elemental concentration of particulate organic matter and concentration of total suspended matter in rivers leading into Conception Bay.

Sample/ date[10]	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	C/N	TSM (mg/L)	[PON] (μM)	[POC] (μM)
MR 3/27	14.5	-26.2	18.6	0.237	0.28	5.17
CB 4/24	11.8	-25.9	7.7	1.637	1.78	13.63
MR 4/24	17.2	-26.5	9.6	4.570	8.35	79.85
SP 4/24	12.8	-27.9	9.6	0.954	1.70	16.27
CB 5/24		-28.1		1.184		11.75
MR 5/24	13.4	-26.2	11.9	1.986	1.19	14.13
SP 5/24	11.6	-28.0	16.5	0.790	0.97	16.00
CB 7/10	14.7	-25.2	18.8	0.229	0.22	4.07
MR 7/10	9.8	-24.5	16.3	0.393	0.43	7.06
SP 7/10	11.2	-25.1	10.1	0.575	0.93	9.35
CB 8/16	8.5	-25.1	13.2	0.825	0.83	11.03
MR 8/16	6.4	-25.1	15.5	0.647	1.06	16.46
SP 8/16	8.5	-24.5	11.0	0.406	0.76	8.37
Average	11.7	-26.0	13.2	1.110	1.54	16.40
Std. Dev.	2.9	1.2	3.6	1.119	2.10	18.75

[10] MR = Manuels River; CB = Conway Brook; SP = St. Phillips River. See Fig. 1 for locations.

Table 19. Concentration and isotopic composition of dissolved inorganic carbon and nitrogen in rivers leading to Conception Bay.

Sample/ Date	$[NH_4^+]$ (μM)	$[NO_3^-]$ (μM)	$[NO_2^-]$ (μM)	$\delta^{15}N$-NO_3^- (‰)	[DIC] (mmol/kg)	$\delta^{13}C$-DIC (‰)
CB 3/27	1.7	18.9	0.1	1.5	0.06	-9.1
MR 3/27	5.1	7.9	0.2	4.3		
CB 4/24	3.9	22.8	0.2	-0.9	0.25	-21.7
MR 4/24	3.4	9.5	0.2	-2.6	0.04	-8.5
SP 4/24	1.7	15.4	0.1	3.3	0.05	-23.2
CB 5/24	1.1	19.4	0.1	0.3		
MR 5/24	1.5	7.1	0.1	-1.7		
SP 5/24	1.2	6.6	0.0	-0.3		
CB 7/10	0.9	15.5	0.0	-0.2	0.05	-10.4
MR 7/10	2.8	7.6	0.1	0.5	0.35	-8.5
SP 7/10	0.7	14.3	0.2	3.4	0.05	-7.1
CB 8/16	1.4	22.4	0.0	-0.7	0.16	-10.1
MR 8/16	1.4	4.0	0.2	-2.9	0.15	-9.1
SP 8/16	1.0	15.8	0.0	3.6		-9.4
Average	2.0	14.4	0.1	0.6	0.13	-11.7
Std. Dev.	1.3	4.9	0.1	2.3	0.10	5.4

Table 20. The isotopic composition of 1988 sediment trap material and 1990 seston predicted from the flux weighted average (eq. 4) in comparison to average values.

Sample	Model $\delta^{15}N$	Average $\delta^{15}N$	Model $\delta^{13}C$	Average $\delta^{13}C$
40 m Trap	8.63	9.61	-22.73	-23.28
80 m Trap	10.36	10.31	-22.11	-22.68
150 m Trap	9.00	9.79	-22.12	-22.53
240 m Trap	nd[11]	8.85	-22.39	-22.72
Seston (all depths)	11.65	12.67	-23.66	-23.92
Seston within the Chl. max. 3/29- 4/30	9.00		-22.75	
Sediments (0-1cm)		8.57		-21.44

[11] nd indicates not determined. The entire set of 240m trap samples could not be analyzed for $\delta^{15}N$ due to insufficient material.

Figure 1. A model of the benthic nitrogen cycle in Conception Bay. Values for rates of transfer between resevoirs are from Pomeroy et al. (1991).

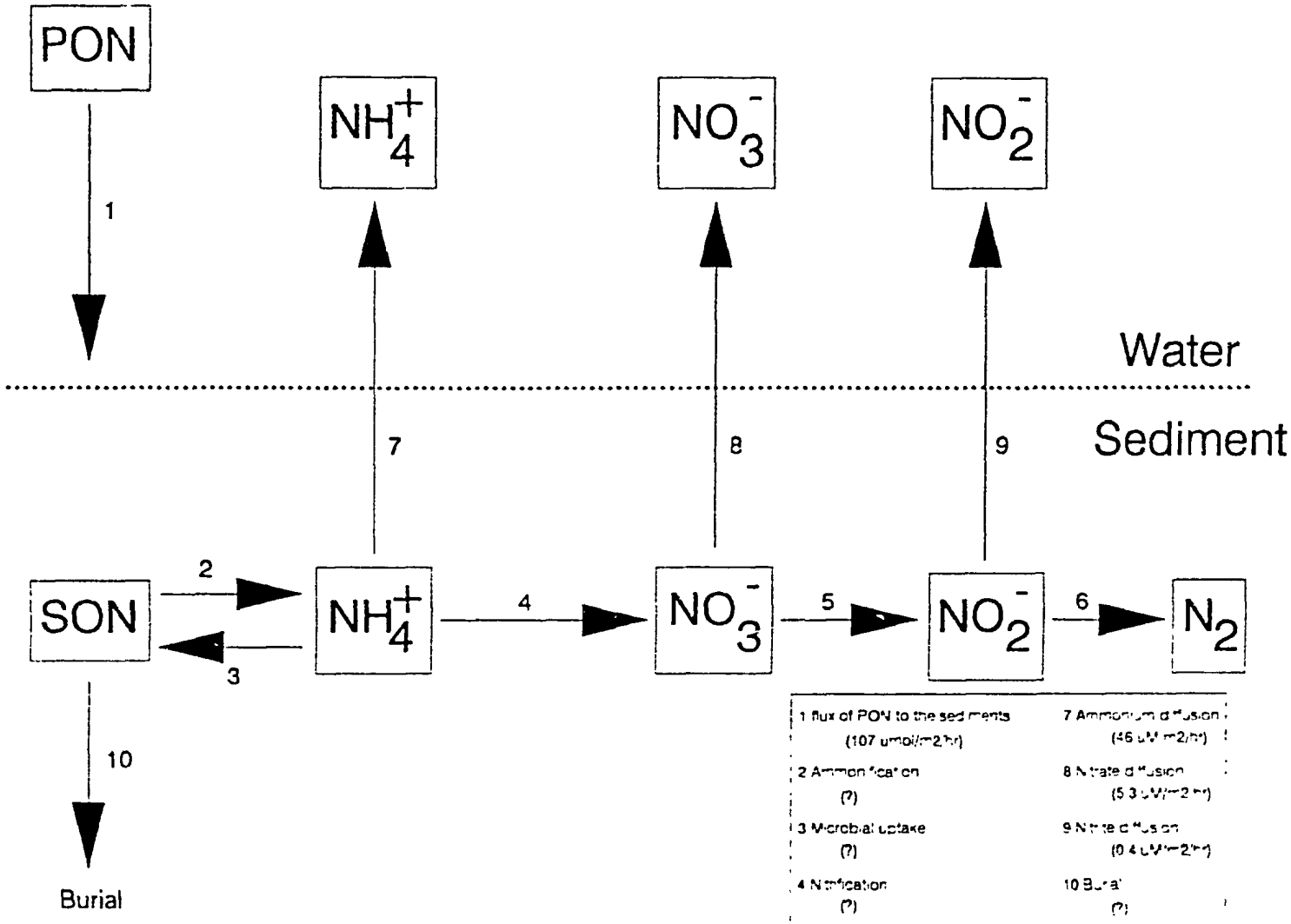

PON
NH_4^+
NO_3^-
NO_2^-
1
Water
Sediment
7
8
9
SON
2
3
NH_4^+
4
NO_3^-
5
NO_2^-
6
N_2
10
Burial
1 flux of PON to the sediments (107 umol/m2/hr)
2 Ammonification (?)
3 Microbial uptake (?)
4 Nitrification (?)
5 and 6 Denitrification (58 umol/m2/hr)
7 Ammonium diffusion (46 uM/m2/hr)
8 Nitrate diffusion (5.3 uM/m2/hr)
9 Nitrite diffusion (0.4 uM/m2/hr)
10 Burial (?)

Figure 2. A model of sources and processes affecting the concentration and isotopic composition of DIC in the ocean.

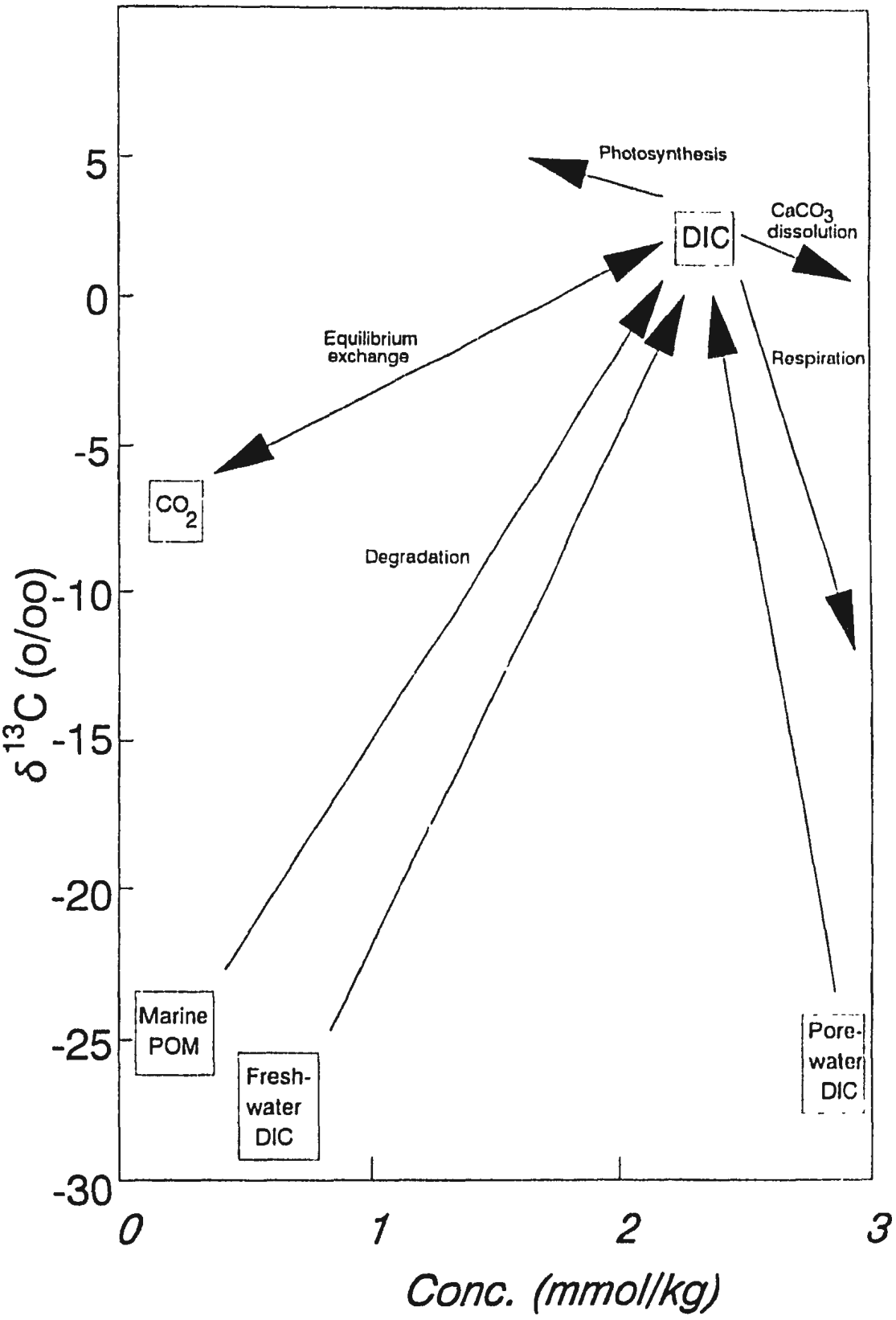

Photosynthesis
DIC
CaCO3 dissolution
Equilibrium exchange
Respiration
CO2
Degradation
Marine POM
Fresh-water DIC
Pore-water DIC
δ13C (o/oo)
5
0
-5
-10
-15
-20
-25
-30
0
1
2
3
Conc. (mmol/kg)

Figure 3. Map of Conception Bay, Newfoundland showing locations of sampling stations. Primary stations are emphasized in bold. Freshwater stations are indicated by SP (St. Phillips River), MR (Manuels River), and CB (Conways Brook).

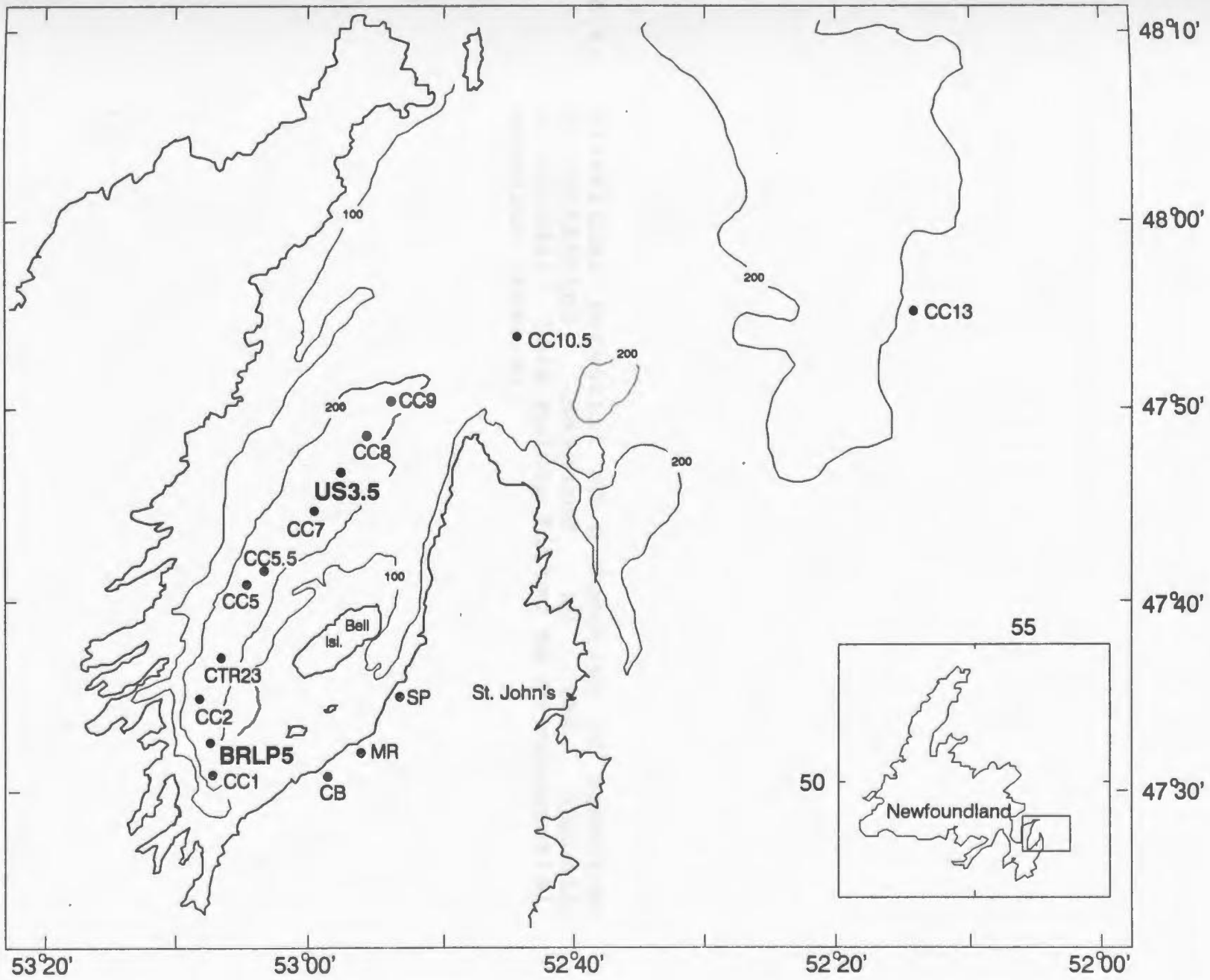

48°10'
48°00'
47°50'
47°40'
47°30'
53°20'
53°00'
52°40'
52°20'
52°00'
100
200
CC13
CC10.5
CC9
CC8
US3.5
CC7
CC5.5
CC5
Bell Isl.
CTR23
CC2
BRLP5
CC1
SP
MR
CB
St. John's
55
50
Newfoundland

Figure 4. Electrical potential as a function of ammonium concentration (measured by the ammonia electrode). Data points fitted to an exponential equation (base e).

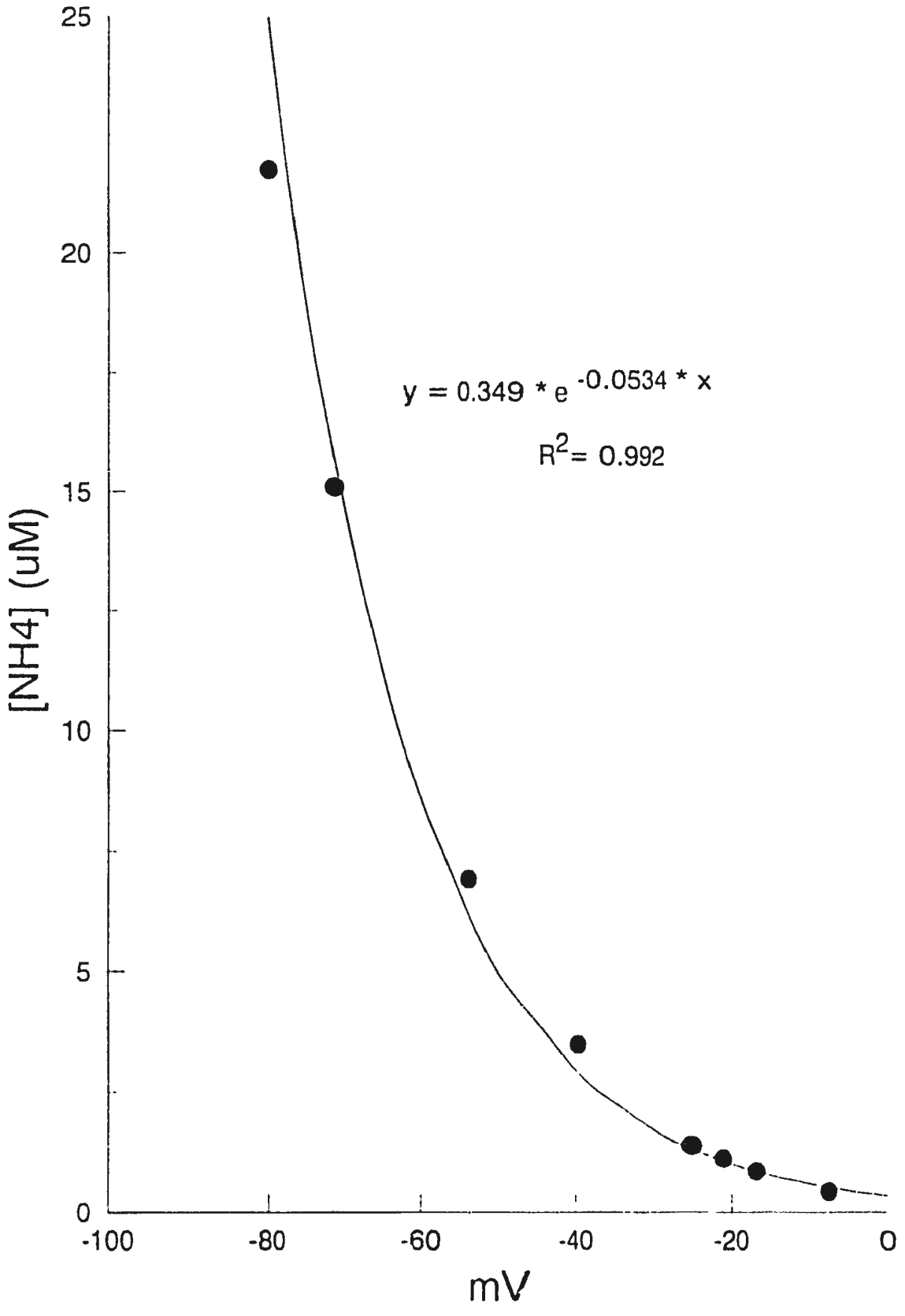
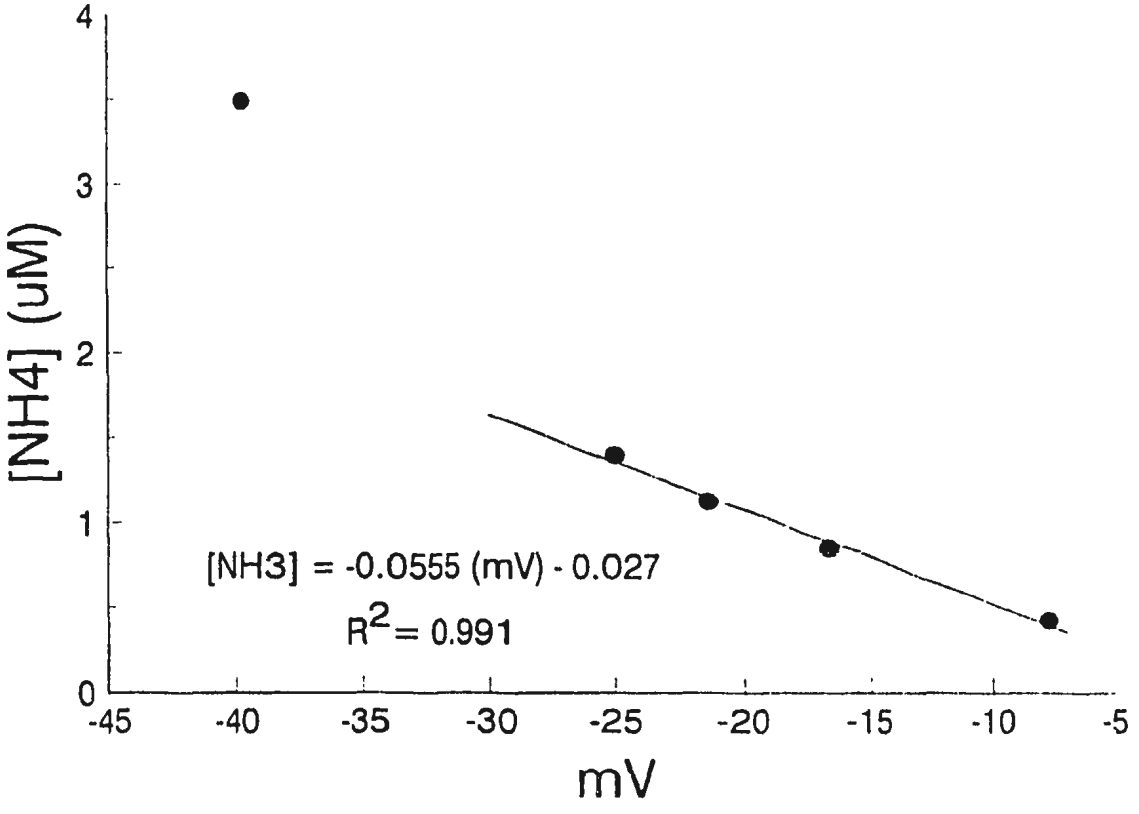

25
20
15
10
5
0
[NH4] (uM)
y = 0.349 * e -0.0534 * x
R2= 0.992
-100
-80
-60
-40
-20
0
mV

Figure 5. Electrical potential as a function of ammonium concentration for value less than 1.8 μM (above) and the log of the concentration for values greater than 1.8μM. Data points fitted to a linear equations.


[NH4] (uM)
4
3
2
1
0
[NH3] = -0.0555 (mV) - 0.027
R2= 0.991
-45
-40
-35
-30
-25
-20
-15
-10
-5
mV

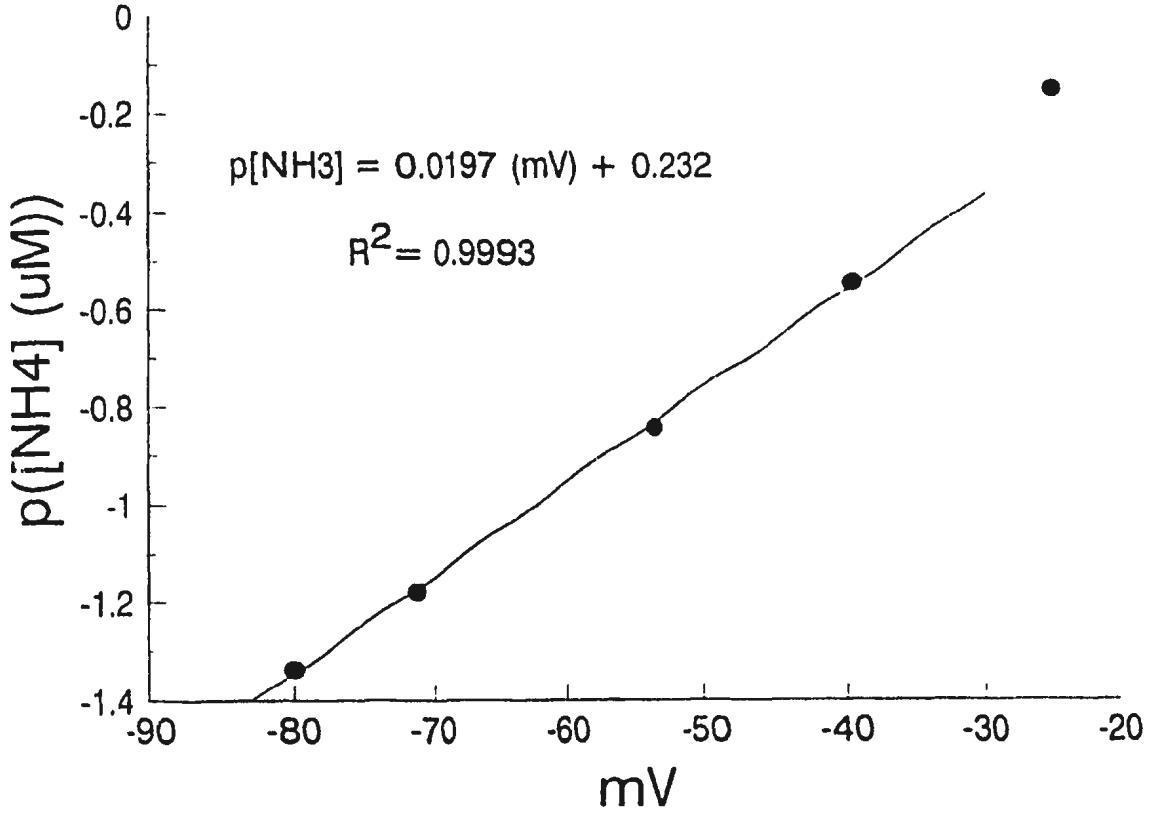

p([NH4] (uM))
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
p[NH3] = 0.0197 (mV) + 0.232
R2= 0.9993
-90
-80
-70
-60
-50
-40
-30
-20
mV

Figure 6. Diagram of distillation apparatus used to determine the $\delta^{15}N$ of nitrate and ammonium in natural waters.

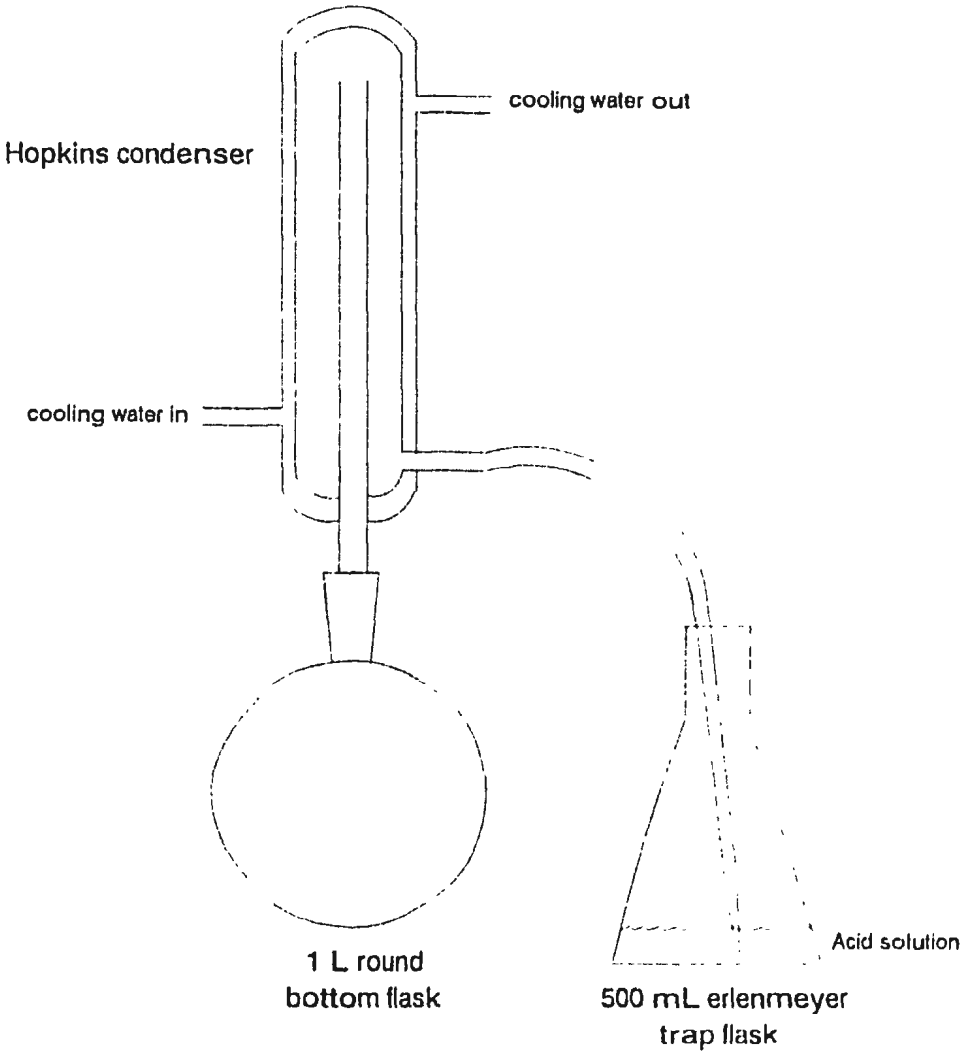

Hopkins condenser
cooling water out
cooling water in
1 L round
bottom flask
Acid solution
500 mL erlenmeyer
trap flask

Figure 7. Carbon and nitrogen isotopic and elemental data for surficial sediments collected over several years along a transect from head to mouth of Conception Bay, Newfoundland.

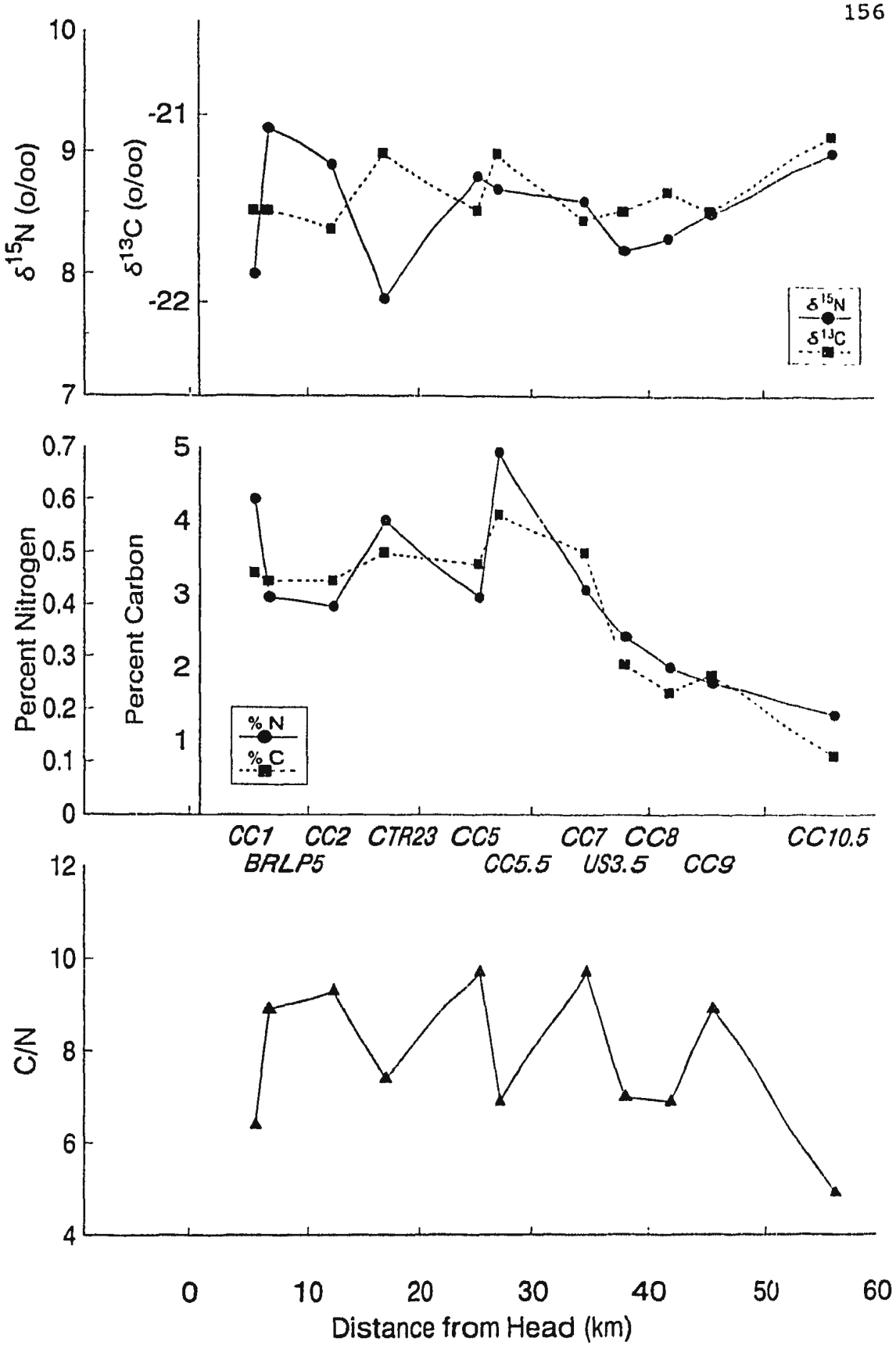

δ15N (o/oo)
δ13C (o/oo)
-21
-22
δ15N
δ13C
Percent Nitrogen
Percent Carbon
%N
%C
CC1
CC2
CTR23
CC5
CC7
CC8
CC10.5
BRLP5
CC5.5
US3.5
CC9
C/N
Distance from Head (km)

Figure 8. Carbon and nitrogen isotopic and elemental data for a boxcore collected at station BRLP5 on April 29.

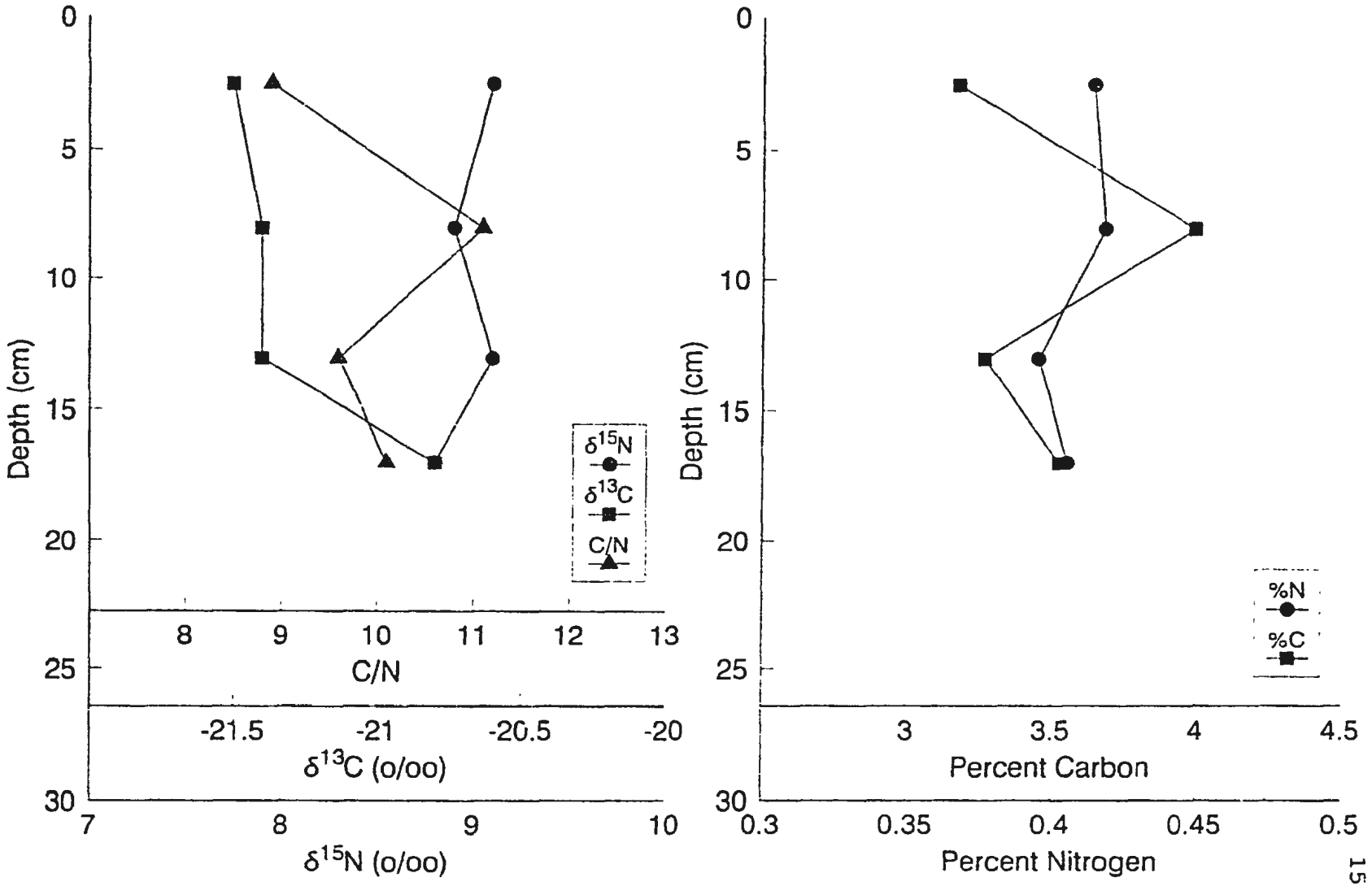

BRLP5 4/29
Depth (cm)
0
5
10
15
20
25
30
δ15N
δ13C
C/N
8
9
10
11
12
13
C/N
-21.5
-21
-20.5
-20
δ13C (o/oo)
7
8
9
10
δ15N (o/oo)
%N
%C
3
3.5
4
4.5
Percent Carbon
0.3
0.35
0.4
0.45
0.5
Percent Nitrogen

Figure 9. Carbon and nitrogen isotopic and elemental data for a boxcore collected at station CC5 on May 4.

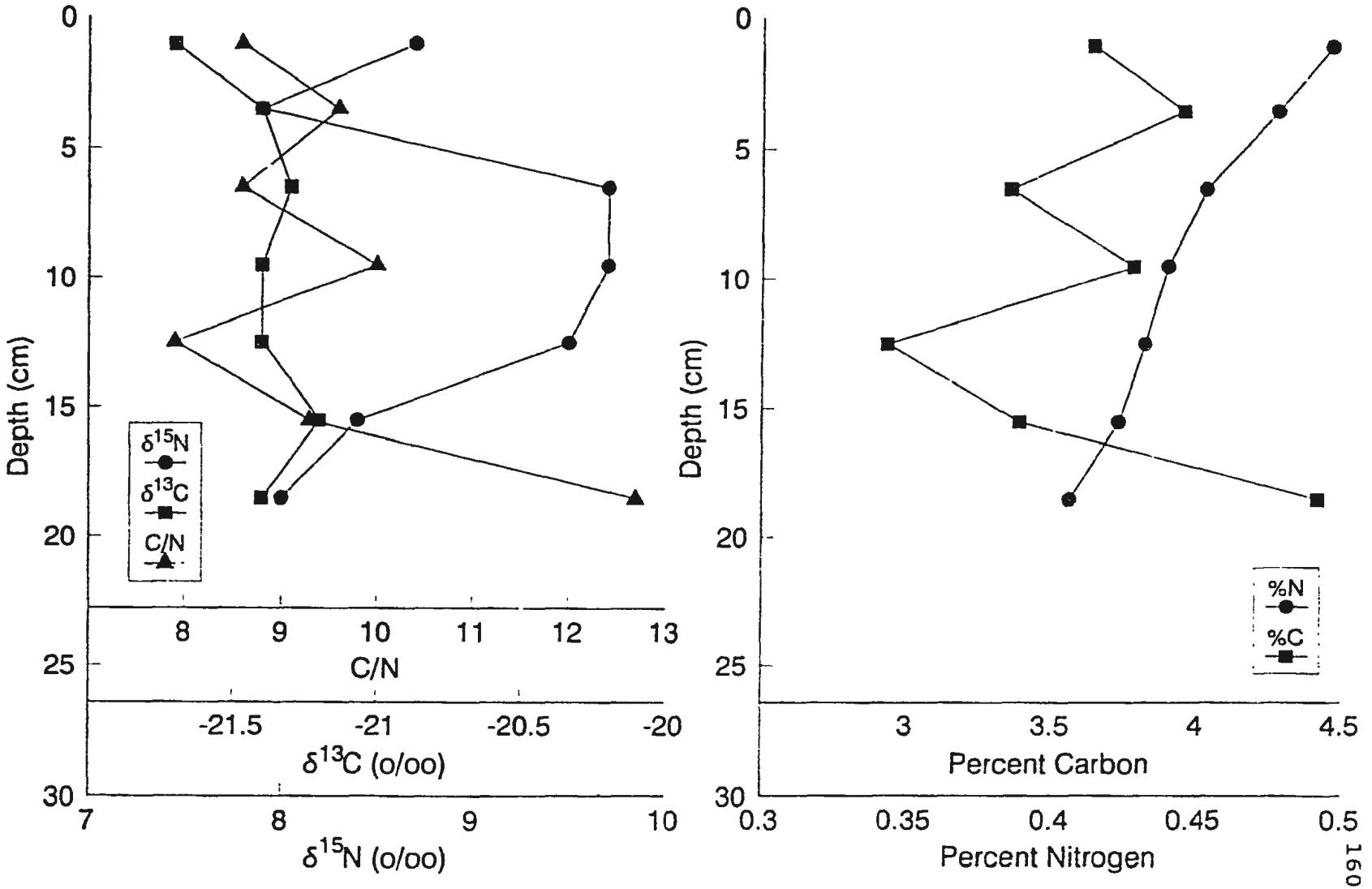

CC5 5/4
Depth (cm)
0
5
10
15
20
25
30
δ15N
δ13C
C/N
8
9
10
11
12
13
C/N
-21.5
-21
-20.5
-20
δ13C (o/oo)
7
8
9
10
δ15N (o/oo)
%N
%C
3
3.5
4
4.5
Percent Carbon
0.3
0.35
0.4
0.45
0.5
Percent Nitrogen

Figure 10. Carbon and nitrogen isotopic and elemental data for a boxcore collected at station CC5 on May 7.

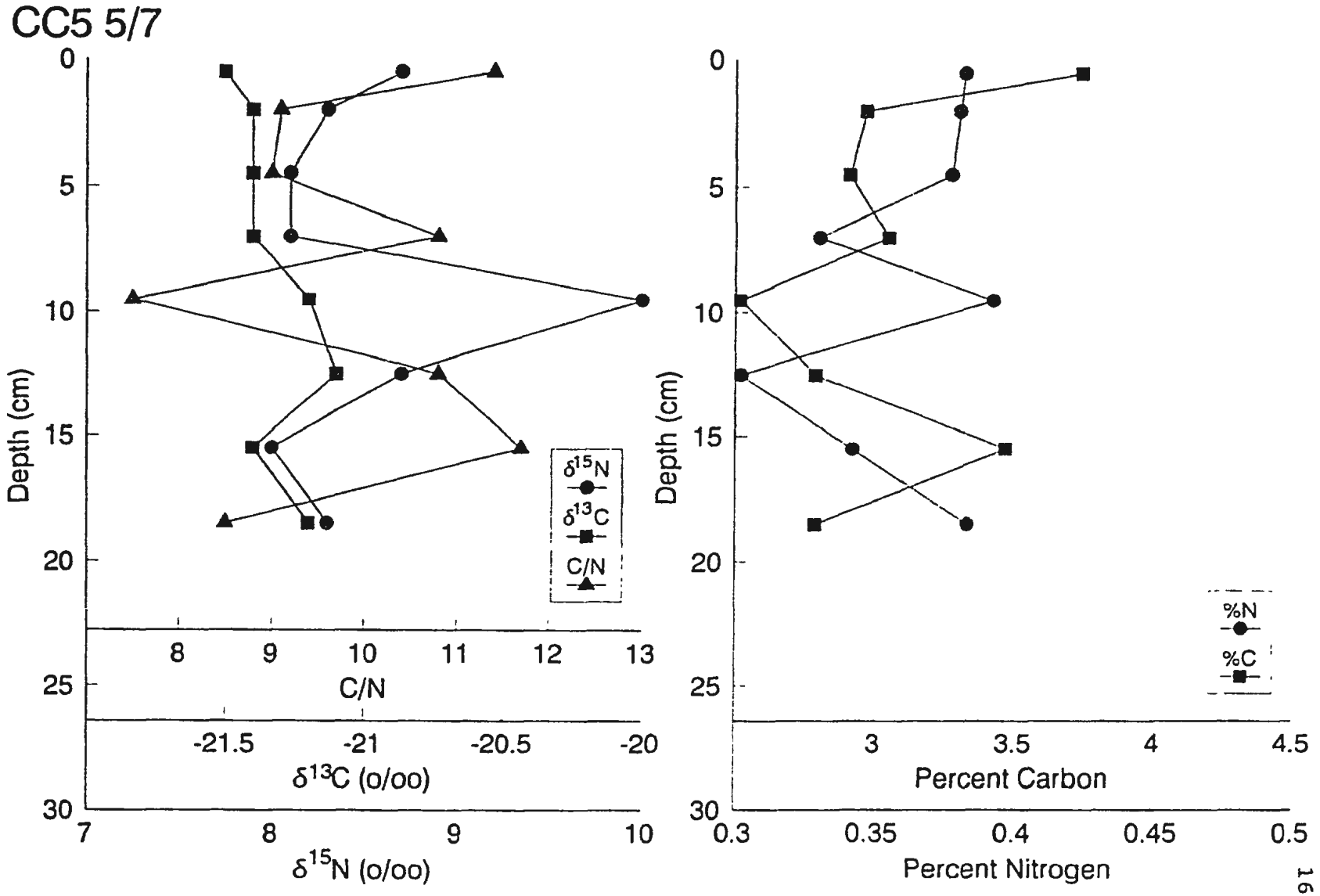

CC5 5/7
Depth (cm)
0
5
10
15
20
25
30
δ15N
δ13C
C/N
8
9
10
11
12
13
C/N
-21.5
-21
-20.5
-20
δ13C (o/oo)
7
8
9
10
δ15N (o/oo)
%N
%C
3
3.5
4
4.5
Percent Carbon
0.3
0.35
0.4
0.45
0.5
Percent Nitrogen

Figure 11. Concentrations on dissolved inorganic nitrogen (DIN) and $\delta^{15}N$ of NH_4^+ in porewaters from a boxcore collected at station BRLP5 on April 29.

