SEASONAL VARIATIONS OF PARTICULATE AND DISSOLVED FRACTIONS OF PHOSPHORUS AND RELATED HYDROCHEMICAL PARAMETERS IN THE NORTHEASTERN MEDITERRANEAN SHELF ZONE

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Approval of the Graduate School of Marine Sciences

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ABSTRACT

SEASONAL VARIATIONS OF PARTICULATE AND DISSOLVED FRACTIONS OF PHOSPHORUS AND RELATED HYDROCHEMICAL PARAMETERS IN THE NORTHEASTERN MEDITERRANEAN SHELF ZONE

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Spatial and temporal changes in principal hydro-chemical parameters were monitored at three time-series stations on the largest shelf zone of the Northeastern Mediterranean between December 2001 and December 2003 and four deep reference stations in December 2003 to fill systematic information gap on fractions of total phosphorus, sensitive phosphate measurements and compound-specific studies on the composition of organic matter. Precise and accurate measurements of very low concentrations of reactive phosphate by the MAGIC method and elemental composition (C/N/P ratio) of particulate organic matter (POM) in oligotrophic seas are essential to assess which parameter primarily controls phytoplankton growth in the NE Mediterranean shelf waters during the late winter-early spring period and less productive seasons as well as the composition of bulk POM sinking to depths below the euphotic zone. The systematic data reveal that POM composition and nutrient concentrations were highly variable in the nearshore water fed by riverine input with relatively high NO_3/PO_4 (N/P: 70-3000) molar ratios. Major components (dissolved and particulate fractions) of total phosphorus measured in the shelf clearly demonstrate that the dissolved-P fraction (TDP: 56-97%) dominates the phosphorus pool and organic-P (DOP) was principally the major constituent of the TDP in the shelf water column. However, organic-P (POP) has a remarkable contribution to the particulate-P pool having pronounced PIP% in the nearshore zone fed by riverine inputs. PON/POP (N/P) molar ratio mostly ranged between 20-50 in the shelf, exceeding the Redfield ratio (as 16/1) and thus strongly suggesting phosphorus-limited primary production in the NE Mediterranean shelf waters.

Keywords: Northeastern Mediterranean Shelf, Nutrients, Particulate Organic Matter, Phosphorus Fractions.

ÖZ

KUZEYDOĞU AKDENİZ KITA SAHANLIĞINDA PARTİKÜL VE ÇÖZÜNMÜŞ FOSFOR FRAKSİYONLARI VE İLİŞKİLİ HİDROKİMYASAL PARAMETRELERİN MEVSİMSEL DEĞİŞİMİ

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Toplam fosfor fraksiyonları, hassas fosfat ölçümleri ve organik madde kompozisyonu üzerine olan bilgi açığını doldurmak amacıyla, hidro-kimyasal parametrelerdeki değişimler, Kuzeydoğu Akdeniz'in en geniş kıta sahanlığı kuşağında yer alan üç zaman serisi istasyonunda Aralık 2001 ve Aralık 2003 döneminde ve dört referans istasyonda Aralık 2003'de izlenmiştir. Besin maddesince fakir (oligotrofik) Kuzeydoğu Akdeniz'de üretimin az olduğu mevsimler ve kış sonu-ilkbahar başlangıcı sırasında fitoplankton gelişimini hangi parametrelerin kontrol ettiğini ve öfotik zonun altına çöken partikül organik maddenin (POM) kompozisyonunu değerlendirmek için, MAGIC yöntemi kullanılarak oldukça düşük konsantrasyonda olan reaktif fosfatın ve POM element kompozisyonunun (C/N/P oranı) doğru ve kesin ölçümü gereklidir. Sistematik veriler, yüksek NO_3/PO_4 (N/P: 70-3000) molar oranına sahip nehir girdisiyle beslenen, kıyı istasyonda POM kompozisyonu ve besin maddesi derişimlerinin oldukça değişken olduğunu göstermektedir. Kıta sahanlığında ölçülen toplam fosforun ana bileşenleri (çözünmüş ve partikül fraksiyonlar), fosfor havuzunda çözünmüş-P fraksiyonunun (TDP: 56-97%) baskın ve su kolonunda TDP'un ana bileşeninin organik-P (DOP) olduğunu açıkça ortaya koymuştur. Bununla birlikte, organik-P (POP), nehir girdisiyle beslenen belirgin PIP yüzdesine sahip kıyı istasyonda, partikül-P havuzuna önemli katkı yapar. PON/POP (N/P) molar oranı, Redfield oranının (16/1) üstüne çıkarak, kıta sahanlığında genellikle 20-50 aralığında değişir ve Kuzeydoğu Akdeniz kıta sahanlığı sularında birincil üretimin fosfor tarafından kontrol edildiğini ortaya koyar.

Anahtar Kelimeler: Kuzeydoğu Akdeniz Kıta Sahanlığı, Besin Elementleri, Partikül Organik Madde, Fosfor Fraksiyonları.

“I was a childbearing PhD student studying on light bearing element (phosphorus).”

To My Parents
&
My Twin Daughters

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DO: Dissolved oxygen

SDD: Secchi Disc Depth

TP: Total phosphorus

TDP: Total Dissolved Phosphorus

TPP: Total Particulate Phosphorus

DIP: Dissolved Inorganic Phosphate

DOP: Dissolved Organic Phosphorus

PIP: Particulate Inorganic Phosphorus

POP: Particulate Organic Phosphorus

POM: Particulate Organic Matter

POC: Particulate Organic Carbon

PON: Particulate Organic Nitrogen

CHAPTER 1

INTRODUCTION

1.1 General Features of the Mediterranean Sea

1.1.1 Uniqueness of the Mediterranean Sea

The Mediterranean Sea lies between mountainous areas to the north and deserts to the south (Figure 1.1.a), with a wide range of climatic variations (Ketchum, 1983). It, although relatively small (2.5 million km^2 area, 3.7 million km^3 volume, and a mean depth of 1500 m with maximum 5267 m), is of sufficient size for its circulation to be governed by large-scale ocean dynamics. It is among the most interesting of our planet's semi-enclosed seas because of the great range of processes and interaction, which occur within it (Malanotte-Rizzoli and Robinson, 1988). Most physical processes, which characterize the global general ocean circulation, occur directly or analogously in the Mediterranean Sea (POEM Group, 1992). The Mediterranean Sea is connected with the North Atlantic Ocean through the narrow Gibraltar Strait to the Red Sea via the Suez Canal and through the narrow Bosphorus Strait to the smaller enclosed Black Sea. The Strait of Gibraltar restricts the exchange of Atlantic and Mediterranean waters, which has an important role to play in the circulation and productivity of the Mediterranean Sea (Figure 1.1.b).

The Mediterranean Sea is composed of two similar size basins (eastern and western) separated by the shallow and narrow Strait of Sicily. The eastern Mediterranean is thus itself an isolated basin with multiple forcings and water mass formations driving the processes and interactions of global interest (POEM Group, 1992). Because of the west-east salinity and nutrient gradients (Krom *et al.*, 1991; Moutin *et al.*, 2002) there is west-east gradient in species diversity (Ben-Tuvia, 1983) and productivity of the Mediterranean Sea (Turley, 1999; Van Wambake *et al.*, 2002). The eastern

Mediterranean consists of two major basins, the Levantine and Ionian Sea (POEM Group, 1992). The hydrodynamics and hydrochemistry within the northern Levantine Sea display three regions of distinct behaviour: the cyclonic Rhodes basin, the anticyclonic Cilician basin and the transitional area between them (Antalya bay or its offshore neighbourhood) (Ediger and Yılmaz, 1996).

Figure 1.1 (a) Composite satellite image of the Mediterranean Sea and (b) A satellite image of the Mediterranean Sea taken from the side of the Straits of Gibraltar; at right, Africa, at left, Europe (http://en.wikipedia.org/wiki/Mediterranean_Sea).

The eastern Mediterranean Sea has attracted the attention of marine scientists because it is characterized as one of the least productive seas in the world (Krom *et al.*, 1992; Levitus *et al.*, 1993; Béthoux *et al.*, 1998; Yılmaz and Tuğrul, 1998; Ediger *et al.*, 1999; Psarra *et al.*, 2000; Tselepides *et al.*, 2000; Karafistan *et al.*, 2002; Krom *et al.*, 2005). The eastern Mediterranean Sea has a number of distinct characteristics:

- Its deep waters have high nitrogen to phosphorus ratio ranging from 25 to 29, compared to the standard N/P Redfield ratio of 16.
- It is located at the southern edge of Europe and is influenced by air masses from anthropogenic sources of Central and Eastern Europe (Mihalopoulos *et al.*, 1997). Atmospheric input of anthropogenic nutrients to areas located downwind of populated and urbanized regions can lead to or shift towards greater phosphorus limitation (Fanning, 1989; Markaki *et al.*, 2003).
- Its arid climate with little natural freshwater (nutrient-rich) runoff, most of which is now intercepted for use by man (Herut *et al.*, 1999a). Therefore, aeolian inputs of nutrients (with relatively high N/P ratios of about 100) in the area are by far the most effective external source (Herut *et al.*, 2002; Markaki *et al.*, 2003; Herut *et al.*, 2005).

- Its general west-east anti-estuarine circulation with an inflow of surface waters from the Atlantic whose nutrient content was filtered on the way and left with relatively poor nutrient content and a counterbalancing outflow of relatively nutrient-enriched LIW and LDW (Özsoy *et al.*, 1993; Crispi *et al.*, 1998; Yılmaz and Tuğrul, 1998; Herut *et al.*, 1999a).
- Oligotrophy of the euphotic zone determines low values of phytoplankton biomass and primary production (Lefevre *et al.*, 1997; Crispi *et al.*, 1998), except for coastal areas, due to the influence of major rivers, and in some open sea regions, because of permanent gyres and upwellings.

Understanding of the medium- and long-term trends in the main biogeochemical features of the Mediterranean can be realized by knowing the general circulation, principal hydrographical and hydrochemical processes controlling the whole marine ecosystem (Margalef, 1985; Crispi *et al.*, 2002).

1.1.2 Circulation and hydrography of the Mediterranean Sea

General circulation of the Mediterranean Sea is largely influenced by the existence of straits with sills (Lacombe, 1988). The inflow of Atlantic surface waters drives the so-called Atlantic Stream System (ASS) in a nearby region to Gibraltar, Alboran Sea. During its transport to the Levantine Basin, the branch of ASS entering Strait of Sicily forms the Atlantic-Ionian Stream (AIS) (Figure 1.2). It travels across the basin and becomes the main current, namely Mid-Mediterranean Jet (MMJ), which influences the eastern Mediterranean. The MMJ flows eastward between the cyclonic Rhodes gyre on the north and the anticyclonic Mersa-Matruh and Shikmona gyres on the south (Figure 1.2). A branch of the MMJ moves towards the north in the eastern side of Cyprus; it forms the Asia Minor Current (AMC), which flows westward along the Turkish coast (POEM Group, 1992; Demirov and Pinardi, 2002; Pinardi *et al.*, 2005).

Air-sea interaction is vigorous in the Mediterranean Sea and both deep water and intermediate water masses are formed. Increased density due to saltiness caused by intense surface evaporation is important for water mass formations and for the main thermohaline cell analogously to the global ocean processes (POEM Group, 1992).

In the eastern Mediterranean, surface waters are characterized by warm (16-25 °C) and saline (38.8-39.4 psu) feature called Levantine surface water (LSW). Below this layer, Atlantic water (AW) -which can be identified as salinity minimum- is observed with a temperature of about 17 °C and salinity between 38.5 and 39.0 psu (Özsoy *et al.*, 1993; Robinson and Golnaraghi, 1994). Below the Atlantic water, the Levantine intermediate water (LIW) is situated with salinity of about 39.1 psu and typical temperature of about 15.5 °C, throughout the year (Özsoy *et al.*, 1993; Robinson and Golnaraghi, 1994; Malanotte-Rizzoli *et al.*, 1999). Levantine deep water (LDW) has a temperature of ≤ 13.8 °C and salinity of ≤ 38.74 psu. These water bodies can be easily identified from the temperature and salinity (T-S) diagrams and can be found in different depths during different seasons and different places (Özsoy *et al.*, 1991; Robinson and Golnaraghi, 1994; Herut *et al.*, 2000). But roughly LSW found at 0-100 m range, AW at 20-100 m, LIW at 100-400 m and lastly LDW at the depths below 600-700 m (Özsoy *et al.*, 1991).

Figure 1.2 Schematic of the surface circulation from recent observational data and model simulations. Names of structures and currents are listed (Pinardi *et al.*, 2005).

1.1.3 Hydrochemistry of the Mediterranean Sea

Across the strait of Gibraltar, the mean salinity is 36.2 psu in the Atlantic inflow and 37.9 psu in the Mediterranean outflow (Béthoux, 1980). Salt balance requires an Atlantic inflow 5% greater than the Mediterranean deep outflow this difference being equal to the freshwater deficit over the sea. The mean total phosphorus concentrations estimated by Coste *et al.* (1988) were 0.36 and 0.44 µM for surface inflow and deep outflow, respectively. The Atlantic input of phosphorus may compensate for about 86% of the Mediterranean deep outflow. By contrast, the organic phosphorus in Atlantic inflow was neglected and the mean concentrations of phosphate were estimated as 0.05 and 0.27 µM in the surface inflow and deep outflow, respectively (Béthoux, 1989). In this case, the Atlantic inflow only accounts for 19% of PO_4 by the deep outflow.

Mediterranean production is characterized by two annual extremes nutritive limits. The first corresponds to winter mixing, which determines the initial stock of nutrients. Quantity of nutrient in the photic zone mainly depends on the depth reached by cooling waters. The second limit corresponds to the maximum summer stratification and to the lower availability of new nutrients (Özsoy *et al.*, 1993; Yılmaz and Tuğrul, 1998; Moutin and Raimbault, 2002).

Among the above mentioned water bodies in Section 1.1.2, the nutrient-poor LIW is well defined in the anticyclonic regions (e.g. Cilician Basin) but it does not form in cyclonic regions (e.g. Rhodes Gyre). The nutrient concentrations of this layer remain almost constant with depth down to the permanent nutricline, but vary with season and region (Ediger and Yılmaz, 1996). Nutrient content of the LDW is relatively high, although it is 5 times lower than the deeper layers of the Atlantic Ocean (Salihoglu *et al.*, 1990). On the other hand, past studies showed that the physical characteristics of the region overlapped on the biochemical characteristics specially the central parts of the Rhodes cyclonic gyre. Nutrient distributions in the region are strongly associated with the hydrographic features (Ediger and Yılmaz, 1996; Yılmaz and Tuğrul, 1998). Additionally, the cyclonic areas and peripheries of cyclones are relatively high in nutrient content and productivity, besides this, anticyclones are very poor (Salihoglu *et al.*, 1990).

Sarmiento *et al*. (1988) divide basins into what they term “desert” and “nutrient trap” basins. Desert basins have a combination of inputs and losses that result in low nutrient concentrations, while nutrient trap dynamics result in high nutrient concentrations. On a regional scale the Mediterranean is a desert basin. In the Mediterranean Sea, surface waters are depleted in phosphate, nitrate and silicate due to anti-estuarine water circulation and biological activity. Preformed nutrient concentrations, if they exist, are probably very low and deep-water concentrations mainly result from the mineralization of organic matter formed in the euphotic layer (Béthoux *et al*., 2002). Despite early observations of P limitation (Berland *et al*., 1973; Fiala *et al*., 1976; Berland *et al*., 1980), recent works suggest that the western Mediterranean surface waters are nitrogen-limited (Owens *et al*., 1989). In fact, there is growing evidence that the eastern Mediterranean is P-limited (Krom *et al*., 1991) whereas western Mediterranean is probably N-limited (Raimbault and Coste, 1990; Thingstad and Rassulzadegan, 1995). However, limitation may shifts from nitrogen to phosphorus and vice versa depending on the period of the year (Fiala *et al*., 1976; Dolan *et al*., 1995) or the area considered (Woodward and Owens, 1989). The uniquely high levels of N/P ratios in the eastern Mediterranean (25-27) compared with other open ocean averages (15) may reflect this situation, and are probably evidence of P limitation (Guerzoni *et al*., 1999). Bioassays in offshore and coastal waters in the eastern Mediterranean (Zohary and Robarts, 1998) as well as nutrient stoichiometry (Krom *et al*., 1991; Kress and Herut, 2001) have also suggested that biological production in the region is limited by phosphorus availability. Zohary and Robarts (1998) reported P-turnover times below 7 h in severely P-deficient regions of the Eastern Mediterranean, whereas P-replete areas like the Rhodes Gyre had P-turnover times longer than 100 h.

An experimental way to demonstrate nutrient limitation in aquatic systems is to add the suspected limiting nutrient and demonstrate growth beyond that recorded for an unfertilized control. In most cases, either N or P will be limiting to phytoplankton growth. However, in ultraoligotrophic systems like the Eastern Mediterranean (Yacobi *et al*., 1995) where the ambient concentrations of both dissolved inorganic N and P are exceptionally low (Krom *et al*., 2003), co-limitation or near co-limitation is likely, i.e. that the addition of the primary limiting nutrient will immediately lead to limitation by the other, and substantial growth will occur only when both nutrients are added. Psarra *et al.* (2005) reported that, there was no significant pool of bioavailable N available to the phytoplankton in the Eastern Mediterranean even when excess phosphate was added. The immediate response was an increase in the P-starved heterotrophic community of bacteria and micrograzers. This resulted in an increased grazing rate that caused the numbers and biomass of the dominant picoplankton to decrease. Although there was a small increase in larger nanoplankton and microplankton as ammonia was released by grazers, their initial numbers were so small that these changes were relatively insignificant. After seven days all these biological changes disappeared as the patch relaxed and was diluted away.

The microbial loop has been proposed as a second major pathway of energy and carbon flow in the pelagic food web as opposed to the classic grazing food chain (phytoplankton-copepods). In oligotrophic seas, the microbial loop is usually assumed to dominate over the classic food chain (Pitta *et al.*, 2005; and references therein). Both phytoplankton and bacteria in the Mediterranean Sea are limited by the availability of phosphorus (Thingstad and Rassoulzadegan, 1995).

Particulate matter in the oceans is constituted of living organisms and detrital material such as organic fragments, clays and carbonates, on which organic substances, colloids and metals may be fixed or absorbed. Particulate matter may have an autochthonous origin from living organisms or from physico-chemical transformations involving the colloids or may be allochthonous deriving from riverine or atmospheric inputs (Giani *et al.*, 2003). In the shallow coastal zone, POM undergoes transformations and degradation both during settling and at the water-sediment interface leading to nutrient regeneration. POM in the surface waters is not solely composed of phytoplankton; throughout most of the year, excluding the bloom period, bacteria, microzooplankton, protozoa and detrital material constitute a major fraction of the total POM inherent in the euphotic zone (Vostokov and Vedernikov, 1988; Polat *et al.*, 1998). The abundance and chemical composition of particulate organic matter (POM) in marine environments are controlled by complex physical and biochemical processes interacting in the upper layer as well as nutrient supplies from various sources (Tselepides *et al.*, 2000; Ediger *et al.*, 2005). Thus, particulate concentrations in the Mediterranean upper layer increase in more productive western regions and seasons (Rabitti *et al.*, 1994; Socal *et al.*, 1999). Concentrations of particulate organic carbon (POC) in the western Mediterranean generally range from 1.9-3.9 μM in less productive open sea to 1.4-9.2 μM in the more productive basins receiving more nutrients from deep waters and land-based sources (Rabitti *et al.*, 1994; Socal *et al.*, 1999). Naturally, similar spatial and temporal trends appear in the nitrogen (PON) component of bulk POM in the euphotic zone of the western Mediterranean (Socal *et al.*, 1999; Doval *et al.*, 1999), with values ranging between 0.1 and 1.8 μM PON in the stratified period. Limited particulate data from the oligotrophic eastern Mediterranean indicate that the upper waters contain low concentrations of bulk POM (Abdel-Moati, 1990; Ediger *et al.*, 1999). Moreover, particulate profiles exhibit coherent peaks within the deep chlorophyll maximum (DCM) zone, constituting a remarkable fraction of total POM in the upper layer (Abdel-Moati, 1990; Ediger *et al.*, 2005). The Levantine basin of the NE Mediterranean Sea is characterized by its large seasonal and regional variability in hydro-dynamical and biochemical properties, extending from the surface layer down to at least 1000-m depth. Bulk POM from the nutrient-depleted surface mixed layer possess relatively high C/N ratios, indicating that POM pool is dominated by detritus, bacteria and zooplankton (Ediger *et al.*, 2005).

1.1.4 The N/P ratio in the Mediterranean Sea

The N/P (NO_3/PO_4) molar ratio of the Mediterranean deep water is around 22 in the western Mediterranean and 24 in the eastern basin, instead of 16 in the ocean world. This is one of the most intriguing biogeochemical peculiarities of the Mediterranean Sea. The selective enrichment in dissolved organic nitrogen of waters of Adriatic origin is particularly noteworthy because it suggests a possible role of the Adriatic Sea in contributing to support the N/P ratio anomaly in the Eastern Mediterranean (Civitarese *et al.*, 1998; Herut *et al.*, 2002). The results of Degobbis and Gilmartin (1990) suggest that the anomaly in the N/P ratio could originate, at least in part, directly in the formation sites of the Eastern Mediterranean deep water, i.e. the Adriatic Sea, because of a selective enrichment in due to freshwater inputs, and the active role of the Adriatic shelf in the efficient removal of phosphorus from the water column via burial in the bottom sediments. Thus, the coastal and shelf areas of the Adriatic could influence the entire Eastern Mediterranean, the biogeochemical imprint being carried within the closed deep conveyor belt (Civitarese *et al.*, 1998).

In addition to the general depletion of nutrients observed, phosphate usually runs out slightly before nitrate in the Mediterranean when nutrients become depleted in surface waters; that is, subsurface N/P is significantly greater than the usual value of 14-16 generally found in most of the world ocean (Yılmaz and Tuğrul, 1998; Moutin and Raimbault, 2002).

On the other hand, the N/P ratios of bulk POM (PON/POP) in the eastern Mediterranean were lower than the Redfield ratio during winter and summer and this suggest luxury uptake by algae in P-limited waters when nutrient rich deep waters are supplied to the upper layer and some fraction of phosphorus in bulk POM might be non-biogenic origin via adsorption of inorganic phosphate on particles. These estimated ratios are inconsistent both with higher N/P ratios of deep waters and P-limited algal growth in the euphotic zone (Ediger *et al.*, 2005). In other words, P-rich particle snow during bloom period does not help the establishment of high N/P ratios (28-29) in the LDW. These sources could be result of slow recycling of nitrogen in the euphotic zone (Yılmaz and Tuğrul, 1998) and atmospheric deposition with very high N/P ratios (Markaki *et al.*, 2003).

1.2 Background Information on Phosphorus

1.2.1 Phosphorus in the sea

In the ocean, phosphorus is found in particulate and dissolved forms. Particulate P (PP) is mainly composed of an organically bound form derived from biological materials. Dissolved P includes free orthophosphate, polyphosphates, and a variety of organic compounds. Soluble reactive P (SRP) is the operationally defined P component that forms a molybdophosphoric acid complex under acidic conditions (Murphy and Riley, 1962; Strickland and Parsons, 1972). Free orthophosphate is the main component of SRP and thought to be the most bioavailable form for planktonic microorganisms. SRP includes P released from organic or inorganic compounds through acid hydrolysis during molybdophosphoric acid complex formation. Dissolved P that does not form molybdophosphoric acid complexes under acid conditions is defined as soluble non-reactive P (SNP). This non-reactive P fraction is commonly equated to dissolve organic P (DOP). Many previous studies have focused on the abundance of SRP in seawater or metabolic rates of SRP uptake by microorganisms to examine P availability in marine ecosystems (e.g., Perry and Eppley, 1981; Sorokin, 1985; Harrison and Harris, 1986). DOP is another potentially important P source, because its concentration can be more than an order of magnitude higher than SRP concentrations in oligotrophic oceanic ecosystems (Michaels *et al.*, 1996; Cavender-Bares *et al.*, 2001; Suzumura and Ingall, 2004). DOP can be utilized by cultured marine phytoplankton and bacteria assemblages to satisfy their P requirements (Björkman and Karl, 1994). A number of studies have provided evidence that enzymatic remineralization is a key process in the utilization of DOP by various microorganisms (Ammerman and Azam, 1985; Martinez and Azam, 1993; Mulholland *et al.*, 2002). P cycling at the North Pacific subtropical gyre was studied by Benitez-Nelson and Karl (2000) using cosmogenic ^{32}P and ^{33}P isotopes, suggesting that the DOP pool is a potentially important source for sustaining productivity (Suzumura and Ingall, 2004). In typical marine environments, PP produced in the euphotic zone is lost through three processes, remineralization, dissolution of soluble components, and settling of bulk particulate matter. The combination of these processes results in PP concentrations decreasing rapidly with depth. Particulate organic phosphorus (POP) is usually present at relatively low concentrations, typically 10-20 nM in oligotrophic environments and 1-2 orders of magnitude higher in productive zones. As with DOP, POP is under sampled and more poorly understood than particulate organic nitrogen (PON) (Michaels *et al.*, 1996).

Phosphorus is an essential macronutrient for all living organisms. In the cell, P is incorporated into a broad spectrum of organic compounds with vital metabolic functions, including structure (membrane lipids), catabolism (sugars and fatty acids), energetics (nucleotides), and cellular coordination (nucleic acids). Under certain environmental conditions more exotic, otherwise nonessential P containing compounds such as phosphonates, polyphosphates, regulatory nucleotides, and phosphorylated proteins can also be produced by selected groups of marine microorganisms. Consequently, through the normal processes of cell growth, exudation, and cell death by the combined contributions of autolysis, viral infection, and grazing there is a continual production of dissolved P compounds, especially in the upper portion of the world ocean (Karl and Yanagi, 1997).

In the sea, P growth requirements can be met by the uptake and assimilation of a variety of inorganic and organic P compounds, in addition to the most readily assimilated and favored orthophosphate (HPO_4^{2-}) ion (Figure 1.3). Because most phosphorylated organic compounds cannot be assimilated intact by microorganisms (although there are notable exceptions), cell membrane-associated enzymes are responsible for facilitiating uptake by a variety of coupled hydrolysis-transport mechanisms. Alkaline phosphatase (APase) and other phosphohydrolyses present in both *bacteria* (heterotrophic bacteria and cyanobacteria) and *eucarya* (eucaryotic algae and zooplankton) and 5-nucleotidase (5Ndase) predominantly present in *bacteria* are considered to be the two most important enzyme classes in aquatic environments. These enzymatic reactions have been suggested to sustain the P cycle in seawater (Karl and Yanagi, 1997).

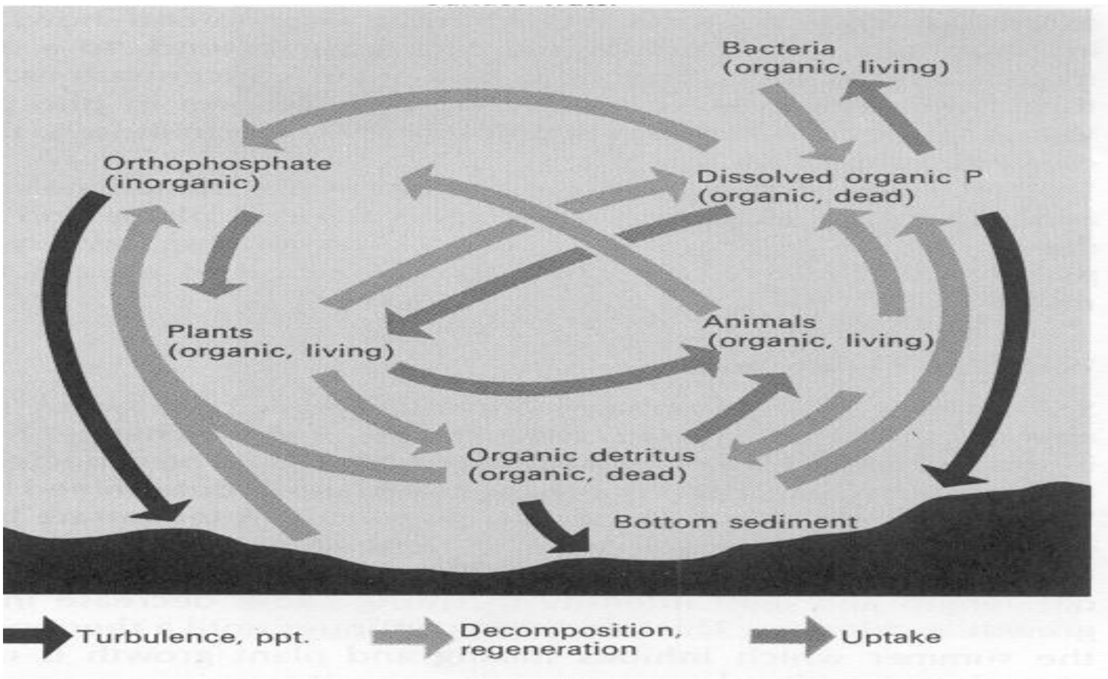


Figure 1.3 Phosphorus cycle in the sea (Davis Jr, 1972).

The total phosphorus concentration in marine ecosystems, ranging from oligotrophic seas to estuaries varied 650-fold (0.03-20 μM) (Downing, 1997; Scanlan and Wilson, 1999). In the marine environment, dissolved P can exist as free orthophosphoric acid (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$) (Figure 1.4), inorganic polyphosphate and in combination with a variety of organic derivatives, including purines and pyrimidines, sugars and lipids. Both inorganic polyphosphate and most dissolved organic phosphorus (DOP) compounds can be used to satisfy the P requirements of marine bacteria and phytoplankton, albeit at variable rates and efficiencies (Björkman and Karl, 1994).

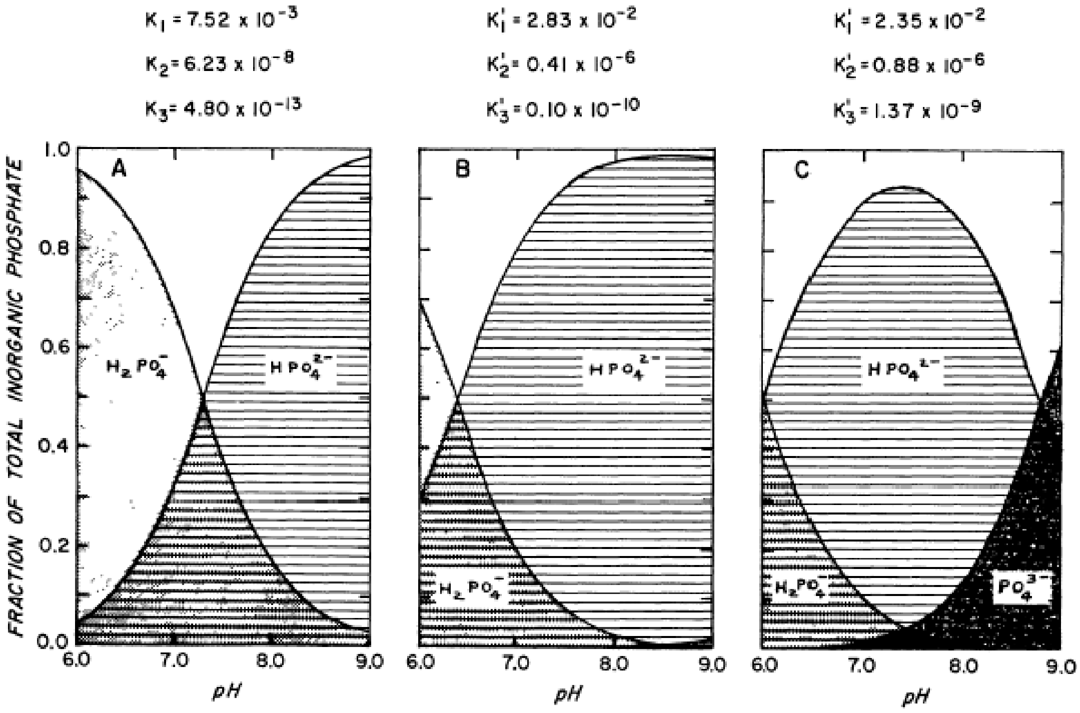


Figure 1.4 Distribution of phosphate species at 20ºC. A) Pure water B) O.68 M NaCl. C) Artificial seawater, 33‰ salinity (Kester and Pytkowicz, 1967).

Sediments receive a mixture of labile and refractory organic and inorganic phosphorus compounds from the overlying water and surrounding land masses (Sundby *et al.*, 1992). Some of these compounds behave as inert material and are simply buried in their original form. Others decompose or dissolve and release phosphate ions to the sediment pore water. The regenerated phosphate may be released to the overlying water, reprecipitated within the sediment as an authigenic phase, or adsorbed by other constituents of the sediment (Figure 1.5) (Sundby *et al.*, 1992). Adsorption on metal oxides in the sediment has been identified as one of the principal reactions involving phosphate (Sundby *et al.*, 1992).

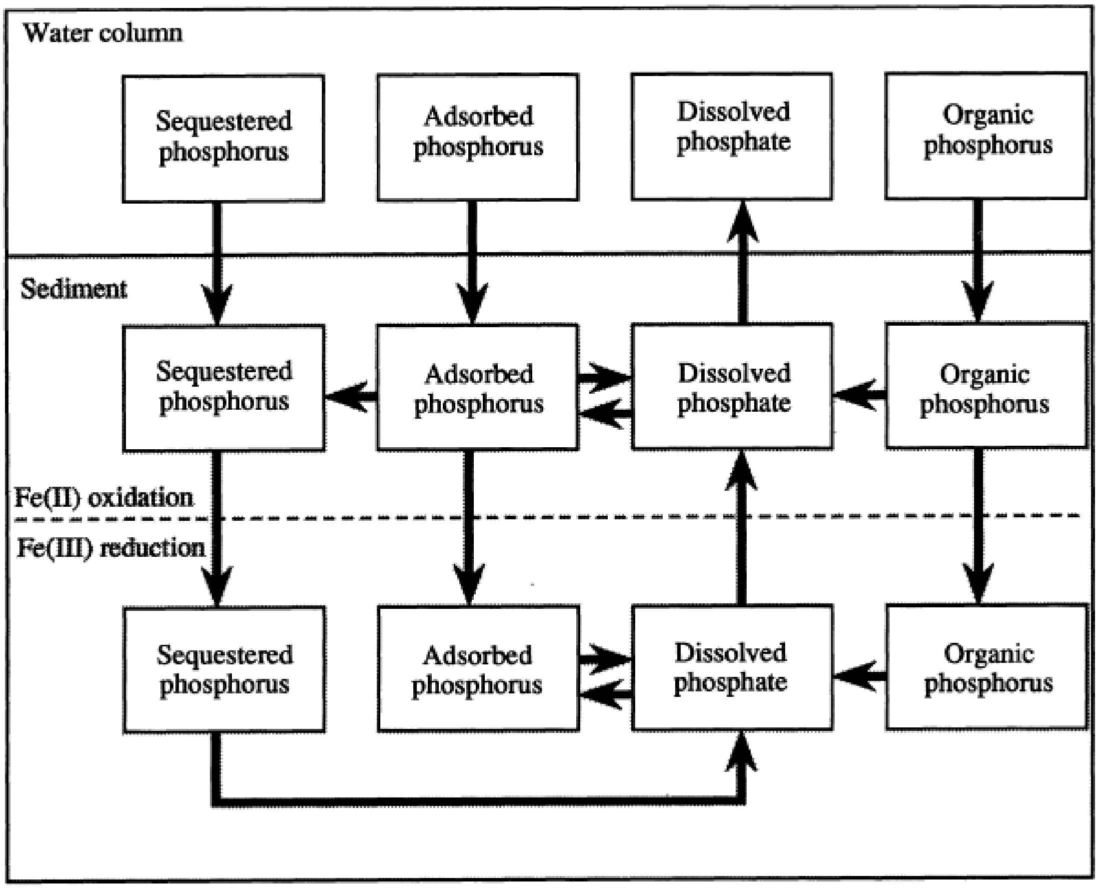


Figure 1.5 Summary diagram of P fluxes within the sediment and across the sediment-water interface. Inert P is not shown (Sundby *et al.*, 1992).

Phosphorus contents in the studied sediments obtained from the Arctic seas (Barents, Kara, and Norwegian), intercontinental seas (Baltic, White, Aral, Caspian, Black, Azov, and Mediterranean), and marginal seas of the Pacific and Indian oceans (Bering, Sea of Okhotsk, and Arabian) range from 0.1 to 0.9%. Commonly, the P content has a positive correlation with the organic-rich pelite fraction. The average phosphorus content in marine sediments is 0.07%. This corresponds to its average content in sedimentary rocks from continents (Turekian and Wedepohl, 1961; Vinogradov, 1962; Baturin, 2003).

1.2.2 Riverine and atmospheric input of phosphorus

Riverine transport is the principal pathway of suspended and dissolved elements from land to the sea. Changes in riverine end-member nutrient concentrations and their ratios may affect coastal ecosystems (Liu *et al.*, 2003). Traditionally budgets and residence time estimates for nutrients in the oceans have been based on riverine fluxes and have ignored atmospheric inputs. However, for most major and minor components of seawater the atmosphere has generally been assumed to be a secondary source (Jickells, 1995). The relative importance of atmospheric input of nutrients to the Mediterranean increases from the shoreline to the open sea with the decreasing influence of riverine inputs, and from active mixing zones (margin ‘upwellings’, frontal zones) to oligotrophic ‘stable’ zones (Martin *et al.*, 1989; Jickells, 1995; Guerzoni *et al.*, 1999). On an annual scale, the nitrogen atmospheric input is significant for oligotrophic zones, in which it may account for up to 60% of new production, whereas atmospheric phosphorus may account for a maximum of 25% (Guerzoni *et al.*, 1999). It is evident that the impact of the atmospheric input of nutrients to the open Mediterranean is difficult to detect, and would in any case be negligible during the period of intense primary production because of mixing with deep rich waters. But during the summer and early fall stratification of the Mediterranean, atmospheric inputs represent a non-negligible source of nutrients (up to 4000 $\mathrm{mmolNm^{-2}d^{-1}}$), which may trigger small but detectable phytoplankton blooms (Martin *et al.*, 1989; Guerzoni *et al.*, 1999).

When aerosols come in contact with raindrops, a part of the particulate inorganic phosphorus associated with the particles can dissolve into orthophosphate form (PO_4^{3-}) (denoted as dissolved inorganic phosphorus [DIP]) that may be assimilated by the biological community (Ridame *et al.*, 2003). Although Saharan air masses can episodically bring high amounts of dust (up to 3 g m^{-2} for a single rain event; Loÿe-Pilot and Martin, 1996), it is now recognized that P associated with soil-derived and/or Saharan inputs exhibits low solubility (Bergametti *et al.*, 1992; Herut *et al.*, 1999a, Migon and Sandroni, 1999). Owing to the combination of precipitation and adsorption processes, detritic aeolian dust may also act as a sink for P, with partly removing dissolved phosphate from surface marine layer (Krom *et al.*, 1991; Herut *et al.*, 1999b; Migon and Sandroni, 1999; Migon *et al.*, 2001). The debate on whether Saharan events are likely to trigger measurable bloom of phytoplankton is still open. By contrast, anthropogenic P emission sources (i.e. foodstuff residues, incinerators, fertilisers, chemicals, detergents, pesticides) may be responsible for an efficient spreading of soluble P over marine areas (Viturtia *et al.*, 1992; Dojlido and Best, 1993), in particular through urban-dominated rain events (Migon *et al.*, 2001).

Atmospheric input can be by wet or dry deposition and the relative importance of these varies from place to place (depending predominantly on rainfall frequency), and from element to element. In general wet deposition is more important than dry for components associated with smaller particles, which are mainly those produced by gas to particle conversion. Such particles, therefore, include many elements and chemical species whose atmospheric sources are dominated by anthropogenic sources (Church, *et al.*, 1990; and references therein). Crustal and marine-derived aerosols are characteristically associated with larger aerosols and are more efficiently dry deposited (Arimoto and Duce, 1986; Jickells, 1995). The wet deposition of total inorganic phosphorus to the Southeastern Mediterranean (SEMED), estimated from 2 years of measurements on the northern coast of Israel was 0.6 $mmolm^{-2}d^{-1}$ and dry deposition was 1.2 $mmolm^{-2}d^{-1}$, giving a total rate of 1.8 $mmolm^{-2}d^{-1}$ (Herut and Krom, 1996).

Phosphorus values of Saharan dust range from 0.04% found in the SEMED to 0.07% from Libyan Desert material (Herut and Krom, 1996). Values as high as 0.25-0.40% were found in Saharan dust collected in the Northwestern Mediterranean (NWMED). Saharan dust may act as a trap for soluble phosphorus by adsorption of PO_4^{-3} on to Fe-rich particles, whereas Lepple (1971) found that up to 8% of Saharan dust phosphorus is soluble in seawater.

1.3 Molar Ratios of Nutrients and Particulate Organic Matter in the Sea

An essential tool for the calculation of oceanic fluxes in biological models is the Redfield ratio (Redfield *et al.*, 1963), since it describes a fixed covariation of the elements C, N, and P in a ratio of 106:16:1. The Redfield ratio implies a reciprocal interaction between the elemental composition of marine biota and their dissolved nutrition resources. Organisms or, more generally, particulate organic matter (POM) leaving the upper mixed layer should export this ratio to the deep ocean and leave its imprint on the stoichiometry of remineralization products. Indeed, in the deep ocean the covariation of the major nutrients nitrate and phosphate and the amount of oxygen used (AOU) for oxidation of organic carbon seem to reflect this ratio almost perfectly (Engel *et al.*, 2002). By applying the Redfield ratio as a criterion for stoichiometric nutrient balance, one can distinguish between P-deficient, N-deficient, and Si-deficient waters, and those having a well balanced nutrient composition (Rabalais *et al.*, 2002). The combined patterns of variation of total N/P ratios in marine and freshwater environments provide a model of the global N/P cycle. In upstream freshwaters where input is mostly derived from high N/P precipitation and high N/P run-off from undisturbed soils (Downing and McCauley, 1992), P concentrations are low, N/P is high and production is strongly P-limited. As water moves downstream, it is enriched by high P, low N/P run-off from terrestrial systems, P increases and N/P declines, resulting in frequent N-limitation of primary production (Elser *et al*., 1990) and blooms of N-fixing cyanobacteria (Smith, 1983). This enrichment may proceed to a varying degree, depending upon the size, land use, and human inhabitation in the drainage system (Peierls *et al*., 1991; Downing, 1997).

It was suggested that N/P molar ratio of nutrients is very high in oligotrophic, open seas but often very low in estuaries and coastal ecosystems. Estuarine, coastal, or enclosed parts of the sea had N/P ratios less than the required cellular ratio of 16:1 significantly more frequently than samples taken from the surface waters of the open ocean (Downing, 1997).

Particulate and dissolved organic N/P can be very high at a variety of oligotrophic sites in the open sea (Copin-Montégut and Copin-Montégut, 1983; Jackson and Williams, 1985).

If the organisms that comprise the bulk of the organic biomass in sinking material have N/P elemental concentrations near the Redfield ratio of 16, the reminalization of this biomass will lead to the production of 16 moles of nitrate for every mole of phosphate produced. If organisms such as nitrogen-fixing *cyanobacteria* create biomass that is richer in nitrogen (more correctly, phosphate-poor) this could yield the reminalization of more than 16 moles of nitrate for every mole of phosphate. Conversely, denitrification would remove nitrate with respect to phosphate and decrease the in situ elemental ratio (Michaels *et al*., 1996).

The influence of organisms on the composition of seawater is determined by physiological influences and consequently exhibits the regularity inherent in organic processes. Elements are withdrawn from seawater by the growth of marine plants in the proportions required to produce protoplasm of specific composition and are returned to it as excretions and decomposition products of an equally specific nature. The elementary composition of unicellular algae can be varied by changing the composition of the medium in which they grow. If one element is markedly deficient in the medium, relative to its need by the organism, cell growth and cell division can proceed for a limited period of time. The cells produced under these conditions contain less of the deficient element than do normal cells. When an element is provided in excess in the medium, luxury consumption can increase its content in the cells (Redfield *et al*., 1963). The range in C/N/P stoichiometry is much wider under nutrient-limited conditions than in nutrient-replete cells in which the concentrations of organic nutrients in solution are several fold greater than the half-saturation constants for nutrient assimilation. Mass balance calculations, based on the physiologically achievable range of the dominant biochemical macromolecules in the cell, point to a range of N/P from 10 to 40. The lower boundary of this range in N/P can be raised to 16 at a protein content of 40-50% of organic matter, which is expected in nutrient-replete cells, and at an intermediate range of phospholipid and nucleic acid. The lowest N/P ratios observed in the nutrient-replete cultures can be reconciled with the biochemical analysis only by invoking the intracellular storage of phosphorus. The critical N/P ratio will be observed when cells are simultaneously N- and P-limited, and is expected to reflect a biochemical composition that is dominated by nucleic acids, phospholipids and protein but where no N and P storage products are present. Based on protein contribution 40-60% of organic matter, one expects the critical N/P to take a value between 10 and 50 depending on the nucleic acid and phospholipid contents. The ratio could be higher for cells with significant contents of N-containing osmolytes (Geider and La Roche, 2002).

The variability of the C/N/P composition of phytoplankton can arise either from changes in the concentrations of N- and P-containing organic macromolecules or from the accumulation nutrient reserve (polyphosphate, nitrate) or energy reserve (starch or triglyceride) pools. While C is significant component in all classes of organic macromolecules (24-80% of dry weight), N and P enriched in some compounds but notably absent in neutral lipids and carbohydrates. The elemental composition of marine phytoplankton cultures indicate that (Geider and La Roche, 2002):

1- The physiological range of N/P in phytoplankton is from <5 under severe N-limitation to >100 under severe P-limitation, however, the N/P ratio of particulate matter from N- and P-rich waters and the nitrate/phosphate draw-down ratio tend to be <16, whereas the N/P of marine particulate matter from nutrient-poor oligotrophic regions tends to be >16.
2- The N/P ratio of nutrient-replete phytoplankton ranges from about 5 to 19, with most observations falling below the Redfield ratio of 16.
3- The range becomes increasingly restricted as the species-specific maximum growth rate is approached.
4- The critical N/P ratio that marks the transition between N- and P-limitation appears to be in the range 20-50, and thus exceeds the Redfield ratio of 16.
5- The C/N ratio, although variable (3-17), has a typical value that is close to that of the Redfield ratio under nutrient-replete conditions.

1.4 Previous Works

1.4.1 Previous works in the Eastern Mediterranean

Özsoy *et al*. (1993) reported that surface measurements, satellite images and the mass field indicated an entire range of scales of dynamical features in the Levantine Basin. The complexity of the circulation was consistent with the basin-wide and mesoscale heterogeneity of the hydrographic properties. The interannual variability of Levantine Intermediate Water (LIW) formation in the region appeared correlated with the changes in the circulation. Wintertime convective overturning of water masses reached intermediate depths and constituted a dominant of LIW formation, especially in anticylonic eddies and along the coast of the northeastern Levantine Basin.

There have been various suggestions on the high N/P ratios in the deep waters of the eastern Mediterranean. Béthoux *et al*. (1992) have reported that nitrogen fixers have protein reserves and rather low C/N ratio; they probably present a high N/P ratio, which could explain the peculiar N/P molar ratio in the Mediterranean deep waters, about 21 to 27, instead of 15 in the open ocean and in the Atlantic inflowing water.

Nutrient chemistry of the Mediterranean Sea has been studied extensively since 1980. Krom *et al.* (1991) studied in the southeastern Mediterranean and found that all the PO_4^{3-} was removed from the upper water column during the winter phytoplankton bloom in the core and boundary of warm-core eddy, while measurable NO_3^- (0.3-0.6 μM) remained. The N/P ratio in the core and boundary of the Cyprus eddy was estimated as 27.4 and the slope of the linear portion of the N vs. P scattergram was 25.5. A similar N/P ratio (28-29) and slope (21-23) was found for the water column across much of the southern Levantine basin. They have concluded that the southern Mediterranean is strongly P limited. The degree of P limitation increases from west to east across the entire basin. They suggested that removal of PO_4^{3-} by adsorption on Fe-rich dust particles may be an important process controlling the concentration of P in the water column.

Ediger and Yılmaz (1996) have examined the vertical distributions of chlorophyll-a throughout the northern Levantine Basin of the eastern Mediterranean in the period of October 1991-March 1994. The well developed deep chlorophyll maximum (DCM) was observed in the northeastern Levantine basin, with concentrations greater than 1 μg/L at depths ranging from 45 to 100 m on average. In cyclonic regions, the depths of the DCM and the nutricline coincided and relatively high chl-*a* concentrations were observed at shallower depths at relatively high percentages of surface light. In anticyclonic regions, the DCM was located at the base of the euphotic zone (EZ) and much above the nutricline. They found that the EZ was nutrient depleted and the concentrations were close to detection limits (e.g. 0.02 μM for phosphate and 0.05 μM for nitrate) and in general did not show significant seasonal variations. The nutricline was located at the base of the EZ in cyclonic region (Rhodes Gyre). In anticyclonic regions, the main nutricline was as deep as 600 m.

Yılmaz and Tuğrul (1998) have reported that the nutrient distribution and phytoplankton production in the Levantine Sea of the eastern Mediterranean have been principally determined by the duration and the intensity of deep winter mixing in the quasi-permanent anticyclonic and cyclonic eddies. The nutricline is much sharper and shallower in the cyclonic Rhodes Gyre. In the severe winters of 1992 and 1993, the LDW with its associated chemical properties and abnormally high nutrient concentrations (NO_3=3.8-4.7 μM; PO_4=0.14-0.16 μM and Si=7.3-7.8 μM) occupied the euphotic zone of the cyclonic Rhodes Gyre. However, the surface nutrient concentrations of the anticyclonic regions were raised merely from the summer-autumn values of <0.02 μM and nearly 0.2 μM to about 0.03 μM and 0.8 μM for phosphate and nitrate, respectively. The molar ratios of nitrate to phosphate in the water column ranged between 5 and 20 in the euphotic zone but exhibited well-defined peak values (as large as 40-120) at the top of the nutricline for most of the year. Below the nutricline the N/P ratios decrease regularly and reach an almost constant deep value (=28) over the basin. The mean ratio, derived from linear regression of the pooled phosphate and nitrate data from March 1991 to March 1994 was about 23.6, substantially higher than deep ocean values. Relatively low N/P ratios -with respect to Redfield ratios- determined in bulk POM from the Levantine surface layer suggested that there should be another source for the observed high N/P ratios in the Levantine deep water. The most probable source was the sinking water, selectively enriched with labile, dissolved organic and inorganic nitrogen constituents at the origin.

Zohary and Robarts (1998) experimentally tested the hypothesis that phosphorus was the primary nutrient limiting phytoplankton and bacterial growth in the eastern Mediterranean Sea, and examined the spatial variability in P limitation during winter. Complementary measurements were employed using water sampled during January 1995 from nine pelagic stations east of the Straits of Sicily. Ambient concentrations of inorganic P in the upper 50 m of the water column in seven stations were 20-40 nM. The upper limit of bioavailable P ranged from 6 to 18 nM, suggesting severe P shortage. Orthophosphate turnover time ranged from 2 to 7 h in those P-depleted waters. In nutrient-enrichment bioassays using subsurface water from the Ionian and Levantine basins, P addition caused significant increases in bacterial activity, bacterial numbers, and chl *a* relative to unenriched controls. It was concluded that in the pelagic waters of the Eastern Mediterranean in winter, P was the primary limiting nutrient when other factors (such as light or grazing) did not control microbial biomass or activity.

Çoban-Yıldız *et al.* (2000a) determined the relative concentrations of pyrolysis products (termed markers), characteristic of chlorophyll, lipid, carbohydrate, and protein components of suspendent particulate organic matter (SPOM) in the eastern Mediterranean Sea in 1996. The vertical distribution of lipid markers of bulk POM was uniform in the Mediterranean surface waters. The relative concentrations of chlorophyll markers increased consistently within the chlorophyll maximum zone where the carbohydrate markers were less abundant in bulk POM. Relatively lower and constant C:N ratios were determined in SPOM from the thicker euphotic zone of the Mediterranean Sea.

Moutin and Raimbault (2002) investigated the distribution of primary production, particulate carbon export from the photic zone to deeper layer, and nutrient concentrations in the Mediterranean Sea during May-June 1996. A decrease in integrated primary production, particulate carbon export and nutrient availability towards the eastern part of the Mediterranean Sea was observed, while integrated chlorophyll *a* remains rather constant. Integrated primary production ranging from 350 to 450 $mgCm^{-2}day^{-1}$ in the western Mediterranean decreased toward the east to a value of about 150 $mgCm^{-2}day^{-1}$. The latter value may appear as a limit for primary production rates under strong oligotrophic conditions. Particulate carbon export represented 4.0±2.9% of integrated primary production. Up to 90–95% of primary production was then sustained by internal recycling of organic matter. Evidence of a limitation of production by phosphate was obtained from differences between depth of nitracline and phosphacline and by enrichment experiments. The wide range of oligotrophic conditions in the Mediterranean Sea provided a case study for links between C, N and P-cycles.

Marty and Chiavérini (2002) reported that the increase of carbon assimilation rate per unit of chlorophyll *a* appeared as linked to the period of phosphorus-limited ecosystem, and vertical distribution of taxonomic pigments suggested a possible role of *cyanobacteria*. A possible shift of primary production towards a more regeneration-dominated system was suggested for recent years.

Markaki *et al.* (2003) measured total and dissolved inorganic phosphorus in both rainwater and aerosol samples collected from two remote coastal areas: on the island of Crete (Greece) and at Erdemli (Turkey). The results indicated that (i) in both wet and dry deposition, the DIN/DIP molar ratio ranged between 217 and 294 at Erdemli, exceeding by a factor of up to 22 the N/P ratio observed in seawater (ranging from 25 to 28) and (ii) atmospheric deposition of DIP could reasonably account for a significant part of the new production (up to 38%) observed during the summer and autumn period (i.e., when water stratification was at its maximum). These results were in agreement with the conclusions by Bergametti *et al.* (1992) for the northwestern Mediterranean.

Ridame *et al.* (2003) found that Saharan particles did not represent a significant sink for seawater phosphate in the western Mediterranean Sea. This result was in agreement with that determined from a similar approach conducted in the eastern basin. As a consequence, the unusual N/P ratio measured in the whole Mediterranean Sea (up to 29) cannot be explained by the adsorption process of seawater phosphate onto Saharan dust.

Ediger *et al.* (2005) performed POM, nutrients, chlorophyll-a (CHL) and primary production measurements in the upper layer of three different regions (cyclonic, anticyclonic and frontal+peripherial) of the NE Mediterranean Sea in 1991-1994. Depth profiles of bulk POM exhibited a subsurface maximum, coinciding with the deep chlorophyll maximum (DCM) established near the base of the euphotic zone of the Rhodes cyclone and its periphery where the nutricline was situated just below the euphotic zone for most of the year. Moreover, the POM peaks were broader and situated at shallower depths in late winter-early spring as compared to its position in the summer-autumn period.