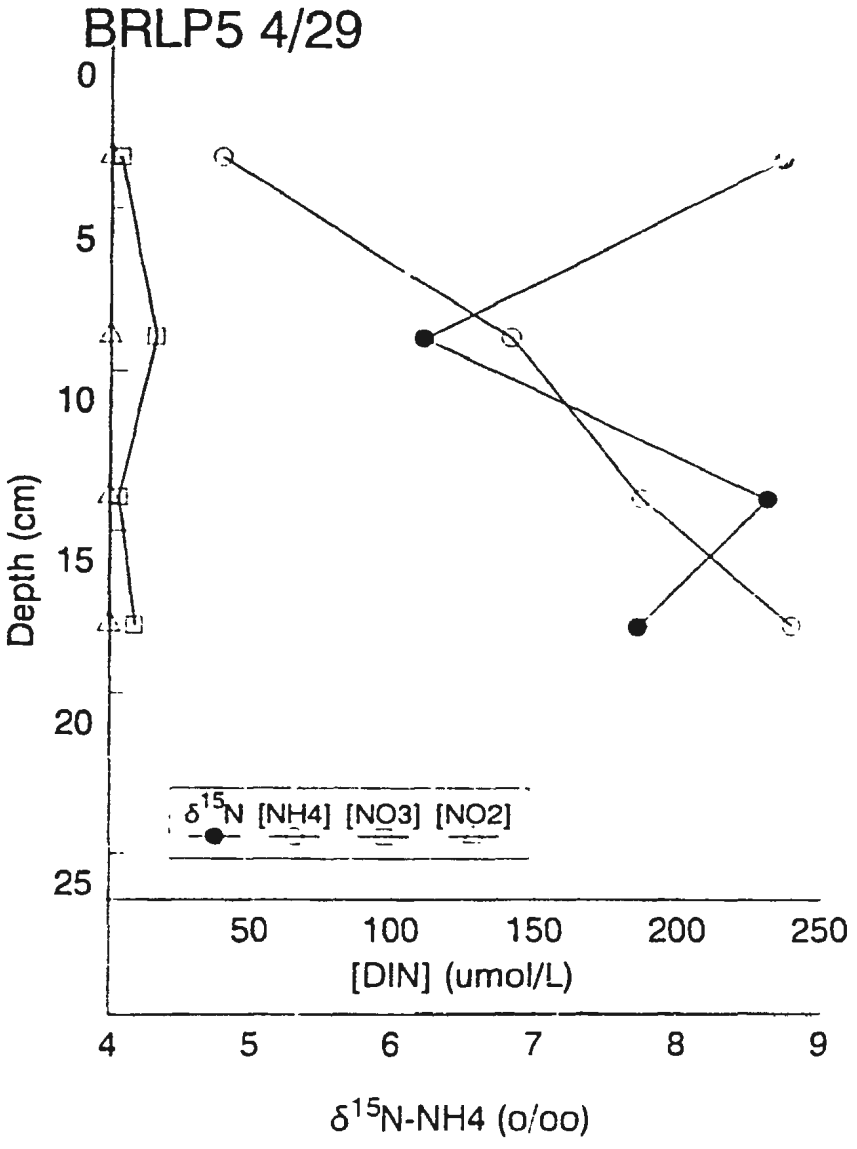

BRLP5 4/29
0
5
10
15
20
25
Depth (cm)
δ15N [NH4] [NO3] [NO2]
50
100
150
200
250
[DIN] (umol/L)
4
5
6
7
8
9
δ15N-NH4 (o/oo)

Figure 12. Concentrations on dissolved inorganic nitrogen (DIN) and $\delta^{15}N$ of NH_4^+ in porewaters from a boxcore collected at station CC5 on May 4.

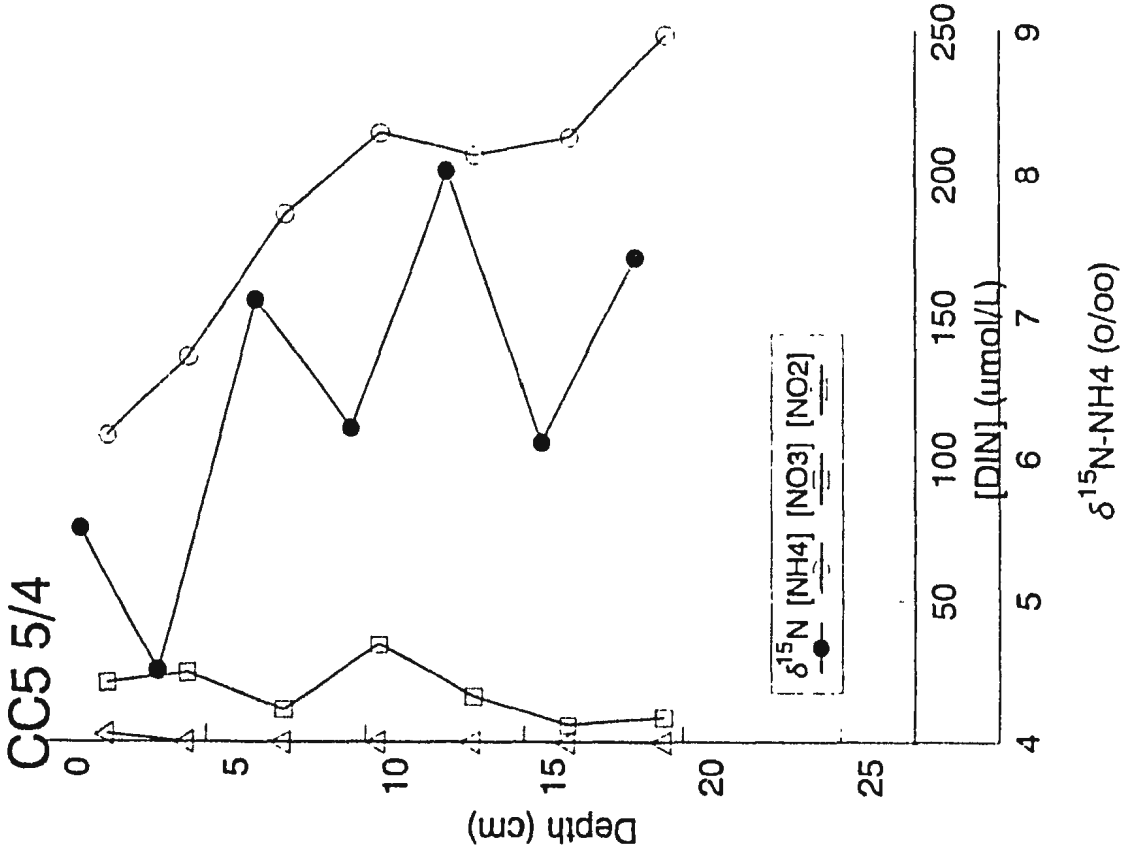

CC5 5/4
Depth (cm)
0
5
10
15
20
25
[DIN] (umol/L)
50
100
150
200
250
δ15N-NH4 (o/oo)
4
5
6
7
8
9
δ15N [NH4] [NO3] [NO2]

Figure 13. Concentrations on dissolved inorganic nitrogen (DIN) and $\delta^{15}N$ of NH_4^+ in porewaters from a boxcore collected at station CC5 on May 7.

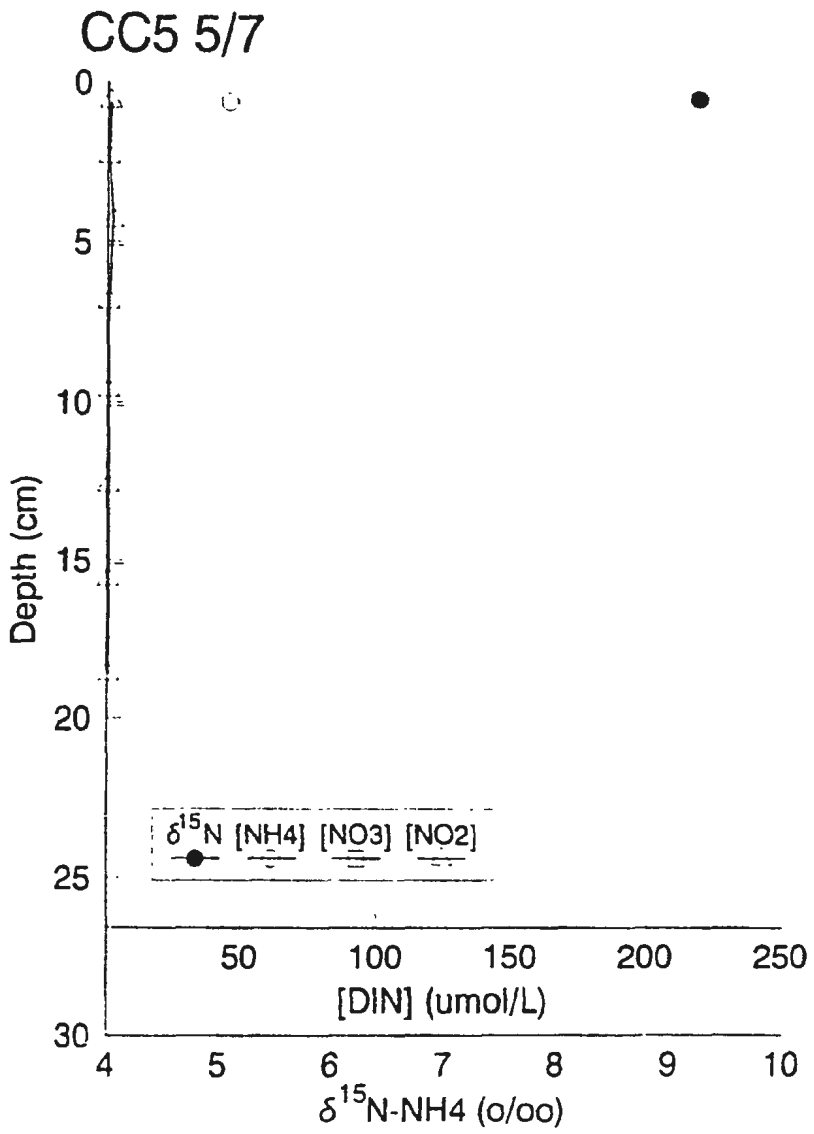

CC5 5/7
Depth (cm)
0
5
10
15
20
25
30
δ15N [NH4] [NO3] [NO2]
50
100
150
200
250
[DIN] (umol/L)
4
5
6
7
8
9
10
δ15N-NH4 (o/oo)

Figure 14. Salinity, temperature, and density as a function of water column depth for station BRLP5 on March 23.

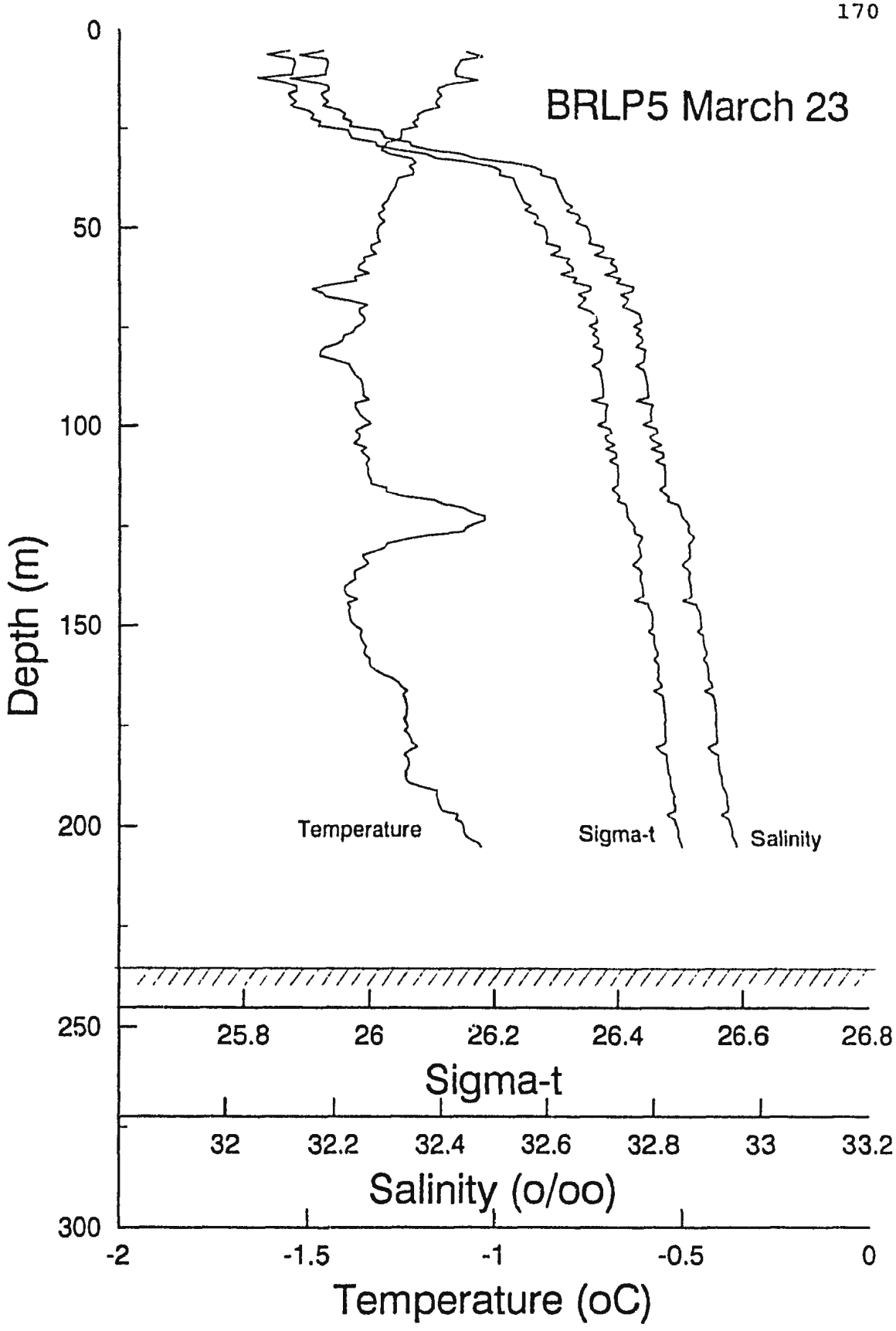

BRLP5 March 23
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
Temperature (oC)

Figure 15. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on March 23. Oxygen saturation (Sat.) is the difference, in μM, between measured concentrations and theoretical concentrations for oxygen in atmospheric equilibration at in situ temperatures and salinities (calculated from Weiss, 1970). The dotted line represents the zero saturation level.

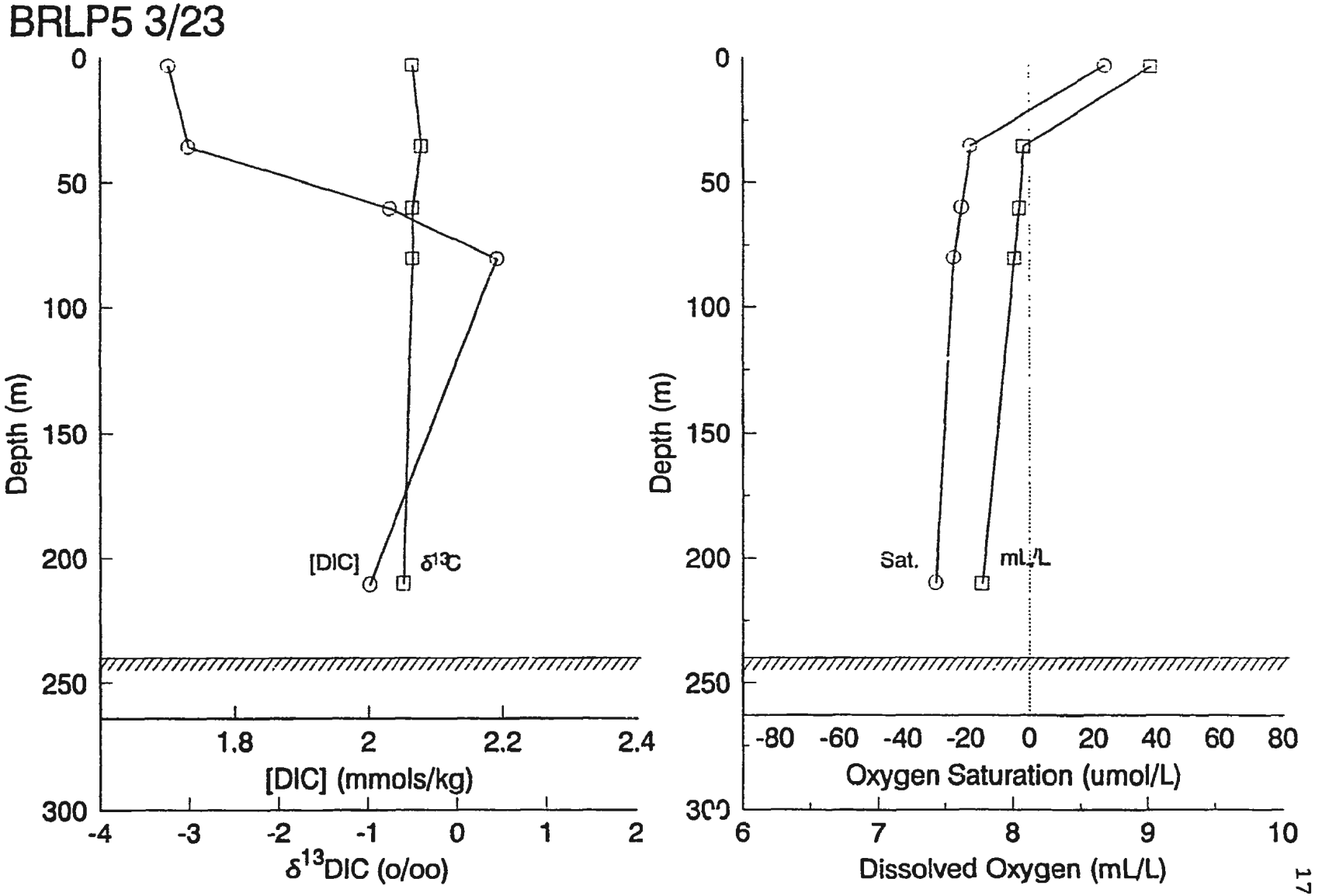

BRLP5 3/23
Depth (m)
0
50
100
150
200
250
300
[DIC]
δ13C
1.8
2
2.2
2.4
[DIC] (mmols/kg)
-4
-3
-2
-1
0
1
2
δ13DIC (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 16. Percent transmittance and concentrations of particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on March 23.

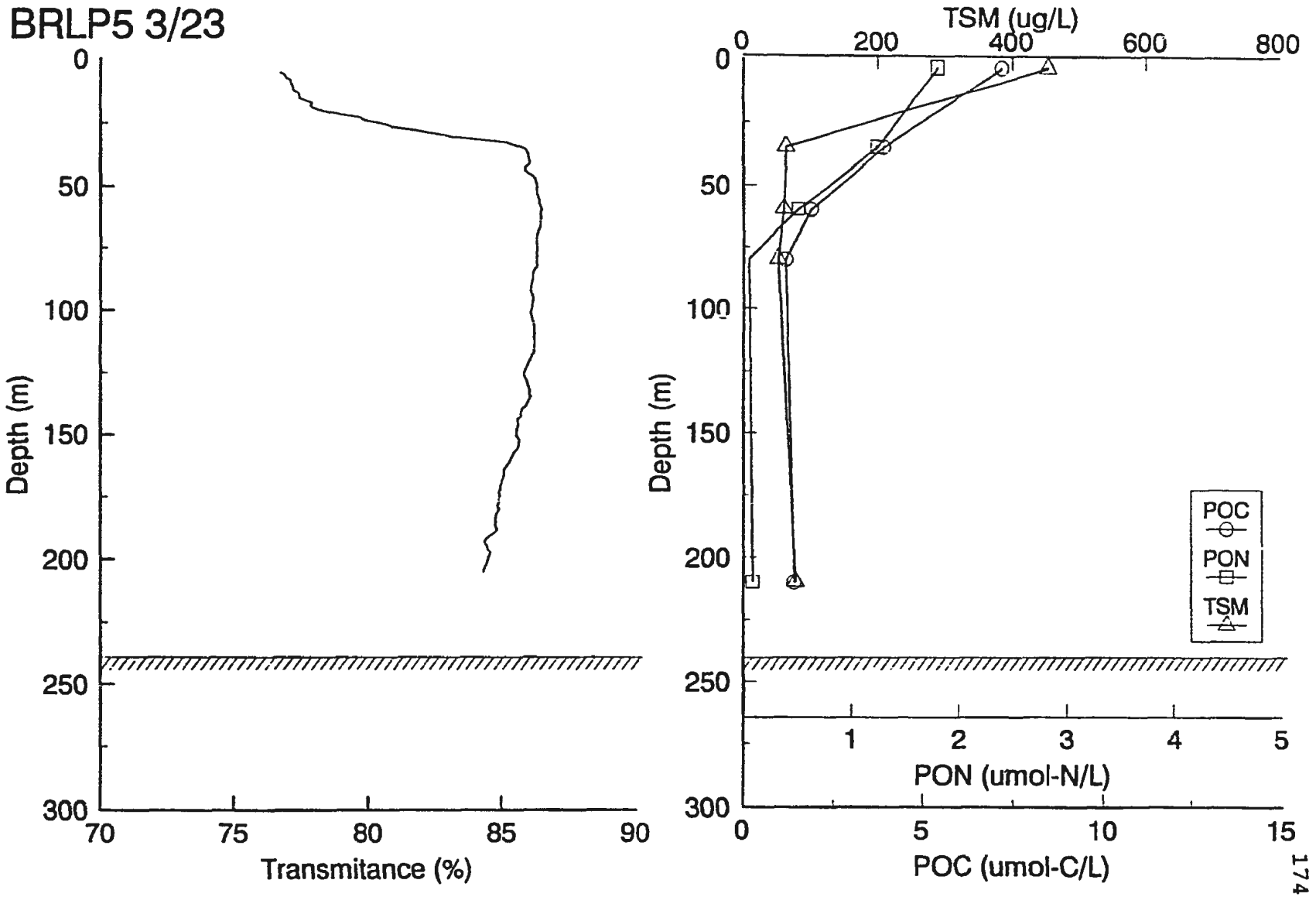

BRLP5 3/23
Depth (m)
0
50
100
150
200
250
300
70
75
80
85
90
Transmitance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 17. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on March 23.

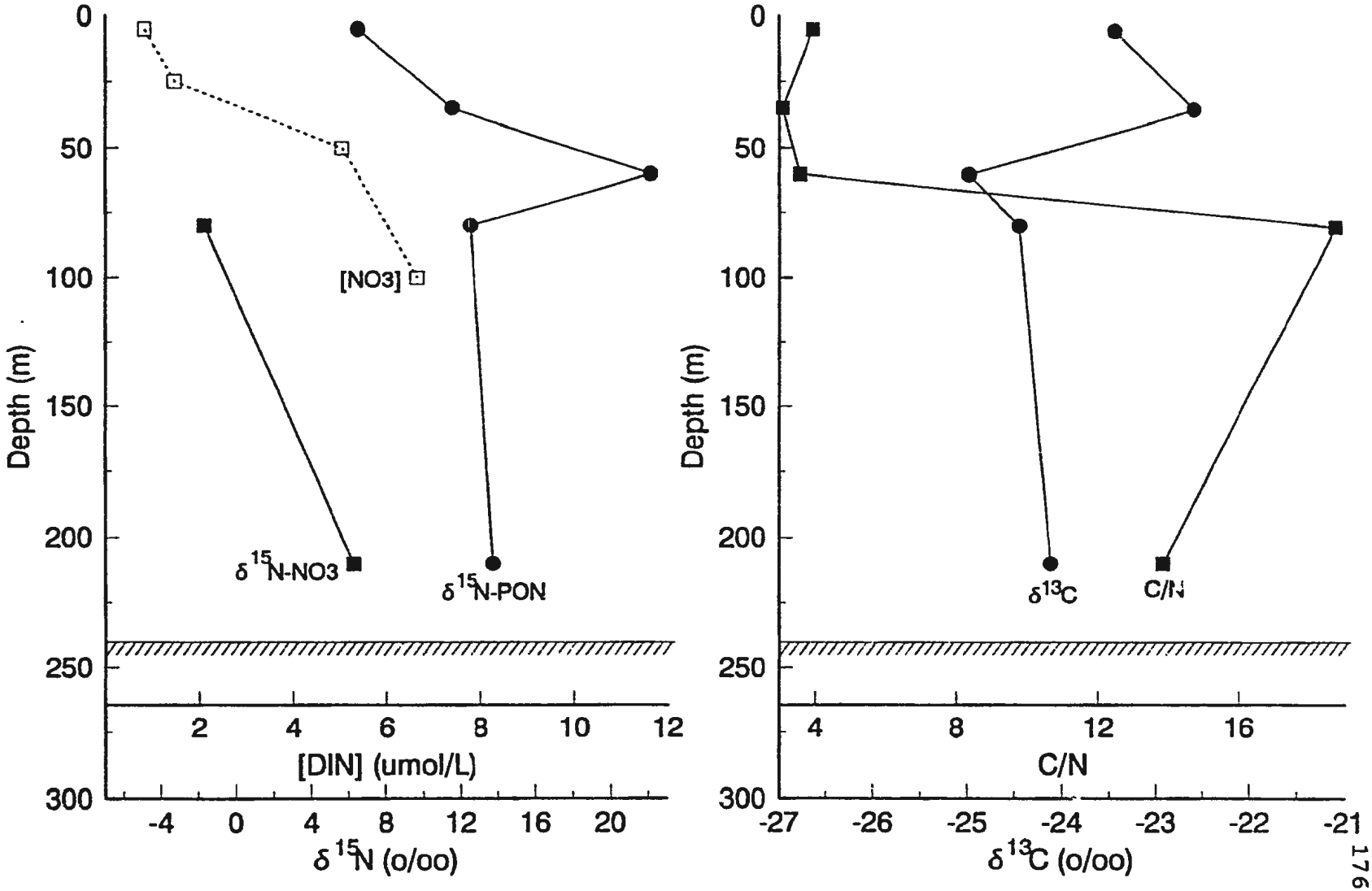

BRLP5 3/23
Depth (m)
0
50
100
150
200
250
300
[NO3]
δ15N-NO3
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
δ13C
C/N
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 18. Salinity, temperature, and density as a function of water column depth for station BRLP5 on March 29.

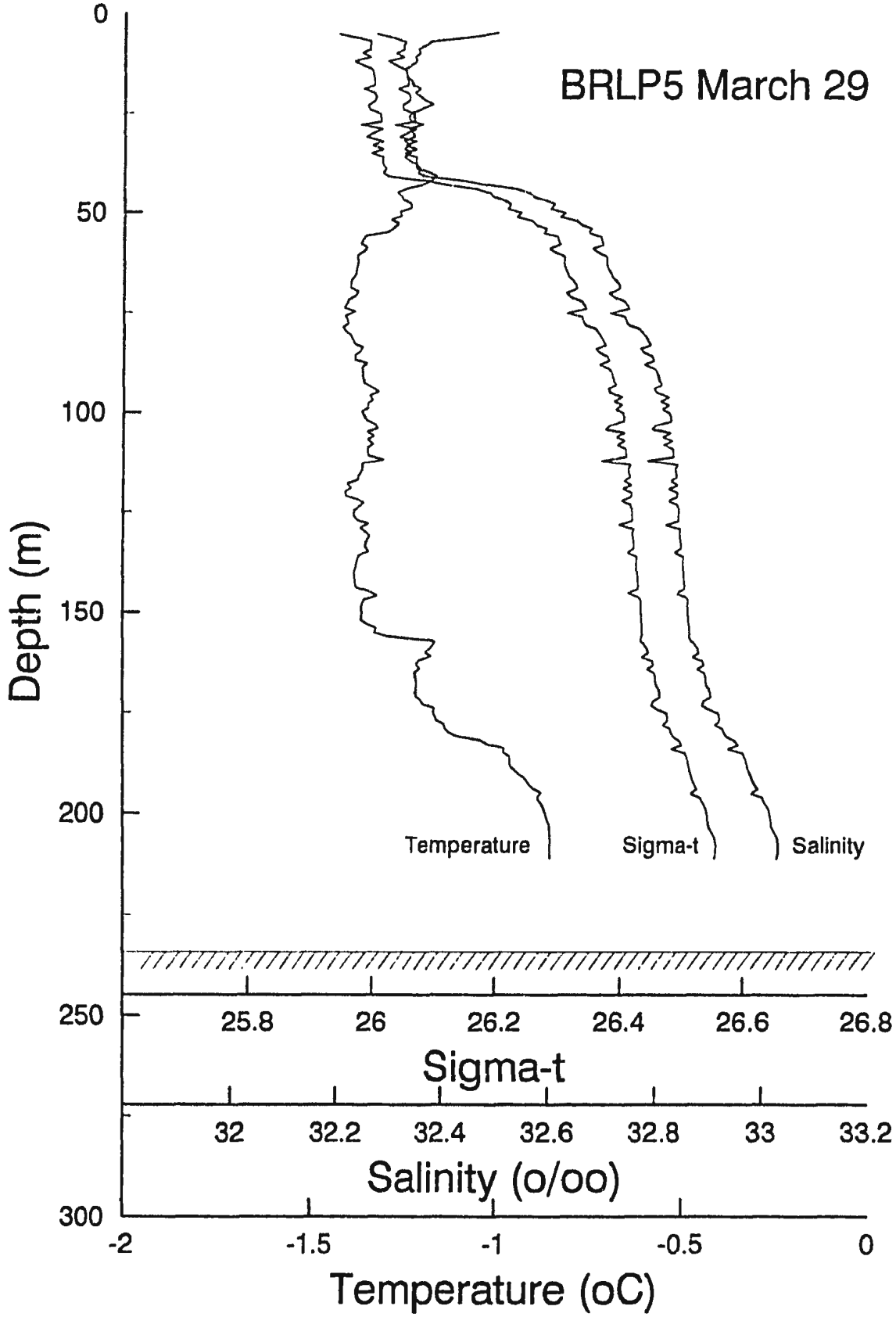

BRLP5 March 29
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
Temperature (oC)

Figure 19. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on March 29.

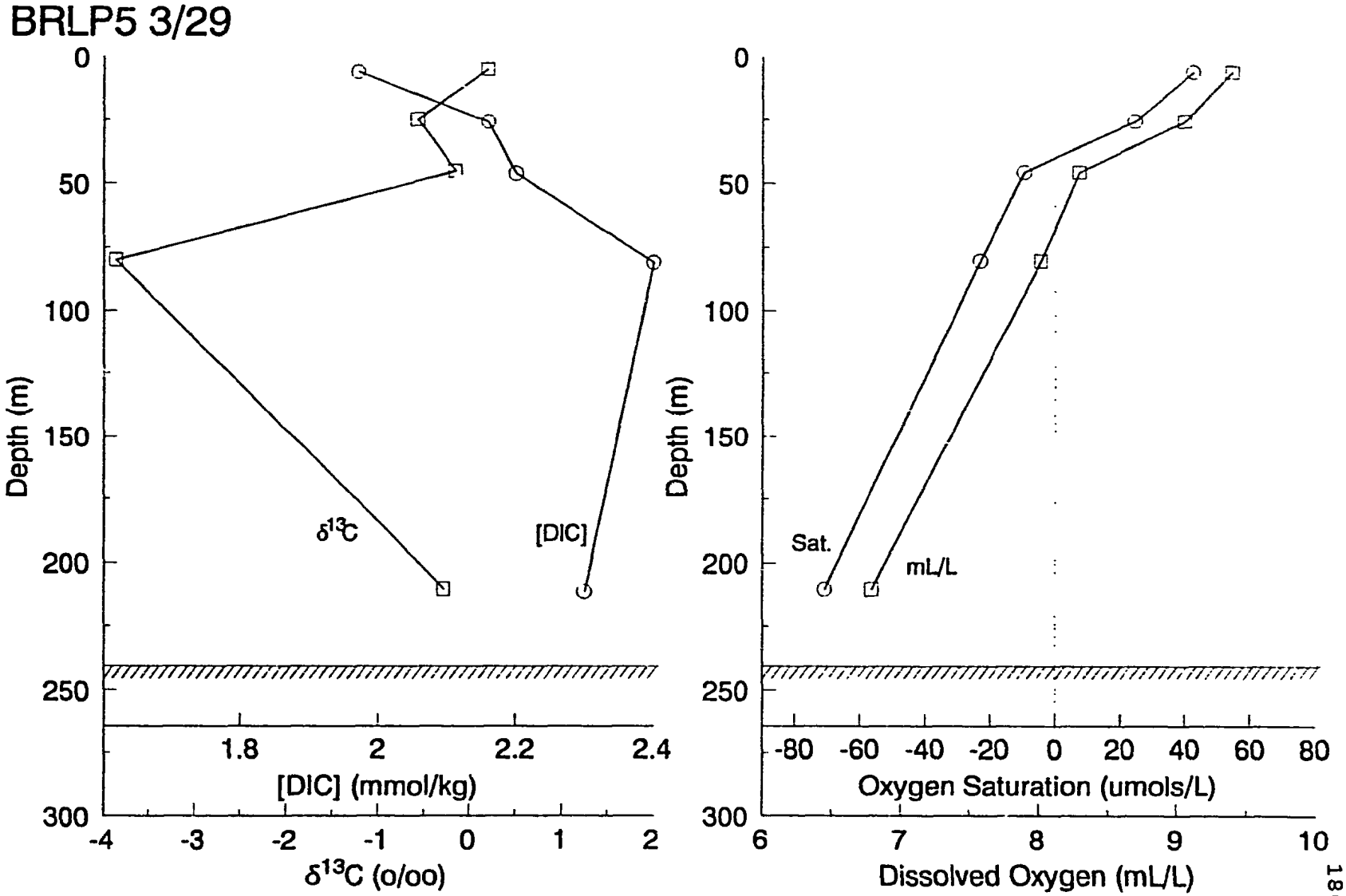

BRLP5 3/29
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umols/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 20. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on March 29.

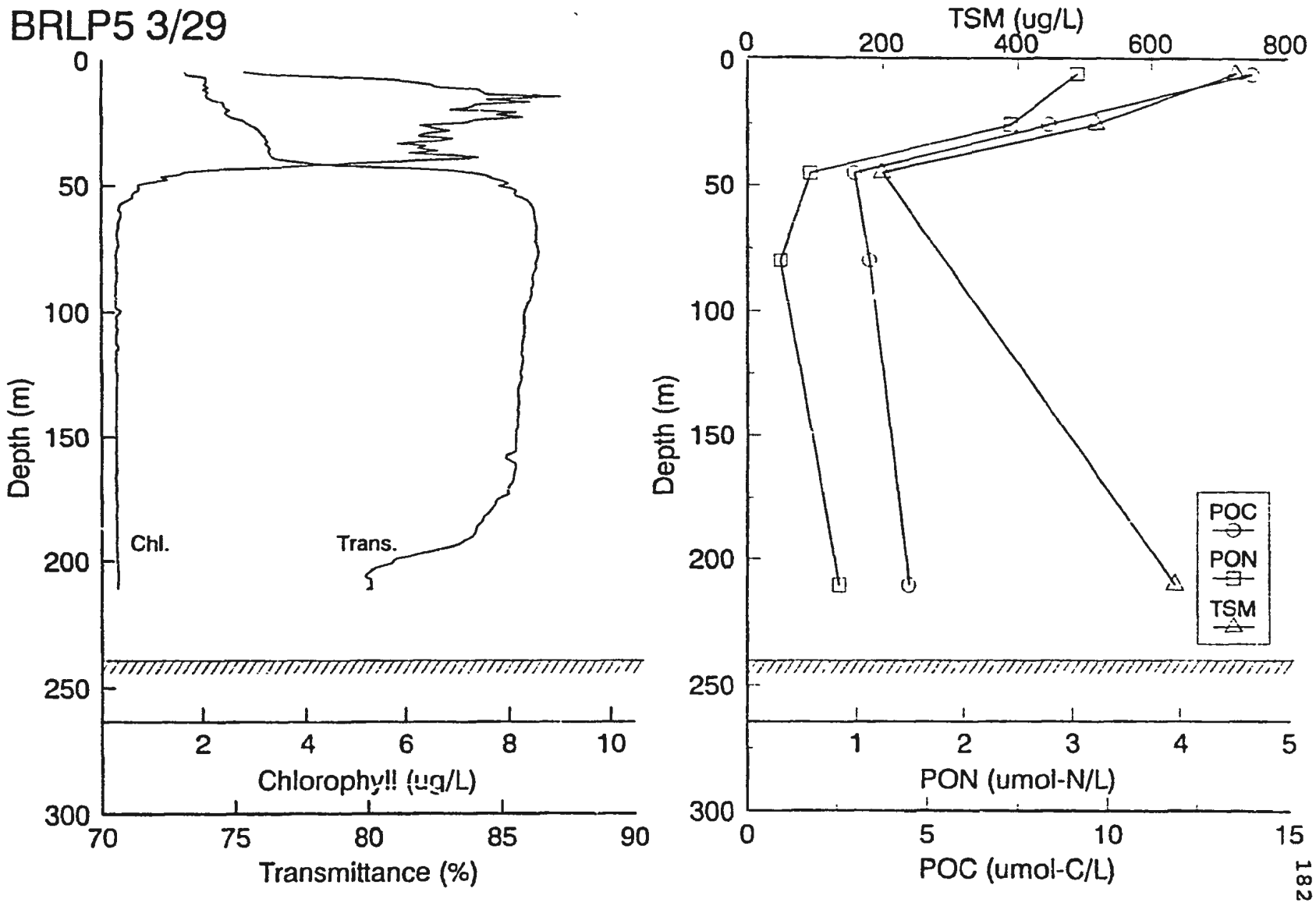

BRLP5 3/29
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
2
4
6
8
10
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 21. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on March 29.

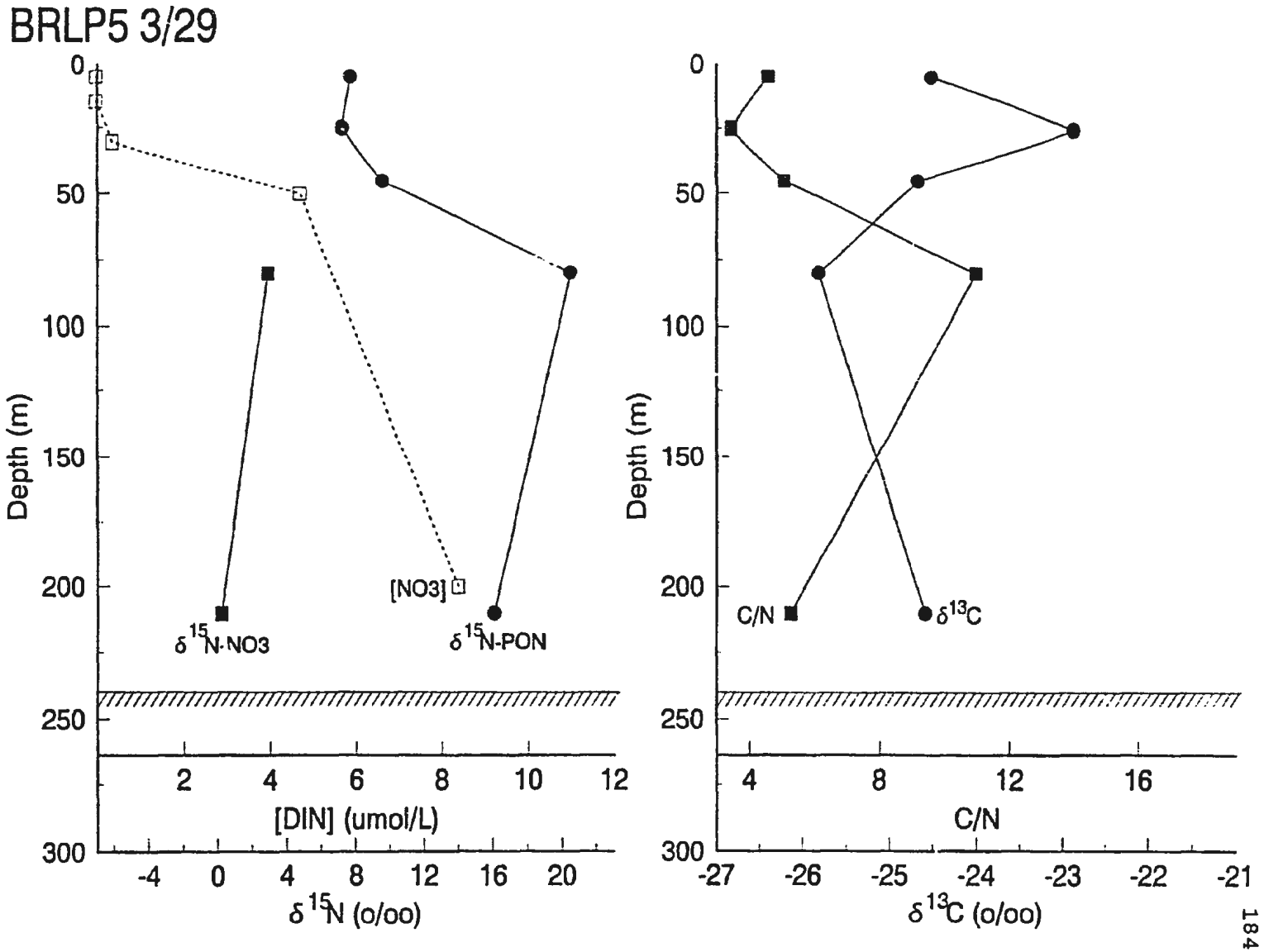

BRLP5 3/29
Depth (m)
0
50
100
150
200
250
300
[NO3]
δ15N-NO3
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 22. Salinity, temperature, and density as a function of water column depth for station BRLP5 on April 4.

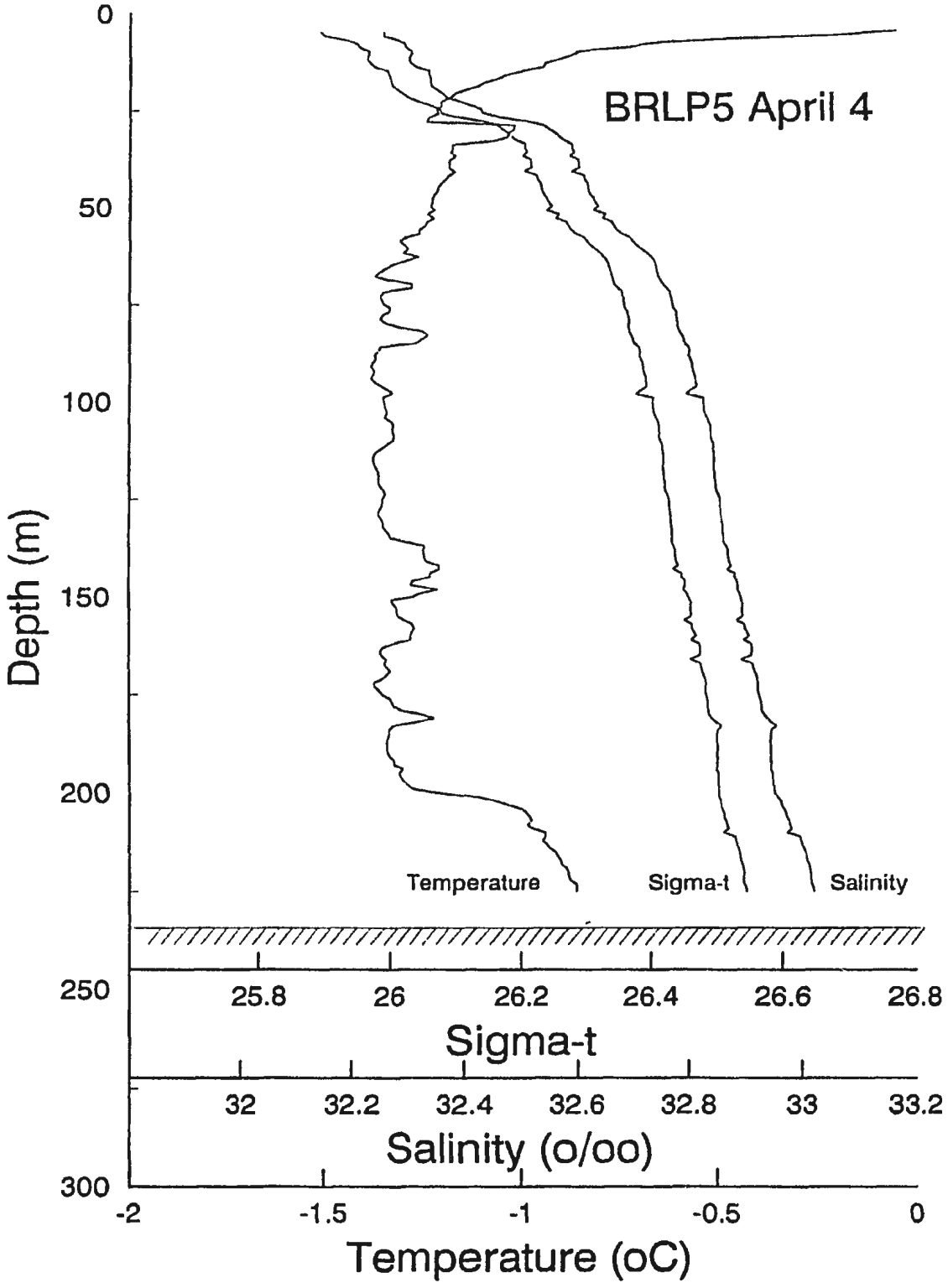

BRLP5 April 4
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
Temperature (oC)

Figure 23. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on April 4.

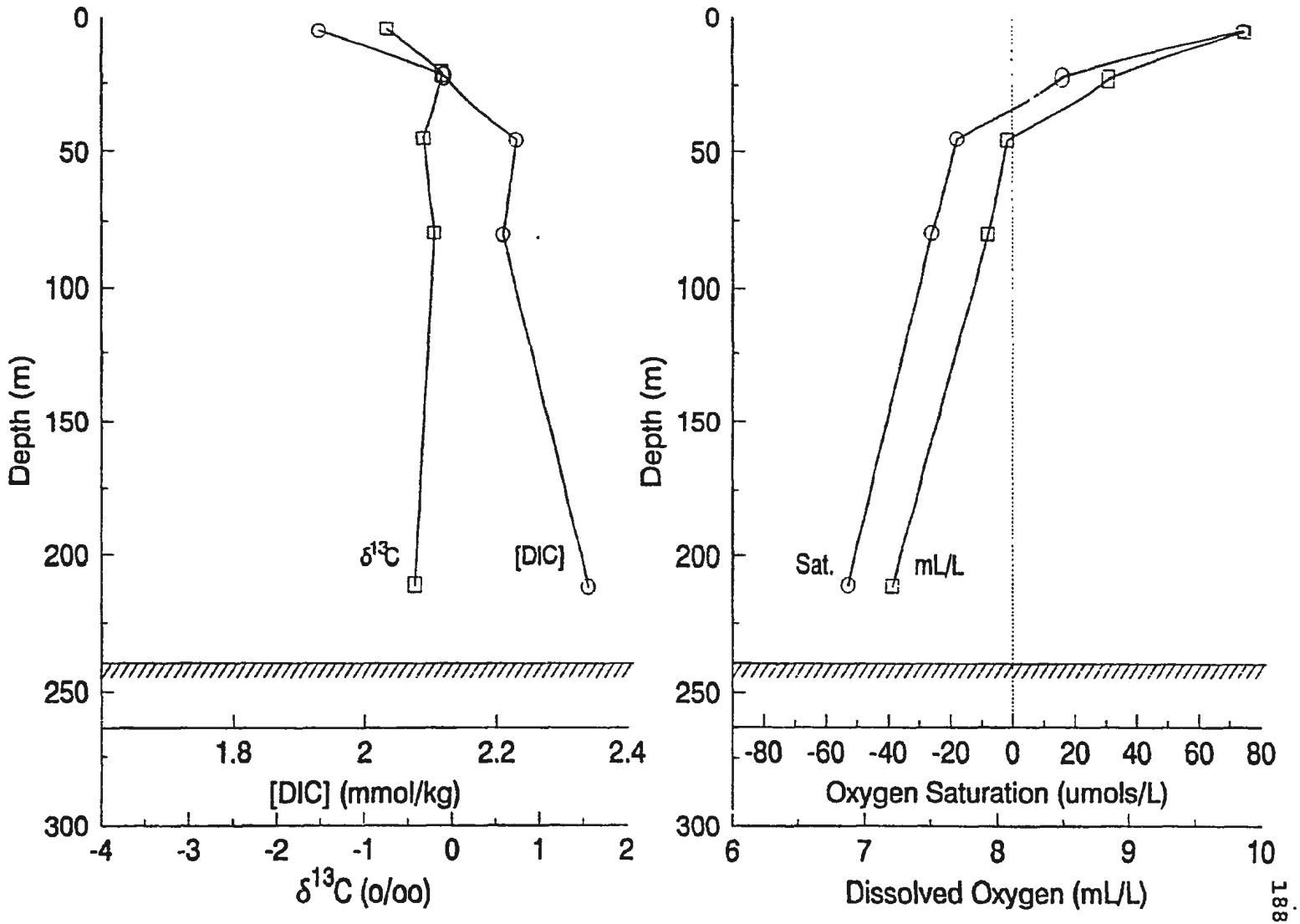

BRLP5 4/4
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umols/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 24. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on April 4.

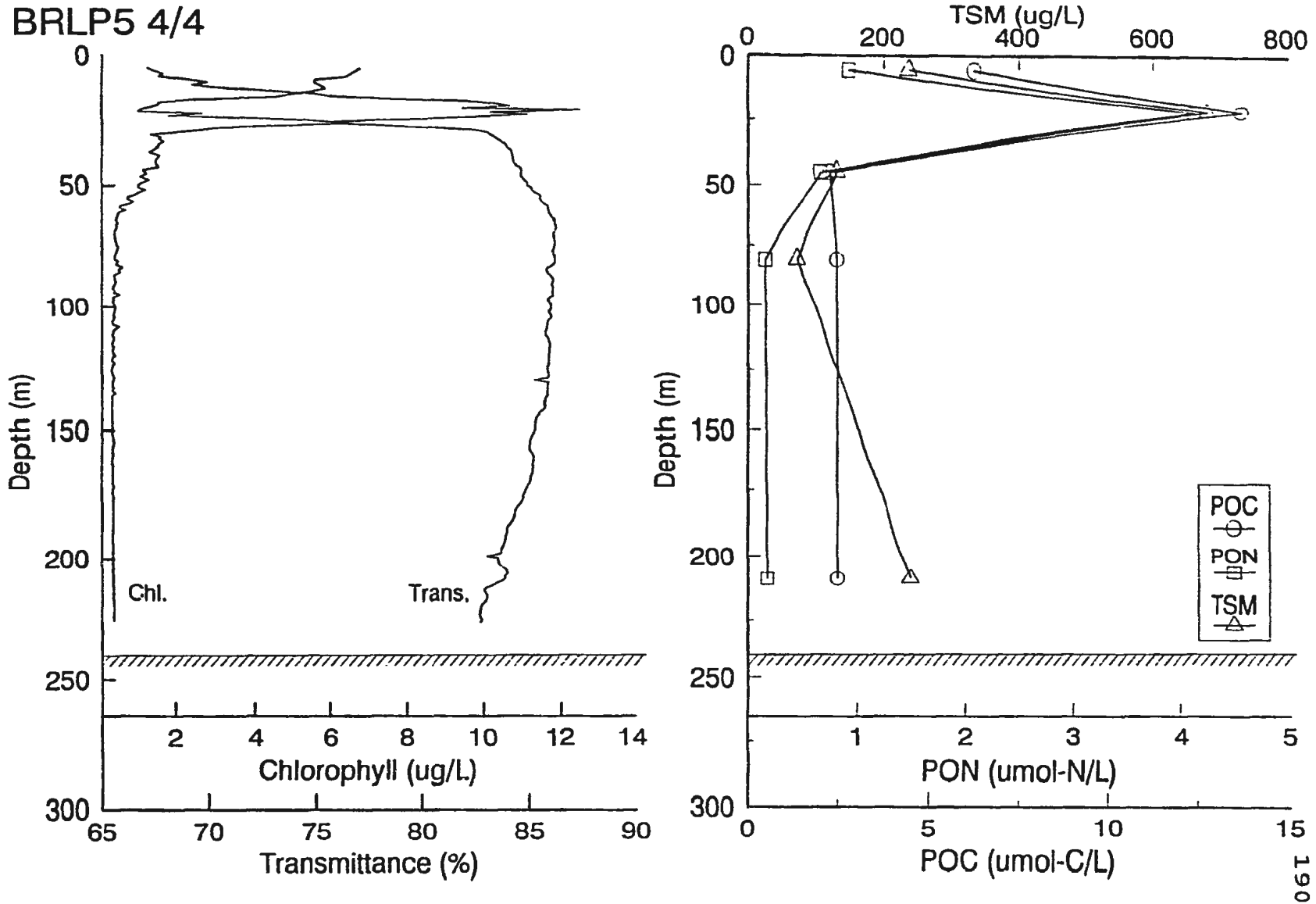

BRLP5 4/4
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
2
4
6
8
10
12
14
Chlorophyll (ug/L)
65
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)
POC
PON
TSM

Figure 25. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on April 4.

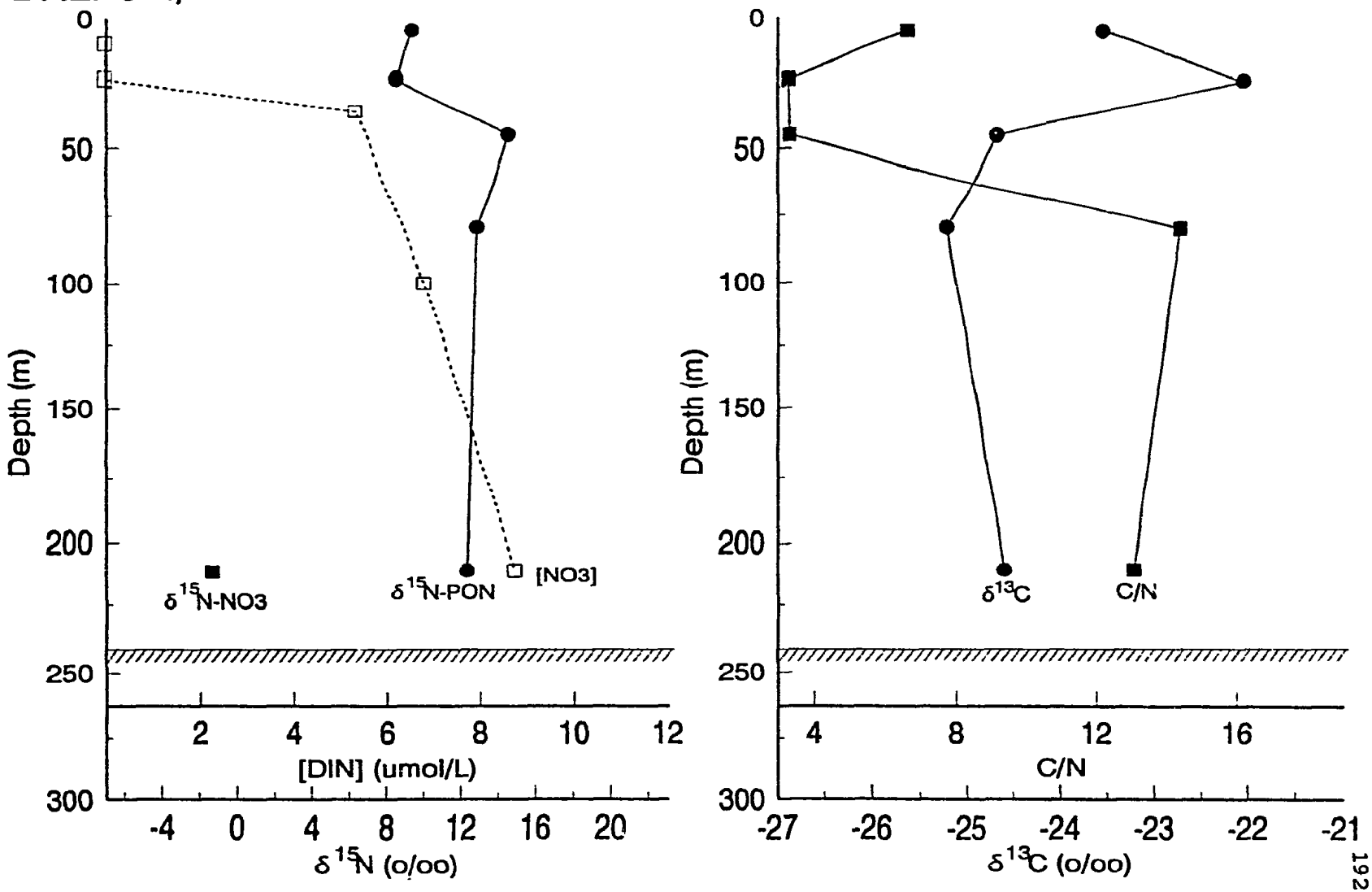

BRLP5 4/4
Depth (m)
0
50
100
150
200
250
300
δ15N-NO3
δ15N-PON
[NO3]
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
δ13C
C/N
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 26. Salinity, temperature and density as a function of water column depth for station BRLP5 on April 18.

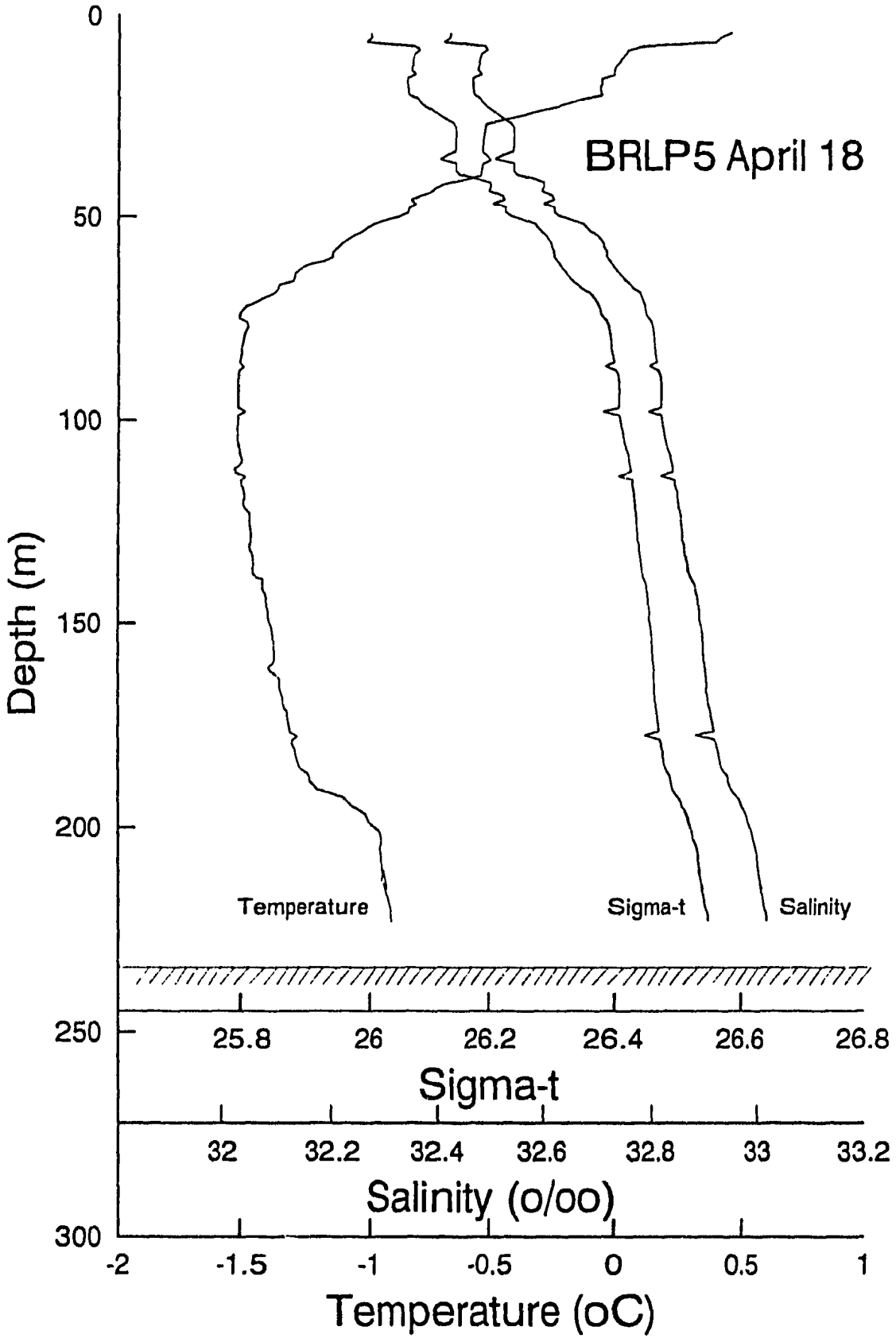

BRLP5 April 18
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
0.5
1
Temperature (oC)

Figure 27. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on April 18.

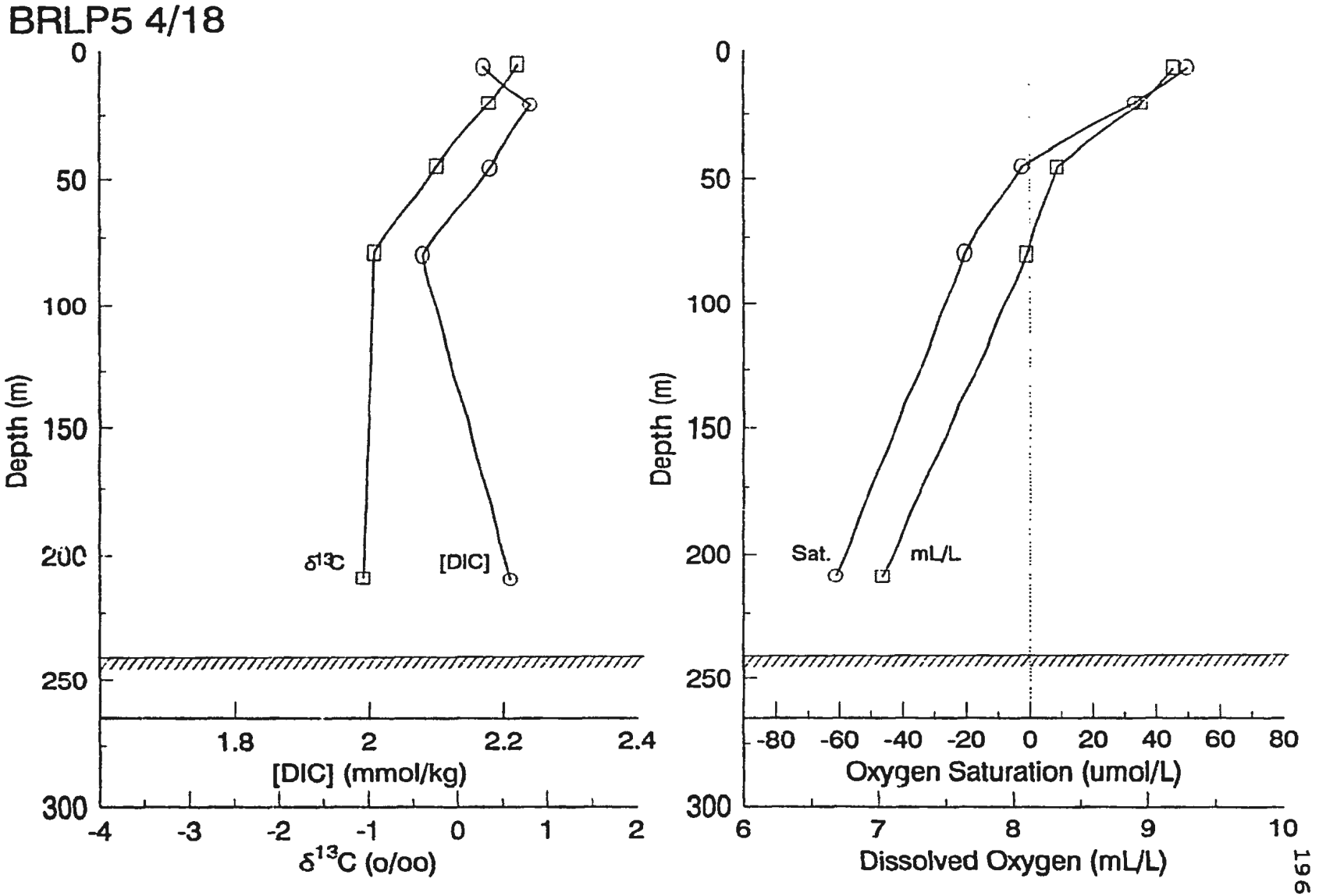

BRLP5 4/18
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 28. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on April 18.

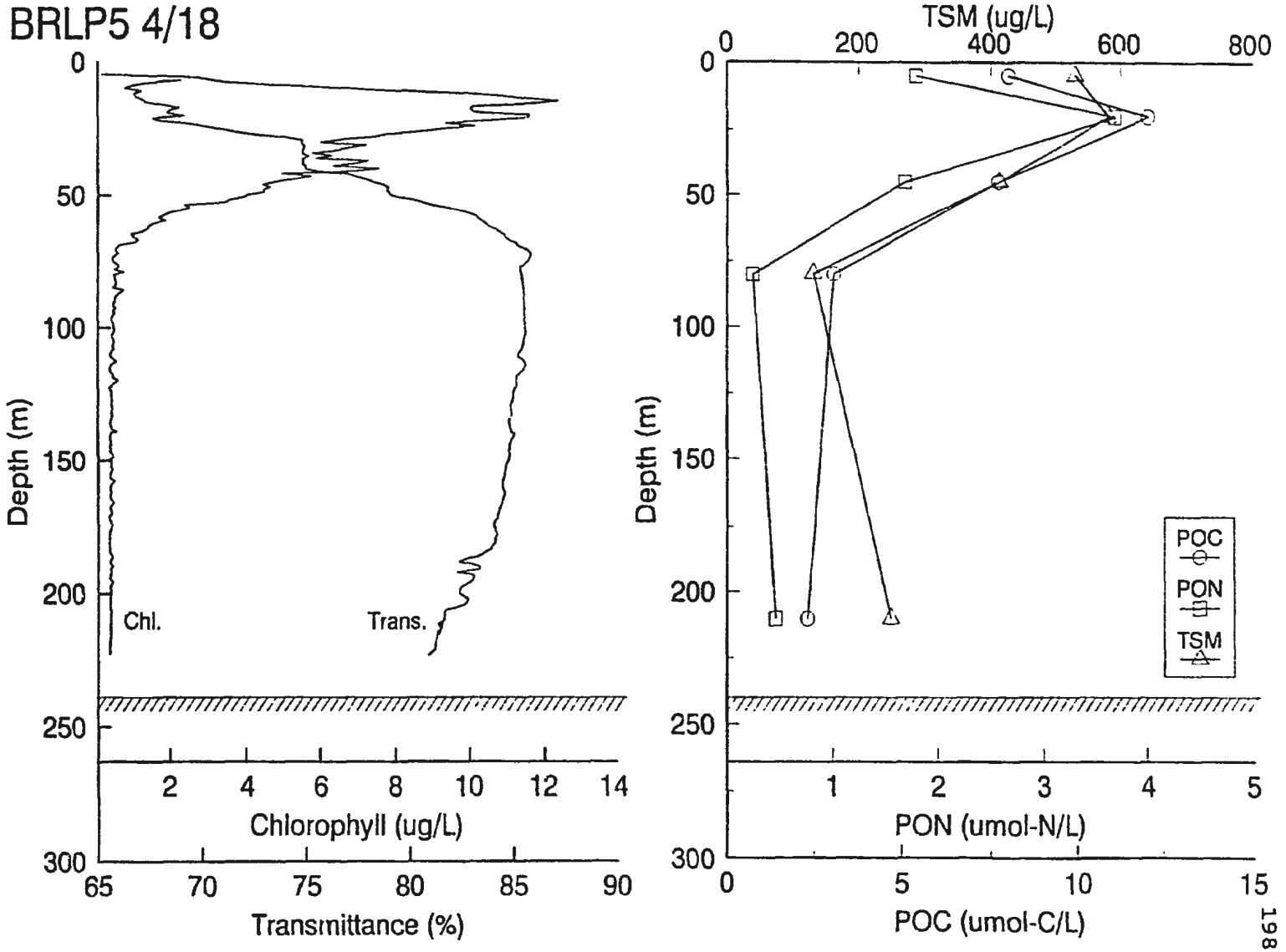

BRLP5 4/18
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
2
4
6
8
10
12
14
Chlorophyll (ug/L)
65
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)
POC
PON
TSM

Figure 29. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on April 18.

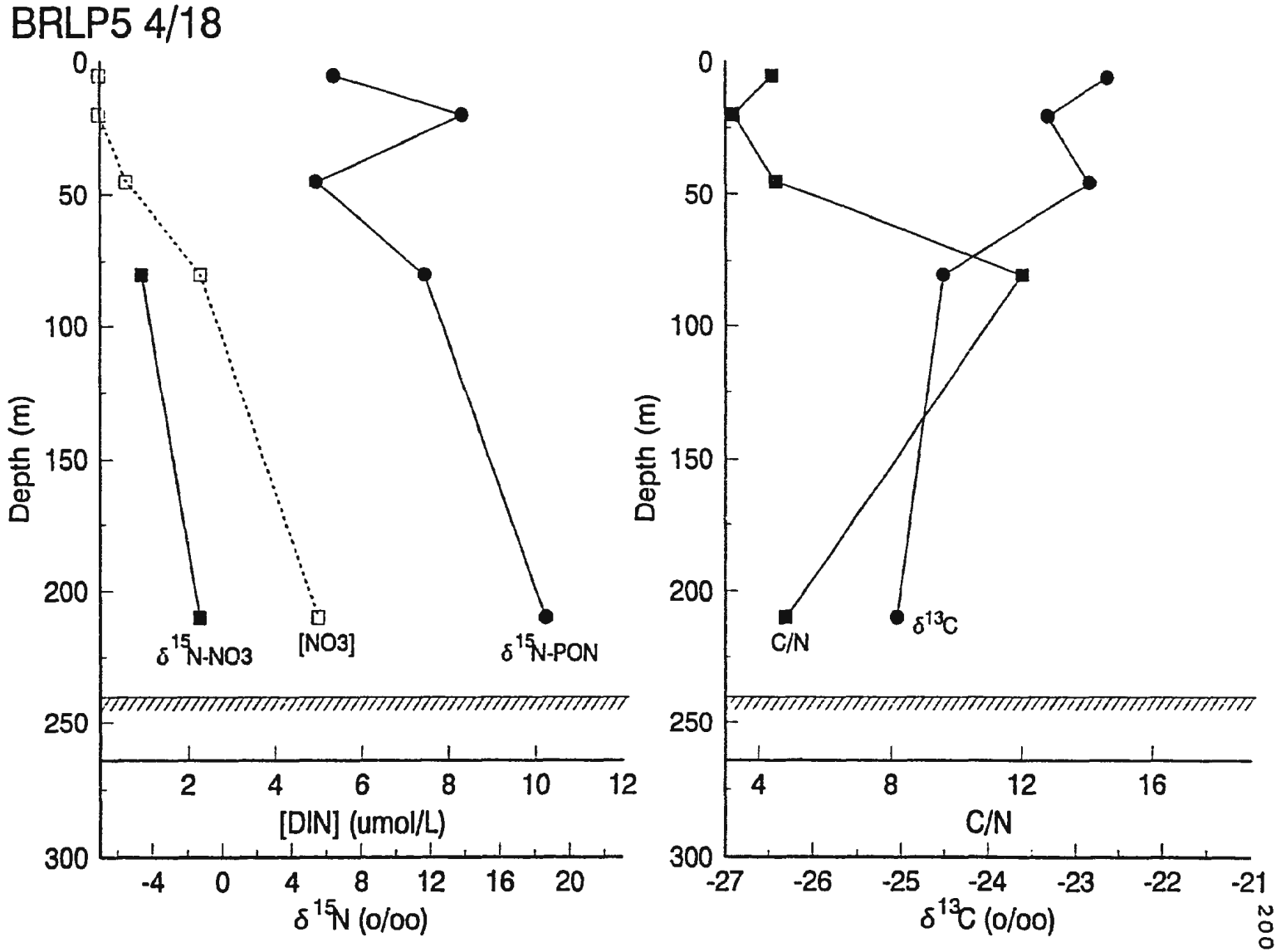

BRLP5 4/18
Depth (m)
0
50
100
150
200
250
300
δ15N-NO3
[NO3]
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 30. Salinity, temperature and density as a function of water column depth for station BRLP5 on April 29.

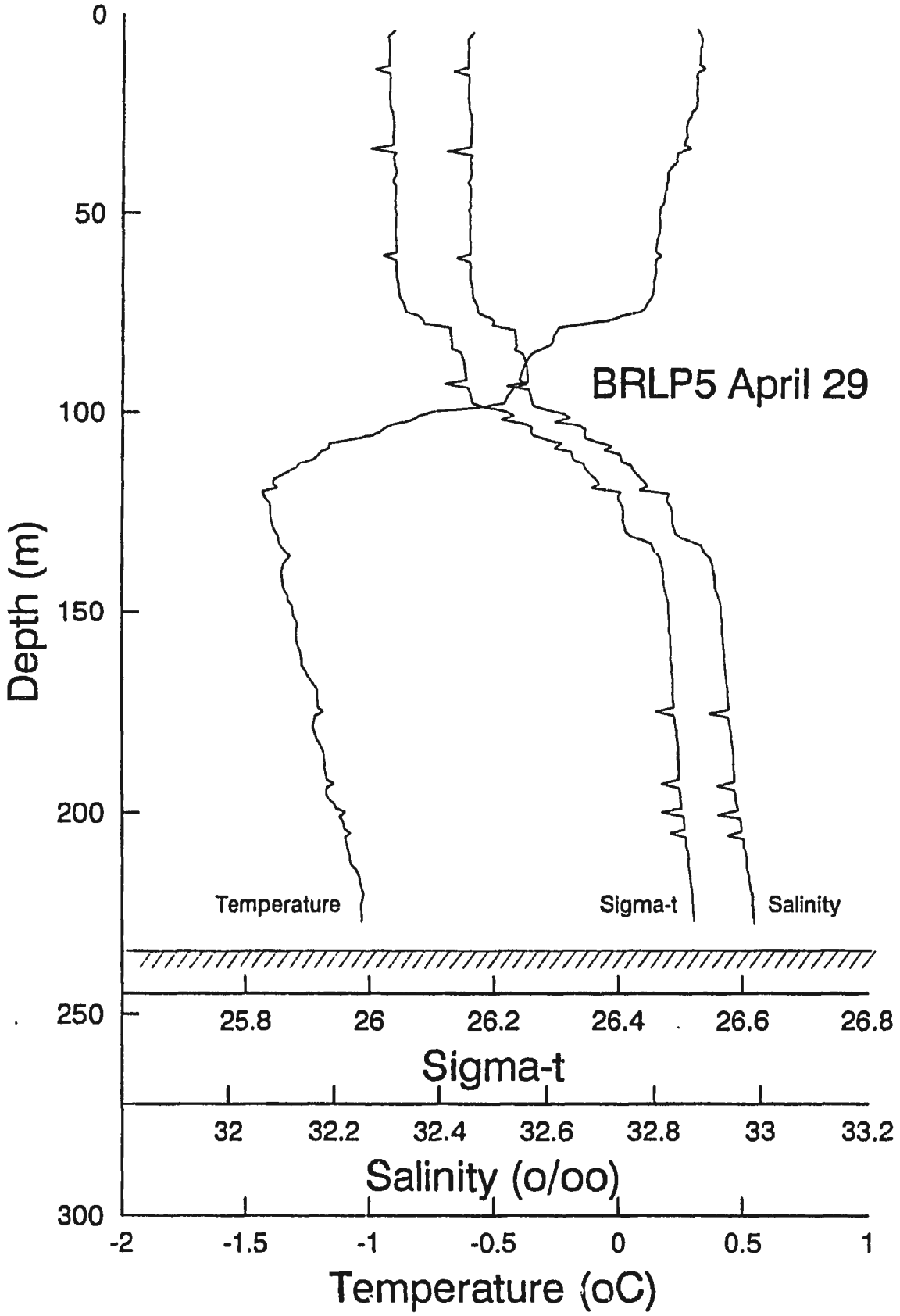

BRLP5 April 29
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
0.5
1
Temperature (oC)

Figure 31. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on April 29.

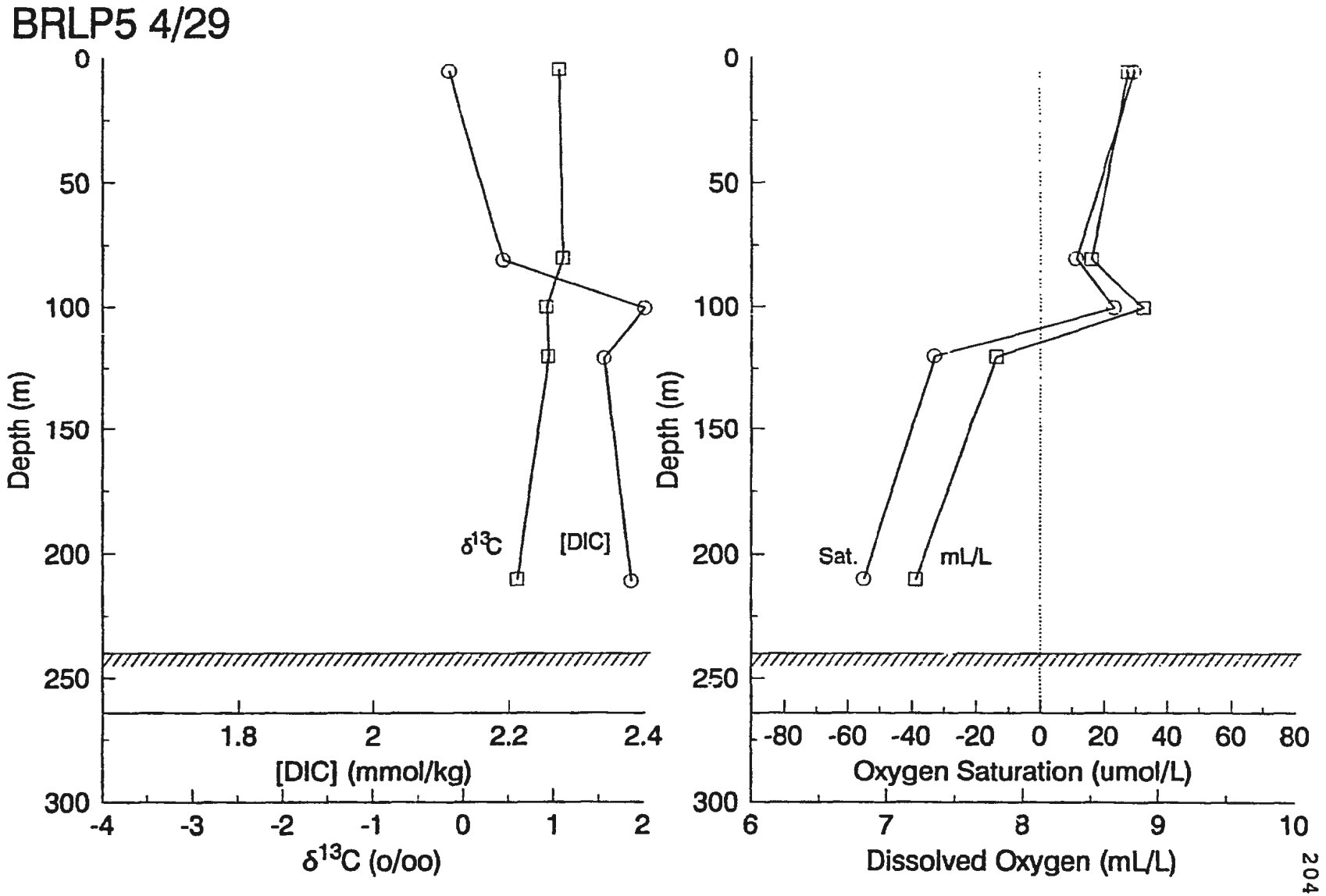

BRLP5 4/29
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 32. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on April 29.

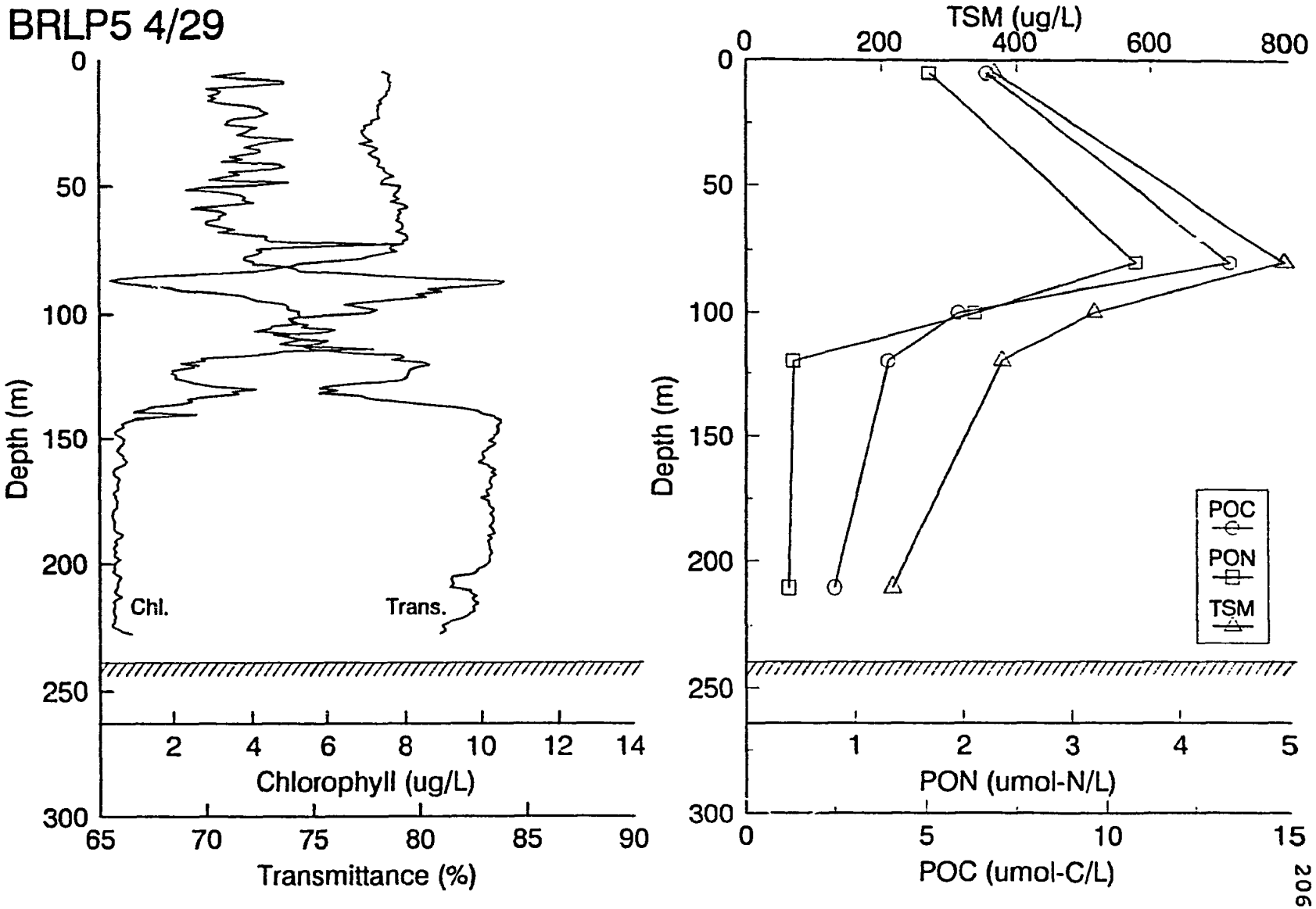

BRLP5 4/29
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
2
4
6
8
10
12
14
Chlorophyll (ug/L)
65
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 33. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on April 29.

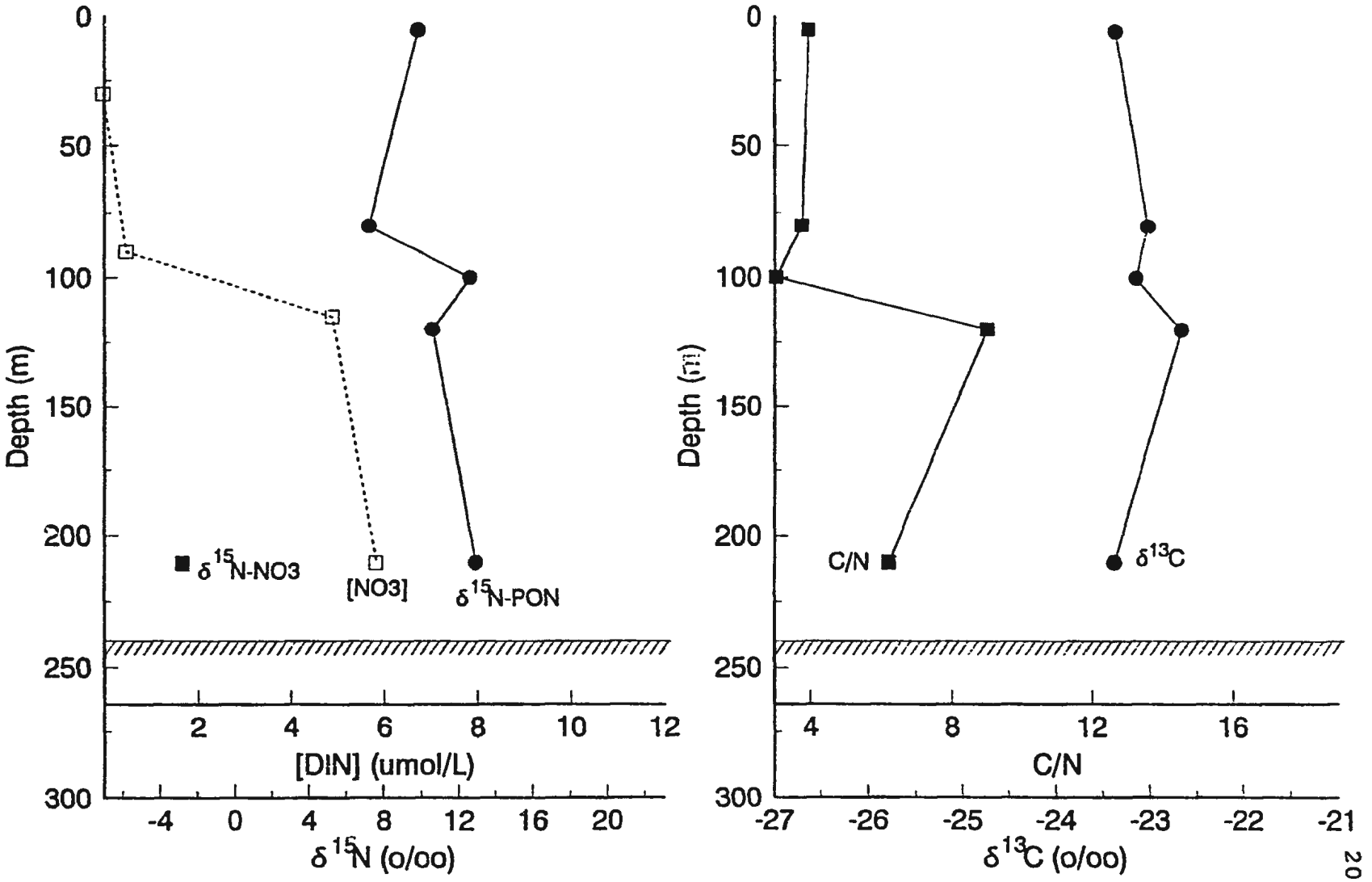

BRLP5 4/29
Depth (m)
0
50
100
150
200
250
300
δ15N-NO3
[NO3]
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 34. Salinity, temperature and density as a function of water column depth for station BRLP5 on May 2.

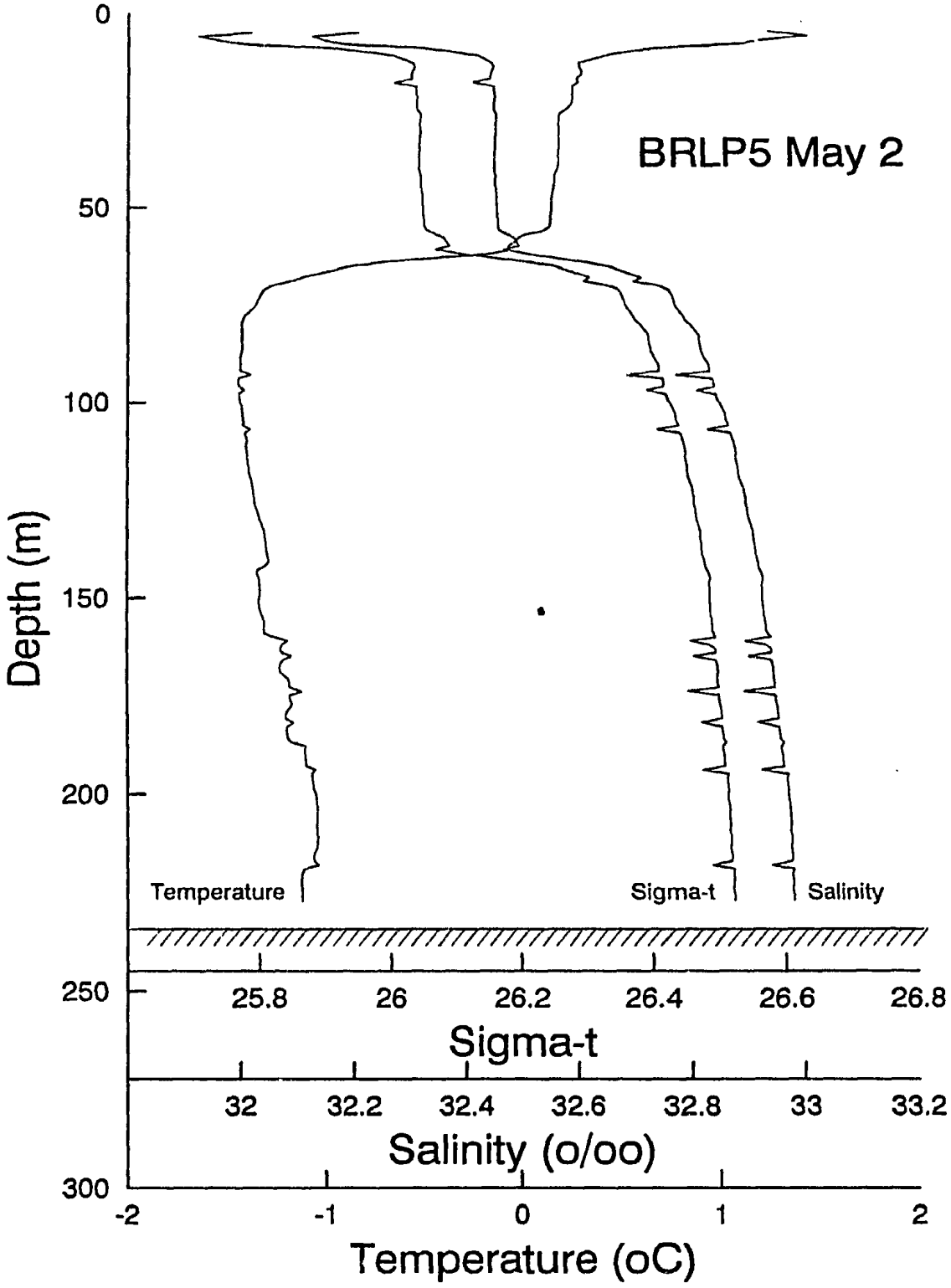

BRLP5 May 2
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1
0
1
2
Temperature (oC)

Figure 35. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on May 2.

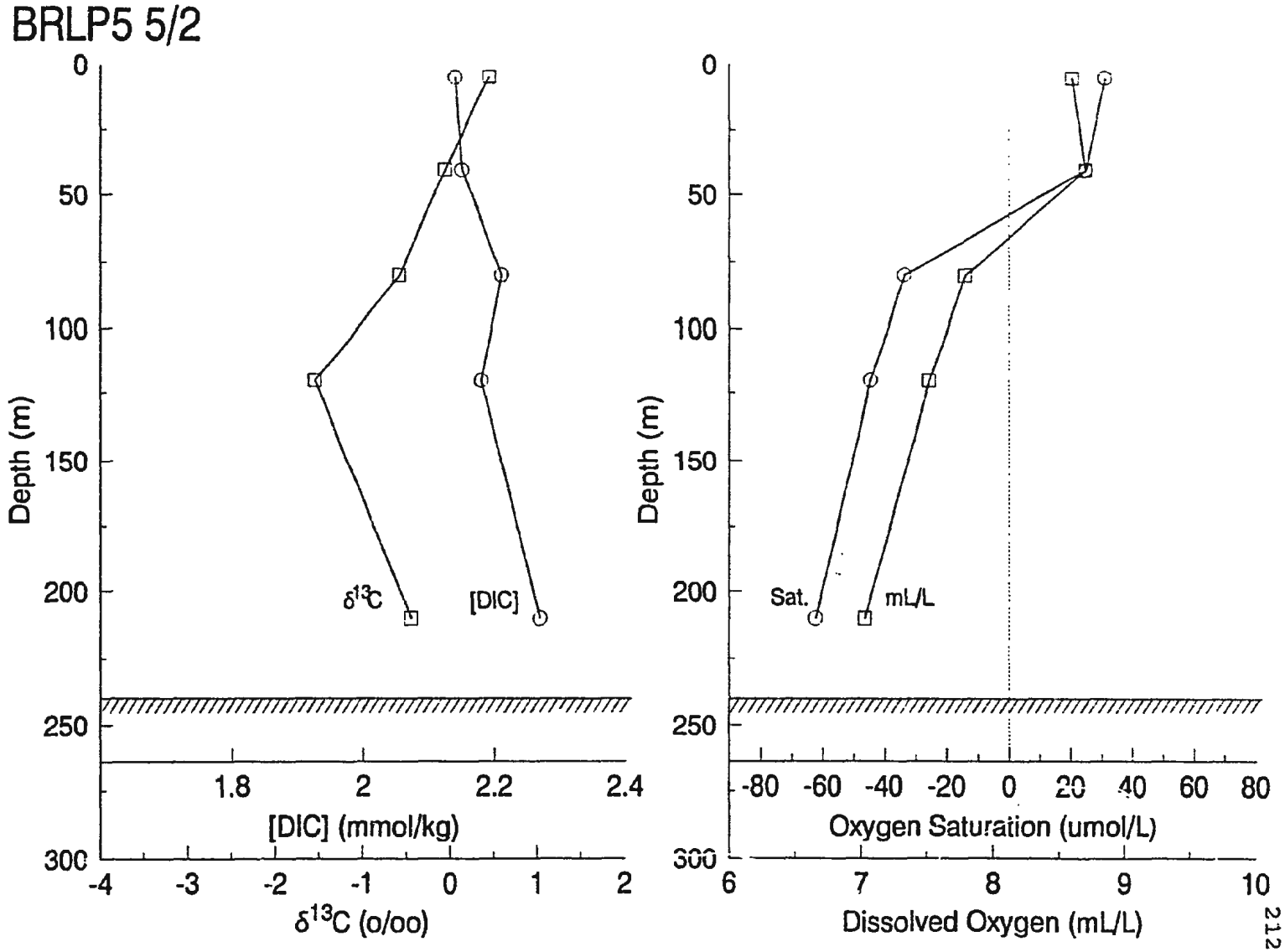

BRLP5 5/2
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 36. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on May 2.