The results of CYCLOPS project show that the phosphate, although added to the eastern Mediterranean surface waters, was rapidly taken up by the microbial biota, there was a small but significant decrease in chlorophyll *a* and no increase in primary production, together with an increase in heterotrophic bacterial activity, ciliate numbers and in the gut fullness and egg numbers in the zooplankton community. A microcosm experiment carried out using within-patch and out-of-patch water showed that the phytoplankton community was N and P co-limited, while the bacteria and micrograzers were P-limited. Thus this system tends to N and P co-limitation of phytoplankton productivity in summer possibly caused by bioavailable DIN being converted into non-bioavailable forms of DON.

Krom *et al*. (2005) reported that the results from the first extensive deployment of on-board nanomolar nutrient measurements in this low nutrient low chlorophyll (LNLC) system showed that free ammonia (50-80 nM) was present in the surface waters while nitrate was less than 10 nM, confirming the results obtained elsewhere in the CYCLOPS addition experiment that grazing/nutrient recycling is a dominant process in this system. The total DIN:DIP ratio in the nutrient depleted waters above the chlorophyll maximum was predominantly greater than 16:1, denoting that the system has not switched to N-limitation.

1.4.2 Previous works in the Northeastern Mediterranean shelf zone

Köksalan (2000) studied temporal variability in *Synechococcus* spp. abundances and nutrients in the Northeastern Levantine Basin, based on time-series observations in 1998 at three stations off Erdemli. It was found that nutrients seemed to have no direct relationship with the *Synechococcus* cell abundance as their high surface to volume ratio permit them to survive even at very low nutrient concentrations. The abundance of *Synecoccocus* spp. (cyanobacteria) was much higher ($39x10^6$ cells l^{-1}) at the same shelfbreak station during 1998 than at the same nearshore station ($18x10^6$ cells l^{-1}).

Eker-Develi (2004) studied in the same region, at the nearshore and offshore zone of the shelf, during March-June 1999 and December 2000-April 2002. It was reported that phosphate concentration was mostly below detection limit (0.02 μM) of the conventional method at the offshore stations. Thus, N/P ratios could not be computed reliably. However, it was found that the 1999 period was more productive than 2001. The highest nitrate, phosphate, chlorophyll-*a*, phytoplankton abundance and biomass values were determined in 1999 (probably due to the much stronger river influence as well as water dynamics). High biomass values were also observed in January-April period of 2002, probably due to heavier precipitation as well as strong vertical mixing, compared to 2001 which was a relatively calm period.

Eker-Develi *et al*. (2006) also studied that the effects of atmospheric deposition and other environmental factors on phytoplankton dynamics in the shelf waters between December 2000 and December 2001. Data on phytoplankton, chlorophyll *a*, nutrients, temperature and salinity were obtained at bi-weekly or more intense intervals during 1 yr, whilst transport of Saharan dust towards the sampling region was monitored daily by SeaWiFS (sea-viewing wide field-of-view sensor) images. Diatoms were the group of highest average biomass during the entire investigation period. Although coccolithophores (mainly *Emiliania huxleyi*) numerically dominated at the open station during the study period, the intensity of dust transport was observed to be highest in spring. Less intense transports were observed in summer and autumn. It was suggested that the impact of atmospheric nutrient input on phytoplankton in the Mediterranean was rather low on a yearly basis.

Uysal (2006) studied the vertical distributions of the unicellular cyanobacteria *Synechococcus* in the NE Mediterranean shelf waters during October 2000 and September 2002. Cell abundances varied significantly on both vertical and horizontal scales in all physically and spatially discrete water masses. Epifluorescence microscope cell counts clearly showed that majority of the population remains suspended in the surface-mixed layer and decreases gradually towards the base of the euphotic zone. Changes in abundance in the mixed layer were small compared to the abrupt changes below the halocline. The major population remained suspended above the depth of fluorescence maximum.

Yılmaz (2006) studied at the same nearshore and shelfbreak stations during December 2001-December 2003 as cooperative of the present study. Temporal variations of phytoplankton in the NE Mediterranean shelf was examined using pigment biomarkers in the sea. It was found that phytoplankton abundance was higher in the surface water of both stations. However, the biomass decreased markedly towards offshore station from spring to late summer. Diatoms and coccolithophores were the major phytoplankton groups at both stations. Chl-*a* concentrations were low at the shelfbreak station and a weak deep chlorophyll maximum was observed around 100 m depth during summer of 2002 and 2003. Primary production in the nearshore station surface layer (180±176 $mgCm^{-3}d^{-1}$) was much higher than the shelfbreak station (6.0±3.1 $mgCm^{-3}d^{-1}$).

1.5 Purpose and Objectives of the Present Study

1.5.1 Major gaps in nutrient chemistry of the Northeastern Mediterranean

In the upper layer of the NE Mediterranean:

☐ Sensitivity and detection limit of the conventional colorimetric method (about 15-20 nM) are insufficient to measure PO_4 accurately in the surface and intermediate waters of the eastern Mediterranean. New approaches are needed to assess NO_3/PO_4 (N/P) ratio reliably and systematically in the upper layer waters of the region as well as to model the P-limited marine ecosystem of the NE Mediterranean.

☐ It is not known yet why the nitracline onset appears at greater depths relative to that of phosphate gradient, resulting abnormally high N/P ratio in the upper nutricline zone. The phosphate-deficiency in the system may be a factor for this shift.

☐ Contribution of particulate inorganic phosphorus (PIP) in the total particulate-P (TPP=PIP+POP) pool of the NE Mediterranean is not known due to lack of data. Therefore, it is yet undefined what % of TPP is composed of PIP and thus what % of PON/TPP ratios originates from PIP in suspended particles collected on filters. It appears that PIP-corrected PON/POP ratios should be computed to understand the role of phoshate limitation on the elemental composition of bulk POM produced in the water column of the NE Mediterranean shelf. This knowledge is highly essential for a sound understanding of P-cycle in the NE Mediterranean Sea and thus modeling of the phosphate-limited marine ecosystems.

In the deep layer of the NE Mediterranean:

☐ NO_3/PO_4 (N/P) ratio is as high as 25-28, much greater than the conventional Redfield N/P molar ratio of 16. But it is as yet unclear what processes dominate the high N/P ratios in the deep layers of the eastern Mediterranean though there are various suggestions for P-deficiency in the deep waters (Yılmaz and Tuğrul, 1998; Herut *et al.*, 1999a; Ediger *et al.*, 2005; Krom *et al.*, 2005).

Nutrients and particulate matter have systematically been measured in the open NE Mediterranean Sea since the beginning of 1980 and the measurements are available in the databank of Institute of Marine Sciences. However, the conventional colorimetric method is not sensitive enough to detect ortho-phosphate (PO_4) precisely below 50 nM (detection limit: 20 nM). The present data bank has contained only orthophosphate (PO_4^{3-}, hereinafter referred to as DIP) determined by the conventional method and the concentrations being undetectable (DIP<20 nM). Therefore, previous data sets are inadequate to assess N/P ratios reliably in the surface waters for sound understanding of potential limiting nutrients and for bio-assay experiments. This study aims to meet the demand for accurate determination of DIP in the oligotrophic NE Mediterranean Sea.

1.5.2 Objectives of this study

Principal objectives of this study are

- to provide systematic nutrient, particulate organic matter (POM) and P-fractions data in the NE Mediterranean shelf off Erdemli,
- to further understand spatiotemporal and interannual variations of fraction of phosphorus and related hydro-chemical parameters in 2-year-long time series,
- to identify the most important water-column formation and transformation processes influencing the nutrient pool of the NE Mediterranean shelf. One contrasting marine environment located along the coast of Northern Cyprus has also been investigated for comparison.
- to measure specific phosphate (DIP) at nM levels by co-precipitation method that is about 20 times more sensitive than the conventional automated method,
- to estimate NO_3/PO_4 molar ratios reliably across the shelf: It is essential for examination of potential limiting nutrients for the NE Mediterranean as well as uptake ratios of inorganic nutrients by phytoplankton, and
- to estimate PON/TPP and PON/POP ratios of bulk POM and elemental composition of organic matter, based on POM data and regression analysis of particulate C, N and P data sets obtained in the NE Mediterranean shelf. They are essential parameters for mass fluxes in the system and for modeling of algal production in the region.

CHAPTER 2

EXPERIMENTAL

2.1 Data Sampling Strategy

This study aimed to investigate spatial and temporal variations in different forms of phosphorus in the total P-pool and related parameters in the NE Mediterranean shelf waters (off Erdemli). A sampling program has been, therefore, designed to determine hydrographical and bio-chemical parameters across the shelf off Erdemli so that environmental factors affecting P cycle in the shelf ecosystem could be understood in space and time. For this goal, long-term data have been provided by a 2-year (from December 2001 to December 2003) monitoring and research programme. Data sets including salinity, temperature, density, DIP^{AA}, NO_3, Si, POC and PON (unpublished data from IMS-METU; Tuğrul *et al.*, 2004) have been used for linkage with the present P-fractions data in this study.

2.2 Sampling Locations

Systematic field surveys were carried out monthly from the nearshore (0.5 nautical mile off the coast, >20 m, 36^{o} 57' N 34^{o} 27' E) to the shelfbreak stations (~9 nautical miles off the coast, >200 m, 36^{o}50’N and 34^{o}38’E) during the period of December 2001-December 2003, using R/V Lamas and R/V Erdemli research vessels. The nearshore station (St 1) was approximately 25 m deep, which was influenced by the small Lamas River. It should also be noted that the samples were collected at the middle station on the shelf (~4 nautical miles off the coast, >100 m, 36^{o}43’N 34^{o}36’E) during September 2002-December 2003 (Figure 2.1). Complementary sampling was conducted at four open (reference) stations (R1, R2, R3 and R4), located along the coast of Northern Cyprus (Figure 2.2), aboard R/V Bilim in

December 2003. Rainwater and the Lamas River water samples were also collected between 2002 and 2003 to evaluate the effects of external input on the system.

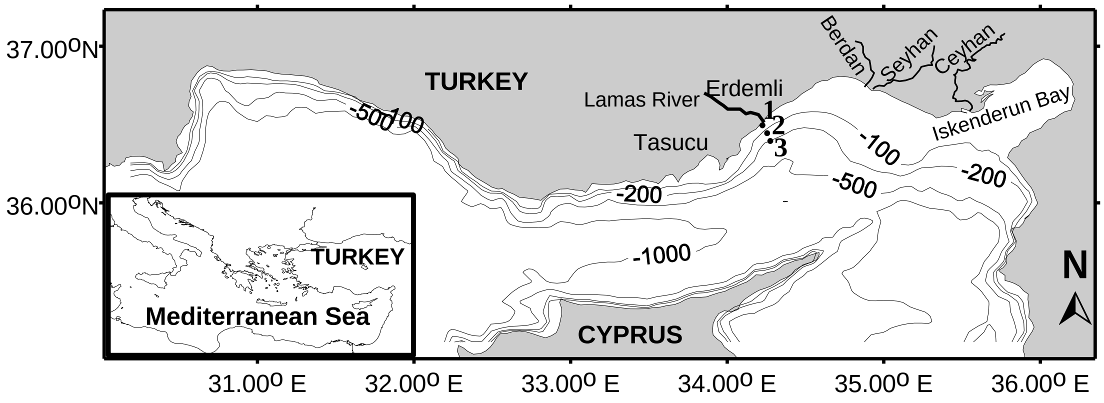


Figure 2.1 The locations of sampling stations (1: Nearshore, 2: Middle and 3: Shelfbreak) on the NE Mediterranean shelf off Erdemli.

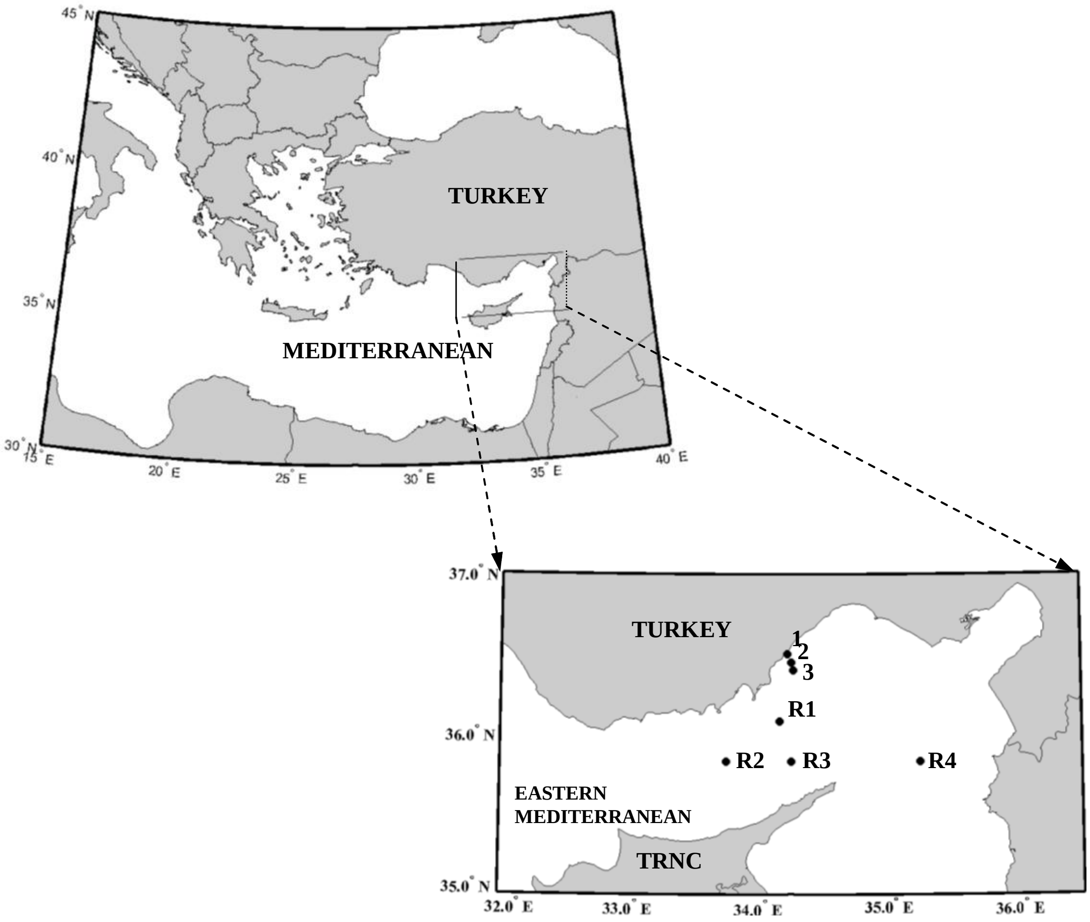


Figure 2.2 The locations of reference stations (R1, R2, R3, and R4) visited in Cilician Basin of the NE Mediterranean.

2.3 Sampling of Hydro-Chemical Parameters

2.3.1 Hydrographic and Bio-Optical sampling and measurements

Continuous *in-situ* sampling and measurements of water column salinity, temperature and density were performed with a Sea-Bird model CTD probe. The CTD probe system was equipped with external temperature, conductivity, dissolved oxygen, fluorescence sensors and with an internal pressure sensor. During the R/V Bilim cruise in December 2003, the CTD system and 12 bottles rosette system was deployed on a 3-conductor cable allowing for the real-time display of CTD data and acquisition, and for tripping the bottles in areas of interest in the water column. CTD data were recorded during both down and up casts. However, water samples were taken on the upcast.

The Secchi disc is a simple instrument used to measure water transparency and provides a rough estimate of light penetration in the water column. The Secchi disc depths (SDD) were noted to obtain light penetration depth for stations. LICOR sensor attached on the Sea-Bird CTD system was used for measuring Photosynthetically Active Radiation (PAR). Dissolved Oxygen (DO) sub-samples were taken initially using tygon tubing. The 5-L Niskin bottles were conveniently mounted on a rosette (which also carry other instrumentation such as CTD), and lowered down through the water column by the ship’s winch. In this case, the sample bottles were closed through commands issued from the surface deck-unit, and transmitted to the rosette through a conductive cable.

2.3.2 Sampling for dissolved inorganic nutrients

Seawater samples seeking accurate determinations of dissolved inorganic nutrients were subsampled directly from the Niskin bottles into 125-mL polyethylene storage bottles (Kartell, Italy) that had been acid-washed (10% HCl vol/vol) and rinsed with deionized-distilled water (DDW) before use. Each bottle was rinsed three times with sample waters before final filling; care was taken to avoid contamination. If immediate analyses were not possible, the nutrient samples were kept upright in a -20 °C freezer. These sampling and storage protocols have been shown to be ideal for quantitative measurements of nutrients in oligotrophic seawaters (Strickland and Parsons, 1972; Dore *et al.*, 1996).

2.3.3 Sampling for Particulate Organic Matter (POM)

Seawater samples, collected by the Niskin bottles, were transferred directly to acid-cleaned polyethylene carboys through 200 μm mesh for removing larger particles. The contents were then filtered under low pressure (<0.5 atm) through combusted/preignited in-line acid rinsed Glass Fiber Filters (Whatman, GF/F) having 47 mm diameter and 0.7 μm pore size. Contamination is the primary problem to be avoided with these samples. Combusted (450 ^oC for 4.5 h) acid rinsed filters should be used. All sampling bottles, forceps, tubing and filtration bottles have also to be acid rinsed.

Particulate organic carbon (POC) and nitrogen (PON) samples were collected on the same filter in order to achieve the same conditions for sampling and filtering efficiently. The volume of the filtered water depended on the particle content of the station and sampling depth (Ormaza-González and Statham, 1996). Generally, 5 to 10 liters of the seawater was sufficient to collect POC and PON from the Northeastern Mediterranean, while up to 40 liters of water has been filtered from the Mediterranean open (reference) stations. Following filtration, clean forceps were used to transfer each filter to a combusted 16 x 100 mm glass test tube, which was then covered with a 3.5 cm square piece of combusted foil. Each sample was labeled and kept frozen on board (-20 ^oC) and then dried overnight at about 40 ºC and stored in a vacuum desiccator until analysis. Any water remaining in the carboy is measured to calculate the volume filtered. This information and any other appropriate data are entered on the data sheet.

2.3.4 Sampling for phosphorus fractions

Contamination is the primary concern with P determinations. This is particularly true with samples collected from the euphotic zone where dissolved inorganic phosphate (DIP) concentrations are extremely low (<20 nM). In order to avoid contamination, sample bottles have to be cleaned with dilute HCl, rinsed with DDW before use and aged with low nutrient seawater (LNSW) to minimize adsorption-desorption until analysis.

Collected at discrete depths in the Niskin bottles seawater samples, which were not filtered, for total phosphorus (TP) analysis were taken into acid washed (10% HCl) 125 mL bottles. They were stored in a deep-freezer at about -20 ^{o}C until the analysis. Their analyses were completed in 2 weeks after the arrival of samples to the laboratory.

The seawater samples were pressure filtered through combusted acid-rinsed GF/F filters for subsequent analysis of total particulate phosphorus (TPP) and particulate phosphorus (PIP) in the same manner as previously described in Section 2.3.3. Each filter was put in labeled sterile petri dishes, kept frozen on board (-20 ^{o}C). The filters were then dried overnight at ca. 40 ºC after arrived in the laboratory and stored in a vacuum desiccator till the analysis.

Non-filtered seawater samples were taken into acid washed (10% HCl) 1000 mL measuring cylinders for DIP analysis by using the MAGIC method (DIP^{MAGIC}). The samples were immediately analysed and not kept in a -20 °C freezer (see Section 2.5.5).

2.4 Analysis of Bio-Chemical Parameters

2.4.1 Dissolved inorganic nutrient analysis

Currently, nutrient samples collected at the selected stations were analyzed at the laboratory of the Institute of Marine Science. Technicon model 3-channel autoanalyzer II (Bran Luebbe, Germany) has been used to perform analyses. For nutrient analyses, as well as standard methods proposed by Bran Luebbe for autoanalyzer applications for phosphate (method no: G-175-96, MT18), nitrate (G-172-96, MT19) and silicate (G-177-96, MT19), colorimetric methods described by Strickland and Parsons (1972) and Grasshoff *et al*. (1983) have been used to analyze the samples. Frozen samples were completely thawed at room temperature or in a water bath before analysis. The samples were run against low nutrient sea water as baseline and wash.

2.4.1.1 Orthophosphate (PO_4-P) analysis

The automated procedure for the determination of orthophosphate (PO_4^{3-}, hereinafter referred to as DIP) is based on the colorimetric method in which a blue color is formed by the reaction of DIP, molybdate ion and antimony ion followed by reduction with ascorbic acid at pH<1 (Strickland and Parsons, 1972; Grasshoff *et al.* 1983; Koroleff, 1983). The absorbance of the reduced blue phosphomolybdenum complex is read at 880 nm. The analytical detection limit of the automated technique is 20 nM (Bran Luebbe Method no: G-175-96); so, it is not sensitive enough for precise determinations of the very low DIP concentration (<20-30 nM) of the eastern Mediterranean upper layer waters. Therefore, the magnesium-induced coprecipitation (MAGIC) technique recently developed by Karl and Tien (1992) for phosphate-depleted surface waters, which is much more sensitive (detection limit 1.0 nM) than the automated method, has also been applied for the first time to determine these low DIP levels (see Section 2.5.5, Figure 2.3).

2.4.1.2 Total Oxidized Nitrogen (NO_3+NO_2-N) analysis

The automated determination of total oxidized nitrogen (NO_3+NO_2-N, hereinafter referred to as nitrate) is based on the quantitative reduction of nitrate to nitrite ions by means of a heterogeneous reaction in a copper-cadmium reductor. Then the total nitrite ions are reacted with sulfanilamide under acidic conditions to form a di-azo compound. This compound then couples with N-1-naphthyl-ethylenediamide dihydrochloride to form a reddish-purple azo-dye, which is measured colorimetrically at 550 nm (Strickland and Parsons, 1972; Grasshoff *et al.* 1983). The analytical detection limits are 0.05 μM for NO_3 and 0.01 μM for NO_2 (Bran Luebbe Method no: G-172-96).

2.4.1.3 Reactive Silicate ($Si(OH)_4$-Si) analysis

In natural seawater silicon exists predominantly as reactive silicate ($Si(OH)_4$-Si, silicate thereafter). The automated procedure for the determination of silicate is based on the reduction of silicomolybdate in acidic solution to molybdenum blue by ascorbic acid. Oxalic acid is introduced to the sample stream before the addition of ascorbic acid to minimize interference from phosphate. The absorbance of blue color complex is measured colorimetrically at 660 nm (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983). The analytical detection limit of silicate is 0.30 μM (Bran Luebbe Method no: G-177-96).

2.4.2 Elemental (C, N, P) analysis of Particulate Organic Matter (POM)

POM samples collected at the studied stations were analyzed at the laboratory of Institute of Marine Science. Quantitative analysis of particulate organic carbon (POC) and nitrogen (PON) were performed by the dry combustion technique, high temperature flash combustion (Polat and Tuğrul, 1995; Polat *et al.*, 1998), using a Carlo Erba EA 1108 model CHN analyzer. Moreover, the particulate organic phosphorus (POP) was calculated from the total particulate phosphorus (TPP) and the particulate inorganic phosphorus (PIP) fractions.

2.4.2.1 Particulate Organic Carbon (POC) and Nitrogen (PON) analysis

The dried filters (see Section 2.3.3) were cut into two pieces for POC and PON analysis. Pieces of pre-weighed filters were fumed with concentrated HCl in a desiccator for an hour in order to remove any organic carbon in the filters. Re-dried samples were then encapsuled into tin foil cups and were analyzed. For each set of samples, at least 3 standards (acetilanilide, with 71.09% C, 10.36% N, and 6.71% H) were used (Carlo Erba EA 1108 Instruction Manual; Polat and Tuğrul, 1995; Çoban-Yıldız *et al.*, 2000a; Ediger *et al.*, 2005). The details of the experimental procedure and calculation have been given in some thesis on these subjects (Polat, 1995; Çoban, 1997; Çoban-Yıldız, 2003).

2.4.2.2 Particulate Organic Phosphorus (POP)

The P fraction of the particulate organic matter (POP) was not analysed. The measurements of TPP and PIP in seawater were used to calculate POP (see Section 2.5).

2.5 Analysis of Phosphorus Fractions

Different forms of total phosphorus in the seawater were determined in this study:

- Total phosphorus, TP: the total of dissolved plus particulate phosphorus compounds in a water sample,
- Total particulate phosphorus, TPP: the sum of particulate inorganic and organic phosphorus compounds in seawater,
- Dissolved inorganic phosphate, DIP: a measure of monomeric inorganic phosphorus in seawater,
- Particulate inorganic phosphorus, PIP: a measure of inorganic phosphorus in particulate matter

The measurements of TP, TPP, DIP and PIP in seawater were used to calculate:

- Total dissolved phosphorus, TDP: the difference between TP and TPP.
  TDP=TP-TPP=calculated value.
- Dissolved organic phosphorus (DOP): the difference between TDP and DIP.
  DOP=TDP-DIP=calculated value.
- POP: the difference between TPP and PIP.
  POP= TPP-PIP= calculated value.

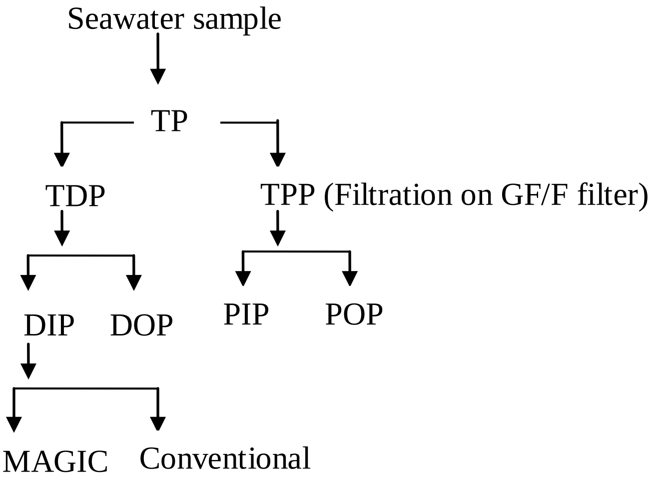


Figure 2.3 Flowchart showing the fractions of phosphorus in seawater.

Quantitative analyses of P-fractions in seawater have traditionally relied on the formation of a 12-molybdophosphoric acid (12-MPA) complex and its subsequent reduction to yield a highly colored blue solution, the extinction of which is measured by absorption spectrophotometry, according to the methodology of Koroleff (1983). This procedure measures all forms of phosphorus, which can be released by combustion and acid hydrolysis. The greatest advantage of using ascorbic acid as reductant is that the blue phosphomolybdic complex is stable for hours and that the color intensity is not influenced by variations in salinity.

2.5.1 Chemicals and reagents

- Distilled water: Double-distilled in all-glass apparatus, has proved satisfactory.
- MQ water: MQ water is used for the preparation of samples and solutions.
- Natural seawater, low in phosphate: Open-sea surface water after a period of high biological activity usually has very low phosphate content. To avoid salinity effect, Low Nutrient Sea Water (hereinafter referred to as LNSW) for standard preparations were used.
- HCl (10% vol/vol) for cleaning
- Kaliumperoxidisulphate, $K_2S_2O_8$ (E. Merck, Darmstadt, Germany, Prod No. 105090) for total phosphorus analysis
- Phenolphthalein indicator solution: Dissolve 2.5 g phenolphthalein, [O.CO. $C_6H_4.C.(C_6H_4.OH)_2$] (BDH, England, Prod. No. 20089), in 250 mL 95% ethyl alcohol and add 250 mL MQ water.
- Suprapur® sodium hydroxide monohydrate, $NaOH.H_2O$ (E. Merck, Darmstadt, Germany, Prod No. 106466), and suprapur® hydrochloric acid, HCl 30% (E. Merck, Darmstadt, Germany, Prod. No. 100318) for nanomolar P determinations.
- Ammonium molybdate solution: Dissolve 12.5 g of ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] (BDH, England, Prod. No. 10028) in 125 mL MQ water.
- Potassium antimony tartrate solution: Dissolve 0.5 g of ACS potassium antimony tartrate [$K(SbO)C_4H_4O_6$] (BDH, England, Prod. No. 10042) in 20 mL MQ water.
- Sulphuric acid, 4.5 M: Carefully add 250 mL concentrated sulphuric acid, H_2SO_4 98% (E. Merck, Darmstadt, Germany) to 750 mL MQ water. Allow to cool and dilute to 1 L. Store in a polyethylene bottle.
- Mixed reagent: Add the molybdate solution 350 mL sulphuric acid (4.5 M), stirring continuously. Add the tartrate solution and mix well. Store in lab glass bottle. This mixed reagent is stable for several months.

- Acidified ascorbic acid solution: Dissolve 10 g of ACS ascorbic acid -$C_6H_8O_6$ (Fluka, Prod. No. 95210)- in 50 mL MQ water, then add 50 mL sulphuric acid (4.5 M). Store in an amber lab glass bottle in a refrigerator, whereby the reagent is stable for at least a week and can be used as long it remains colourless.
- Sodium thiosulphate solution: Dissolve 2.4 g suprapur® sodium thiosulphate pentahydrate, $Na_2O_3S_2.5H_2O$ (E. Merck, Darmstadt, Germany, Prod. No. 106509), in 100 mL MQ water. Add and dissolve 50 mg sodium carbonate, Na_2CO_3 (E. Merck, Darmstadt, Germany, Prod No. 106398), as a preservative. Stored cold in an amber lab glass bottle the reagent is stable for weeks.
- Phosphorus stock solution (10 mM): Potassium dihydrogen phosphate, KH_2PO_4 (E. Merck, Darmstadt, Germany), is dried in an oven at 110 ˚C then in a desiccator. Exactly 136.1 mg of KH_2PO_4 is dissolved in MQ water into which 0.2 mL sulphuric acid (4.5 M) prepared beforehand has been added. Finally dilute to 100 mL. Store cold (at 4 ^{o}C) in a dark glass bottle, through which light cannot penetrate, the solution is stable for months.
- Working phosphate standard (10 μM): Working standards are prepared daily by volumetric dilutions of the stock using glass pipettes and a volumetric flask. All pipettes and volumetric flasks are acid-washed (10% HCl vol/vol) and gravimetrically calibrated prior to use. Dilute 0.1 mL of the stock standard to 100 mL (use volumetric flask). Then dilute the working standard to prepare a series of standards to cover a range of P concentrations.

All reagents were of at least analytical grade as well as being tested for P contamination. Distilled deionized water (DDW), MQ quality, was used in the preparation of reagents and standards.

2.5.2 Total Phosphorus (TP) analysis

For determining total phosphorus (TP), persulphate digestion (Menzel and Corwin, 1965; APHA, 2005) was performed to liberate orthophosphate (DIP) from the particulate and dissolved organic P fractions and then DIP was measured by the conventional ascorbic acid method (Grasshoff *et al.*, 1983; Koroleff, 1983) by using a spectrophotometer set at 880 nm. This well-known analytical technique of TP is, briefly, as follows:

a) The frozen samples are thawed; then 0.5 g $K_2S_2O_8$ is added to 50 mL sample.
b) Samples are kept for ~30 min in 50-60 ^{o}C water bath (if the samples were in polyethylene bottles) and then transferred to glass beakers to complete the digestion on a heating block (hot plate).
c) The temperature should be kept at moderate levels in order to avoid boiling of samples.
d) The digestion step is completed when ~80% of solution has evaporated; samples are then diluted to a certain level and left to cool.
e) To neutralize the samples, first, a few drops of phenolphthalein indicator solution are added to the sample and then the pH of the solution is adjusted to about 8.0 with dilute NaOH.
f) Final volume is adjusted to the initial value (50 mL) by adding MQ water.
g) 1 mL of the reducing agent (acidified ascorbic acid) is added to the pH and volume adjusted samples and then mixed vigorously.
h) 1 mL of mixed reagent is also added and mixes well to initiate phosphomolybdic acid formation. This acid is then reduced to molybdenum blue by ascorbic acid.
i) The sample absorbance is measured photometrically at 880 nm with a 5 or 10 cm cell as soon as possible after a reaction time of 10 min but within about half an hour.
j) All spectrophotometric measurements should be referenced against MQ water.
k) Calibration is achieved with working standard prepared in range of 0.2-1 μM P by using digested and undigested MQ water (MQW) and low nutrient natural seawater (LNSW) (Figure 2.4).

TP concentrations of seawater samples were converted to DIP and calculated as follows:

TP (μM)= (x-b)/m

where:

x = blank-corrected absorbance of sample (A_s-A_b)

b = y intercept of the regression line

m = slope of the regression line (Figure 2.4)

If sample absorbances are high, the intercept can be ignored.

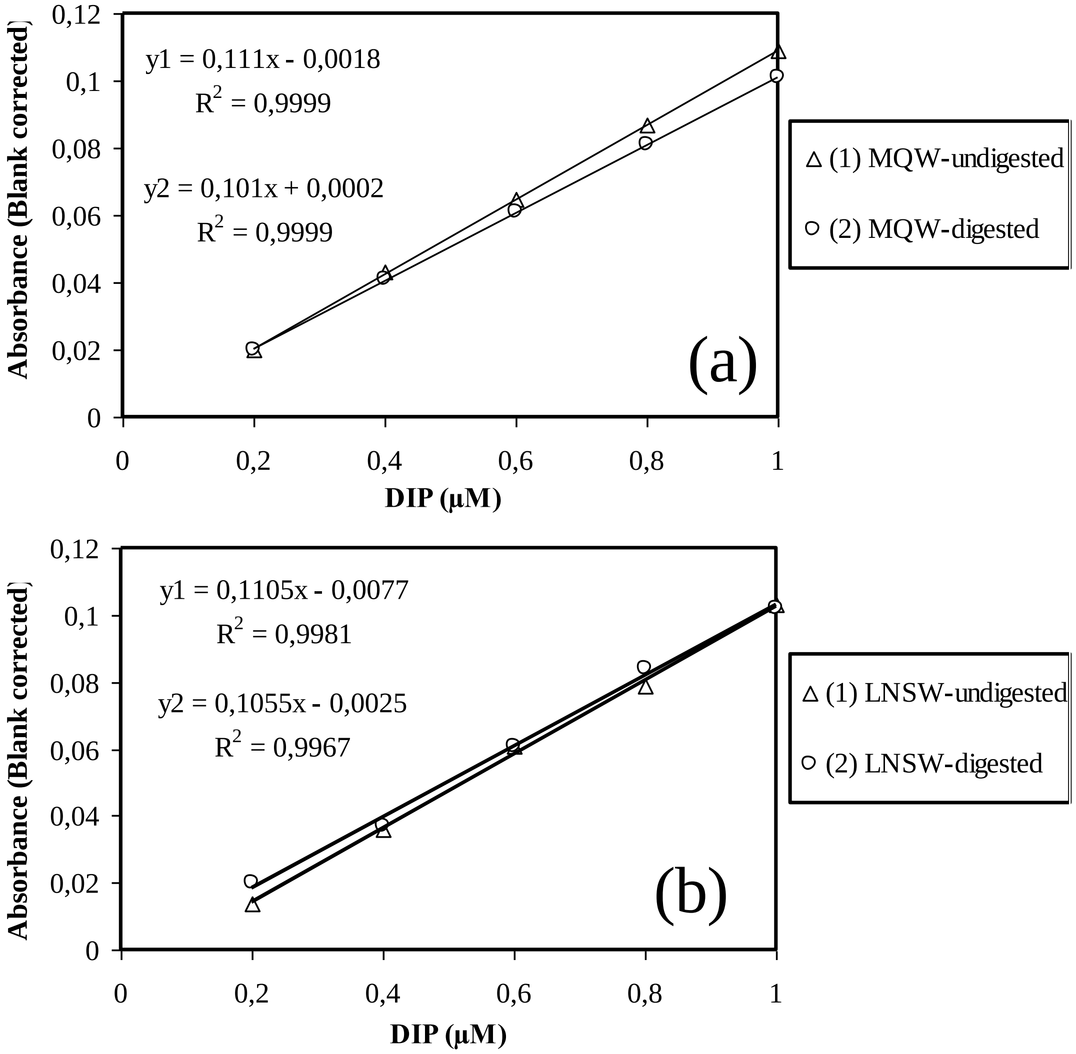


Figure 2.4 Calibration curves of phosphorus standards prepared in (a) MQ water (MQW) and (b) low nutrient seawater (LNSW).

2.5.3 Total Particulate Phosphorus (TPP) analysis

The TPP analysis procedure presented here is a modification of the method followed by the Hawaii Institute of Marine Biology Analytical Services laboratory at the University of Hawaii (Karl *et al.*, 1990). The method relies on the release of organically-bound phosphorus compounds as orthophosphate (DIP), by high temperature combustion at 450-500 ^{o}C. The orthophosphate is then extracted with 0.5 N HCl at 90 ^{o}C. The liberated orthophosphate reacts with a mixed reagent of molybdic acid, ascorbic acid and trivalent antimony to form phosphomolybdic acid. This heteropoly acid is then reduced to the colored molybdenum blue complex by ascorbic acid and the solution is measured spectrophotometrically (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983; Koroleff, 1983; Karl *et al.*, 1990). The analytical technique used for TPP determination can be described step by step as follows:

a) Placed in sterile petri dishes filters are transferred in acid-washed glass test tubes and then combusted at 450 ^{o}C for 4.5 hours in a muffle furnace to oxidize organic phosphorus compounds to the inorganic form.
b) The samples are allowed to cool overnight and immersed in 10 mL of 0.5 M HCl.
c) The test tubes are then heated for 60 minutes at 90 ^{o}C in a water bath for the extraction of orthophosphate.
d) The samples are allowed to cool again, and centrifuged for 30 min at 2800 g. This centrifuge procedure is repeated two more times with the addition of sufficient HCl to yield optimum acid extract.
e) Obtained supernatant is volumetrically subsampled into another combusted acid washed test tube.
f) After processing all the samples, 1 drop of phenolphthalein indicator solution is added to each test tube and they are then neutralized with NaOH solution to a light pink color for pH at about 8.0.
g) The tubes are then filled with MQ water to 20 mL level.
h) In this procedure the samples are converted into DIP, then TPP in the sample can be measured quantitatively by following conventional method of DIP (Koroleff, 1983):

h.1) 0.4 mL of the reducing agent (acidified ascorbic acid) are added to the samples and standards and mixed thoroughly.

h.2) 0.4 mL of mixed reagent is also added and mixed well.

h.3) The sample absorbance is read at 880 nm with a 5 cm cell against MQ reference.

i) Standards are corrected for reagent blanks, while samples are corrected for field filter blanks. At least, 2 reagent blanks are prepared and individual standard absorbances are corrected by the mean blank value (Karl *et al.*, 1990).
j) The mean absorbance from three field filter blanks, stored and processed in the same manner as samples, are used to correct individual sample absorbance for filter, reagent and systematic procedural contamination (Karl *et al.*, 1990).
g) Calibration is achieved with working standard by using MQ water (MQW) (Figure 2.5).

TPP concentrations of the samples are calculated using the following equation:

$\mu M \text{ TPP} = [(a/m \times 20/1000 \times b/c)-d]/e$

where:

a= absorbance of sample

m= slope of the regression line (Figure 2.5)

b= total filter weight

c= filter weight when filter is cut

d= absorbance of filter blank, and

e= filtered volume of seawater

2.5.4 Particulate Inorganic Phosphorus (PIP) analysis

The measurement of only the weak acid extractable fraction of the TPP collected on the filters, which may partly represent particulate inorganic phosphorus (PIP) (Sharp, 1991; Liebezeit, 1991), depends on the release of orthophosphate (DIP). The liberated DIP was analysed by the conventional ascorbic acid method (Grasshoff *et al.*, 1983; Koroleff, 1983) by using a spectrophotometer set at 880 nm. PIP analysis steps described as follows (Keefe *et al.*, 2004):

a) Filters of samples are placed in acid-washed glass tubes (Do not combust the samples).
b) 10 mL of cold 1 N HCl is added to each sample tube containing a filter.
c) Tubes are capped and stand for a minimum of 24 hours. They are shaken several times during the 24-hour period.
d) Then, the samples are centrifuged at ~4500 rpm.
e) 5 mL of supernatant are transferred to sampling tubes with a Pasteur pipette. Then, 5 mL of MQ water is added.
f) To neutralize the 10 mL samples, first, one drop of phenolphthalein indicator solution is added and then the pH of the solution is adjusted to about 8.0 with dilute NaOH.
g) Final volume is adjusted to 20 mL by using MQ water.
h) When converted into DIP, PIP in the sample can be measured quantitatively in the same manner following procedure in Section 2.5.3 Steps h.1 through h.3.
i) PIP concentrations are calculated by using same equation in Section 2.5.3.

2.5.5 Dissolved Inorganic Phosphate (DIP) analysis

DIP concentrations were measured by two independent methods:

(1) Direct measurements of DIP by the conventional manual or the automated flow method (Bran Luebbe Method no: G-175-96; Strickland and Parsons, 1972),

(2) Pre-concentration of DIP in seawater by magnesium-induced coprecipitation (MAGIC) method with followed by spectrophotometric determination (Grasshoff *et al*., 1983; Koroleff, 1983; Karl and Tien, 1992).

Direct measurements of DIP in seawater, rain and river waters were carried out either using a 3-channel Technicon model Autoanalyzer II continuous flow system (Bran Luebbe, Germany) or a spectrophotometer (Helios, UVD 103917, England) with 1-cm, 5-cm and 10-cm cuvettes. Both methods are based on the standard molybdenum blue procedure. However, slight modifications have been incorporated to achieve the optimum range and sensitivity for each nutrient at concentration levels specific for the time series seawaters.

In oligotrophic oceanic environments, DIP determinations are poorly reliable because the ambient phosphorus concentrations approach the limit of analytical detection (20 nM) with the conventional colorimetric method. At these low concentrations, the variability of replicate determinations can be ±25% or greater. Consequently, several modifications and new analytical procedures have been introduced to improve the detection limit and precision of DIP analysis in surface waters.

A new and straightforward method, known as magnesium-induced coprecipitation (MAGIC), has been developed for the precise determination of DIP in seawater at low concentration levels. This sensitive method is based upon the quantitative removal of DIP from solution by in vitro of brucite $[Mg(OH)_2]$, initiated by the addition of high purity sodium hydroxide (NaOH) to seawater samples. The concentrations calculated for DIP in the studied region are lower than the detection limit of the chemical method, even when using the MAGIC procedure (Karl and Tien, 1992). Therefore, the volume of seawater processed in the MAGIC procedure was increased and some modifications were done to increase the sensitivity by from

10 to 20-fold, depending on the enrichment factor, thereby providing a method that can reliably detect 1 nM DIP of seawater (Doğan-Sağlamtimur and Tuğrul, 2004).

The modified pre-concentration MAGIC method was applied in this study to determine DIP accurately and precisely and to increase assay sensitivity, as follows (Doğan-Sağlamtimur and Tuğrul, 2004):

- 1 L seawater samples (typically 3 replicates) are transferred from Niskin bottles to measuring cylinders (plastic-PMP) (see Section 2.3.4)
- 5 mL high purity NaOH solution (1 M) are added and mix vigorously to form $Mg(OH)_2$. Sound results were obtained for routine P determinations (20-times conc.), after various successful experiments by the addition of 5 mL of 1 M NaOH. This procedure is effective for the quantitative removal of PO_4^{3-} from the samples.
- The samples are kept overnight to collect insoluble $Mg(OH)_2$ (brucite) containing the adsorbed P.
- Two phases are developed in the measuring cylinder. Then, the phase on the top contained P-free seawater is taken by peristaltic pump.
- Remained precipitate (pellet) is then dissolved in 5 mL of high-purity 1 M HCl.
- At this point, the triplicate samples are treated to eliminate arsenate reactivity using the method of Johnson (1971).
- The concentrated DIP samples are transferred to volumetric flasks and then volume was adjusted to 50 mL by adding MQ water.
- The concentrated and pH adjusted samples are treated exactly as the direct DIP measurement in seawater adding the standard Koroleff molybdenum blue reagents (Grasshoff, 1983; Koroleff, 1983). Conventional DIP method is applied (see Section 2.5.2, step g-k).

The presence of Mg^{2+} in the concentrated seawater samples has no effect on the quantitative determination of DIP as assessed by the direct comparison of the PO_4^{3-} standard curves taken through the entire MAGIC procedure with control MQ water or seawater-based PO_4^{3-} standards. The daily regression standards were prepared by MQ water (MQW) and low nutrient natural seawater (LNSW) for comparison of the slopes of the regression lines. The P-free phase from a NaOH-treated seawater sample (PFSW thereafter) was used as the dilutents to provide a low-level P standard curve (Figure 2.6). The linear regressions of the standards were applied to calculate DIP in the seawater samples measured under similar analytical conditions. Typical correlations produced r^2 values that were between 0.998 and 1.0. Corrections for arsenic interference are made with thiosulfate reduction according to the method of Johnson (1971). Moreover, reagent blank in MQ water was subtracted from sample absorbance before DIP calculation from standard calibration curve.

DIP concentrations of seawater samples were calculated as follows:
DIP (μM) = (x-b) / (m/n)
where:
x = blank-corrected absorbance of sample (A_s-A_b)
b = y intercept of the regression line
m = slope of the regression line (Figure 2.5)
n = 20 (pre-concentration factor = 1000 mL seawater/50 mL solution)

Calibration, Data Reduction and Calculations

Typical examples of the standard calibration curves in the MQ water -with the additions of 1 M NaOH and HCl as in the MAGIC samples- obtained from the long-term calibration data between 2002 and 2003 by using phosphorus (KH_2PO_4) stock solution are depicted in Figure 2.5. The comparison of calibration curves obtained by using low nutrient natural seawater (LNSW), MQ water (MQW), phosphorus-free seawater (PFSW), METU-IMS Harbour Seawater (MIHSW) are displayed in Figure 2.6. The slopes of the regression lines are very consistent, indicating insignificant matrix effect in DIP determination. In order to increase data quality, the calibration curves of phosphorus standards were compared periodically, using different P stock solutions of the chemistry laboratory of IMS-METU (Figure 2.7).

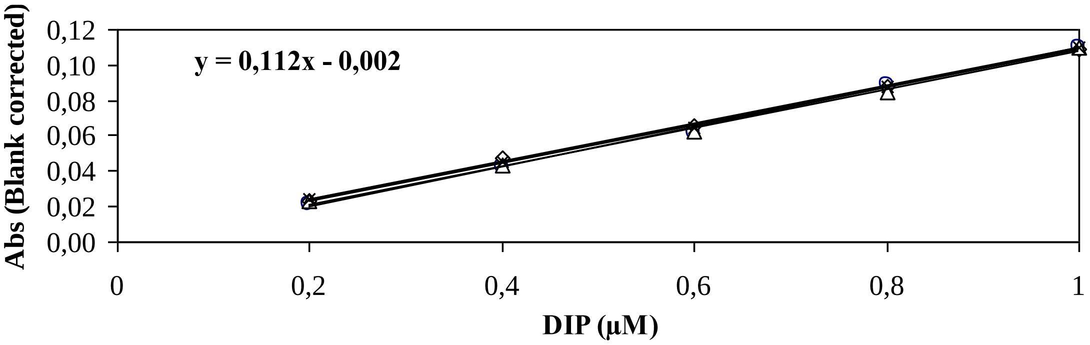


Figure 2.5 DIP calibration curves averaged from long term calibration data between 2002 and 2003.

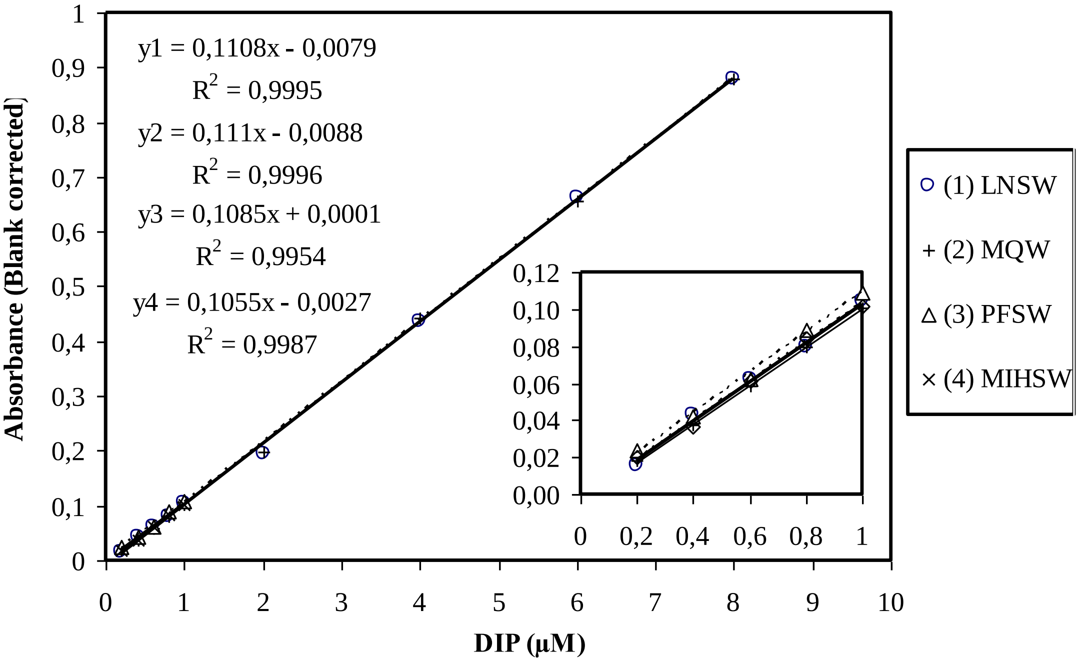


Figure 2.6 Calibration curves for DIP prepared by using LNSW (1); MQW (2); PFSW (3); MIHSW (4).

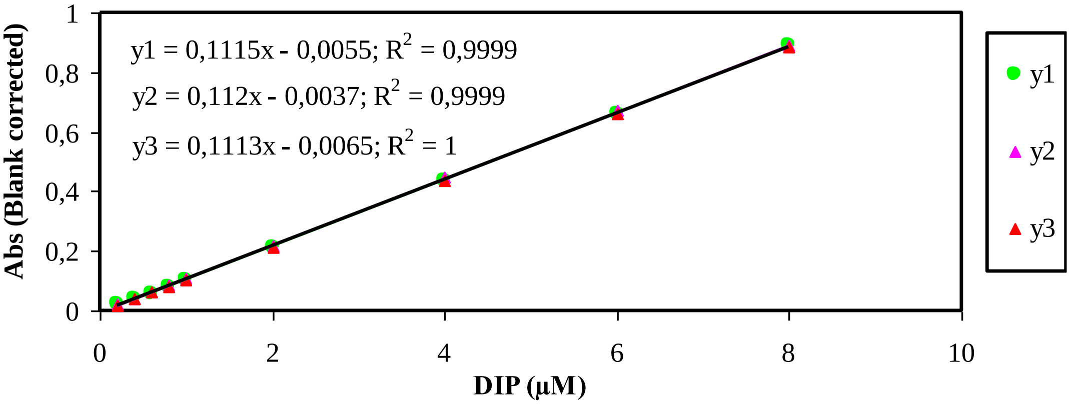


Figure 2.7 Comparative calibration curves for DIP prepared from different P stocks used in the Chemical Oceanography Department of IMS at Erdemli.

2.6 Quality Control/Quality Assurance

The primary objective of the study was to collect and interpret biochemical and hydrographic time-series data. The first step of this goal was to provide quality assurance of all data sets. Good accuracy and precision in the analysis of data is difficult to obtain, and highly dependent on how successfully the contamination control is achieved during cleaning procedures, sub-sampling, sample handling and analytical steps. To provide good precision and accuracy in the analysis:

a) Contamination of samples should be avoided: Systematic errors in the analysis mainly originate from an improper cleaning of the glassware, from difficulties during the sub-sampling and from the prolonged storage of the untreated samples. Contamination from the sampling equipments, ship and shipboard activities were avoided while sampling was undertaken.
b) Adequate sub-sampling protocol: Firstly DO samples using tygon tubing and then in order of nitrite, other nutrients were taken.
c) Sample handling on board: DIP concentrations in the samples were analyzed as quickly as possible after collection. If immediate analysis was not possible, nutrient samples were frozen in “aged” and “tested” polyethylene bottles. Particulate samples were firstly frozen, then dried and kept in vacuum desiccator until analysis.
d) Chemical measurements: All spectrophotometric measurements were referenced against MQ water. To avoid salinity effect, LNSW was used for standard preparations and as wash-water in the automated method. Full “procedural blank” including sample bottle blank filled with LNSW was obtained and treated as samples. Suprapure chemicals were used.

The second step of this goal is to obtain quality control of all data sets:

a) Repeatability: As an internal quality monitor, three replicate samples were studied in all the P-fractions data to ensure the repeatability of sampling and analysis and accuracy & precision of the data (Table 2.1).
b) Reference samples: Intercalibration experiments by using certified reference matter provided IAEA-Monaco were carried out and published in Tuğrul *et al*. (2005).

Table 2.1 Accuracy and precision (A&P) tests for different P-fractions

A&P of the analytical method	**A&P of the sampling**			
	TP	**TPP**	**PIP**	**DIP**
0.2 μM standart	**Nearshore st/0 m/Jan 2003**	**Nearshore st/0 m/Jan 2003**	**Nearshore st/0 m/Jan 2003**	**Nearshore st/0 m/Jan 2003**
Measured concentration	**Measured concentration***	**Measured concentration***	**Measured concentration***	**Measured concentration***
0.27	0.378	0.029	0.013	0.028
0.30	0.390	0.031	0.017	0.027
0.27	0.366	0.025	0.010	0.029
0.26				
0.29	Mean ± SD: 0.378 ± 0.012	Mean ± SD: 0.029 ± 0.004	Mean ± SD: 0.013 ± 0.004	Mean ± SD: 0.028 ± 0.001
	Blank: 0.018	Blank: 0.016	Blank: 0.003	Blank: 0.009
Mean ± SD: 0.28 ± 0.016				
	Middle st/0 m/Jan 2003	**Middle st/0 m/Jan 2003**	**Middle st/0 m/Jan 2003**	**Middle st/0 m/Jan 2003**
Measured blank	**Measured concentration***	**Measured concentration***	**Measured concentration***	**Measured concentration***
0.085	0.220	0.018	0.008	0.022
0.086	0.225	0.014	0.011	0.022
0.083	0.216	0.022	0.005	0.021
0.070	Mean ± SD: 0.220 ± 0.005	Mean ± SD: 0.018 ± 0.004	Mean ± SD: 0.008 ± 0.003	Mean ± SD: 0.022 ± 0.0006
0.090	Blank: 0.018	Blank: 0.016	Blank: 0.003	Blank: 0.009
Mean ± SD: 0.083 ± 0.008	**Shelfbreak st/0 m/Jan 2003**	**Shelfbreak st/0 m/Jan 2003**	**Shelfbreak st/0 m/Jan 2003**	**Shelfbreak st/0 m/Jan 2003**
	Measured concentration*	**Measured concentration***	**Measured concentration***	**Measured concentration***
Blank corrected concentration:	0.207	0.017	0.006	0.022
0.197 μM	0.201	0.025	0.009	0.020
Recovery: ~ 99%	0.210	0.013	0.004	0.023
	Mean ± SD: 0.207 ± 0.007	Mean ± SD: 0.017 ± 0.004	Mean ± SD: 0.006 ± 0.003	Mean ± SD: 0.022 ± 0.002
	Blank: 0.018	Blank: 0.016	Blank: 0.003	Blank: 0.009

* indicates blank corrected concentration values

CHAPTER 3

RESULTS

In order to understand the factors controlling nutrient cycling and fractions of total-P pool in the NE Mediterranean shelf zone, the time series data of hydrographic and bio-chemical parameters were obtained monthly/seasonally in the course of December 2001-December 2003 at three stations (nearshore, middle and shelfbreak) selected across the shelf. However, field surveys could not be carried out in March 2002, October and November 2003 at all the stations and, in April 2003 at the middle and the shelfbreak stations. Complementary data were collected in December 2003 at four open (reference) stations located in the deep Cilician basin (see Figure 2.2), representing typical oligotrophic characteristics of the NE Mediterranean.