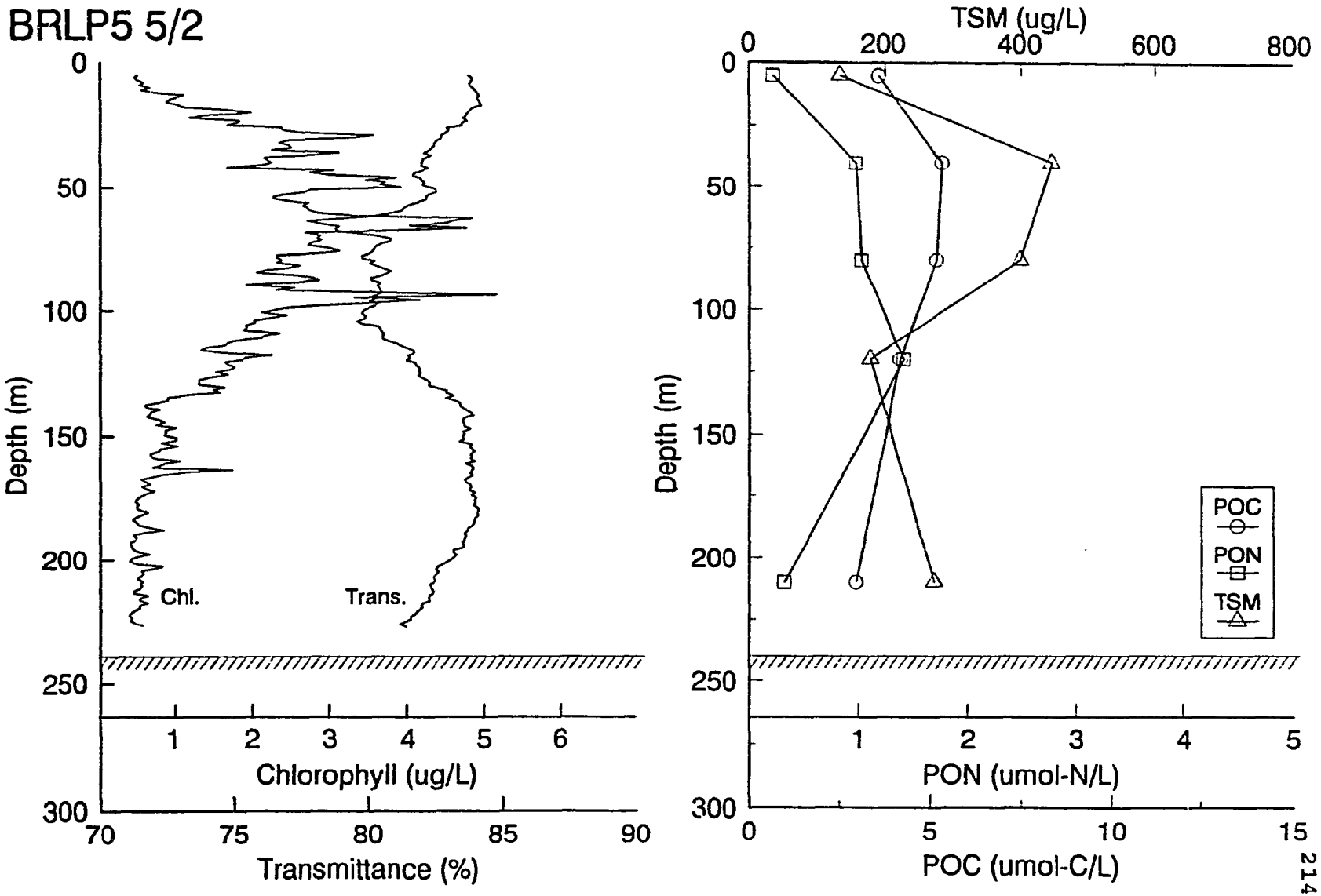

BRLP5 5/2
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
1
2
3
4
5
6
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 37. Isotopic composition of PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on May 2.

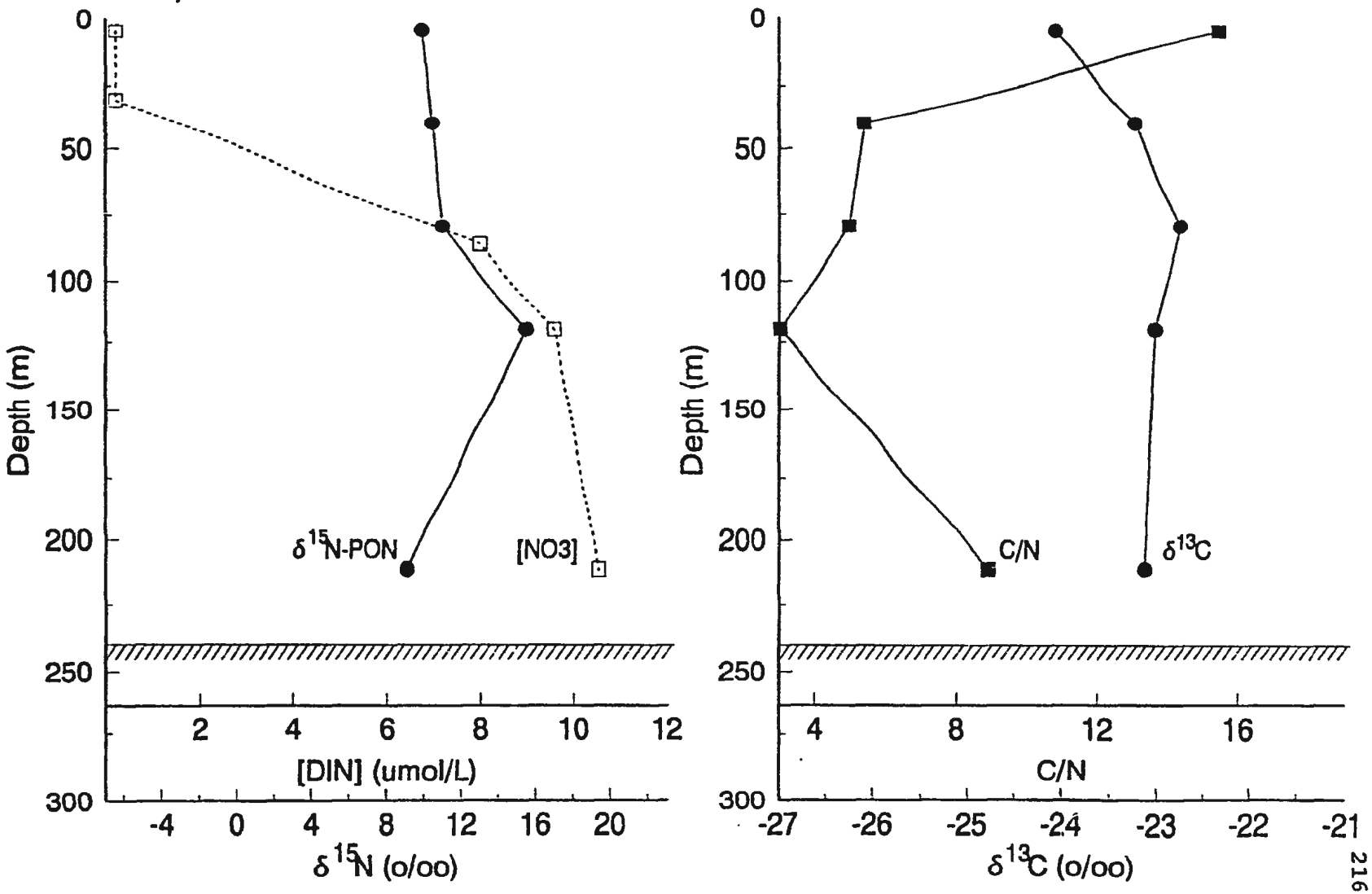

BRLP5 5/2
Depth (m)
0
50
100
150
200
250
300
δ15N-PON
[NO3]
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 38. Salinity, temperature and density as a function of water column depth for station BRLP5 on May 6.

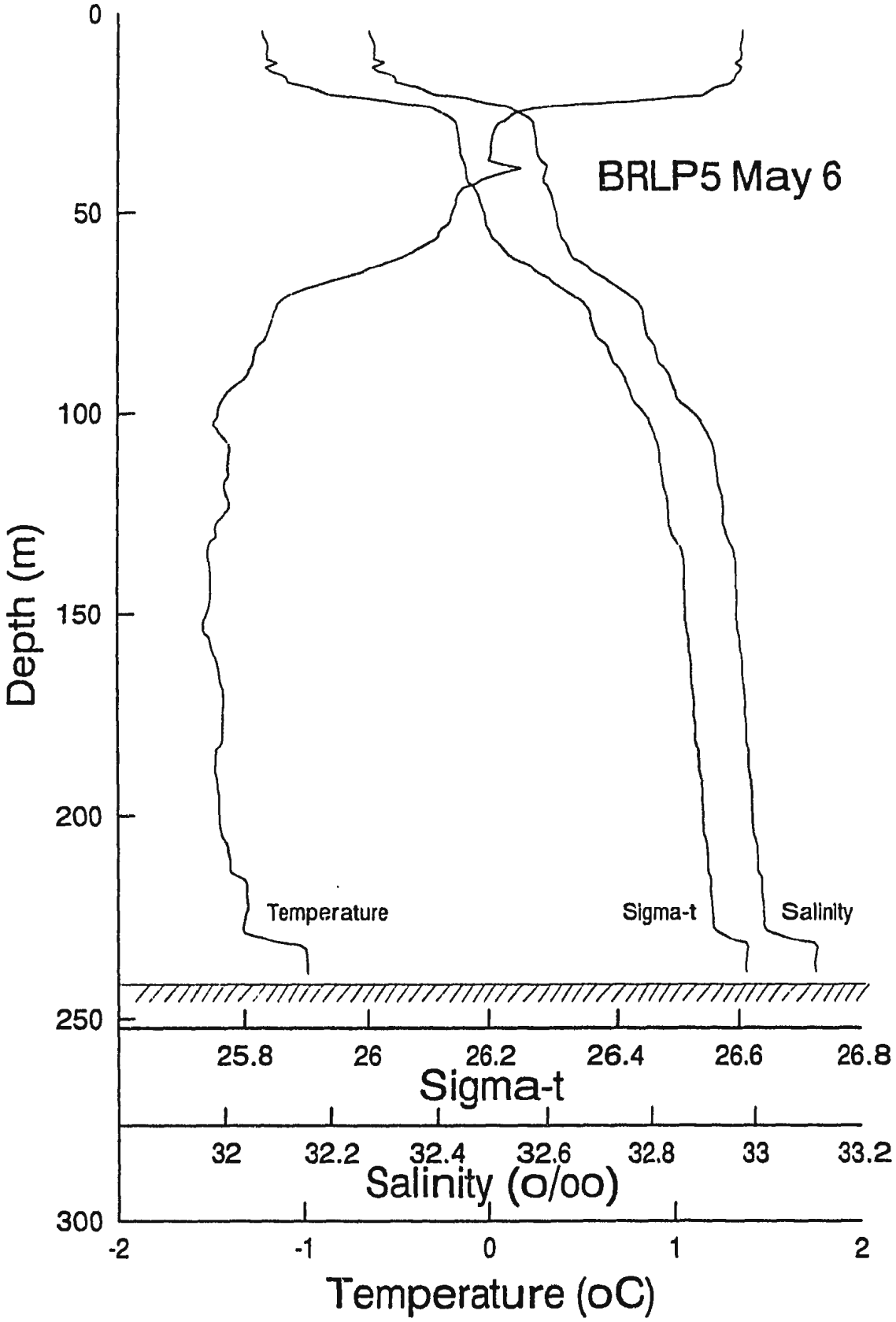

BRLP5 May 6
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1
0
1
2
Temperature (oC)

Figure 39. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on May 6.

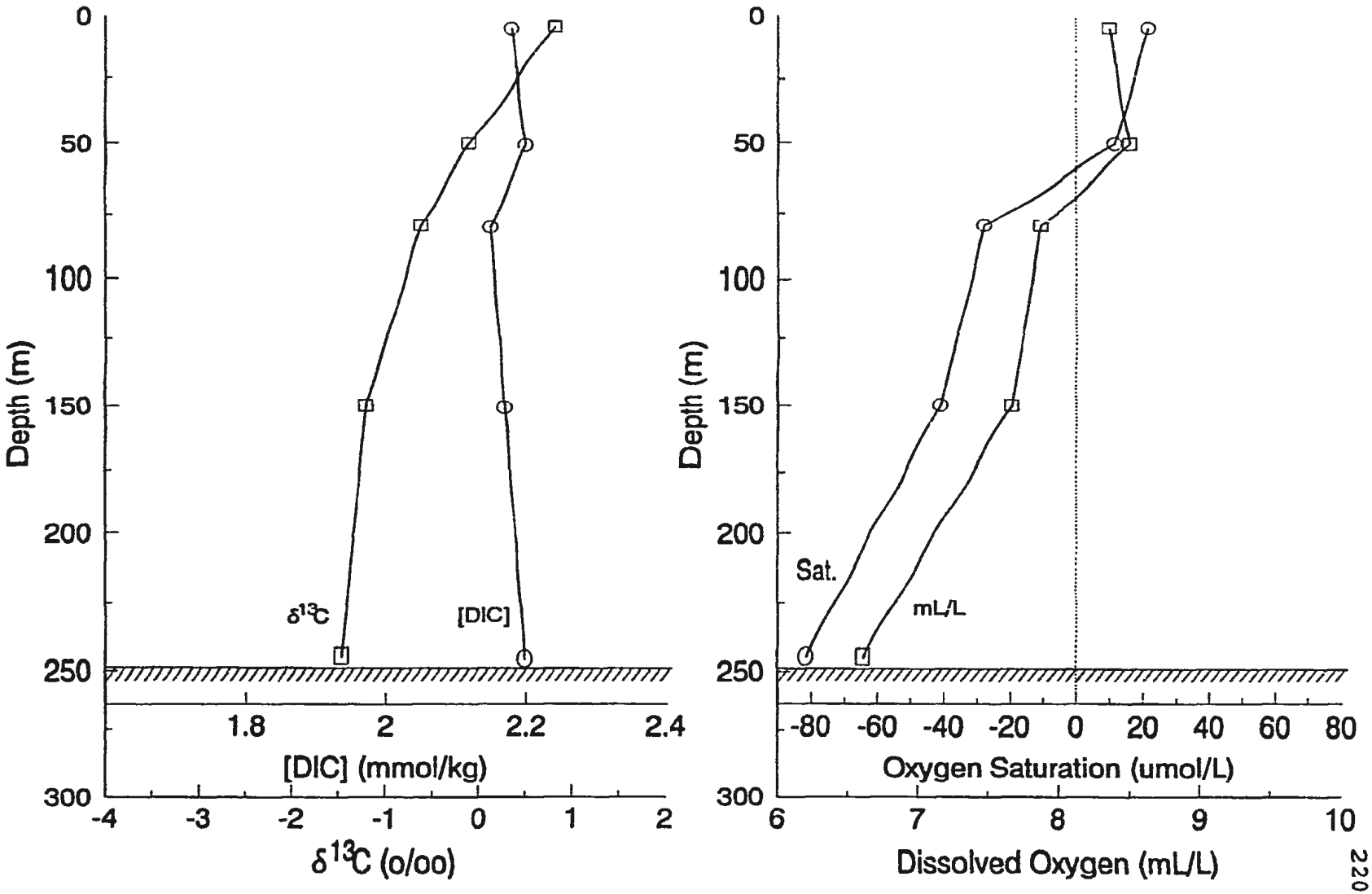

BRLP5 5/6
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 40. Concentrations of particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on May 6.

BRLP5 5/6

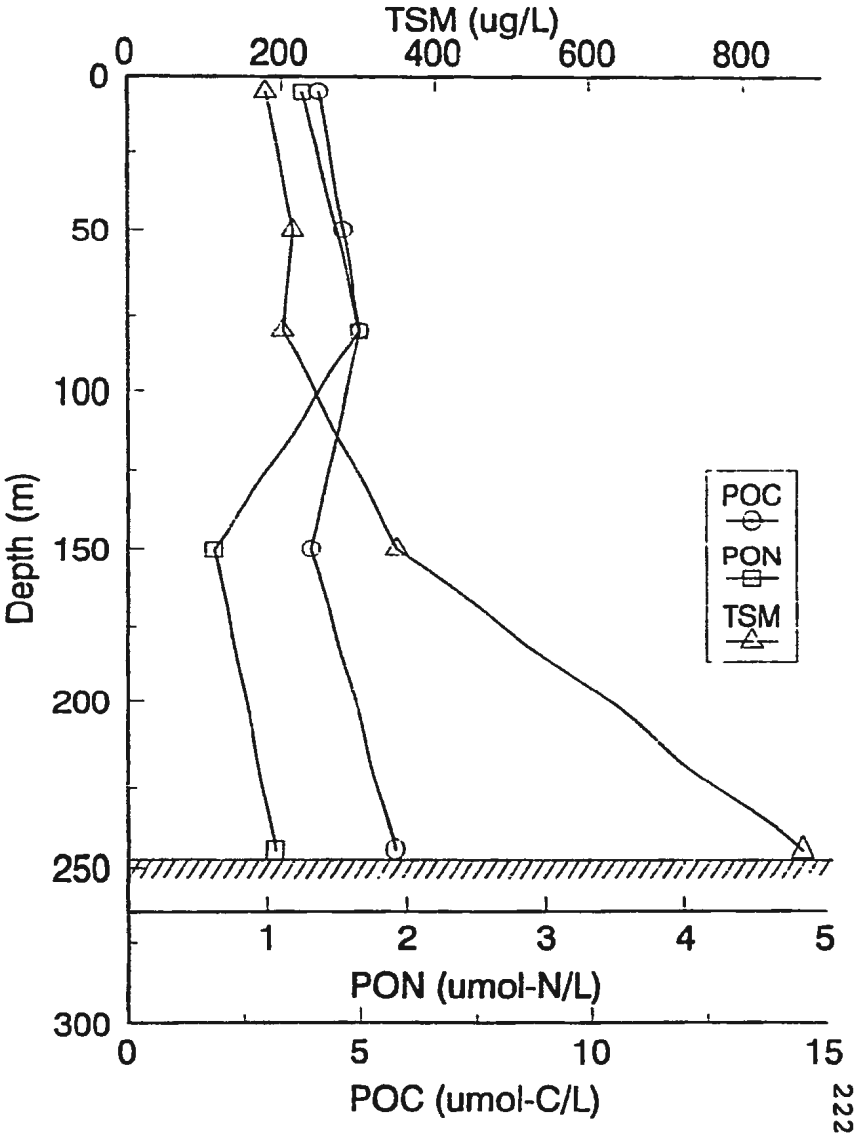

TSM (ug/L)
0
200
400
600
800
0
50
100
150
200
250
300
Depth (m)
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 41. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on May 6.

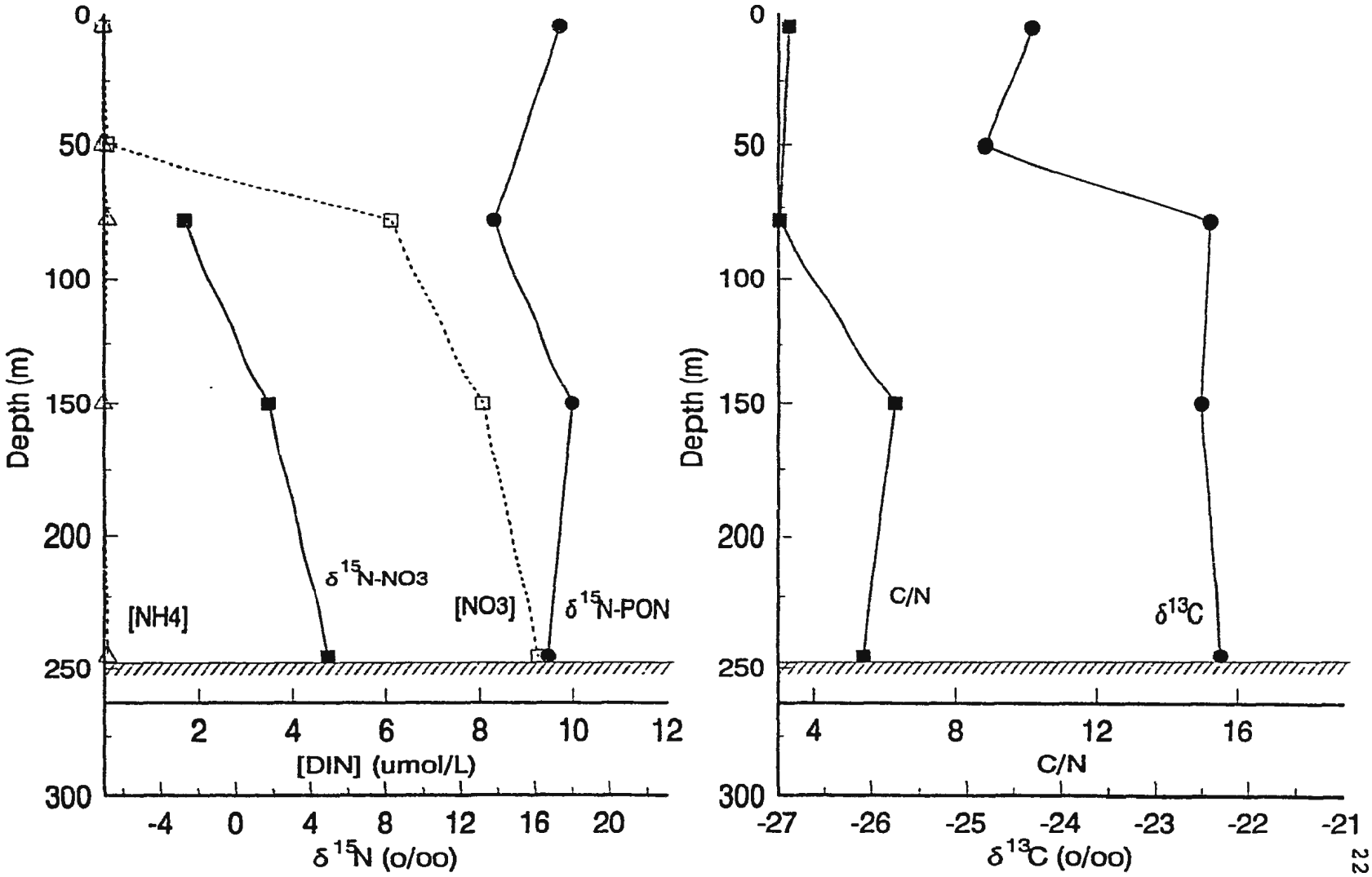

BRLP5 5/6
Depth (m)
0
50
100
150
200
250
300
[NH4]
δ15N-NO3
[NO3]
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 42. Salinity, temperature and density as a function of water column depth for station BRLP5 on May 20.

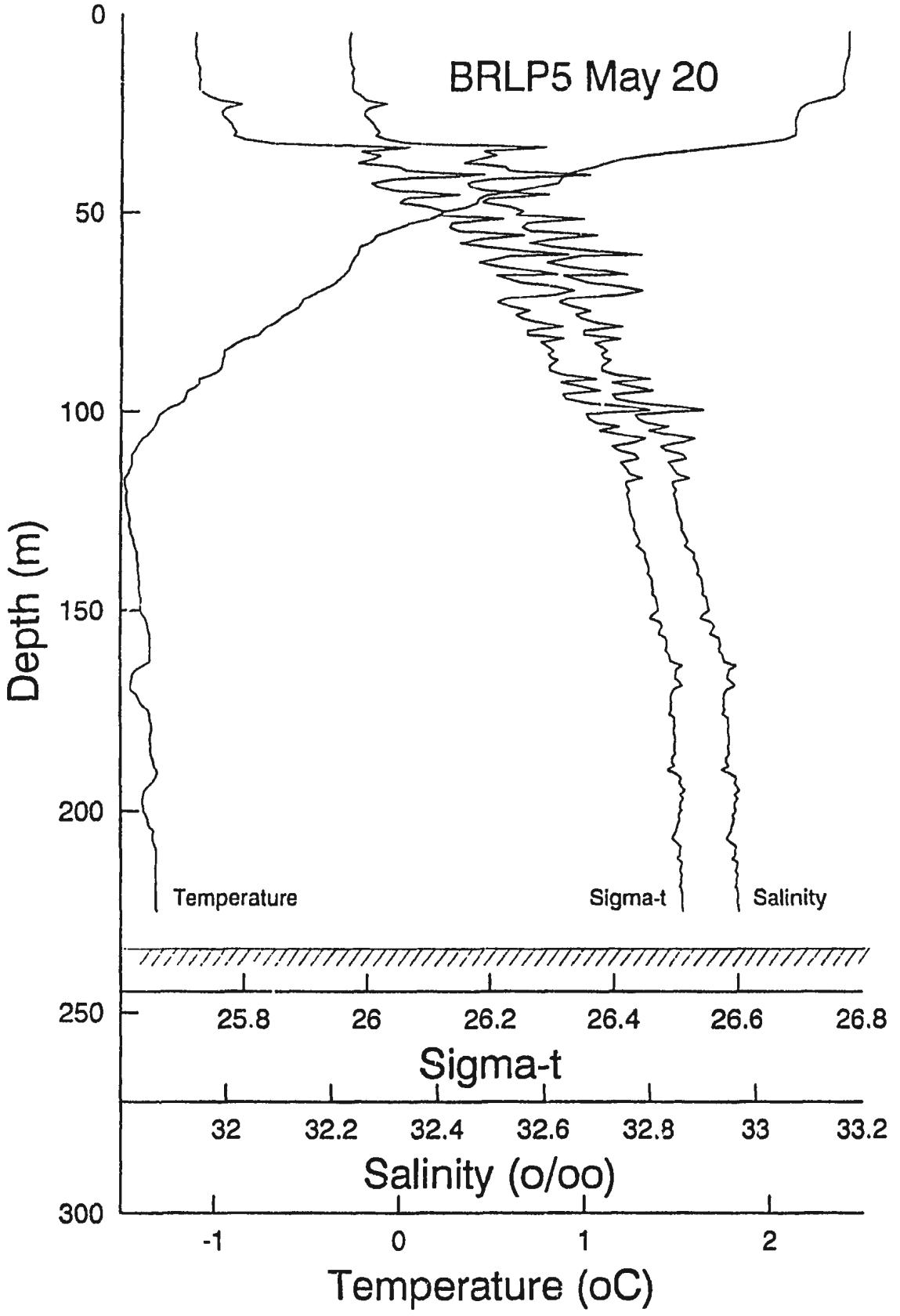

BRLP5 May 20
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-1
0
1
2
Temperature (oC)

Figure 43. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on May 20.

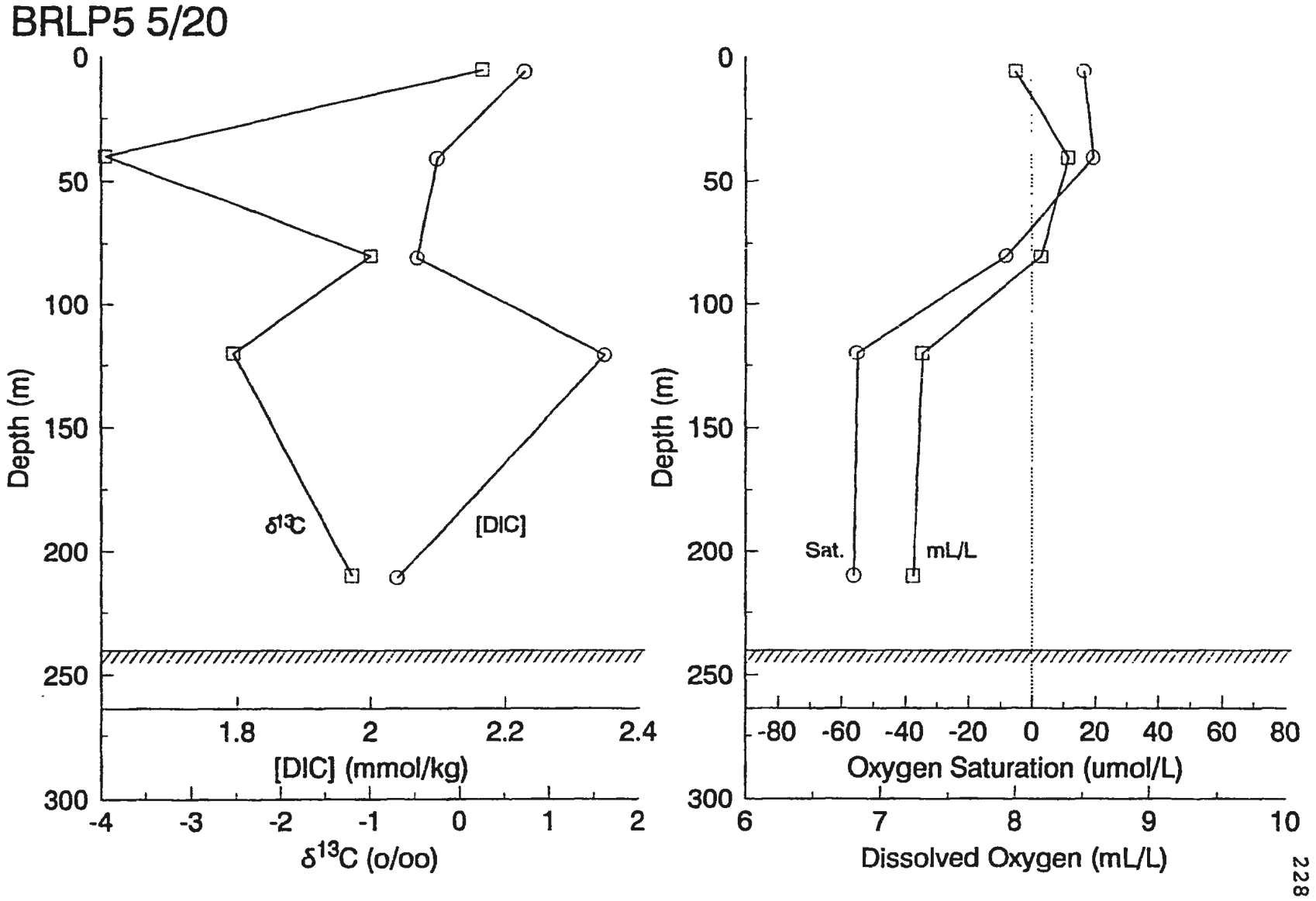

BRLP5 5/20
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 44. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on May 20.

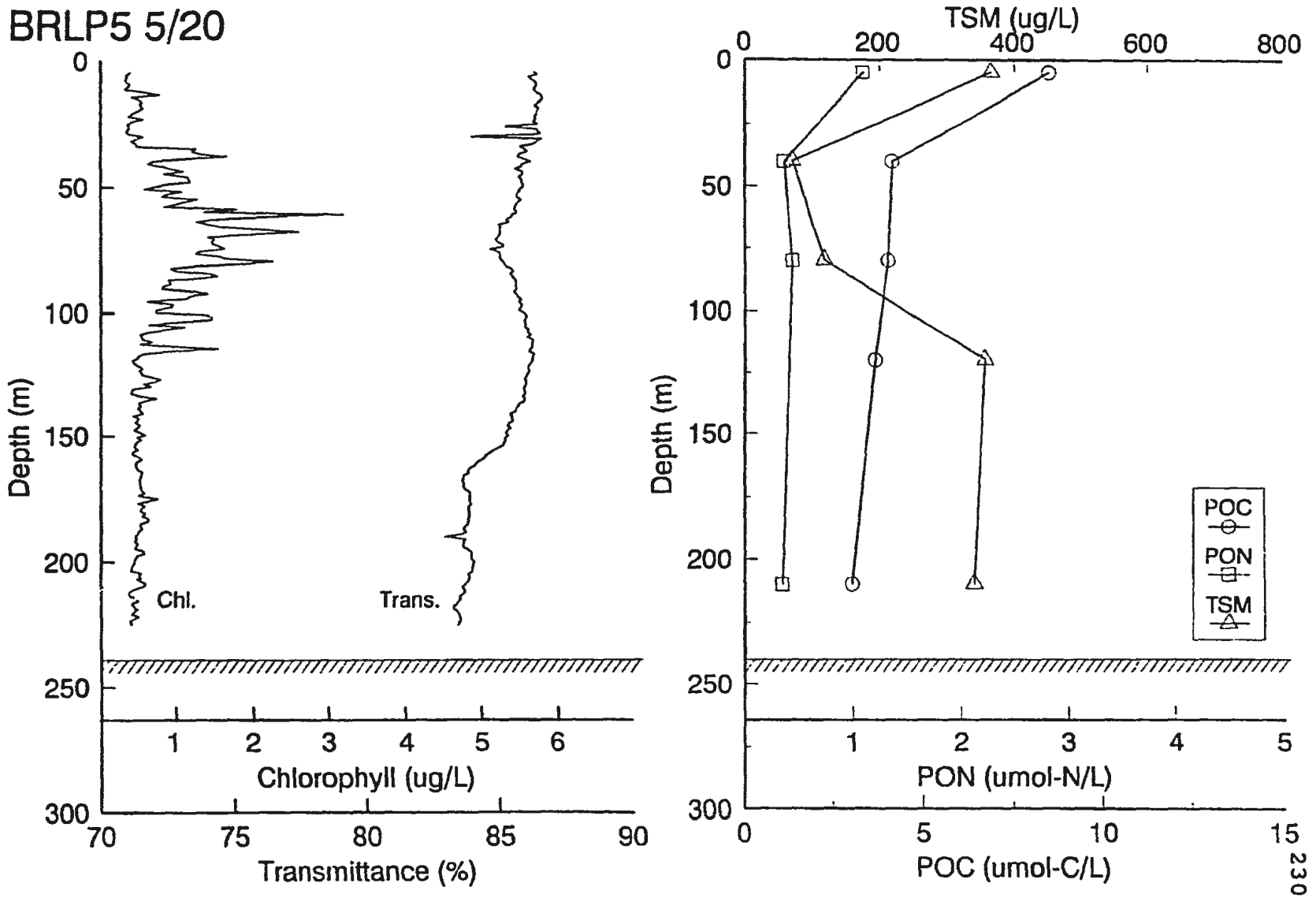

BRLP5 5/20
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
1
2
3
4
5
6
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 45. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on May 20.

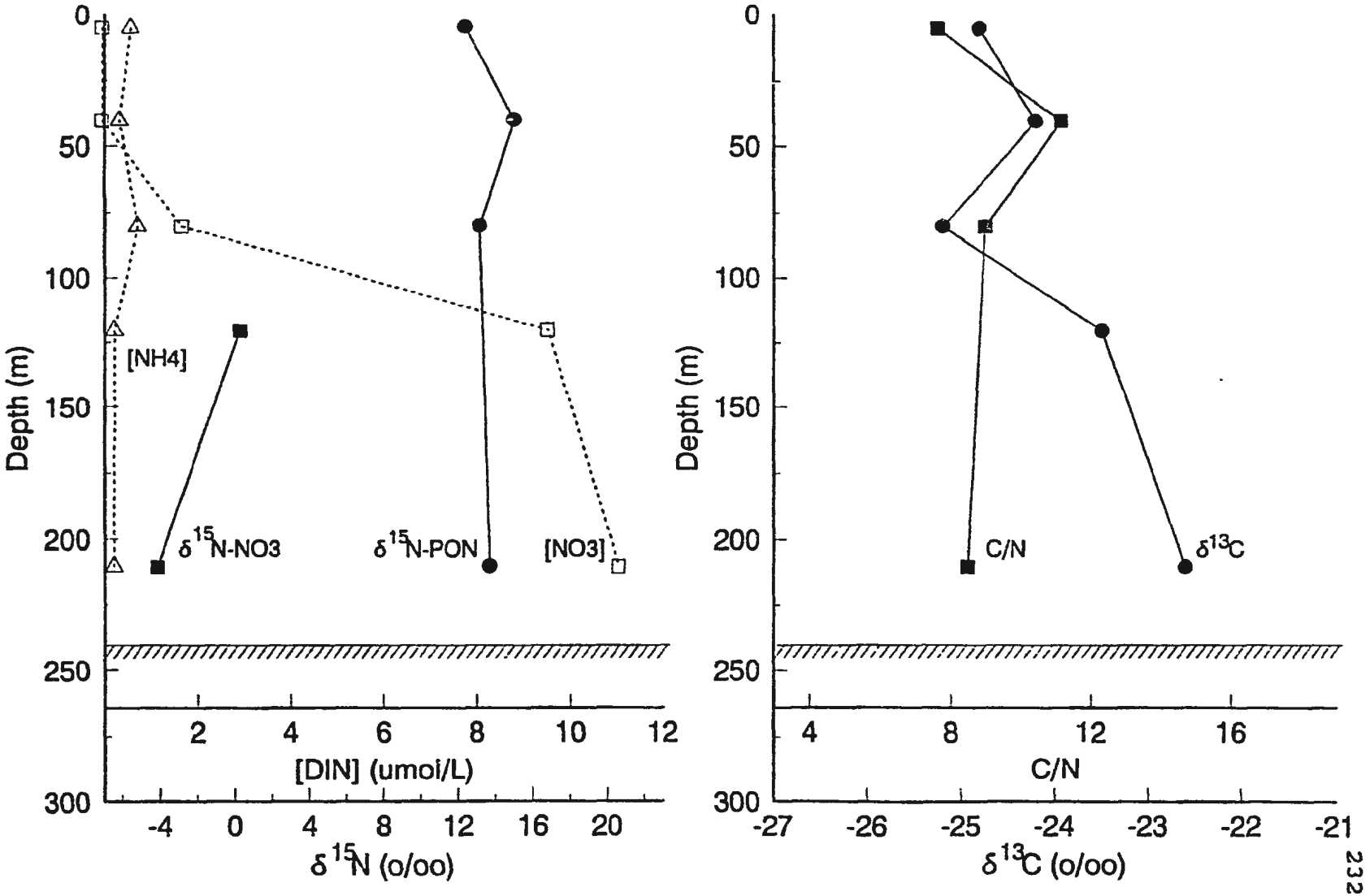

BRLP5 5/20
Depth (m)
0
50
100
150
200
250
300
[NH4]
δ15N-NO3
δ15N-PON
[NO3]
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 46. Salinity, temperature and density as a function of water column depth for station BRLP5 on June 24.

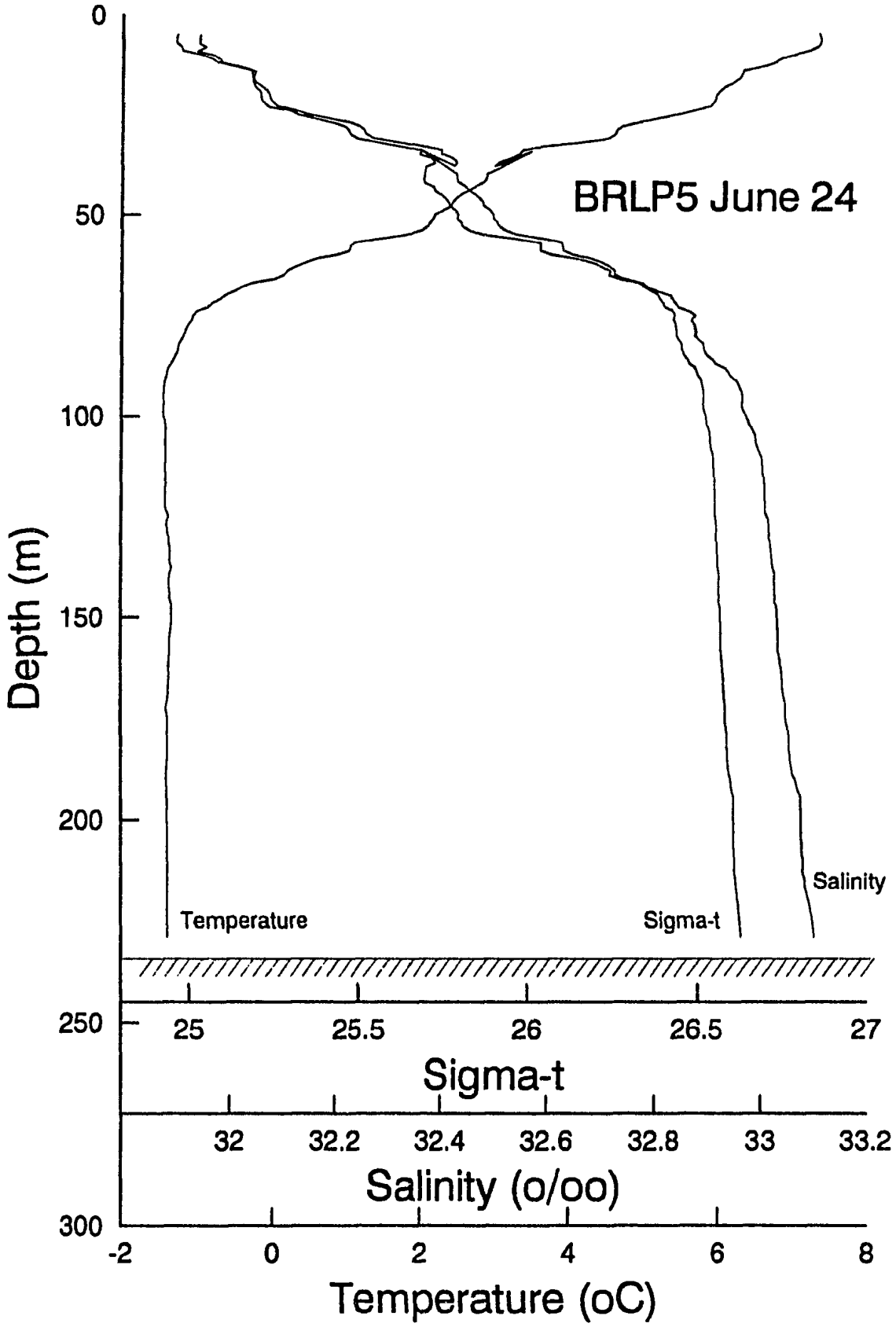

BRLP5 June 24
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25
25.5
26
26.5
27
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
0
2
4
6
8
Temperature (oC)

Figure 47. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on June 24.

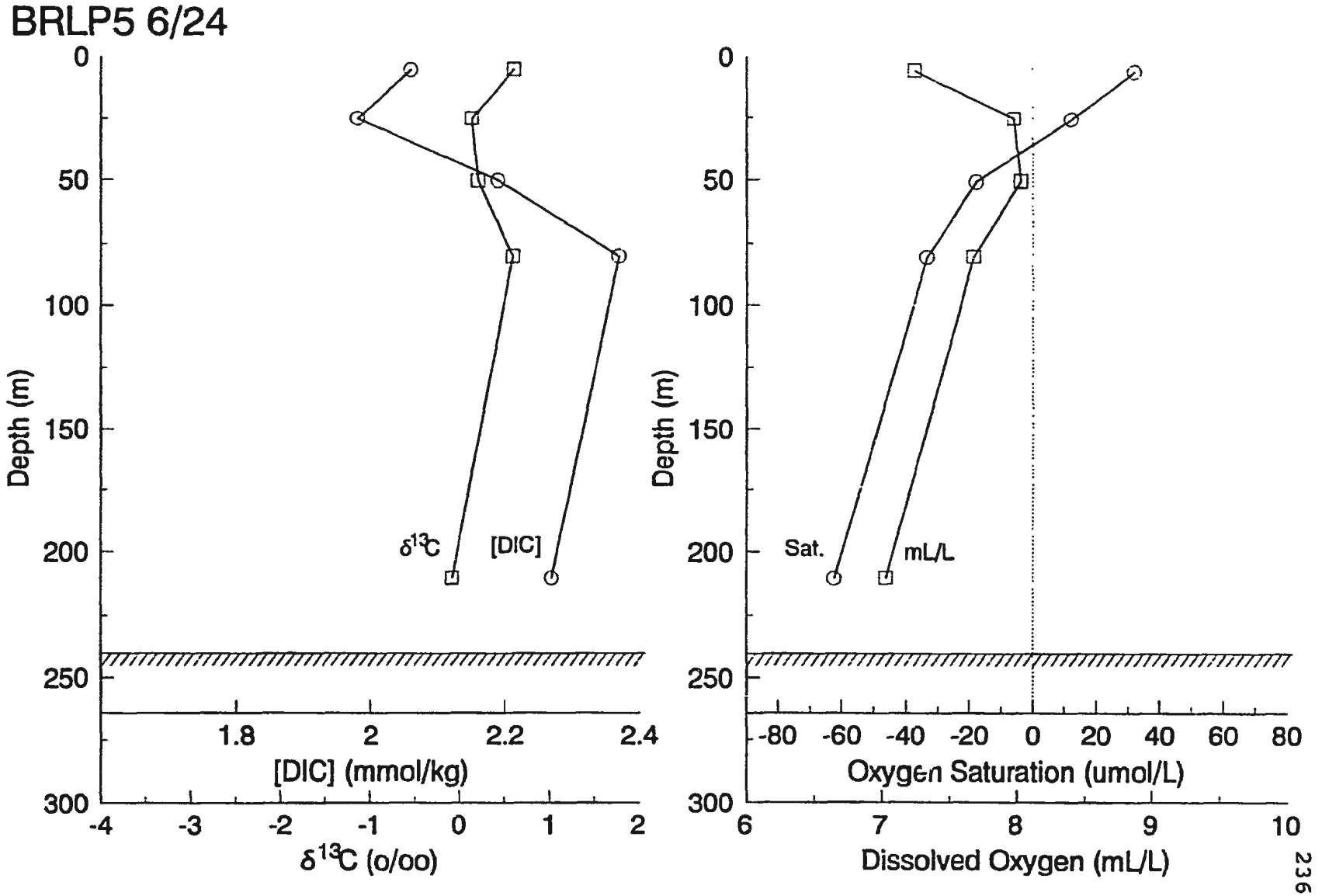

BRLP5 6/24
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 48. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on June 24.

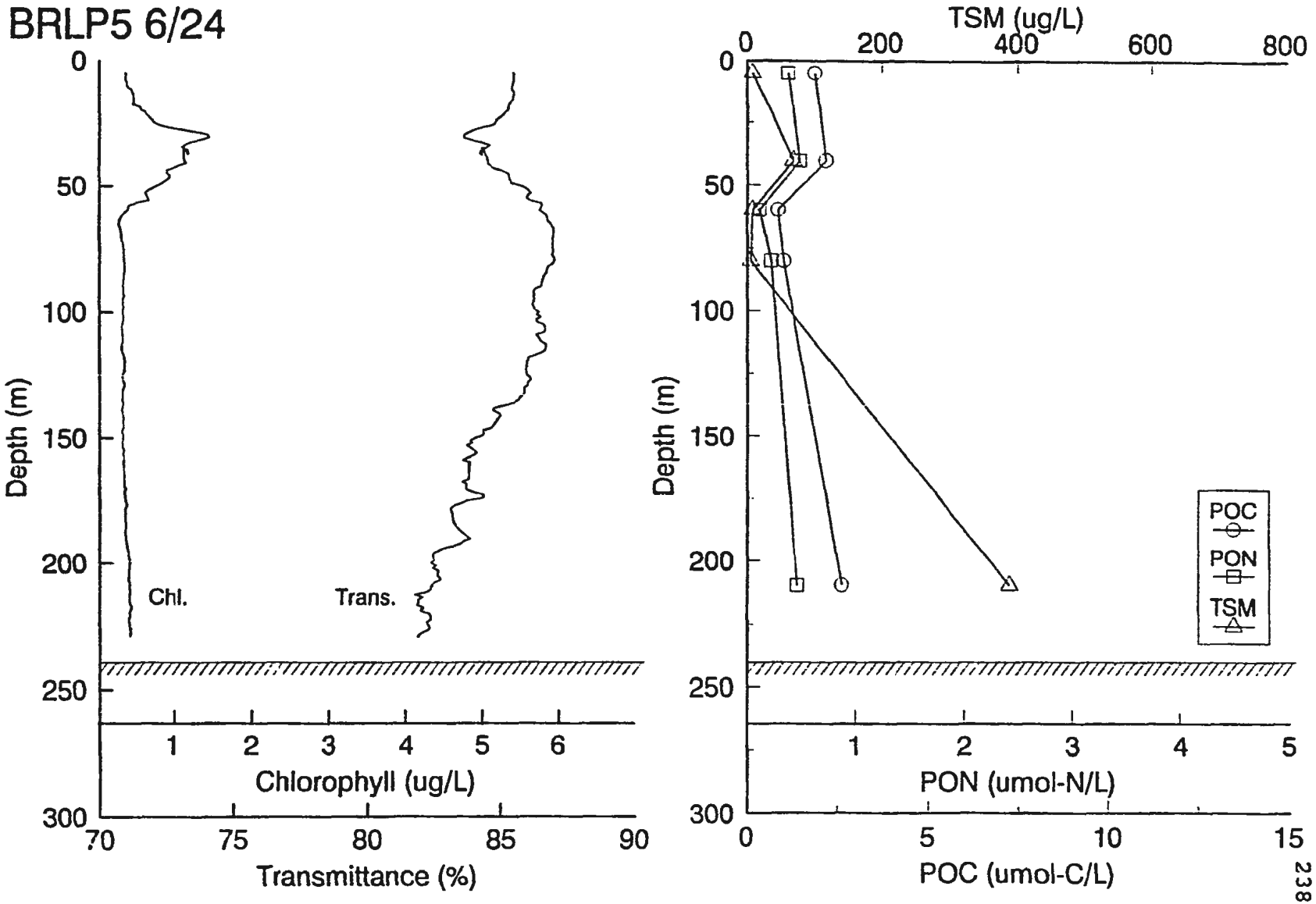

BRLP5 6/24
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
1
2
3
4
5
6
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 49. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on June 24.

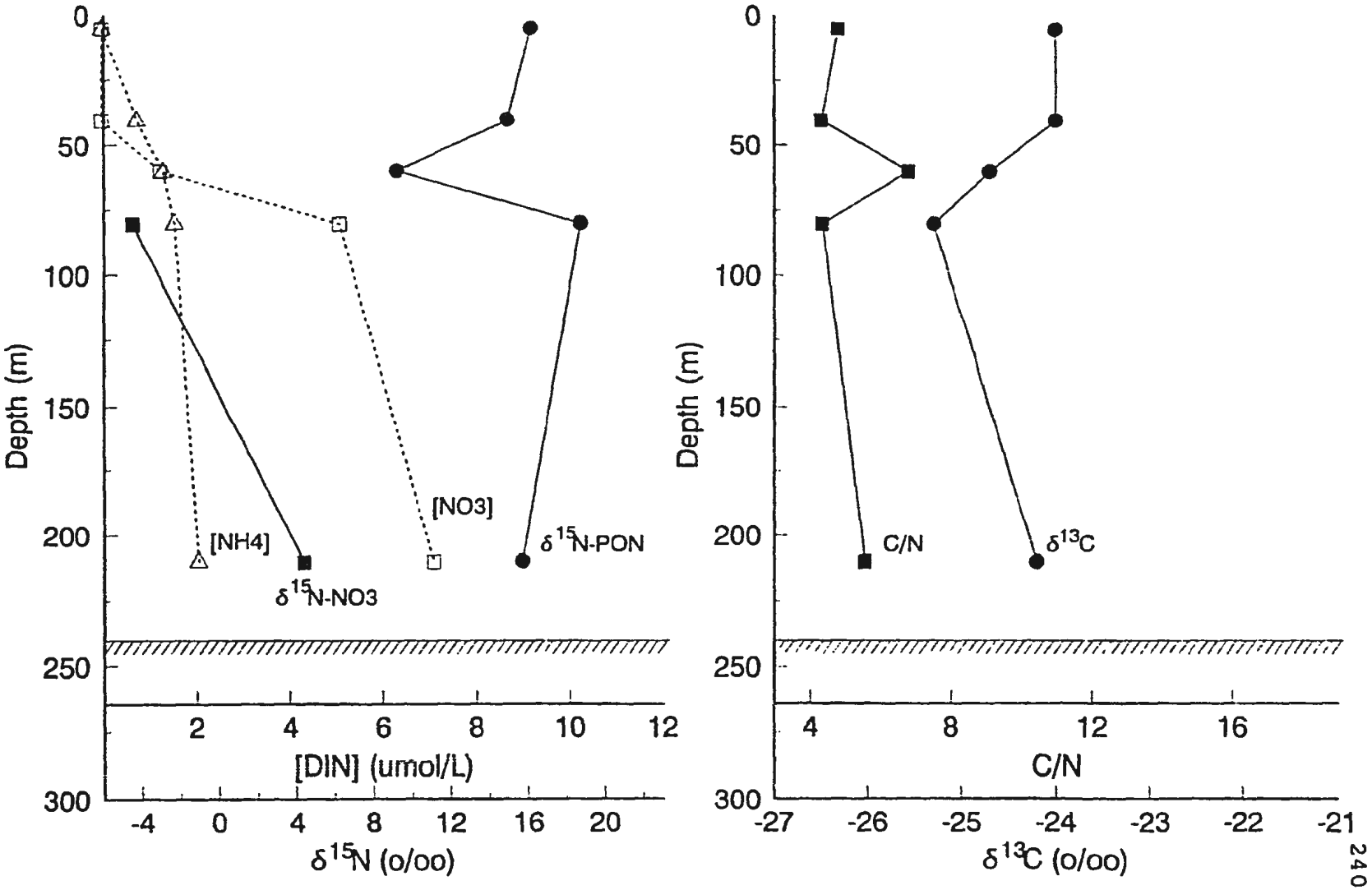

BRLP5 6/24
Depth (m)
0
50
100
150
200
250
300
[NH4]
[NO3]
δ15N-NO3
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 50. Salinity, temperature and density as a function of water column depth for station BRLP5 on July 27.

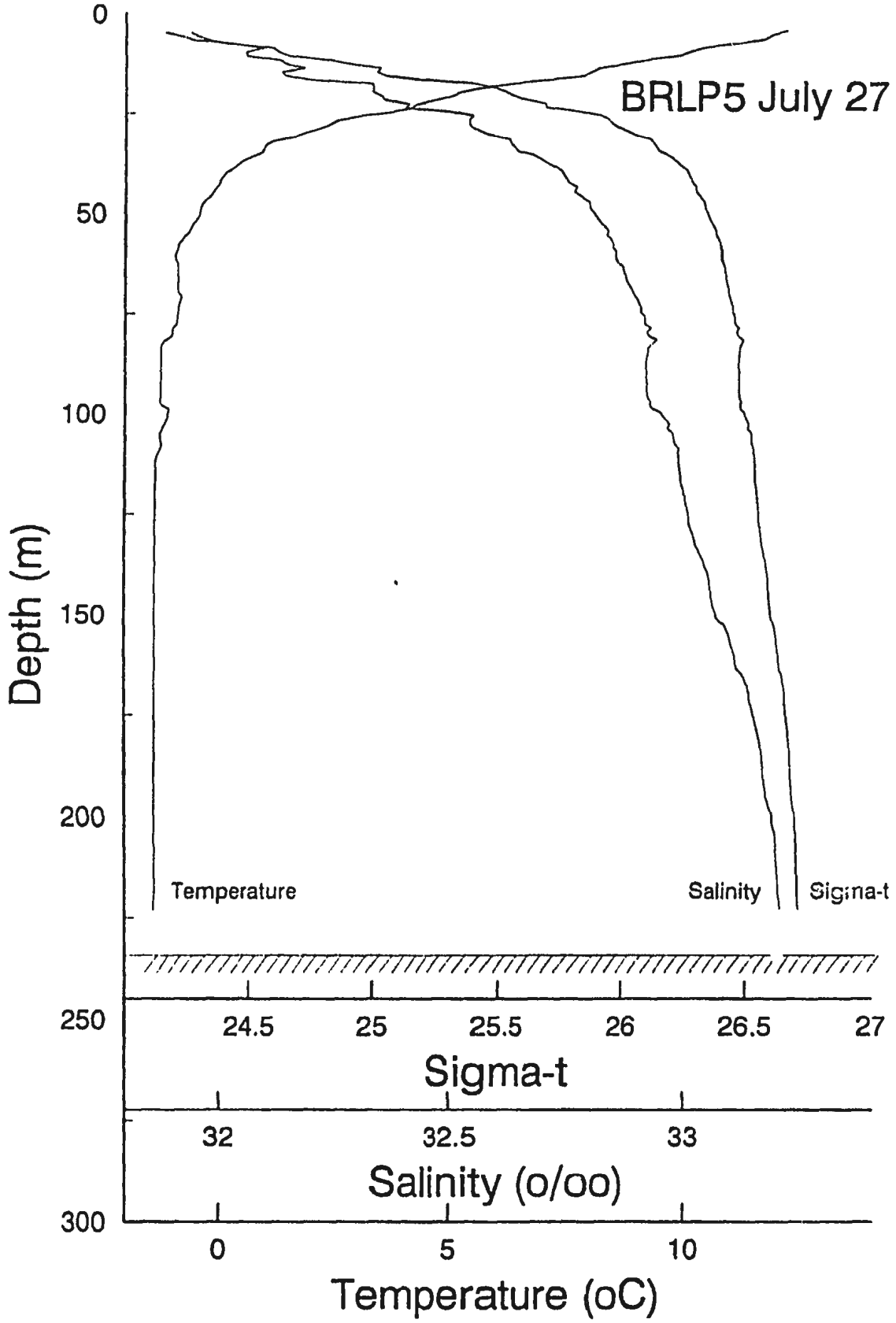

BRLP5 July 27
Depth (m)
0
50
100
150
200
250
300
Temperature
Salinity
Sigma-t
24.5
25
25.5
26
26.5
27
Sigma-t
32
32.5
33
Salinity (o/oo)
0
5
10
Temperature (oC)

Figure 51. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on July 27.

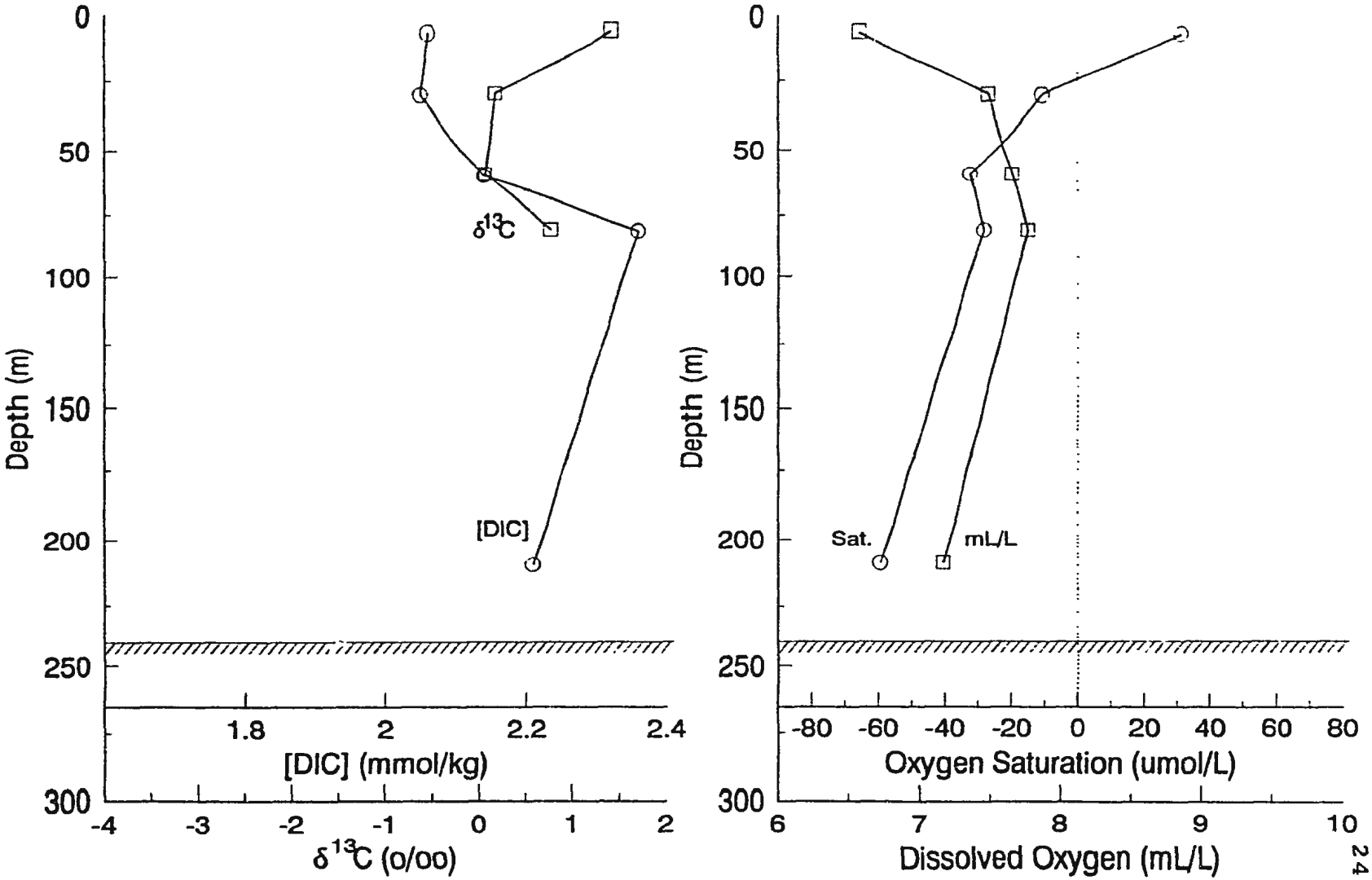

BRLP5 7/27
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 52. Percent transmittance and concentrations of chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on July 27.

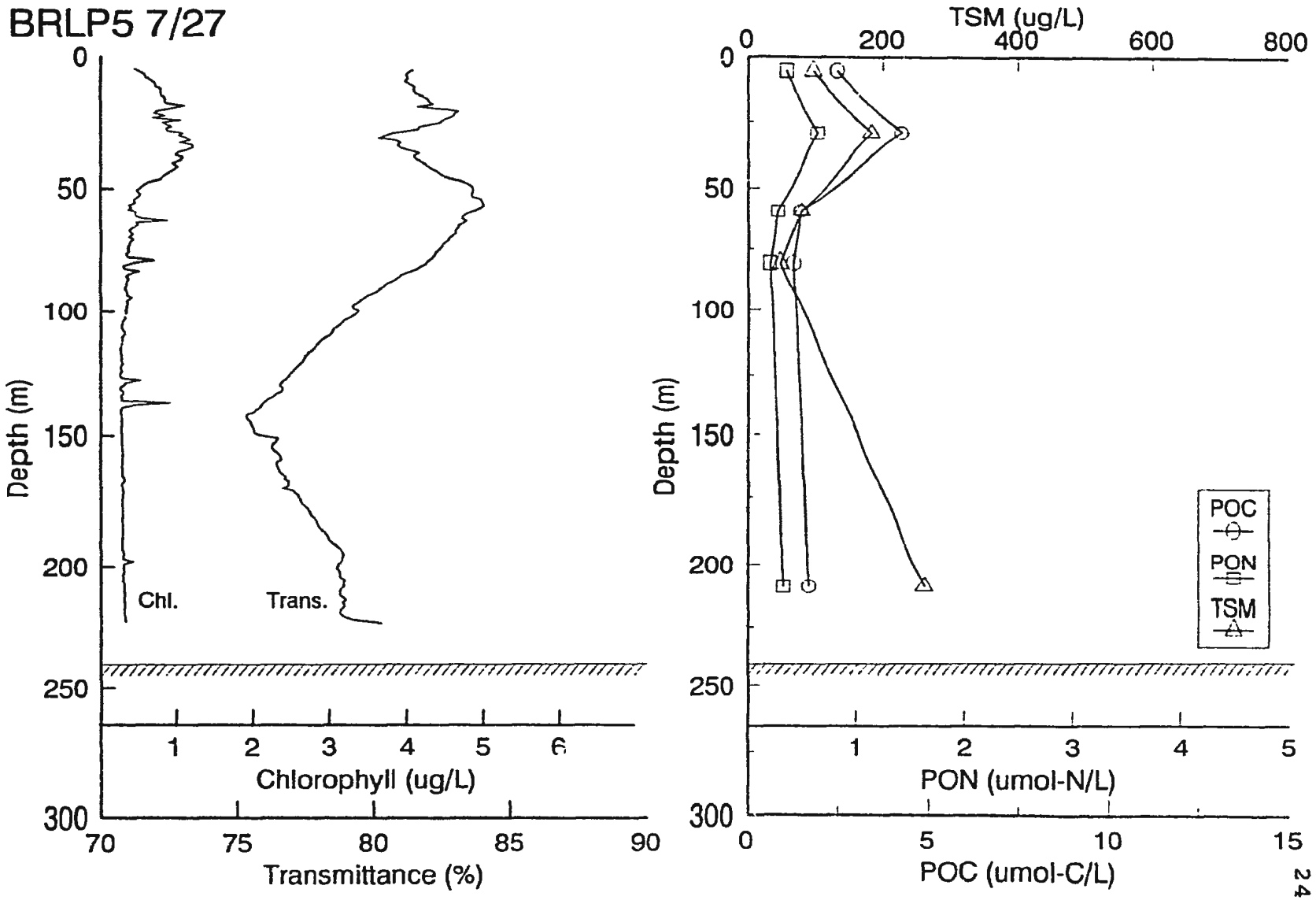

BRLP5 7/27
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
1
2
3
4
5
6
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 53. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), ammonium ($\delta^{15}N$-NH_4), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on July 27.

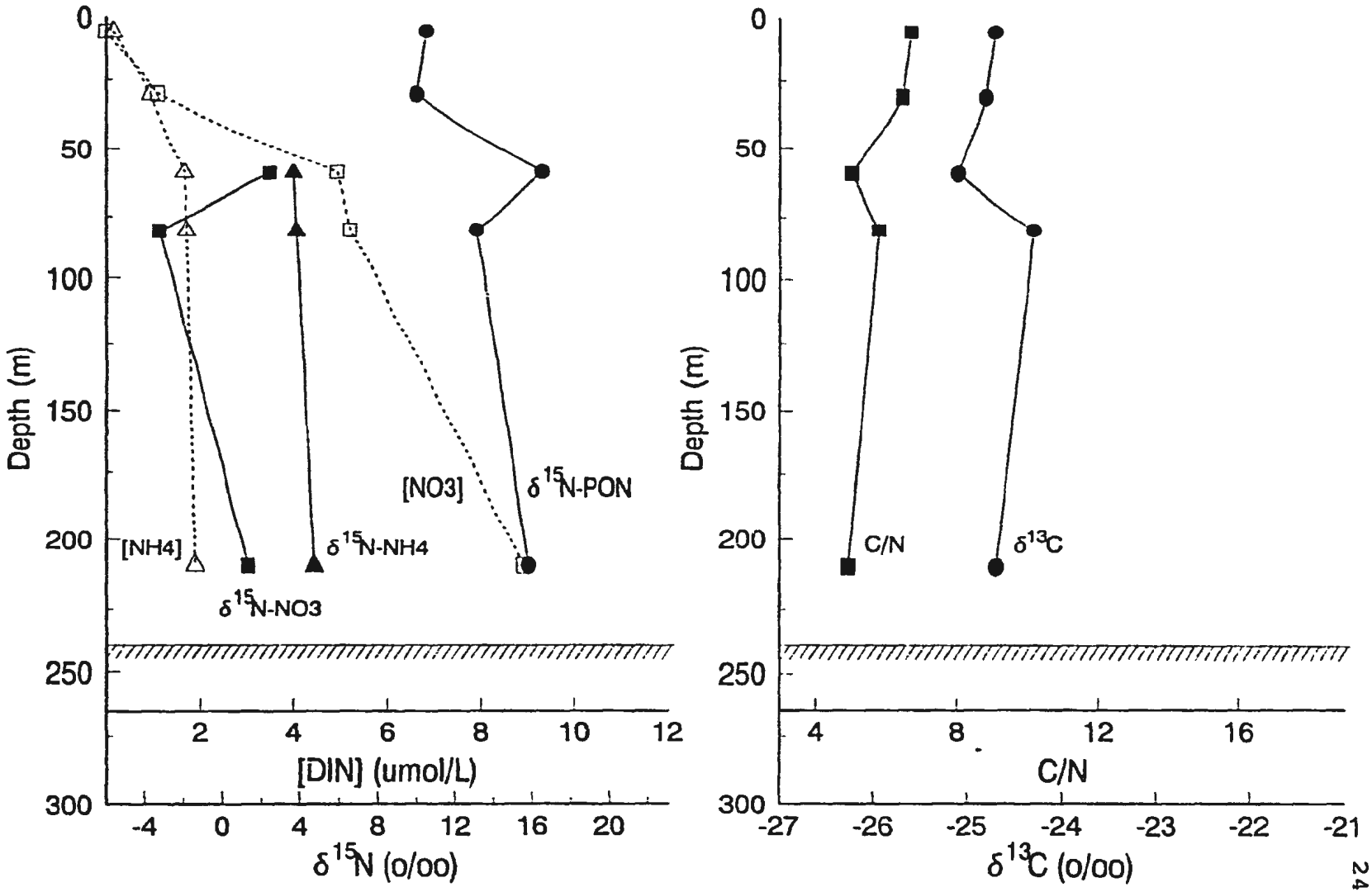

BRLP5 7/27
Depth (m)
0
50
100
150
200
250
300
[NH4]
[NO3]
δ15N-NO3
δ15N-NH4
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 54. Salinity, temperature and density as a function of water column depth for station BRLP5 on August 30.

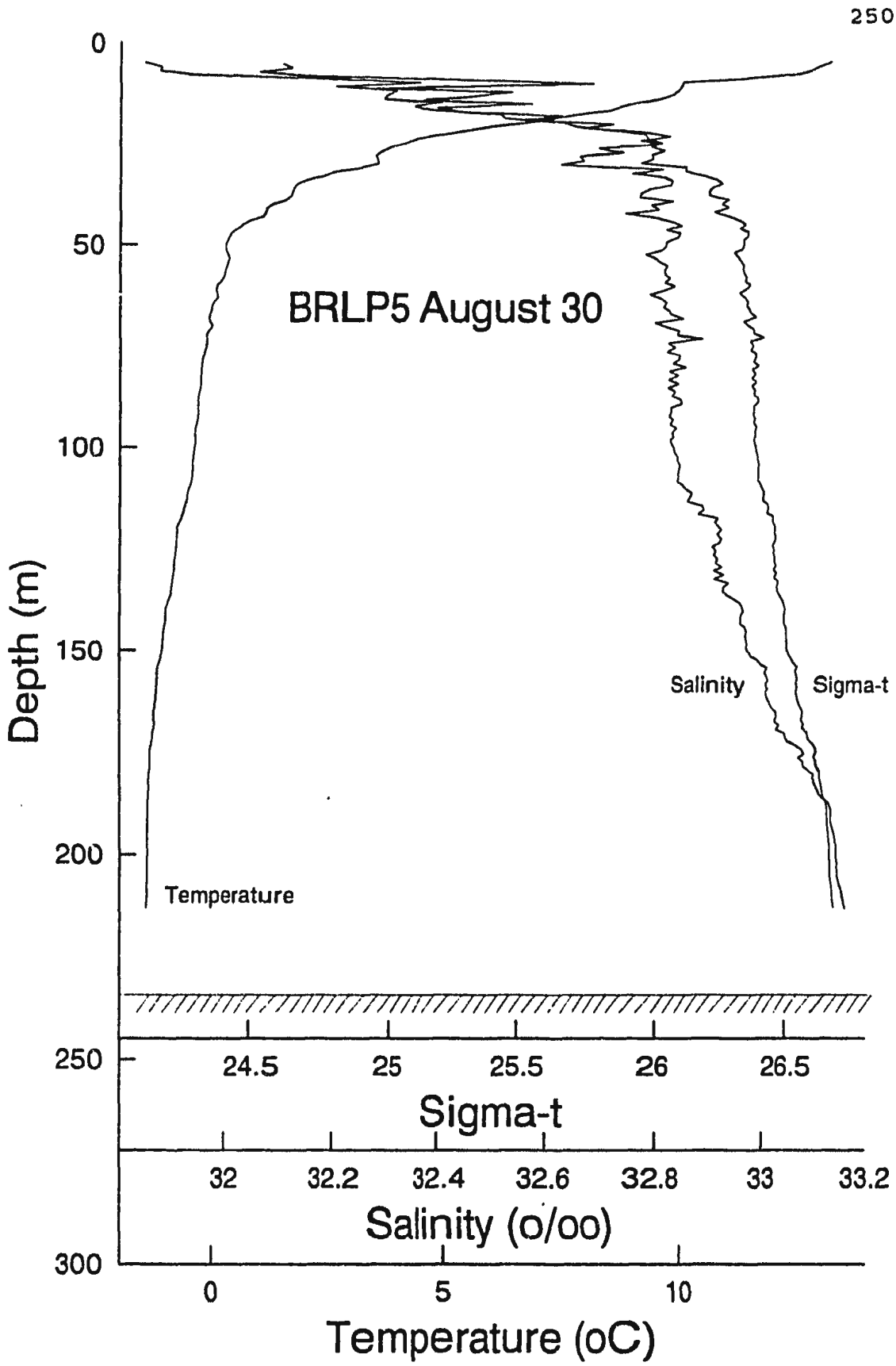

250
0
50
100
150
200
250
300
Depth (m)
BRLP5 August 30
Salinity
Sigma-t
Temperature
24.5
25
25.5
26
26.5
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
0
5
10
Temperature (oC)

Figure 55. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station BRLP5 on August 30.

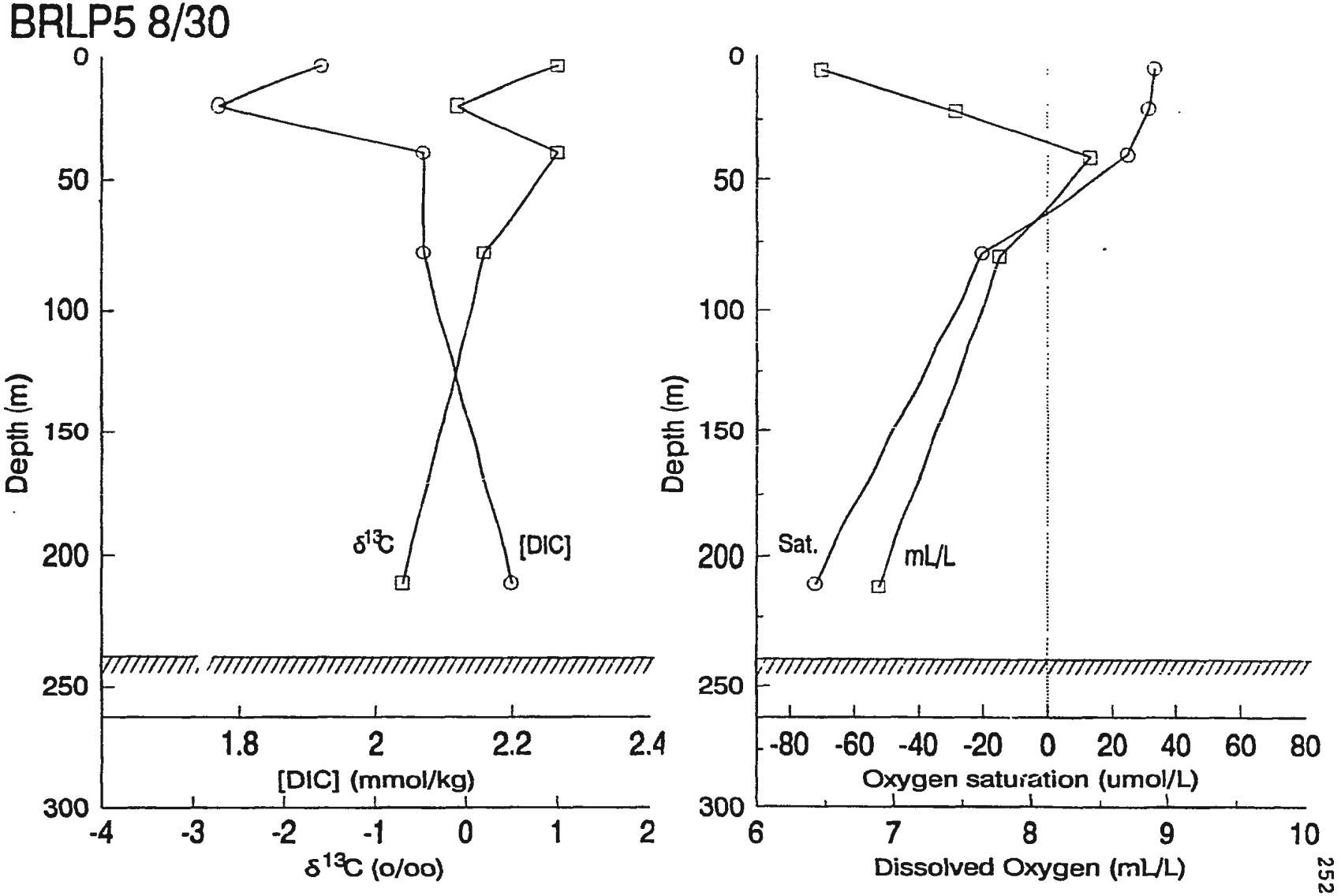

BRLP5 8/30
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 56. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station BRLP5 on August 30.

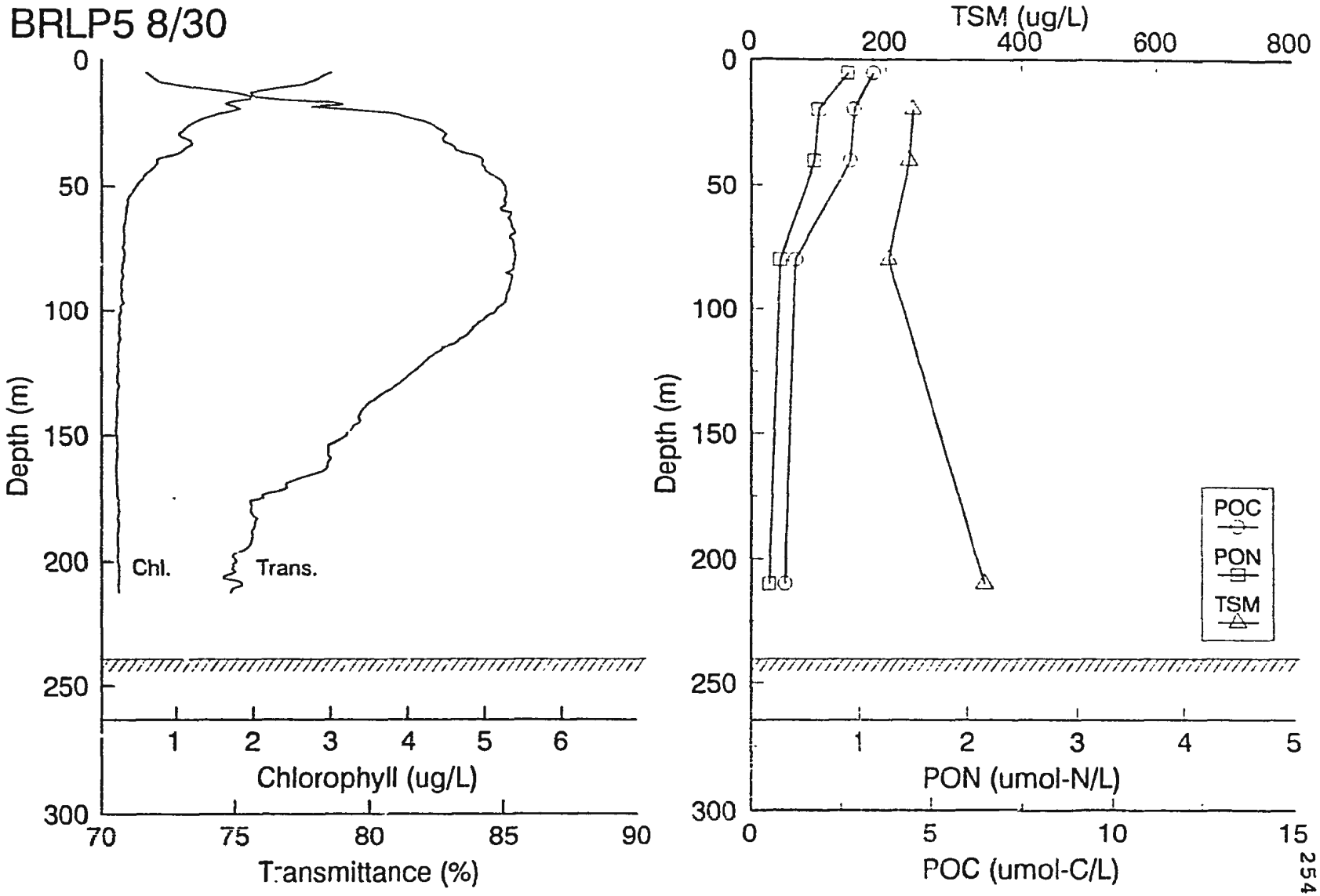

BRLP5 8/30
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
1
2
3
4
5
6
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 57. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), ammonium ($\delta^{15}N$-NH_4), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station BRLP5 on August 30.

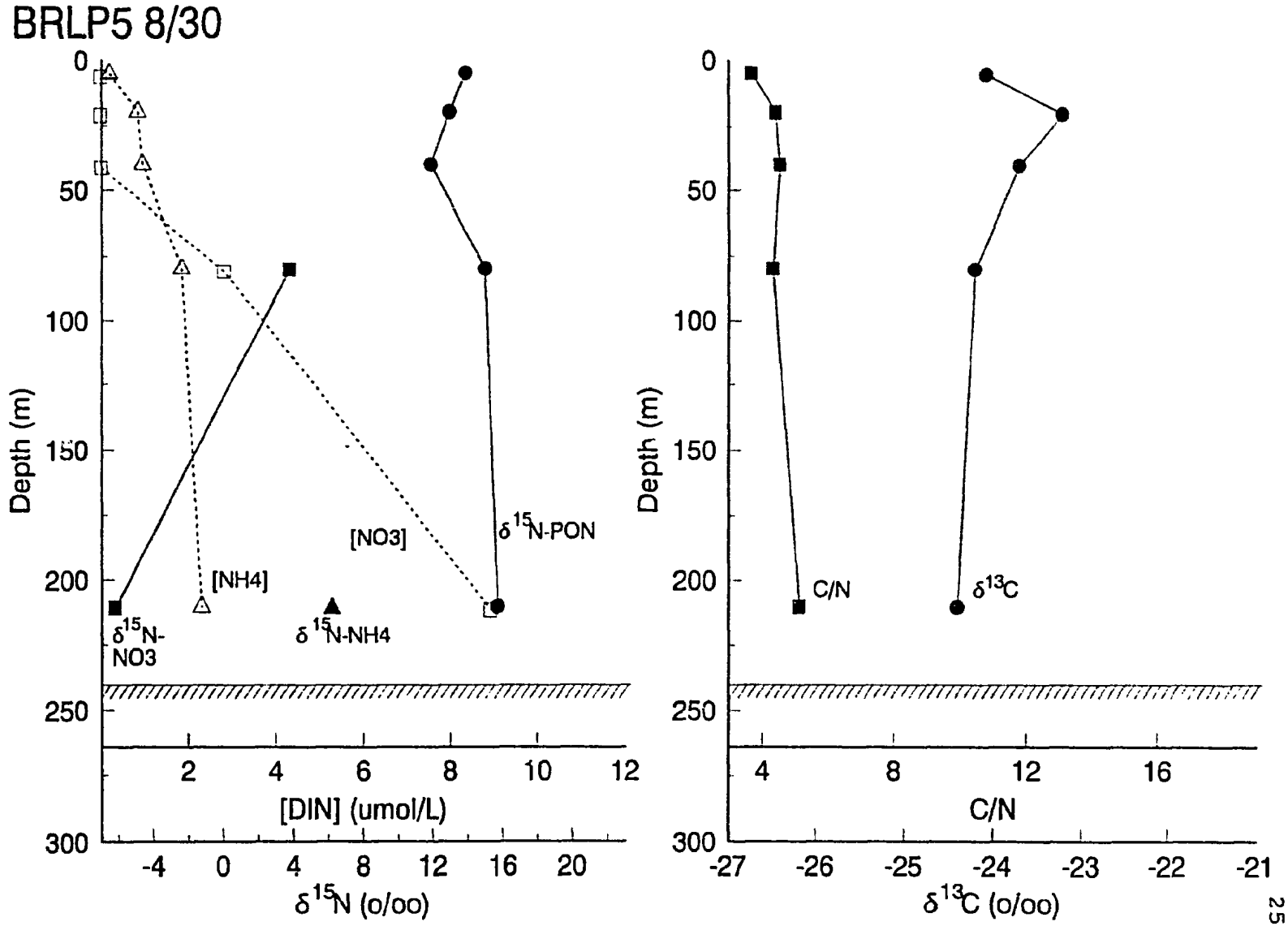

BRLP5 8/30
Depth (m)
0
50
100
150
200
250
300
[NO3]
[NH4]
δ15N-PON
δ15N-NO3
δ15N-NH4
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 58. Salinity, temperature and density as a function of water column depth for station US3.5 on May 1.

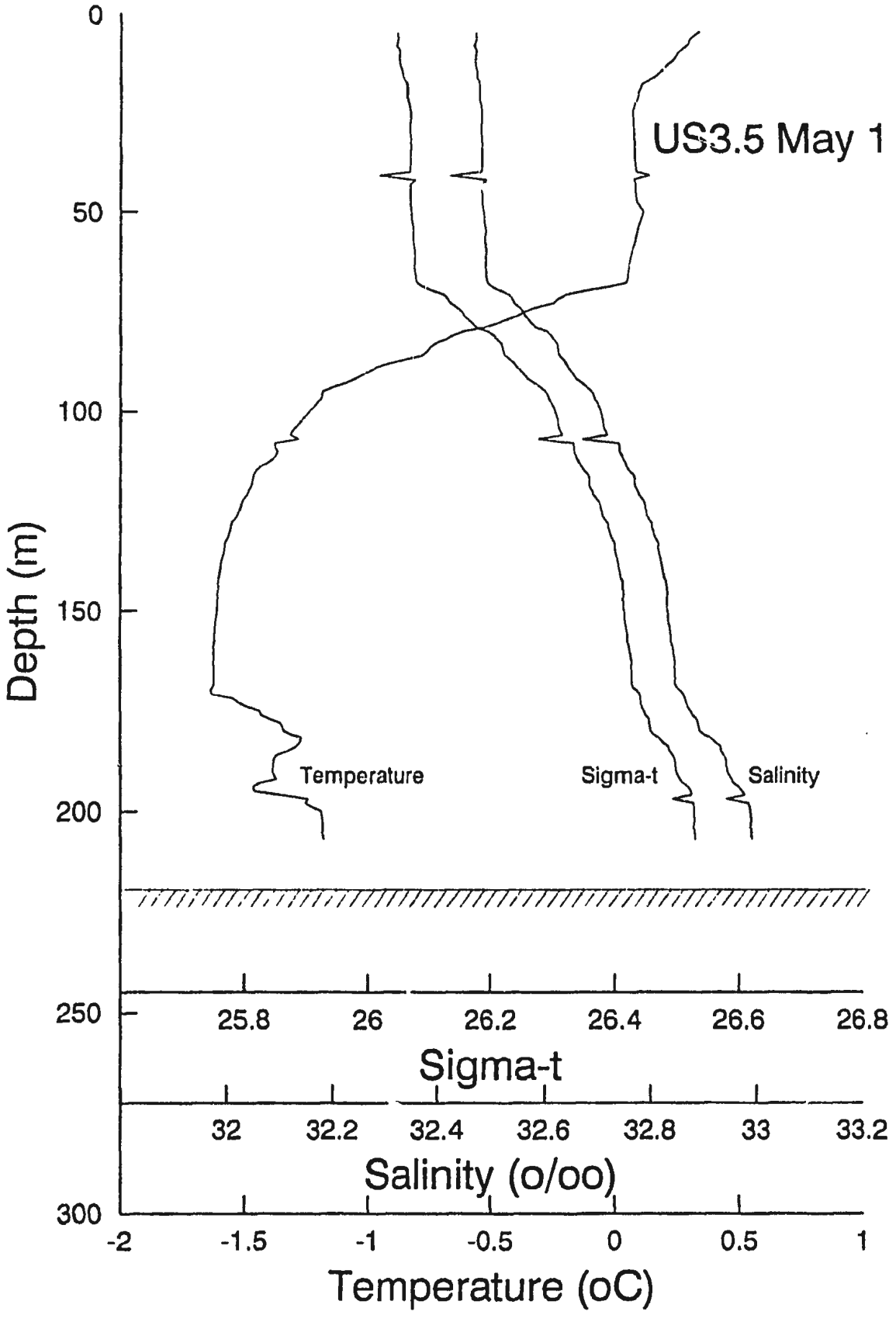

US3.5 May 1
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
0.5
1
Temperature (oC)

Figure 59. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station US3.5 on May 1.

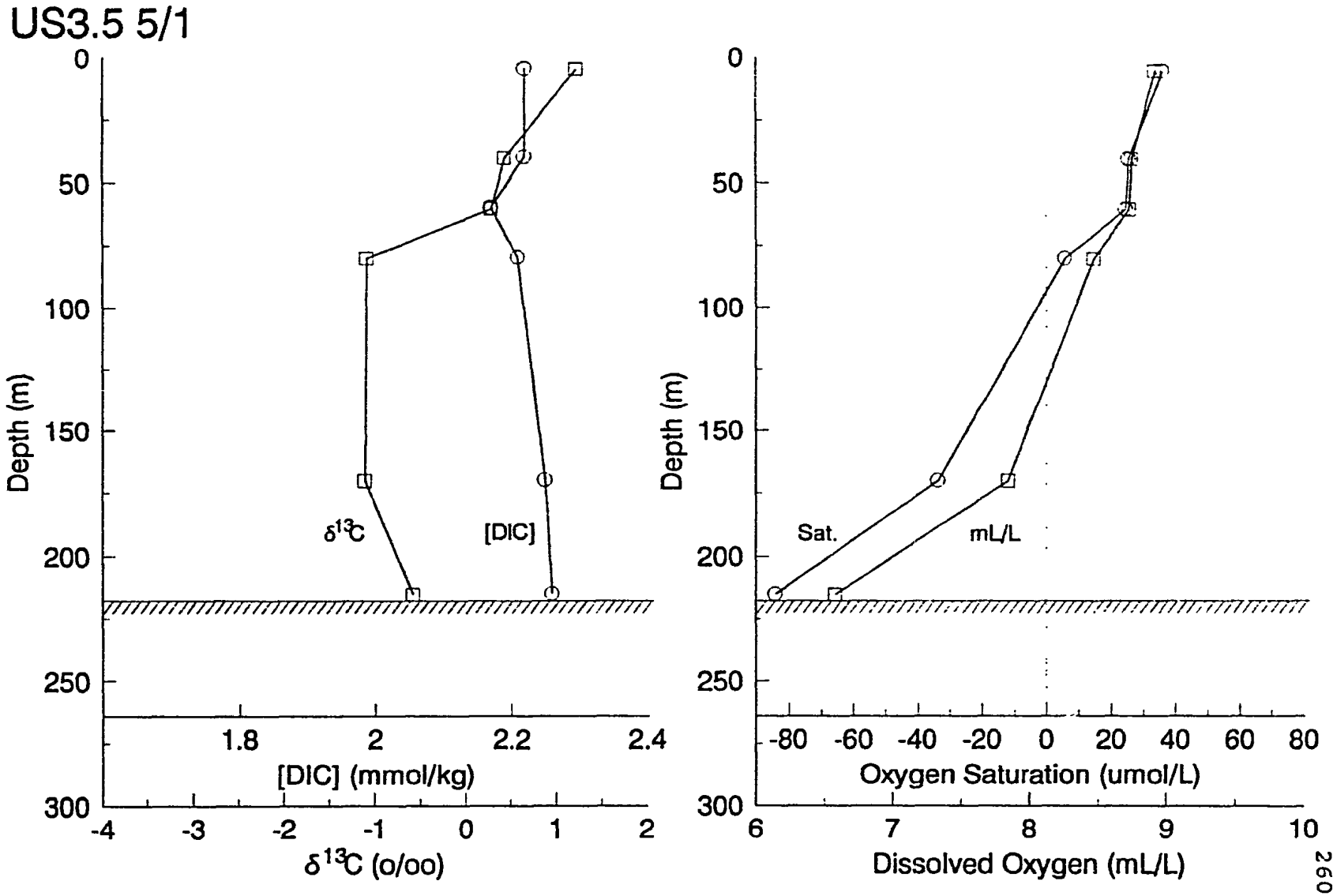

US3.5 5/1
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 60. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station US3.5 on May 1.

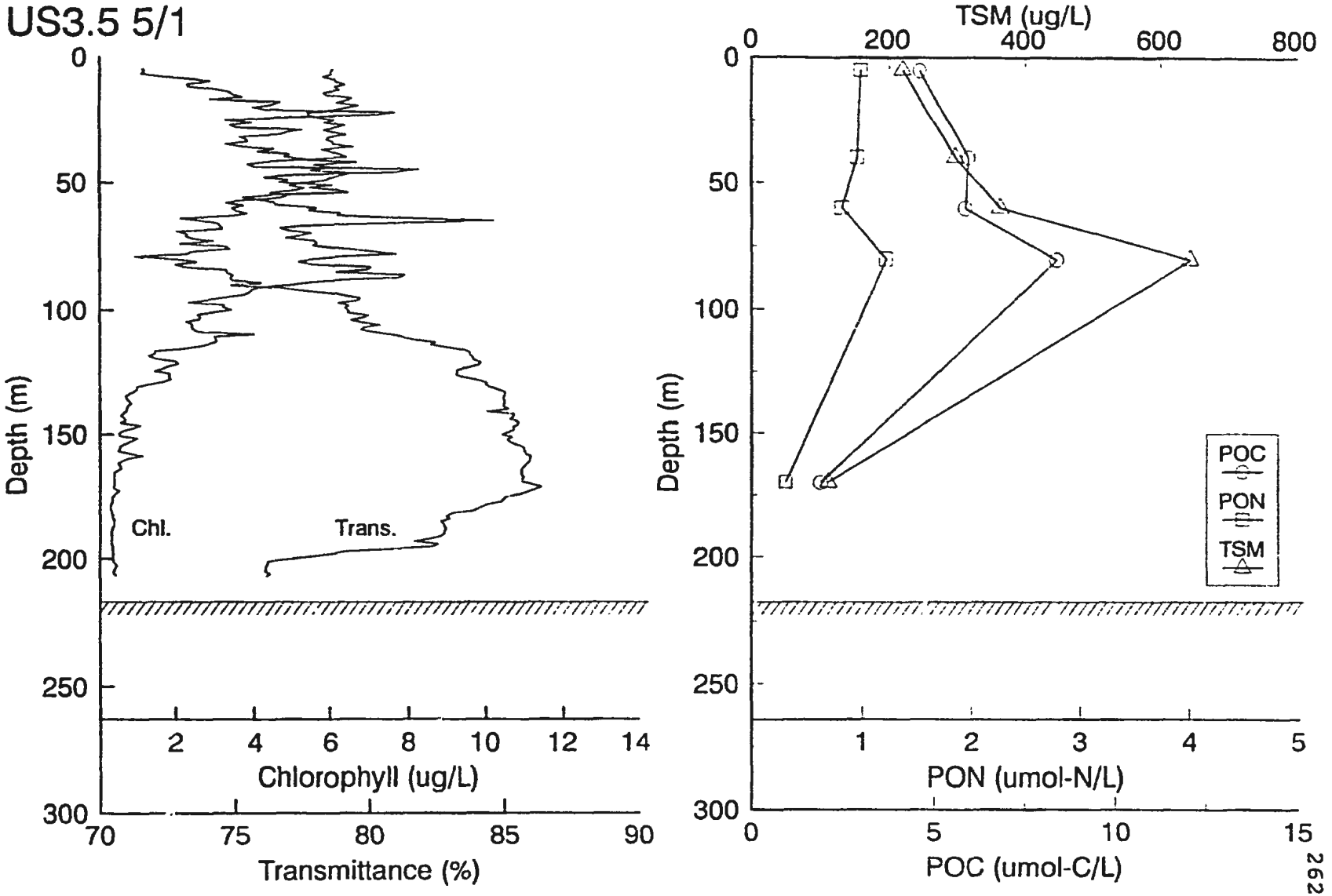

US3.5 5/1
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
2
4
6
8
10
12
14
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 61. Isotopic composition of PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station US3.5 on May 1.