In this chapter, monthly profiles of hydrographical data, measurements of Secchi disc depth (SDD), dissolved oxygen (DO), nutrients, particulate organic matter (POM) and phosphorus fractions have been evaluated at the time-series stations off Erdemli, and the reference stations.

3.1 Evaluation of Hydrographic Data

3.1.1 Nearshore station

Seasonal variations of hydrographic parameters in the water column of the nearshore station are presented in Figures 3.1 to 3.2 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Physical Oceanography department). The results show that the nearshore station is influenced by the small Lamas River having an annual volume flux of about $2.2x10^8$ m^3 per year (Doğan-Sağlamtimur and Tuğrul, 2004;

Tuğrul *et al*., 2004); seasonal volume flux of this river increases in spring months (Tuğrul *et al*., 2005). However, the Lamas River effect is limited to the nearshore zone as compared to the other major rivers (Seyhan, Ceyhan and Göksu), which feed the NE Mediterranean shelf zone. The riverine inflow is evidenced by the less saline surface water (35.8-37.0 psu in 2002, 37.0-37.4 psu in 2003) overlying the saltier near-bottom water (36.0-38.9 psu in 2002 and 38.1-38.4 psu in 2003) (Figure 3.1). The hydro-physical parameters measured in the water column during 2002 varied from 35.8 to 39.4 psu for salinity, 16.6 to 30.7 °C for temperature and 22.8 to 28.4 for density, respectively, whereas in 2003, these values ranged between 37.0 and 39.3 psu for salinity, 15.0 and 29.6 °C for temperature and 23.6 and 28.8 for density, respectively.

Surface salinity varied throughout the year from 35.8 to 38.7 psu in 2002 and 37.2 to 39.3 psu in 2003 (Figure 3.1). In winter 2002, surface salinity was in the range of 37.8-38.7 psu; the highest surface salinity (38.7 psu) was observed in January. In spring-early summer period, increased river inflow produced a less saline, thin surface layer ranging between 36-37 psu. Surface salinity values remained low between 35.8-36.1 psu until July 2002, and then increased markedly to 38.5 psu in August 2002. In autumn, the salinity values varied slightly from 38.3 to 38.7 psu due to decreased flow of the river. Salinity in the near-bottom waters (at 5-10 m) showed a similar decreasing trend in the March-May 2002 period when the Lamas River highly influenced the surface layer. In 2003, the surface water salinity remained high in the range of 38.4-39.1 psu due to intense winter vertical mixing. In spring months, a typical reduction (down to 37.0-37.4 psu) in the river-induced surface layer salinity was observed. However, surface salinity during the summer months of 2003 was relatively high (38.9-39.3 psu) and remained almost constant at 39.1-39.3 psu during rest of the year.

Water temperature at the shallow station varied seasonally, ranging from 16.6 to 30.7 °C in 2002 and between 15.5-29.6 °C in 2003 (Figure 3.1). In the winter 2002, surface water temperature varied slightly between 16.6 and 18.7 °C. Especially much cooler water was brought from the Taurus Mountains nearby Lamas River, which affected water temperature distribution at the coastal zone (Köksalan, 2000). Surface temperature increased in spring to levels of 17.6 °C in April to 23.2 °C in May. The water kept heating in summer. The highest surface temperature was observed in August (30.7 °C), because of increase in atmospheric temperature in summer. However, in autumn, the surface water started to cool steadily, decreasing from 27.7°C in September to 25.2 °C in October, and then to 22.1°C in November 2002. In 2003, it cooled down to 15.5-18.7 ^{o}C in winter period. The surface temperature increased again from 15.9 °C in March to 24.9 °C in May, and remained high (22.9-29.6 ^{o}C) in summer months, reaching its maximum in August. In autumn, surface water temperature had a steady decreasing trend from 27.6 °C in September to 19.8 °C in December 2003 due to decrease in atmospheric temperature (Figure 3.1).

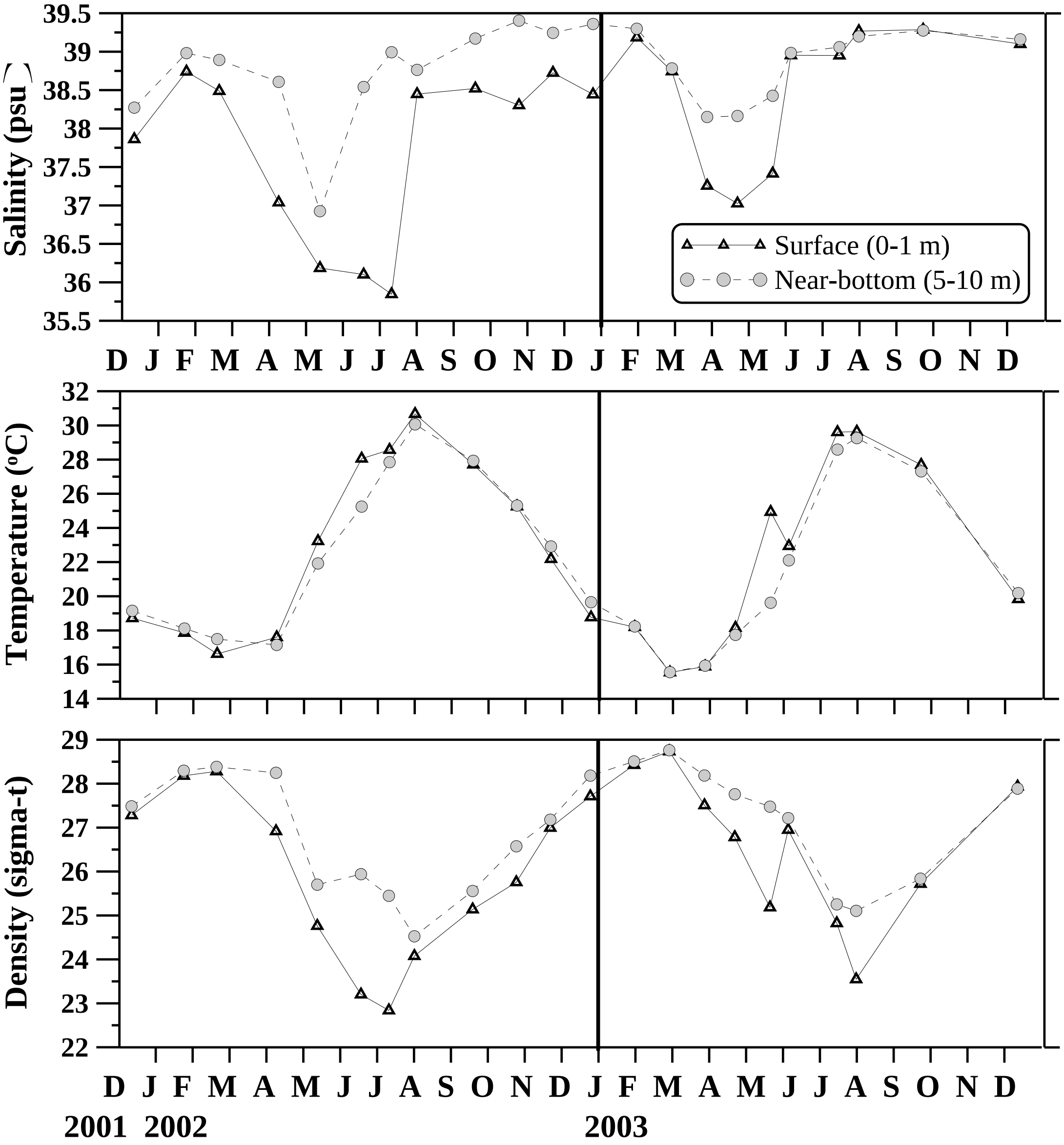


Figure 3.1 Monthly variations of salinity, temperature and density at the nearshore station in the course of December 2001-December 2003.

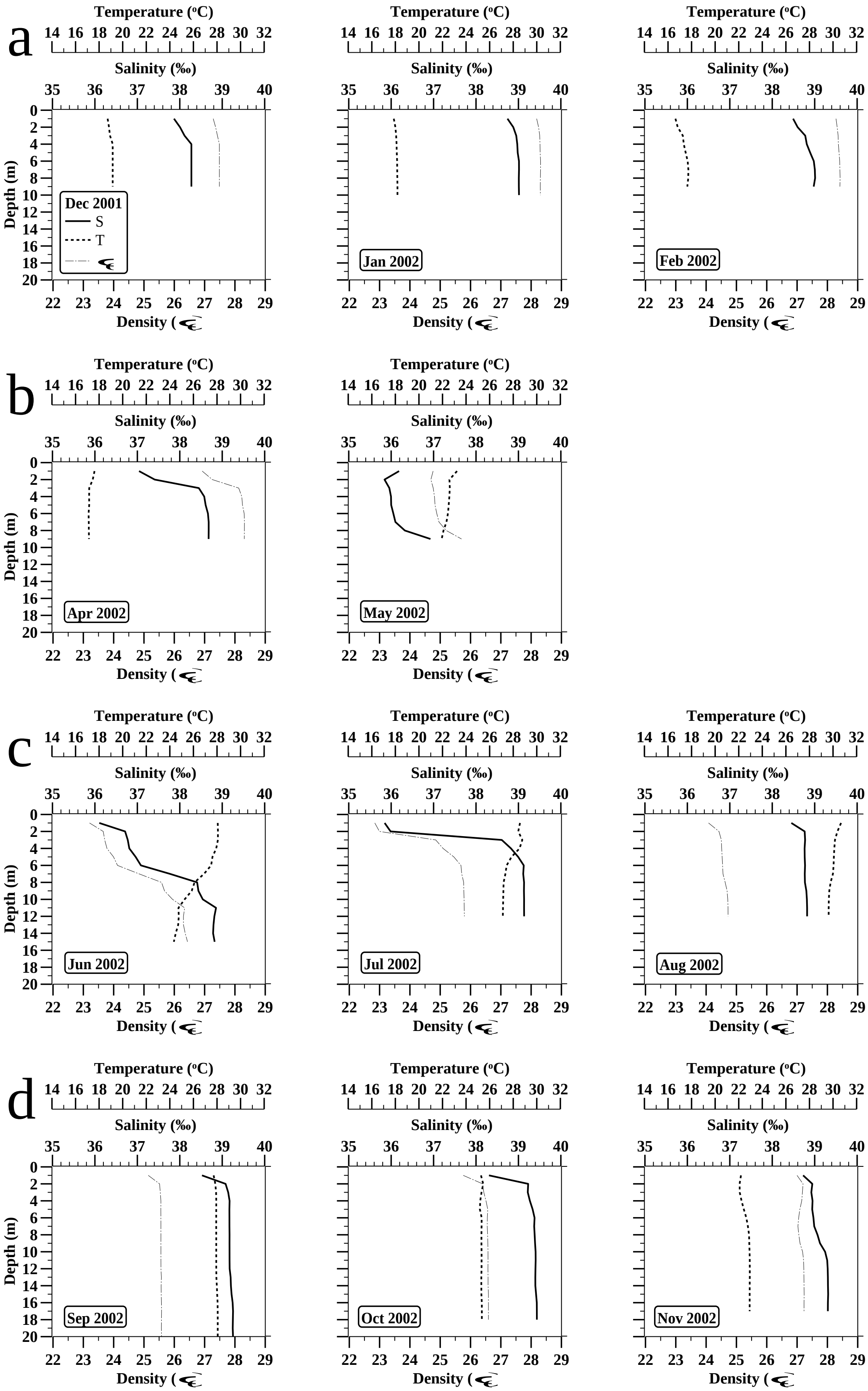


Figure 3.2.a Vertical profiles of hydrographic parameters at the nearshore station in 2002 (a: Winter, b: Spring, c: Summer, d: Autumn).

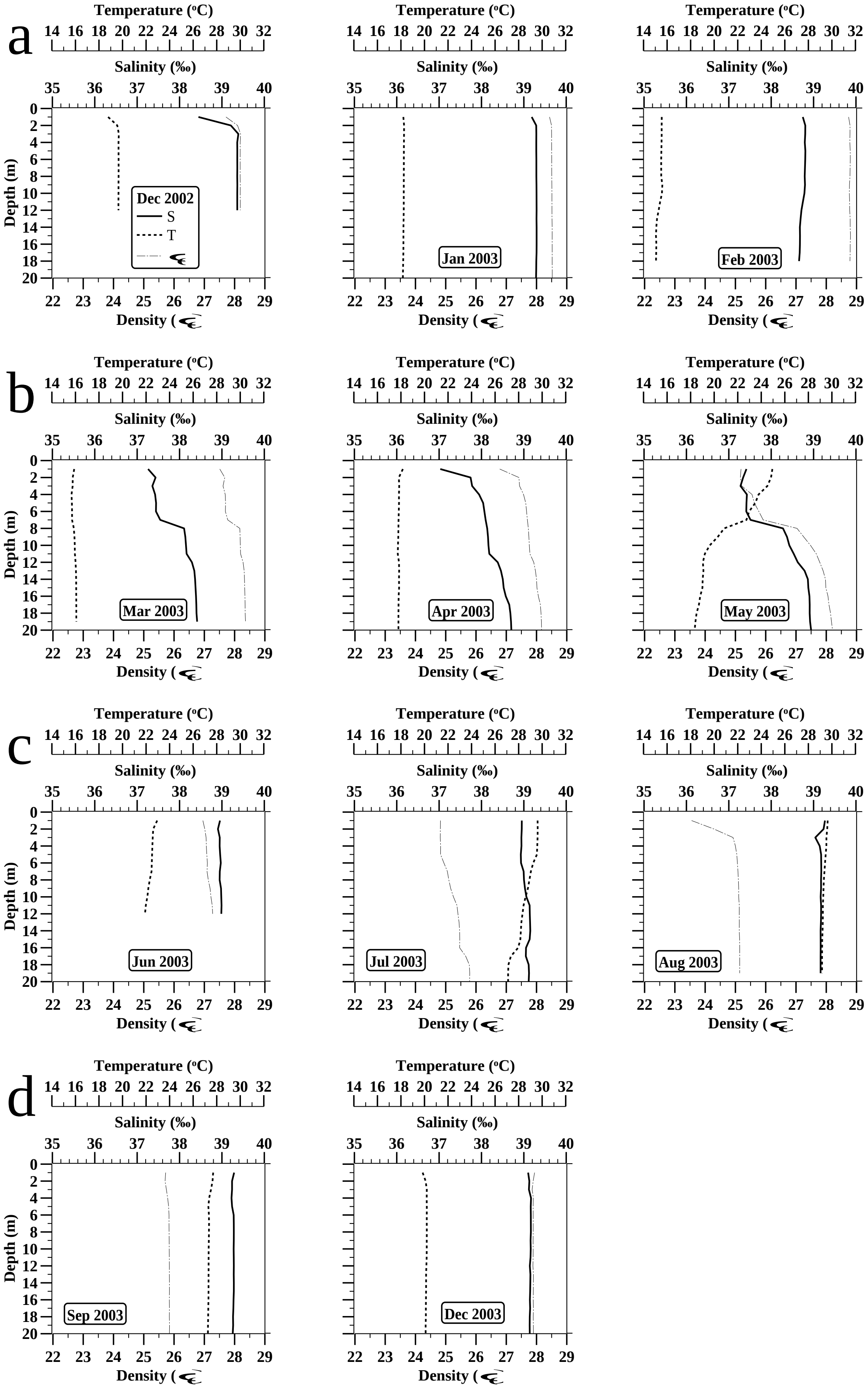


Figure 3.2.b Vertical profiles of hydrographic parameters at the nearshore station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

Water density (sigma-t) is dependent on salinity and water temperature. It ranged between 22.8 and 28.7 during 2002-2003 (Figures 3.1-3.2). In winter of 2002, surface density was as high as 27.3-28.3, later, decreasing to 23.2-26.9 in spring and then to levels of 22.8-24.0 in summer. However, it increased again from 25.1 in September to 26.9 in late-autumn. In 2003, the surface density was greater in winter, ranging between 27.7 and 28.7; then it decreased to 25.1 in May, 24.8 in July and 23.5 in August due to increase in water temperature. But it increased again from 25.7 in September to 27.9 in December when waters started cooling down (Figure 3.1).

Typical salinity vs. depth profiles of the near-shore station in Figure 3.2.a clearly show that salinity was influenced significantly by vertical mixing, resulting in a vertically uniform profile (38-39 psu) in winter 2002. In spring, the hydrographic characteristics of this shallow zone were affected by the Lamas river inflow. Salinity stratification was formed in summer (36 to 39 psu) and lasted until December 2002. However, it almost disappeared in the summer-autumn period of 2003. In winter 2003, this two layer hydrographic feature almost disappeared due to strong mixing events where salinity ranged between 38.5-39 psu in the water column (Figure 3.2.b). The spring 2003 salinity profiles displayed an increasing trend from the surface to bottom (37.2-38.4 psu in March, 37.0-38.7 psu in April, and 37.4-38.9 psu in May), as experienced in the spring of 2002. The steep halocline was established again in spring due to river inflow. As compared to 2002 results, salinity was higher in the water column, ranging between 38.9-39.2 psu in summer, showing almost homogeneous distribution. In autumn, the salinity profiles were still uniform, varying slightly between 39.1-39.3 psu.

Vertical profiles clearly show that temperature was almost uniform in winter and decreased from 19 °C in December 2001 to 16 °C in February 2002 (Figure 3.2.a). In early spring, temperature was evenly distributed throughout the water column at 17°C in April. A seasonal thermocline was formed between 2 and 8 m during late spring and summer periods (23 to 22 °C in May, 28 to 24 °C in June, 28 to 27 °C in July and 30 to 29 °C in August). In autumn, water column started mixing and cooling; the surface temperature dropped from 28 °C in September to 22 °C in November. In winter of 2003, temperature ranged between 18-19 °C in December 2002 and then was almost homogeneous at about 18 °C in January and 15 °C in

February 2003 (Figure 3.2.b). In early-spring, the water column had still a vertically uniform temperature; ~16 °C in March and ~18 °C in April. A seasonal thermocline was formed in late spring at 7 m where temperature dropped from 24 to 18 °C. In summer, water column was well mixed and the temperature remained uniform at around ~22 °C in June and ~29 °C in August. However, it decreased slightly from 29 to 27 °C in July, towards to bottom. Water temperature did not show much variation in September (~27 °C) and in December (~20 °C).

As seen in Figure 3.2.a, the density showed almost uniform distribution (~27-28) in the water column during December 2001-February 2002 period (~28). In April, it was 27 in the near-surface layer, rising to 28 in the near-bottom waters. In late-spring and summer period, less dense water was present in surface layer due to thermal stratification. The density in the water column changed between 25-26 in May, and 22-26 in early-summer, being homogeneous (~24) in August 2002. The water density became vertically constant in autumn with the values of ~25 to ~27. Vertically uniform density profiles (almost 28) lasted in the winter months of 2003 (Figure 3.2.b). Then a pycnocline was formed in spring due to high flow of the Lamas River; the density varied from 27 to 28 in March, between 26-28 in April, and 25-28 in May. The density ranged between 24 and 25 in July and from 23 to 25 in August, while it was uniform in September (~25) and December 2003 (~28).

3.1.2 Middle station

Seasonal variations of hydrographic parameters in the water column at the middle station are presented in Figures 3.3 to 3.4 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Physical Oceanography department). The middle station was located outside the direct effect area of the River Lamas and other fresh water discharges. Collection of time-series data at the middle station started in September 2002. The hydro-physical parameters, measured during 2002, ranged between 38.8-39.7 psu for salinity, 17.4-27.9 °C for temperature and 25.6-28.5 for density in the water column. Similar variations were recorded in 2003, ranging from 37.8 to 39.3 psu for salinity, 16.0 to 29.0 °C for temperature and 25.0 to 28.0 for density.

The surface salinity slightly varied from 39.3 to 39.7 psu during the autumn 2002, exceeding the deep water values (Figure 3.3). Then, it ranged between 37.8 and

39.3 psu during 2003. It decreased from 39.3 to 39.0 psu in winter 2003 and 38.6 to 37.8 psu in spring. The lowest surface salinity (37.8 psu) in 2003 was observed in May, indicating that Seyhan, Berdan, and Deliçay rivers waters reach up to this region via general and wind-induced surface currents. Afterwards, it increased markedly from 38.8 to 39.1 psu in June-July period, reaching the highest level (39.3 psu) in September 2003 due to rise in evaporation. The surface salinity remained constant at 39.2-39.3 psu during rest of the year. Salinity in the deep layer showed a similar temporal trend in 2003, decreasing to level of 39.0 psu in May. However, it reached the lowest value (38.7 psu) in September. The deep water salinity displayed less temporal variations than the surface layer.

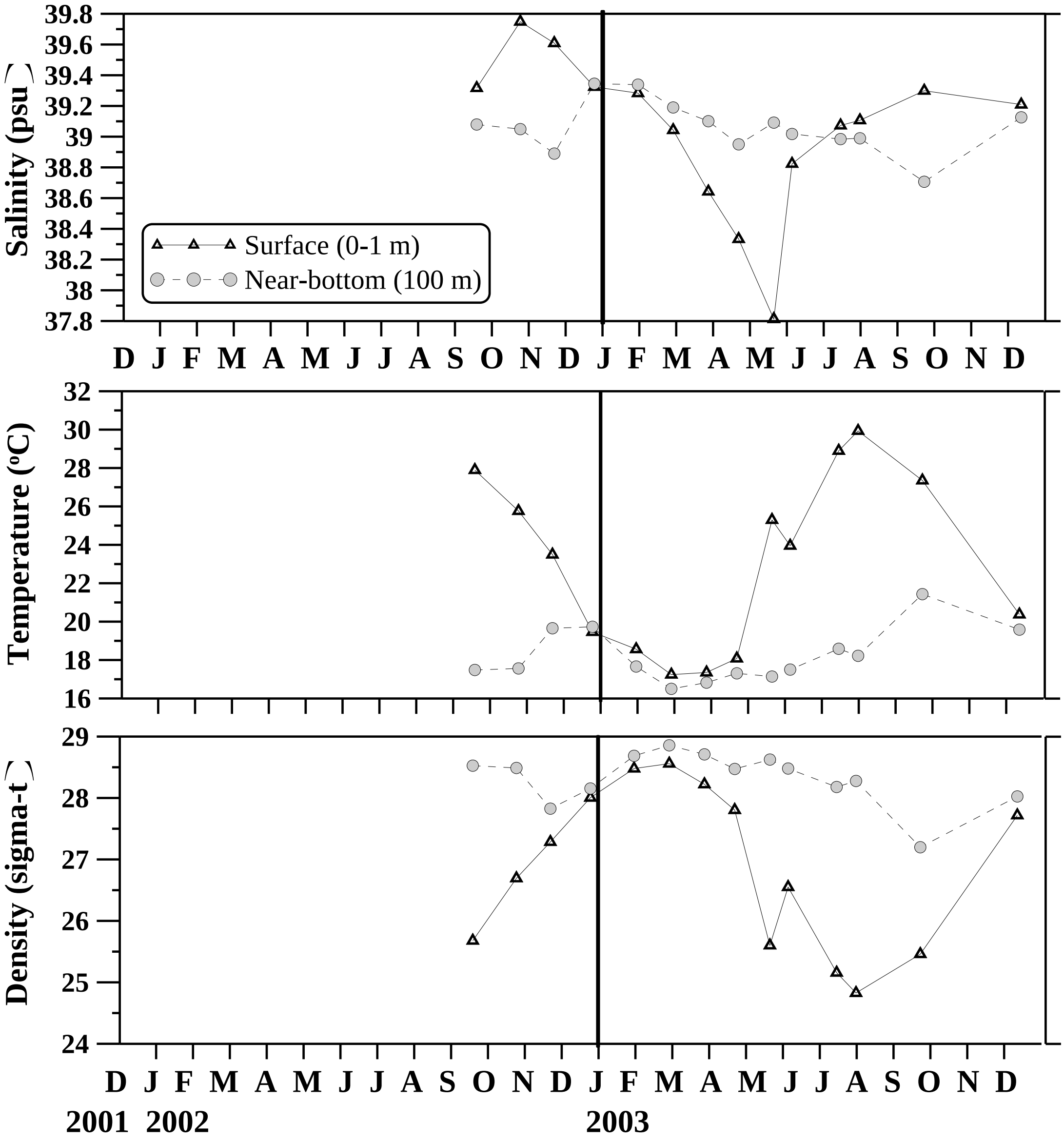


Figure 3.3 Monthly variations of salinity, temperature and density at the middle station in the course of December 2001-December 2003.

The surface temperature declined from 27.8 °C in September to 23.5 °C in December 2002 (Figure 3.3). Then, it ranged seasonally between 17.2-29.9 °C in 2003. The surface water kept cooling during autumn-winter months, descending to the lowest value of 17.2 °C in February 2003. The surface temperature increased slightly from March (17.3 °C) to April (18.0 °C), increasing steadily in May 2003 (25.3 °C) due to rise in air temperature. In summer, the surface water temperature was between 23.9-29.9 °C; then it displayed a decreasing trend from 27.3 °C in September to 20.3 °C in December 2003.

The surface density (in sigma-t unit) varied between 25.6 and 27.2 during autumn 2002 (Figure 3.3). It fluctuated between 24.8 and 28.5 throughout 2003. The surface water density, displayed a maximum of 28.5 in the winter, and then decreased to the lowest value of 24.8 in late summer due to warming of the surface water. Later, it increased again to 25.4 in September and 27.7 in December 2003, as the result of surface water cooling.

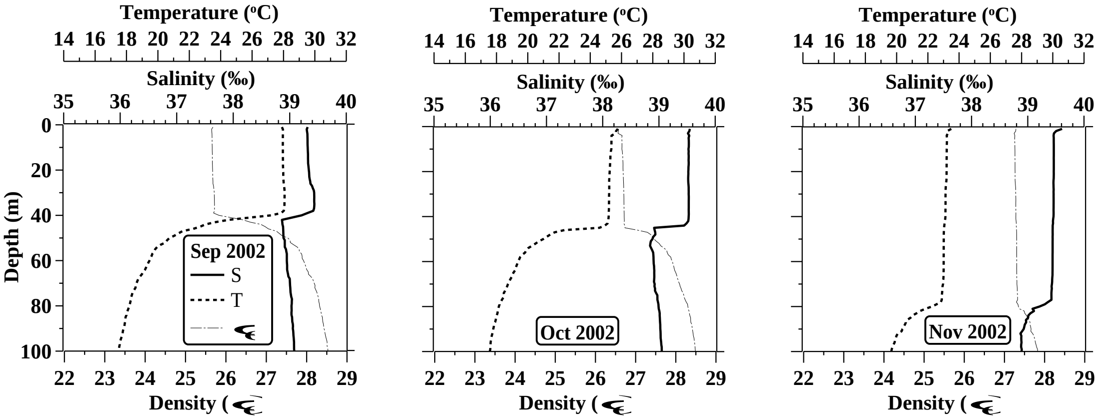


Figure 3.4.a Vertical profiles of hydrographic parameters at the middle station in the autumn of 2002.

Depth profiles of salinity, temperature and density in Figure 3.4 clearly demonstrates that a steep halocline developed around 40 m during September and October 2002 (Figure 3.4.a). The salinity decreased markedly from 39.7 to 38.9 psu and remained almost unchanged in subhalocline zone. In November 2002, as a result of vertical mixing of the upper layer, the halocline deepened as far as 80 meters where salinity changed from 39.6 to 38.8 psu. In 2003, the winter salinity profiles showed a vertically uniform distribution (~39.3 psu in December 2002 and January 2003) in the entire water column (Figure 3.4.b). However, in February 2003, deep minimum was evidenced at 80 m where the salinity decreased from 39.2 to 39.0 psu. In spring, less saline water occupied the upper 20 meters, ranging between 38.3-39.0 psu. The seasonal halocline was formed apparently in May at 20 meters. In summer, the halocline formation almost disappeared where the salinity ranged between 38.8 and 39.1 psu. In September 2003, the halocline was established at about 40 meters, as observed during 2002 where the salinity decreased from 39.3 to 38.6 psu. Then, the water column was well mixed in December 2003, having a salinity of 39.1 psu.

In 2002, a seasonal thermocline developed at the depth of the halocline that was around 40 m in September and October and then moved down to 80 m in November (Figure 3.4.a). In autumn, temperature decreased within the thermocline layer, ranging from 27.9 to 21 °C. The deep water temperature ranged between 17.4, 17.5 and 19.5 °C in autumn of 2002. Temperature was vertically uniform throughout the water column at about 18-19 °C in early-winter 2003 (Figure 3.4.b). However, in February, a deep minimum (~16 °C) was recorded, coinciding with the salinity minimum, indicating intrusion of less saline Atlantic water. The temperature remained almost constant at 16-18 °C in March through April in the water column. In May 2003, salinity and temperature both exhibited different vertical structures; the surface layer became warmer and less saline, indicating the effect of river inflow. A seasonal thermocline became apparent at 20 m where the temperature declined from 25 to 18 °C in May. This feature moved down to 30 m in summer, then to 40 m in September, and then disappeared in December 2003 due to cooling of the surface water and consequent effective vertical mixing.

In 2002, a sharp pycnocline was formed, depending on salinity and temperature changes (Figure 3.4.a). The water density increased from 25.6 at the surface to 28.5 at the near-bottom depths in autumn 2002. Then, the water column was naturally well mixed (sigma-t: ~28) from December 2002 to March 2003 (Figure 3.4.b). In spring and summer of 2003, the water density displayed an increasing trend with depth, ranging from 25 to 28. The density became vertically uniform (~28) in the entire water column in December 2003.

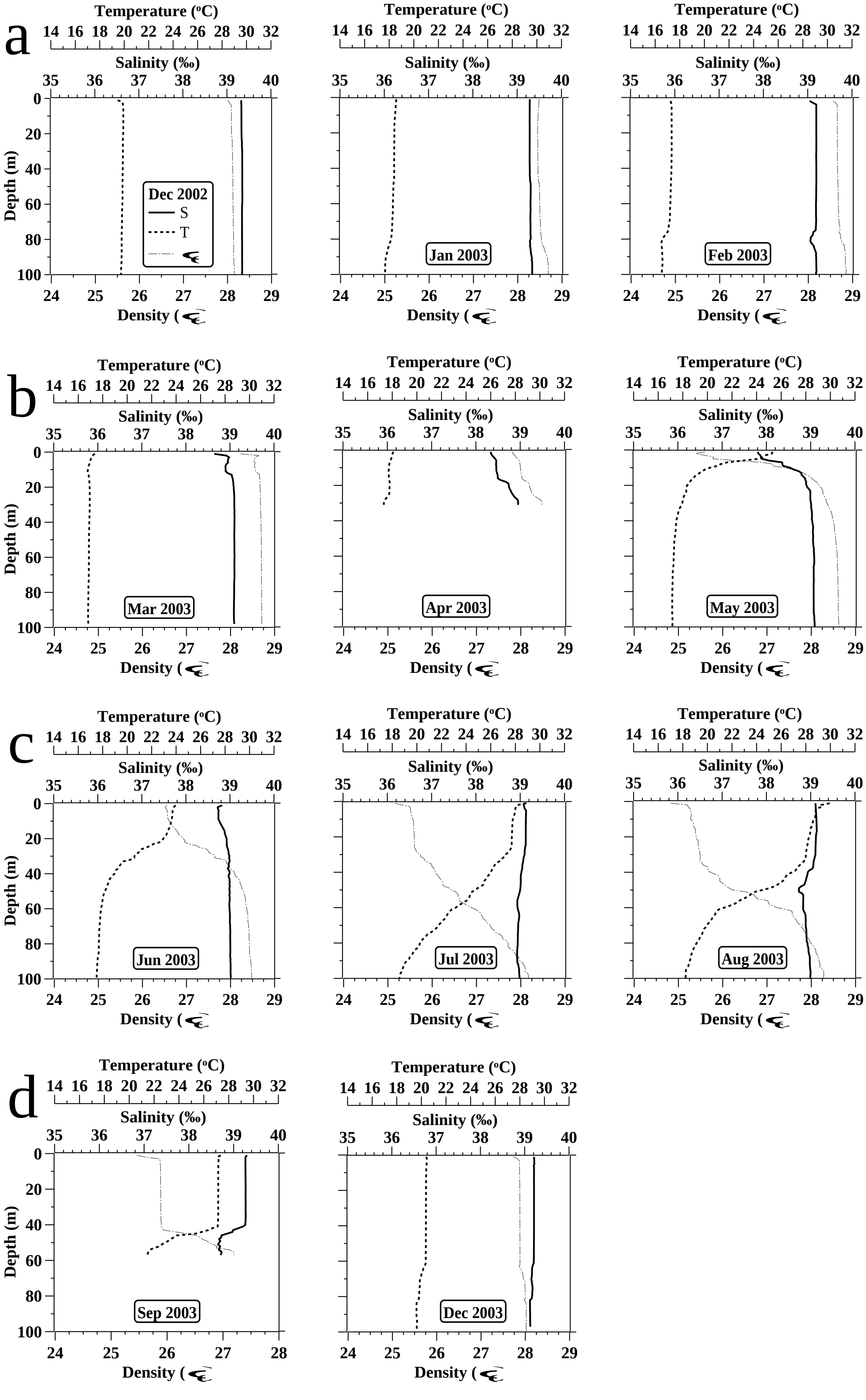


Figure 3.4.b Vertical profiles of hydrographic parameters at the middle station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

Briefly salinity, temperature and density showed significant seasonal variations in the surface layers. However, there were no significant seasonal changes in salinity (38.8-39.2 psu), temperature (16-20 °C) and density (27-29) values of the near-bottom waters (Figures 3.3-3.4).

3.1.3 Shelfbreak station

Monthly measurements of hydrographic parameters in the water column at the shelfbreak station are presented in Figures 3.5 and 3.6 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Physical Oceanography department), indicating apparent seasonal variations in the upper layer of this location. The surface salinity data show that the shelfbreak station is much less influenced by the river inflows of the region. Therefore, surface water salinity was higher than those of the nearshore and middle stations. The hydrographic measurements in the water column ranged between 38.1-39.6 psu for salinity, 15.8-29.6 °C for temperature and 25.1-28.9 for density during 2002, whereas they were in the ranges of 38.6-39.6 psu for salinity, 15.7-29.2 °C for temperature and 25.5-28.9 for density in the course of 2003.

Surface salinity varied throughout the year between 38.0-39.5 psu in 2002 and 38.5-39.3 psu in 2003 (Figure 3.5). In winter 2002, the surface salinity ranged between 38.9-39.0 psu, decreasing to a minimum of 38.0 psu in May 2002, indicating high flow period of the major rivers (Seyhan, Ceyhan) in the region. Then, the surface water became more saline during July and October 2002 (39.1-39.3 psu) due to the excessive evaporation. The salinity enhanced in autumn, ranging slightly between 39.4 to 39.5 psu and exhibiting a maximum of 39.6 psu in October 2002. In winter of 2003, the surface salinity decreased slightly to levels of 39.2-39.3 psu; then, in spring, a typical reduction in salinity (38.5-38.8 psu) was observed in the river-induced surface layer. The surface salinity increased again in the summer months (38.8-39.1 psu), which remained almost constant at 39.2 psu during the autumn months of 2003. Figure 3.5 demonstrates that two evident salinity minima (38.0 and 38.5 psu) were situated in the surface layer in May 2002 and May 2003. However, the near-bottom salinity (at 200 m) exhibited small temporal fluctuations, increasing slightly in the winter 2003.

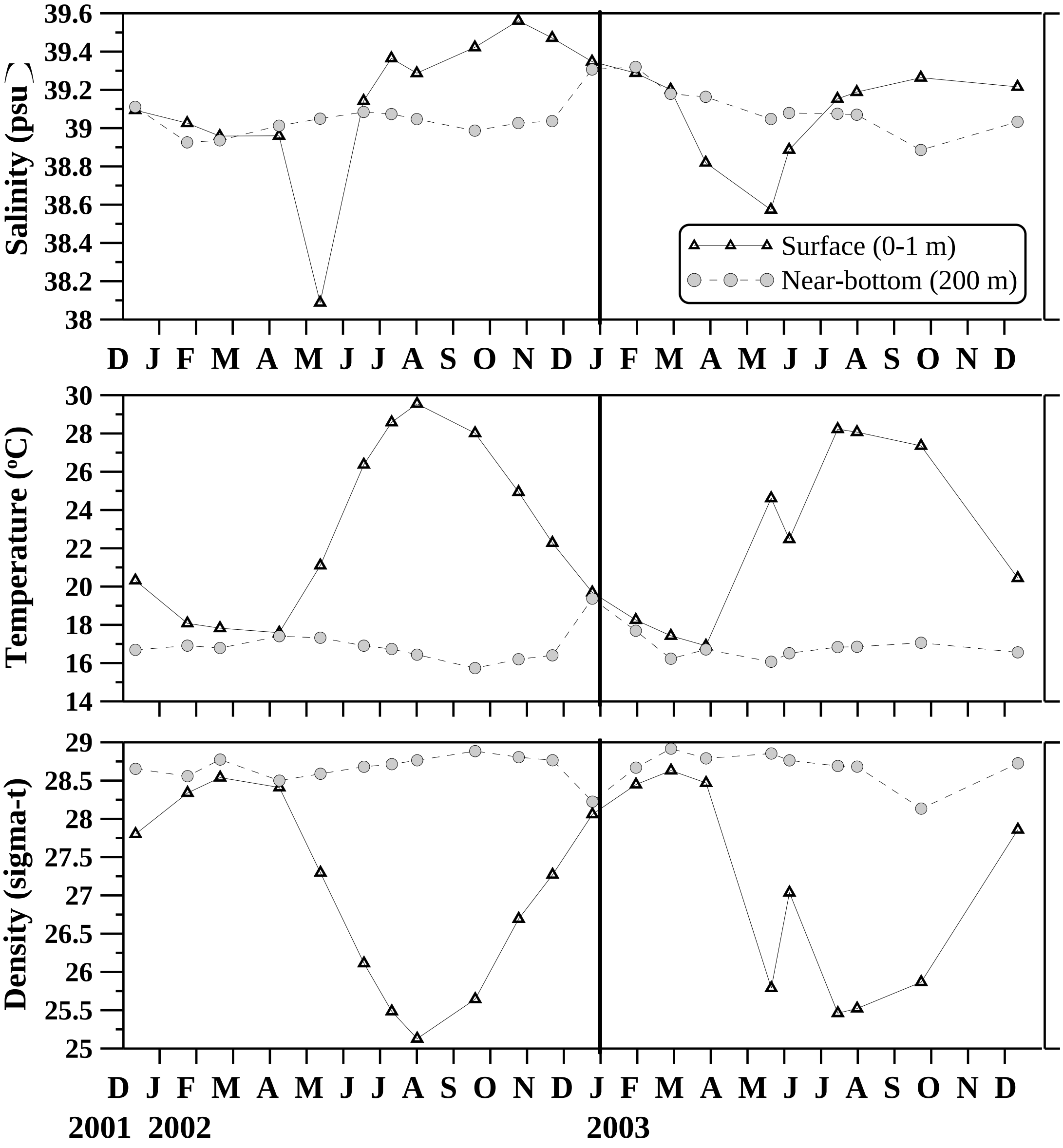


Figure 3.5 Monthly variations of salinity, temperature and density at the shelfbreak station in the course of December 2001-December 2003.

Surface water temperature varied seasonally at the shelfbreak station, ranging from 17.5 to 29.5 °C in 2002 and 16.9 to 28.2 °C in 2003 (Figure 3.5), respectively. Surface waters cooled down to ~18 °C in winter months of 2002, which was about 17.5 °C in April, and then started warming to 23.2 °C in May 2002. The surface temperature reached to the highest value of 29.5 °C in August due to increase in air temperature in summer. However, in autumn, the surface temperature started declining from 24.9 °C in October to ~22.2 °C in November 2002. In the winter of 2003, it dropped to levels of 17.4-19.7 °C, and then to minimum of 16.9 °C in March. The surface temperature increased again to 24.6 °C in May, reaching ~22 °C in June and ~28 °C in July. Following the summer maximum, surface water started cooling during autumn; the surface temperature dropped to 27.3 °C in September and 20.4 °C in December 2003, in parallel to decrease in air temperature. The near-bottom water temperatures ranged between 38.9-39.3 °C during the 2002-2003 period (Figure 3.5), exhibiting small increases in the winter of 2003 due to rise in salinity.

Surface water density ranged between 25.1-28.5 in 2002 and 25.4-28.6 in 2003 (Figure 3.5). In winter of 2002, the surface density was as high as 27.8-28.5, and then decreased to 28.4-27.2 in spring and to minimum levels of 26.1-25.1 in summer. However, the surface density increased again from 25.6 in September to 27.2 in November 2002. It kept enhancing in winter of 2003 to the levels of 28.6, then exhibited a decreasing trend in spring from 28.4 in March to 25.8 in May due to fresh water inflow from the major rivers. It decreased further in summer to the levels of 25.4 in July and 25.5 in August due to increasing water temperature, which increased again from 25.8 in September to 27.8 in December 2003 when water started cooling (Figure 3.5).

Typical salinity profiles at the shelfbreak station (Figure 3.6.a) clearly show that the winter profiles were vertically uniform (at ~39 psu) in the upper layer down to 100-160 m depth. However, the cooler and less saline waters of Atlantic origin (POEM Group, 1992; Özsoy *et al.*, 1993; Robinson and Golnaraghi, 1994; Yılmaz and Tuğrul, 1998; Pinardi *et al.*, 2005) may occasionally occupy the intermediate depths of the NE Mediterranean shelf by the lateral intrusions and circulations. This deep minimum was located at 100 m with salinity value of 38.9 psu in December 2001, then moving down to 160 m with 38.8 psu in January 2002 and 170 m with 38.6 psu in February. In April 2002, the water column was still well mixed; but the river inflow influenced the surface layer (0-6 m) in May. Modified Atlantic water (MAW) became apparent in the water column in September-December months. A weak halocline started to develop in July-August 2002; it became well pronounced in September-November period. The steep halocline was located at 40 m in September (39.4 to 38.9 psu), 43 m in October (39.5 to 38.9 psu) and 85 m in November (39.4 to 38.8 psu) due to the increased vertical mixing of the upper layer. In the winter of 2003, the halocline disappeared due to strong mixing processes

(Figure 3.6.b). MAW was traced in December 2002 by a primary deep minimum at ca. 100 m and a secondary deep minimum at ca. 186 m where the salinity decreased from 39.3 to 39.1 psu. This feature persisted during January and February 2003 at 170-180 m. In spring 2003, the river effect was confined to the upper 10-20 m of the water column. Therefore, a salinity gradient was established at about 20 m in May, perfectly coinciding with the thermocline. In summer 2003, the surface 20 m-layer was saltier and warmer due to evaporation. However, a less saline layer was present between 20 to 40 m during July and August 2003. Below the seasonal thermocline, the salinity decreased to 38.6 psu in September, slightly rising to 38.8 psu in December 2003 (Figure 3.6.b).

In 2002, the upper water column was homogenized thoroughly in winter (Figure 3.6.a). In December of 2001, the temperature profile was almost uniform with 20.3 °C in the upper 100 m to 18.9 °C in the near-bottom water. It was observed that the thermocline moved further down to 170 m in January and February 2002 (18.0 to 16.0 °C). In April, the temperature profile was uniform at ~17 °C in the whole water column. Later, it increased to 21 °C in the upper layer in May 2002, declining to 17 °C below the thermocline. In summer, the upper layer temperature increased to 29 °C, while the deep water temperature remained at almost constant (16-17 °C). The seasonal thermocline that was formed in May 2002 lasted until November 2002, deepening down to 80 m. In winter 2003, when the surface waters cooled down, the upper layer of 170 m was homogenized thoroughly (Figure 3.6.b). The winter temperature, which was around 20 °C in the upper water column, decreased to ~17-18 °C below the salinity minimum and temperature gradient zones. In early spring, temperature was still uniform throughout the water column at 16-17 °C during March of 2003. The seasonal thermocline was observed from May up to September 2003. In May, the temperature decreased with depth from 24 °C in the near-surface water to 16 °C below the seasonal thermocline (6 m) where the salinity exhibited an opposite trend with depth. The thermocline that was very thin at shallower depths during May and June descended down to ~60 m during summer. By September 2003, gradual cooling of surface waters eroded the seasonal thermocline and surface waters were homogenized, and subsequently deepened down to the bottom (see Figure 3.6.b for December 2003) during autumn and early-winter.

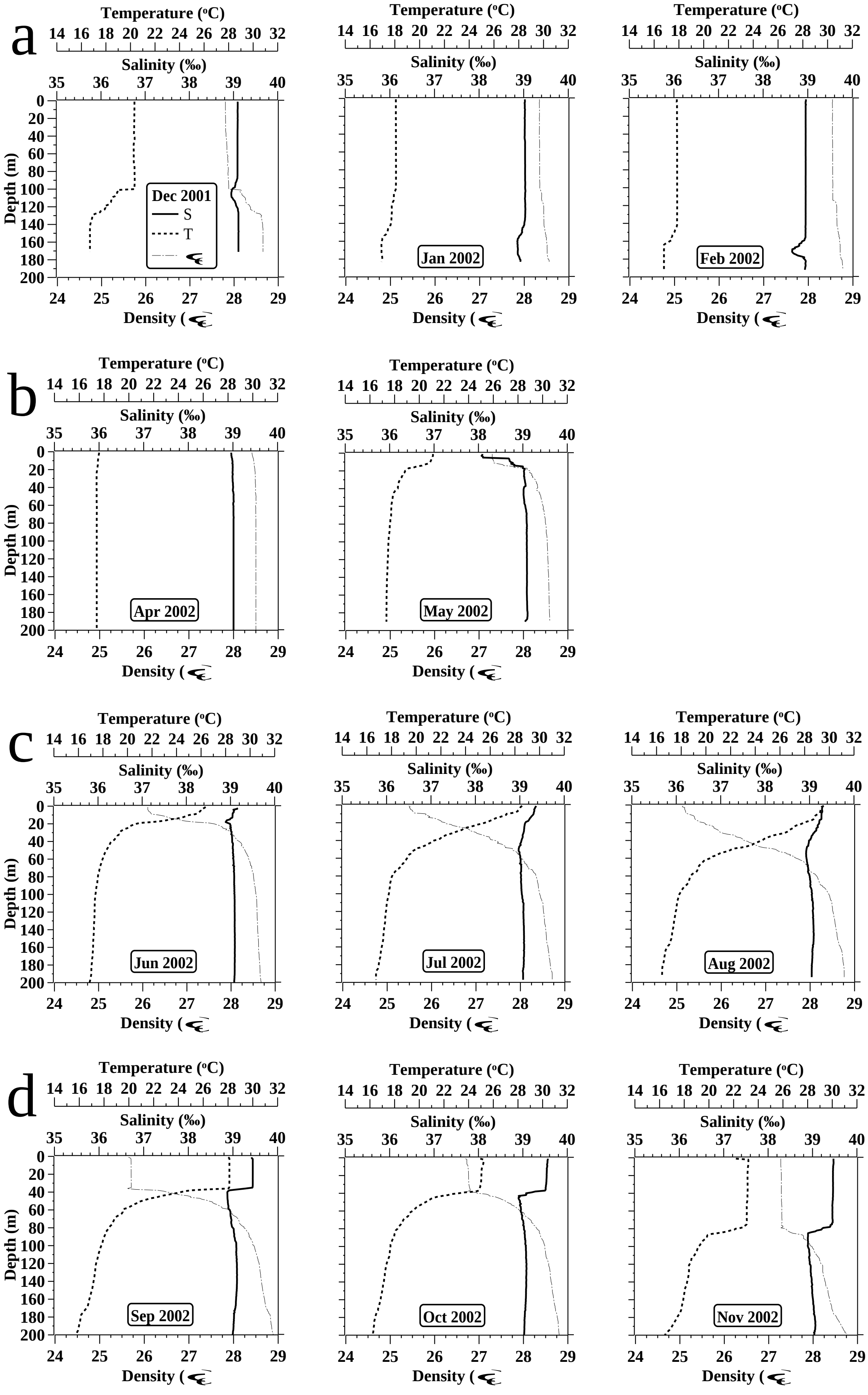


Figure 3.6.a Vertical profiles of hydrographic parameters at the shelfbreak station in 2002 (a: Winter, b: Spring, c: Summer, d: Autumn).

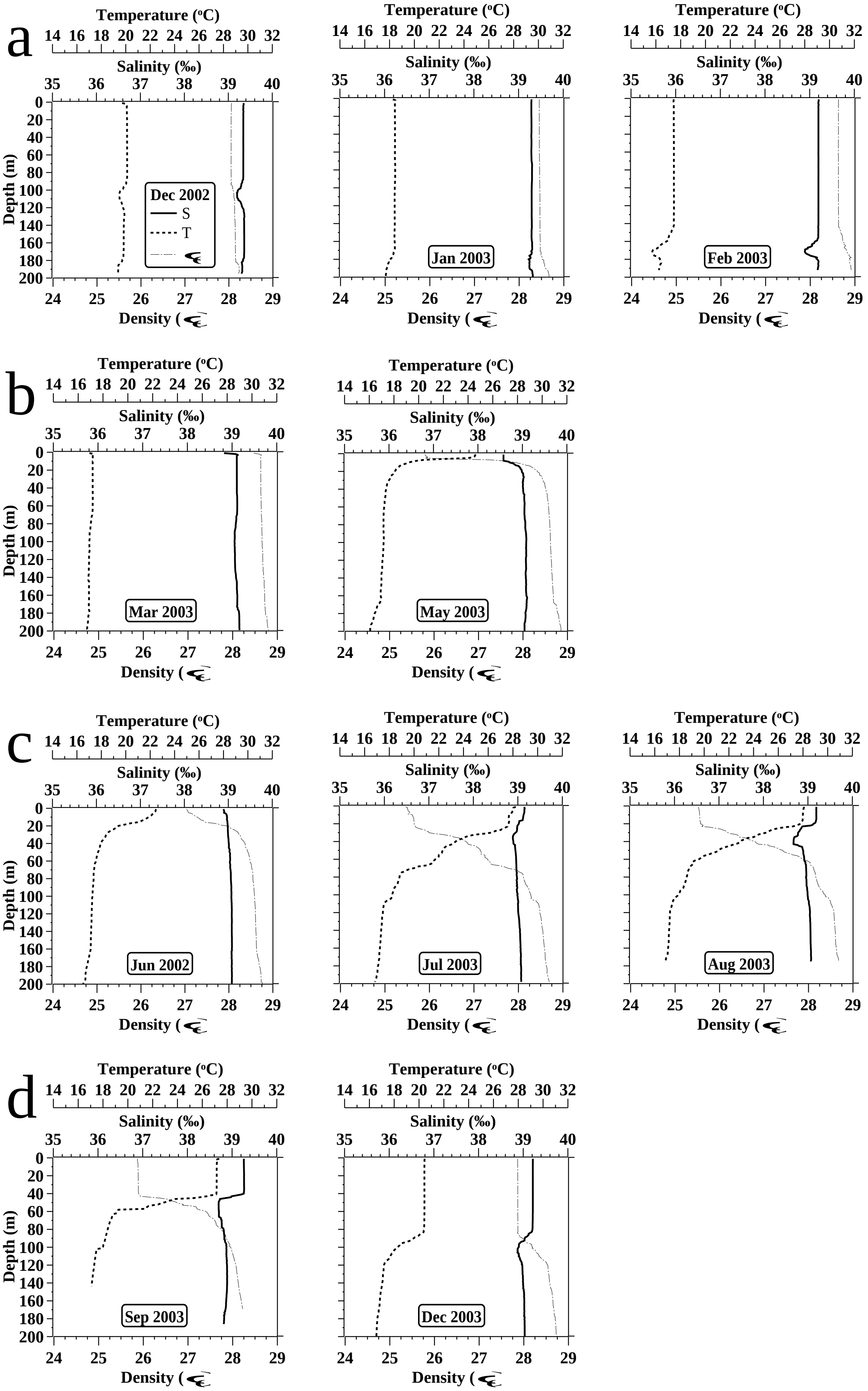


Figure 3.6.b Vertical profiles of hydrographic parameters at the shelfbreak station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

The water column density values ranged between 26.1-28.6 in June, 25.4-28.7 in July and 25.1-28.7 in August 2002 (Figure 3.6.a). A seasonal pycnocline was formed in the near-surface layer during spring; it deepened about 40 m depth during September and October and then moved down to 80 m in November 2002. The winter density profiles were almost vertically uniform at the shelfbreak zone; however, the bottom layer of ca. 15-20 m was occupied by more dense water (28.8) (Figure 3.6.b). The winter pycnocline was very weak in December 2002, but established at depth of 170 m in January and February 2003. The seasonal density stratification started again in May 2003. The density gradient zone was very broad during the period of July-September 2003; then it weakened and got thinner by late autumn.

3.2 Evaluation of Secchi Disc Depth (SDD) Data

3.2.1 Nearshore station

The Secchi Disc Depth (SDD) is a rough indicator of light permeability of the water column. It ranged from 3 to 17 m at the nearshore station during the study period (Table 3.1). It deepened to depths of 15-17 m in December 2002 and January 2003, indicating the solar light penetrated down to the bottom when the nearshore waters were slightly influenced by the Lamas River inflow. However, it was merely 3 to 4 m in February and March 2003 when Lamas River carried large amounts of particulate matter and nutrients to the inshore waters, which limit light penetration in the water column.

Table 3.1 Monthly variations of SDD between December 2001 and December 2003 at the time-series stations (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Date (dd/mm/yy)	**Nearshore**	**Middle**	**Shelfbreak**	**Date (dd/mm/yy)**	**Nearshore**	**Middle**	**Shelfbreak**
11/12/01	3		34	24/12/02	17	19	19
23/01/02	3		19	29/01/03	15	24	23
19/02/02	12		28	27/02/03	4	15	21
09/04/02	-		21	28/03/03	3	14	22
18/06/02	-		36	21/05/03	7	9	10
11/07/02	3		25	05/06/03	7	14	19
01/08/02	-		23	15/07/03	7	18	36
18/09/02	7	13	21	31/07/03	9	21	32
24/10/02	5	37	37	22/09/03	12	20	29
21/11/02	4	28	24	11/12/03	12	24	32

3.2.2 Middle station

The SDD varied between 9 and 37 m during September 2002 and December 2003 (Table 3.1). The lowest value was measured as 9 m in May 2003 when plankton production increased in the near-surface waters. In October 2002, when plankton production and particulate matter concentration were very low, the SDD was ca. 37 m. During November 2002 to March 2003, more nutrients were supplied from the bottom to the upper layer via vertical mixing; but solar light intensity was limited. Therefore, the SDD ranged monthly between 14 and 28 m. In spring period of 2003, the SDD decreased to 9 m due to increasing concentration of suspended particulate matter of plankton origin; then it steadily increased to 14 m in June, 18 m in July and 20 m in September 2003, when primary production of plankton decreased in the upper layer.

3.2.3 Shelfbreak station

The SDD at the shelfbreak station varied seasonally between 12 and 37 m (Table 3.1). It was measured as 21 m in September 2002, reaching the maximum value of 37 m in October 2002. It ranged between 16 and 23 m in winter months; the lowest depth of 12 m was recorded in May 2003 when particulate matter concentration increased in surface waters. In the summer of 2003, the SDD was 19 m in June, rising up to 36 m in July due to decreasing of primary production and thus POM concentration in the Euphotic Zone (EZ). In the beginning of August, the SDD decreased slightly to 32 m and then to 29 m in September 2003.

3.3 Evaluation of Dissolved Oxygen (DO) Data

3.3.1 Nearshore station

Dissolved oxygen (DO) values were higher than 200 μM both in the surface and in the deep waters in 2002 and 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department). The oxygen values were at the saturation level of seawater, increasing in winter, and then descending in summer when the seawater got warmer (see Appendix E).

3.3.2 Middle station

DO varied monthly between 183 and 255 µM from September 2002 to December 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department). DO profiles were vertically uniform in winter. It increased from the surface to the bottom in spring. DO concentrations increased towards the base of the EZ and then displayed a decreasing trend to the bottom. Since salinity showed small variations below the EZ, DO variations were determined by changes in both water temperature and respiration processes (see Appendix E).

3.3.3 Shelfbreak station

DO concentrations varied seasonally and vertically between 173 to 264 µM at the shelfbreak station (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department). DO concentration exceeded mostly 200 µM in the water column. The values less than 200 µM were occasionally recorded in the warmer upper layer waters in September 2002. DO concentrations in the surface water were at saturated levels during spring and summer months, ranging between 220 to 239 µM; below the thermocline it ascended in the cool waters of intermediate depths. It showed a decreasing trend in the near-bottom water due to respiration. As water column was homogenous in winter, the DO concentration distributed uniformly in the entire water column of the shelf (see Appendix E).

3.4 Evaluation of Bio-Chemical Parameters

The time series data of dissolved inorganic nutrients and particulate matter determined at the three stations between December 2001 and December 2003 are evaluated in this section for each location.

3.4.1 Evaluation of dissolved inorganic nutrients

3.4.1.1 Nearshore station

Dissolved inorganic nutrients measured in the water column (sampled only surface and 5 to 10 m depths) of the nearshore station are depicted in Figure 3.7, indicating prominent seasonal fluctuations. Concentrations of dissolved inorganic phosphate (DIP, o-PO_4), total oxidized nitrogen (NO_3+NO_2, referred to as nitrate or NO_3), and reactive silicate (Si) were relatively high in the river-induced surface waters during December 2001-May 2003, then decreasing apparently in the summer-autumn of 2003. DIP was measured by the sensitive (detection limit 1.0 nM or 0.001 μM) Magnesium-Induced Coprecipitation (MAGIC) technique and by the automated (AA) method (see Appendix A). The sensitive MAGIC results allow evaluating spatial and temporal variations of DIP more precisely in the P-depleted surface waters.

The shallow nearshore station was directly influenced by the small Lamas River. Long-term (2002-2003 period) river data reported recently in Tuğrul *et al.* (2004) demonstrate that the river has high nitrate (63-121 μM; annual mean 93 μM) and reactive silicate (62-118 μM; mean 91 μM) but low phosphate (0.03-1.16 μM; mean 0.21 μM) (Table 3.2).

Rainwater is another external source of nutrients for the studied shelf region. Tuğrul *et al.* (2004) reported that phosphate, nitrate and reactive silicate concentrations of rainwater samples measured during 2002-2003 ranged from 0.15 to 9.00 μM (mean 1.19), 6.8 to 675 μM (mean 74.4) and 0.02 to 17.72 μM (mean 2.52), respectively (see Appendix B).

DIP contents of the surface seawaters that were measured by the sensitive MAGIC method varied between 0.036-0.230 μM in 2002 and from 0.018 to 0.162 μM in 2003 (Figure 3.7). The surface DIP values were apparently high in winter period, reaching 0.230 μM in December 2001 and descending from 0.166 μM in January 2002 to 0.055 μM in February. In spring, surface DIP was as low as 0.072 μM in

April, and then displayed a secondary maximum of 0.130 µM in May. Surface DIP values declined again to 0.077 µM in June and remained low at levels of 0.036-0.053 µM in July-August period. The low surface DIP (0.036-0.077 µM) concentrations of the nearshore station were similar to the near-bottom values of 0.042-0.073 µM during the summer-autumn period of 2002. The DIP concentration in the water column increased to 0.097-0.101 µM in February and 0.14-0.16 µM in March 2003. In the spring months, surface DIP declined from 0.071 to 0.058 µM in May. It decreased further from 0.061 to 0.039 µM in August. It remained almost low at 0.043 µM level in September, further dropping to 0.018 µM in December 2003 (Figure 3.7).

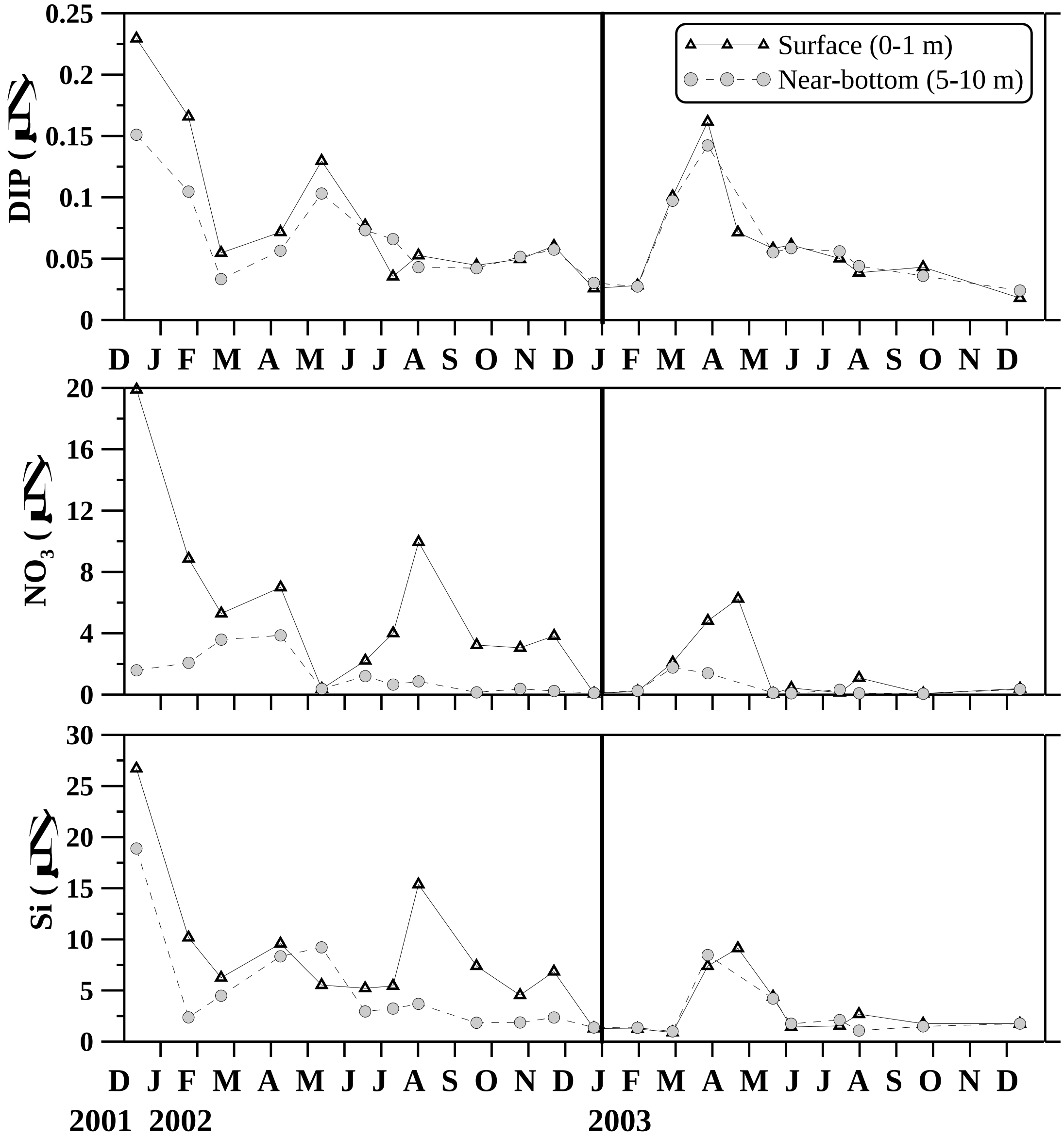


Figure 3.7 Monthly variations of DIP, NO$_3$ and Si at the nearshore station in the course of December 2001-December 2003.

NO_3 content of the nearshore station varied seasonally between 0.15-19.9 µM in 2002, and between 0.06-6.26 µM for the 2003 period (Figure 3.7). In 2002, the surface NO_3 was markedly high (19.9 µM) in December 2001, descending steadily to 8.87 µM in January 2002 and to 5.30 µM in February 2002. It was still high (7.0 µM) in April and then dropped to a minimum of 0.38 µM in May 2002. The surface NO_3 increased again from 2.22 µM in June to 9.96 µM in August. However, it remained still high at levels of 3.06-3.84 µM in autumn. Then, it declined to levels of 0.08 µM in December 2002 and 0.22 µM in January 2003; the winter nitrate values increased again to 2.10 µM in February and to 4.82 µM in March (Figure 3.7). The highest value of 6.26 µM was reached in April 2003. Later, it dropped to very low values of 0.13-0.44 µM in early summer. After a slight increase in August (1.10 µM), it stayed low until the end of the year, ranging from 0.08 µM in September to 0.40 µM in December 2003. In the near-bottom waters, NO_3 concentrations were notably lower than the surface values. The higher values were in the range of 1.59-3.59 µM in the winter of 2002, decreasing to the lowest values of 0.06-0.38 µM in the autumn periods of 2002 and 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Reactive Si values of surface waters ranged between 1.85 and 26.72 µM in 2002 and from 0.91 to 9.14 µM in the course of 2003 (Figure 3.7). The maximum Si concentration (26.72 µM) was recorded in December 2001, indicating large riverine input. Then, it decreased steadily to levels of 10.2 µM in January 2002, 6.26 µM in February. The surface Si values remained almost constant at levels of 5.23-5.54 µM in late-spring and early-summer months. However, it increased again to 15.4 µM in August 2002. The near-bottom values were between 1.85-3.70 µM during summer-autumn period. The water column Si values were low and similar in the winter of 2003, ranging between 0.91 and 1.39 µM (Figure 3.7). However, Si concentrations in March were rather high (7.40-8.48 µM) in the water column due to river input and vertical mixing. Then, the surface and near-bottom Si values declined to 4.41 µM level in May, further decreasing to levels of 1.44-2.70 µM in the summer months. The low Si values lasted in the water column during the period of September-December 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Table 3.2 Composite data of nutrient, particulate organic matter, P-fractions and elemental ratios in the Lamas River (Tuğrul *et al.*, 2004).

Date (dd/mm/yyyy)	**TP (µM)**	**TDP (µM)**	**DOP^{AA} (µM)**	**DIP^{AA} (µM)**	**NO$_3$ (µM)**	**Si (µM)**	**N/P^{AA}**	**Si/N**	**POC (µM)**	**PON (µM)**	**TPP (µM)**	**POP (µM)**	**PIP (µM)**	**C/P (POC/TPP)**	**C/P (POC/POP)**	**C/N (POC/PON)**	**N/P (PON/TPP)**	**N/P (PON/POP)**
04/04/2003	6.694	3.281	2.121	1.16	82.80	88.00	71.4	1.06			3.41	2.100	1.313					
07/04/2003	6.315	2.505	1.975	0.53	63.28	76.8	119	1.21	270.6	33.4	3.81	2.020	1.790	71.1	1340	8.1	8.8	16.6
28/05/2003	0.520	0.361	0.271	0.09	81.67	92.66	907	1.13	55.5	1.61	0.16	0.124	0.035	349	449	34.5	10.1	13.0
30/05/2003	0.460	0.248	0.168	0.08	85.72	100.7	1072	1.17	44.5	2.37	0.21	0.164	0.048	210	271	18.8	11.2	14.4
03/06/2003	3.856	0.492	0.202	0.29	86.89	92.28	300	1.06	124.9	13.8	3.36	2.391	0.973	37.1	52.2	9.1	4.1	5.8
14/07/2003	0.410	0.296	0.216	0.08	79.78	105.1	997	1.32	22.0	1.16	0.11	0.069	0.045	193	321	19.0	10.2	16.9
01/08/2003	0.350	0.263	0.163	0.10	71.74	99.02	717	1.38	19.0	0.83	0.09	0.070	0.017	218	272	22.9	9.5	11.9
02/09/2003	0.333	0.131	0.045	0.09	110.3	93.48	1226	0.85	19.9	1.71	0.17	0.166	0.036	98.9	120	11.7	8.5	10.3
22/09/2003	0.288	0.128	0.058	0.07	121.4	118.4	1734	0.97	13.3	1.16	0.16	0.130	0.030	83.1	103	11.5	7.3	8.9
28/10/2003									10.9	1.13			0.030			9.7		
06/11/2003									6.48	0.93			0.021			7.0		
01/12/2003	0.252	0.165	0.135	0.03	92.9	107.3	3100	1.15	6.83	1.04	0.09	0.060	0.027	78.5	114	6.6	12.0	17.3
11/12/2003	0.340	0.274	0.174	0.10	91.9	106.6	919	1.16	5.97	1.01	0.07	0.039	0.027	90.5	153	5.9	15.3	25.8
29/12/2003	0.640		0.450	0.19	103.7	108.9	546	1.05										

3.4.1.2 Middle station

Seasonal variations of nutrients in the water column of the middle station are presented in Figures 3.8 and 3.9. All nutrient data, including DIP concentrations by the two methods, are given in Appendix A. The DIP data that were obtained by the MAGIC method are evaluated in the text. Located outside the direct effect area of Lamas River, nutrient concentrations at the middle station were lower than those determined at the nearshore station. Nutrient concentrations in the water column were in the ranges of 0.014-0.066 μM for DIP, 0.04-0.88 μM for NO_3, and 0.80-3.83 μM for Si during 2002-2003.

The surface DIP concentration varied from 0.014 to 0.033 μM during the autumn of 2002 (Figure 3.8). It ranged between 0.015 and 0.041 μM throughout the year in 2003. The DIP concentrations decreased in the surface and the near-bottom from September to November 2002. In 2003, the surface DIP increased slightly from 0.017 to 0.023 μM in winter and then to levels of 0.032-0.041 μM in March-May 2003 (Figure 3.8). Surface DIP concentrations were low and almost constant (0.026-0.028 μM) during June-August period. The surface DIP was measured as 0.033 μM in September and declined to 0.015 μM in December 2003. DIP concentrations in the deep layer were higher than the surface values during September 2002-February 2003. However, the surface DIP exceeded the near-bottom water concentrations in April-May 2003 when the less saline waters occupied the surface layer. Near-bottom DIP reached the highest value of 0.066 μM in August, and then exhibited a secondary peak of 0.059 μM in December 2003.

The surface NO_3 concentration ranged from 0.10 to 0.47 μM during the autumn of 2002, then varied between 0.06 and 0.78 μM with season in 2003 (Figure 3.8). In the autumn of 2002, the surface NO_3 showed a decreasing trend from 0.47 μM in September to 0.10 μM in November, then it remained low (0.08 μM) in December. In 2003, the surface NO_3 increased apparently from 0.08 to 0.63 μM in the winter (Figure 3.8) and kept its high level in March (0.58 μM) whilst the near-bottom NO_3 was as low as 0.23 μM. In the region, the NO_3 concentration displayed a maximum of 0.78 μM in April and then declined markedly in May (0.08 μM) and kept its low level (0.06-0.09 μM) in the summer and early-autumn period of 2003. Then, the surface water was partly enriched in NO_3 (0.34 μM) in December due to internal input via vertical mixing. The highest NO_3 concentrations in the near-bottom water were observed in May and December 2003 as 0.88 and 0.67 μM, respectively (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

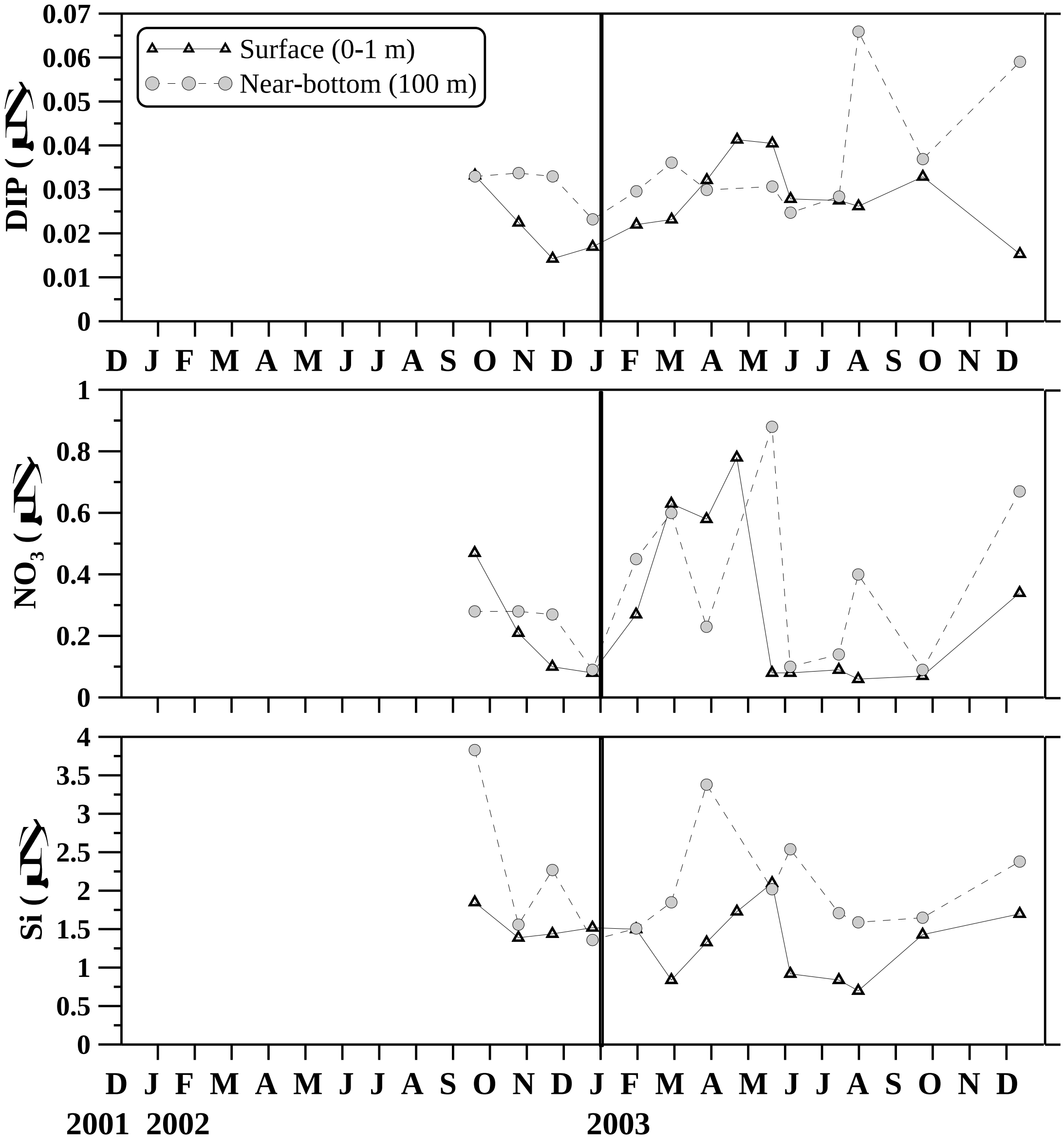


Figure 3.8 Monthly variations of DIP, NO_3 and Si at the middle station in the course of September 2002-December 2003.

The surface Si concentrations varied slightly from 1.39 to 1.85 μM during the autumn 2002, and then ranged seasonally between 0.84 and 1.70 μM in 2003 (Figure 3.8). During September-October 2002 period, the Si showed a decreasing trend from

1.85 to 1.39 µM in the surface water, but from 3.83 to 1.56 µM in the near-bottom water. In the winter of 2003, the surface Si concentration was 1.52 µM in January, decreasing to 0.84 µM in February (Figure 3.8). It increased again in the spring months from 1.33 µM in March to 1.73 µM in April and 2.10 µM level in May 2003, indicating riverine input. In summer months, the surface Si declined to levels of 0.92 µM in June, 0.84 µM in July and 0.70 µM in August 2003. It increased slightly to 1.43 µM in September and 1.70 µM in December 2003 through the river discharges being at minimum levels. The Si in the near-bottom waters (at 100 m) was in the range of 1.36-3.83 µM during the course of 2002-2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Nutrient profiles showed vertically uniform distribution in the Euphotic Zone (hereinafter referred to as EZ, the depth to which 1% of the surface light penetrates) but exhibited remarkable variations with season. Table 3.3 shows that the EZ thickness ranged between 43-86 m (Tuğrul *et al.*, 2004; Yılmaz, 2006). In 2002, DIP concentrations in the EZ varied slightly between 0.021-0.033 µM in September and October. Then, it ranged from 0.014 to 0.041 µM in November. Below the EZ, it was nearly constant value of 0.033 µM in the autumn 2002 (Figure 3.9.a). In the winter of 2003, when water column was well mixed, DIP content of the EZ ranged slightly between 0.016-0.023 µM. The winter DIP was determined between 0.023-0.036 µM in the bottom waters (Figure 3.9.b). In the spring 2003, the DIP decreased from the surface to the bottom of the EZ from 0.032 to 0.016 µM in March and from 0.040 to 0.024 µM in May; it was about 0.030 µM in the bottom water. In the summer of 2003, the EZ thickness was between 60-76 m where the DIP ranged between 0.019-0.046 µM. The DIP in the EZ varied from 0.028 to 0.035 µM in September, ~0.015 µM in December; the DIP concentration increased to levels of 0.037-0.059 µM in the bottom water (Figure 3.9.b).

NO_3 profiles in Figure 3.9.a show that the EZ concentrations varied between 0.06 and 0.47 µM in the autumn of 2002. The near-bottom concentration was about ~0.3 µM. In the winter of 2003, the EZ values of NO_3 were in the range of 0.1-0.3 µM in December 2002 and in January 2003 when the water column was well mixed (Figure 3.9.b). However, the values of NO_3 in February and March ranged between 0.08-0.66 µM in the water column. In late-spring and early-autumn period of 2003, the NO_3 in the EZ was very low (0.05-0.13 µM), increasing to ~0.33 µM level in December (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Si concentrations in the EZ of the middle station were slightly variable with depth and time, ranging between 1.83-2.03 μM in September, 1.29-1.68 μM in October and 1.44-2.21 μM in November 2002 (Figure 3.9.a). The highest near-bottom Si values were recorded in September 2002 (3.83 μM) and March 2003 (3.38 μM). In the winter period, the EZ values were between 1.43 and 1.89 μM in December 2002, 1.47-1.53 μM in January and 0.79-1.02 μM in February 2003 (Figure 3.9.b). In the spring of 2003, the Si concentration in the EZ ascended with depth from 0.85 to 1.68 μM in March and from 0.85 to 2.75 μM in May 2003. The summer Si contents of the EZ were in the range of 0.70-1.23 μM, rising to levels of 1.43-1.70 in the autumn of 2003. However, below the EZ, the Si concentration generally increased with depth (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Table 3.3 Thickness of the Euphotic Zone (EZ; 1% light depth) at the middle station between September 2002 and December 2003 (Tuğrul *et al.*, 2004; Yılmaz, 2006)

Date (dd/mm/yyyy)	EZ thickness (m)	Date (dd/mm/yyyy)	EZ thickness (m)
18/09/2002	72	21/05/2003	72
24/10/2002	86	05/06/2003	74
21/11/2002	86	15/07/2003	76
24/12/2002	85	31/07/2003	60
29/01/2002	70	22/09/2003	43
27/02/2003	71	11/12/2003	57
28/03/2003	71		

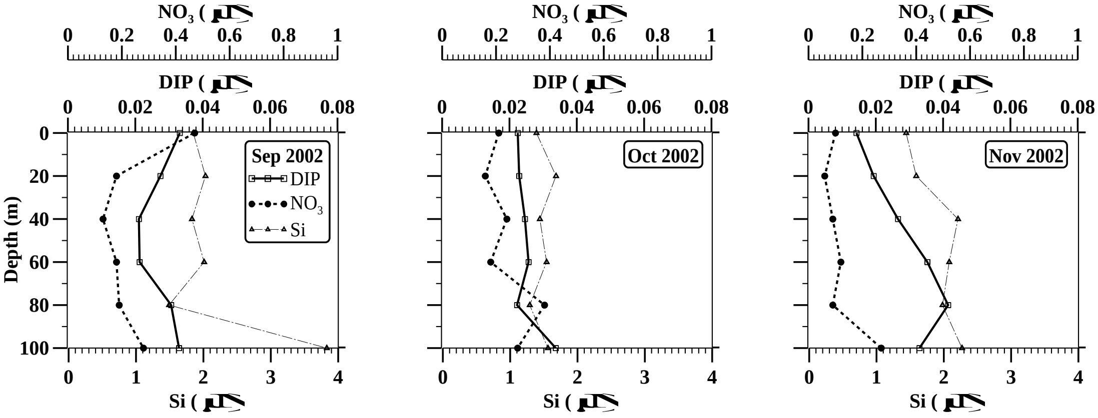


Figure 3.9.a Vertical profiles of dissolved inorganic nutrients at the middle station in the autumn of 2002.

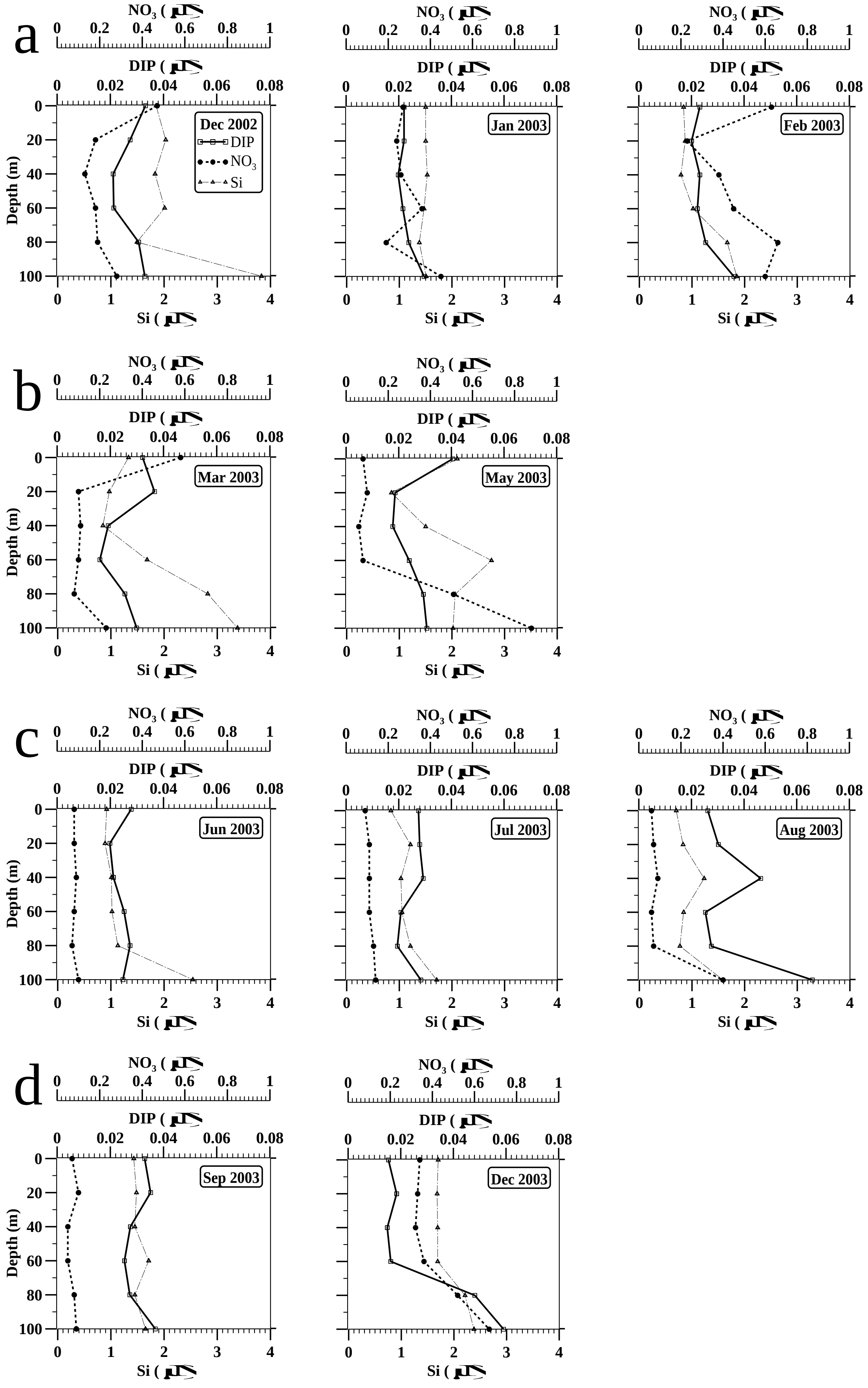


Figure 3.9.b Vertical profiles of dissolved inorganic nutrients at the middle station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

3.4.1.3 Shelfbreak station

Seasonal variations of nutrients in the water column of the shelfbreak zone (station 3 in Figures 2.1-2.2) are presented in Figures 3.10 and 3.11. In addition, nutrient concentrations, including DIP measured by the MAGIC method, are tabulated in Appendix A. DIP, NO_3 and Si concentrations in the surface waters of this station were lower than the values of the other two stations on the near-shore zone. It is located outside the river effect but in a direct interaction with Mediterranean open water system. The nutrient concentrations measured in 2002-2003 were in the ranges of 0.009 to 0.068 μM for DIP, 0.05 to 3.61 μM for NO_3, and 0.54 to 5.79 μM for Si in the water column.

The nutrient contents of the surface waters were generally similar to the values measured at the middle station. The surface DIP concentrations varied from 0.012 to 0.036 μM in the period of 2002-2003 (Figure 3.10). The surface DIP was 0.012 μM in December 2001, increasing to 0.028 μM in January 2002; then it declined slightly to level of 0.012 μM in February 2002, followed by a small rise to 0.017 μM in spring. The surface DIP in summer increased slightly from 0.020 μM in June to 0.029 μM in July, and then decreased to 0.015 μM in August. The surface water had higher DIP in September (0.032 μM), declining to 0.018-0.023 μM levels in October and November. It should be noted that these small DIP values at μM scale could be detectable only by MAGIC method. The surface DIP concentrations were relatively low in the winter months of 2003, ranging from 0.017 to 0.025 μM (Figure 3.10). The DIP in the surface water was as low as 0.014 μM in March, and then reached the highest concentrations in May, with the values of 0.036 μM in the surface and 0.068 μM in the near-bottom water, when the river input apparently influenced the marine ecosystem. In the summer months of 2003, the surface DIP concentrations were as low as 0.017-0.026 μM. The surface DIP, which was 0.032 μM in September, was about 0.018 μM in December 2003. The DIP contents of the near-bottom water, which ranged between 0.021 and 0.068 μM and exhibited two major maxima in January 2002 and May 2003, were consistently greater than the surface concentrations.

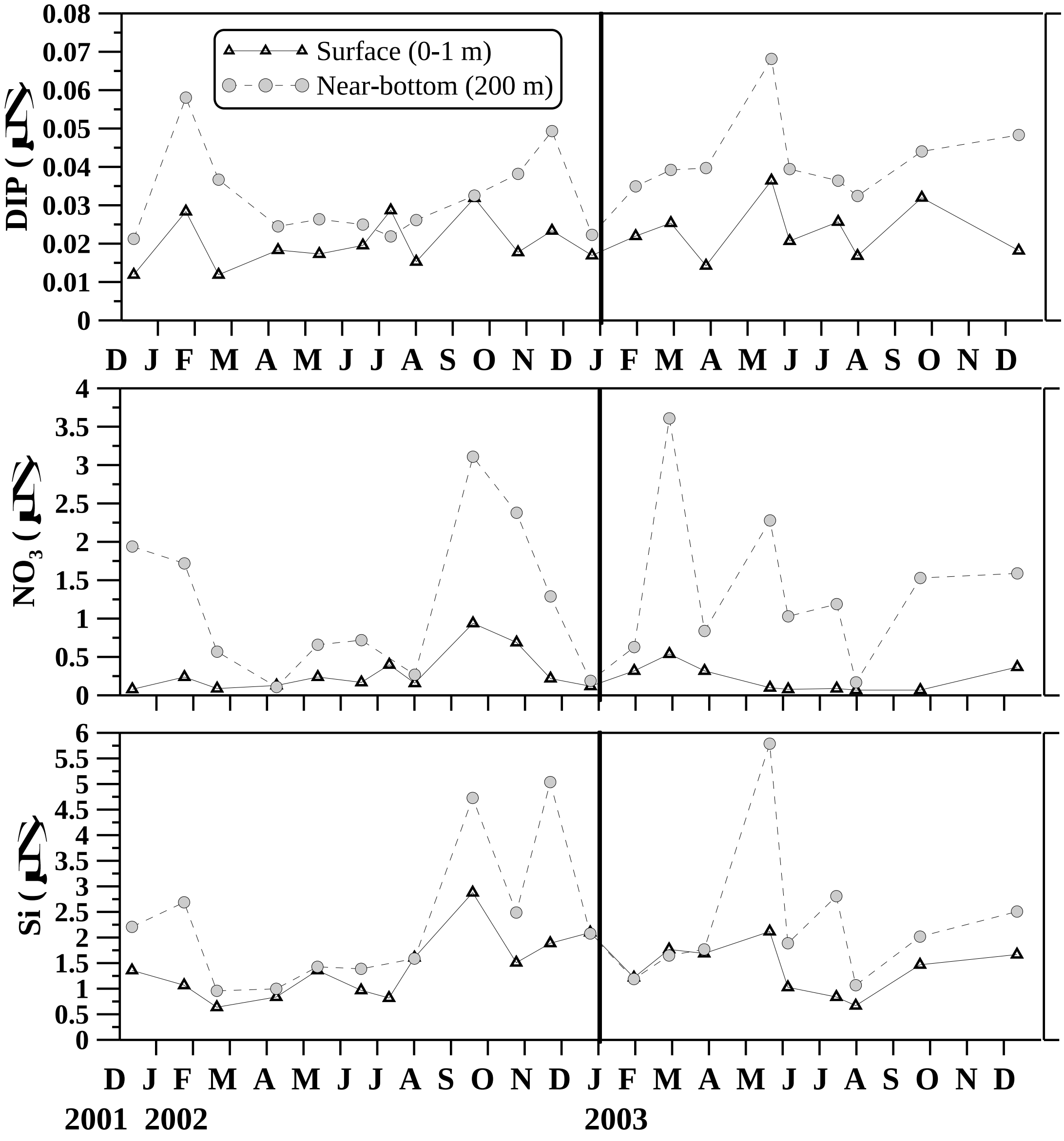


Figure 3.10 Monthly variations of DIP, NO_3 and Si at the shelfbreak station in the course of December 2001-December 2003.

NO_3 content of the surface water was consistently less than the near-bottom water values. The surface NO_3 varied markedly between 0.07 and 0.94 µM in 2002-2003 (Figure 3.10). In the winter of 2002, the surface NO_3 concentrations were relatively low, ranging from 0.08 µM in December 2001 to 0.24 µM in January 2002. However, the near-bottom waters were relatively rich in NO_3 (0.57-1.94 µM). In the period of spring-summer 2002, the surface NO_3 concentrations varied merely between 0.13-0.40 µM, with the highest value in July. The surface NO_3 increased markedly (0.69-0.94 µM) in the autumn, then declined to 0.22 µM in November 2002. In 2003, it was between 0.12-0.54 µM in the winter-spring months. It was very low throughout the summer months and September (0.07-0.09 μM), then increased again to 0.37 μM in December 2003 (Figure 3.10). It should be noted that NO_3 concentrations in the surface and near-bottom waters became similar in April and December 2002, and August 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Reactive Si concentrations varied between 0.64 and 2.88 μM in the surface and, 0.96 and 5.79 μM in the near-bottom water in the course of 2002-2003 (Figure 3.10). The surface Si ranged between 0.64-1.36 during December 2001-July 2002. Then it displayed a maximum of 2.88 μM in September 2002, decreasing to levels of 1.51-1.89 μM during October-November period. Si content of the entire water column was uniform (2.1 μM) in December 2002. Then it varied between 1.19-1.77 μM during January-March 2003 period (Figure 3.10), displaying maxima of 2.12 μM in the surface and 5.79 μM in the near-bottom water in May 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Nutrients showed considerable seasonal variations in the EZ whose thickness ranged between 50 to 119 m (Table 3.4). DIP concentrations in the EZ were always low, ranging between 0.006-0.018 μM in December 2001, 0.023-0.028 μM in January, and 0.012-0.018 μM in February 2002 (Figure 3.11.a). A small subsurface minimum was observed in December 2001 and in January 2002. In the spring, the DIP concentrations were expectedly low in the EZ (0.01-0.02 μM). Below the EZ, DIP exhibited an insignificant variation with depth, ranging between 0.017-0.028 μM. DIP values in the EZ ranged between 0.017 and 0.033 μM in the autumn 2002 and in the period of January-February 2003. In the spring of 2003, when the EZ boundary was situated at 89-95 m, DIP concentrations ranged between 0.014 μM and 0.036 μM in the EZ, rising to 0.040-0.068 μM at 200 m. In the summer, DIP in the EZ was in the range of 0.012-0.026 μM. In this period, DIP concentrations displayed an increasing trend towards the bottom, to levels of 0.036-0.039 μM. In September, DIP concentrations varied between 0.024-0.041 μM in the EZ then increased to 0.044 μM in the bottom water. In December 2003, DIP was relatively low in the EZ (0.015-0.018 μM), rising to 0.048 μM in the bottom water (Figure 3.11.b).

In 2002, NO_3 values were low and vertically almost uniform in the EZ, ranging monthly between 0.06-0.46 μM in winter, it increased markedly in the deep water (0.57-1.94 μM) (Figure 3.11.a). The spring and summer values of NO_3 in the EZ ranged between 0.12-0.61 μM. Below the EZ, it reached the levels of 0.41-1.04 μM. In the autumn, NO_3 profiles displayed a decreasing trend from the surface to the bottom of the EZ from 0.94-0.18 μM to 0.69-0.06 μM levels in September and October, respectively; however it was less variable in November 2002 (0.22-0.07 μM). Below the EZ, NO_3 reached to the highest values of 3.11 μM in September, 2.38 μM in October and 1.29 μM in November in the deep water. NO_3 concentrations in the EZ were very low in December 2002 (0.06 to 0.12 μM), increasing slightly to levels of 0.27-0.54 μM in January and February 2003 (Figure 3.11.b). Below the EZ, the winter NO_3 concentrations remained almost constant in the water column due to intense winter mixing; however, a maximum of 3.61 μM was observed in the bottom water in February 2003. In the spring, NO_3 was uniformly distributed in the well-mixed EZ (0.27-0.32 μM) in March; however it was variable (0.07-0.60 μM) in May. The bottom NO_3 values were as high as 0.84-2.28 μM in March-May period. The summer NO_3 concentrations in the EZ were in the range of 0.05-0.27 μM. A prominent nutricline was located at the bottom of the EZ in May and June. Near-bottom NO_3 concentrations were as high as 1-1.2 μM in June-July period. NO_3 concentrations were uniform in the EZ in September (0.07-0.08 μM) and December 2003 (0.34-0.39 μM) (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Table 3.4 Thickness of the Euphotic Zone (EZ; 1% light depth) at the shelfbreak station between December 2001 and December 2003 (Tuğrul *et al.*, 2004; Yılmaz, 2006).

Date (dd/mm/yyyy)	EZ thickness (m)	Date (dd/mm/yyyy)	EZ thickness (m)
11/12/2001	92	29/01/2003	68
23/01/2002	50	27/02/2003	84
19/02/2002	76	28/03/2003	89
09/04/2002	55	21/05/2003	95
13/05/2002	70	05/06/2003	101
18/06/2002	96	15/07/2003	83
10/07/2002	100	31/07/2003	119
01/08/2002	62	22/09/2003	70
18/09/2002	99	11/12/2003	56
24/10/2002	119		
21/11/2002	96		
24/12/2002	65		

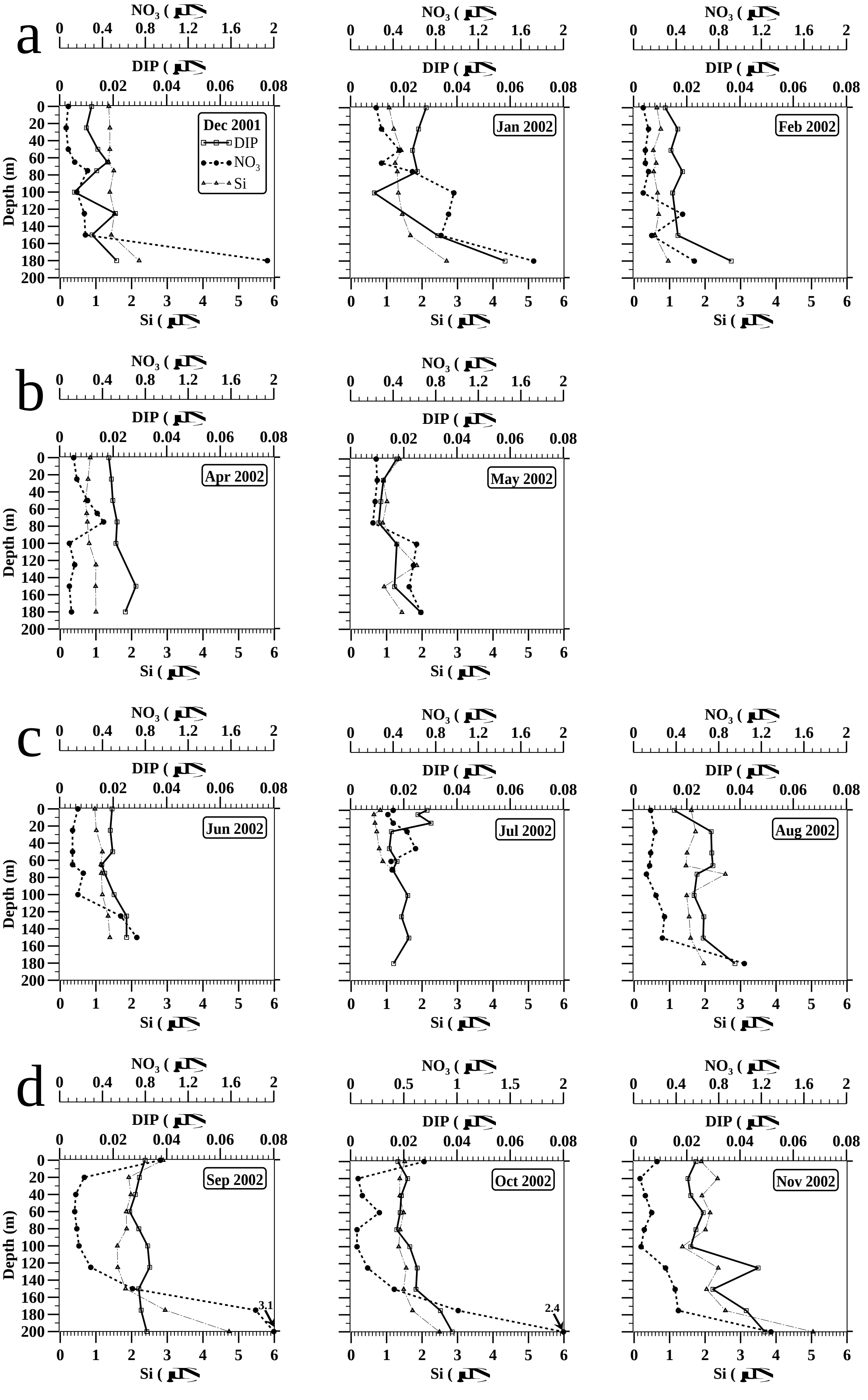


Figure 3.11.a Vertical profiles of dissolved inorganic nutrients at the shelfbreak station in 2002 (a: Winter, b: Spring, c: Summer, d: Autumn)

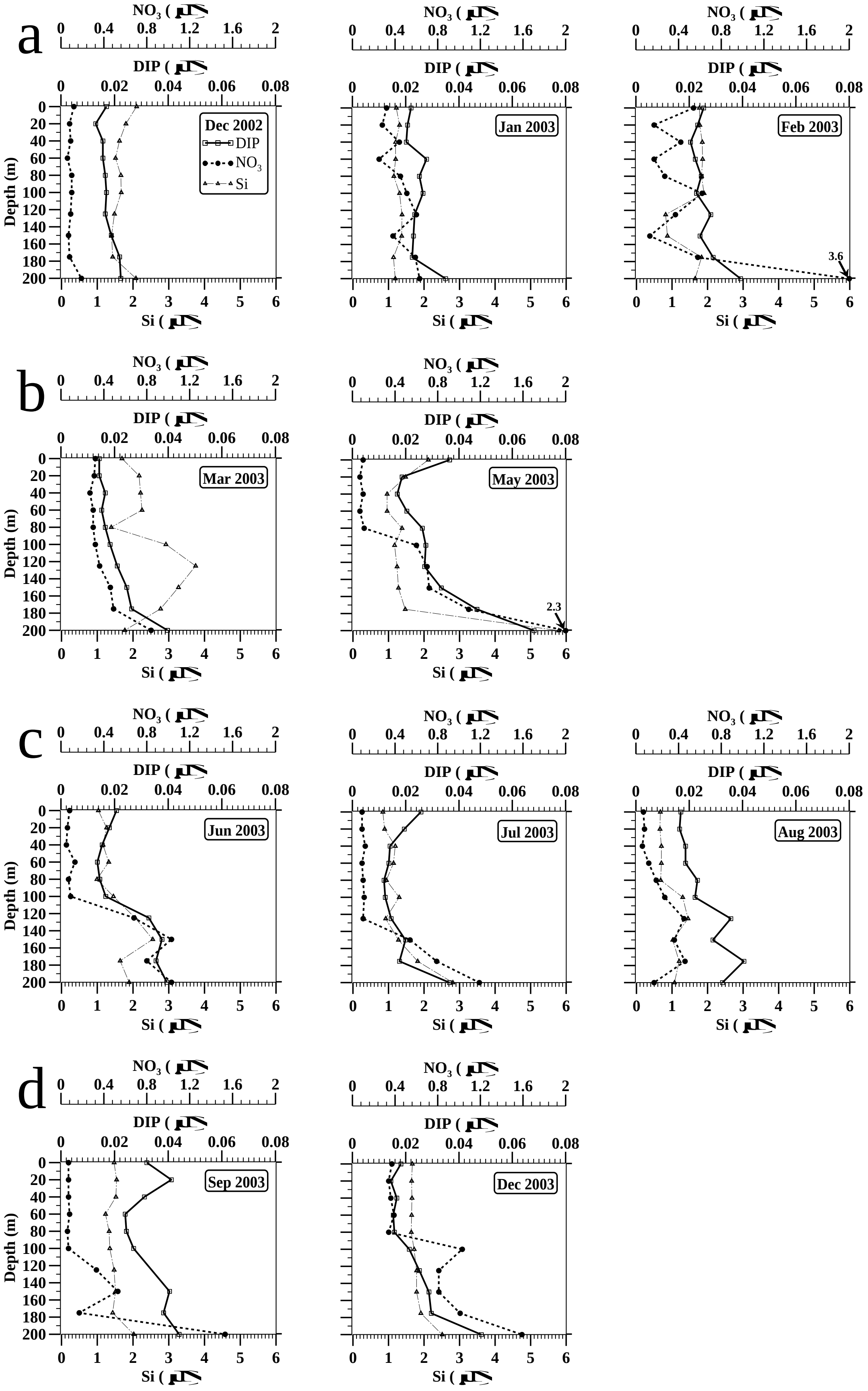


Figure 3.11.b Vertical profiles of dissolved inorganic nutrients at the shelfbreak station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn)

The silicate concentration in the water column of shelfbreak station was generally above 1.0 µM. In the winter of 2002, Si concentrations in the EZ ranged between 1.07-1.41 µM in December 2001-January 2002 period (Figure 3.11), declining to levels of ~0.6 µM in February 2002 (Figure 3.11.a). Si concentration increased steadily in the bottom layer to levels of 2.2-2.7 µM. It was relatively low (0.7-1.0 µM) in February and April, ranging between 0.89-1.36 µM in the EZ for May 2002. In the summer, Si concentrations in the EZ were in the range of 0.63-1.73 µM. The autumn Si concentrations ranged between 1.3-2.9 µM in the EZ, with higher concentrations in the surface waters. The bottom water values were as high as 2.5-5.0 µM in the autumn. In the winter of 2003, Si distribution was naturally homogeneous in the EZ due to winter mixing, ranging monthly from 1.2 to 2.1 µM, showing small fluctuations in the water column (Figure 3.11.b). In March, the Si concentrations varied slightly between 1.4 and 2.3 µM in the EZ. In May, Si concentration decreased apparently from 2.12 µM in the surface to 1.17 µM at the bottom of the EZ; then, it reached to 5.79 µM in the bottom water. The Si for the summer period fluctuated between 0.67-1.45 µM in the EZ, increasing to levels of 1.89-2.81 µM in the bottom waters. In the autumn, Si concentrations were between 1.23-1.54 µM in the EZ (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

3.4.2 Evaluation of particulate matter data

Spatial and temporal variations of time-series POM data (in terms of particulate organic carbon, particulate organic nitrogen, and total particulate phosphorus) were collected from the NE shelf waters off Erdemli between 2002 and 2003. The particulate organic carbon (POC) and particulate organic nitrogen (PON) results evaluated here are based on unpublished data of the IMS-METU Chemical Oceanography department and data reported in Tuğrul *et al*. (2004).

3.4.2.1 Nearshore station

Seasonal POM data obtained at the surface and 5 to 10 m depths of the nearshore station are given in Figure 3.12, indicating prominent seasonal fluctuations in concentrations of particulate organic carbon (POC), particulate organic nitrogen (PON), and total particulate phosphorus (TPP).

The nearshore station was directly influenced by the small Lamas River with associated chemical properties, which showed seasonal fluctuations (Tuğrul *et al.*, 2004). POM data in Table 3.2 show that POC concentrations in the Lamas River ranged between 6.0 and 270 µM, whereas PON results varied significantly from 0.83 to 33.4 µM and TPP changed seasonally between 0.07 and 3.81 µM. The Lamas River flowing to this region had high POM in April and June 2003 (Table 3.2). POM concentrations in the river were relatively low during the dry summer and autumn months. Annual means of POM for the river water were 50 µM for POC, 5 µM for PON and 0.8 µM for TPP. However, if the extremely high values are excluded, the annual means will be 13 µM, 1 µM and 0.1 µM for POC, PON and TPP, respectively.

POM in the nearshore water ranged monthly between 2.5-114 µM for POC, 0.4-10 µM for PON and between 0.026-0.153 µM for TPP (see Appendix C, Figure 3.12), exhibiting almost similar temporal changes in the course of 2002-2003. Surface and near-bottom POC concentrations were in the range of 2.5-4.5 µM during December 2001-January 2003 period. The POC displayed a steep increase in January, implying riverine input, and then dropped markedly to 11-13 µM levels in the water column in February 2002. In the spring, POC was 21.28 µM in the surface and 15.98 µM at the near-bottom in April, reaching the peak values of 90.4 µM and 114 µM in the surface and near-bottom waters in May 2002. In the summer of 2002, the surface POC concentrations decreased from 24.83 µM in June to 5.89 µM in August; also the near-bottom values displayed a similar temporal trend. In September, the POC concentration increased slightly to 10.7 and 11.97 µM in the surface and near-bottom waters. In the following months, it displayed decreasing trend, when the riverine inflow was at minimal levels. The surface POC exhibited a secondary peak of 29.73 µM in February 2003, while the near-bottom POC increased slightly to 8.13 µM (Figure 3.12). In the spring, the surface POC decreased from 23.22 to 12.53 µM in March-April period; then it displayed a weak maximum of 24.25 µM in May. POC concentrations in the near-bottom water were generally low in 2003, showing a small rise in May. In the summer-autumn period of 2003, POC concentrations were relatively low, ranging between 3.30-20.91 µM in the water column; the surface value descended further to 3.85 µM in December (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

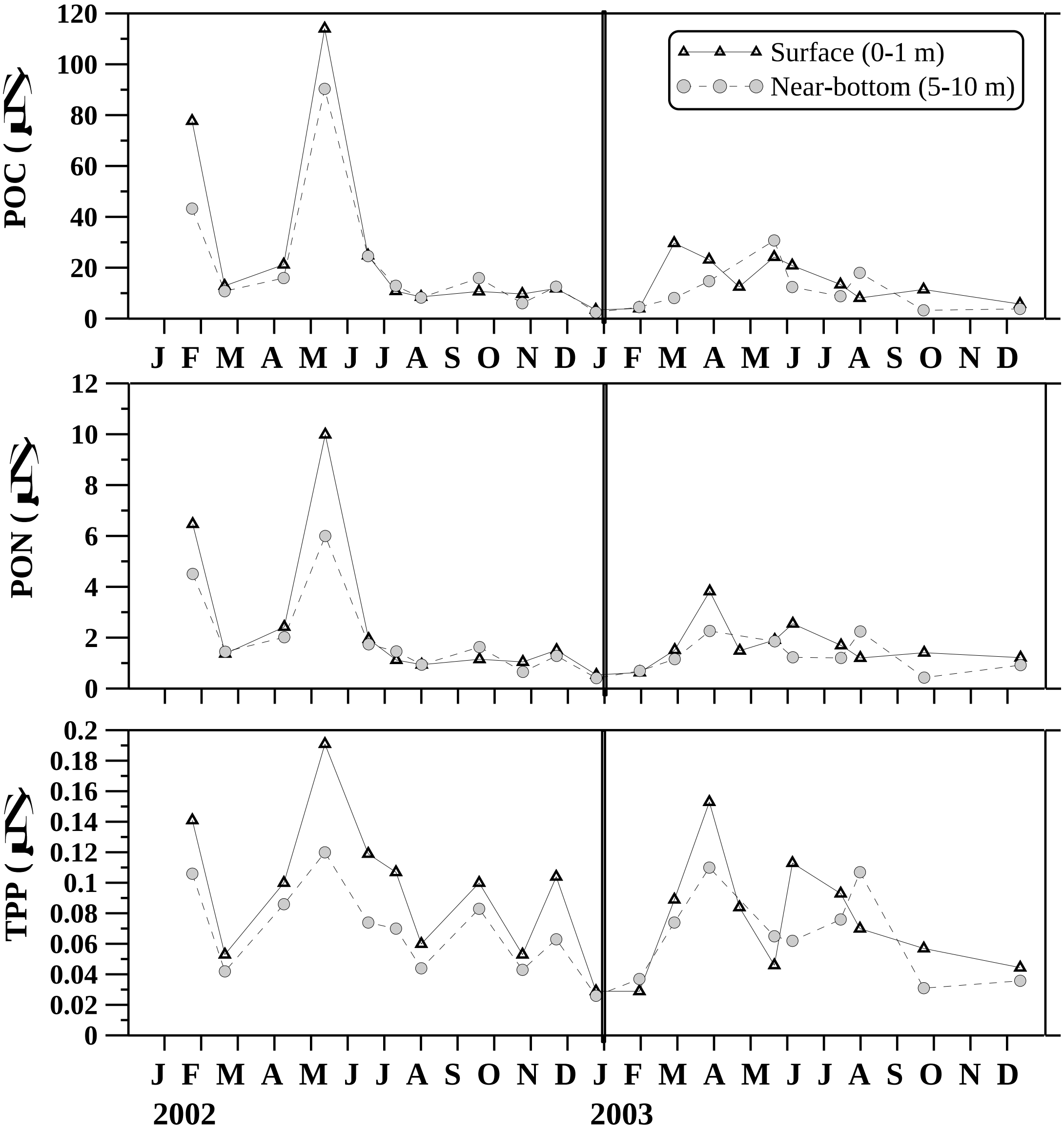


Figure 3.12 Monthly variations of POC, PON and TPP at the nearshore station between January 2002 and December 2003.