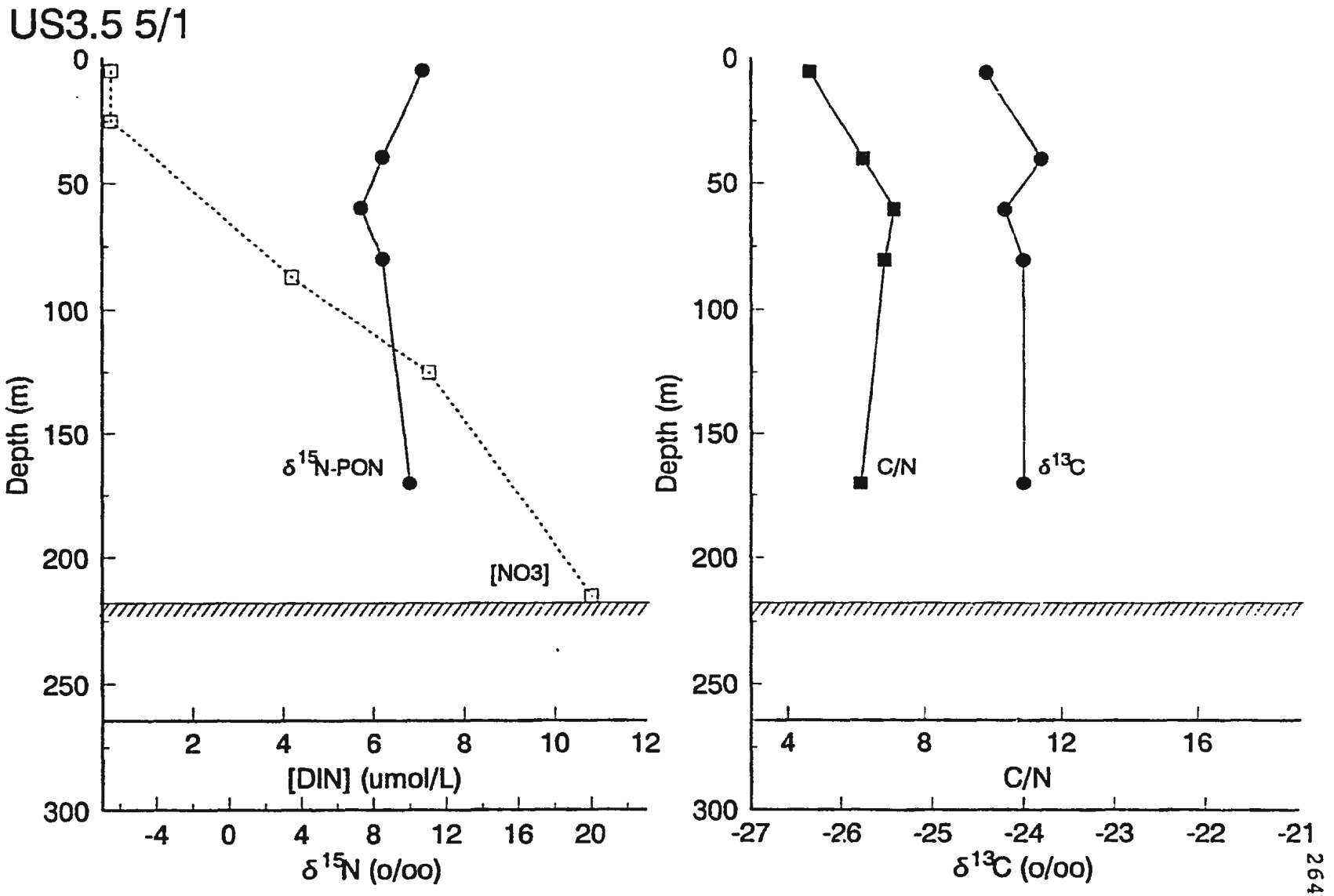

US3.5 5/1
Depth (m)
0
50
100
150
200
250
300
δ15N-PON
[NO3]
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 62. Salinity, temperature and density as a function of water column depth for station US3.5 on May 6.

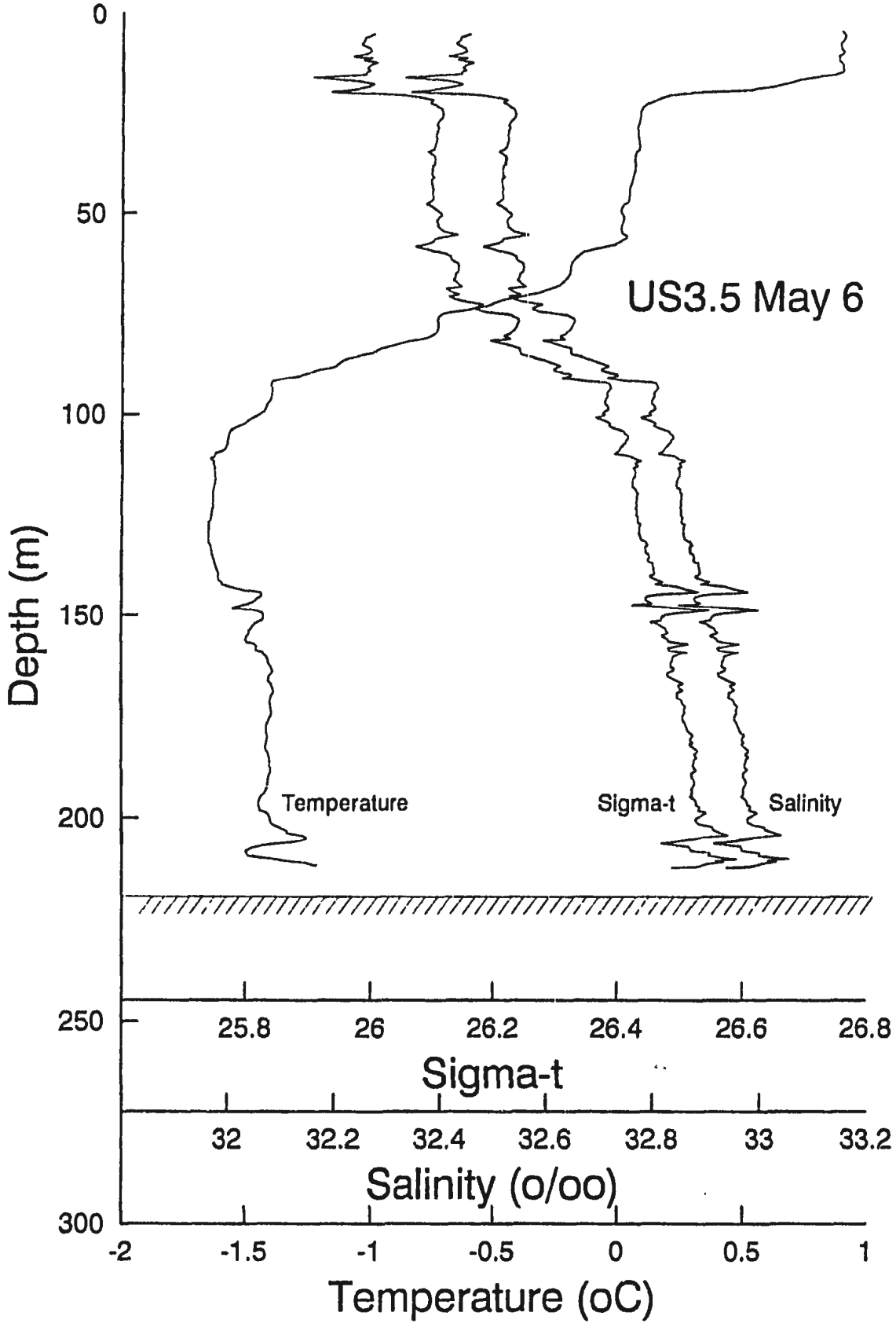

US3.5 May 6
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
0.5
1
Temperature (oC)

Figure 63. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station US3.5 on May 6.

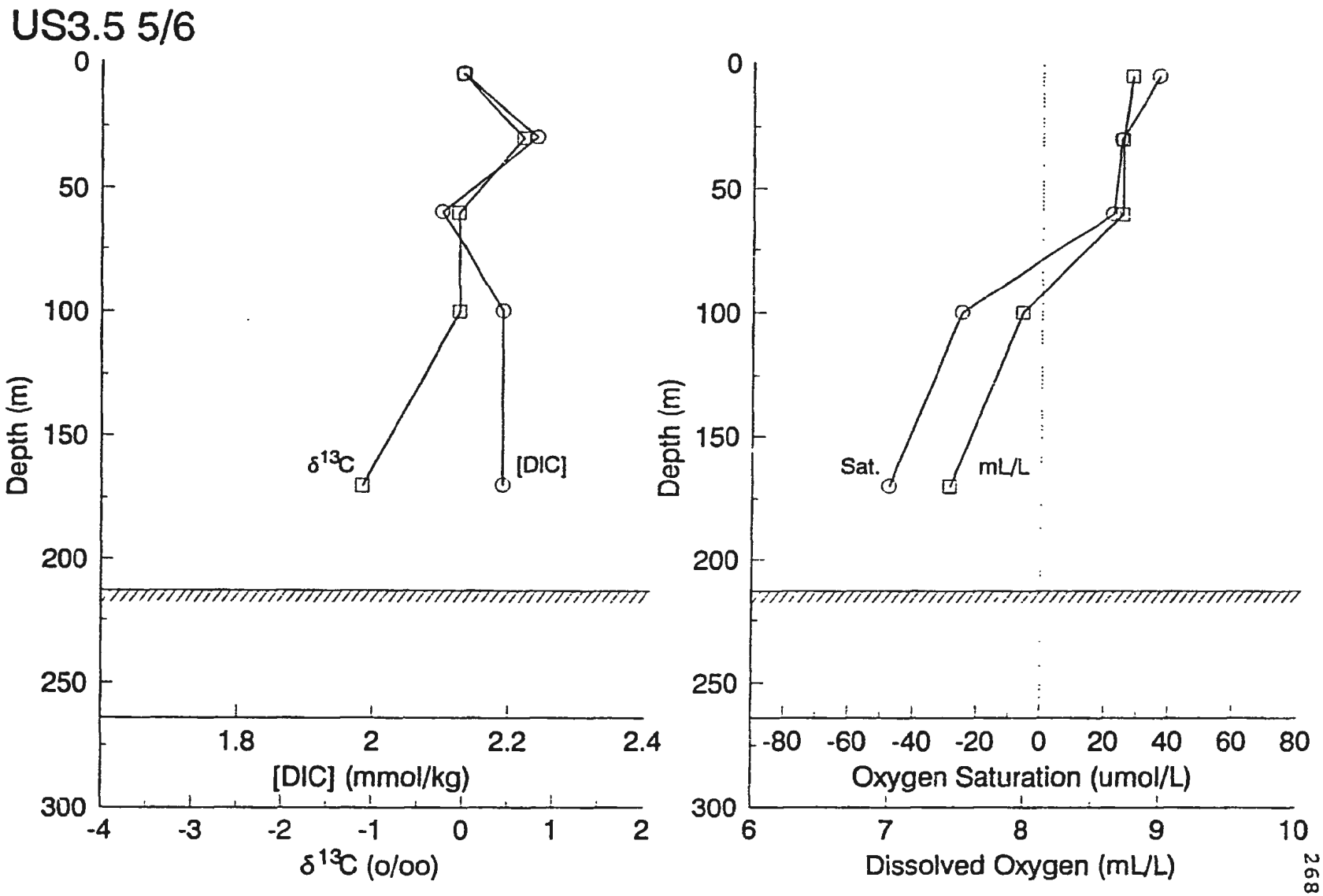

US3.5 5/6
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 64. Concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station US3.5 on May 6.

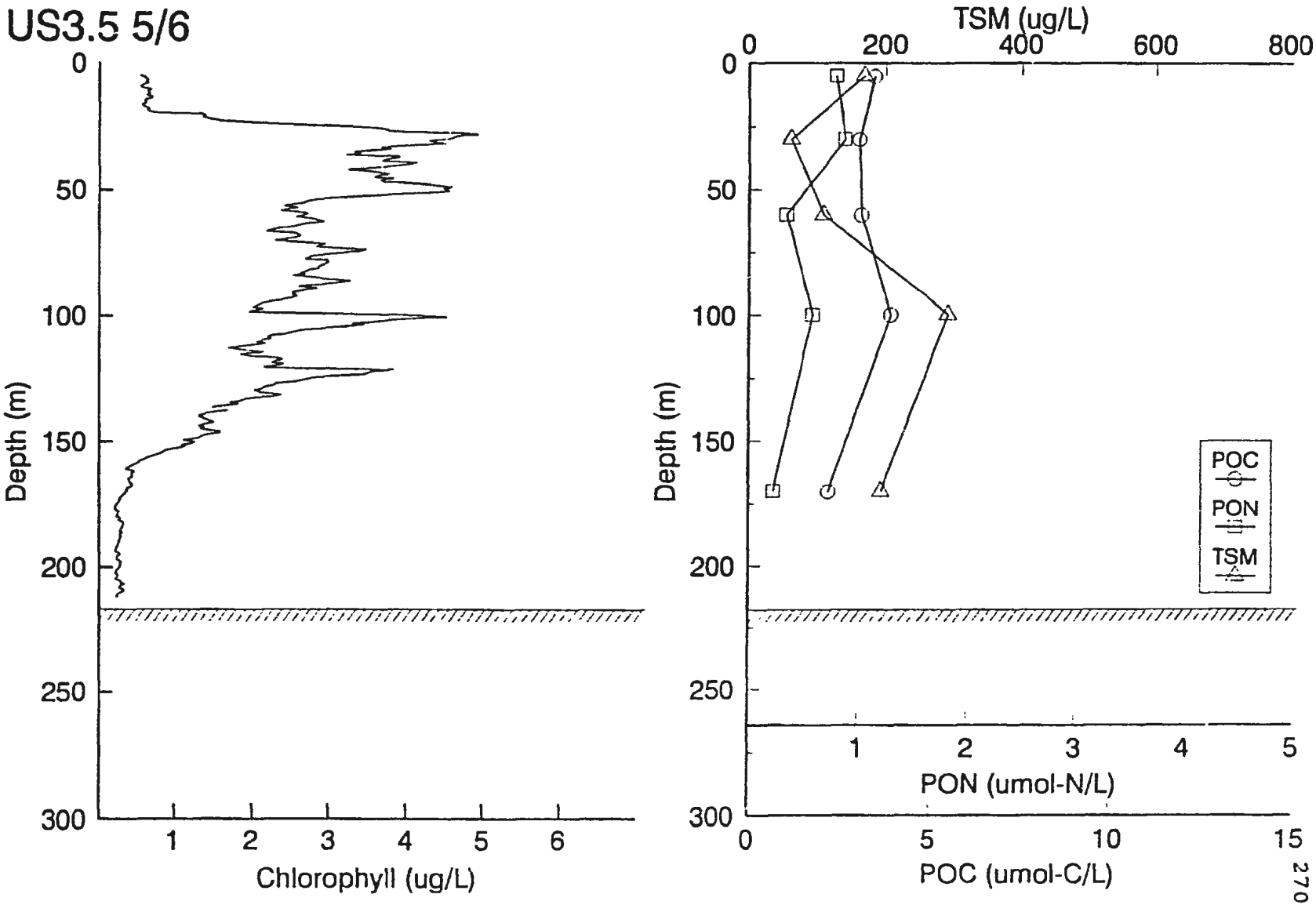

US3.5 5/6
Depth (m)
0
50
100
150
200
250
300
1
2
3
4
5
6
Chlorophyll (ug/L)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 65. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station US3.5 on May 6.

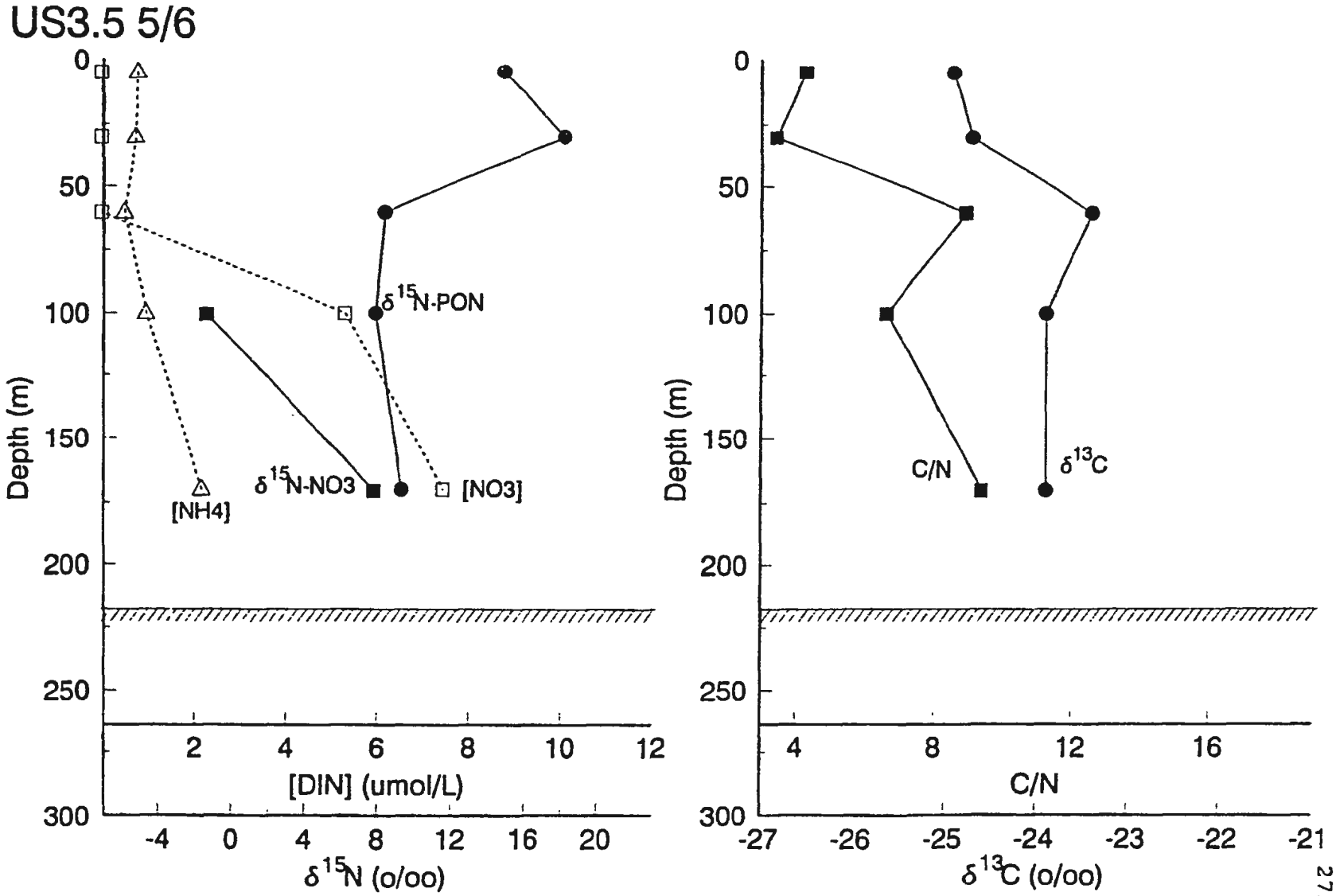

US3.5 5/6
Depth (m)
0
50
100
150
200
250
300
δ15N-PON
[NH4]
δ15N-NO3
[NO3]
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 66. Salinity, temperature and density as a function of water column depth for station US3.5 on May 21.

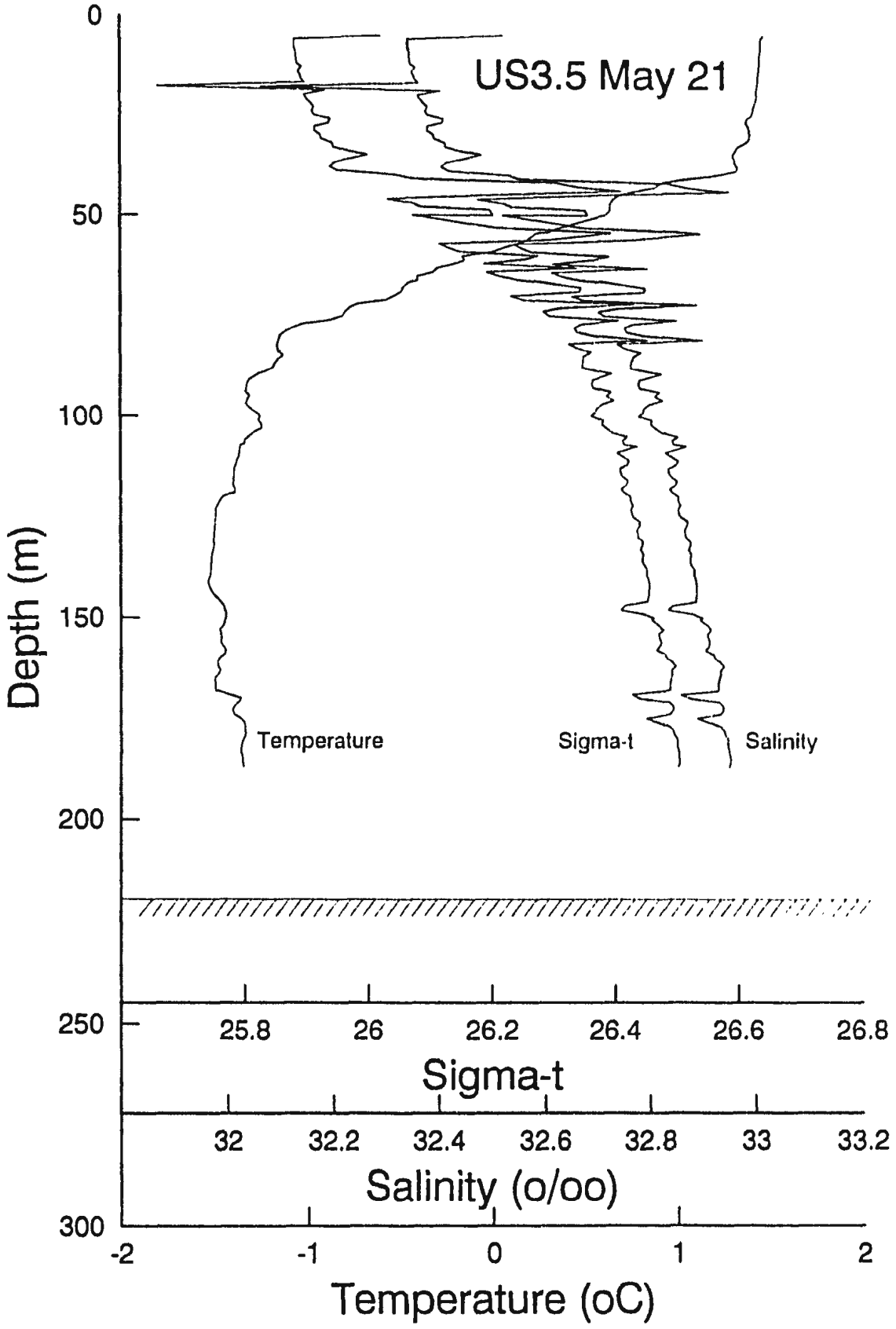

US3.5 May 21
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1
0
1
2
Temperature (oC)

Figure 67. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station US3.5 on May 21.

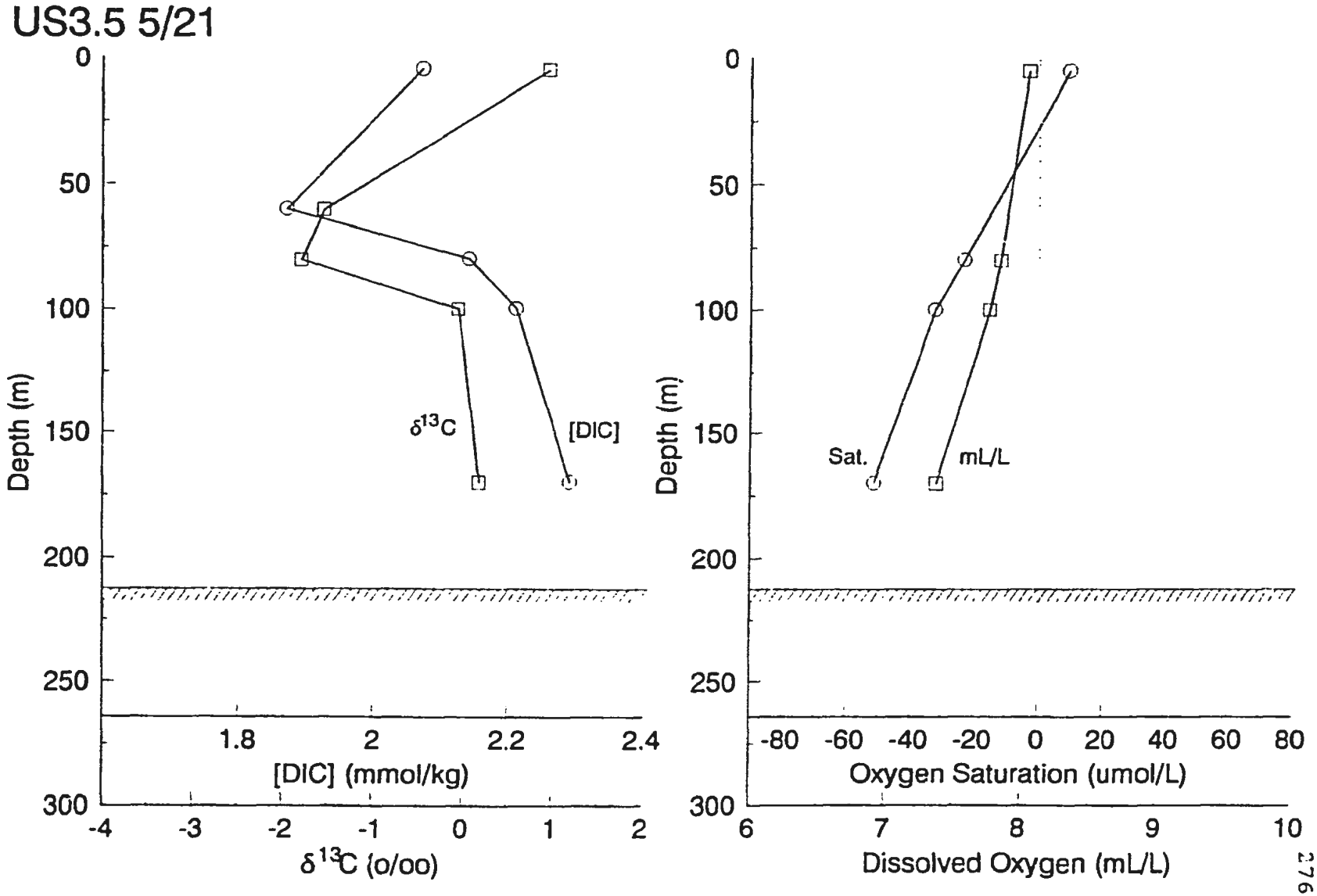

US3.5 5/21
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 68. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station US3.5 on May 21.

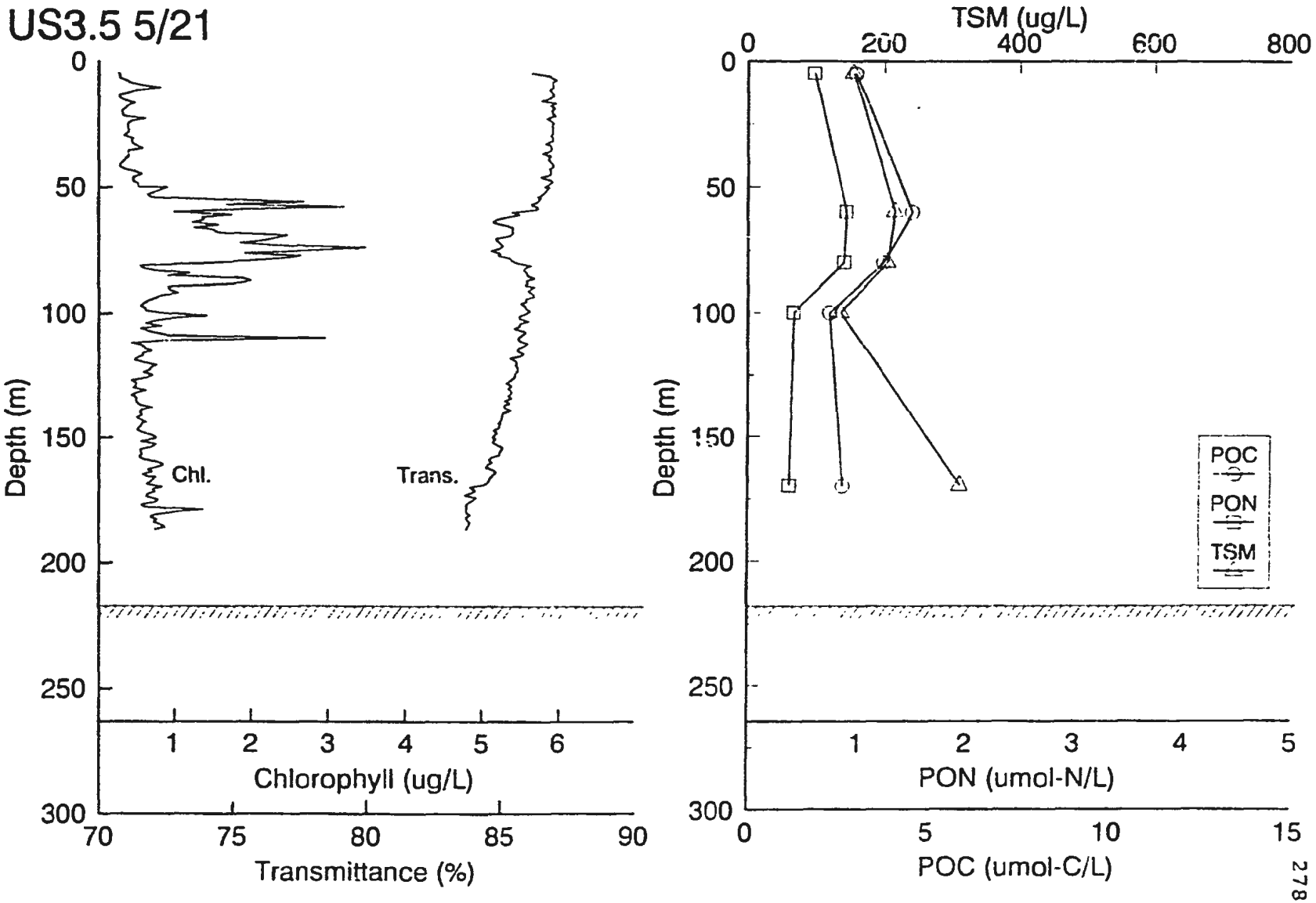

US3.5 5/21
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
1
2
3
4
5
6
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 69. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station US3.5 on May 21.

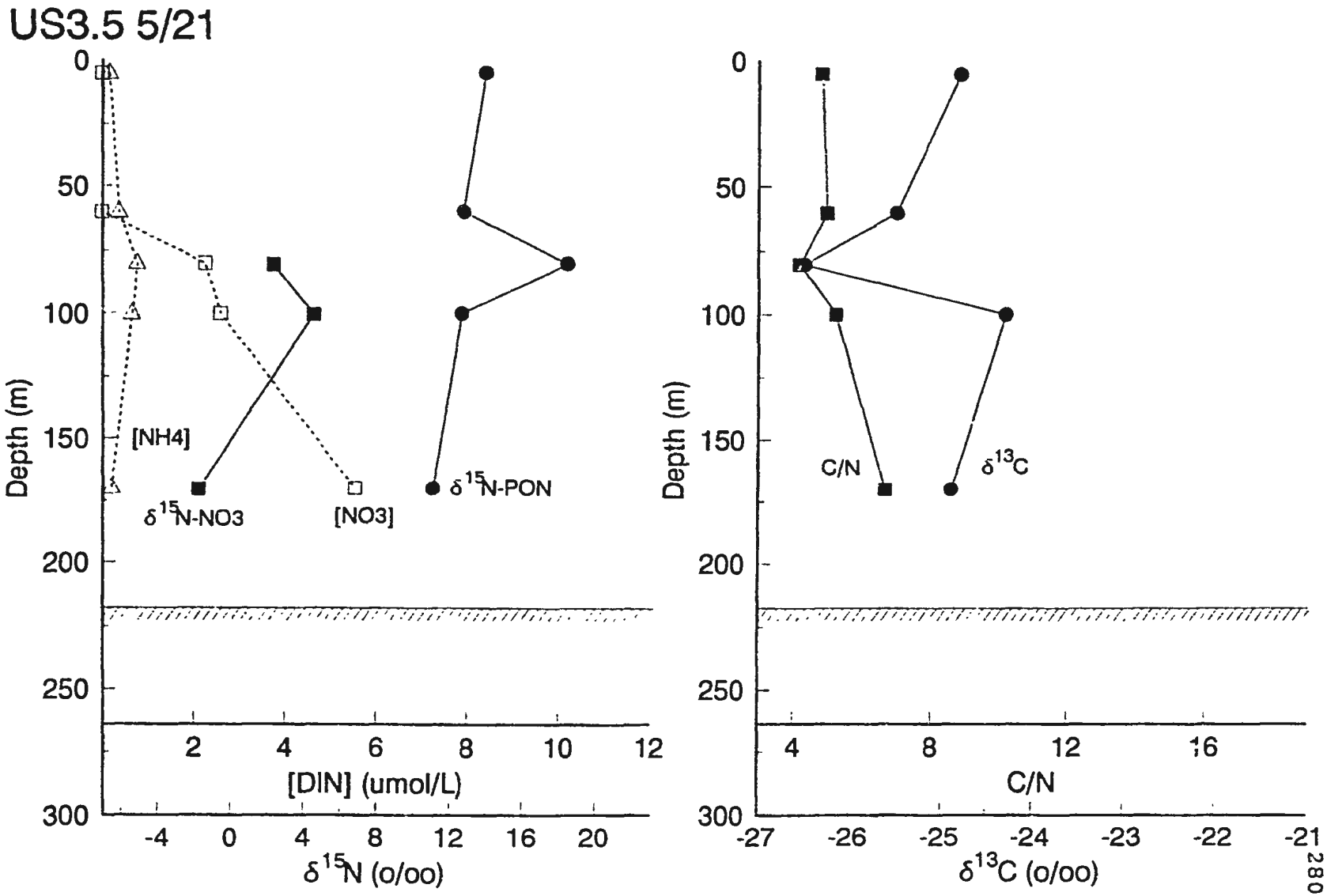

US3.5 5/21
Depth (m)
0
50
100
150
200
250
300
[NH4]
δ15N-NO3
[NO3]
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 70. Salinity, temperature and density as a function of water column depth for station US3.5 on June 24.

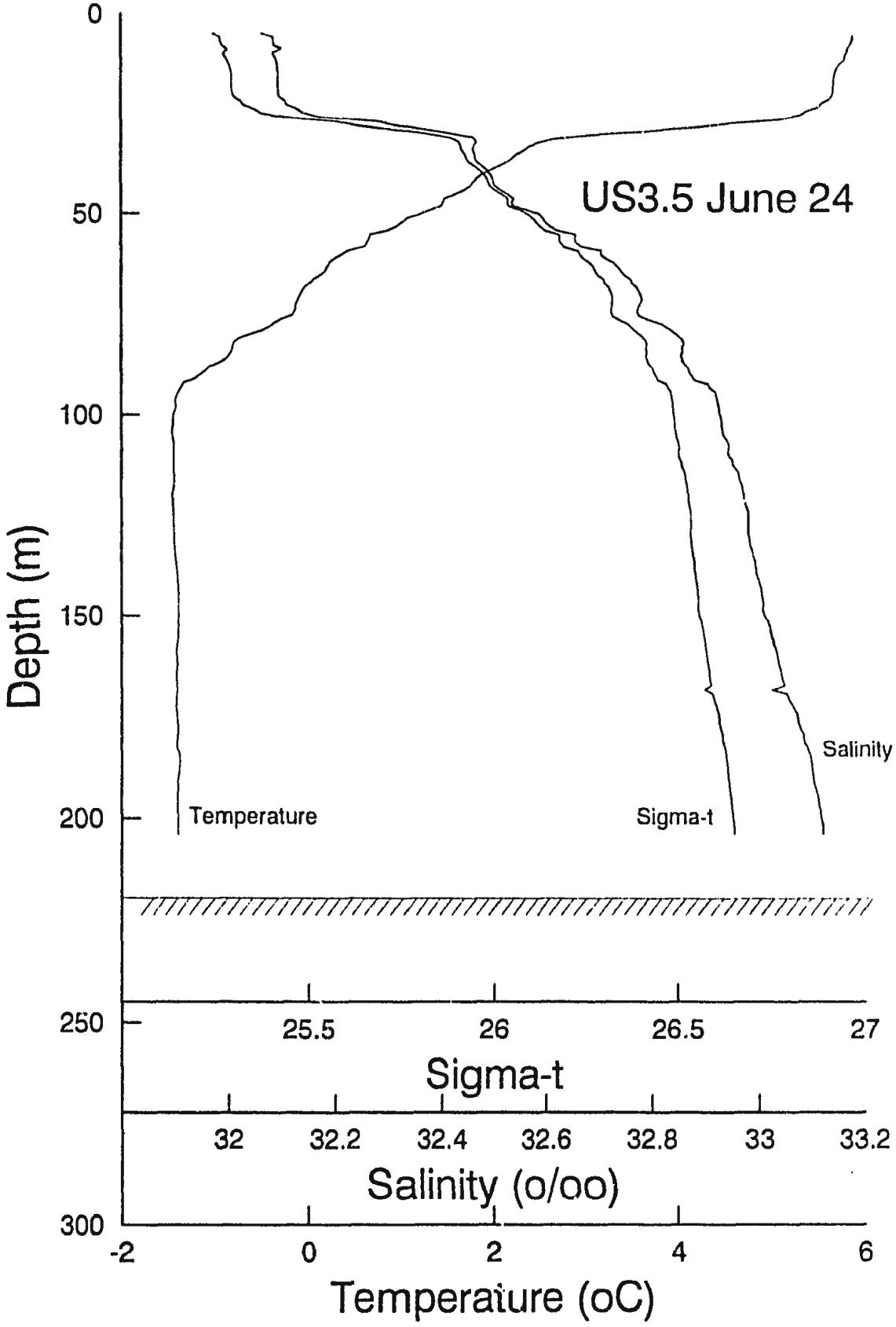

US3.5 June 24
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.5
26
26.5
27
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
0
2
4
6
Temperature (oC)

Figure 71. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station US3.5 on June 24.

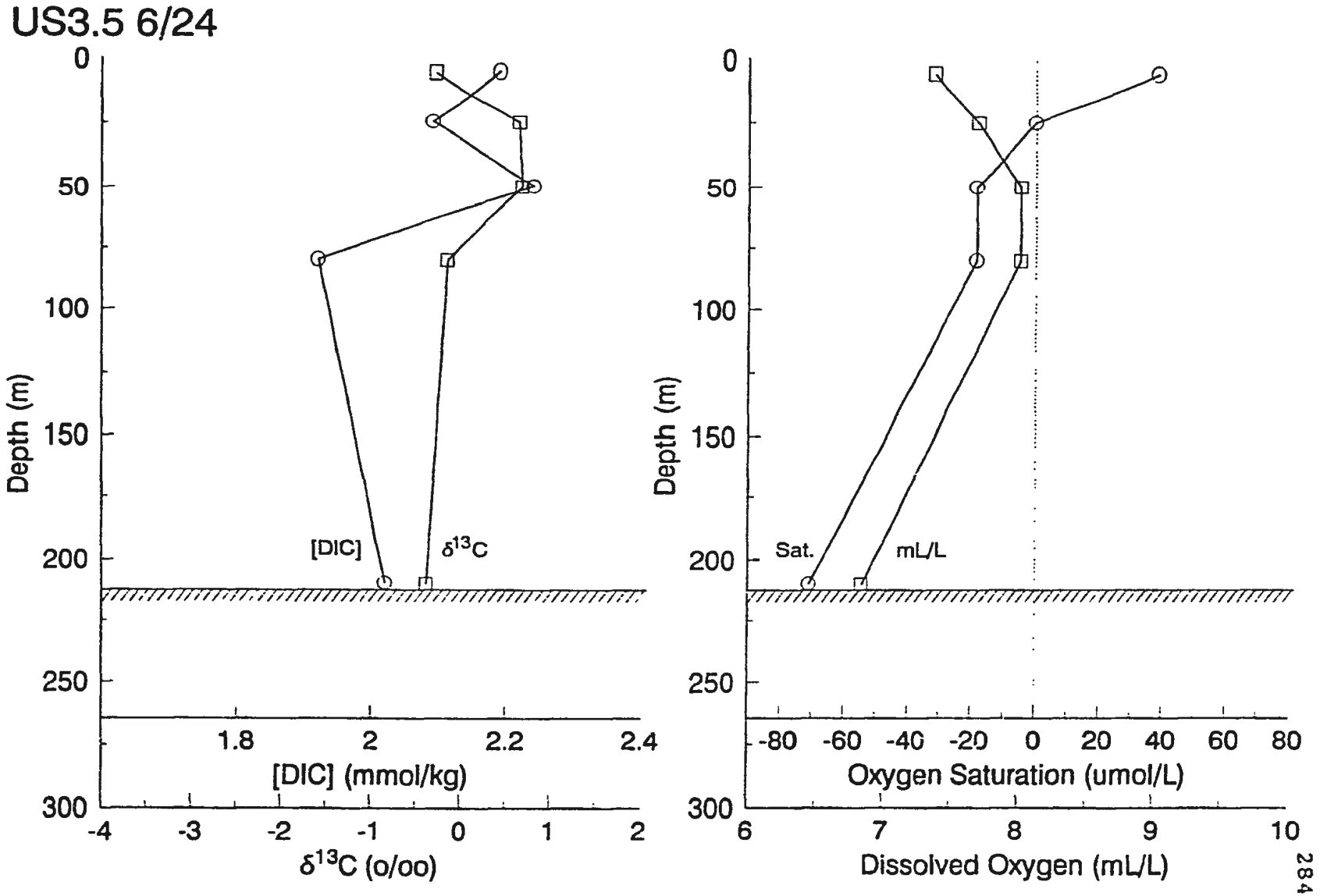

US3.5 6/24
Depth (m)
0
50
100
150
200
250
300
[DIC]
δ13C
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 72. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station US3.5 on June 24.

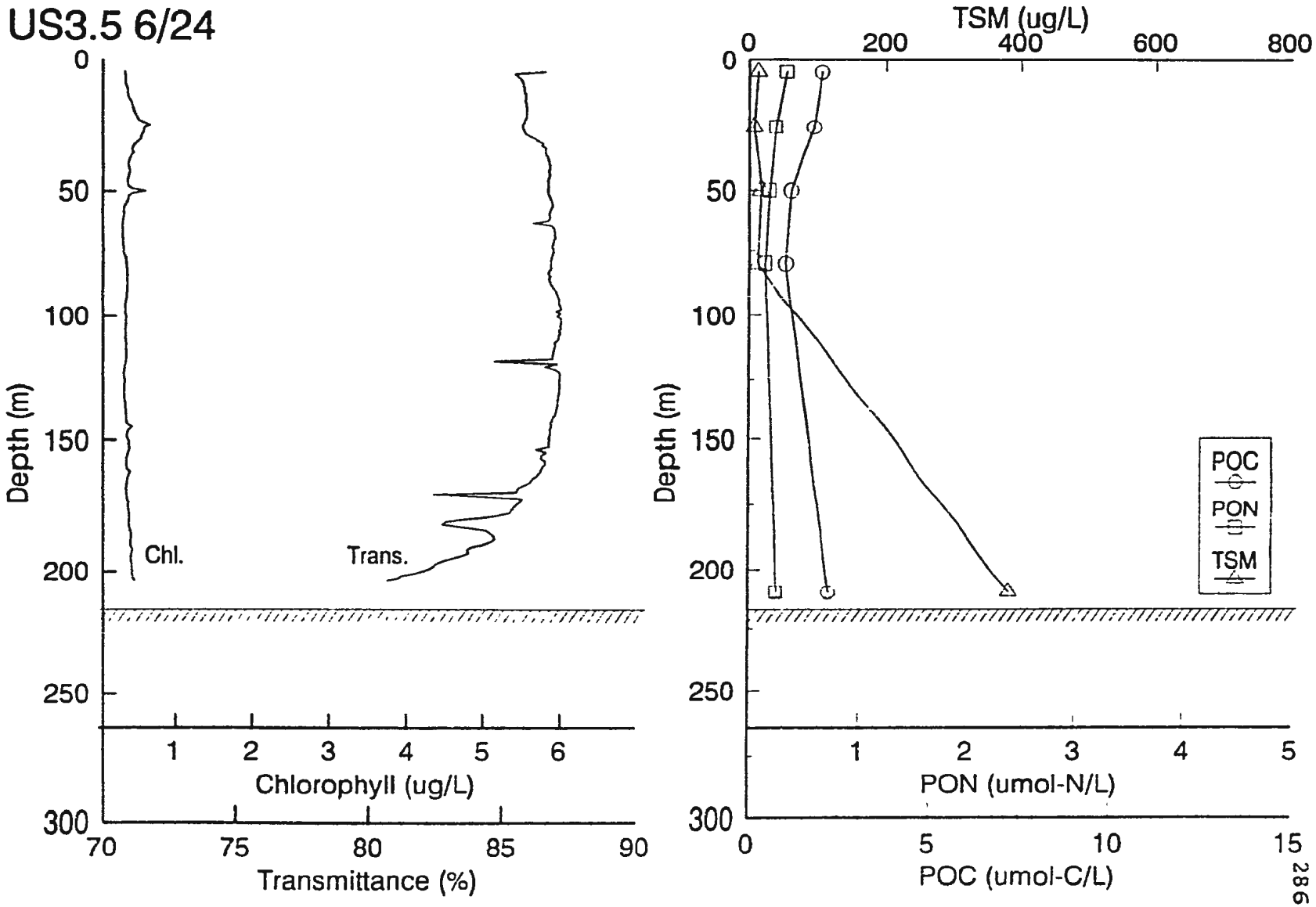

US3.5 6/24
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
1
2
3
4
5
6
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 73. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station US3.5 on June 24.

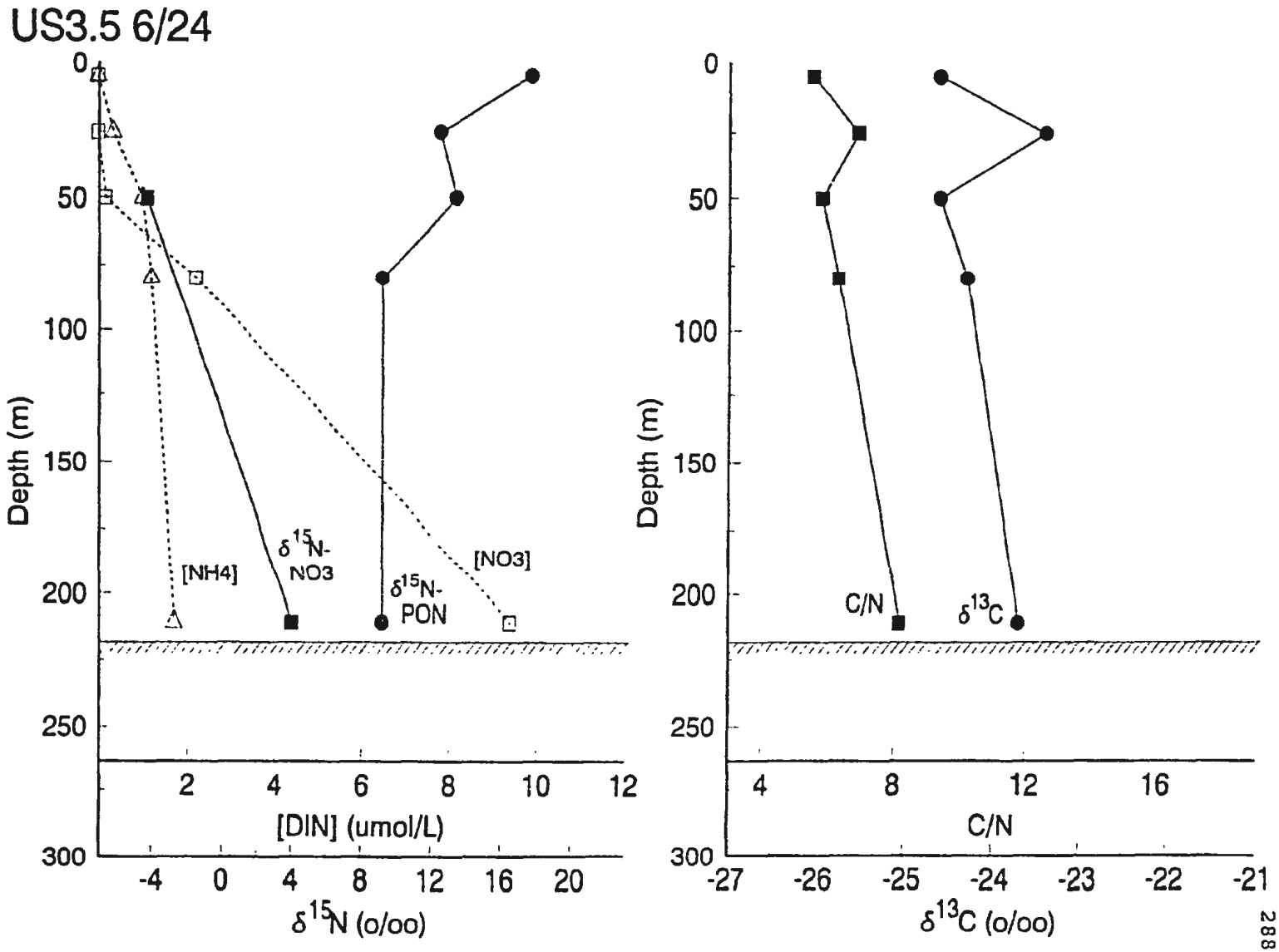

US3.5 6/24
Depth (m)
0
50
100
150
200
250
300
[NH4]
δ15N-NO3
δ15N-PON
[NO3]
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 74. Salinity, temperature and density as a function of water column depth for station CTR23 on April 30.