PON concentrations fluctuated seasonally at the nearshore station, ranging between 0.54-9.99 µM in the surface and 0.41-6.00 µM in the near-bottom water in the period of 2002-2003, with the lowest values in 2003 (Figure 3.12). The PON maxima coincided with POC peaks observed in 2002. In 2003, a secondary peak of PON (3.82 µM) in the surface water was recorded in March. In the summer-autumn, it decreased markedly to levels of 0.9-1.95 µM, which were consistent with the near-bottom values in the course of 2002-2003, except for September 2002 and August 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

TPP concentrations were highly variable, ranging between 0.029 and 0.191 µM in the surface, 0.026 and 0.120 µM in the near-bottom water during 2002-2003 (Figure 3.12). The peak values of TPP in the water column were recorded in January 2002, May 2002 and March 2003. The lowest values were determined in December 2002, January 2003 and September-December period of 2003.

3.4.2.2 Middle station

POM data from the water column of the middle station are depicted in Figures 3.13 and 3.14. Concentrations of bulk POM at the middle station were expectedly lower than the nearshore measurements. POM values of the water column ranged between 1.40-24.41 µM for POC, 0.16-1.85 µM for PON, and 0.013-0.072 µM for TPP during 2002-2003 (see Appendix C).

Time-series data in Figure 3.13 show that surface and near-bottom POC concentrations varied markedly with season from 1.99 to 24.4 µM and from 1.69 to 17.15 µM, respectively, during 2002-2003. The POC in the near-bottom water displayed a maximum in November 2002 and then varied little by December 2003. In the winter of 2003, the surface and near-bottom POC were very similar and low, varying from 3.66 to 3.38 µM in December 2002 and from 1.99 to 4.40 µM in January 2003 (Figure 3.13). In spring, surface POC concentrations increased markedly from 6.62 µM in March to a maximum of 24.41 µM in May as the near-bottom POC varied little between 2.11 and 5.23 µM. Surface and near-bottom POC values displayed a similar trend during August-December 2003, remaining low in the range of 4.28-5.17 µM (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

Temporal variations of the surface and near-bottom PON data are very consistent with the POC changes. The PON ranged from 0.23 to 1.85 µM in the surface water and from 0.17 to 0.86 μM in the near-bottom water during 2002-2003 (Figure 3.13). The surface PON was relatively high (0.99 μM) in September 2002, then fluctuated between 0.23 and 0.69 μM during October 2002-February 2003. In this period, a rising trend of PON was observed in the near-bottom waters from 0.17 μM in September to 0.69 μM in November. In the spring, the surface PON reached the peak values of 1.67 and 1.85 μM in April-May months then declined steeply to levels of 0.38 μM in the dry summer months. However, the near-bottom PON values ranged merely between 0.33-0.67 μM during spring-summer period, then displayed an increasing trend in December 2003 (after Tuğrul *et al*., 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

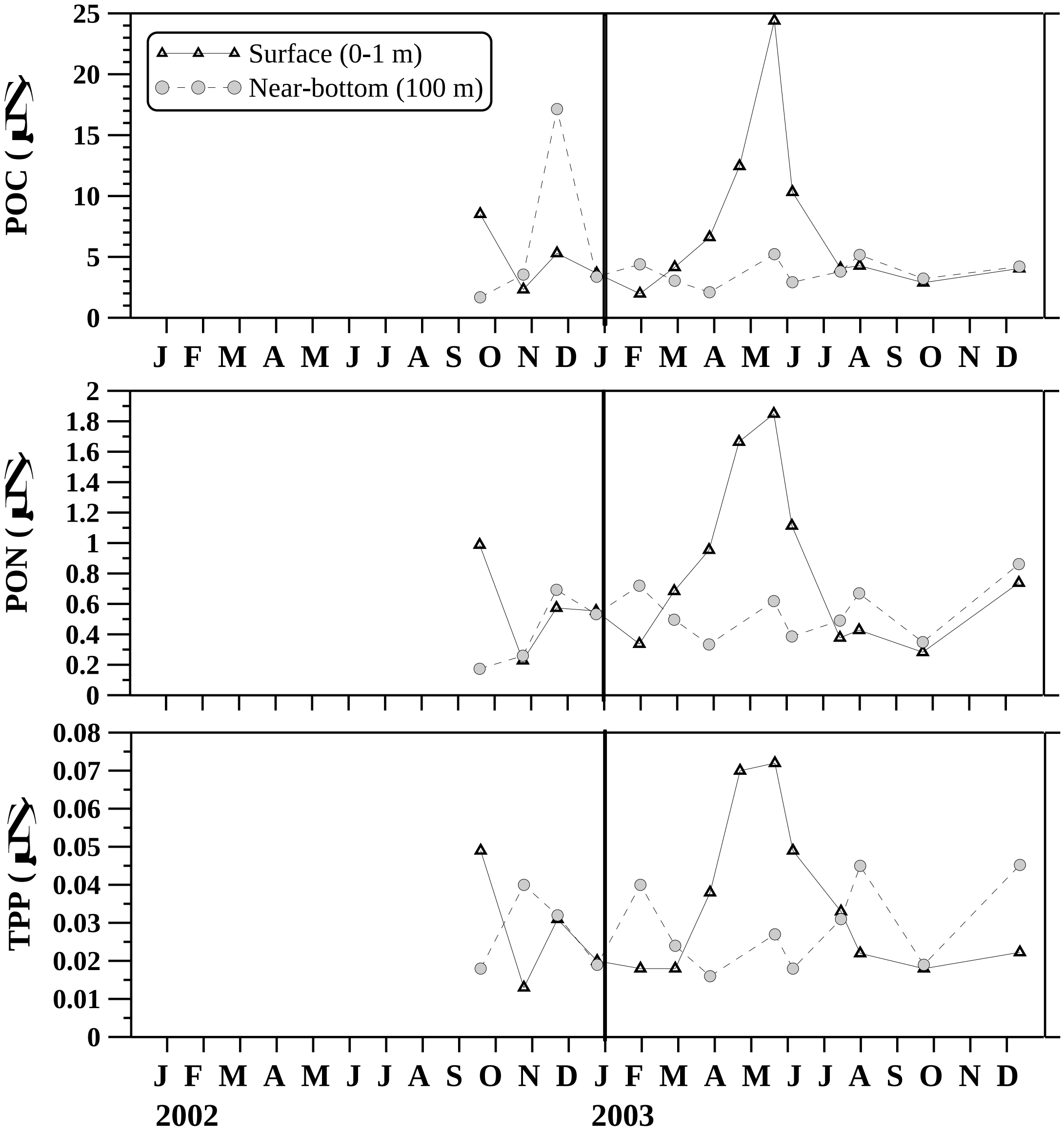


Figure 3.13 Monthly variations of POC, PON and TPP at the middle station between September 2002 and December 2003.

Monthly changes in the surface and near-bottom TPP concentrations were consistent with those of POC and PON, varying from 0.013 to 0.049 µM and from 0.018 to 0.040 µM, respectively, during autumn 2002 (Figure 3.13). Then they were between 0.018 and 0.020 µM in the surface, and 0.019 and 0.040 µM in the near-bottom waters in 2003. The surface TPP showed a decreasing trend from 0.049 µM in September to 0.018 µM in October, as the near-bottom TPP ascended from 0.018 to 0.040 µM in the same period. The surface TPP was almost similar (0.018-0.020 µM) in the winter of 2003, then displayed a coherent maximum of ~0.07 µM in April-May 2003, followed by a steep decline in the summer months to levels of 0.022 µM. It remained almost unchanged in the autumn months (between 0.018-0.022 µM). The near-bottom water concentrations were more variable in 2003, ranging between 0.016 and 0.045 µM, exhibiting peak values in August and December 2003.

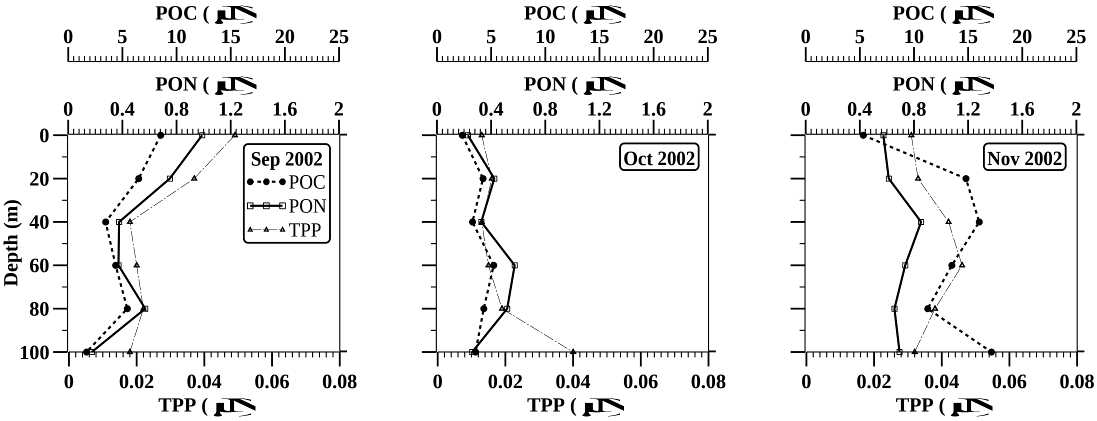


Figure 3.14.a Vertical profiles of particulate matter at the middle station in the autumn of 2002.

Abundance of POM in the EZ, whose thickness varied seasonally between 43-86 m. (Table 3.3), showed remarkable fluctuations with depth during 2002-2003. In September 2002, POC declined to 4.37 µM in the bottom of the EZ (Figure 3.14.a). In October 2002-February 2003 period, vertical changes in POC concentrations were less pronounced in the EZ, ranging monthly between 2-16 µM (Figure 3.14.b). In the spring, POC concentration decreased from 6.62 µM in the surface to 3.59 µM at the bottom of the EZ in March. However, it was markedly high (24.41 µM) in the surface water in May. The summer POC profiles in the EZ showed a steady decreasing trend from 10.34 to 3.66 µM in June, from 4.07 to 2.48 µM in July, and from 4.28 to 3.73 µM in August. The POC varied little in the autumn, between 2.90-3.68 µM in September-December 2003 period (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

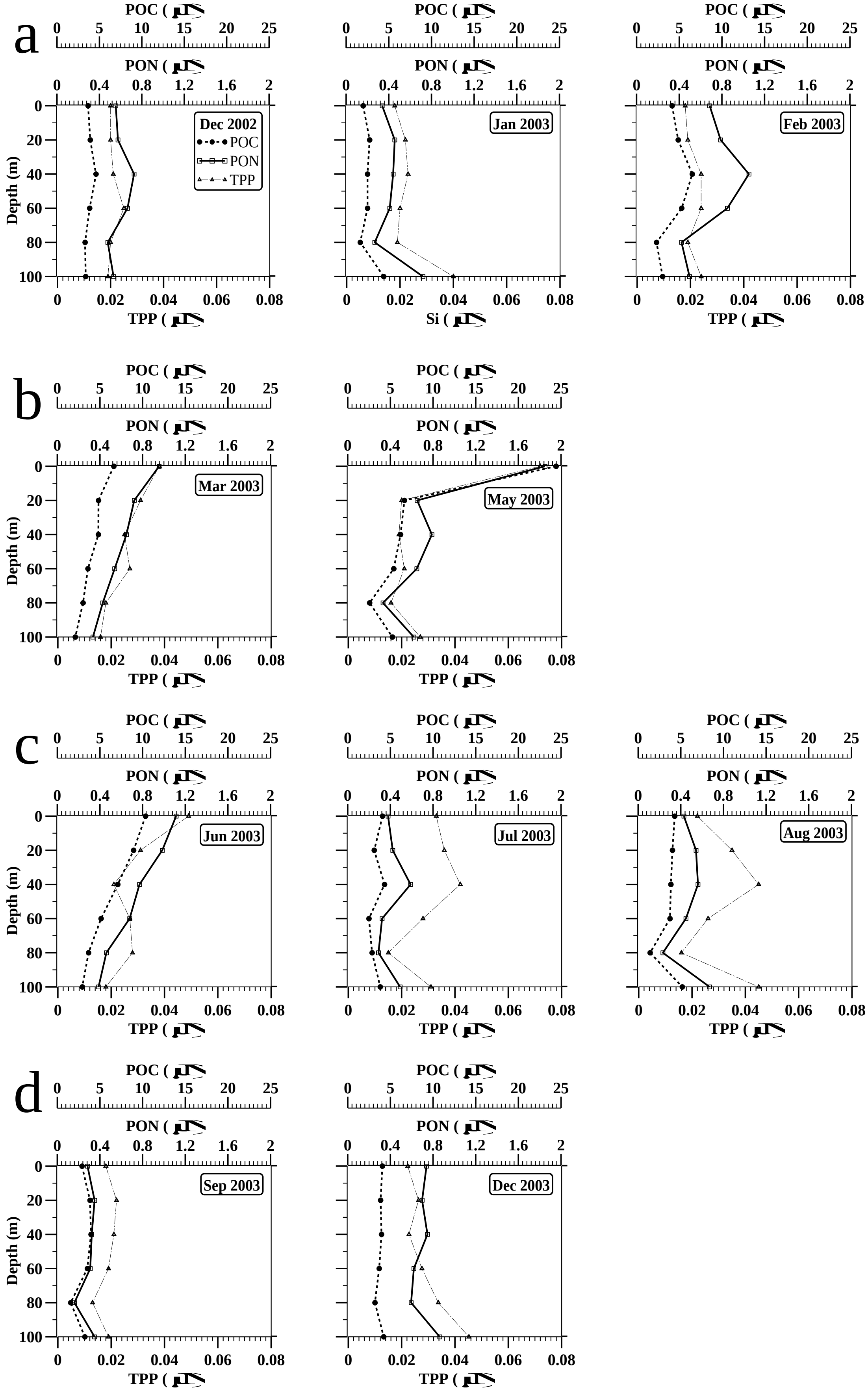


Figure 3.14.b Vertical profiles of particulate matter at the middle station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

Temporal PON profiles were similar to those of POC, declining in the EZ from 0.99 to 0.37 µM in September 2002 (Figure 3.14.a). Vertically uniform PON distributions were observed in December 2002-January 2003, ranging between 0.34-0.48 µM (Figure 3.14.b). However, PON concentration increased to levels of 0.69-1.05 µM in February. The spring PON displayed a decreasing profile in the EZ from 0.95 to 0.54 µM in March; this trend became more pronounced in May (Figure 3.14.b). The summer PON concentrations were variable in the EZ, fluctuating between 0.46 and 1.11 µM in June, and between 0.29-0.59 µM in July-August 2003 period. The PON in the EZ was still uniformly distributed in September (between 0.28-0.35 µM) and in December (0.62-0.75 µM) (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

In the autumn of 2002, TPP concentrations in the EZ dropped from 0.049 to 0.020 µM in September, but varied little between 0.013 and 0.019 µM in October and ranged between 0.031-0.046 µM in November (Figure 3.14.a). TPP had a broad maximum (0.046 µM) at 60 m in November. The TPP concentrations in the EZ were distributed almost uniformly with depth (~0.018-0.025 µM) in December 2002-February 2003 (Figure 3.14.b). In the spring and early-summer, TPP displayed a decreasing trend with depth in the EZ, from 0.038 to 0.025 µM in March, from 0.072 to 0.019 µM in May, from 0.049 to 0.021 µM in June, and from 0.042 to 0.015 µM in July 2003. An opposite trend was observed in August, rising from 0.022 to 0.045 µM in the EZ. However, a subsurface maximum in the range of 0.042-0.045 µM in July and August was recorded in the EZ. The TPP profile was vertically uniform (0.018-0.022 µM) in September; but it varied slightly in December 2003, with values of 0.022-0.028 µM in the EZ.

3.4.2.3 Shelfbreak station

Temporal variations of POM in the water column of the shelfbreak station are presented in Figures 3.15 and 3.16. Particulate concentrations in the surface waters of this station were expectedly lower than the values measured at the other two stations on the inner-shelf zone. POM concentrations measured in the water column ranged monthly from 1.0 to 20.49 µM for POC, 0.11 to 1.83 µM for PON, and 0.007 to 0.065 µM for TPP in 2002. Particulate concentrations varied between 1.41-18.07 µM for POC, 0.23-1.15 µM for PON, and 0.010-0.048 µM for TPP in 2003 (see Appendix C).

Figure 3.15 demonstrates that POC concentrations at the shelfbreak station varied from 2.07 to 18.07 μM in the surface water and from 0.98 to 10.21 μM in the near-bottom water during 2002-2003 period. In the winter of 2002, surface POC decreased from 8.75 μM in January to 3.82 μM in February, while deep POC ranged between 10.2 and 8.1 μM. In the spring, the surface POC concentrations varied slightly between 6.6-6.9 μM during March-May 2002. However, the near-bottom POC declined apparently from 7.04 μM in April to 4.87 μM in May 2002. In the summer, a slight rising trend was observed in the surface POC from 4.93 μM in June to 6.70 μM in August. In this period, the near-bottom POC was relatively low, ranging from 1.74 μM in June to 3.29 μM in July and then decreasing to 1.50 μM in August. In the autumn months, the surface POC dropped slightly from 3.51 μM in September to 2.16 μM in November. However, after decreasing from 3.85 μM in September to 0.98 μM in October, the near-bottom POC increased to 7.71 μM in November 2002. In the winter of 2003, both surface and near-bottom POC values reached the peak values of 7.40 and 16.59 μM in December 2002 (Figure 3.15). In January-March months, POC values remained almost unchanged at levels of 2.37-2.67 μM in the surface, 4.45-5.15 μM in the near-bottom water. A peak value of 18.07 μM in the surface water was recorded in May 2003. A contrary view appeared in the near-bottom water, decreasing from 3.64 μM in March to 1.70 μM in May. In summer months, the surface POC descended from 6.70 μM in June to 3.41 μM in August. However, the near-bottom POC varied slightly between 5.0-5.8 μM in June-July, and then displayed a maximum of 10.18 μM in August. The surface and near-bottom POC concentrations were very similar in September (2.76 μM and 2.45 μM); the former was 2.80 μM and the latter was 4.45 μM in December 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

PON contents of the surface and near-bottom water varied from 0.11 to 1.15 μM and from 0.13 to 1.68 μM in the course of 2002-2003 (Figure 3.15). Principally both POC and PON concentrations showed similar temporal changes; however, the surface PON displayed more fluctuations in 2002. Briefly, in the winter of 2002, surface PON decreased from 1.09 to 0.54 μM, whilst the near-bottom water concentrations remained at 0.90 μM level. In the spring-summer period, PON varied between 0.42-1.02 μM in the surface, but declined steadily from 0.67 to 0.21 μM in the near-bottom water. The near-bottom PON values were relatively low (0.14-0.32 µM) during June-July. In September and October, the surface PON values stayed constant (0.27 to 0.25 µM); then it dropped to 0.11 µM in November. The near-bottom PON exhibited a small decreasing trend during September and October period from 0.29 to 0.13 µM, and then increased to 0.67-0.51 µM in November and December 2002. The near-bottom PON displayed a maximum of 1.68 µM in December 2002. In the winter of 2003, the surface PON remained low between 0.49-0.62 µM (Figure 3.15). In the spring, while PON increased from the lowest (0.29 µM) to the peak value of 1.15 µM in the surface water, an opposite trend was observed in the near-bottom water, decreasing from 0.42 to 0.28 µM. The summer PON concentrations ranged between 0.59 and 0.43 µM in the surface water, showing an upward trend in the near-bottom water, reaching the peak value of 1.0 µM in August. Both surface and near-bottom PON concentrations increased in the late 2003 from 0.33-0.59 µM in September to 0.38-0.86 µM in December 2003 (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

TPP data obtained in the course of 2002-2003, show significant temporal variations, ranging from 0.009 to 0.060 µM in the surface, 0.008 to 0.064 µM in the near-bottom water (Figure 3.15). Monthly changes were more pronounced in the near-bottom water. In the winter of 2002, surface TPP decreased from 0.025 µM in January to 0.015 µM in February 2002, while the near-bottom concentration remained unchanged at about 0.038 µM. In the spring, TPP concentrations showed a similar increasing trend in April and May both in surface (0.018-0.026 µM) and near-bottom water (0.017-0.029 µM. The surface TPP concentrations varied little between 0.022-0.029 µM in the summer 2002 and decreased in October to 0.009 µM level. The near-bottom TPP data displayed a coherent maximum of 0.064 µM in September, and then declined to the lowest value of 0.008 µM in October 2002. TPP increased again in the surface and near-bottom water in November (0.034 and 0.039 µM). In the winter months of 2003, TPP decreased from 0.030 to 0.015 µM in the surface where in the near-bottom water TPP exhibited another peak of 0.060 µM in December 2002, and then dropped to 0.026 µM in January 2003. In the spring, TPP showed opposite trends. While the surface concentrations increased from 0.014 to 0.041 µM, near-bottom water TPP decreased from 0.023 to 0.012 µM in March-May.

In the summer, surface and near-bottom TPP were relatively low in June (0.015 and 0.036 µM), increasing in July (0.031 and 0.047 µM). Surface TPP remained relatively unchanged during the rest of the year (0.023 µM in September and 0.025 µM in December 2003) whereas the near-bottom TPP concentration varied between 0.025-0.034 µM (Figure 3.15).

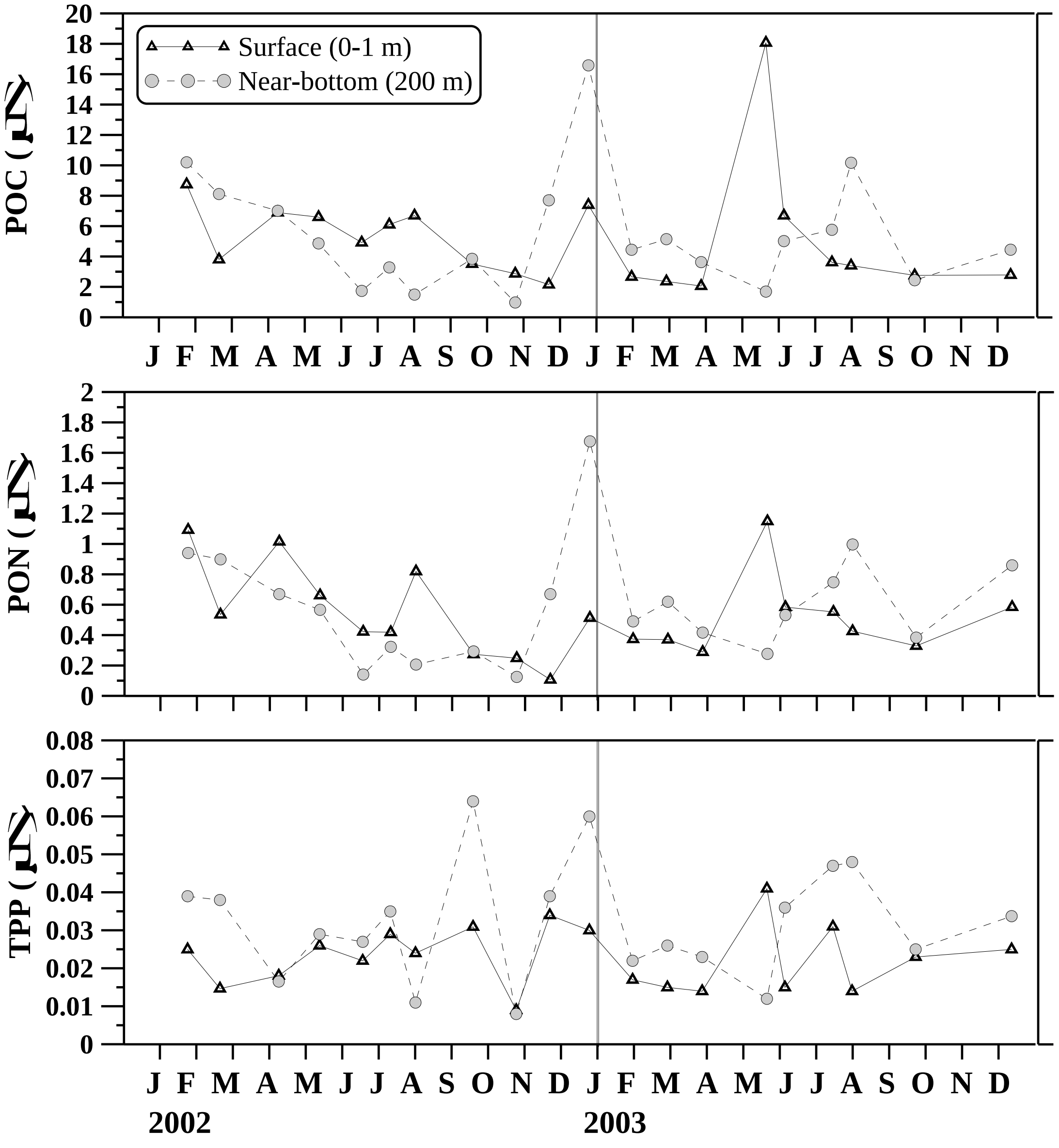


Figure 3.15 Monthly variations of POC, PON and TPP at the shelfbreak station between January 2002 and December 2003.

POM showed seasonal variations in the EZ, depending on nutrient input from different sources and primary production in the lighted zone. The EZ thickness varied monthly between 55-119 m (Table 3.4). POC concentrations in the EZ fluctuated between 8.75 and 7.17 µM in January 2002 (Figure 3.16.a), exhibiting a peak value of 20.49 µM at 25 m and then dropping to less than 10 µM at the bottom of the EZ. In February, POC ranged between 3.82-6.16 µM in the EZ. The spring POC profile showed an increasing trend (from 6.90 to 8.05 µM) in April, whilst an opposite trend (from 6.60 to 3.57 µM) appeared in May 2002. In the summer months, POC in the EZ varied from 2.89 to 5.49 µM in June, 2.88 to 6.11 µM in July and 3.60 to 6.70 µM August. In the autumn months, vertical changes in POC were relatively low, ranging from 2.1 to 5.6 µM. In the winter of 2003, POC concentrations were uniformly (~2 µM) distributed in the EZ (Figure 3.16.b). Similar vertical distribution was observed in March (1.75 to 2.91 µM). In May, POC decreased steeply from 18.07 µM in the surface to 1.75 µM at the base of the EZ. The summer POC profiles in the EZ fluctuated from 2.67 to 6.70 µM in June, 2.96 to 4.10 µM in July and 2.42 to 4.73 µM in August 2003. Higher POC was recorded in the bottom water. POC distribution showed similar trend in September and December, ranging between 2.22 to 4.57 µM in the EZ (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

PON profiles down to 200 m at the shelfbreak station are depicted in Figure 3.16, very consistent with variability of POC with depth. In the winter of 2002, PON decreased in the EZ with depth in January (1.09 to 0.80 µM). A vertically homogeneous profile appeared in February, at levels of 0.54-0.58 µM in the EZ (Figure 3.16.a). In the spring, PON concentrations showed variations in the EZ, ranging between 0.93 and 1.44 µM in April, 0.23 and 0.66 µM in May; and then it varied from 0.23 to 0.82 µM in the summer. In the autumn, PON in the EZ fluctuated between 0.25 to 0.54 µM in September-October and 0.11 to 0.44 µM in November 2002. PON concentrations in the EZ ranged between 0.29 and 0.51 µM during December 2002-February 2003 (Figure 3.16.b). The spring profiles were similar to winter features in March (0.027 to 0.039 µM). The summer PON contents of the EZ water varied from 0.30 to 0.59 µM in June, exhibiting a maximum (0.72 µM) below the EZ. In July, the PON in the EZ was distributed uniformly between 0.47-0.59 µM, decreasing slightly to 0.3-0.4 µM level in August. Then, it ranged from 0.25 to 0.42 µM in September, rising to 0.52-0.65 µM in December 2003, exhibiting vertically uniform profiles (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department).

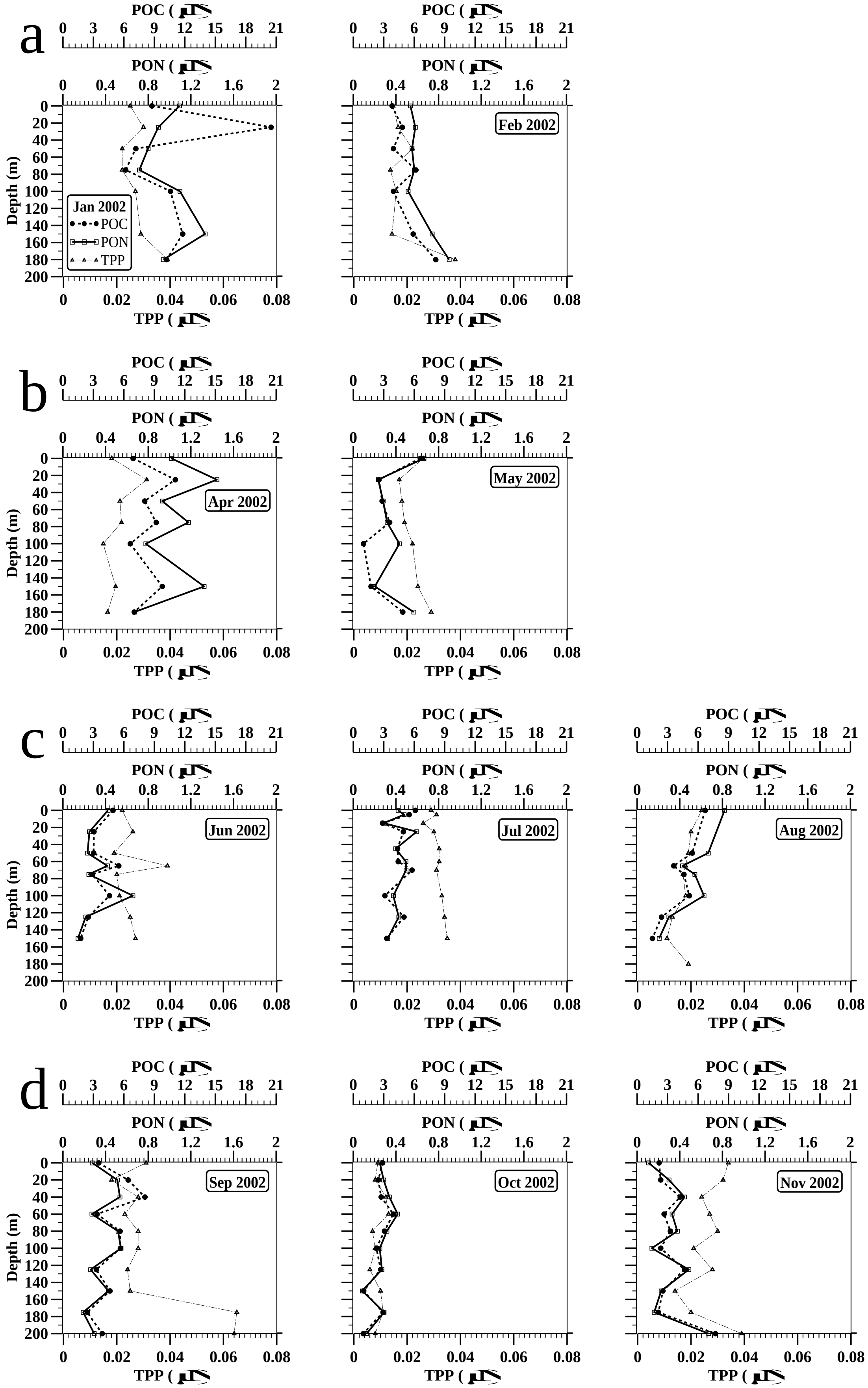


Figure 3.16.a Vertical profiles of particulate matter at the shelfbreak station in 2002 (a: Winter, b: Spring, c: Summer, d: Autumn).

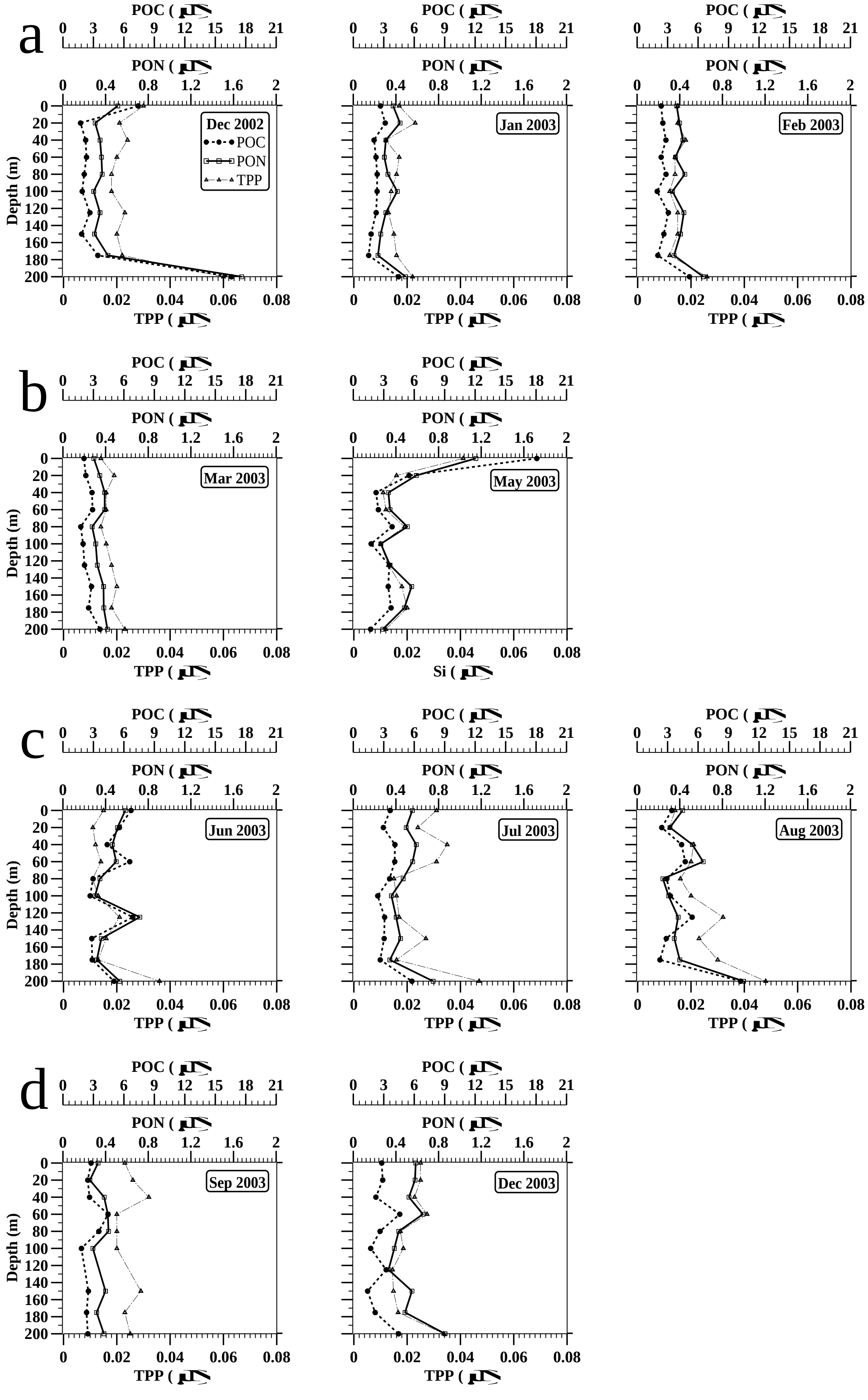


Figure 3.16.b Vertical profiles of particulate matter at the shelfbreak station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn)

Figure 3.16 demonstrates the vertical profiles of TPP in the shelfbreak zone. Depth distributions of TPP in the EZ were almost uniform, ranging between 0.022-0.030 µM in January, and between 0.014-0.022 µM in February (Figure 3.16.a). Below the EZ, TPP concentrations increased to levels of 0.039 µM in January, 0.038 µM in February. The April profile was almost same as the winter feature, varying from 0.018 to 0.031 µM in the EZ. However, in May, the concentration was slightly high in the surface (0.026 µM), declining to 0.019 µM at the bottom of the EZ. In summer, TPP distributed uniformly in the EZ (~0.022 µM), ranging between 0.018-0.033 µM. In the autumn, the TPP contents of the EZ water were at levels of 0.018-0.031 µM in September, decreasing to 0.007-0.013 µM in October and then rising again to 0.021-0.034 µM levels in November. In this period, TPP displayed an increasing trend in the bottom water to 0.039-0.064 µM levels. In the winter of 2003, TPP distribution was vertically uniform in the well-mixed water column, ranging between ca. 0.014 to 0.017 µM in the EZ (Figure 3.16.b). TPP concentrations in the EZ were high and slightly variable in December 2002, rising to 0.060 µM in the bottom water. TPP concentrations in March were similar within the EZ (~0.016 µM) and then partly increased in the bottom water (0.023 µM). In May, TPP was apparently high (0.041 µM) in the surface water, declining to 0.010 µM at the base of the EZ. In the summer, TPP concentrations were variable in the EZ, ranging between 0.011-0.035 µM. It was high in the bottom water, fluctuating between 0.036-0.048 µM. TPP contents of the water column were almost constant during the remaining of the year, ranging between 0.020-0.027 µM. However, bottom water values were as high as 2.0-2.5 µM in December 2003.

3.5 Evaluation of Phosphorus Fractions

Time-series data of total phosphorus fractions in seawater (total phosphorus, total dissolved phosphorus, dissolved inorganic phosphate, dissolved organic phosphorus, total particulate phosphorus, particulate inorganic phosphorus, particulate organic phosphorus) collected at 3 stations on the NE shelf zone off Erdemli, between January 2002 and December 2003, are presented here.

3.5.1 Nearshore station

Monthly measurements of different forms of total phosphorus in the water column (only surface and 5-10 m depth) of the nearshore station are depicted in Figures 3.17 and 3.18, indicating prominent fluctuations with time and depth.

The nearshore station visited in this study was directly influenced by the small Lamas River. Table 3.2 shows this freshwater source has high total phosphorus (TP) and thus its components during wet periods, after heavy rains in the region, as experienced in April 2003. Contributions of dissolved and particulate phosphorus to TP were nearly similar. However, in dry period TP was relatively low in the Lamas River water, TDP became the major constituent of TP (Table 3.2). The annual averages of POC/PON and POC/POP ratios in the river water were estimated as 14 and 206, respectively.

Concentration ranges of different forms of phosphorus in the nearshore water for the period of 2002 were between 0.207-0.430 µM for TP, 0.124-0.300 µM for TDP, 0.055-0.245 for DOP, 0.011-0.044 µM for POP, 0.003-0.069 µM for PIP, 0.009-0.058 µM for DIP and, 0.013-0.049 µM for TPP in the water column (Appendix D). In 2003, they ranged between 0.117-0.270 µM for TP, 0.092-0.243 µM for TDP, 0.051-0.219 µM for DOP, 0.024-0.136 µM for POP, 0.002-0.028 µM for PIP, 0.033-0.230 µM for DIP and, 0.026-0.153 µM for TPP.

Figure 3.17 shows that surface and near-bottom water TP concentrations varied seasonally from 0.243 to 0.430 µM and 0.207 to 0.396 µM, respectively in 2002; they were between 0.198-0.396 µM and 0.225-0.360 µM, respectively, in 2003. The surface TP values for 2002 were consistently greater than the near-bottom water concentrations, displaying coherent maximum of 0.4 µM in May 2002. Then they declined to minimal levels of 0.2 µM in September-October months. TP concentrations increased to levels of 0.3 µM in December 2002. In the winter of 2003, the surface TP kept increasing from 0.333 to 0.396 µM. However, near-bottom TP dropped from 0.306 to 0.270 µM in December 2002-January 2003 period, then increased again to 0.324 µM in February 2003. In spring, the surface TP concentration was still high (0.378 µM) in March; then a steep decrease to 0.2 µM level was observed in April, followed by an increasing trend in May-June period. Near-bottom TP ranged from 0.360 μM in March to 0.288 μM in May 2003. In summer, TP in the surface water displayed a peak of 0.351 μM in June; then it decreased slightly from 0.288 to 0.243 μM in July-August and 0.225 to 0.198 μM in September-December 2003. Near-bottom TP was low (0.270 μM) in June; it ranged between 0.297-0.306 μM in the period of July-December 2003 (Figure 3.17).

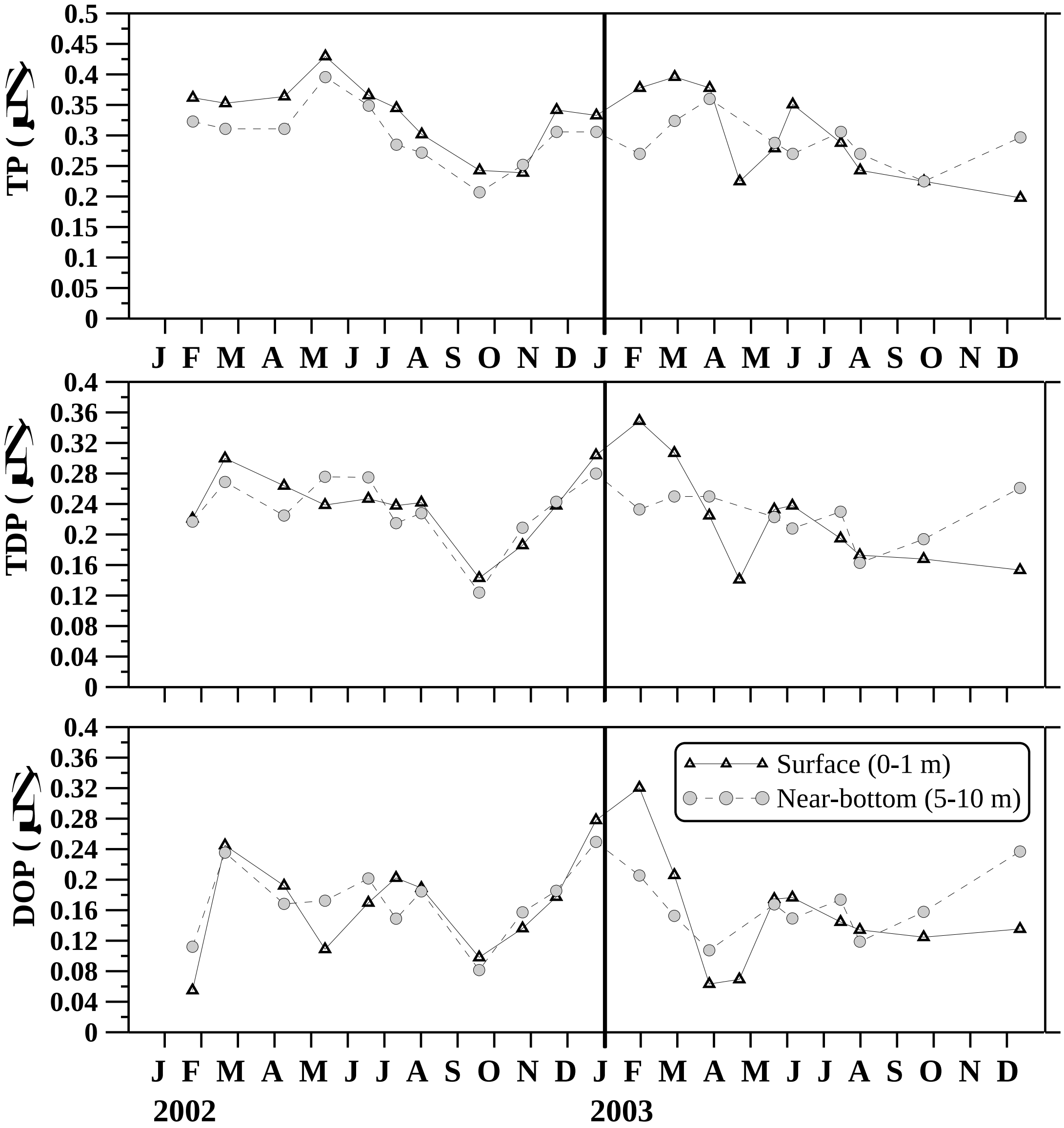


Figure 3.17 Monthly variations of TP, TDP and DOP at the nearshore station between January 2002 and December 2003.

Temporal variations of TDP concentrations in the surface and near-bottom waters were very similar to TP changes, ranging between 0.143 and 0.300 μM and 0.124

and 0.276 μM for 2002; 0.198-0.396 μM and 0.225-0.360 μM for the period of 2003 (Figure 3.17). In the winter-spring of 2002, TDP was relatively high in the surface (0.221 to 0.300 μM) and near-bottom waters (0.217 to 0.276 μM). In the summer, an apparent decrease in TDP concentrations was observed in the surface (0.247 to 0.238 μM) and near-bottom waters (0.275 to 0.215 μM) in June-July period. In August, TDP increased to 0.242 μM in the surface and 0.228 μM in the near-bottom water. In September, TDP dropped to its lowest levels of 0.12-0.14 μM in the surface and near-bottom waters. In autumn, an increasing trend in TDP was noted, ranging from 0.143 to 0.238 μM in the surface and 0.124 to 0.243 μM in the near-bottom water. The surface TDP was displayed a maximum of 0.349 μM in January 2003, then a coherent minimum in April, followed by an increase to 0.233 μM in May. The near-bottom TDP was also high in January-February 2003, keeping its high level (0.25 μM) in March. During April-December 2003, slightly varying concentrations of TDP were recorded (Figure 3.17).

Surface and near-bottom DOP concentrations varied seasonally in the shallow zone, ranging from 0.055 to 0.245 μM and 0.082 to 0.236 μM respectively in 2002, and between 0.063-0.321 μM and 0.108-0.250 μM respectively in 2003 (Figure 3.17). In the winter of 2002, the surface DOP increased almost fivefold from 0.055 μM in January to 0.245 μM in February, whereas changes were about twofold in the near-bottom water (0.112 to 0.236 μM). In the spring, DOP variation in the surface (0.109 to 0.192 μM) was different from the concentration changes in near-bottom water (0.168 to 0.173 μM). In the summer, the surface (0.170 to 0.202 μM) and near-bottom water concentrations (0.149 to 0.202 μM) showed a fluctuation trend. The surface and near-bottom DOP concentrations were at the lowest levels (0.098 and 0.082 μM) in September, and then displayed a pronounced increasing trend by January 2003. The surface DOP was at the highest level (0.321 μM) in January 2003, while DOP in the deep water concentration was about 0.206 μM. DOP concentrations in the water column dropped dramatically from late-winter to early-spring of 2003. In following months, the concentrations increased to 0.175 μM in the surface and 0.168 μM in the near-bottom waters. In the summer of 2003, the surface DOP showed a slight decrease to 0.134 μM, then remained almost constant (0.12 μM) in the autumn. The near-bottom DOP exhibited an apparent increase from 0.119 μM in August to 0.257 μM in December 2003 (Figure 3.17).

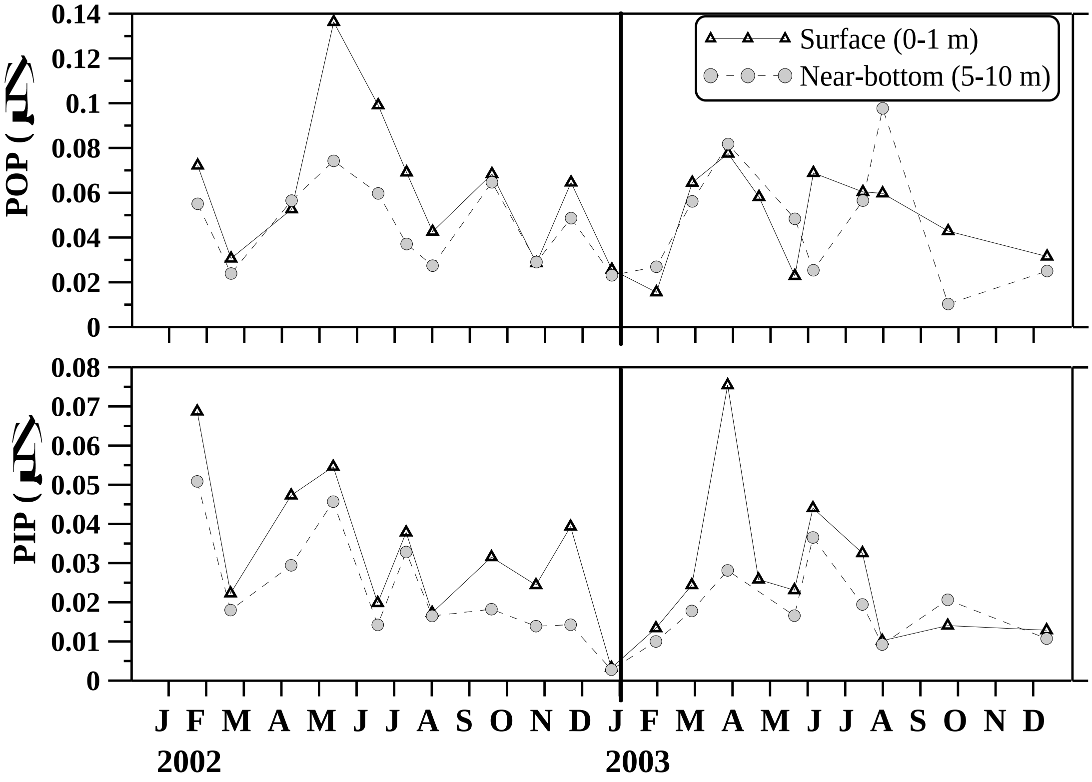


Figure 3.18 Monthly variations of POP and PIP at the nearshore station between January 2002 and December 2003.

POP concentrations were highly variable with season, ranging between 0.016 and 0.136 µM in the surface and between 0.010 and 0.098 µM in the near-bottom water in 2002-2003 (Figure 3.18). Winter data showed a decreasing trend in the surface (0.072 to 0.031 µM) and the near-bottom water (0.055 to 0.024 µM). The spring values were similar (0.053 and 0.057 µM) in March, reaching the peak values of 0.136 and 0.074 µM respectively in May. In summer, a steep decrease was seen in the water column concentration from 0.099 to 0.043 µM in the surface and from 0.060 to 0.027 µM in the near-bottom water. The autumn POP values fluctuated between 0.029 and 0.068 µM in the water column. The surface POP increased from 0.016 µM in January to 0.078 µM in March 2002; then a decreasing trend was recorded in May. In the summer-autumn period, the surface POP displayed a steady decreasing trend from 0.069 to 0.032 µM by December 2003. However, fluctuating near-bottom water concentrations displayed a maximum of ~0.1 µM in August 2003, and then a decreasing trend to levels of 0.01-0.02 µM in late autumn (Figure 3.18).

Seawater PIP concentrations highly fluctuated with season at the nearshore station, ranging from 0.003-0.075 µM in the surface water and 0.003-0.051 µM in the near-bottom water during 2002-2003 (Figure 3.18). The surface and near-bottom PIP were as low as 0.02-0.07 µM in January-February 2002 period. In the spring, PIP enhanced again to 0.047-0.055 µM level in the surface and to 0.029-0.046 µM level in the near-bottom water. PIP concentration that was depleted in June (0.020 µM in the surface, 0.014 µM in the near-bottom) increased to the levels of 0.033-0.038 µM in July and then declined to about 0.017 µM in August. In the autumn, surface and near-bottom PIP showed a decreasing trend from 0.032 to 0.024 µM and from 0.018 to 0.014 µM respectively during September-October 2002. The surface PIP reached to 0.039 µM and near-bottom PIP remained unchanged (0.014 µM) in November 2002. In December 2002, both surface and near-bottom PIP dropped to the lowest value of 0.003 µM. The winter 2003 values of PIP increased to 0.024 µM level in the surface and to 0.018 µM level in the near-bottom waters. The surface and near-bottom PIP values reached the maximum levels of 0.075 and 0.028 µM respectively in March; then it dropped to 0.023 and 0.017 µM in May 2003. The summer concentrations ranged from 0.033 to 0.044 µM in the surface and between 0.019 and 0.037 µM in the near-bottom water during June-July 2003. They were very low (0.010 µM and 0.009 µM) in August, and then increased slightly to the levels of 0.014 and 0.021 µM in September 2003. The water column concentrations were almost similar (0.013 and 0.011 µM) in December 2003 (Figure 3.18).

Monthly distributions of DIP and TPP in the nearshore station were previously evaluated in the Section 3.4.1.1 and 3.4.2.1, respectively (Figures 3.7 and 3.12); they expectedly showed remarkable temporal variations.

3.5.2 Middle station

Time series data of different forms of total phosphorus measured at the middle station are depicted in Appendix D. Seasonal fluctuations of P-fractions in the water column of the middle station are presented in Figures 3.19 to 3.21.

Concentrations of total-P in the water column ranged between 0.117 and 0.288 µM for 2002-2003. In this period, the dissolved and particulate constituents of TP varied from 0.092 to 0.243 µM for TDP, 0.051 to 0.246 µM for DOP, 0.005 to 0.054 µM for POP, 0.002 to 0.028 µM for PIP, 0.009 to 0.068 µM for DIP, and 0.013 to 0.070 µM for TPP (see Appendix D).

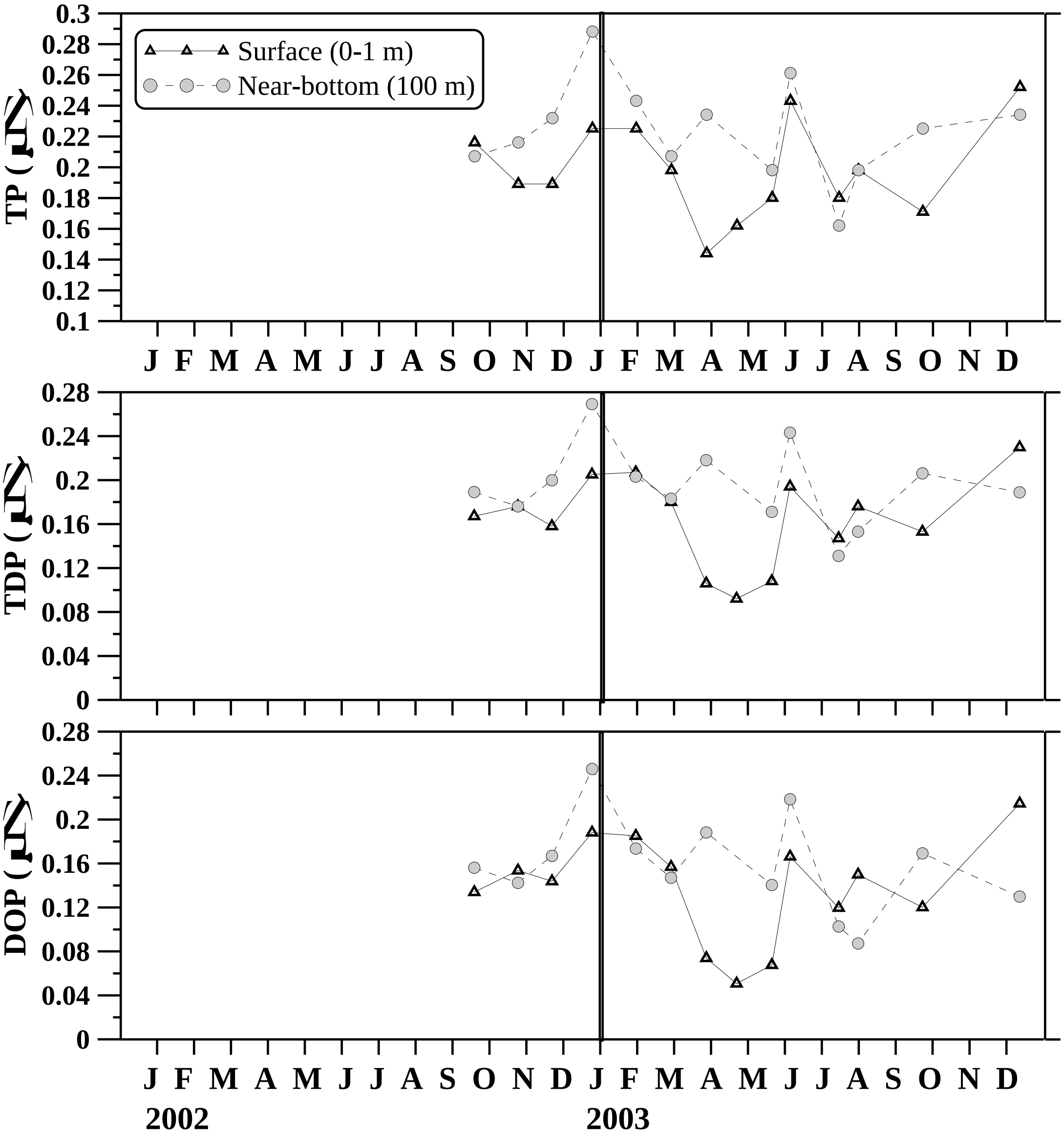


Figure 3.19 Monthly variations of TP, TDP and DOP at the middle station between September 2002 and December 2003.

Figure 3.19 shows that TP varied between 0.189 and 0.216 µM in the surface water and between 0.207-0.232 µM in the near-bottom water during the autumn of 2002. The surface TP ranged from 0.144 to 0.252 µM, whereas the near-bottom TP values were between 0.162 and 0.288 µM in 2003. The surface TP remained unchanged (0.189 µM) during October-November 2002 period, which was less than the near-bottom water values (0.216-0.232 µM). The surface TP decreased slightly from 0.225 µM in December 2002 to 0.198 µM in February 2003; a similar trend (0.288 to 0.207 µM) was observed in the near-bottom water. A steep increase was observed from 0.144 µM in March to 0.243 µM in June, then the surface TP declined to

0.180-0.198 μM during July-August 2003 period. In September, TP in the surface (0.171 μM) was less than the near-bottom TP concentration (0.225 μM).

TDP concentration varied between 0.092 and 0.230 μM in the surface water, and between 0.103 and 0.269 μM in the near-bottom water during 2002-2003 (Figure 3.19). TDP changes were consistent with that of TP. A winter maximum of 0.2 μM was observed in January 2003. However, in February, surface and near-bottom TDP values dropped to levels of about 0.18 μM. The surface values decreased steeply in the spring, forming a minimum of 0.092 μM in April 2003. The surface TDP enhanced again to 0.19 μM levels in summer months. The deep TDP ranged between 0.131 and 0.243 μM during spring-autumn of 2003, with an apparent decrease in July. In September-December period, the surface TDP fluctuated between 0.153 and 0.230 μM, exceeding the annual mean of 0.18 μM in December 2003.

The DOP contents of the water column varied seasonally between 0.051 to 0.215 μM in the surface and between 0.087 and 0.246 μM in the near-bottom water during 2002-2003 (Figure 3.19), with the average values of 0.14 and 0.16 μM respectively for this period. The surface DOP increased from 0.134 μM in September to 0.19 μM in December 2002-January 2003 period. A similar trend was observed in the near-bottom water, displaying a maximum of 0.246 μM in December 2002. The near-bottom concentrations fluctuated between 0.087 and 0.219 μM in 2003. The surface DOP displayed a marked decrease to levels of 0.051-0.074 μM in the spring, then a rising trend to levels of 0.120-0.166 μM in summer and reached to 0.215 μM level in December 2003.

Seasonally variable POP concentrations ranged between 0.010-0.054 μM for the surface and 0.008-0.035 μM for the near-bottom water in the course of 2002-2003 (Figure 3.20). In the autumn of 2002, while POP decreased in the surface from 0.044 μM in September to 0.011 μM in October, it increased in the near-bottom water from 0.014 to 0.035 μM. In November, it remained unchanged (0.026 μM) in the surface and near-bottom water. The surface POP declined to minimal levels of 0.01 μM in January-February 2003. The near-bottom POP fluctuated between 0.017 and 0.031 μM in winter. In the spring, a steep increase of 0.054 μM was observed in April; then it decreased from 0.044 μM in May to 0.015 μM in August.

However, the near-bottom POP concentration was highly variable in 2003, rising to about 0.035 µM in August and December 2003.

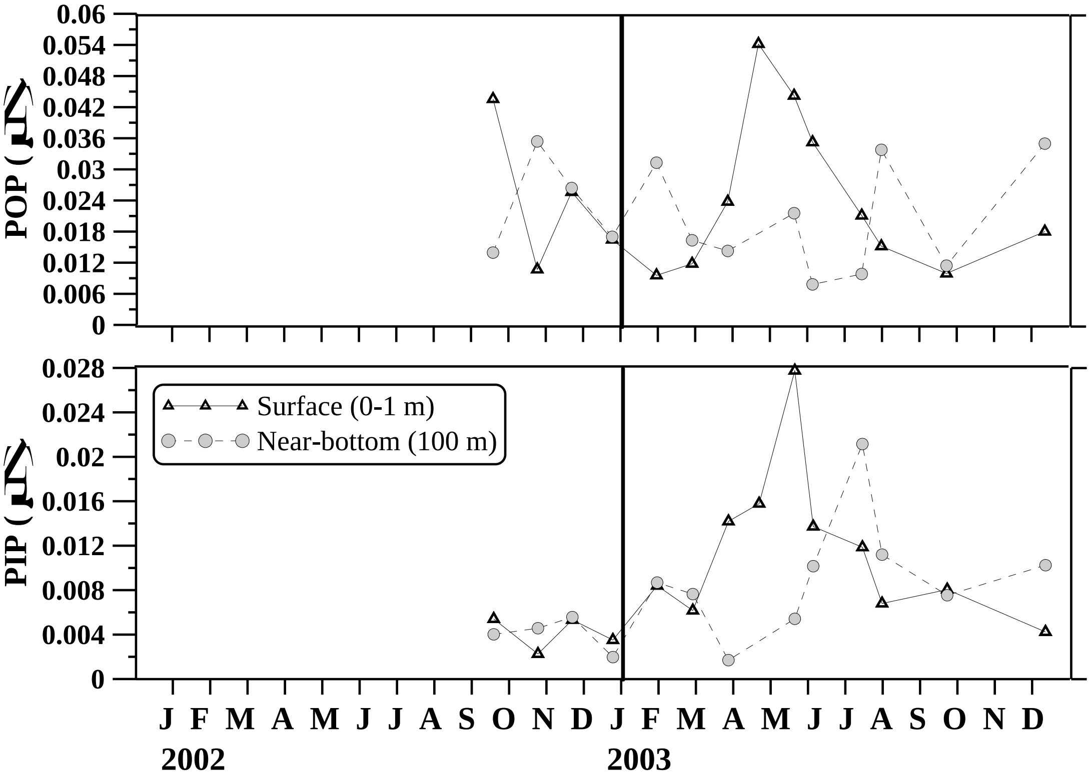


Figure 3.20 Monthly variations of POP and PIP at the middle station between September 2002 and December 2003.

The surface and near-bottom water PIP was relatively low, ranging between 0.002 and 0.005 µM, and from 0.004 to 0.006 µM, respectively, during the autumn of 2002 (Figure 3.20). However, PIP varied apparently from 0.004 to 0.028 µM in the surface and between 0.002 and 0.021 µM in the near-bottom water in 2003. The surface and near-bottom PIP concentrations were very low (0.002-0.004 µM) in December 2002, but they increased to 0.008-0.009 µM level in January 2003, and then declined to the level of 0.006-0.008 µM in February. In the spring, PIP showed an apparent rise in the surface water from 0.014 to 0.028 µM, whereas the near-bottom concentration remained at minimal levels (0.002-0.005 µM). After reaching the peak level in May 2003, a steep decrease (0.014 to 0.007 µM) was observed in the PIP contents of surface water. The near-bottom PIP was 0.010 µM in June, rising to the highest value of 0.021 µM in July, and then decreased the June's level (0.011 µM). In September, surface and near-bottom PIP values were very similar (0.008 µM). In December 2003, the PIP concentrations increased from the surface (0.004 µM) to the near-bottom water (0.010 μM), which were comparable with the average (0.007 μM) for the study period (Figure 3.20).

The fractions of phosphorus showed remarkable fluctuations in the EZ waters (Figure 3.21). The September 2002 TP profile in the EZ decreased with depth from 0.216 μM in the surface to 0.153 μM at the bottom of the EZ; however, an opposite feature was observed in November, increasing from 0.189 to 0.230 μM (Figure 3.21.a). Depth profiles of the EZ descended slightly in January 2003 (0.225 to 0.207 μM) and February (0.198 to 0.166 μM) (Figure 3.21.b). The March TP concentration ranged from 0.144 to 0.178 μM in the EZ. In May, an apparent decrease was observed from the surface to the base of the EZ. The summer TP values in the EZ increased in June (0.221 to 0.270 μM) and then declined in August (0.198 to 0.171 μM). In September, higher concentrations were determined towards the bottom of the EZ (0.171 to 0.202 μM). In December 2003, TP fluctuated slightly between 0.207 and 0.252 μM in the EZ.

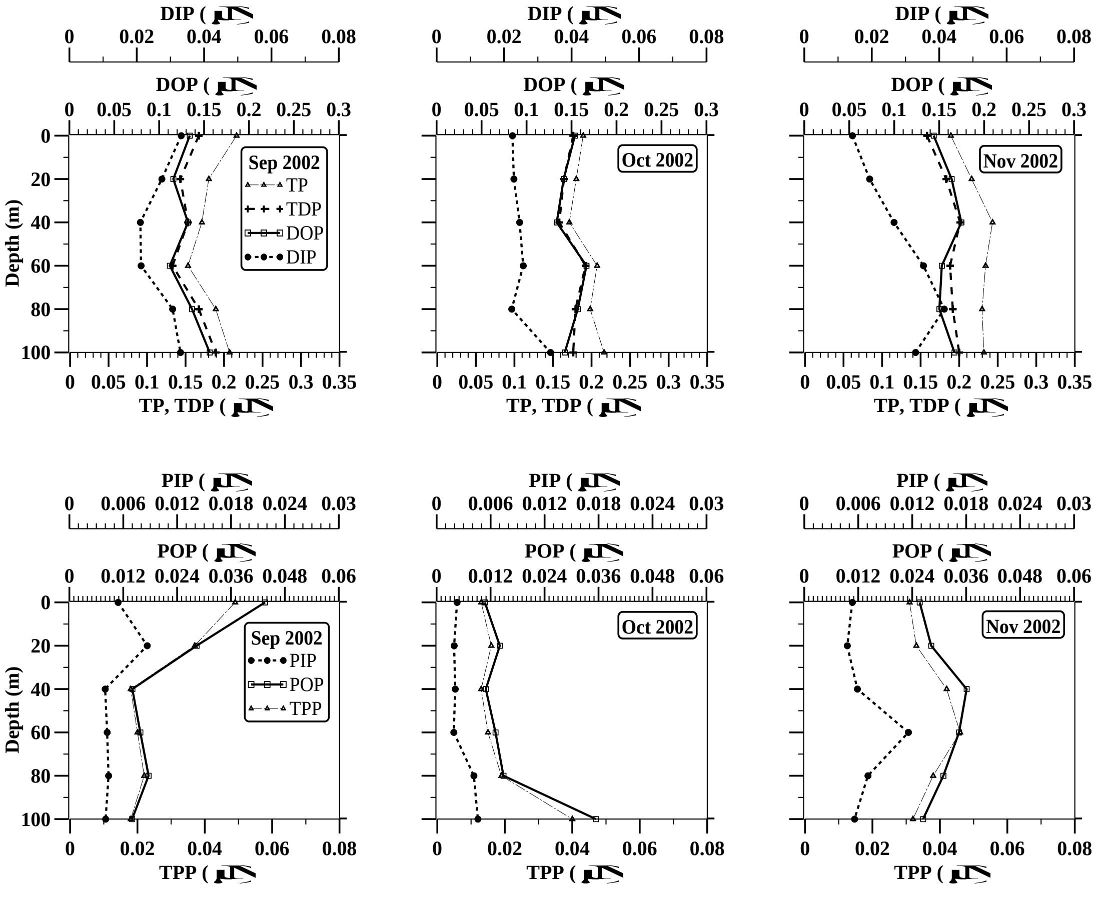


Figure 3.21.a Vertical profiles of fractions of phosphorus at the middle station in the autumn of 2002.

In the autumn of 2002, the TDP in the EZ decreased from 0.167 μM in the surface water to 0.133 μM at the EZ boundary in September 2002, remaining at levels of 0.158-0.192 μM in October, and then showing an increasing trend between 0.158 and 0.201 μM in November (Figure 3.21.a). TDP distribution in the EZ was almost uniform in December 2002 (0.178 to 0.214 μM), showing a decreasing trend in January (0.207 to 0.187 μM) and February 2003 (0.180 to 0.142 μM) (Figure 3.21.b). The spring profile displayed an opposite trend in the EZ, increasing from 0.106 to 0.151 μM in March. In summer, TDP concentrations were variable in the EZ, ranging between 0.194 and 0.242 μM in June, between 0.147 and 0.180 μM in July, and from 0.126 to 0.176 μM in August 2003. TDP contents of the EZ increased from 0.153 μM to 0.181 μM in September, and then descended from 0.230 to 0.184 μM in December 2003 (Figure 3.21.b).

Figure 3.21.a demonstrates that DOP concentrations in the EZ ranged between 0.112 and 0.167 μM during September-November 2002 that were not much different from the surface mean of 0.138 μM for 2002-2003. DOP expectedly displayed a temporal change similar to TP and TDP in the EZ; it increased in December 2002 (0.162 to 0.195 μM) and then descended in January 2003 (0.185 to 0.166 μM) and February (0.157 to 0.120 μM) (Figure 3.21.b). The spring DOP distribution in the EZ showed an increasing trend in March (0.074 to 0.135 μM) and May (0.068 to 0.081 μM). The summer-early autumn period DOP concentrations ranged between 0.166-0.215 μM in June, 0.120-0.154 μM in July, and from 0.080 to 0.150 μM in August. An opposite trend was observed from the surface to the boundary of the EZ in September (0.120 to 0.153 μM) and December 2003 (0.215 to 0.181 μM).

The POP concentrations in the EZ ranged between 0.011-0.044 μM in the autumn of 2002 (Figure 3.21.a). The winter POP values in the water column varied monthly from 0.010 to 0.031 μM, but had uniform distribution with depth in the EZ. It exhibited a decreasing trend in March (0.024 to 0.014 μM) and May 2003 (0.044 to 0.022 μM). The summer POP concentrations were variable in the EZ, ranging between 0.005-0.035 μM; it was almost uniform in September (from 0.010 to 0.013 μM) and December 2003 (0.018 to 0.021 μM) (Figure 3.21.c).

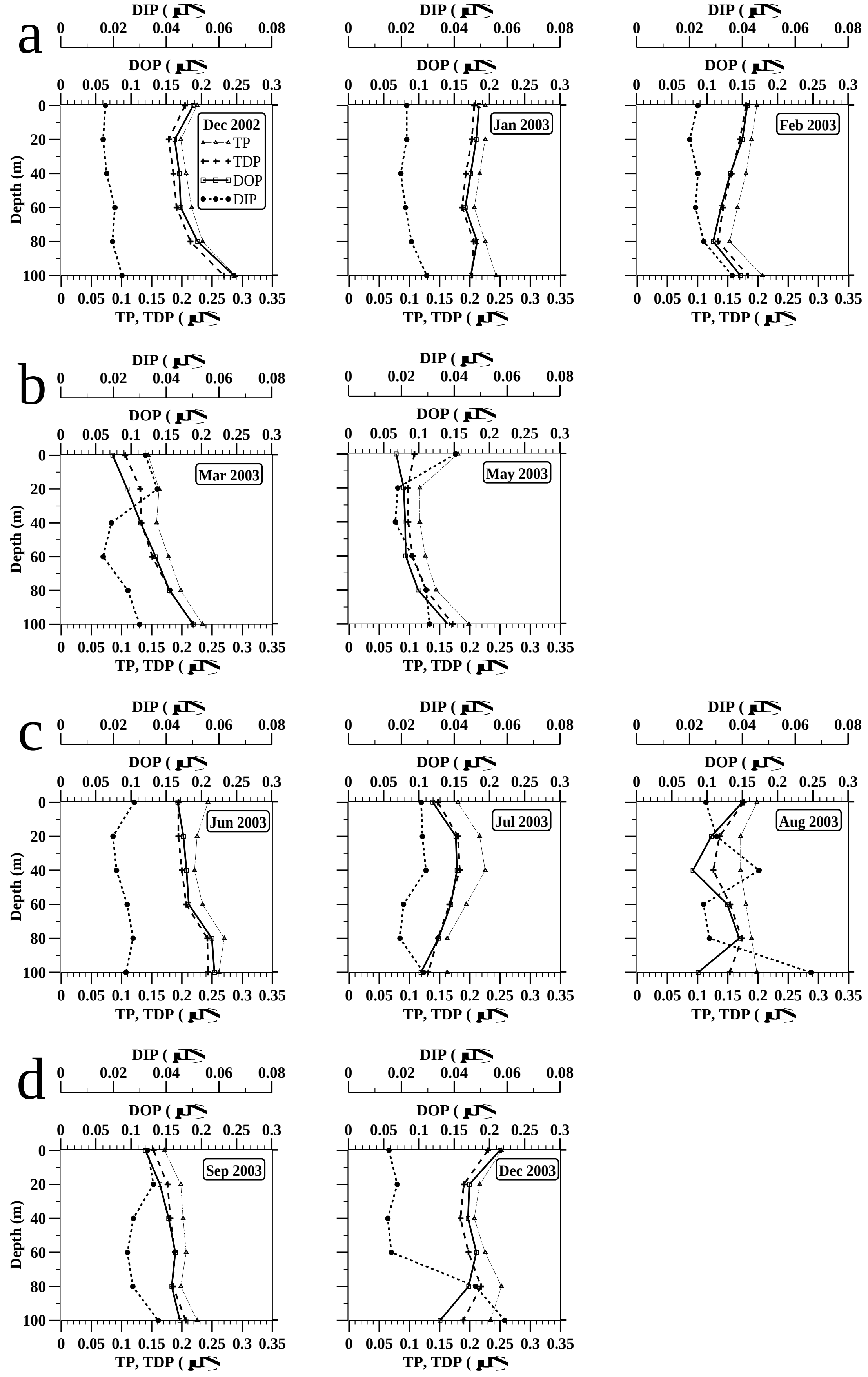


Figure 3.21.b Vertical profiles of fractions of phosphorus at the middle station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn)

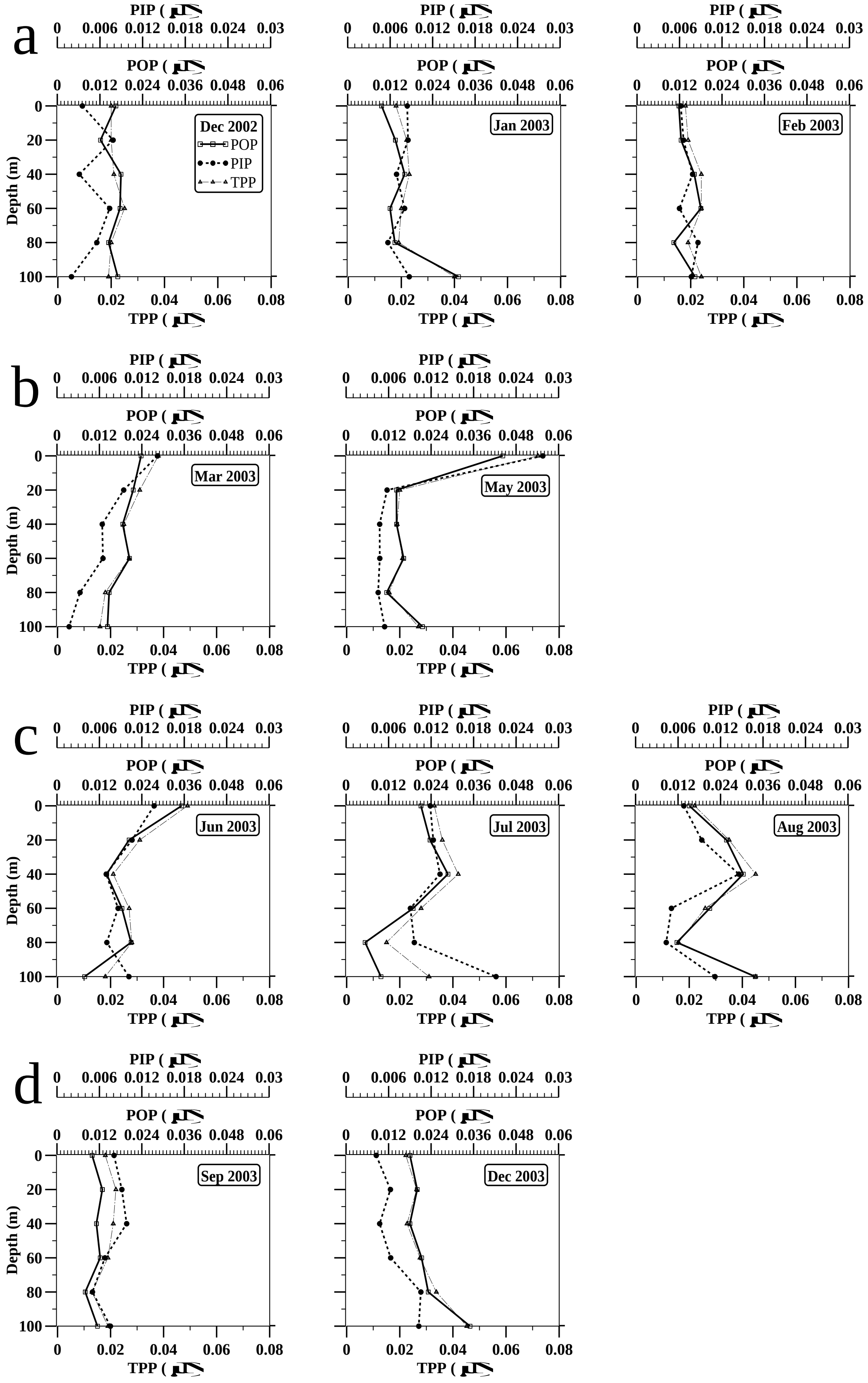


Figure 3.21.c Vertical profiles of fractions of phosphorus at the middle station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

In the autumn of 2002, PIP remained almost constant (~0.005 μM) in the EZ where it ranged between 0.002 and 0.004 μM in October, 0.005 and 0.012 μM in November (Figure 3.21.a). PIP values in the EZ ranged between 0.003 and 0.008 μM in December 2002, increasing to 0.006-0.009 μM level in January and February 2003, when the water column was well mixed (Figure 3.21.c). In the spring, PIP concentration decreased from the surface to the boundary of the EZ in March (0.014 to 0.007 μM). After decreasing in the EZ; the concentrations remained unchanged down to the bottom water in May 2003. The summer concentrations displayed a decreasing trend in the EZ from 0.014 to 0.007 μM in June, 0.013 to 0.009 μM in July, and rising in the bottom water (0.010 μM in June and 0.021 μM in July). In August, PIP was low (0.005 to 0.015 μM) in the EZ, but almost homogeneous in the entire water column (0.007-0.008 μM) in September. The concentrations were still low in the EZ (0.004 to 0.006 μM), slightly increasing to 0.010 μM in the near bottom water in December 2003 (Figure 3.21.c).

Temporal and depth distributions of DIP and TPP at the middle station are evaluated extensively in Sections 3.4.1.2 and 3.4.2.2, respectively.

3.5.3 Shelfbreak station

Concentrations of different forms of total phosphorus pool of the water column are given in Appendix D. TP in the water column ranged from 0.108 to 0.315 μM during 2002-2003. TDP and DOP were the major fractions of TP in the water column of the shelfbreak station. TDP fraction varied between 0.074-0.277 μM; whereas DOP fluctuated seasonally between 0.066-0.253 μM. Contents of the remaining P-fractions ranged from 0.006 to 0.065 μM for TPP, between 0.005-0.053 μM for POP, 0.001-0.027 μM for PIP, 0.006-0.068 μM for DIP. Temporal variations of P-fractions in the water column at the shelfbreak station are depicted in Figures 3.22 to 3.24.

TP concentrations in the surface water were consistently less than those in the near-bottom water. The surface TP varied from 0.108 to 0.260 μM (mean: 0.187 μM) where the near-bottom TP ranged between 0.132 and 0.315 μM (mean: 0.225 μM) for the period of 2002-2003 (Figure 3.22). They showed small temporal variability during winter-spring 2002. The surface TP decreased from spring to summer (0.238 to 0.157 μM); it displayed a minimum of 0.108 μM in late-autumn. However, the near-bottom TP displayed an increasing trend in autumn (0.189 to 0.279 μM). The surface and near-bottom TP values reached their highest level (0.234 and 0.315 μM) in December 2002; then they dropped to 0.117 and 0.216 μM level in spring, exhibiting small peaks in May 2003. They showed insignificant temporal changes by December 2003.

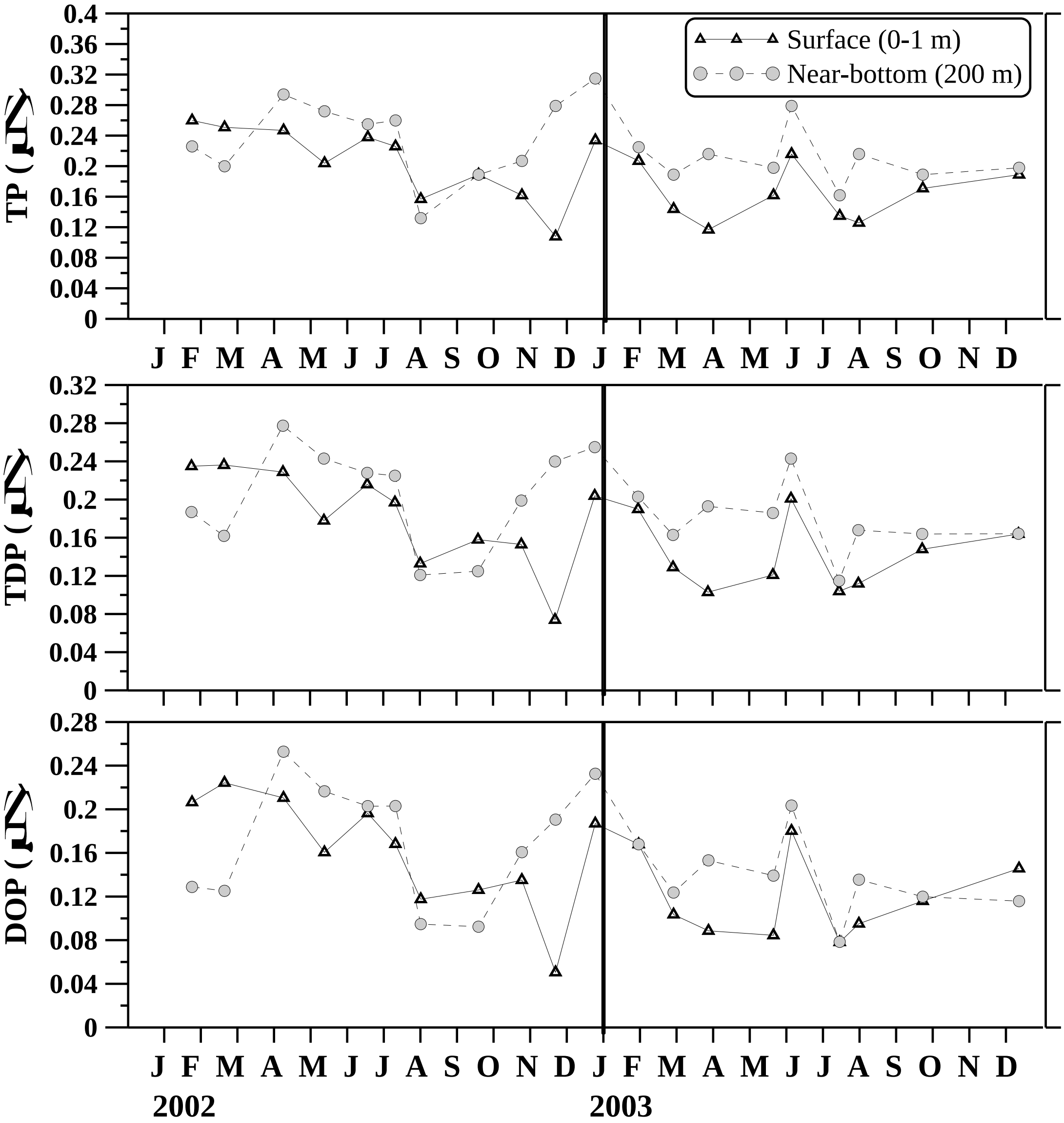


Figure 3.22 Monthly variations of TP, TDP and DOP at the shelfbreak station between January 2002 and December 2003.

The surface and near-bottom TDP concentrations ranged from 0.074 to 0.236 μM (mean: 0.164 μM) and 0.115 to 0.277 μM (mean: 0.193 μM) in 2002-2003 (Figure

3.22), consistent with temporal changes of TP. The surface TDP varied slightly between 0.178 and 0.236 µM in the winter-spring of 2002, whereas the near-bottom TDP displayed a coherent increase to 0.277 µM in April. In late summer, a declining trend was observed, ranging from 0.216 to 0.133 µM in the surface and 0.228 to 0.121 µM in the near-bottom water. The surface TDP decreased to a minimal level of 0.074 µM in November 2002 whilst the near-bottom TDP displayed an apparent increasing trend. TDP concentrations were relatively low in the spring of 2003, ranging between 0.103-0.121 µM in the surface and between 0.186-0.193 µM in the near-bottom waters. In 2003, the peak surface and near-bottom values were observed in June. In autumn, TDP displayed small temporal and spatial changes in the surface and the deep layer waters (0.148-0.164 µM) (Figure 3.22).

Surface and near-bottom DOP concentrations ranged between 0.051-0.224 µM (mean: 0.142 µM) and 0.079-0.253 (mean: 0.157 µM) during 2002-2003 (Figure 3.22). In the winter of 2002, DOP varied slightly between 0.207 and 0.224 µM in the surface water, but as low as 0.125-0.129 µM in the near-bottom water. The surface DOP displayed a decreasing trend from winter to autumn with small fluctuations. The lowest surface concentration (0.051 µM) was observed in November and then displayed a maximum in the winter of 2003. It decreased in the spring of 2003, followed by a sharp increase in June. The near-bottom DOP was relatively high in spring of 2002, then declining to minimal levels of 0.092-0.095 µM in August-September 2002. The DOP reached the peak level in winter 2003 in the surface water. Temporal changes in DOP were less pronounced in 2003, exhibiting a secondary peak (0.204 µM) in June and a minimum (0.079 µM) in July 2003. Then it was almost constant in autumn 2003 (0.120 µM) (Figure 3.22).

POP varied from 0.007 to 0.028 µM (mean: 0.017 µM) in the surface water and 0.007 to 0.053 µM (mean: 0.023 µM) in the near-bottom water in 2002-2003 (Figure 3.23). POP showed higher seasonal variations in 2002, reaching the highest surface values of 0.028 and 0.030 µM in September and November 2002 as the near-bottom POP values as high as 0.049 and 0.053 µM in September and December 2002. The surface and near-bottom water declined to the background levels of 0.011-0.017 µM in January-February 2003 and reached maximum values of 0.022 µM in July for the former and 0.037 µM in August 2003 for the latter.

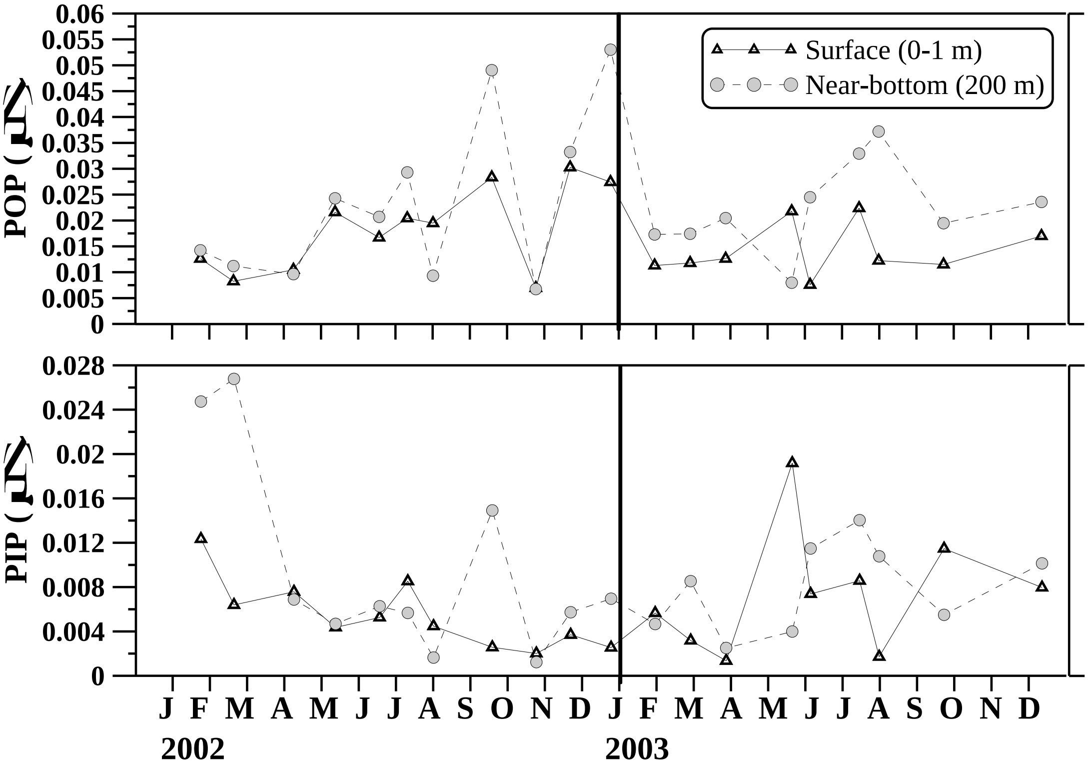


Figure 3.23 Monthly variations of POP and PIP between January 2002 and December 2003 at the shelfbreak station.

The surface and near-bottom PIP ranged from 0.001 to 0.019 µM (mean: 0.006 µM) and 0.001 to 0.027 µM (mean: 0.009 µM) in 2002-2003, mostly 0.010 µM level (Figure 3.23). The surface PIP concentrations dropped to the lowest levels of 0.002-0.004 µM in autumn 2002 and ascended to a maximum of 0.019 µM in May 2003. It fluctuated between 0.002 and 0.011 µM in spring-autumn 2003. The near-bottom water concentration of PIP was higher in winter 2002, declining to levels of 0.002-0.006 µM in summer 2002. A peak value of 0.015 µM was recorded in September 2002. The winter 2003 values were not much different from the average of 2002-2003. The near-bottom PIP increased to 0.014 µM in summer 2003 then dropped to levels of 0.006 µM in autumn 2003.

Concentrations of phosphorus fractions in the water column showed temporal variations in the EZ whose thickness ranged seasonally between 50 and 119 m (Table 3.4). In January 2002, TP concentrations were very similar in the EZ (0.255 to 0.260 µM), exhibiting a subsurface minimum of 0.213 µM at 25 m (Figure 3.24.a). In February, TP decreased slightly from 0.260 to 0.213 µM in the EZ and then to 0.200 µM in the deep water. In spring, TP in the EZ showed small increasing trend in

April (0.247 to 0.255 µM), and then an opposite trend in May (0.204 to 0.128 µM). In summer, TP in the EZ ranged from 0.230 to 0.268 µM in June, 0.191 to 0.255 µM in July and then dropped to 0.115-0.157 µM level in August 2002. In autumn, TP content of the EZ declined gradually from 0.189 to 0.126 µM in September; it was almost uniform, ranging between 0.162 and 0.198 µM in October, and then increased from 0.108 to 0.198 µM in November. In winter 2003, TP concentrations remained nearly constant in the EZ, between 0.207 and 0.234 µM in December 2002, in the range of 0.108 to 0.144 µM in February 2003 (Figure 3.24.b). However, it displayed a decreasing trend in January from 0.207 to 0.153 µM in the EZ, then forming a peak at 100 m. In March, TP concentrations ranged between 0.117 and 0.135 µM in the EZ. Then in May, TP varied from 0.153 to 0.180 µM in the EZ, which was partly enriched (0.207 to 0.270 µM) in June, then declined to levels of 0.117-0.170 µM in July, 0.126-0.171 µM in August. The bottom water TP concentrations fluctuated between 0.162 and 0.279 µM in summer months. Then, TP contents of the EZ for autumn period were in the range of 0.171-0.225 µM in September and December 2003.

TDP constituted the major fraction of TP in the water column, it showed expected seasonal pattern with the TP and DOP (Figure 3.24.a-b).

Depth distributions of DOP were naturally similar to TDP, because it was the major fraction of TDP. DOP concentrations were variable in the EZ, fluctuating between 0.157 and 0.210 µM in January 2002, from 0.181 to 0.227 µM in February 2002 (Figure 3.24.a). The spring concentrations in the EZ were almost constant at levels of 0.204-0.211 µM in April, then ranging between 0.099-0.161 µM in May. DOP content of the EZ varied from 0.188 to 0.229 µM in June, 0.066 to 0.126 µM during August-September period, and then it was between 0.134-0.169 µM in October 2002. It displayed small changes in December 2002 and January 2003, and then decreased apparently in February 2003 (Figure 3.24.b). In spring, DOP was uniformly distributed in the water column down to 125 m in March; then it ranged from 0.085 to 0.142 µM in May. In summer, DOP content of the EZ was observed to rise to 0.178-0.241 µM levels in June, and then declined to 0.074-0.125 µM levels in July-August period. An increasing trend was recorded in late 2003, reaching levels of 0.163 µM in September and 0.186 µM in December 2003 (Figure 3.24.b).

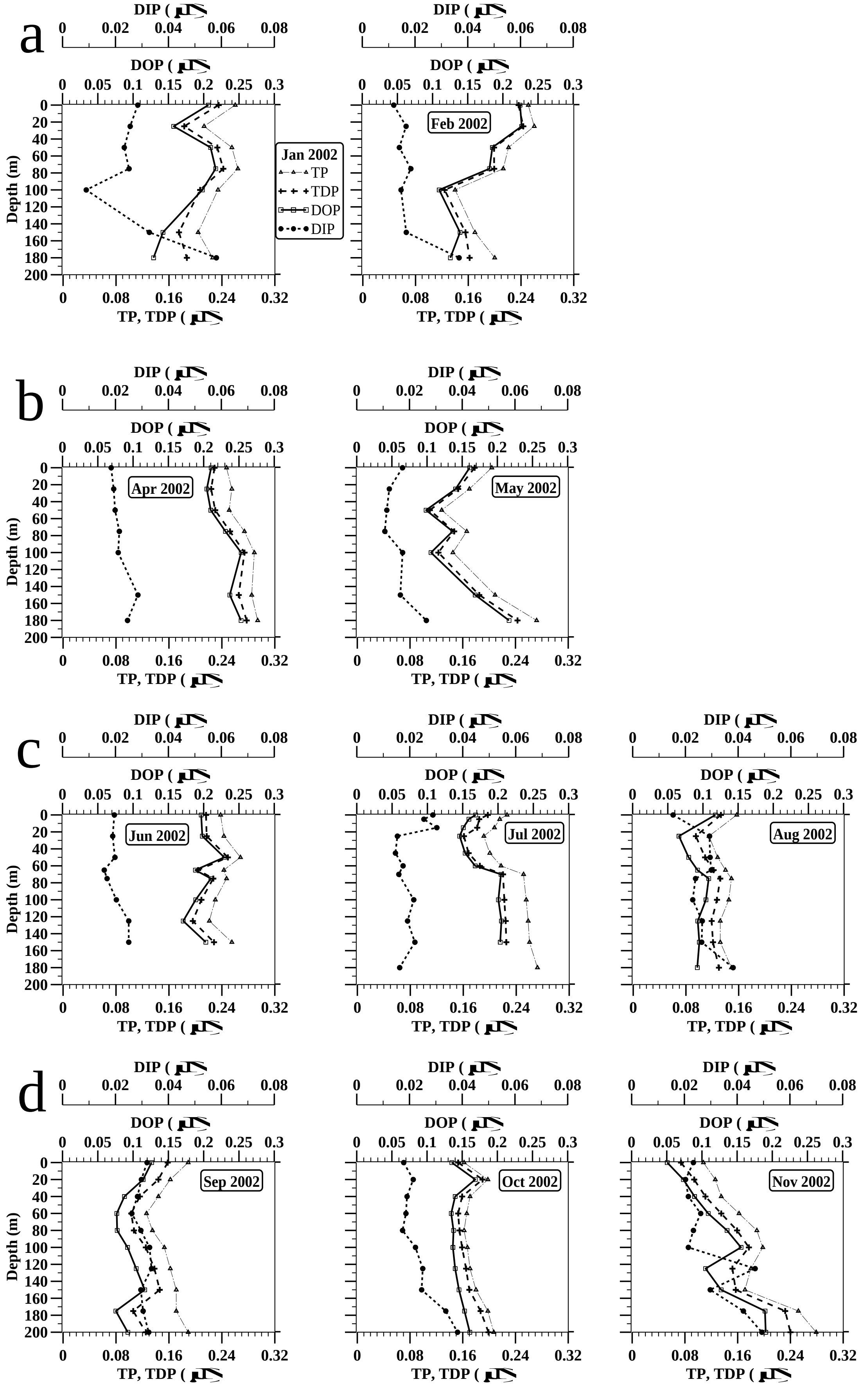


Figure 3.24.a Vertical profiles of fractions of phosphorus at the shelfbreak station in 2002 (a: Winter, b: Spring, c: Summer, d: Autumn).

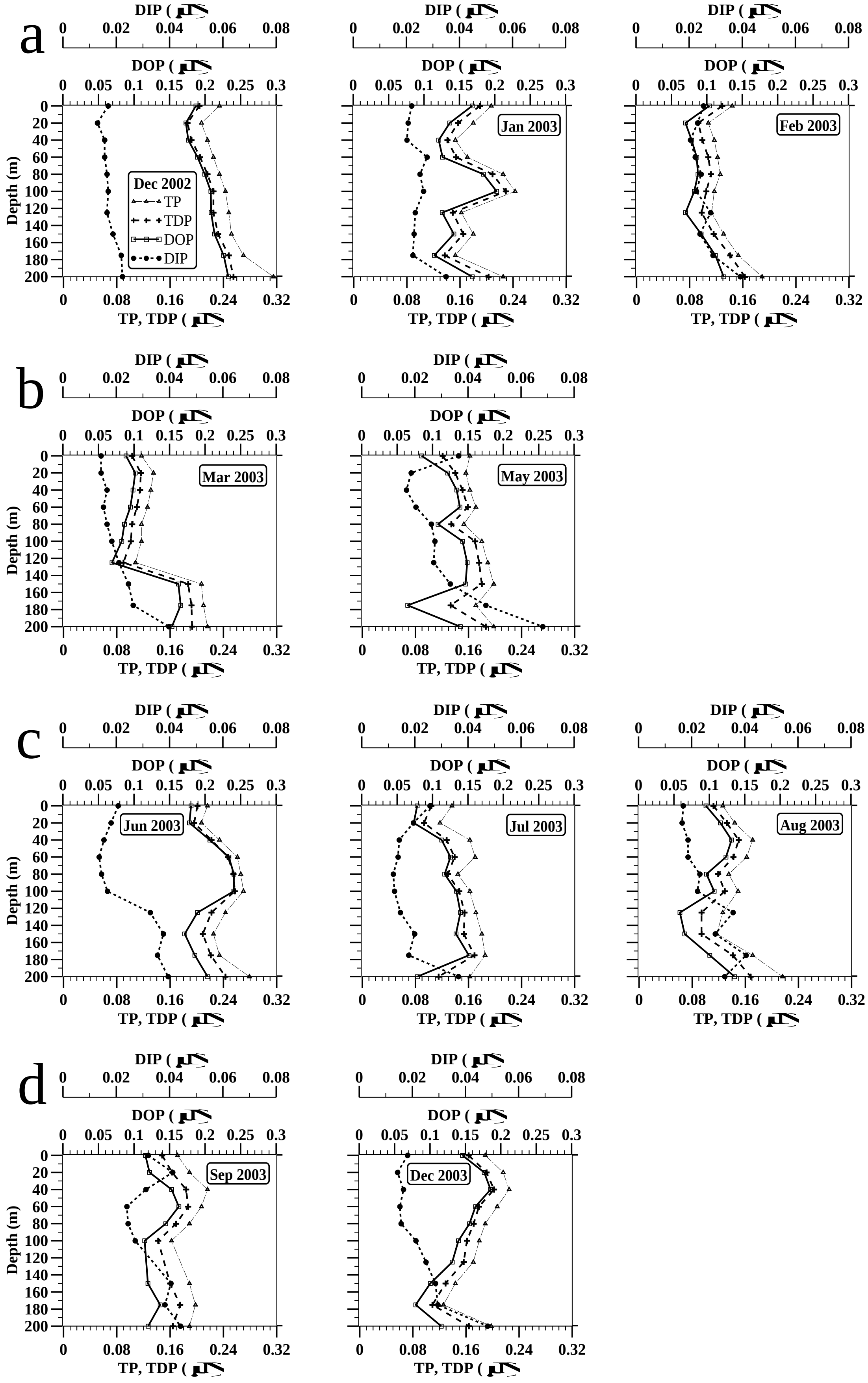


Figure 3.24.b Vertical profiles of fractions of phosphorus at the shelfbreak station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

In the winter of 2002, POP content of the EZ was almost vertically uniform in January (0.012 to 0.016 µM) and February (0.008 to 0.009 µM) (Figure 3.24.c). Then, it fluctuated between 0.010 and 0.024 µM in spring-summer period. In autumn, it ranged between 0.016 and 0.028 µM in September and between 0.019 and 0.030 µM in November; POP increased to 0.033-0.049 µM level in the deep water. In 2003, POP in the EZ varied from 0.016 to 0.027 µM in December 2002; it was as low as 0.009-0.016 µM during February-March period. It ranged between 0.005-0.011 µM in May. The summer POP values in the EZ were between 0.005-0.029 µM (Figure 3.24.d). POP contents of the EZ were fluctuated between 0.012 and 0.020 µM in September, 0.017 and 0.021 µM December 2003.

In winter 2002, PIP was low and almost constant in the EZ, ranging slightly between 0.010-0.014 µM in January 2002, and 0.005-0.014 µM in February 2002; it ascended to levels of 0.025-0.027 µM in the bottom water (Figure 3.24.c). In spring, PIP in the EZ ranged between 0.008 and 0.013 µM in April, 0.002-0.004 µM in May. It was very low (0.003 to 0.005 µM) in June, then slightly increased to 0.006-0.012 µM level in July, followed by a declining trend to 0.002-0.004 µM in August. In autumn 2002, PIP content of the EZ was still very low in the range of 0.002-0.006 µM. However, the summer concentrations were relatively high in the bottom water. The well-mixed waters of winter 2003 contained low PIP values (0.001-0.006 µM) in the EZ (Figure 3.24.d). PIP in the EZ was very low (0.001 to 0.003 µM) in March, then increased in May 2003. In summer, it slightly varied between 0.002-0.009 µM; however the PIP increased to 0.011-0.014 µM level in the bottom water. PIP profile became vertically uniform in December 2003 (0.004-0.009 µM).

Distributions of DIP and TPP at the shelfbreak station were previously mentioned in Section 3.4.1.3 and Section 3.4.2.3, respectively. Also, monthly variation of DIP and TPP in the shelfbreak station are depicted in Figures 3.11 and 3.16, respectively.

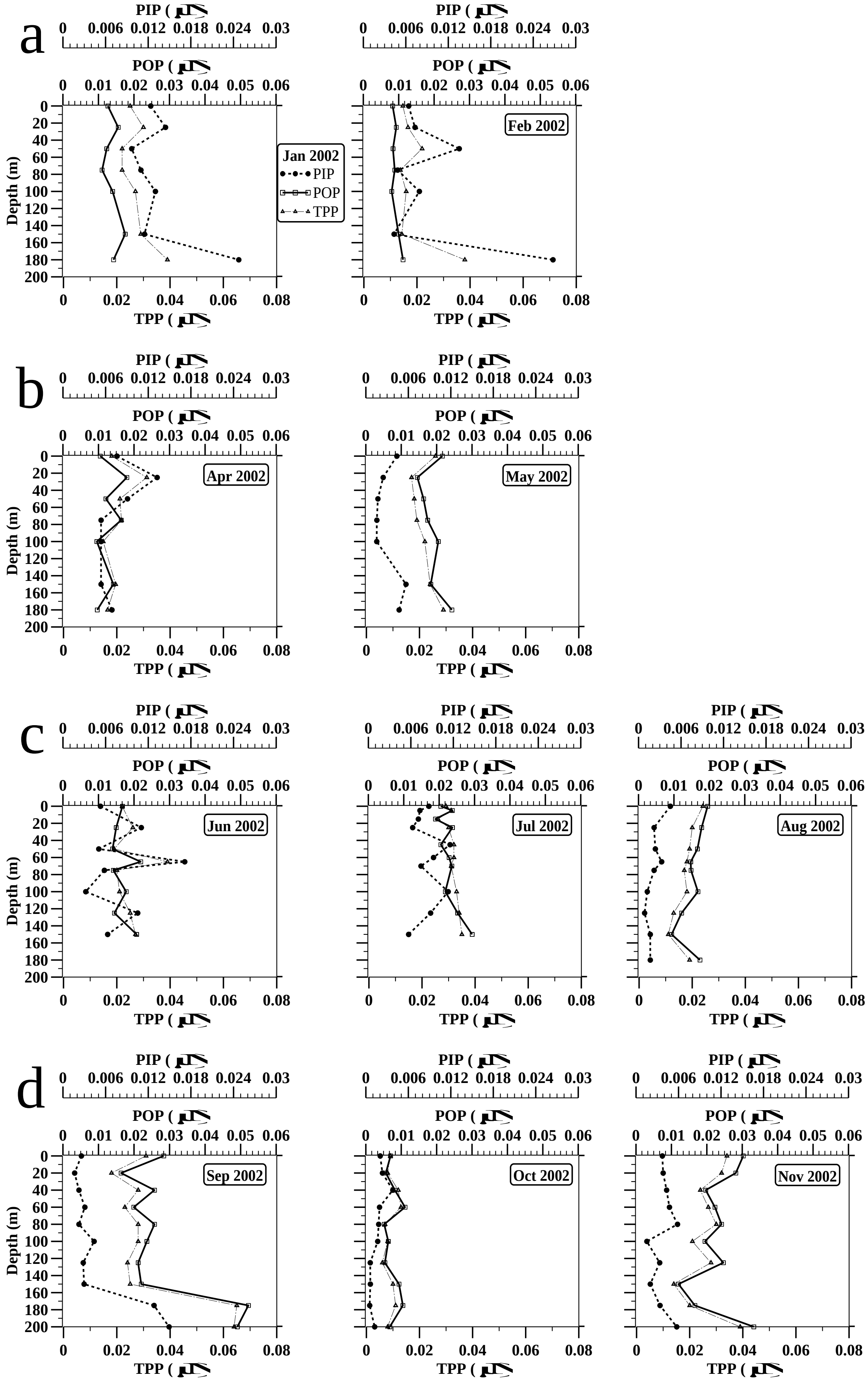


Figure 3.24.c Vertical profiles of fractions of phosphorus at the shelfbreak station in 2002 (a: Winter, b: Spring, c: Summer, d: Autumn).