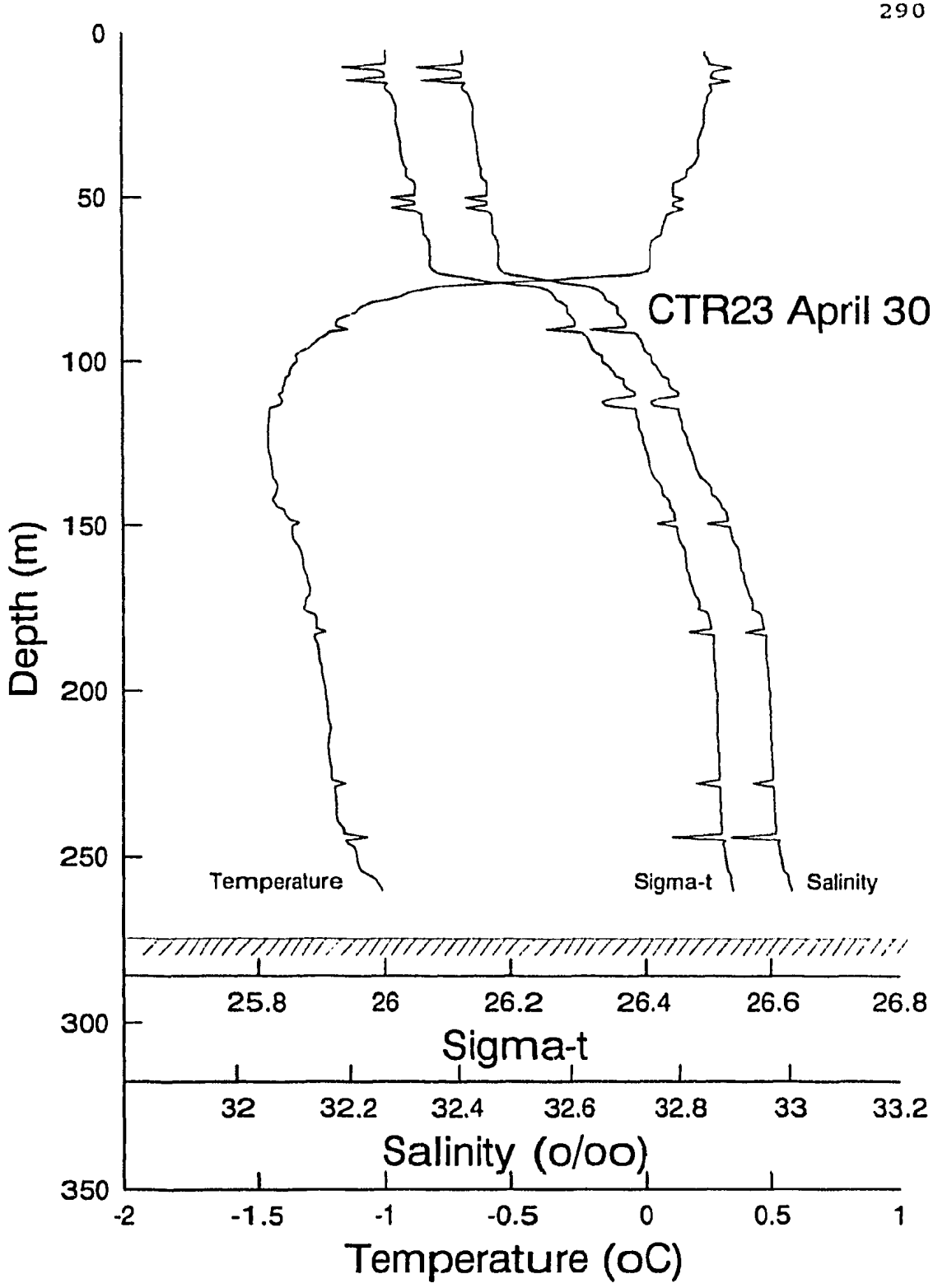

CTR23 April 30
Depth (m)
0
50
100
150
200
250
300
350
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
0.5
1
Temperature (oC)

Figure 75. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station CTR23 on April 30.

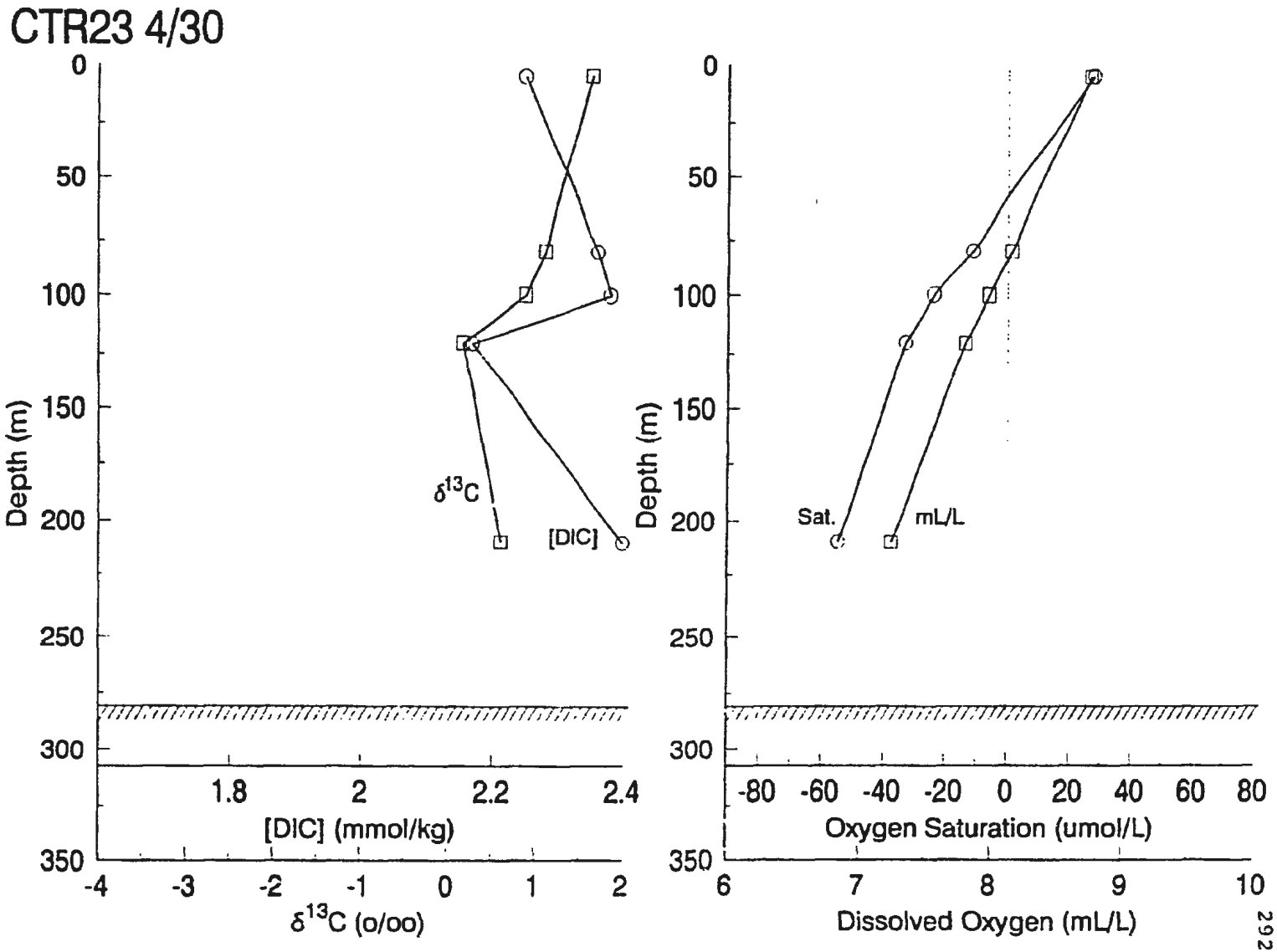

CTR23 4/30
Depth (m)
0
50
100
150
200
250
300
350
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 76. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station CTR23 on April 30.

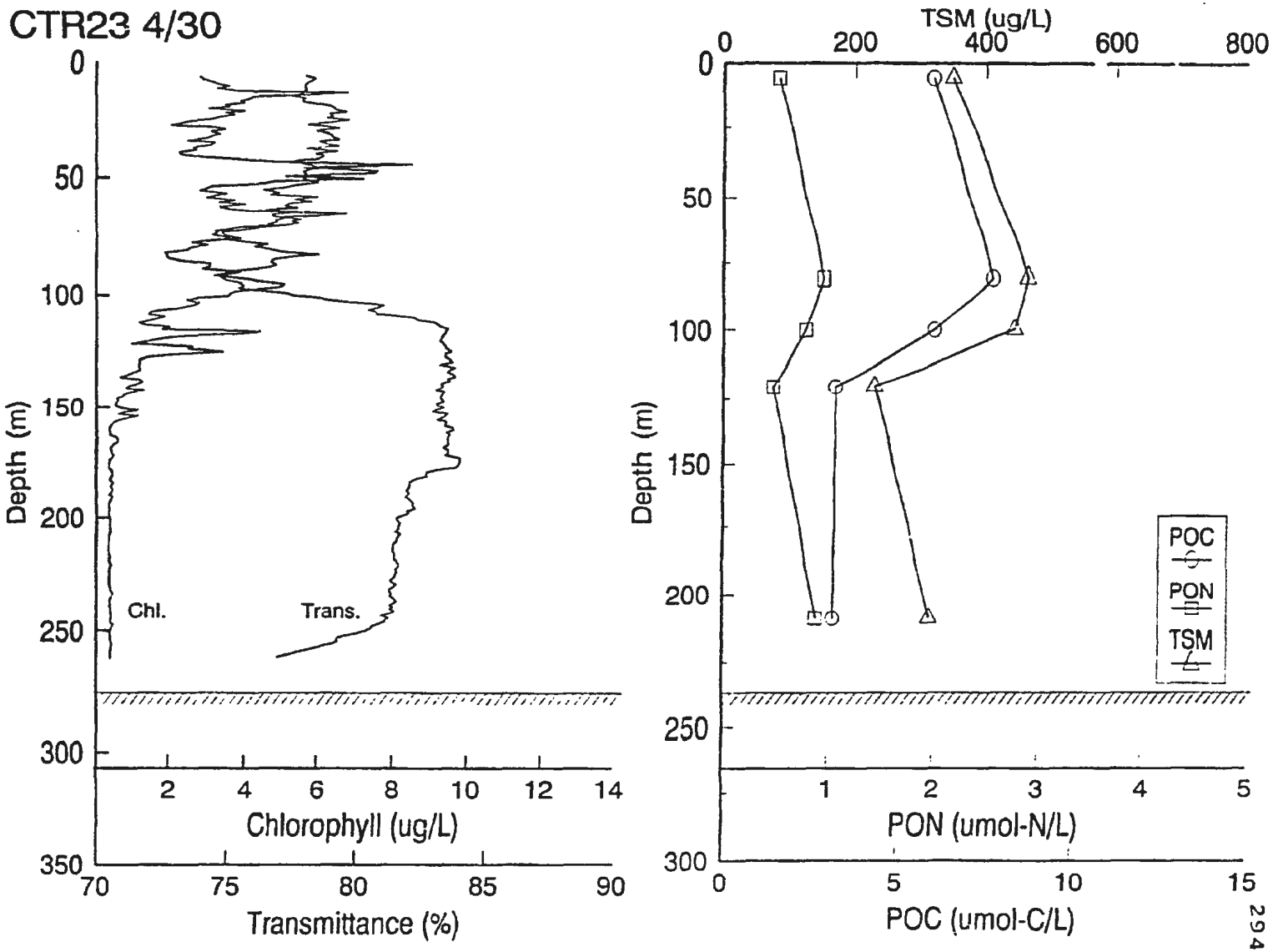

CTR23 4/30
Depth (m)
0
50
100
150
200
250
300
350
Chl.
Trans.
2
4
6
8
10
12
14
Chlorophyll (ug/L)
70
75
80
85
90
Transmittance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 77. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station CTR23 on April 30.

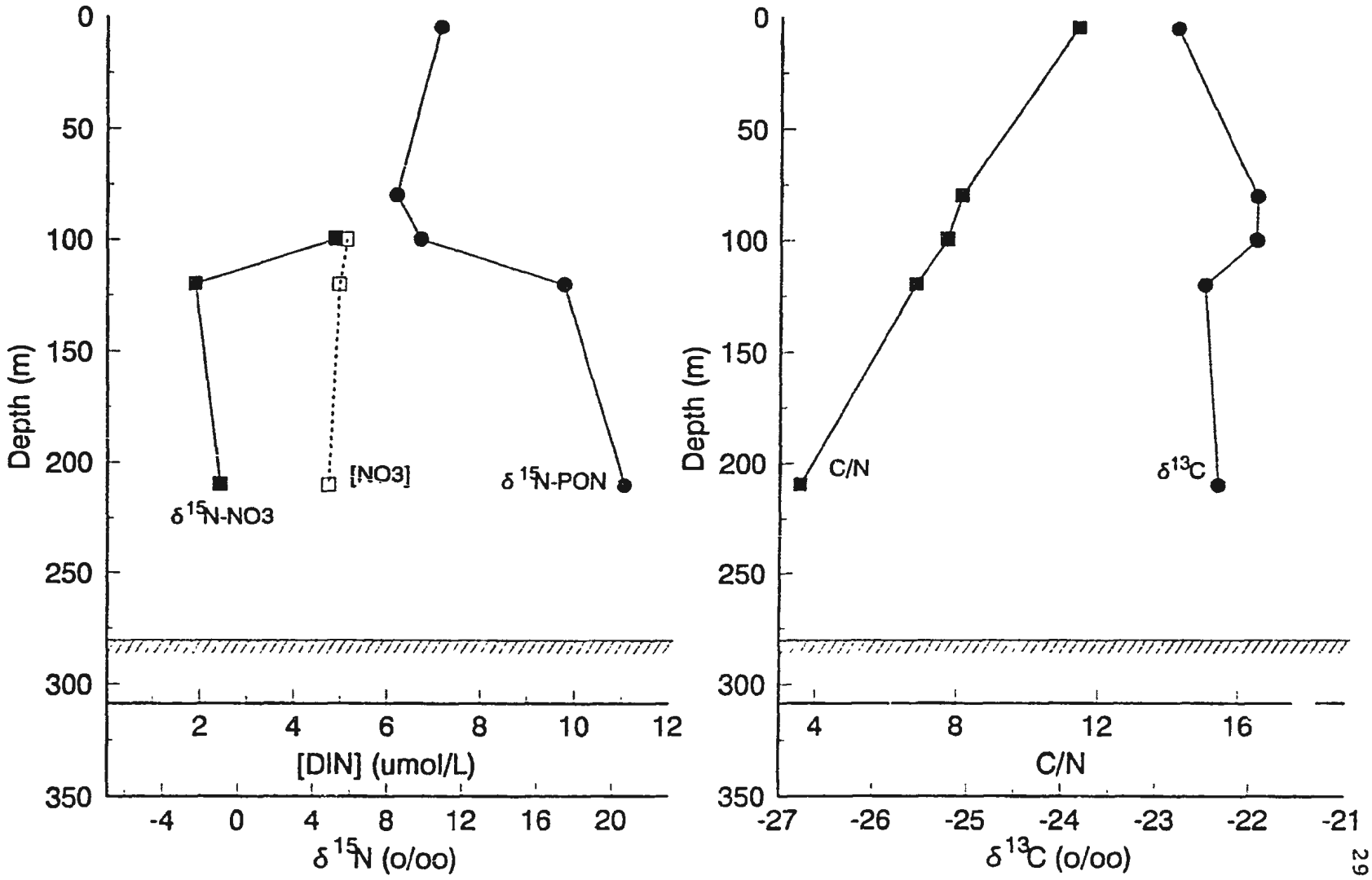

CTR23 4/30
Depth (m)
0
50
100
150
200
250
300
350
δ15N-NO3
[NO3]
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 78. Salinity, temperature and density as a function of water column depth for station CC13 on May 4.

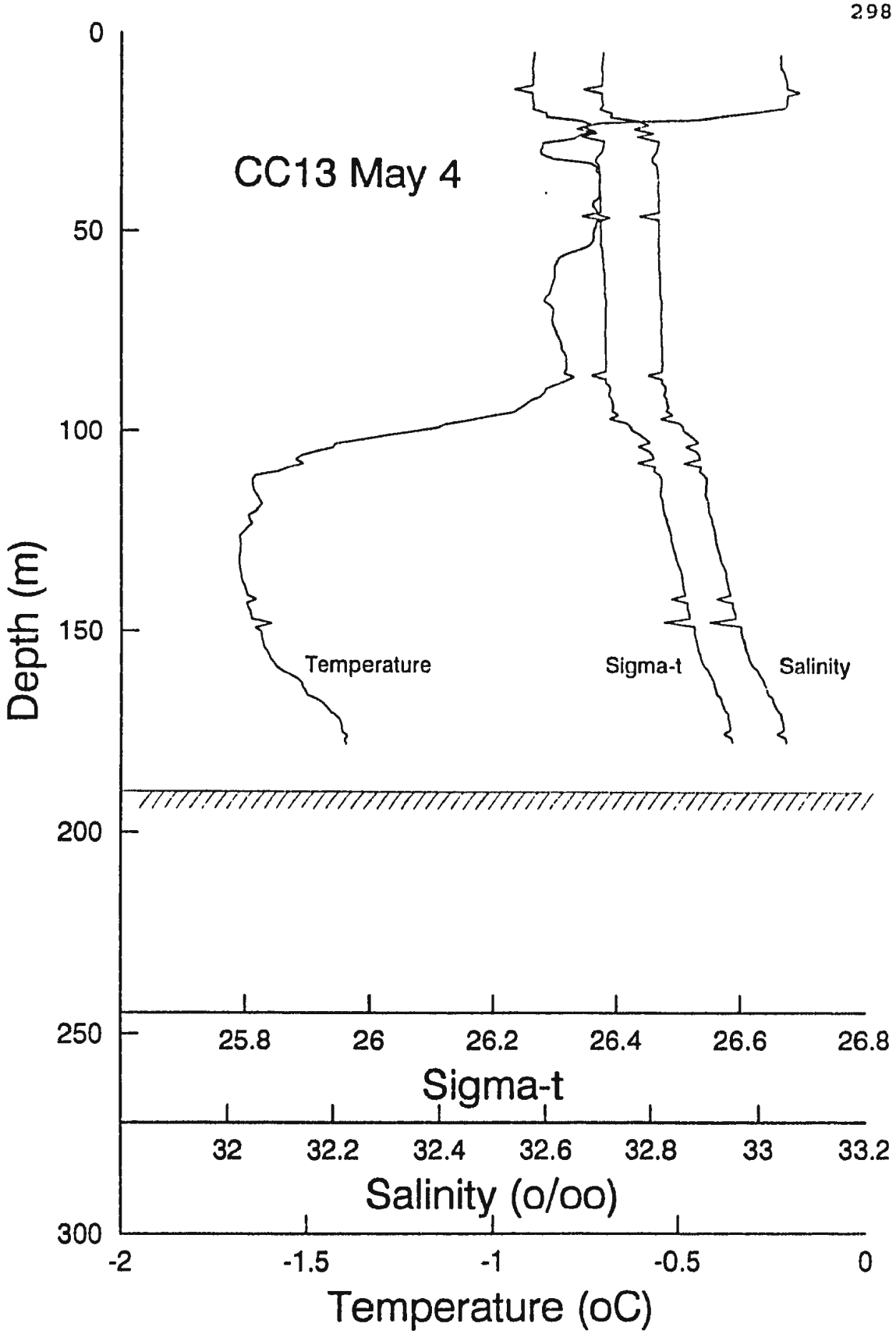

CC13 May 4
Depth (m)
0
50
100
150
200
250
300
Temperature
Sigma-t
Salinity
25.8
26
26.2
26.4
26.6
26.8
Sigma-t
32
32.2
32.4
32.6
32.8
33
33.2
Salinity (o/oo)
-2
-1.5
-1
-0.5
0
Temperature (oC)

Figure 79. Concentration of dissolved oxygen and dissolved inorganic carbon (DIC) and the $\delta^{13}C$ of DIC for station CC13 May 4.

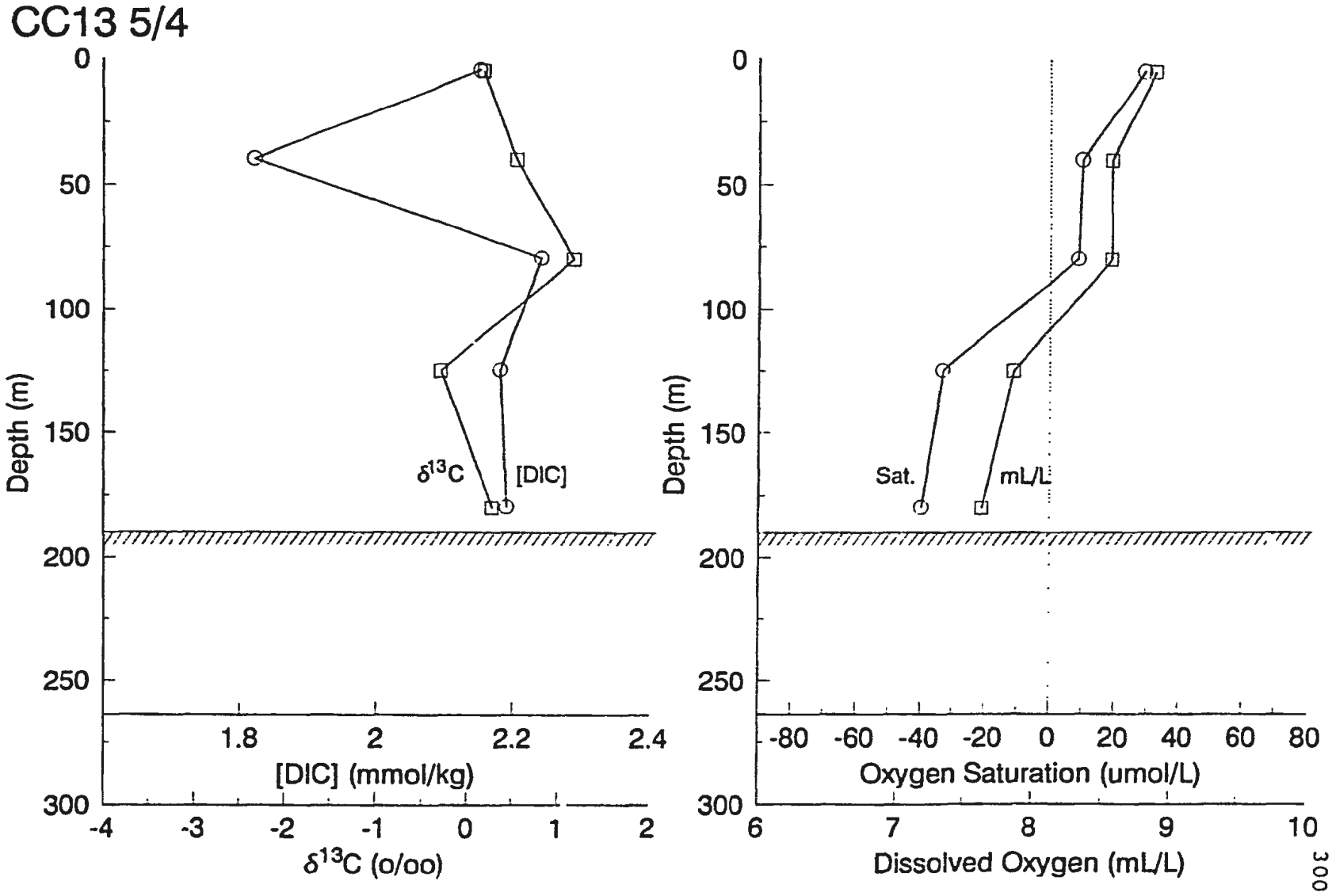

CC13 5/4
Depth (m)
0
50
100
150
200
250
300
δ13C
[DIC]
1.8
2
2.2
2.4
[DIC] (mmol/kg)
-4
-3
-2
-1
0
1
2
δ13C (o/oo)
Sat.
mL/L
-80
-60
-40
-20
0
20
40
60
80
Oxygen Saturation (umol/L)
6
7
8
9
10
Dissolved Oxygen (mL/L)

Figure 80. Percent transmittance and concentrations of Chlorophyll a, particulate organic nitrogen (PON), particulate organic carbon (POC) and total suspended matter (TSM) for station CC13 on May 4.

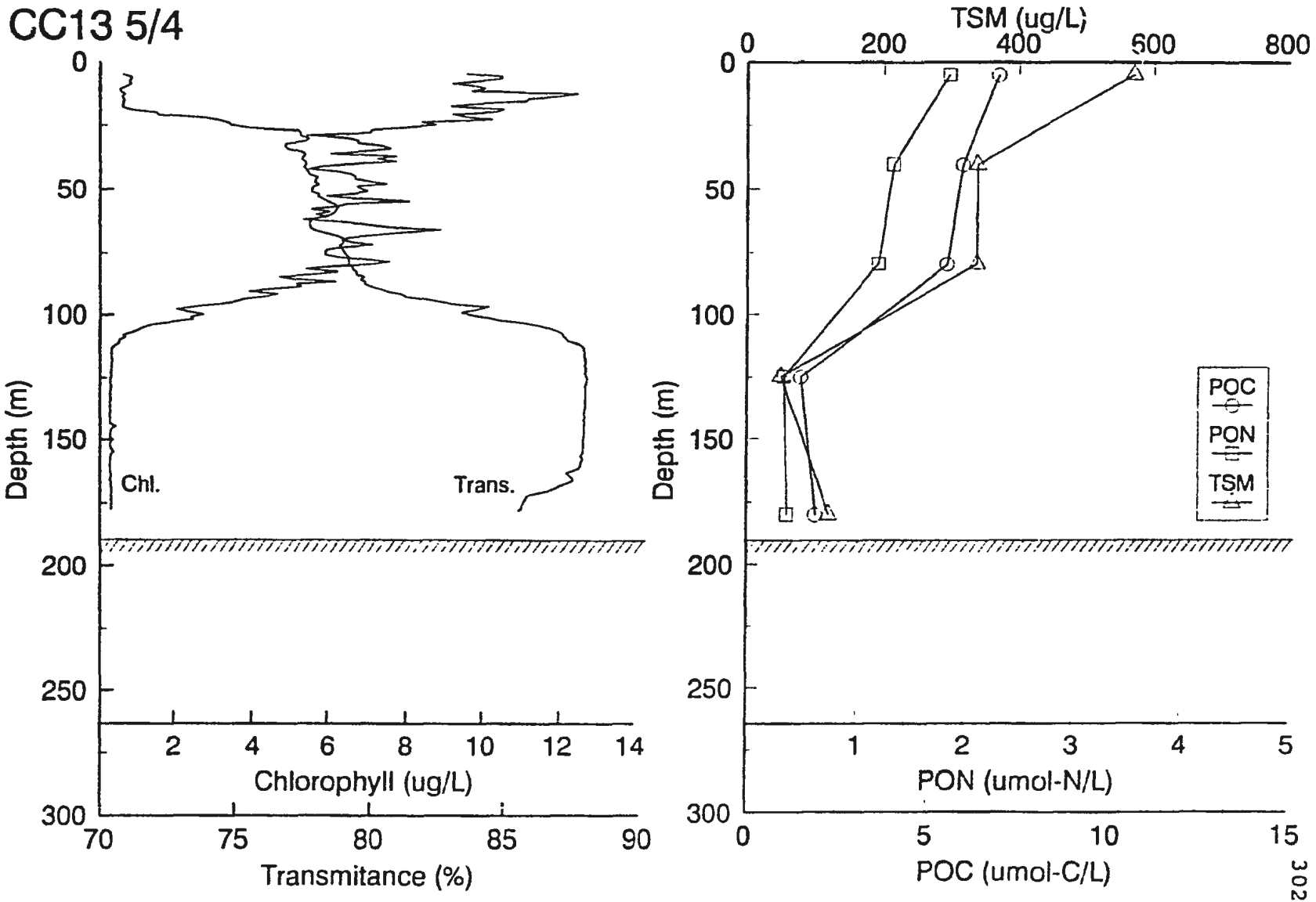

CC13 5/4
Depth (m)
0
50
100
150
200
250
300
Chl.
Trans.
2
4
6
8
10
12
14
Chlorophyll (ug/L)
70
75
80
85
90
Transmitance (%)
TSM (ug/L)
0
200
400
600
800
POC
PON
TSM
1
2
3
4
5
PON (umol-N/L)
0
5
10
15
POC (umol-C/L)

Figure 81. Isotopic composition of dissolved nitrate ($\delta^{15}N$-NO_3), PON and POC, C/N of POM and concentration of dissolved inorganic nitrogen (DIN) for station CC13 on May 4.

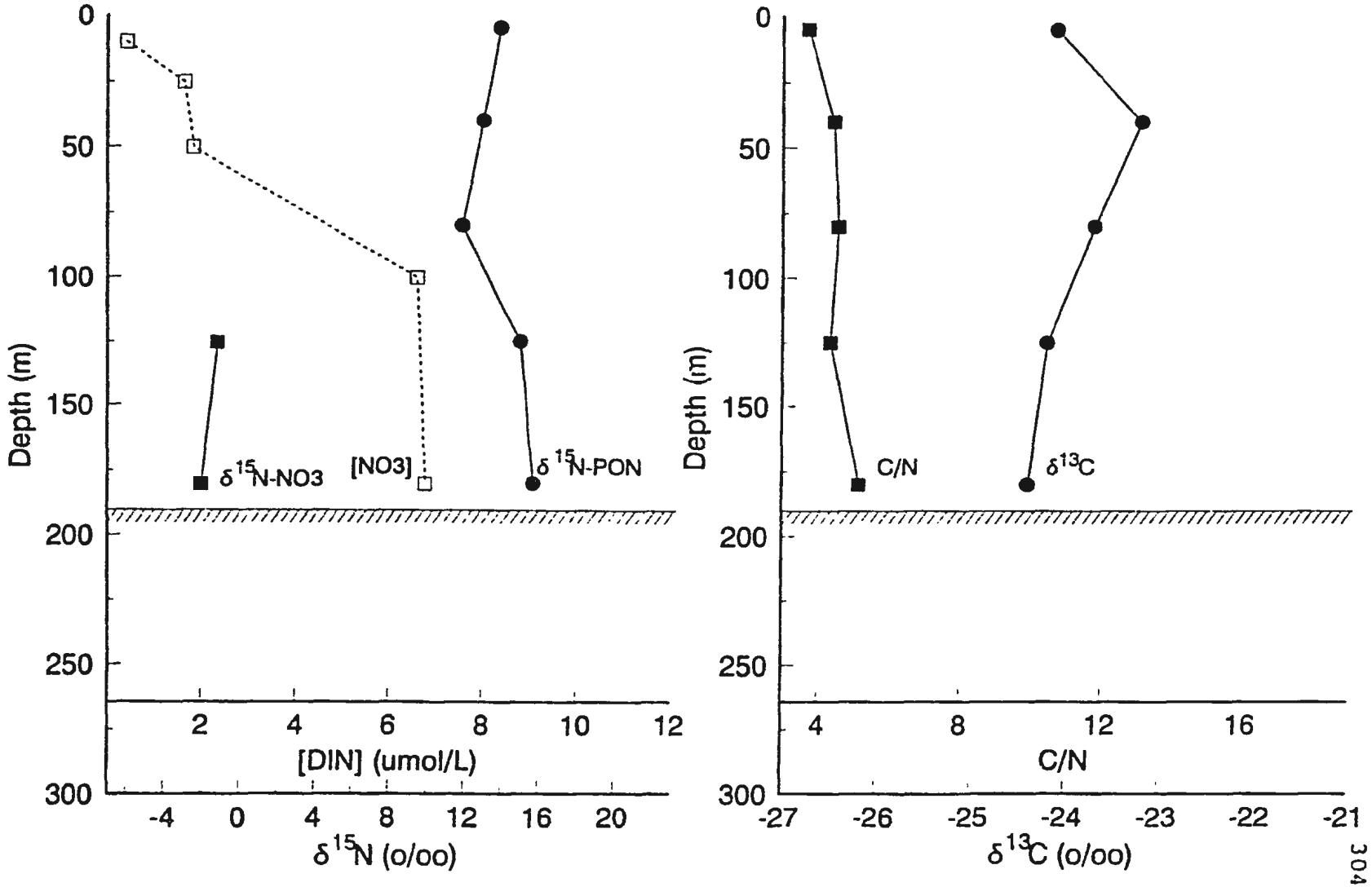

CC13 5/4
Depth (m)
0
50
100
150
200
250
300
δ15N-NO3
[NO3]
δ15N-PON
2
4
6
8
10
12
[DIN] (umol/L)
-4
0
4
8
12
16
20
δ15N (o/oo)
C/N
δ13C
4
8
12
16
C/N
-27
-26
-25
-24
-23
-22
-21
δ13C (o/oo)

Figure 82. Weight averaged $\delta^{15}N$ and $\delta^{13}C$ values (eq. 3) for seston at BRLP5 and US3.5 in 1990 and chlorophyll concentrations integrated over the water column

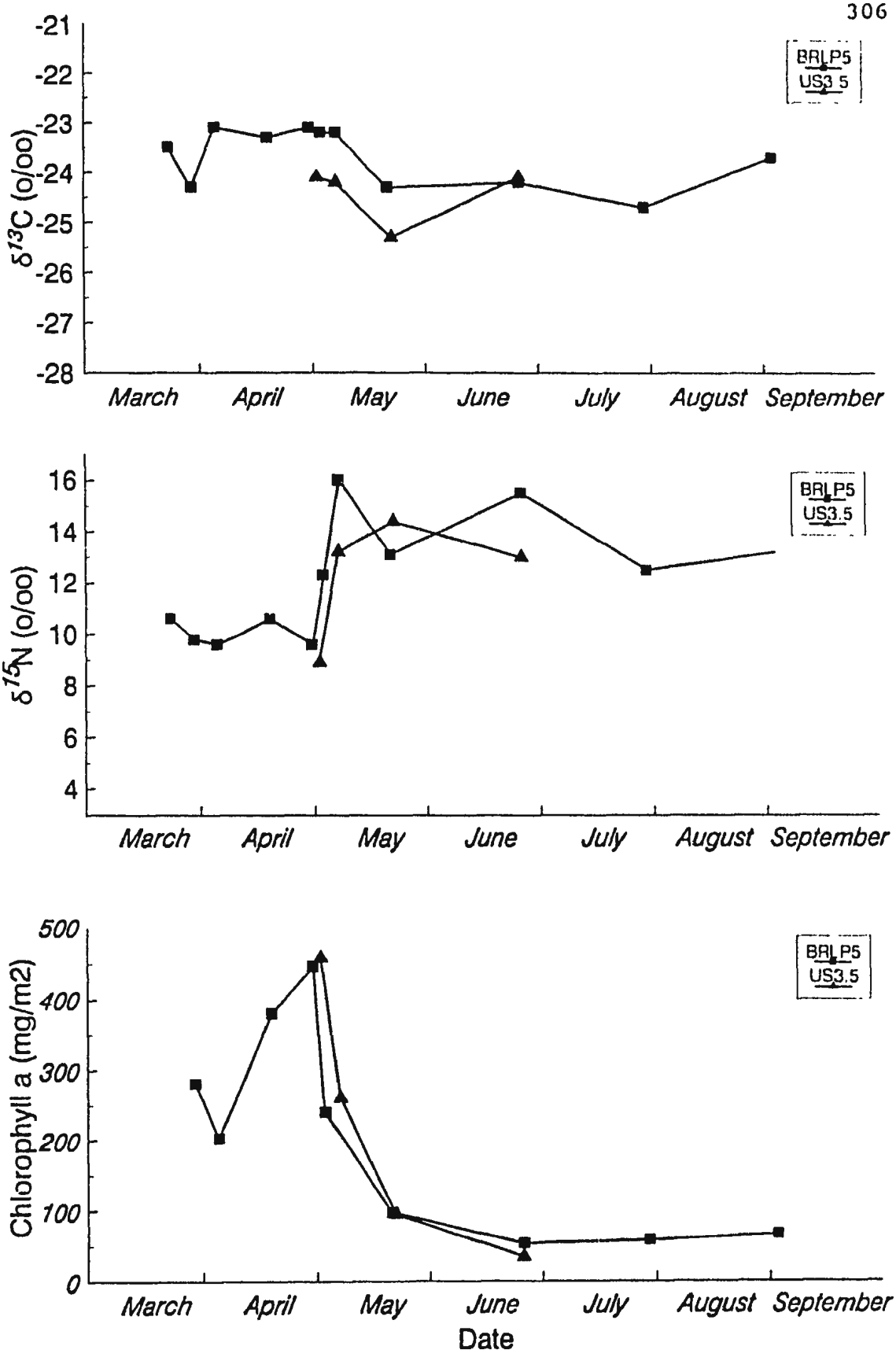

-21
-22
-23
-24
-25
-26
-27
-28
δ13C (o/oo)
BRLP5
US3.5
March
April
May
June
July
August
September
16
14
12
10
8
6
4
δ15N (o/oo)
BRLP5
US3.5
March
April
May
June
July
August
September
500
400
300
200
100
0
Chlorophyll a (mg/m2)
BRLP5
US3.5
March
April
May
June
July
August
September
Date

Figure 83. Carbon and nitrogen isotopic, elemental and flux data determined from sediment trap collections at 40m from station BRLP5 in 1988.

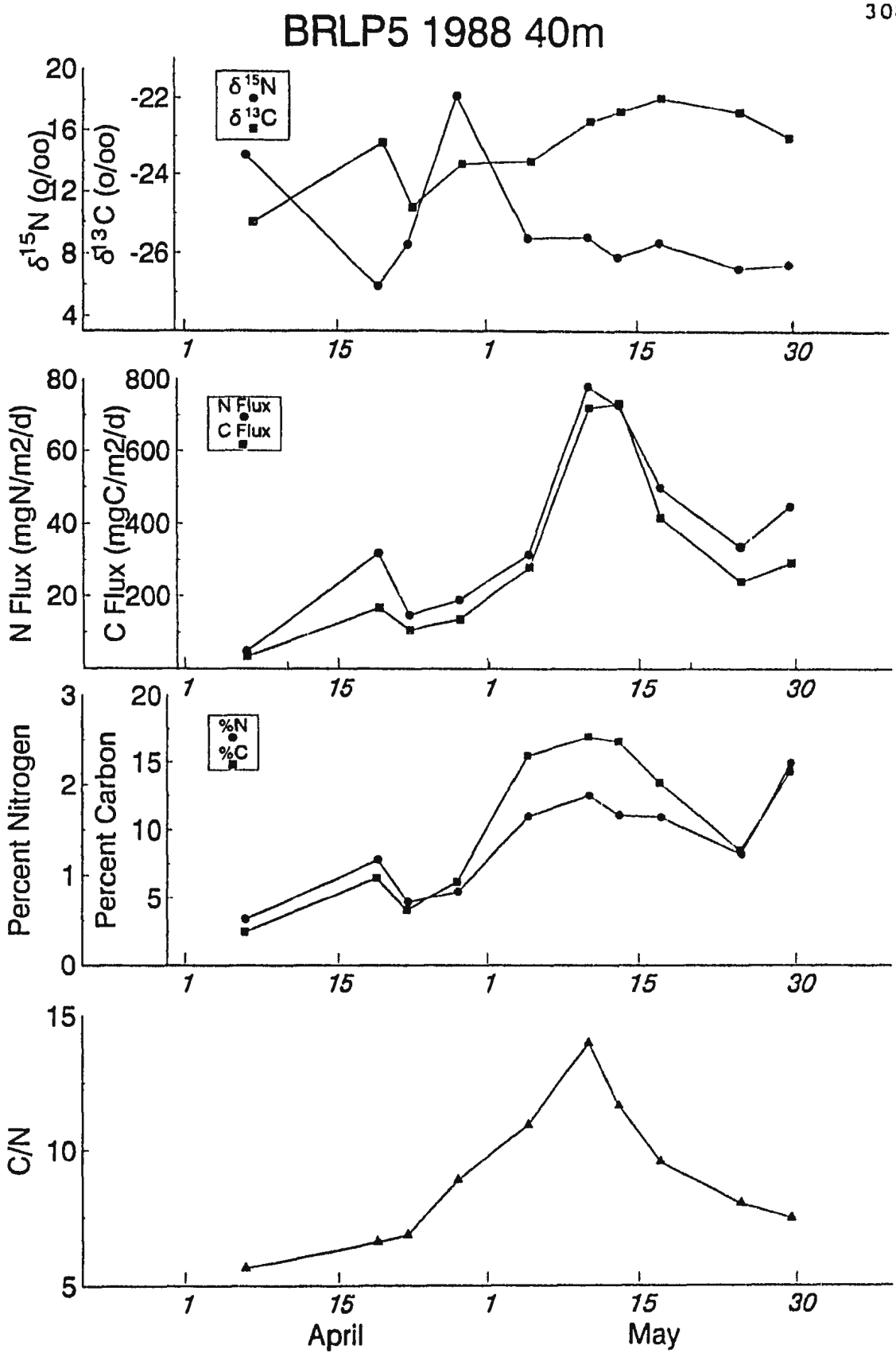

BRLP5 1988 40m
δ15N (o/oo)
δ13C (o/oo)
δ15N
δ13C
N Flux (mgN/m2/d)
C Flux (mgC/m2/d)
N Flux
C Flux
Percent Nitrogen
Percent Carbon
%N
%C
C/N
1
15
1
15
30
April
May

Figure 84. Carbon and nitrogen isotopic, elemental and flux data determined from sediment trap collections at 80m from station BRLP5 in 1988.

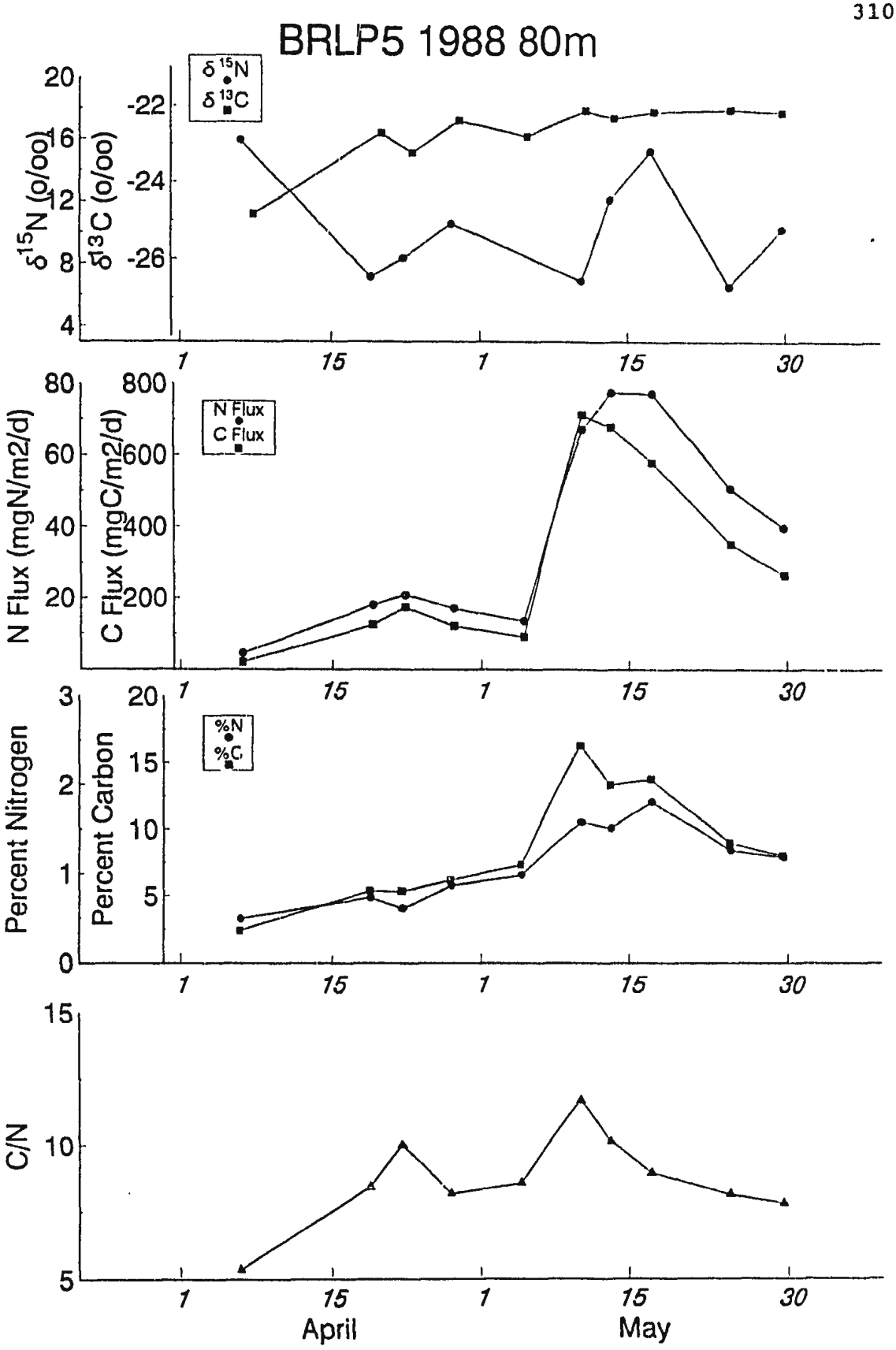

BRLP5 1988 80m
δ 15N
δ 13C
δ15N (o/oo)
δ13C (o/oo)
N Flux
C Flux
N Flux (mgN/m2/d)
C Flux (mgC/m2/d)
%N
%C
Percent Nitrogen
Percent Carbon
C/N
1
15
1
15
30
April
May

Figure 85. Carbon and nitrogen isotopic, elemental and flux data determined from sediment trap collections at 150m from station BRLP5 in 1988.