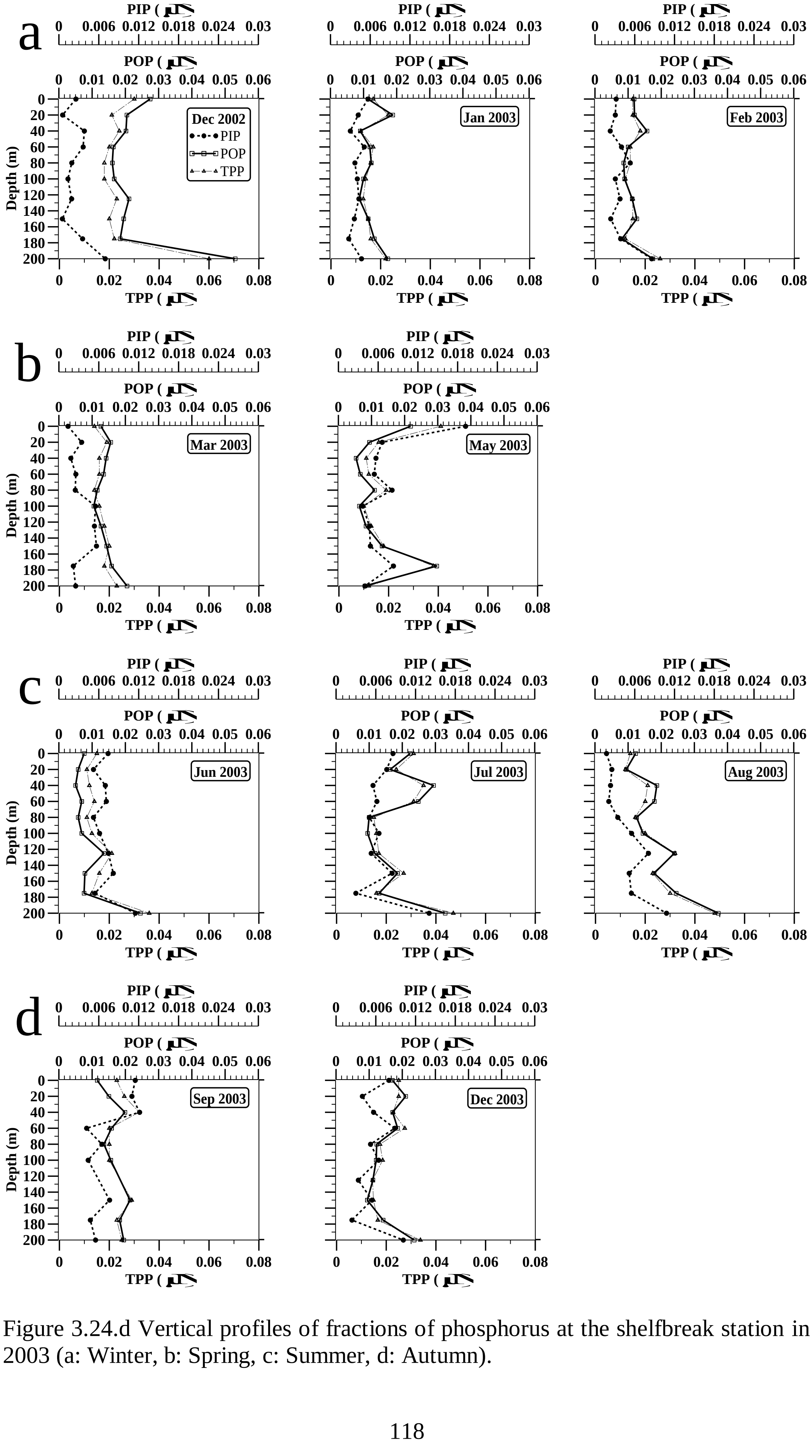


Figure 3.24.d Vertical profiles of fractions of phosphorus at the shelfbreak station in 2003 (a: Winter, b: Spring, c: Summer, d: Autumn).

3.6. Evaluation of Deep Basin Data as Reference Region

The hydrographic, biochemical and phosphorus fractions data collected in December 2003 from the off-shore stations located in the Cilician deep basin of the eastern Mediterranean (Figures 3.25 to 3.27) are presented here to compare with the measurements in the Cilician shelf waters of the NE Mediterranean.

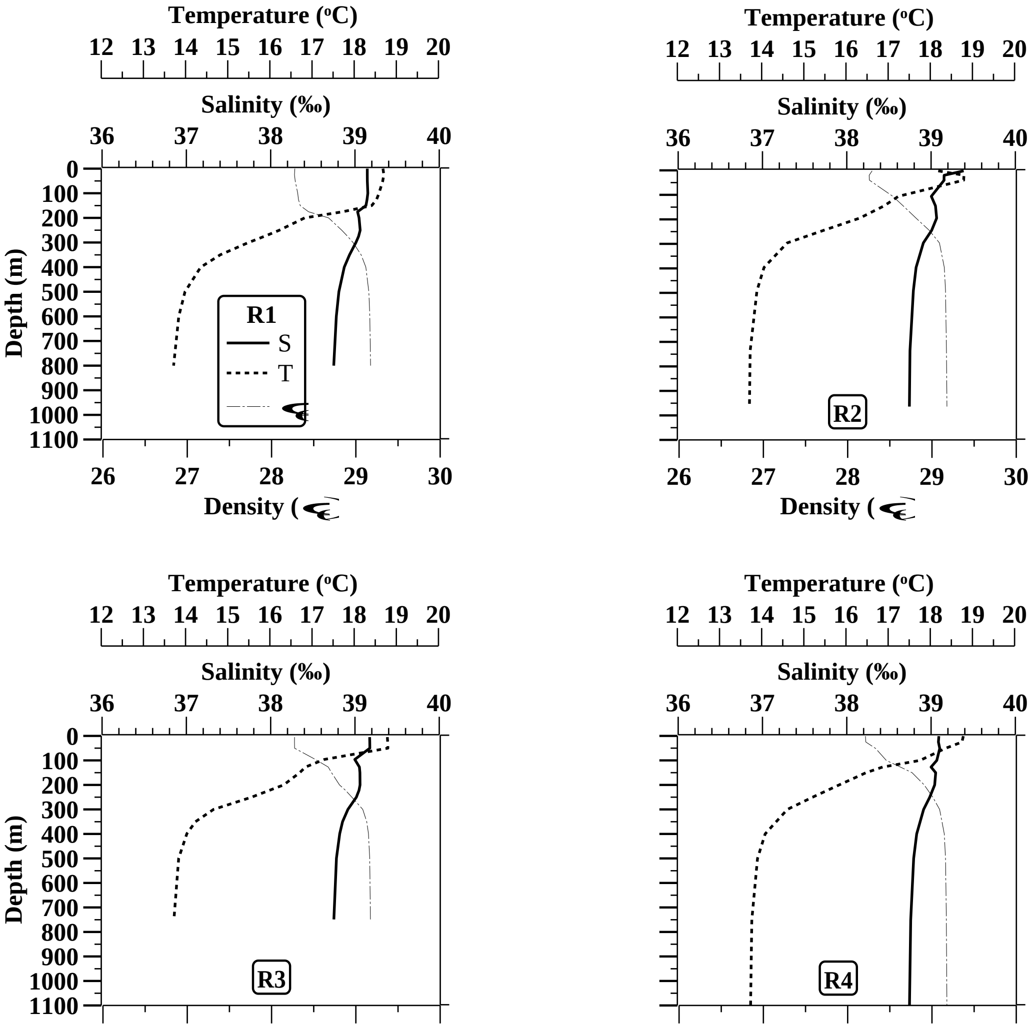


Figure 3.25 Vertical distributions of hydrographic parameters at the reference stations of the Cilician Basin in December 2003.

Depth profiles of hydrographic parameters and nutrients measured at the deep (reference) stations are presented in Figures 3.25 and 3.26. In the open sea, the surface salinity varied from 39.09 to 39.39 psu, while the temperature fluctuated between 18.2 and 18.8 °C. The salinity profile displayed a subsurface minimum at ca. 100 m and then had high salinity values of nearly 39.1 psu; below the halocline at 250 m depth, the salinity remained almost constant (S: 38.7 psu) in the deep layer water. Temperature profiles were partly similar to the salinity distribution with depth. A well pronounce thermocline was formed between ca. 300 and 350 m where temperature decreased from 18.7 °C to ~14.6 °C. Then, the temperature was vertically uniform at ~13.8 °C (Figure 3.25).

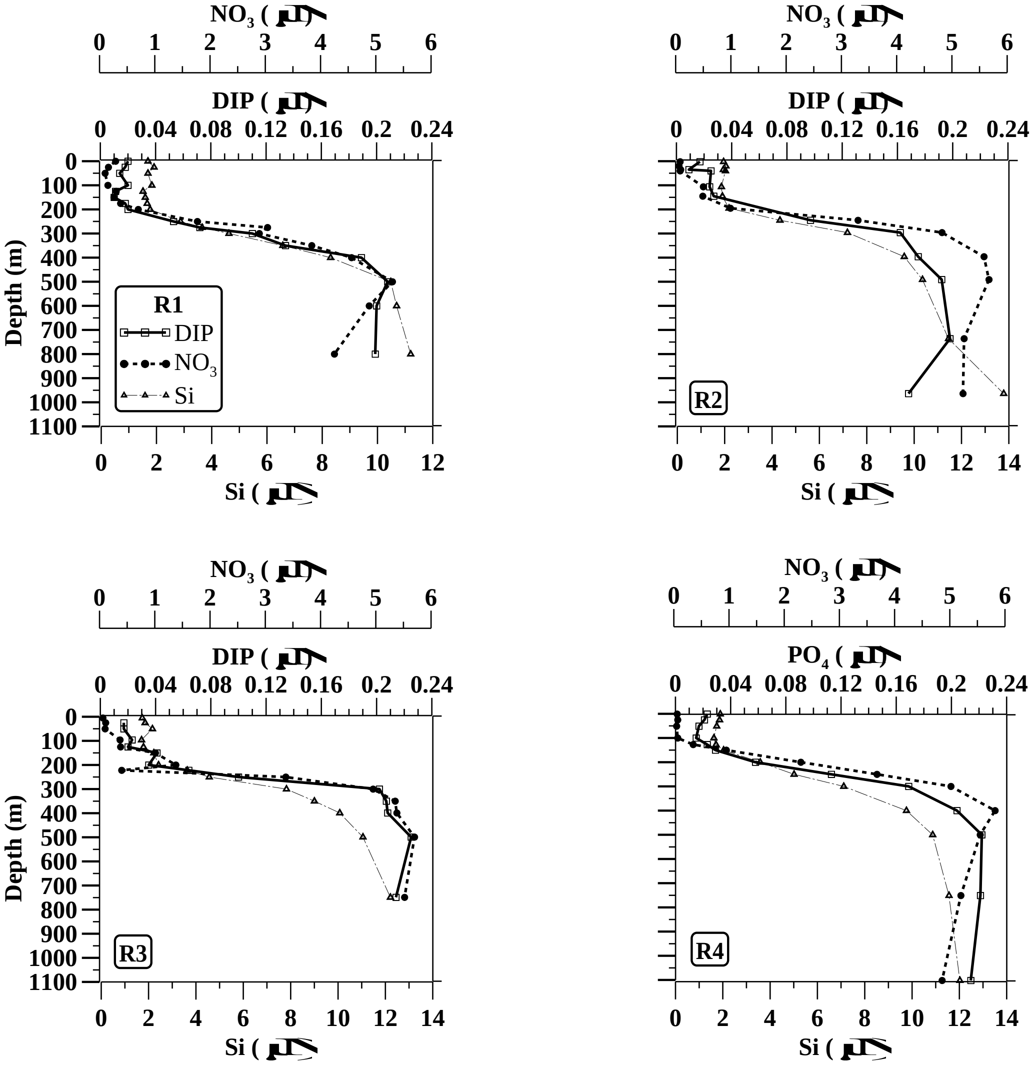


Figure 3.26 Vertical distributions of nutrients at the reference stations of the Cilician Basin in December 2003.

Typical nutrient profiles in the water column of the Cilician deep stations are depicted in Figure 3.26. Concentrations of nutrient were very low in the surface water, ranging between 0.017 to 0.023 μM for DIP, 0.06 to 0.29 μM for NO$_3$ and 1.69 to 1.95 μM for Si. In December 2003, nutrient deficiency continued in the upper

125-150 m; then a nutricline of about 150-200 m thick was located between ca. 125-450 m depth ranges where the nutrient concentrations displayed coherent increases. The concentrations of DIP and NO_3 reached the peak values of 0.192-0.225 μM and 5.30-5.82 μM, respectively, between 400-500 m (Figure 3.26). Then their concentrations varied insignificantly with depth. DIP concentrations reached the levels 0.168-0.214 μM in the deep water where NO_3 and Si values ranged slightly between 4.25-5.52 μM and 11.20-13.78 μM (see Appendix A).

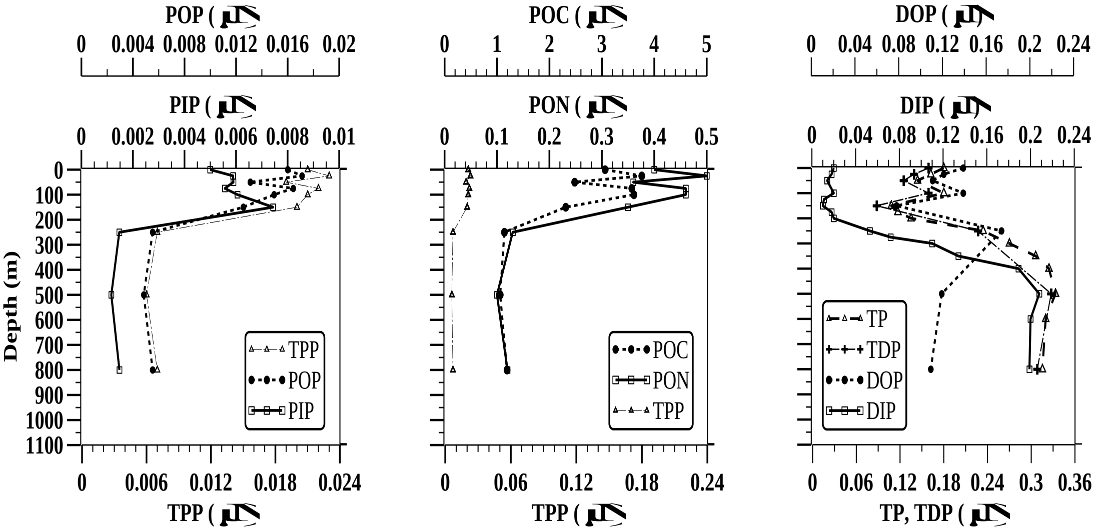


Figure 3.27 Vertical distribution of phosphorus fractions and POM at the reference station (R1) in December 2003.

Vertical profiles of POM and P-fractions determined only at the deep (reference) station 1 (R1) are depicted in Figure 3.27. Particulate phosphorus concentrations slightly varied in the upper 200 m, ranging from 0.019 to 0.023 μM for TPP, 0.013 to 0.016 μM for POP and 0.005 to 0.007 μM for PIP and then dropped to lower values in the deep water (Figure 3.27). POC and PON content of POM displayed similar trends with relatively high values in the upper 200 m, fluctuating between 2.31-3.76 μM for POC and 0.35-0.50 μM for PON. Then they remained almost constant levels of 1.0 and 0.1 μM in the deep layer, respectively (see Appendix C).

TP concentration at the R1 ranged from 0.108 to 0.333 μM in the water column; it fluctuated between 0.108-0.180 μM in the upper 200 m (Figure 3.27). Then it increased to levels of 0.31-0.33 µM in the deep water. At this reference station, the TDP, DOP and DIP followed similar patterns with maximum values of 0.327, 0.119 and 0.208 µM at 500 m and minimum values of 0.088, 0.078 and 0.010 µM at 150 m, respectively (see Appendix D).

3.7. Statistical Evaluations

Descriptive statistics were applied to the data (Zar, 1984) (see Appendix F). The relationships between hydrographic, biochemical and P-fraction variables were analysed with Pearson correlation (see Appendix H-L). Thus, it is possible to understand if there is any relation between changing chemical and physical properties of the water and phosphorus fractions within a time period. Significant correlations and differences observed were given in related part of the Discussion section of the thesis.

CHAPTER 4

DISCUSSION

It is well known that hydrographic and bio-chemical features of the marine environments are controlled by complicated internal and external processes (Redfield *et al.*, 1963; Ketchum, 1983). Despite limited existing studies (Krom *et al.*, 1991; Yılmaz and Tuğrul, 1998; Çoban-Yıldız, 2000b; Eker-Develi *et al.*, 2006; Uysal, 2006), systematic information gap on fractions of total phosphorus, sensitive phosphate measurements and compound-specific studies on the composition of organic matter in the Northeastern Mediterranean shelf water column remains to be filled. This study principally aims; (a) understanding of coastal processes, (b) source and sink terms of nutrient pool in the shelf zone of the Northeastern Mediterranean by studying spatial and temporal variations of the hydrographic and bio-chemical properties from the surface down to the bottom. Because the shelf waters are fed by a few major and small rivers and atmospheric input, the nutrient contents of both rivers and rainwater in the region have been evaluated here to determine their roles on the wide shelf ecosystem of the Northeastern Mediterranean. The open sea, outside the river effect, between Mersin Bay and Cyprus Island, was visited in December 2003 to assess the range of changes from the nearshore to deep basin. In order to understand the influences of internal and external pressures on the nutrient cycles in the Northeastern shelf ecosystem of the oligotrophic eastern Mediterranean, the hydrographic, bio-chemical and phosphorus fractions data obtained systematically at three time-series shelf stations (nearshore, middle, and shelfbreak) off Erdemli and four reference deep stations (R1, R2, R3 and R4) are discussed extensively in this chapter.

The DIP contents of the shelf and the Northeastern Mediterranean deep basin waters were measured by the conventional colorimetric method and the new modified MAGIC (pre-concentration) technique; these data sets were compared to reach conclusive remarks on their sensitivities and reliabilities for P-poor waters of the Northeastern Mediterranean.

4.1 Spatial and Temporal Variations of Hydrographic Properties of the Water Column across the Northeastern Mediterranean Shelf

Changes in hydrographic properties of the water masses were closely related to their source and the residence time (duration) on the shelf. Water circulations on the Northeastern Mediterranean continental shelf zone are dominated by the general circulations in the Cilician basin (Özsoy *et al.*, 1981; Hecht *et al.*, 1988; POEM Group, 1992; Pinardi *et al.*, 2005). The residence time of the near bottom waters on the shelf are very likely to range from week to month depending on both the location and water column depth (Robinson and Golnaraghi, 1994; Béthoux and Gentili, 1999 and references therein; Durrieu de Madron *et al.*, 2003). The seasonal signals seem to be much stronger in the Mediterranean Sea compared to the other seas of the world (Ketchum, 1983; Malanotte-Rizzoli and Robinson, 1988; Ediger *et al.*, 2005).

Temporal variations of the surface salinity, temperature and density (Figure 4.1 to 4.3) demonstrate that the nearshore values range between 35.8-39.3 (38.4±1.0) psu, 16-30 (22.6±4.9) °C, and 22.8-28.7 (26.5±1.7) respectively. Despite the fact that surface water properties exhibit significant seasonal variations, the intermediate and deep waters have moderate salinities (>38.8 psu), temperatures (>18.0 °C), and density (>27) values. Salinity contour plots in Figure 4.1 indicate that the temporal changes in the bottom water of the near-shore zone were much faster and more apparent than in the offshore zone due to both effective wind-induced circulations and vertical mixing in the river-fed shallow zone. Accordingly, the near-bottom water salinity ranged from 36.9 to 39.4 psu at the nearshore station (Figure 4.1). However, the near-bottom water salinity of the shelfbreak station varied slightly between 38.8 and 39.3 psu in 2002-2003. The entire water column was well mixed and became saltier in the winter of 2003, and then the deeper part of the shelf was occupied by less saline water with different hydro-chemical properties during the autumn 2003.

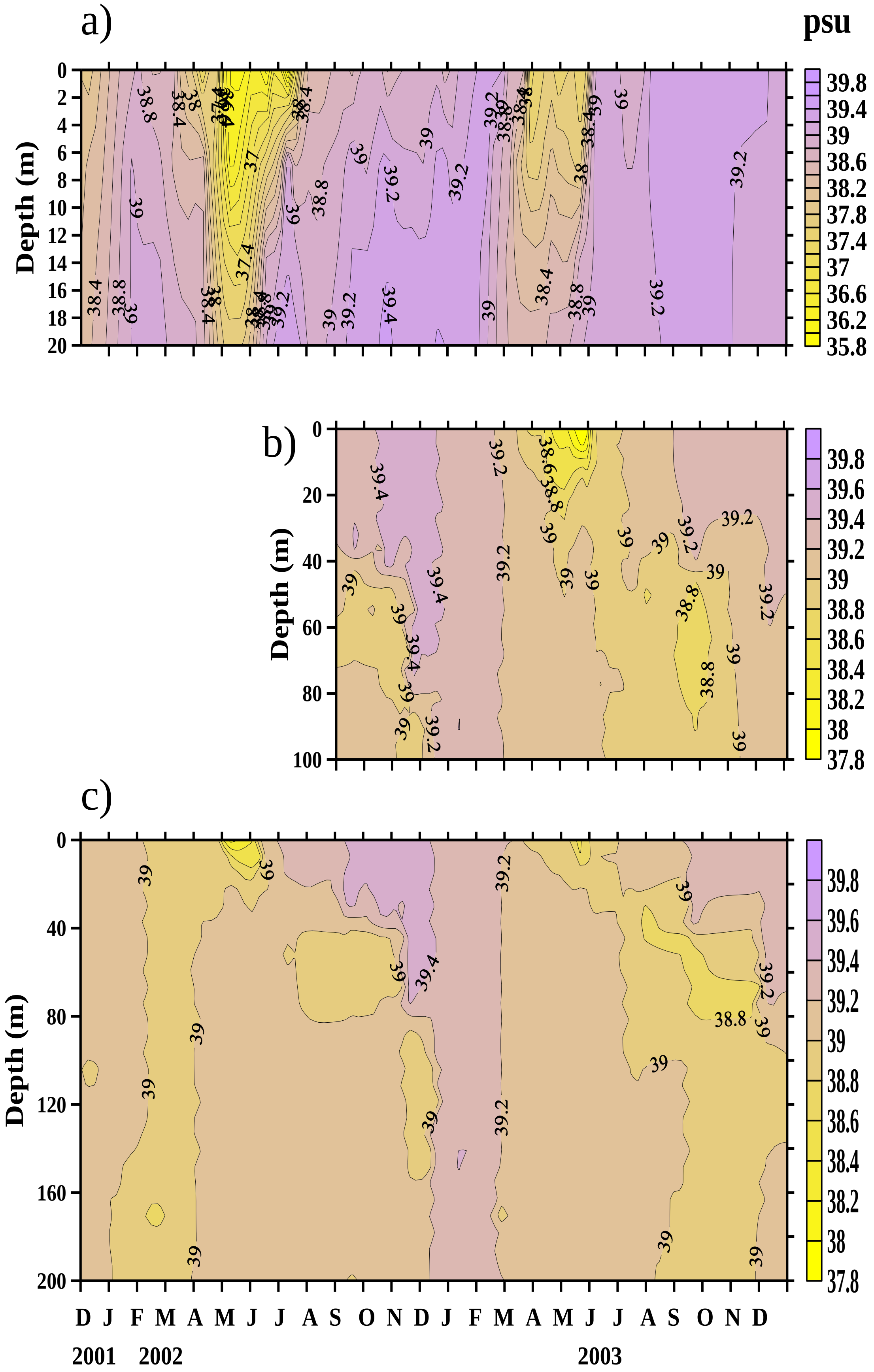


Figure 4.1 Contour plots of the vertical distribution of salinity at the time-series stations (a: Nearshore, b: Middle, c: Shelfbreak).

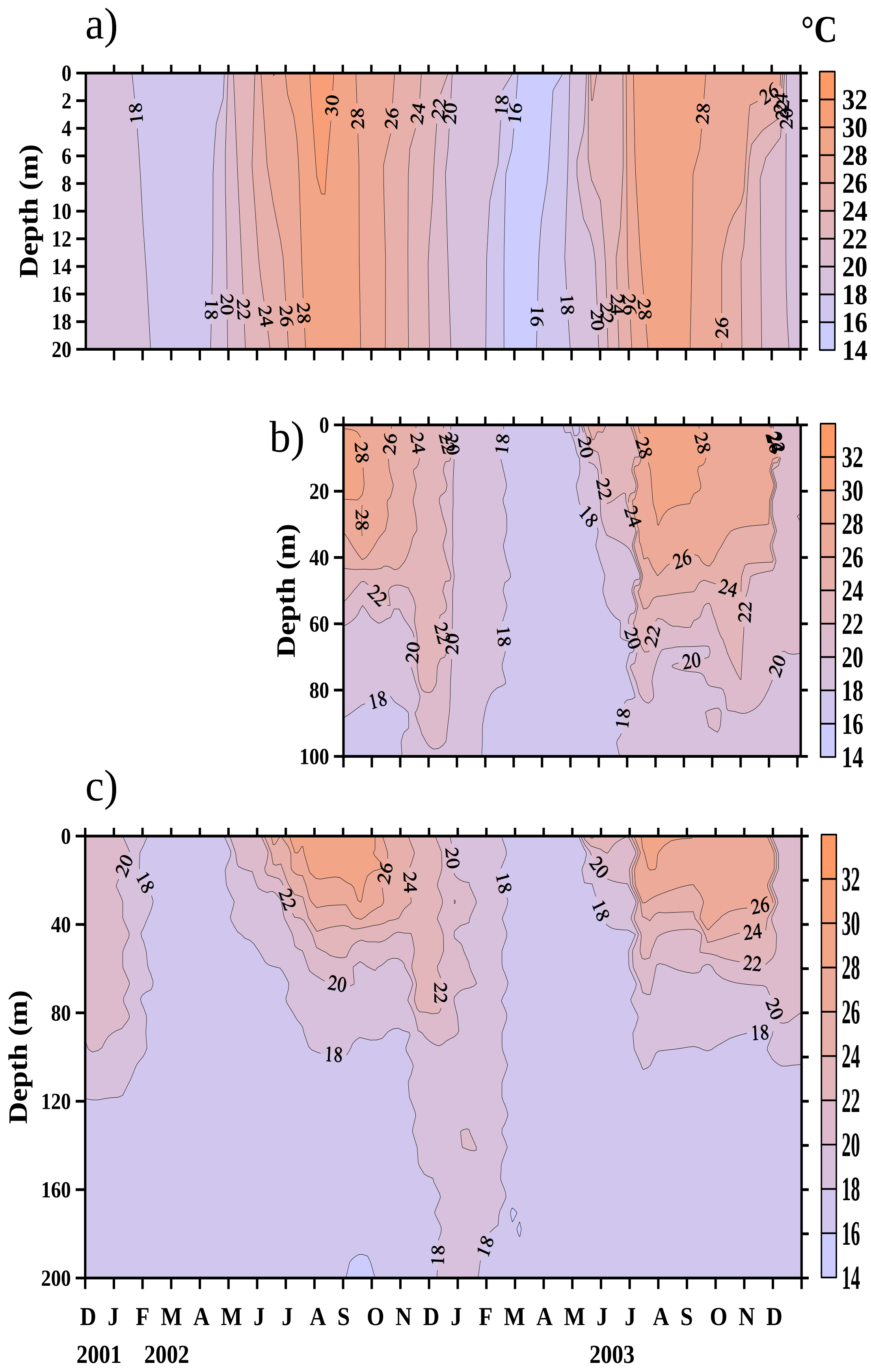


Figure 4.2 Contour plots of the vertical distribution of temperature at the time-series stations (a: Nearshore, b: Middle, c: Shelfbreak).

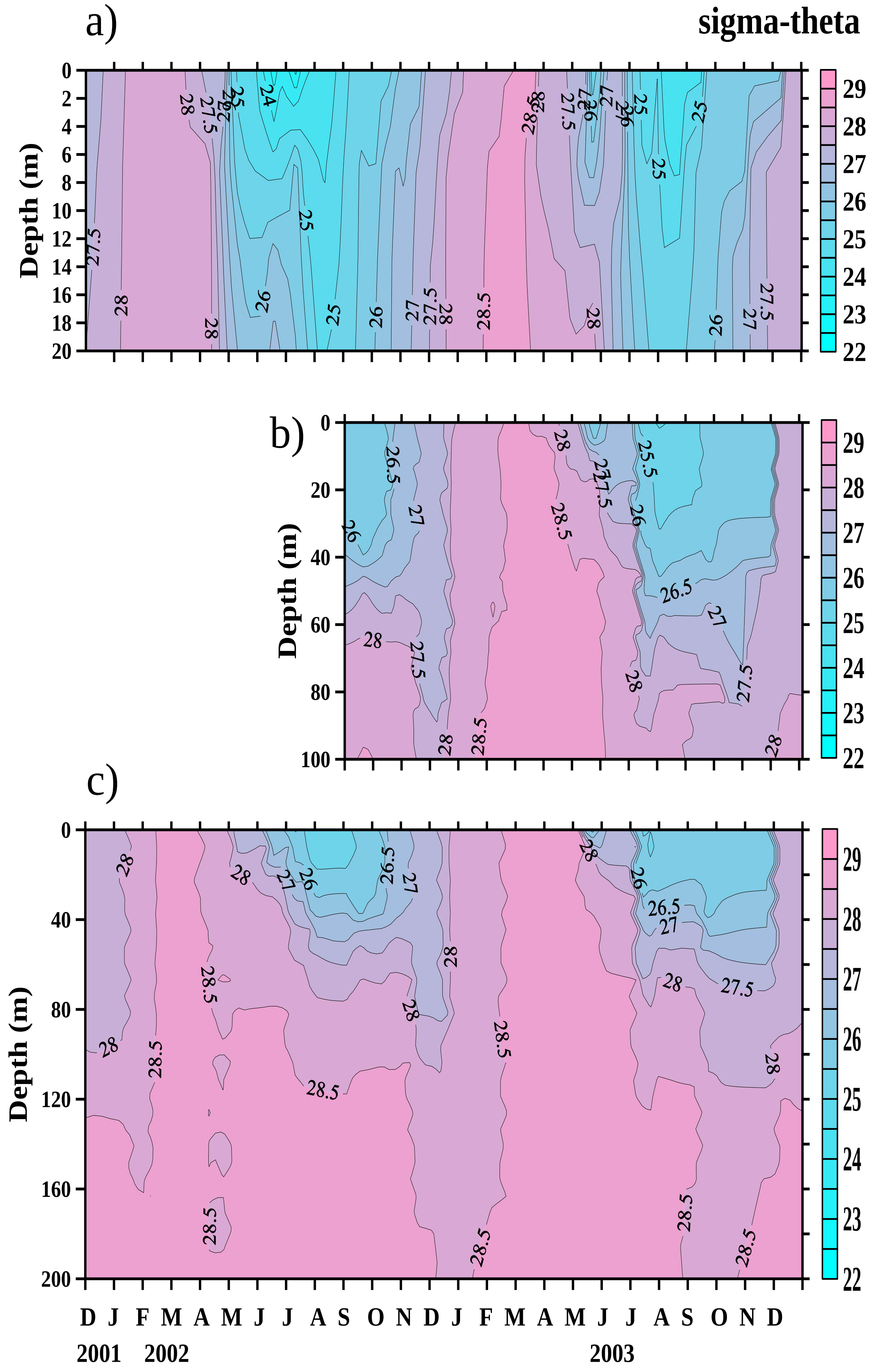


Figure 4.3 Contour plots of the vertical distribution of density at the time-series stations (a: Nearshore, b: Middle, c: Shelfbreak).

The seasonal averages of the Secchi Disc Depth (SDD) in the NE Mediterranean shelfbreak station were estimated as 23±6 m for winter and 32±5 m for summer (Table 3.1). These SDD values are comparable to the previous results reported by Ediger and Yılmaz (1996) and indicate that this station has typical properties of the Mediterranean Sea. At the middle station, SDD ranged monthly between 9 m in May 2003 due to increasing concentration of suspended particulate matter of plankton origin and 37 m in October 2002 when plankton production and particulate matter concentration were very low. At the nearshore zone, when the Lamas River inflows decrease, solar light can penetrate down to the bottom (SDD deepened to depths of 15-17 m).

4.2 Comparison of DIP Data Obtained by MAGIC and Conventional Methods

DIP data obtained by the conventional (direct standard colorimetric) vs. modified MAGIC (magnesium-induced coprecipitation) methods in parallel samples from standard depth of the selected locations at the shelf zone and deep basin of the NE Mediterranean in the period of 2002-2003 are given in Appendix A. It should be noted that the modified MAGIC (pre-concentration) method is about 20 times more sensitive than the direct standard colorimetric method. DIP data sets obtained by the two methods are depicted in Figure 4.4 and Appendix A.

It was estimated that the nearshore, middle and shelfbreak stations contained 0.063±0.043 μM DIP^{MAGIC} and 0.078±0.017 μM DIP^{AA}, 0.027±0.009 μM DIP^{MAGIC} and 0.029±0.011 μM DIP^{AA}, 0.024±0.010 μM DIP^{MAGIC} and 0.038±0.028 μM DIP^{AA}, respectively. It appears that the DIP concentrations obtained by the MAGIC method (DIP^{MAGIC}) in the coastal waters are generally less than the DIP data by the conventional method (DIP^{AA}). Consistent with prior observations (Murphy and Riley, 1962; Strickland and Parsons, 1972; McKelvie *et al.*, 1995 and references therein), this finding strongly suggests that some fractions of labile organic phosphorus in seawater become reactive and form colored P-complexes in acidic reagent solution (pH<1) during the direct colorimetric measurement. In the MAGIC method, however, this labile fraction may have partly remained in liquid phase during the co-precipitation of DIP in the seawater (Benitez-Nelson, 2000; Karl *et al.*, 2001). Close examination of DIP data sets also clearly shows that the positive interferences of labile P-compounds to the reactive DIP values become insignificant when the DIP concentrations exceed 0.1 μM in the coastal and the offshore deep waters (see Figure 4.4 and Appendix A). This implies relatively less interference from the components of P-pool in deep waters of the open sea. It can be concluded from the present study that sensitive and reliable DIP measurements in P-depleted surface waters can only be accomplished by the MAGIC method, leading much more reliable estimates of the N/P ratio for the P-depleted surface waters. However, the conventional colorimetric techniques can be used safely for the NE Mediterranean deep waters with DIP>0.1 μM. On the other hand, the chemical interference is very likely to occur in productive and POM-rich near surface waters due to dissolution of labile organic phosphorus. As a result, it is highly recommended to filter POM-rich surface waters as experienced in the nearshore waters of the polluted Mersin Bay having high concentrations of POM and thus weak-acid soluble organic P-compounds. The findings in this study are partly in accord with low phosphate concentrations measured by the isotope technique (Benitez-Nelson, 2000; Suzumura and Ingall, 2004). This strongly suggests that acid soluble DOP exists in oligotrophic surface waters. In other words, DIP by the MAGIC method is very likely to be composed of dissolved inorganic phosphate and weak acid soluble forms of organic phosphorus that could precipitate during the experiment (Benitez-Nelson, 2000; Karl *et al.*, 2001). In conclusion, the MAGIC data is still insufficient to determine only DIP ions in the surface waters and thus may partly overestimate the N/P ratio whereas the ratios could not be estimated precisely by the standard method in the DIP-depleted surface waters.

Between two methods above mentioned statistical analyses were carried out. DIP^{MAGIC} showed positive correlation with DIP^{AA} in the nearshore ($p<0.001$) and shelfbreak stations ($p<0.001$) (Appendix G.2). Comparisons of DIP concentrations between stations measured by DIP^{MAGIC} and DIP^{AA} showed no difference for the nearshore (t-test, $p>0.05$) and middle stations ($p>0.05$), significant difference ($p<0.001$) for the shelfbreak station (see Appendix G.1). This relation also demonstrates the necessity of the MAGIC method for the DIP-depleted offshore shelf waters for reliable estimates of the N/P ratios and eutrophication modeling studies in coastal waters.

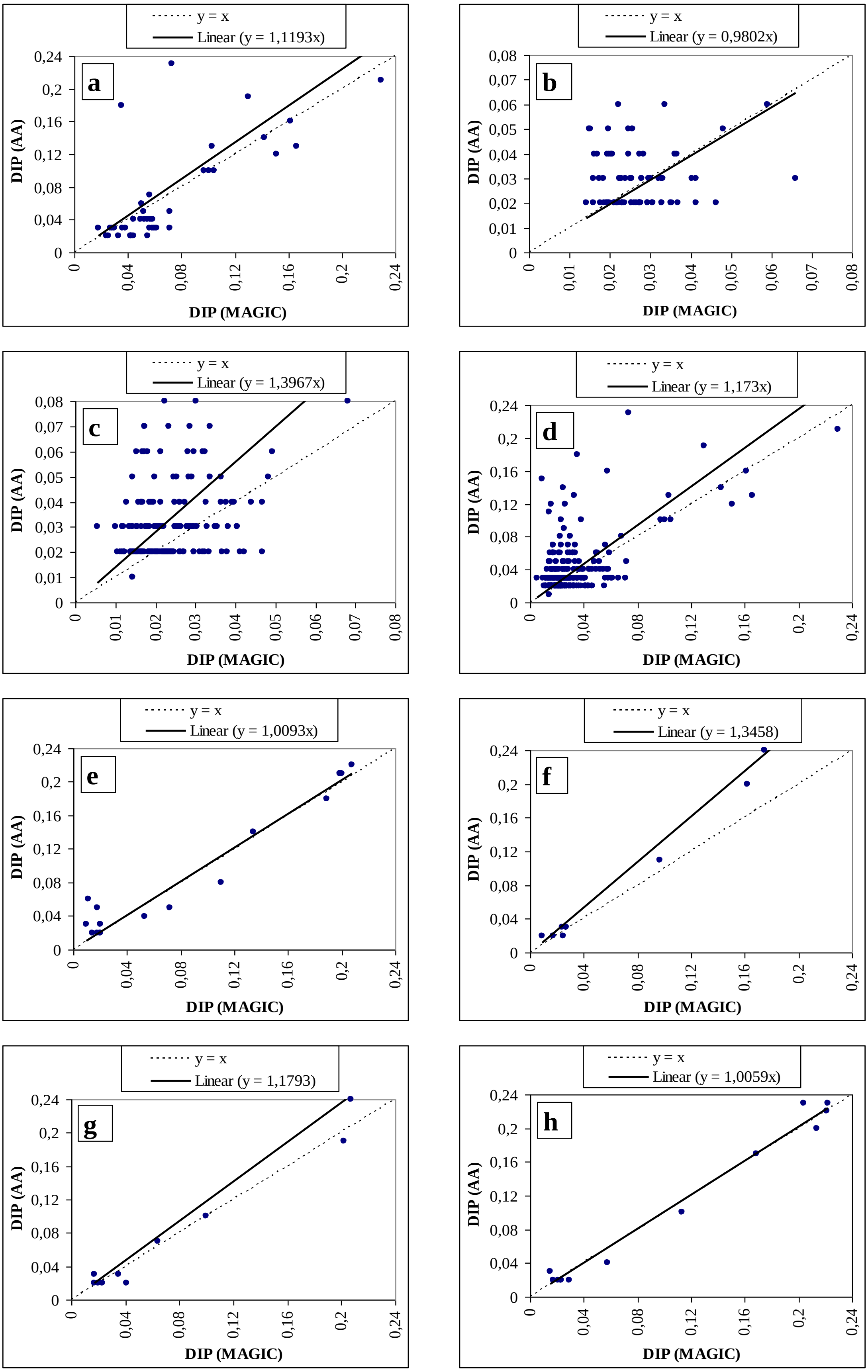


Figure 4.4 Linear relationship between conventional method (AA) and new modified method (MAGIC) for measuring DIP (Time series stations a: Nearshore, b: Middle, c: Shelfbreak, d: All data; Reference stations e: R1, f: R2, g: R3, h: R4).

4.3 Nutrients in the Northeastern Mediterranean Shelf Zone

Most of the phosphorus carried by rivers could be deposited on the continental shelf (Karafistan *et al*., 2002). This could also explain why no evidence of eutrophication due to the river input was noticed either in the northwestern (Lefevre *et al*., 1997) or in the northeastern basins (Yılmaz *et al*., 1992), both of which cover large continental shelf areas. The dissolved inorganic nutrient concentrations of the nearshore zone are consistent with those reported from other coastal margins influenced by riverine inputs (Yılmaz *et al*., 1992; Béthoux *et al*., 1992; Justic *et al*., 1995; Tugrul and Polat, 1995; Cociasu *et al*., 1996; Laznik *et al*., 1999; Monaghan and Ruttenberg, 1999; Stålnacke *et al*., 1999; Çoban *et al*., 2000a; Chen *et al*., 2001; Giani *et al*., 2003; Liu *et al*., 2003; Durrieu de Madron *et al*., 2003).

Table 4.1 Annual averages of nutrient concentrations and N/P ratios in the rivers draining into the NE Mediterranean and in the rainwater (Tuğrul *et al*., 2006).

Sampling Year	**Rainwater**					**The Lamas River**				
	PO_4 (µM)	**NO_3 (µM)**	**Si (µM)**	**N/P**	**N/Si**	**PO_4 (µM)**	**NO_3 (µM)**	**Si (µM)**	**N/P**	**N/Si**
2001	0.91	45.6	0.76	93	60	-	-	-	-	-
2002	0.67	55.4	0.88	138	63	0.81	92.1	62.2	114	1.48
2003	0.99	103	3.90	124	26	0.27	78.1	79.0	362	0.99
Sampling Year	**The Göksu River**					**The Ceyhan River**				
	PO_4 (µM)	**NO_3 (µM)**	**Si (µM)**	**N/P**	**N/Si**	**PO_4 (µM)**	**NO_3 (µM)**	**Si (µM)**	**N/P**	**N/Si**
2001	-	-	-	-		2.20	76.2	144	35.3	0.53
2002	-	-	-	-		0.34	81.4	187	234	0.44
2003	2.98	55.3	109	111	0.51	0.47	111	91.7	234	1.21
Sampling Year	**The Berdan River**					**The Seyhan River**				
	PO_4 (µM)	**NO_3 (µM)**	**Si (µM)**	**N/P**	**N/Si**	**PO_4 (µM)**	**NO_3 (µM)**	**Si (µM)**	**N/P**	**N/Si**
2001	2.40	40.4	61.4	16.8	0.66	0.22	29.0	109	132	0.27
2002	0.65	38.9	117	60	0.33	0.34	87.1	212	285	0.41
2003	0.37	41.6	125	99	0.33	0.16	40.2	152	255	0.26

Before discussing temporal and spatial changes in the shelf water hydro-chemistry, we should know the principal chemical properties of the regional river waters. Annual averages of nutrient data depicted in Table 4.1 (Tuğrul *et al*, 2006) clearly show that fresh waters of the Seyhan, Ceyhan and Berdan rivers, feeding the nutrient pool of Mersin Bay, are poor in phosphate, but very rich in nitrate and reactive silicate, leading to markedly high N/P and Si/P molar ratios in the NE Mediterranean river waters. The Lamas River waters have low phosphate (0.27-0.81 μM), but high nitrate (78.1-92.1 μM) and silicate (62.2-79 μM) concentrations. Thus, estimates of the N/P ratios are consistently higher and ranged between 114 and 362 (Table 4.1). Moreover, the Lamas River, with the lowest chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total suspended solid (TSS) and ammonia (NH_4), represents the least contaminated fresh water properties in the NE Mediterranean region (Tuğrul *et al.*, 2005). Accordingly, its chemical concentrations can be used to assess the level of pollution in the regional rivers in the recent decades. The present nutrient contents of the rivers permit us to distinguish the major origin of nutrients in the shelf waters off Erdemli.

4.3.1 Spatial and temporal variations of dissolved inorganic nutrients in surface water of the Northeastern Mediterranean shelf

The dissolved inorganic nutrient pool of the well oxygenated coastal zone is fed by the inputs from the atmosphere, rivers, direct waste discharges and intrusion from the sediment layer via the resuspension induced by bio-geo-chemical processes (Prastka *et al.*, 1998; Giani *et al.*, 2003). Dissolved inorganic nutrients in the water column are utilized in autotrophic and heterotrophic processes to produce POM (Redfield *et al.*, 1963; Libes, 1992; Scanlan and Wilson, 1999; Çoban-Yıldız *et al.*, 2000b, Geider and La Roche, 2002). Some fractions of POM eventually settle down to the sediment layer (Benitez-Nelson, 2000; Giani *et al.*, 2003; Durrieu de Madron *et al.*, 2003; Slomp and Van Cappellen, 2007). As phosphorus (P) has no stable gaseous form, removal of it, from the world’s oceans is through sedimentary burial. However, this process is inefficient, and less than 1% of the P that reaches the seafloor is ultimately trapped in sediments and removed from the marine P cycle (Benitez-Nelson, 2000). On the other hand, lateral and vertical circulations on the coastal zone and water exchanges with the open sea are the internal source and sink terms of the coastal nutrient pool (Eppley, 1989; Benitez-Nelson, 2000; Herut *et al.*, 2000; Migon *et al.*, 2001). Therefore, salinity changes in the shelf surface waters can be used as a natural tracer to understand the major sources of nutrient increases in the surface layer waters in both space and time.

Offshore and near-shore waters of the same marine environment can differ substantially due to proximity of the latter to natural and anthropogenic sources (Kress *et al.*, 2005). Seasonal variations of the surface salinity values displayed in Figure 4.1 demonstrate that temporal salinity changes at the shallow nearshore station are much more pronounced than those in the middle and shelfbreak stations. In other words, the nearshore surface layer was generally occupied by less saline waters; the Lamas River with relatively low volume flux could modify the hydrographic and bio-chemical properties of the shallow nearshore station (ca. 25 m and 0.5 mile from the coastline). On the other hand, as clearly shown from the satellite pictures in Figure 4.5, the offshore stations located on the Levantine shelf zone off Erdemli are influenced by the NE Mediterranean circulation system carrying discharges of Ceyhan, Seyhan and Berdan rivers (Tuğrul *et al.*, 2005; Özsoy and Sözer, 2006; Örek, 2007).

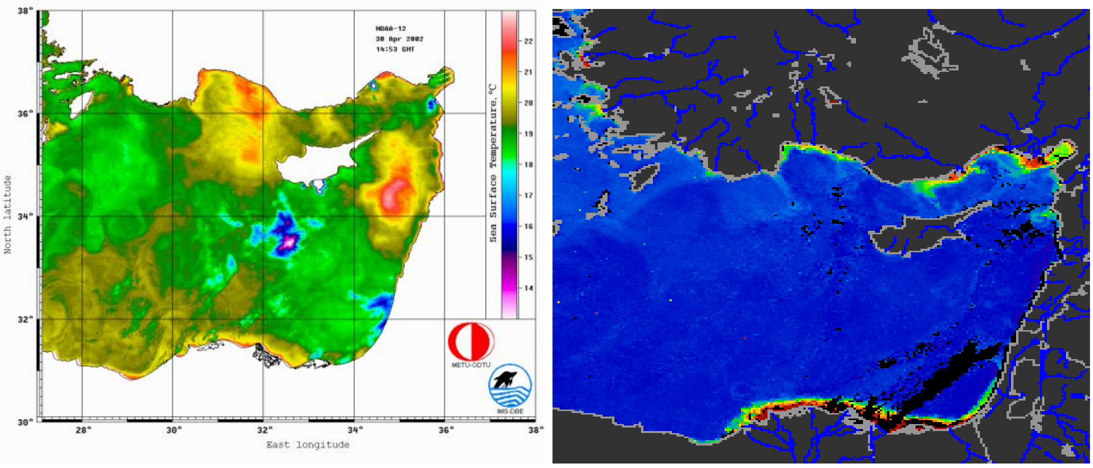


Figure 4.5 Left panel: NOAA-AVHRR Channel 4 images for sea surface temperature circulation dynamics of the NE Mediterranean in spring 2002 (Eker-Develi, 2004). Right panel: Chlorophyll-*a* distribution in the surface waters of the NE Mediterranean in spring 2002 (available from http://marine.jrc.cec.eu.int/cgi-bin/OC/present.pl?2002,04,MEDR).

Correlation analysis was performed between hydrographic parameters and nutrients using the Pearson correlation index (Appendix H). The salinity positively correlated with DIP ($p<0.05$) and Si ($p<0.05$), supported the assumption that the supply of freshwater was the major factor influencing DIP and Si at the nearshore station. In the middle station, salinity showed positive correlation only with DIP ($p<0.01$). On the other hand, NO_3 and temperature are significantly correlated (positively) at the middle and shelfbreak stations ($p<0.01$), suggesting that internal processes have remarkable influences on NO_3 distributions in the productive upper layer waters.

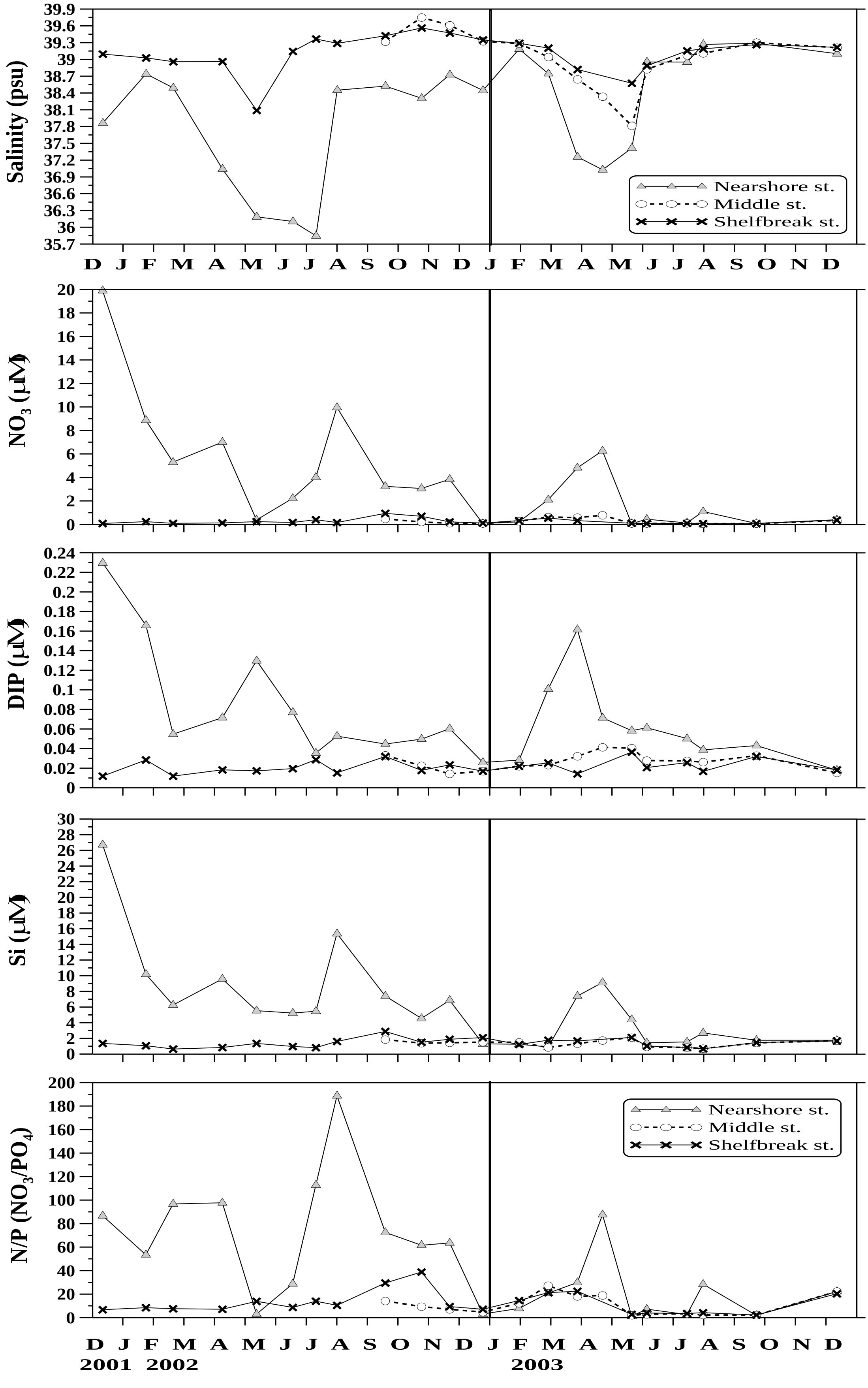


Figure 4.6 Monthly changes of salinity, nutrients and N/P molar ratio in the surface water of the time-series stations on the shelf zone.

River-influenced coastal waters were rich in nitrate originating from the Lamas River and/or the coastal upwelling. The nearshore station, in which P was more prone to become deficient than other offshore stations because of river mixing, showed a higher N/P ratio than that of the other stations. However, their ambient phosphate concentrations were much higher than those of the rest of the stations. Unlike in summer when P was replenished by the coastal upwelling, P in winter was the result of intense mixing. The effect of the river became more apparent during the April-June period of 2002 and March-May of 2003, when the upper layer is thermally stratified and the river plume reached as far as the studied region via wind-induced surface flow. On the other hand, the effect of the river was traced in the offshore surface waters in May 2002 and March-June periods of 2003 (Figures 4.1 and 4.6), indicating that the major rivers of southern Anatolia influenced the entire shelf zone. However, the surface salinity remained relatively high at the shelf zone when the freshwater inflows did not reach as far as the studied region (Figure 4.1 and Figures 4.6-4.7). Satellite pictures of the surface chlorophyll and temperature distributions in Figure 4.5 demonstrate that the NE Mediterranean coastal (shelf) margins can be highly influenced by the river inflows, as reported by Örek (2007). These seasonal variations resulted in evident changes in bio-chemical properties of the wide shallow shelf zone of the NE Mediterranean.

Surface nutrient concentrations of the nearshore and shelfbreak stations become similar when the river effect is at minimal level and internal processes dominate the system (Figure 4.6). For example, nutrient contents of the nearshore surface waters were observed to increase markedly between January and March 2003 due to effective vertical winter mixing and the limited river inflow to the sampling location. However, notable increases (~20 times) were observed in nitrate and silicate contents of the nearshore waters during December 2001, when the river inflow increased drastically after heavy rains in the region. In this period, Eker-Develi (2004) also observed pronounced changes in phytoplankton abundance and composition of the shelf waters due to riverine input of nutrients. Comparison of the nutrient data reveals that phosphate concentrations were always higher in the nearshore waters (See Appendix A). The surface nutrient concentrations reached the peak levels in March and April 2003. However, a maximum of 0.130 μM for DIP was also recorded in May 2002 in surface waters having high POM but very low NO_3 values (Figures 4.6 and 4.8).

Heavy rains can introduce large amounts of phosphorus from land via river runoff and partly by direct precipitation. The Lamas River and rain waters were observed to be selectively enriched in phosphorus when the Saharan dust reached as far as the region (Tuğrul *et al.*, 2005). Kubilay *et al.* (2002) suggested short-term rainfall is necessary for wet deposition of dust minerals; longer duration rainfalls, as in the winter months, may lead to a complete washout of sulfate aerosol particles from the atmosphere. Observations in the region show that the April-May period is the most favorable periods for wet deposition of P-rich Saharan dust via spring rains. For example, before the May-2002 sampling in the sea, the region received some rainfall on May 11, 2002 with high concentration of nitrate (66 μM) and ammonia (40 μM), but very low silicate (0.77 μM) and abnormally high phosphate (3.74 μM) values (Tuğrul *et al.*, 2004), yielding an N/P ratio of 18. This ratio was much less than the natural N/P of the river water and winter rains feeding the region (Tuğrul *et al.*, 2004). Spring rains in the region are expected to increase the phosphate content of the Lamas River. Thus, the P-rich spring rains and the river input could significantly increase the phosphate content of near-surface water in May 2002. Likewise, Migon *et al.* (2001) reported that as the efficiency of atmospheric washout is much higher by means of wet deposition than by dry deposition, a northwest Mediterranean rain event is likely to input within a single day up to 17 μmolm^{-2} of reactive P to surface waters.