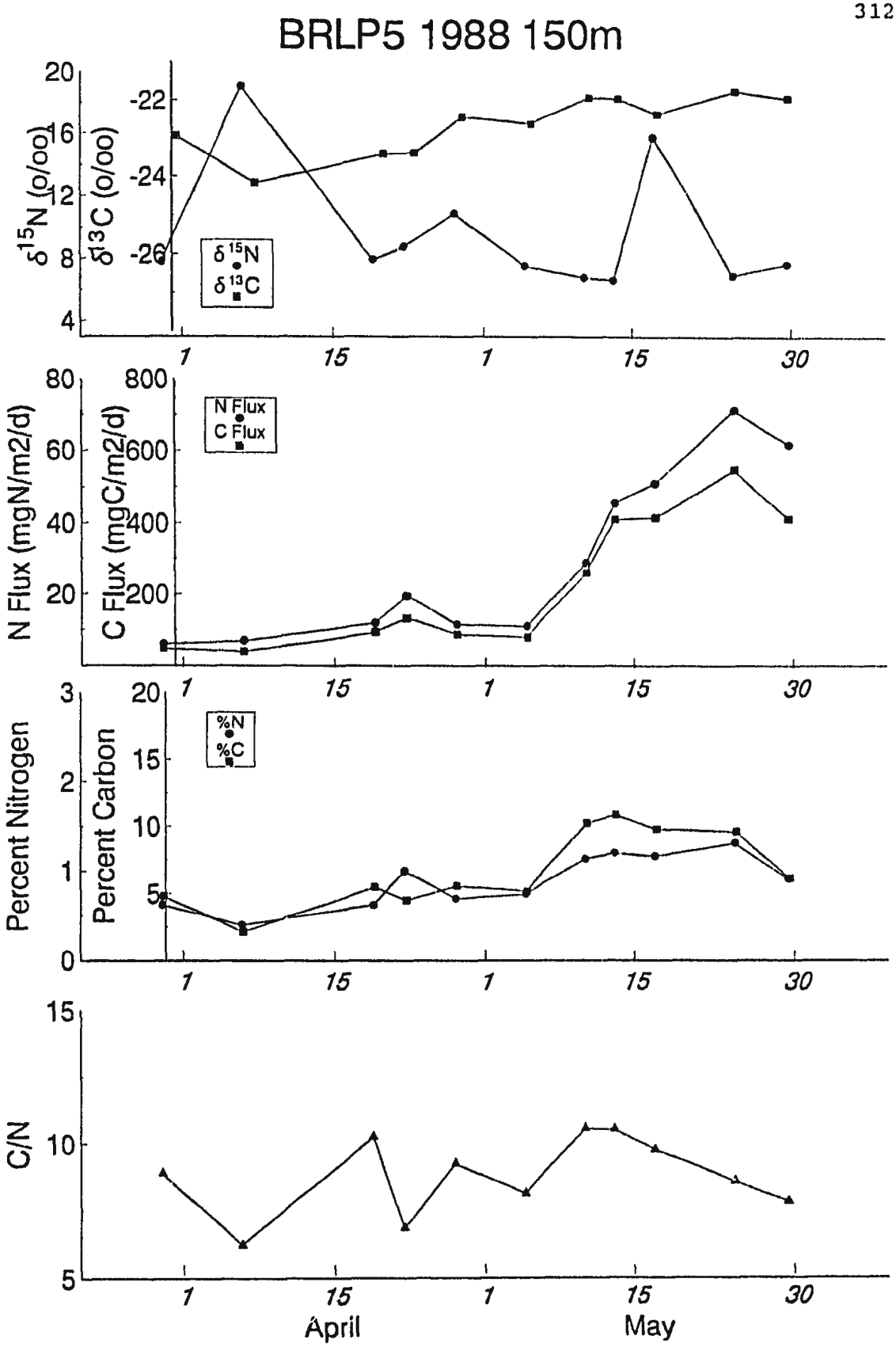

BRLP5 1988 150m
δ15N (o/oo)
δ13C (o/oo)
δ15N
δ13C
N Flux (mgN/m2/d)
C Flux (mgC/m2/d)
N Flux
C Flux
Percent Nitrogen
Percent Carbon
%N
%C
C/N
April
May
1
15
30

Figure 86. Carbon and nitrogen isotopic, elemental and flux data determined from sediment trap collections at 240m from station BRLP5 in 1988.

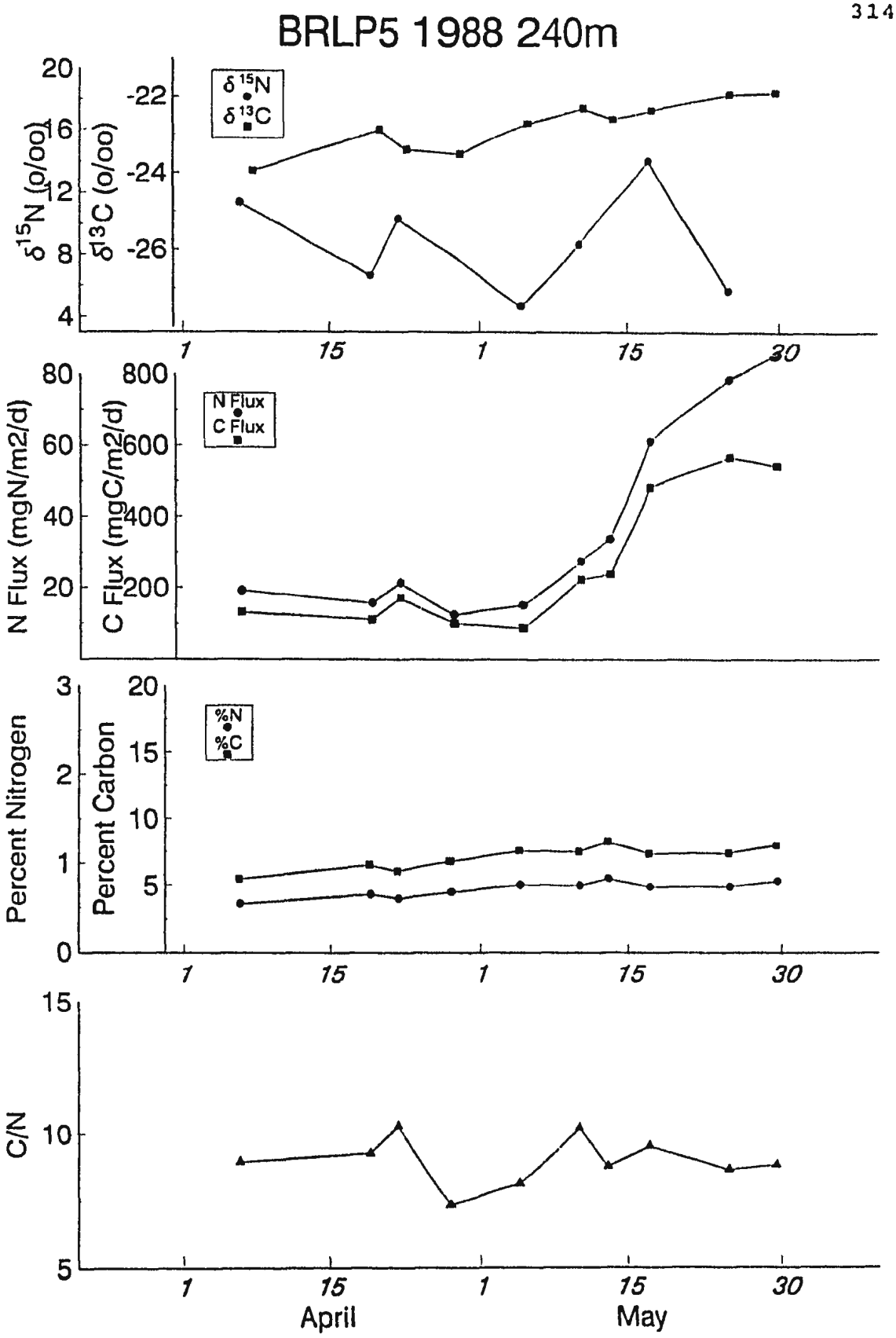

BRLP5 1988 240m
δ15N (o/oo)
δ13C (o/oo)
δ 15N
δ 13C
N Flux (mgN/m2/d)
C Flux (mgC/m2/d)
N Flux
C Flux
Percent Nitrogen
Percent Carbon
%N
%C
C/N
1
15
1
15
30
April
May

Figure 87. Sedimentation rates of bulk material (dry weight) collected in sediment traps at 40 m, 80 m, 150 m, and 240 m at BRLP5 in 1988.

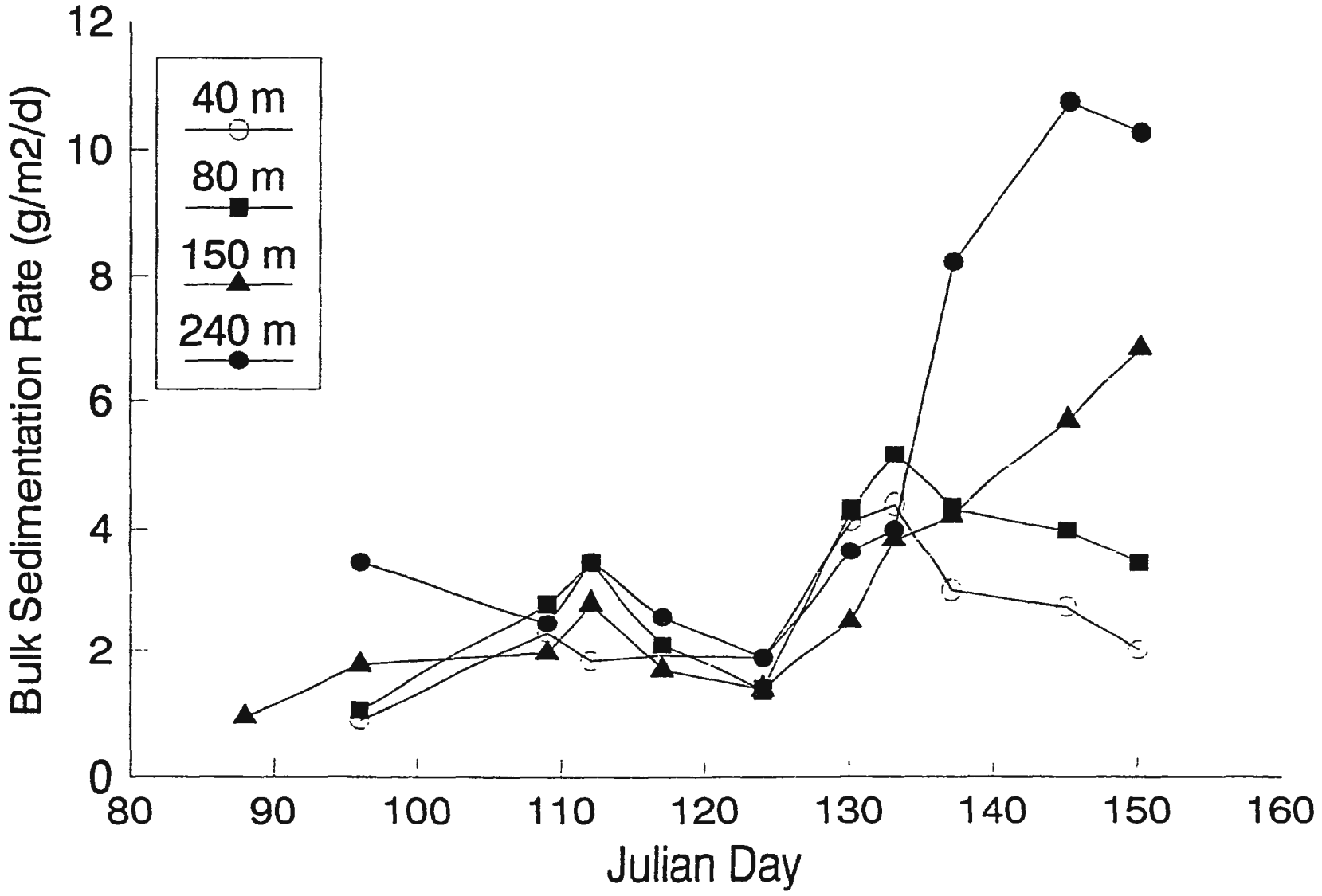
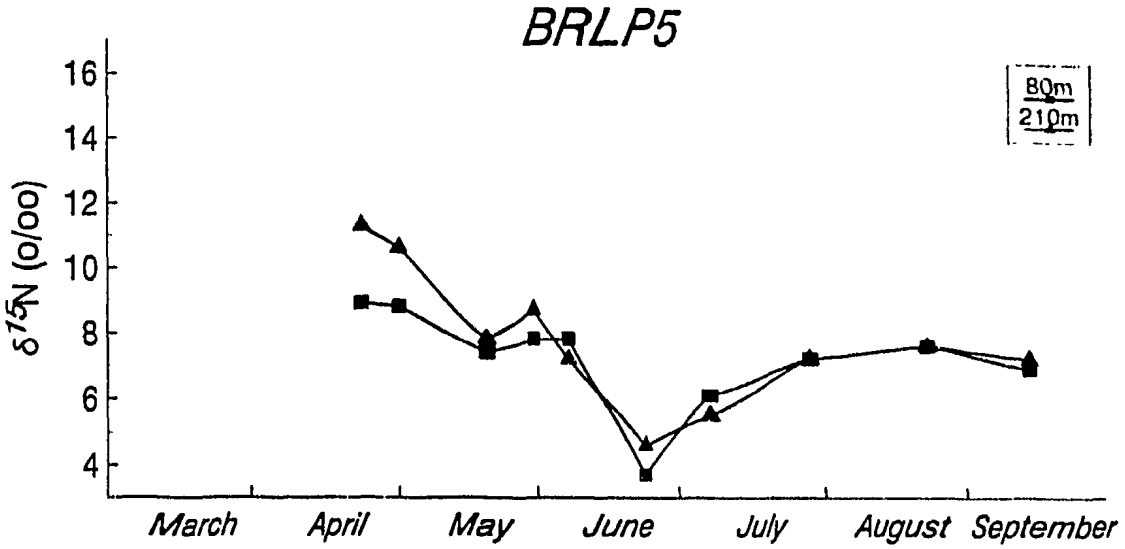

Bulk Sedimentation Rate (g/m2/d)
12
10
8
6
4
2
0
40 m
80 m
150 m
240 m
80
90
100
110
120
130
140
150
160
Julian Day

Figure 88. Nitrogen isotope values for sediment trap material at BRLP5 and US3.5 in 1990.


BRLP5
80m
210m
16
14
12
10
8
6
4
δ15N (o/oo)
March
April
May
June
July
August
September

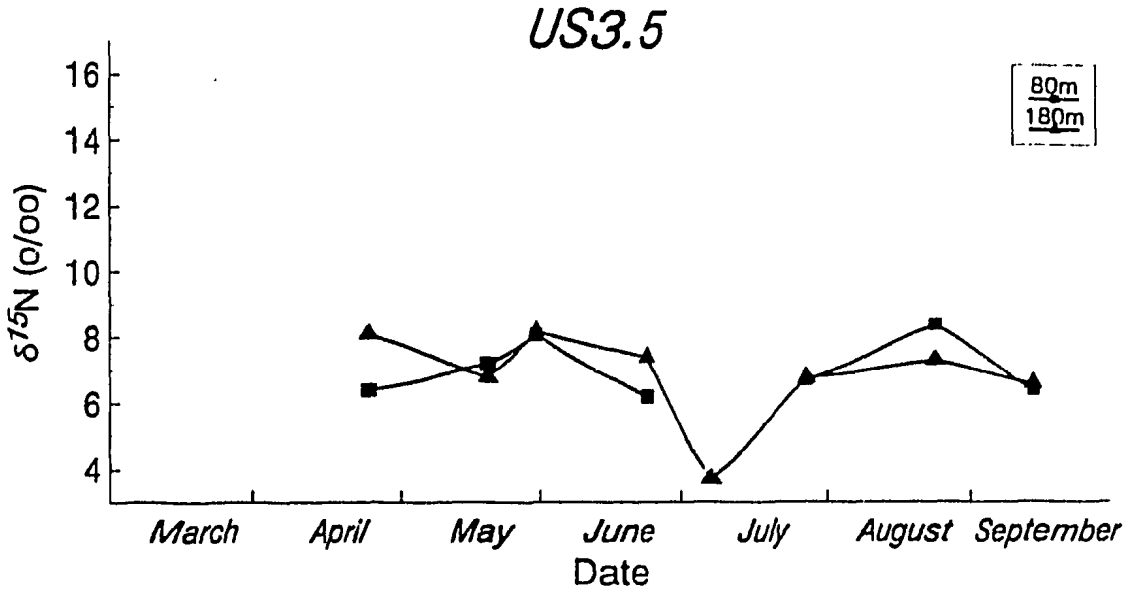
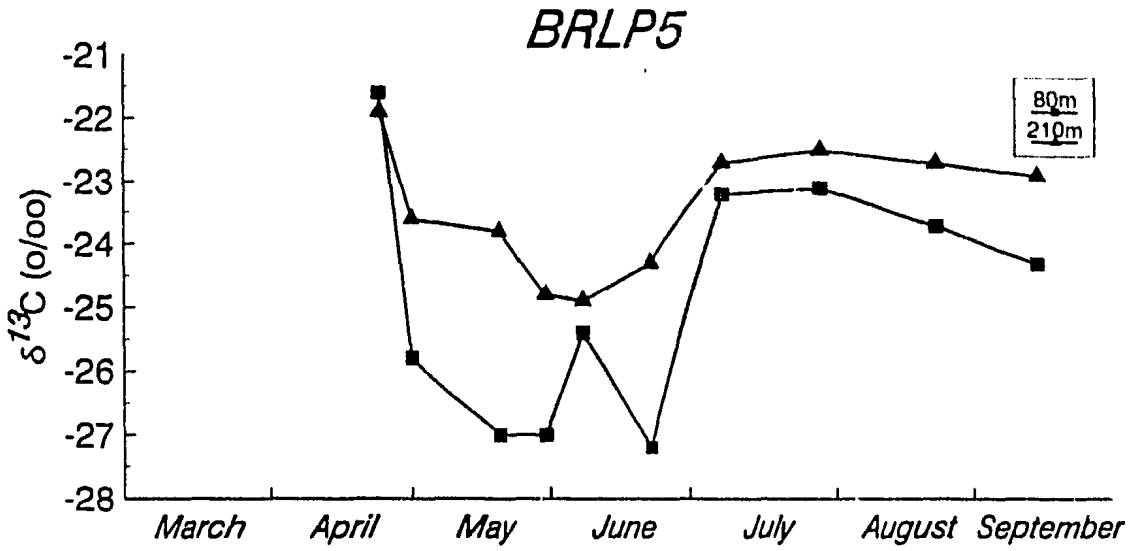
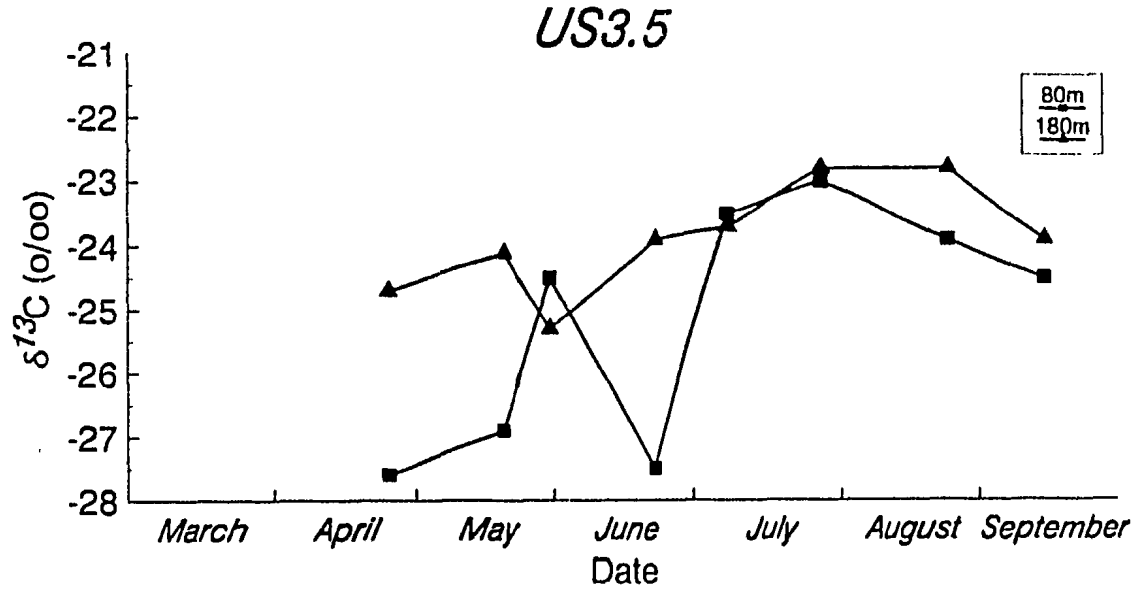

US3.5
80m
180m
16
14
12
10
8
6
4
δ15N (o/oo)
March
April
May
June
July
August
September
Date

Figure 89. Carbon isotope values for sediment trap material at BRLP5 and US3.5 in 1990.


BRLP5
80m
210m
-21
-22
-23
-24
-25
-26
-27
-28
δ13C (o/oo)
March
April
May
June
July
August
September


US3.5
80m
180m
-21
-22
-23
-24
-25
-26
-27
-28
δ13C (o/oo)
March
April
May
June
July
August
September
Date

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Appendix 1. Location of sampling stations in Conception Bay.

Station	Latitude (deg. min. N)	Longitude (deg. min. W)	Depth (m)
CC1	47 30.7	53 07.4	218
BRLP5	47 32.5	53 07.8	238
CC2	47 34.6	53 08.3	275
CTR23	47 36.76	53 07.28	293
CC5	47 41.1	53 05.1	275
CC5.5	47 41.8	53 03.8	nd[1]
CC7	47 45.0	52 59.5	232
US3.5	47 46.65	52 57.8	217
CC8	47 48.3	52 56.8	n.d.
CC9	47 49.9	52 54.7	209
CC10.5	47 53.2	52 44.3	n.d.
CC13	47 55.3	52 15.4	196

[1] nd = not determined

Appendix 2. Carbon and nitrogen isotopic, elemental and flux data determined from sediment trap collections.

Station/ Date	% N	% C	C/N	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	N Flux $mgNm^{-2}d^{-1}$	C Flux $mgNm^{-2}d^{-1}$
1988 40m							
BRLP5 4/6	0.51	2.45	5.65	14.4	-25.2	4.57	23.88
BRLP5 4/20	1.17	6.46	6.59	5.9	-23.2	31.78	158.65
BRLP5 4/23	0.70	4.05	6.83	8.6	-24.8	14.83	96.50
BRLP5 4/28	0.82	6.19	8.88	18.3	-23.7	18.91	127.36
BRLP5 5/5	1.65	15.48	10.93	9.0	-23.6	31.45	271.53
BRLP5 5/11	1.88	16.93	14.01	9.1	-22.6	77.95	712.42
BRLP5 5/13	1.66	16.56	11.65	7.8	-22.3	72.77	725.03
BRLP5 5/19	1.65	13.50	9.57	8.7	-22.0	49.87	408.40
BRLP5 5/26	1.24	8.49	8.02	7.1	-22.4	33.73	232.35
BRLP5 6/1	2.25	14.34	7.46	7.4	-23.0	44.48	284.43
1988 80m							
BRLP5 4/6	0.49	2.27	5.36	15.9	-24.8	5.32	26.57
BRLP5 4/20	0.73	5.26	8.44	7.1	-22.7	18.92	131.25
BRLP5 4/23	0.61	5.20	10.01	8.3	-23.2	21.83	180.59
BRLP5 4/28	0.87	6.07	8.18	10.6	-22.4	17.95	127.43
BRLP5 5/5	0.99	7.20	8.58		-22.8	14.46	97.55
BRLP5 5/11	1.58	16.18	11.70	6.9	-22.1	68.19	720.13
BRLP5 5/13	1.52	13.20	10.18	12.1	-22.3	78.49	686.11
BRLP5 5/19	1.81	13.62	8.95	15.2	-22.2	78.24	586.40
BRLP5 5/26	1.27	8.88	8.15	6.5	-22.1	51.52	359.89
BRLP5 6/1/	1.18	7.92	7.79	10.2	-22.2	40.71	272.77
1988 150m							
BRLP5 3/29	0.62	4.76	8.90	7.8	-22.9	5.99	45.79
BRLP5 4/6	0.40	2.12	6.24	19.1	-24.1	6.90	37.43
BRLP5 4/20	0.62	5.45	10.27	7.9	-23.3	11.73	92.00
BRLP5 4/23	1.00	4.46	6.85	8.8	-23.3	19.41	130.81
BRLP5 4/28	0.69	5.52	9.26	10.9	-22.4	11.29	85.78
BRLP5 5/5	0.74	5.13	8.13	7.5	-22.6	10.89	78.93
BRLP5 5/11	1.14	10.25	10.56	6.8	-21.9	28.76	258.82
BRLP5 5/13	1.21	10.83	10.53	6.6	-21.9	45.43	409.32
BRLP5 5/19	1.17	9.79	9.76	15.8	-22.3	50.92	414.67
BRLP5 5/26	1.32	9.58	8.59	6.9	-21.7	71.22	545.62
BRLP5 6/1/	0.92	6.14	7.82	7.7	-21.9	61.37	410.85
1988 240m							
BRLP5 4/6	0.54	4.13	8.95	12.3	-23.9	18.35	140.59
BRLP5 4/20	0.65	5.17	9.27	7.5	-22.9	15.07	120.04
BRLP5 4/23	0.60	5.26	10.31	9.1	-23.4	20.72	181.29
BRLP5 4/28	0.68	4.27	7.34		-23.5	11.74	110.36

Appendix 2. Continued.

Station/ Date	% N	% C	C/N	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	N Flux $mgNm^{-2}d^{-1}$	C Flux $mgNm^{-2}d^{-1}$
BRLP5 5/5	0.75	5.18	8.11	4.7	-22.7	14.46	97.01
BRLP5 5/11	0.75	6.57	10.23	8.7	-22.3	26.81	233.64
BRLP5 5/13	0.82	6.20	8.75		-22.6	32.99	248.51
BRLP5 5/19	0.73	5.98	9.52	14.1	-22.3	60.44	493.18
BRLP5 5/26	0.74	5.45	8.64	5.7	-21.9	77.91	577.29
BRLP5 6/1	0.80	5.35	8.80		-21.9	85.71	552.99
Date 1st deployed D4/3/90							
1990 80m							
BRLP5 4/23				8.9	-21.6		
BRLP5 4/30				8.8	-25.8		
BRLP5 5/19				7.4	-27.0		
BRLP5 5/29				7.8	-27.0		
BRLP5 6/8				7.8	-25.4		
BRLP5 6/21				3.7	-27.2		
BRLP5 7/5				6.1	-23.2		
BRLP5 7/26				7.2	-23.1		
BRLP5 8/20				7.6	-23.7		
BRLP5 9/11				6.9	-24.3		
1990 240m							
BRLP5 4/23				11.3	-21.9		
BRLP5 4/30				10.6	-23.6		
BRLP5 5/19				7.8	-23.8		
BRLP5 5/29				8.7	-24.8		
BRLP5 6/8				7.2	-24.9		
BRLP5 6/21				4.6	-24.3		
BRLP5 7/5				5.5	-22.7		
BRLP5 7/26				7.2	-22.5		
BRLP5 8/20				7.6	-22.7		
BRLP5 9/11				7.2	-22.9		
1990 80m							
US3.5 4/30				6.4	-27.6		
US3.5 5/19				7.2	-26.9		
US3.5 5/29				8.1	-24.5		
US3.5 6/21				6.2	-27.5		
US3.5 7/5					-23.5		
US3.5 7/25				6.7	-23.0		
US3.5 8/21				8.4	-23.9		
US3.5 9/11				6.4	-24.5		

Appendix 2. Continued.

Station/ Date	% N	% C	C/N	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	N Flux $mgNm^{-2}d^{-1}$	C Flux $mgNm^{-2}d^{-1}$
1990 180m							
US3.5 4/30				8.1	-24.7		
US3.5 5/19				6.8	-24.1		
US3.5 5/29				8.2	-25.3		
US3.5 6/21				7.4	-23.9		
US3.5 7/5				3.7	-23.7		
US3.5 7/25				6.7	-22.8		
US3.5 8/21				7.3	-22.8		
US3.5 9/11				6.6	-23.9		

Appendix 3. Concentration and nitrogen isotopic composition of nitrate and ammonium in water column samples from Conception Bay.

Sample	[NH4] (μM)	[NO3] (μM)	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{15}N\text{-}NH_4^+$ (‰)
BRLP5 3/23 DIN 5		0.9		
BRLP5 3/23 DIN 25		1.5		
BRLP5 3/23 DIN 50		5.1		
BRLP5 3/23 DIN 80			-1.6	
BRLP5 3/23 DIN 100		6.7		
BRLP5 3/23 DIN 210			6.3	
BRLP5 3/29 DIN 5		0.0		
BRLP5 3/29 DIN 15		0.0		
BRLP5 3/29 DIN 30		0.4		
BRLP5 3/29 DIN 50		4.7		
BRLP5 3/29 DIN 80			2.9	
BRLP5 3/29 DIN 200		8.4		
BRLP5 3/29 DIN 210			0.2	
BRLP5 3/29 DIN Sea ice	1.4	0.2		
BRLP5 4/4 DIN 10		0.0		
BRLP5 4/4 DIN 22		0.0		
BRLP5 4/4 DIN 35		5.4		
BRLP5 4/4 DIN 100		6.8		
BRLP5 4/4 DIN 210		8.8	-1.3	
BRLP5 4/18 DIN 5		0.0		
BRLP5 4/18 DIN 20		0.0		
BRLP5 4/18 DIN 45		0.6		
BRLP5 4/18 DIN 80		2.3	-4.7	
BRLP5 4/18 DIN 210		5.0	-1.4	
BRLP5 4/29 DIN 30		0.0		
BRLP5 4/29 DIN 90		0.5		
BRLP5 4/29 DIN 115		4.9		
BRLP5 4/29 DIN 210		5.9	-2.9	
CTR23 4/30 DIN 100		5.2	5.3	
CTR23 4/30 DIN 120		5.0	-2.2	
CTR23 4/30 DIN 210		4.8	-0.8	

Appendix 3. Continued.

Sample	[NH4] (μM)	[NO3] (μM)	$\delta^{15}N-NO_3^-$ (‰)	$\delta^{15}N-NH_4^+$ (‰)
US3.5 5/1 DIN 5		0.2		
US3.5 5/1 DIN 25		0.2		
US3.5 5/1 DIN 87		4.2		
US3.5 5/1 DIN 125		7.2		
US3.5 5/1 DIN 215		10.8		
BRLP5 5/2 DIN 5		0.2		
BRLP5 5/2 DIN 30		0.2		
BRLP5 5/2 DIN 87		8.0		
BRLP5 5/2 DIN 120		9.6		
BRLP5 5/2 DIN 210		10.5		
CC13 5/4 DIN 10		0.4		
CC13 5/4 DIN 25		1.7		
CC13 5/4 DIN 50		1.8		
CC13 5/4 DIN 100		6.6		
CC13 5/4 DIN 125			-1.1	
CC13 5/4 DIN 180		6.8	-2.0	
US3.5 5/6 DIN 5	0.8	0.0		
US3.5 5/6 DIN 30	0.8	0.0		
US3.5 5/6 DIN 60	0.5	0.0		
US3.5 5/6 DIN 100	1.0	5.4	-1.3	
US3.5 5/6 DIN 170	2.2	7.5	7.9	
BRLP5 5/6 DIN 5	0.0	0.0		
BRLP5 5/6 DIN 50	0.0	0.1		
BRLP5 5/6 DIN 80	0.1	6.2	-2.8	
BRLP5 5/6 DIN 150	0.0	8.1	1.7	
BRLP5 5/6 DIN 245	0.1	9.3	4.9	
BRLP5 5/20 DIN 5	0.6	0.0		
BRLP5 5/20 DIN 40	0.4	0.0		
BRLP5 5/20 DIN 80	0.7	1.7	0.3	
BRLP5 5/20 DIN 120	0.3	9.6		
BRLP5 5/20 DIN 210	0.2	11.1	-4.2	
US3.5 5/21 DIN 5	0.2	0.0		
US3.5 5/21 DIN 60	0.4	0.0		
US3.5 5/21 DIN 80	0.8	2.3	2.4	
US3.5 5/21 DIN 100	0.7	2.6	4.6	
US3.5 5/21 DIN 170	0.2	5.5	-1.7	

Appendix 3. Continued.

Sample	[NH4] (μM)	[NO3] (μM)	$\delta^{15}N-NO_3^-$ (‰)	$\delta^{15}N-NH_4^+$ (‰)
US3.5 6/24 DIN 5	0.1	0.0		
US3.5 6/24 DIN 25	0.4	0.0		
US3.5 6/24 DIN 50	1.0	0.2		
US3.5 6/24 DIN 80	1.2	2.2	-4.3	
US3.5 6/24 DIN 210	1.7	9.4	4.0	
BRLP5 6/24 DIN 5	0.0	0.0		
BRLP5 6/24 DIN 40	0.8	0.0		
BRLP5 6/24 DIN 60	1.3	1.3		
BRLP5 6/24 DIN 80	1.6	5.1	-4.4	
BRLP5 6/24 DIN 210	2.1	7.1	4.5	
BRLP5 7/27 DIN 5	0.2	0.0		
BRLP5 7/27 DIN 30	1.0	1.1		
BRLP5 7/27 DIN 60	1.7	5.0	2.5	3.7
BRLP5 7/27 DIN 80	1.7	5.2	-3.2	3.9
BRLP5 7/27 DIN 210	1.9	8.9	1.4	4.8
BRLP5 8/30 DIN 5	0.2	0.0		
BRLP5 8/30 DIN 20	0.0	0.0		
BRLP5 8/30 DIN 40	1.0	0.0		
BRLP5 8/30 DIN 80	1.9	2.9	3.9	
BRLP5 8/30 DIN 210	2.3	8.9	-6.2	6.3

Appendix 4. Concentration of dissolved oxygen and dissolved inorganic carbon and the $\delta^{13}C$ of DIC for all stations.

Station	[O2] (ml/l)	O2 Sat. (μmols/l)	$\delta^{13}C$ (‰)	[DIC] (mmol/kg)
BRLP5 3/23 5	9.03	24.55	-0.5	1.70
BRLP5 3/23 35	8.08	-18.08	-0.4	1.73
BRLP5 3/23 60	8.05	-21.01	-0.5	2.03
BRLP5 3/23 80	8.01	-23.53	0.5	2.19
BRLP5 3/23 210	7.77	-29.14	-0.6	1.99
BRLP5 3/29 5	9.41	43.11	0.2	1.97
BRLP5 3/29 25	9.06	24.96	-0.6	2.16
BRLP5 3/29 45	8.29	-9.30	-0.2	2.20
BRLP5 3/29 80	8.01	-22.88	-3.9	2.42
BRLP5 3/29 210	6.79	-70.50	-0.3	2.30
BRLP5 4/4 5	9.89	74.83	-0.7	1.93
BRLP5 4/4 22	8.85	16.15	-0.1	2.12
BRLP5 4/4 45	8.08	-17.93	-0.3	2.23
BRLP5 4/4 80	7.93	-26.08	-0.2	2.21
BRLP5 4/4 210	7.21	-52.89	-0.4	2.34
BRLP5 4/18 5	9.20	50.54	0.7	2.17
BRLP5 4/18 20	8.96	33.99	0.4	2.24
BRLP5 4/18 45	8.33	-2.07	-0.2	2.18
BRLP5 4/18 80	8.10	-20.06	-0.9	2.08
BRLP5 4/18 210	7.03	-60.71	-1.1	2.21
BRLP5 4/29 5	8.78	30.25	1.1	2.11
BRLP5 4/29 80	8.50	11.65	1.1	2.19
BRLP5 4/29 100	8.89	23.62	0.9	2.40
BRLP5 4/29 120	7.80	-32.50	1.0	2.34
BRLP5 4/29 210	7.21	-54.57	0.6	2.38
CTR23 4/30 5	8.75	27.78	1.7	2.25
CTR23 4/30 80	8.15	-11.30	1.1	2.36
CTR23 4/30 100	7.98	-23.76	0.9	2.38
CTR23 4/30 120	7.80	-32.91	0.2	2.17
CTR23 4/30 210	7.24	-54.57	0.6	2.41

Appendix 4. Continued.

Station	[O2] (ml/l)	O2 Sat. (μmols/l)	$\delta^{13}C$ (‰)	[DIC] (mmol/kg)
US3.5 5/1 5	8.92	36.84	1.2	2.22
US3.5 5/1 40	8.75	26.17	0.4	2.22
US3.5 5/1 60	8.73	25.24	0.3	2.17
US3.5 5/1 80	8.47	6.17	-1.1	2.21
US3.5 5/1 170	7.84	-33.24	-1.1	2.25
US3.5 5/1 215	6.58	-83.79	-0.6	2.26
BRLP5 5/2 5	8.61	31.68	0.5	2.14
BRLP5 5/2 40	8.71	25.51	-0.1	2.15
BRLP5 5/2 80	7.79	-33.32	-0.6	2.21
BRLP5 5/2 120	7.52	-44.16	-1.5	2.18
BRLP5 5/2 210	7.03	-61.97	-0.5	2.27
CC13 5/4 5	8.89	29.57	0.2	2.15
CC13 5/4 40	8.57	10.21	0.5	1.82
CC13 5/4 80	8.57	9.14	1.2	2.24
CC13 5/4 125	7.86	-32.74	-0.3	2.18
CC13 5/4 180	7.63	-39.28	0.3	2.19
CC5 5/4 262	6.44	-87.79	-0.6	2.17
BRLP5 5/4 245	7.21	-53.55	0.2	2.15
US3.5 5/6 5	8.78	36.61	0.0	2.13
US3.5 5/6 30	8.71	24.72	0.7	2.24
US3.5 5/6 60	8.71	22.34	-0.1	2.10
US3.5 5/6 100	7.98	-24.83	0.0	2.19
US3.5 5/6 170	7.45	-47.34	-1.1	2.19
BRLP5 5/6 5	8.36	22.23	0.8	2.18
BRLP5 5/6 50	8.50	11.87	-0.1	2.20
BRLP5 5/6 80	7.87	-27.61	-0.6	2.15
BRLP5 5/6 150	7.66	-40.77	-1.2	2.17
BRLP5 5/6 245	6.61	-81.17	-1.5	2.20
BRLP5 5/20 5	8.01	17.25	0.3	2.23
BRLP5 5/20 40	8.40	20.04	-4.0	2.10
BRLP5 5/20 80	8.19	-7.69	-1.0	2.07
BRLP5 5/20 120	7.31	-54.74	-2.5	2.35
BRLP5 5/20 210	7.24	-55.77	-1.2	2.04

Appendix 4. Continued.

Station	[O2] (ml/l)	O2 Sat. (µmols/l)	$\delta^{13}C$ (‰)	[DIC] (mmol/kg)
US3.5 5/21 5	8.05	9.91	1.0	2.07
US3.5 5/21 60	nd	nd	-1.5	1.87
US3.5 5/21 80	7.94	-22.94	-1.8	2.14
US3.5 5/21 100	7.77	-32.03	-0.1	2.21
US3.5 5/21 170	7.37	-51.06	0.2	2.29
US3.5 6/24 5	7.38	38.98	-0.3	2.19
US3.5 6/24 25	7.70	0.22	0.7	2.09
US3.5 6/24 50	8.01	-18.13	0.7	2.24
US3.5 6/24 80	8.01	-18.13	-0.2	1.92
US3.5 6/24 210	6.84	-70.47	-0.4	2.02
BRLP5 6/24 5	7.24	32.73	0.6	2.06
BRLP5 6/24 40	7.98	12.72	0.1	1.98
BRLP5 6/24 60	8.03	-17.35	0.2	2.19
BRLP5 6/24 80	7.68	-32.97	0.6	2.37
BRLP5 6/24 210	7.03	-61.88	-0.1	2.27
BRLP5 7/27 5	6.58	31.83	1.4	2.06
BRLP5 7/27 30	7.49	-10.44	0.2	2.05
BRLP5 7/27 60	7.66	-32.20	0.1	2.14
BRLP5 7/27 80	7.77	-28.10	0.8	2.36
BRLP5 7/27 210	7.17	-59.25		2.21
BRLP5 8/30 5	6.47	33.64	1.0	1.92
BRLP5 8/30 20	7.45	31.85	-0.1	1.77
BRLP5 8/30 40	8.43	25.20	1.0	2.07
BRLP5 8/30 80	7.77	-20.19	0.2	2.07
BRLP5 8/30 210	6.89	-71.76	-0.7	2.20

Appendix 5. Isotopic composition and concentration of particulate organic nitrogen (PON) and carbon (POC) and concentration of total suspended matter (TSM).

Station	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	C/N (atomic)	PON µmolN/L	POC µmolC/L	TSM mg/L
BRLP5 3/23 5	6.5	-23.4	3.96	1.82	7.20	0.453
BRLP5 3/23 35	11.5	-22.6	3.10	1.26	3.90	0.064
BRLP5 3/23 60	22.1	-25.0	3.59	0.52	1.88	0.061
BRLP5 3/23 80	12.5	-24.5	18.81	0.06	1.17	0.052
BRLP5 3/23 210	13.7	-24.1	13.87	0.10	1.41	0.078
BRLP5 3/29 5	7.7	-24.5	4.59	3.06	14.05	0.726
BRLP5 3/29 25	7.2	-22.9	3.43	2.44	8.37	0.518
BRLP5 3/29 45	9.6	-24.7	5.07	0.58	2.96	0.200
BRLP5 3/29 80	20.5	-25.8	10.98	0.31	3.39	
BRLP5 3/29 210	16.1	-24.6	3.01	1.49	4.48	0.634
BRLP5 3/29 Sea ice	11.7	-26.7		3.59		0.786
BRLP5 4/4 5	9.4	-23.5	6.66	0.94	6.28	0.238
BRLP5 4/4 22	8.5	-22.0	3.31	4.14	13.71	0.681
BRLP5 4/4 45	14.6	-24.7	3.32	0.68	2.27	0.131
BRLP5 4/4 80	12.9	-25.2	14.42	0.17	2.45	0.072
BRLP5 4/4 210	12.3	-24.6	13.09	0.19	2.47	0.240
BRLP5 4/18 5	6.4	-22.6	4.45	1.81	8.03	0.531
BRLP5 4/18 20	13.8	-23.3	3.26	3.70	12.05	0.582
BRLP5 4/18 45	5.4	-22.8	4.55	1.70	7.72	0.414
BRLP5 4/18 80	11.7	-24.5	12.06	0.25	3.05	0.131
BRLP5 4/18 210	18.6	-25.1	4.85	0.47	2.30	0.250
BRLP5 4/29 5	9.8	-23.4	3.93	1.70	6.68	0.368
BRLP5 4/29 80	7.2	-23.0	3.73	3.61	13.45	0.797
BRLP5 4/29 100	12.6	-23.2	2.78	2.12	5.88	0.515
BRLP5 4/29 120	10.6	-22.7	8.98	0.44	3.94	0.378
BRLP5 4/29 210	12.9	-23.8	6.18	0.40	2.46	0.217
CTR23 4/30 5	10.8	-22.8	11.41	0.53	6.00	0.349
CTR23 4/30 80	8.5	-21.9	8.12	0.95	7.73	0.465
CTR23 4/30 100	9.8	-21.9	7.72	0.78	6.04	0.444
CTR23 4/30 120	17.4	-22.5	6.83	0.47	3.23	0.230
CTR23 4/30 210	20.6	-22.3	3.58	0.89	3.17	0.314

Appendix 5. Continued.

Station	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	C/N (atomic)	PON µmolN/L	POC µmolC/L	TSM mg/L
US3.5 5/1 5	10.7	-24.4	4.66	0.99	4.61	0.220
US3.5 5/1 40	8.5	-23.8	6.22	0.96	5.95	0.297
US3.5 5/1 60	7.3	-24.2	7.14	0.82	5.85	0.363
US3.5 5/1 80	8.5	-24.0	6.85	1.22	8.38	0.643
US3.5 5/1 170	10.0	-24.0	6.14	0.31	1.90	0.112
BRLP5 5/2 5	9.9	-24.1	15.48	0.23	3.60	0.135
BRLP5 5/2 40	10.5	-23.2	5.39	0.99	5.33	0.446
BRLP5 5/2 80	11.0	-22.7	4.96	1.04	5.17	0.399
BRLP5 5/2 120	15.5	-23.0	2.92	1.43	4.18	0.179
BRLP5 5/2 210	9.1	-23.1	8.90	0.33	2.96	0.273
CC13 5/4 5	13.9	-24.1	3.73	1.86	6.96	0.571
CC13 5/4 40	13.0	-23.2	4.46	1.34	5.95	0.339
CC13 5/4 80	11.9	-23.7	4.59	1.20	5.52	0.338
CC13 5/4 125	15.0	-24.2	4.37	0.34	1.50	0.050
CC13 5/4 180	15.7	-24.4	5.18	0.37	1.91	0.120
US3.5 5/6 5	14.9	-24.9	4.31	0.80	3.46	0.171
US3.5 5/6 30	18.2	-24.7	3.46	0.88	3.04	0.064
US3.5 5/6 60	8.4	-23.4	8.95	0.35	3.10	0.111
US3.5 5/6 100	7.9	-23.9	6.65	0.59	3.90	0.293
US3.5 5/6 170	9.3	-23.9	9.42	0.23	2.18	0.195
BRLP5 5/6 5	17.3	-24.3	3.27	1.27	4.14	0.179
BRLP5 5/6 50		-24.8			4.64	0.213
BRLP5 5/6 80	13.8	-22.4	2.99	1.67	5.00	0.200
BRLP5 5/6 150	18.0	-22.5	6.27	0.63	3.95	0.347
BRLP5 5/6 245	16.7	-22.3	5.40	1.06	5.74	0.872
BRLP5 5/20 5	12.4	-24.8	7.70	1.11	8.50	0.366
BRLP5 5/20 40	15.0	-24.2	11.21	0.37	4.12	0.071
BRLP5 5/20 80	13.1	-25.2	9.03	0.44	4.00	0.118
BRLP5 5/20 120		-23.5			3.64	0.356
BRLP5 5/20 210	13.7	-22.6	8.54	0.35	3.00	0.340
US3.5 5/21 5	14.0	-24.8	4.83	0.62	2.98	0.156
US3.5 5/21 60	12.8	-25.5	4.98	0.91	4.54	0.217
US3.5 5/21 80	18.5	-26.5	4.20	0.89	3.73	0.206
US3.5 5/21 100	12.7	-24.3	5.24	0.43	2.25	0.137
US3.5 5/21 170	11.1	-24.9	6.68	0.39	2.62	0.313

Appendix 5. Continued.

Station	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	C/N (atomic)	PON µmolN/L	POC µmolC/L	TSM mg/L
US3.5 6/24 5	17.7	-24.6	5.57	0.36	2.00	0.015
US3.5 6/24 25	12.5	-23.4	6.93	0.26	1.79	0.009
US3.5 6/24 50	13.4	-24.6	5.85	0.20	1.17	0.019
US3.5 6/24 80	9.2	-24.3	6.34	0.16	1.03	0.014
US3.5 6/24 210	9.2	-23.7	8.20	0.27	2.20	0.385
BRLP5 6/24 5	16.1	-24.0	4.83	0.39	1.88	0.008
BRLP5 6/24 40	14.9	-24.0	4.34	0.50	2.19	0.069
BRLP5 6/24 60	9.2	-24.7	6.82	0.13	0.86	0.008
BRLP5 6/24 80	18.7	-25.3	4.37	0.23	1.01	0.005
BRLP5 6/24 210	15.7	-24.2	5.58	0.47	2.61	0.386
BRLP5 7/27 5	10.5	-24.7	6.76	0.37	2.48	0.097
BRLP5 7/27 30	10.0	-24.8	6.51	0.65	4.25	0.183
BRLP5 7/27 60	16.5	-25.1	5.06	0.29	1.46	0.080
BRLP5 7/27 80	13.1	-24.3	5.84	0.22	1.26	0.049
BRLP5 7/27 210	15.8	-24.7	4.97	0.34	1.69	0.260
BRLP5 8/30 5	13.9	-24.1	3.73	0.91	3.40	
BRLP5 8/30 20	13.0	-23.2	4.46	0.64	2.86	0.241
BRLP5 8/30 40	11.9	-23.7	4.59	0.60	2.75	0.235
BRLP5 8/30 80	15.0	-24.2	4.37	0.28	1.22	0.204
BRLP5 8/30 210	15.7	-24.4	5.18	0.18	0.94	0.346