Although high amounts of nitrate was supplied to the marine environment via rain and river waters, the rapid turnover of phosphorus in the surface waters may contribute to low N/P ratios. Additionally, in March 2003, the DIP concentration of the NO_3 and the Si-depleted near-shore water column (0.14-0.16 μM) was apparently higher than those of the shelfbreak station (0.014-0.040 μM). However, NO_3 and Si concentrations attained the highest value in the next month (April 2003) in the DIP-depleted surface waters. This shift strongly suggests that the March DIP peak in the well-mixed water column was principally originated from internal processes, mainly the dissolution of reactive phosphate in the sediment layer via turbulent mixing, rather than the external inputs. The biochemical properties of the surface water at the nearshore station become similar to those of the shelfbreak site in December 2002, January 2003, and November 2003, indicating a weak river effect markedly taking place in these periods (Figures 4.6 to 4.9, Appendix A).

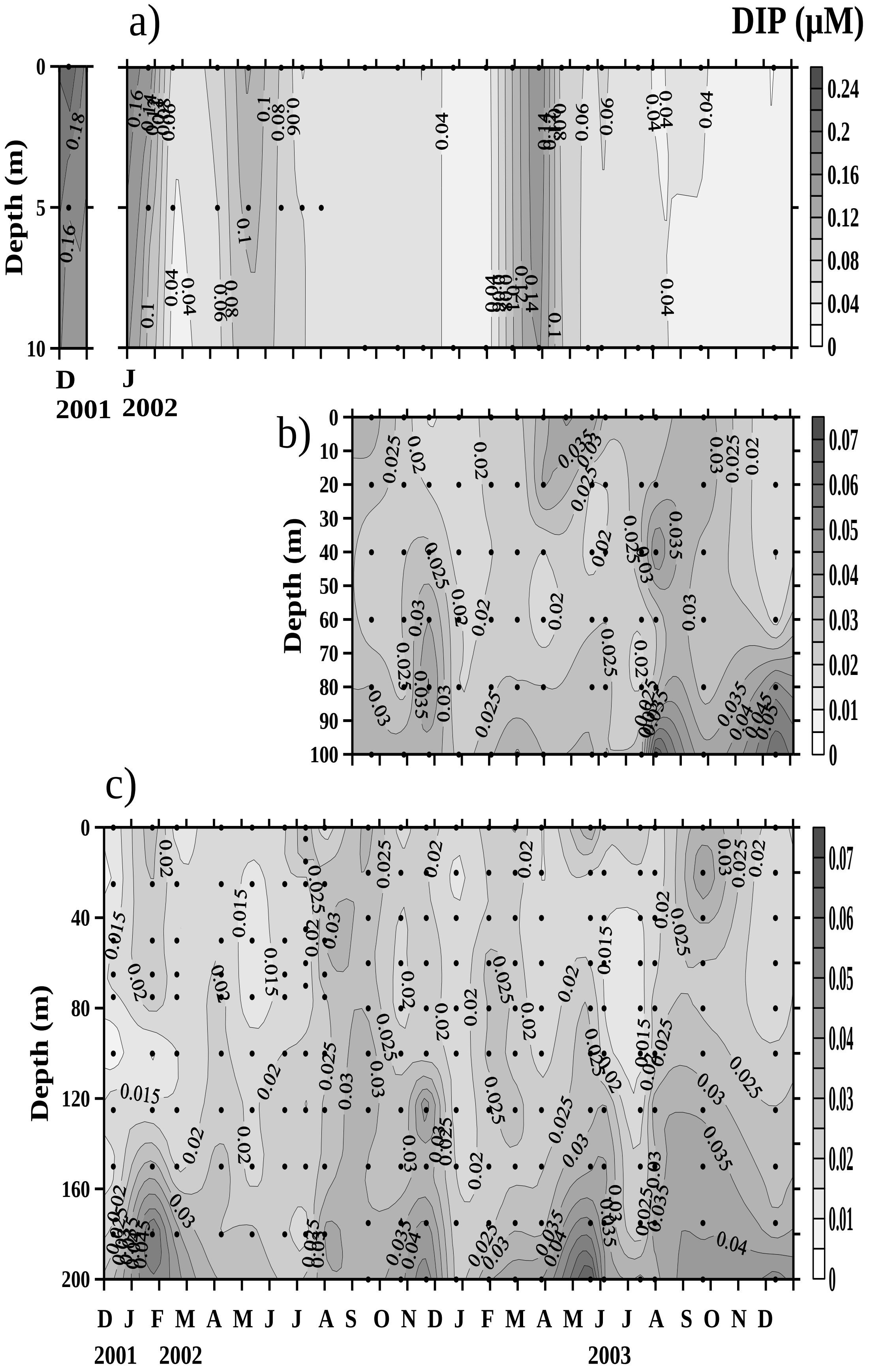


Figure 4.7 Contour plots of the vertical distribution of DIP at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

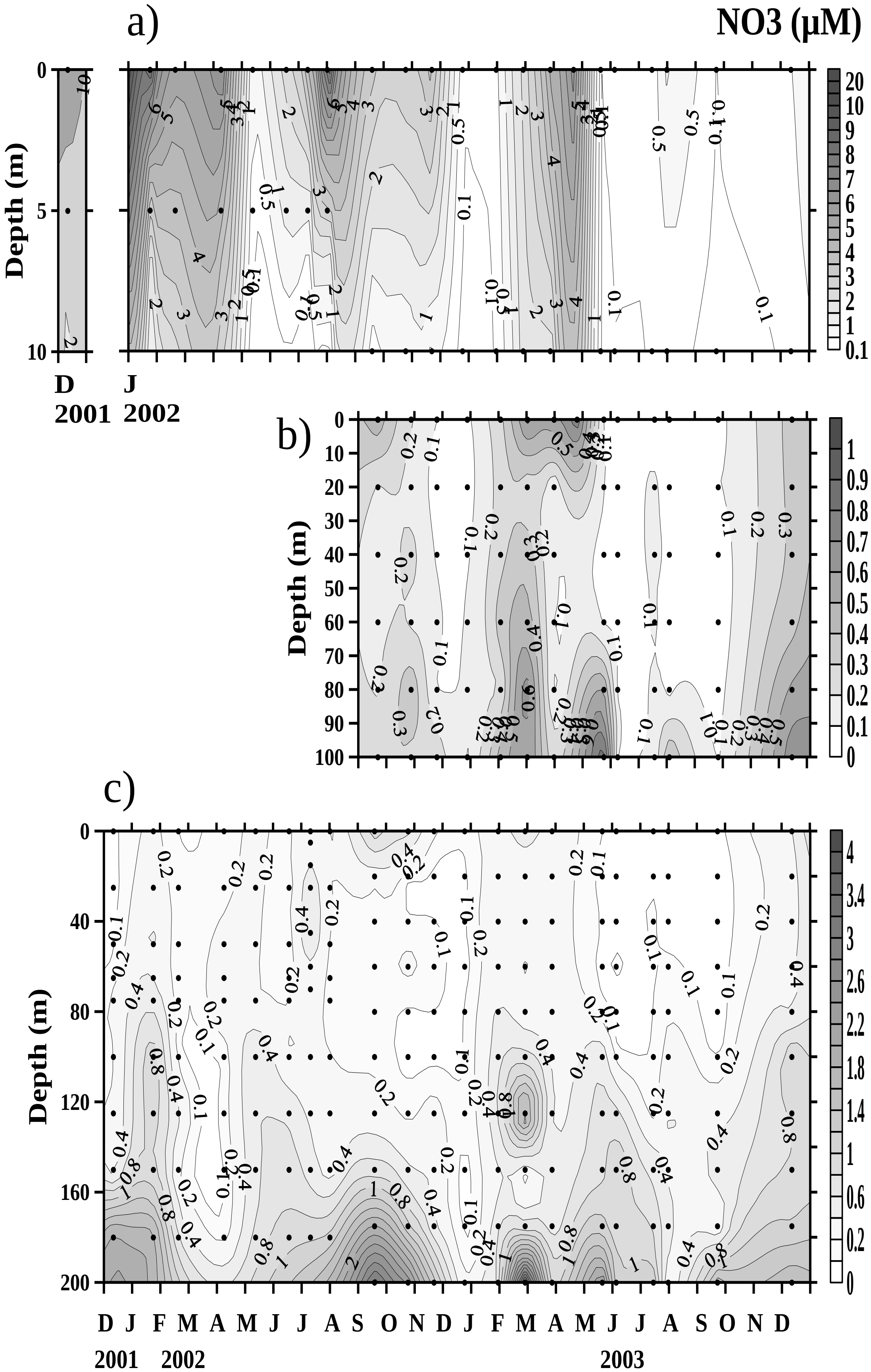


Figure 4.8 Contour plots of the vertical distribution of NO_3 at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

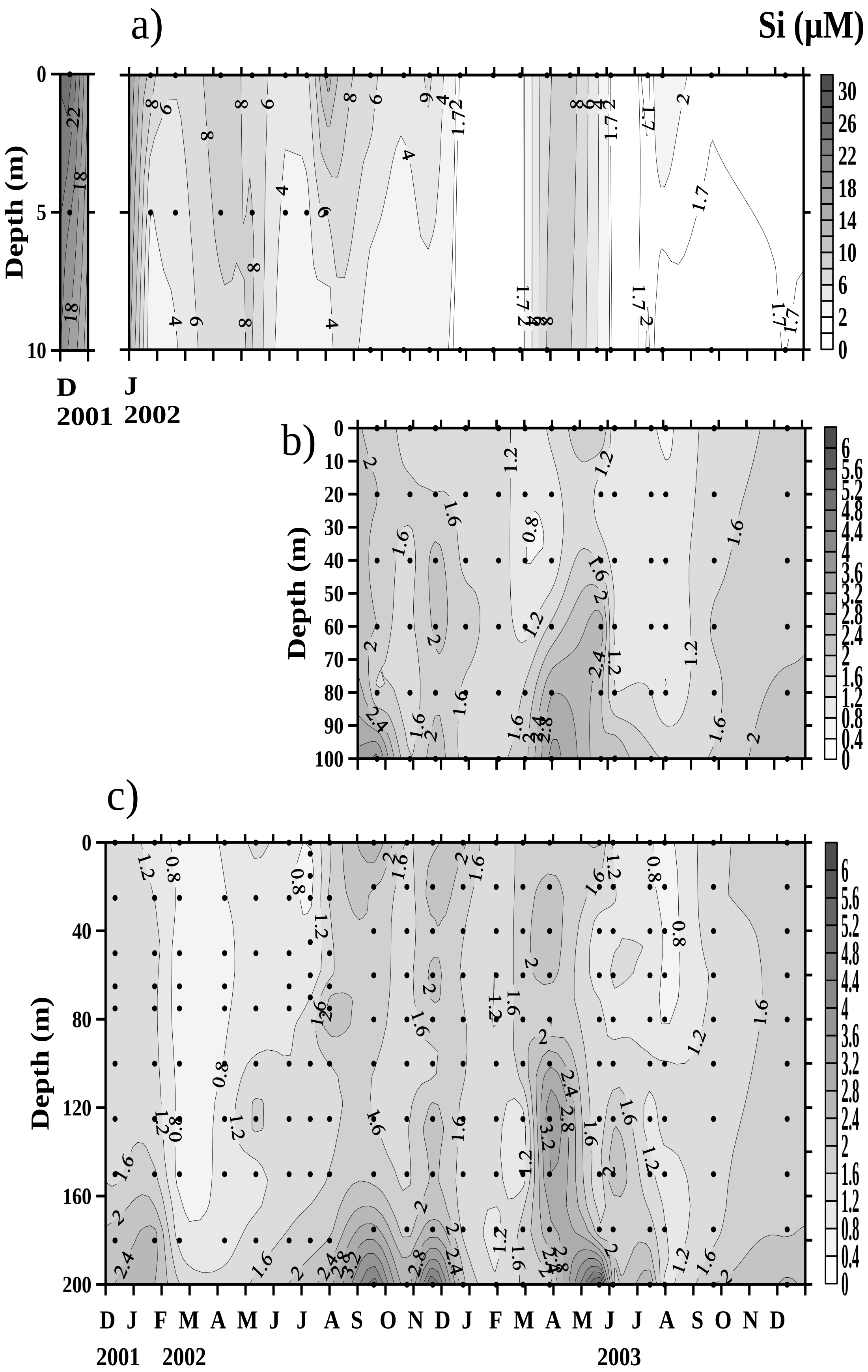


Figure 4.9 Contour plots of the vertical distribution of Si at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

The low salinity, measured in the surface waters of the middle and shelfbreak stations during February and June, indicates the important role of the Seyhan and the Berdan Rivers on the western continental shelf (Figures 4.1 and 4.6). However, the low concentrations of dissolved inorganic nutrients measured in the surface waters of the study region strongly suggest that dissolved inorganic nutrients in the estuarine waters were utilized in photosynthesis and transformed into the organic form until the western shelf region was reached. The major factor for low nitrate and phosphate values measured at the offshore station is that the NE Mediterranean waters are always poor in nutrients during the year (Krom *et al*., 1991; Yılmaz and Tuğrul, 1998), excluding the cyclonic Rhodes Gyre of the winter period (Napolitano *et al*., 2000; Ediger *et al*., 2005).

Comparison of time-series surface data in Figure 4.6 reveals that the surface salinity at the shelfbreak station, ranging between 38.0-39.6 psu in the course of 2002-2003, exhibited less seasonal fluctuations as compared to the nearshore station fed by the Lamas River. However, low salinity and high silicate values were observed in April-May 2003. This feature was the result of the major rivers feeding the eastern shelf region whose effect could be monitored at the western shelfbreak zone off Erdemli (Figures 4.1 and 4.3). Ranges of river effect can be realized from satellite pictures of the NE Mediterranean region (Figure 4.5). However, the nitrate introduced by the river flow was almost consumed in the shallow waters whilst the silicate increase could be monitored in the shelfbreak surface waters during April-May 2003 when the river discharges are at maximal levels.

The river effect on the nearshore hydro-chemistry was traced by apparent increases in nitrate and silicate concentrations in less saline surface waters as compared with the bottom water of the shallow zone and offshore surface waters (Figures 4.8 and 4.9). From the comparison of the Si/NO_3 molar ratios of surface waters (0.02-0.9) with those of the Lamas River waters (0.67-1.38 μM), it can be conclude that the NO_3 consumption in the nearshore waters exceeds the Si removal rate. Similarly, the NO_3/PO_4 molar ratios (N/P) were rather low in the nearshore waters as compared to the river ratios, strongly suggesting faster regeneration of phosphate in the coastal region fed by P-poor water masses. It is well known that the phosphate cycle is much faster than the nitrate turnover in the phosphate depleted surface waters leading to lower N/P ratios in the eastern Mediterranean (Krom *et al.*, 1991; Yılmaz and Tuğrul, 1998; Karafistan *et al.*, 2002; Ediger *et al.*, 2005). The second source of the lower N/P ratios in the surface waters might be due to the overestimation of DIP concentrations in the seawater due to the positive chemical interferences from other forms of phosphorus in the upper layer. Dissolved reactive phosphates measured by the MAGIC technique were very likely to be higher than the real DIP content of the productive (thus dissolved/particulate organic phosphorus rich) surface waters. It has been experienced that some components of DOP and POP in the seawater could be decomposed to DIP by the acid to form a colored DIP complex during the measurement as suggested previously by Vitousek *et al.* (2002) and Moutin *et al.* (2002). This interference becomes less significant when DIP concentrations exceed 0.1 μM in the surface and deep waters having higher DIP than DOP.

4.3.2 Spatial and temporal variations of dissolved inorganic nutrients in the water column of the Northeastern Mediterranean

Because of the imbalance between the supply and removal rates of nutrients, the euphotic zone waters of the NE Mediterranean shelf contained low concentrations of dissolved inorganic nutrients in the course of 2002-2003, as reported by Çoban-Yıldız *et al.* (2000a). The nutrient results given in Appendix A demonstrate the oligotrophic conditions in the shelf EZ waters as well as in the deep basin of the NE Mediterranean Sea (DIP: 0.006-0.041 μM, NO_3: 0.06-0.94 μM and Si: 0.54-2.88 μM). Throughout the study period, mean of nutrient concentrations for the water column were calculated as 0.063±0.043 μM for DIP, 2.08±1.98 μM for NO_3 and 4.42±4.19 μM for Si in the nearshore station, 0.027±0.009 μM for DIP, 0.22±0.19 μM for NO_3 and 1.57±0.57 μM for Si in the middle station, 0.024±0.010 μM for DIP, 0.43±0.35 for NO_3 and 1.51±0.71 μM for Si in the shelfbreak station (see Appendix F). Nutrient-rich waters were generally detected at near-bottom depths of the shelfbreak station (DIP: 0.016-0.068 μM, NO_3: 0.11-3.61 μM and Si: 0.96-5.79 μM) (Figures 4.7 to 4.9). The nutrient profiles in the deep (reference) stations were similar to those reported for the NE Mediterranean (Yılmaz and Tuğrul, 1998; Çoban-Yıldız *et al.*, 2000b; Karafistan *et al.*, 2002; Kress and Herut, 2001; Krom *et al.*, 2005). A nutrient (DIP and NO_3) maximum at ~600 m (Figure 3.26) was formed at the base of the nutricline.

The nutrient data, depicted in Figures 4.7 to 4.9, demonstrate that the near-bottom waters at the shallower station were relatively rich in DIP as compared to the concentrations of the deeper stations. The spatial difference became more evident in the winter period due to DIP inputs from the sediment layer of the shallow zone to the water column by effective vertical mixing as reported for the other coastal seas (Scanlan and Wilson, 1999; Giani *et al*., 2003). The bottom water DIP concentrations at the deeper stations were relatively low, ranging merely between 0.03-0.07 μM during the course of the study. Figure 4.7 also clearly shows that the water column of the deeper stations was depleted in DIP, ranging between 0.02-0.04 μM and with the lowest values at the intermediate depths. The higher DIP concentrations of about 0.05 μM were recorded in the near-bottom waters during the autumn months of 2003. In this period, the bottom layer was occupied by the less saline, cooler water masses of the deep basin origin.

Temporal variations of nitrate in the nearshore water column appeared to be highly determined by the riverine input and intensity of vertical mixing. Figures 4.7 to 4.9 demonstrate that the near-bottom waters of the shallow station were relatively rich in nutrients during winter months because the study region was highly influenced by the river inflow and intensive vertical mixing introduced nutrients from sediment layer to the overlying water column. The influence of riverine discharge and coastal runoff remains significant throughout spring due to snow melt and precipitation events. The deeper shelf zone is slightly affected by riverine inputs. Surface waters of the shelf are subject to input from the deeper layer via circulations and vertical mixing during late autumn-spring period. However, this effect becomes negligible in the summer-early autumn months due to strong density stratification in the upper layer. Comparison of the nearshore and offshore nutrient results in Figure 4.8 reveals that the near-bottom waters of the shallower station were depleted in nitrate during summer-autumn period because the photosynthetic uptake rate exceeded the input rate from internal and external sources to the stratified water column. The bottom waters of the shelfbreak station were far below the euphotic zone boundary. Moreover, the bottom layer at the shelfbreak (~200 m total depth) is also occupied by the relatively nitrate-rich, less saline intermediate waters of the NE Mediterranean Sea (Yılmaz and Tuğrul, 1998; Ediger *et al*., 2005). The lateral intrusions from the deeper layer of the open sea to the interior shelf zone markedly weaken at the middle station (about 100 m water depth) where the signatures of the Mediterranean intermediate waters were not traced clearly. On the other hand, spatial changes in nutrients were less pronounced in the DIP contents of the shelf waters (Figure 4.7) because the Mediterranean intermediate layer waters are well known to be depleted in DIP but relatively rich in nitrate, leading to high N/P ratios in the near-bottom waters of the shelf as experienced in the open sea (Krom *et al.*, 1991; Béthoux *et al.*, 1992; Yılmaz and Tuğrul, 1995; Krom *et al.*, 2005).

The water column concentrations of the shelf waters were almost similar down to 125-150 m depth in winter period because vertical mixing became intensive in the water column and the bottom layer was less influenced by the open sea deep water intrusions. For this reason, the nitrate concentrations of the near-bottom waters at the shelfbreak zone ranged from ca. 0.6 to 2 μM levels in winter months, then rising up to ca. 1-3 μM levels in summer-autumn months. Nitrate concentrations in the upper 100 m of the shelf, however, were almost consistent at similar depths. This feature indicates that the shelf zone was occupied by the water masses with similar hydro-chemical properties changing seasonally.

There are various internal and external sources that can contribute to the nutrient pool of the shelf EZ. Whereas riverine input contributes markedly to primary production in the shallow nearshore regions (Bologa *et al.*, 1995; Cociasu *et al.*, 1997), the major source of nutrients for the EZ of the offshore zone of the shelf is the input from the nutricline depths and sub-halocline layer via strong convective mixing in winter and upwelling processes in winter-early spring months (Eppley, 1989; Herut *et al.*, 2000). Under oligotrophic conditions in summer, a well developed density stratification in the upper marine layer isolates surface waters from the underlying waters (Figures 3.4 and 3.6). Strong stratification limited the nutrient supply to the EZ from aphotic layer having low concentrations of nutrients. As reported by Vedernikov and Demidov (1993) and Oğuz *et al.* (1996), primary production is apparently sustained by the regeneration of nutrients in the EZ. In the eastern Mediterranean Sea, however, the atmospheric deposition may contribute remarkably to biologically available nutrient pool of the EZ of the open sea at dry months when the inputs from rivers and deep layer are very limited (Migon *et al.*, 1989; Bergametti *et al.*, 1992).

Nearshore surface waters fed by the river were always richer in dissolved reactive silicate than the offshore site; the concentrations decreased in the near-bottom waters due to the river input to the near surface layer. This effect disappeared in the winter months because the entire water column was homogenized thoroughly. The lowest nutrient values in the saltier surface waters were observed during summer-autumn of 2003, indicating less riverine input to the study region (Figure 4.6). However, the Si content of the shelf waters mostly exceeded 1.0 μM; the lowest Si values of 0.8-0.9 μM were determined in the spring of 2002 and the autumn of 2003, in the upper layer of 100-160 m of the shelfbreak zone, indicating a net loss of silicate in the upper layer waters (Figure 4.9). The higher Si content of the deep waters at the shelfbreak station was consistent with the temporal variations of nitrate in the shelf, showing a common source of the open sea origin. The Si and nitrate contents of the bottom layer at the shelfbreak zone are similar to those obtained at intermediate depths of the NE Mediterranean open sea (Kormas *et al.*, 2002; Eker-Develi *et al.*, 2004, Krom *et al.*, 2005).

Silicon has not been reported as a limited nutrient in the Mediterranean Sea (Marty *et al.*, 2002). Nevertheless, the seasonal variations of dissolved reactive silicate (Si) concentrations follow the same trends as nitrate and phosphate. There is a depletion of silicates in the surface layers from spring-summer period to December, although it is less pronounced than that of other nutrients. Si remained at low but detectable levels during some months of 2002-2003. Based on the present data set, it is rather difficult to suggest if phytoplankton production is limited by Si in the shelf waters. However, it has been suggested that ratios of dissolved N/P<10 and Si/N>1 indicate N-limitation, that Si/N<1 and Si/P<3 show Si-limitation (Dortch and Whiteledge, 1992; Justic *et al.*, 1995; Herut *et al.*, 2000). The above criteria are based principally on a phytoplankton nutrient uptake in Redfield ratios, as is observed in most oceanic areas. Limiting criteria may deviate with different uptake dynamics of a site-specific biota. In the present study, Si/N (range: 1-39, mean: 8) and Si/P (range: 20-250, mean: 70) were apparently high. According to the above criteria, no Si-limitation was expected to occur in the NE Mediterranean shelf zone during 2002-2003. Put simply, spatio-temporal P and/or N-limitation most probably proceeded in the NE Mediterranean shelf ecosystem off Erdemli.

A highly significant positive correlation (based on Pearson, 2-tailed correlation) was observed between DIP and NO_3, DIP and Si, and NO_3 and Si ($p<0.001$) in the nearshore and shelfbreak stations (see Appendix I). Briefly, the above mentioned significant correlations between nutrients indicated that DIP, NO_3, and Si interact with each other in nearshore and shelfbreak stations. Since the concentration of DIP positively correlated ($p<0.05$) with NO_3 and Si in the middle station, but no correlation was seen between NO_3 and Si ($p>0.05$), it was suggested that the major effect on NO_3 and Si distribution in the middle station was DIP.

4.4 Spatial and Temporal Variations of Particulate Matter Abundance and Composition in the Shelf Waters of the Northeastern Mediterranean

Particulate organic matter (POM), mostly derived from phytoplankton and weakly degraded cells of dead phytoplankton and minor part of bacteria and living or dead zooplankton (Copin-Montégut and Copin-Montégut, 1983; Ediger *et al.*, 1999; Çoban-Yıldız *et al.*, 2000a; Giani *et al.*, 2003), is composed essentially of proteins, carbohydrates, and lipids (Parsons *et al.*, 1977). The abundance and elemental composition (C/N/P ratio) of POM in the marine environments are controlled by complex physical and biochemical processes interacting in the upper layer as well as nutrient supplies from various sources (Tselepides *et al.*, 2000; Karl *et al.*, 2001; Geider and La Roche, 2002; Ediger *et al.*, 2005). In the surface layer, variations in its composition may be due to variations of phytoplankton species or to variable ratios of the constituents of particulate matter. Below the EZ a change in composition is likely because the various molecular species resist biochemical degradation differently. In the deep waters, where detritus is the principal constituent of particulates, the variations are due to the differential decomposition of the material (Copin-Montégut and Copin-Montégut, 1983).

In the NE Mediterranean shelf, concentrations of particulate organic carbon (POC) and nitrogen (PON) generally range from 1-10 μM and 0.08-1.68 μM in less productive open stations to 3-114 μM and 0.41-9.99 μM in the more productive nearshore station receiving more nutrients from deep waters and land-based sources, respectively (Figures 4.10 to 4.12). Naturally, similar spatial and temporal trends appear in PON with values ranging between 0.1 and 4.5 µM as found by Socal *et al*. (1999) and Doval *et al*. (1999) in the western Mediterranean, and 0.06 and 0.68 µM reported by Ediger *et al*. (1999) and Çoban-Yıldız *et al*. (2000b) in the eastern Mediterranean.

POM concentrations were more variable than dissolved inorganic nutrients at the nearshore zone in 2002, exhibiting similar variations in 2003 (Figures 4.10 to 4.12). Moreover, the POM contents of surface waters were markedly high in the nearshore zone fed by the Lamas river inflow (Figure 4.13). The major POM peaks appeared in January and May 2002; the latter peak coincided with the salinity minimum. The surface POC concentrations of the nearshore station showed less pronounced increases in February and March 2003, whereas the increase of PON and TPP concentrations became more apparent in March 2003 (Figures 4.11 and 4.12), suggesting riverine POM input with high C/N ratios in February but nutrient input in March. Autotrophic POM production in March appeared to reduce the Redfield (C/N/P) ratio of bulk POM to levels of the natural POM composition of the marine environments (106/16/1). The POM peak in May 2002 was the result of high algal production during the period of short-term spring rains carrying nutrients from the atmosphere and land-based sources via the river runoff as experienced in the other productive coastal sea (Rabitti *et al*., 1994; Socal *et al*., 1999; Çoban-Yıldız *et al*., 2000b). In this period, NO_3 concentrations in the less saline surface water were nearly consumed by primary producers as the DIP remained at detectable levels, leading to low N/P ratios in the nearshore waters (Figure 4.5). Then, the nearshore POM concentrations apparently declined to levels of 10-15 µM for POC and 1-2 µM for PON in summer and autumn 2002 as the surface salinity was high.

Temporal changes in the POM content of the nearshore waters were much more variable and much higher in 2002 than the observations in saltier water masses (Figures 4.9 to 4.12). The POM increases in the nutrient-rich nearshore waters in spring-summer period occurred with elevated C/N (8-17) and C/P (101-753 as POC/TPP, 136-1217 as POC/POP) ratios, implying remarkable input of suspended POM from land via the river runoff with high concentrations of NO_3 and Si as experienced in other coastal seas (Laznik *et al*., 1999; Giani *et al*., 2001; Rabalais *et al*., 2002). The riverine input in April-May 2003 led to apparent increases in concentrations of POM and TPP in the surface waters of the deeper shelf zone (Figures 4.10 to 4.12 and Figure 4.14); however, the concentrations declined in the deeper part of the euphotic zone (Figures 4.10 to 4.13). These findings imply to the limited effect of riverine input of nutrients on the water column POM distributions. PON changes in the shelf water were principally consistent with POC; however, the TPP displayed more temporal fluctuation than C and N components of bulk POM pool of the shelf. Similar to earlier findings of Giani *et al.* (2003), the POC, PON and TPP concentrations in the coastal waters under the pycnocline declined apparently due to not only stratification but also degradation of settling POM in the water column (Figures 4.10 to 4.12). Moreover, POC, PON, and TPP decrease with increasing depth, as a rule. In the Atlantic Ocean and in the Mediterranean Sea the trend is well described by logarithmic decrease below 150 m, indicating little dissolution of particulates at great depth (Copin-Montégut and Copin-Montégut, 1983).

POM concentrations displayed an apparent decreasing trend from the river-fed nearshore to the shelfbreak zone and from spring to summer-autumn months across the shelf. The levels of spatial changes in the shelf are controlled by the volume flux and thus nutrient loads of the river flowing to the sea, as indicated previous studies in the region and other coastal seas (Abdel-Moati, 1990; Rabitti *et al.*, 1994; Socal *et al.*, 1999; Doval *et al.*, 1999; Ediger *et al.*, 1999; Çoban-Yıldız *et al.*, 2000b; Eker-Develi, 2004).

As was also reported for oligotrophic waters of the North Adriatic by Giani *et al.* (2003), the particulate matter of the EZ in the present study (Table 4.2) is extremely depleted of phosphorus and the deviations of POC (1.7-24.4 μM) concentrations, C/N (10-20), C/P (144-242) and N/P (9-18) ratios from the Redfield ratio were more enhanced than those found previously in the other regions of the eastern Mediterranean (Ediger *et al.*, 1999; Çoban-Yıldız *et al.*, 2000b). In addition to, POC concentrations and, C/N, C/P and N/P ratios at the surface and deep waters were higher than those found by Copin-Montégut and Copin-Montégut (1983) in the location of Borha II and Ligurian Sea of the western Mediterranean Sea (Table 4.2).

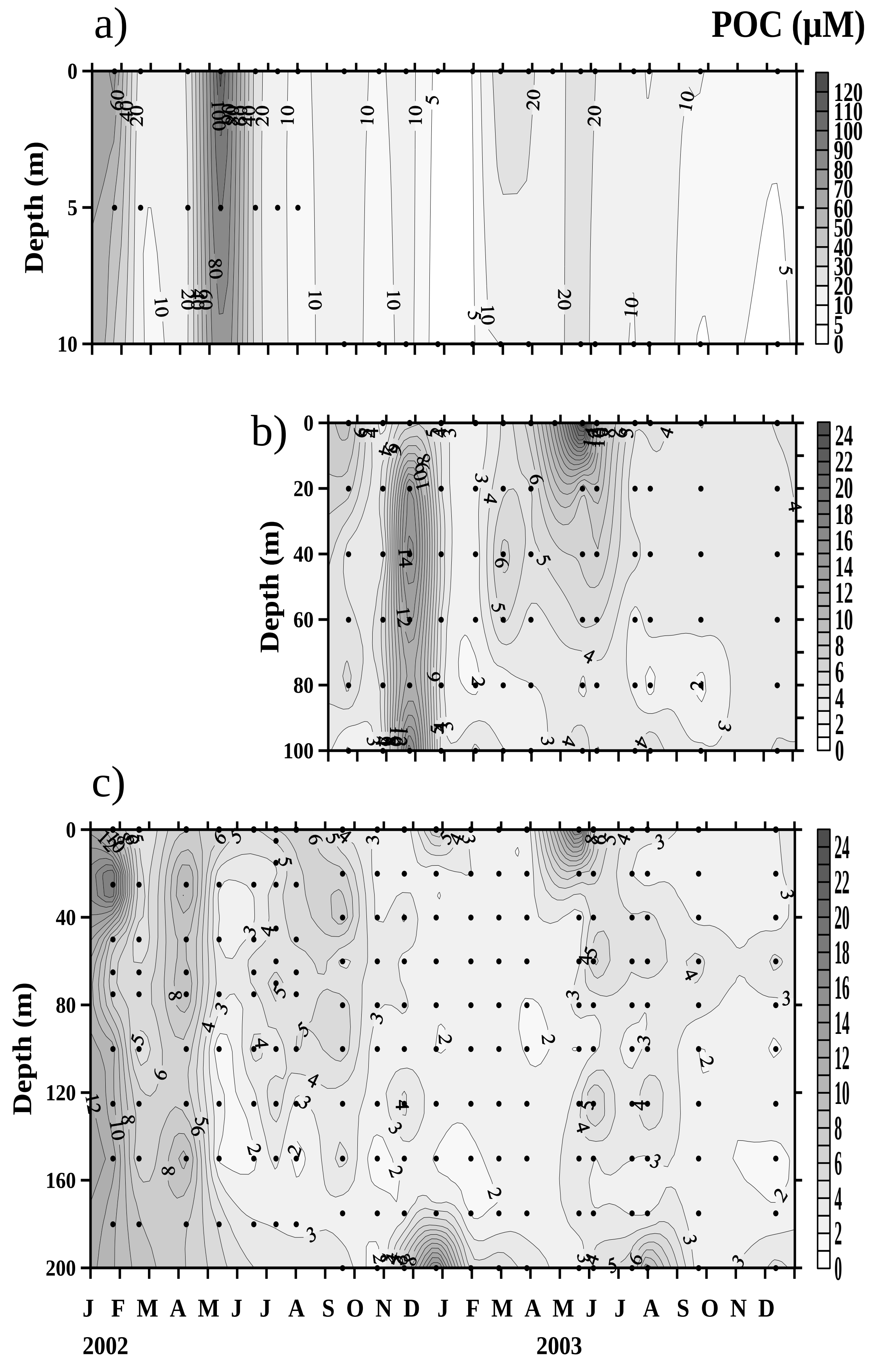


Figure 4.10 Contour plots of the vertical distribution of POC at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

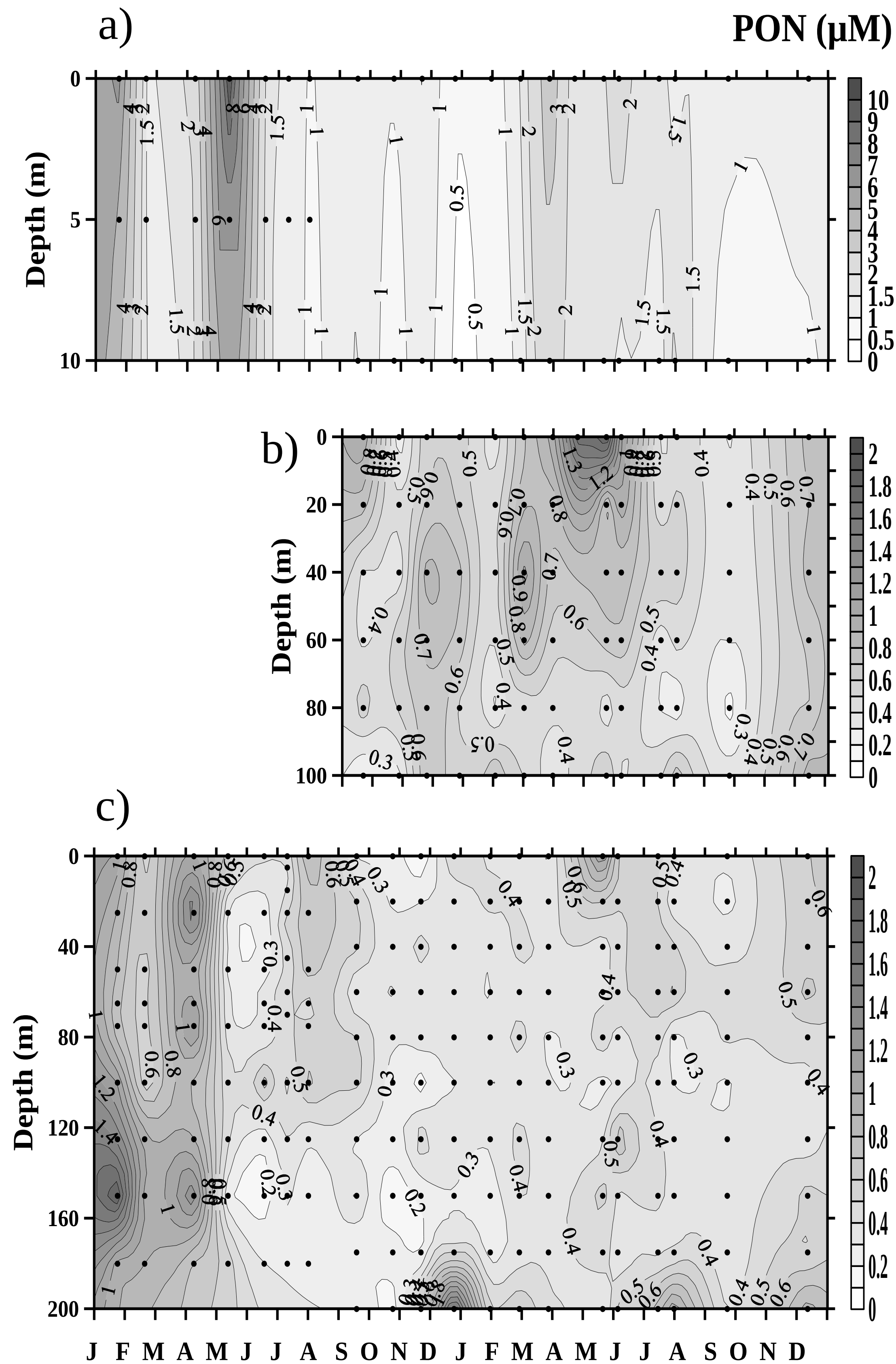


Figure 4.11 Contour plots of the vertical distribution of PON at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

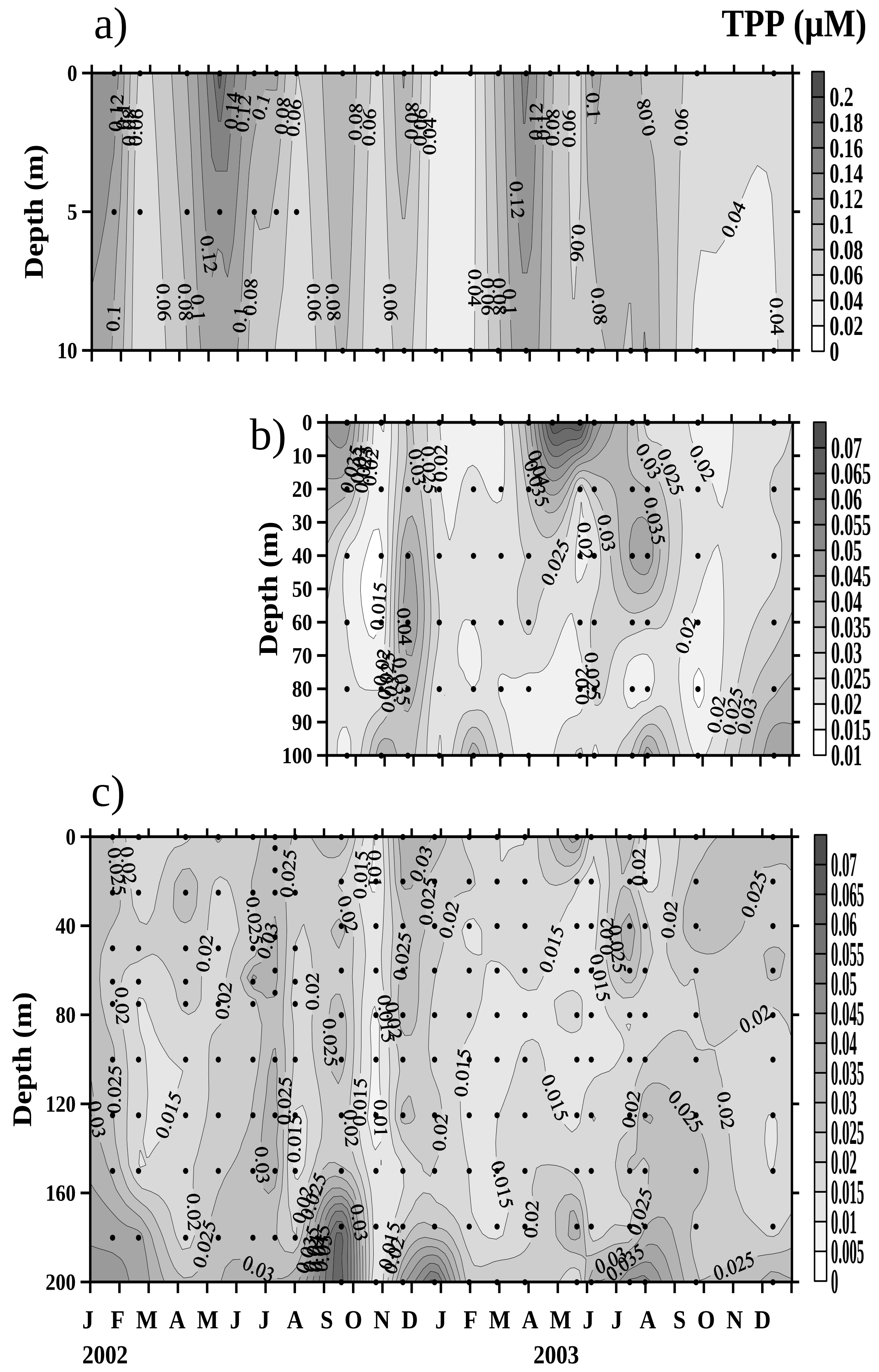


Figure 4.12 Contour plots of the vertical distribution of TPP at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

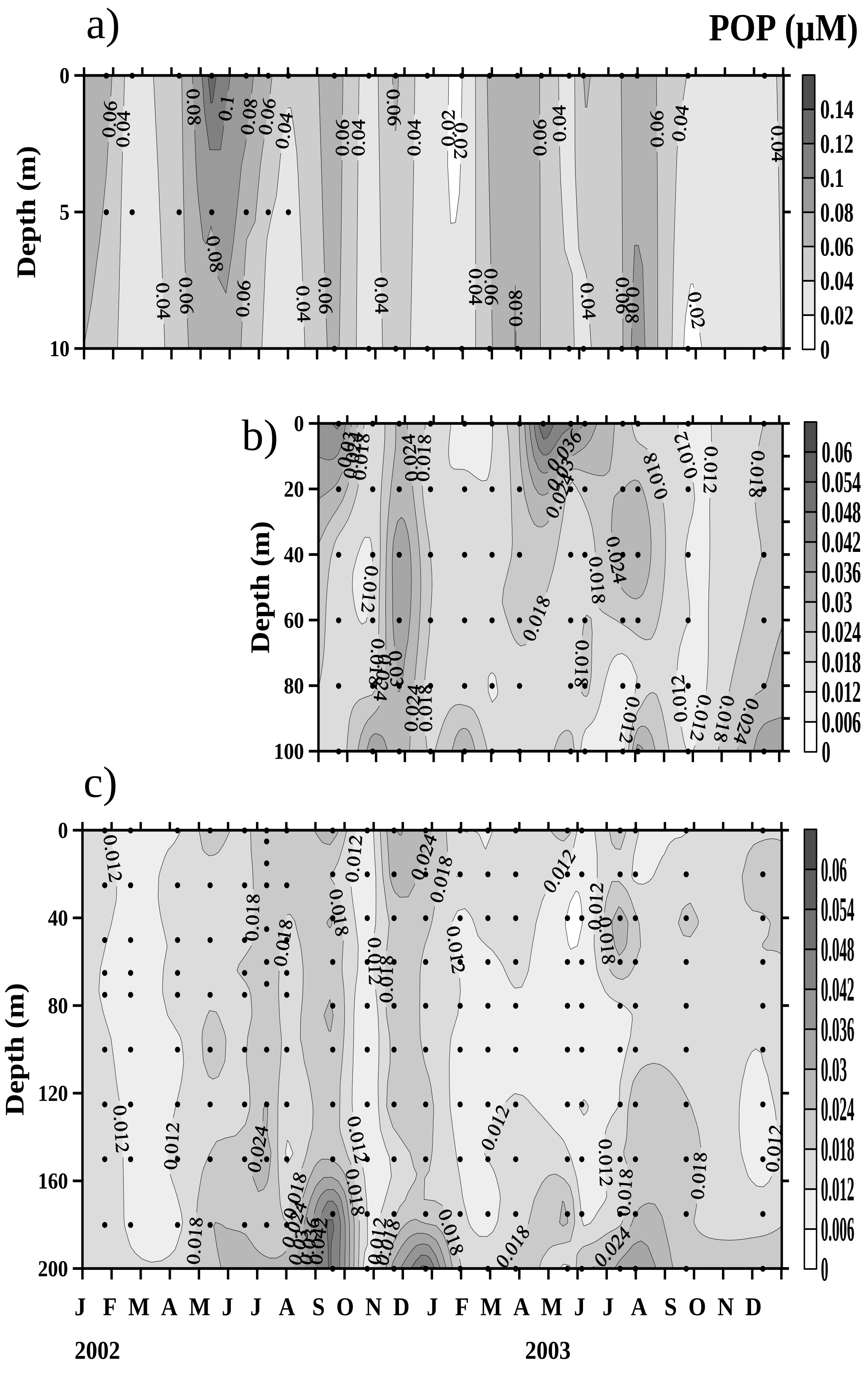


Figure 4.13 Contour plots of the vertical distribution of POP at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

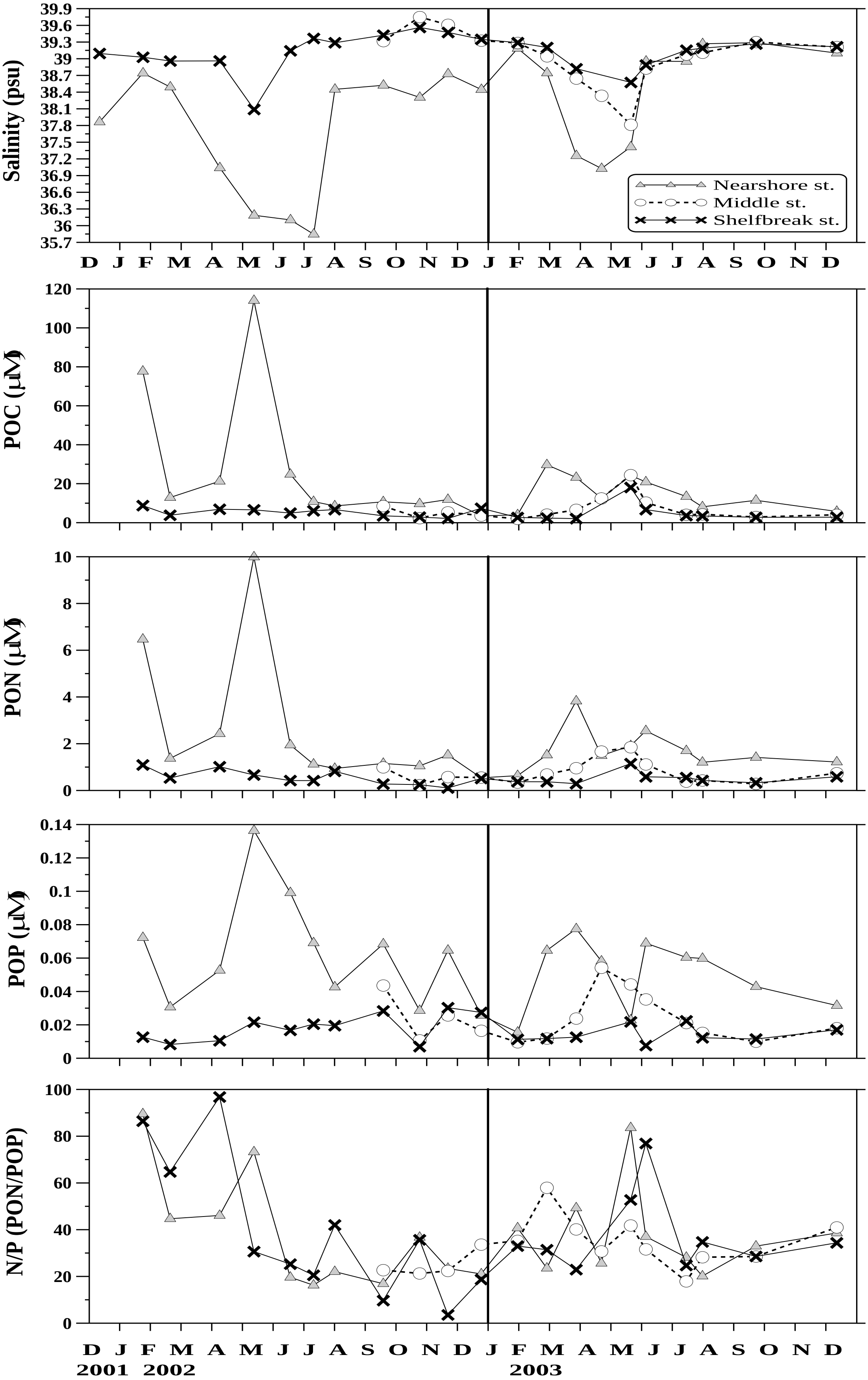


Figure 4.14 Time series distribution of salinity and POM (with N/P molar ratio) in the surface water of the stations.

Table 4.2 Elemental composition (C/N/P ratio) of bulk POM in the Mediterranean Sea derived from regression analyses

Sampling Period	**Area**	**POC (µM)**	**C/N**	**C/P***	**N/P***	**Reference**
December 2001-December 2003	The NE Mediterranean shelf zone (nearshore, middle and shelfbreak stations)	1.9-114 ❶	4.7-19.6 ❶	63.5-551 ❶	8.9-56.2 ❶	Present study
		1.7-24.4 ❷	10.2-19.9 ❷	144-242 ❷	8.9-18.4 ❷	
		1.0-90.4 ❸	4.2-24.7 ❸	60.2-624 ❸	11.5-50 ❸	
1990-1998	The NE Mediterranean (Levantine Basin, nearshore and offshore)	1.4-5.2 ❷	5.8-11.0 ❷	52-113 ❷	7-15 ❷	Çoban-Yıldız *et al.* (2000b)
October 1991-March 1994	The NE Mediterranean (Rhodes Cyclone, Cilician Basin and off Antalya)	1.5-3.9 ❷	6.0-9.9 ❷	107-123 ❷	11-17 ❷	Ediger *et al.* (1999)
August 1975	The Western Mediterranean Sea (Location of the Borha II)	-	5.1-12.7 ❶	89-168 ❶	19-20 ❶	Copin-Montégut and Copin-Montégut (1983)
			6.1-6.3 ❸	95-108 ❸	17-18 ❸	
April 1973	The Western Mediterranean Sea (Ligurian Sea)	-	6.2-6.3 ❶			Copin-Montégut and Copin-Montégut (1983)
			6.5-6.7 ❸	118-124 ❸	17-19 ❸	

P* : TPP
❶ : Surface layer
❷ : Euphotic zone
❸ : Bottom/deep layer

Regeneration of POM in the water column is a continuous source for the pool of dissolved inorganic nutrients. Eventually, a small fraction of settling is exported to the sediment layer. This could thus explain why no seasonal change is observed in the deep phosphate contents of the shelf waters having limited residence time. On the other hand, remineralisation of N and P components of POM occurs more rapidly than POC remineralisation as particles settle throughout the deep water column, leading to increases in C/N and C/P ratios of POM at depths below the EZ (Copin-Montégut and Copin-Montégut, 1983; Karafistan *et al.*, 2002). Comparison of temporal and spatial distributions of the abundance and elemental composition of bulk POM in the shelf margin reveals that changes in POM abundance across the NE Mediterranean shelf occurred with similar C/N ratios. The higher C/N ratios (8-20) were observed in 2002 and spring-summer 2003 (Figure 4.15). Geider and La Roche (2002) suggested previously that C/N ratios for phytoplankton cells isolated from oligotrophic regions tended to exceed the Redfield ratio slightly. High C/N ratios were determined occasionally due to (i) terrigenous organic matter, (ii) the increasing contributions of carbon-rich POM input by the river runoff, (iii) autotrophic production of POM with high C/N ratios, (iv) accumulation of degraded POM in the water column (Libes, 1992; Çoban-Yıldız *et al.*, 2000b; Ediger *et al.*, 2005). However, during summer-autumn 2003, the shelf ecosystem was poor in POM having lower C/N ratios (ranging between 5 and 9). This feature implies that: (i) the POM pool was dominated by autotrophic production fed by regenerated nutrients, (ii) bulk POM was essentially autochthonous origin from living organisms or from pysico-chemical transformations involving the colloids as suggested previously by Frascari *et al.* (2002). These C/N values are consistent with the canonical Redfield ratio of approximately 6.7 estimated for the productive oceans (Geider and La Roche, 2002; Giani *et al.*, 2003).

There is an aggrement among investigators (Copin-Montégut and Copin-Montégut, 1983; references therein) that the C/N ratio may range ca. from 5 to 8 in the surface layer. The variability is greater for the deep waters, but an increase with depth to values between 8 and 15 or even more has been generally observed. The increase suggests a more rapid utilization of proteins than carbohydrates. There are more discrepancies in the variations of the C/P ratio with depth, but the most recent results show that the ratio increases more rapidly than C/N. In general, C/N variations in particulate composition of the present study are consistent with these findings, ranging from ca. 5 to 11 in the surface layer and 5 to 25 in the bottom waters of the middle and shelbreak stations.

In this study it was determined that, the particulate matter in the surface waters of the NE Mediterranean was depleted in phosphorus and the deviations of C/P ratios from the classical Redfield ratios were coherent as recently observed in the oligotrophic waters of the North Adriatic (Giani *et al.*, 2003). Sanudo-Wilhelmy *et al.* (2004) reported that P-limited cultures had higher total cellular C/P ratios very close to the increased intracellular values in the field collections. Supported this assumption, calculated C/P ratios of bulk POM were higher than the Redfield ratio of 106 in the present study (Figure 4.16). The ratio was apparently high in the surface waters (Figure 4.14), indicating P-limited production and P-deficiency in the POM pool of the NE Mediterranean shelf ecosystem.

Close examination of bulk POM data in the surface water across the shelf show that the N/P ratio was markedly variable and high (PON/TPP: 26-46, PON/POP: 45-90) in winter 2002. This feature remained unchanged in the POM-rich nearshore surface waters (Figure 4.14). The lower C/N but higher N/P ratios of bulk POM across the shelf strongly suggest that biologically reactive phosphate was the potential limiting nutrient for POM production in the NE Mediterranean shelf waters (Figures 4.15 and 4.17). This suggestion is supported by the high NO_3/PO_4 (N/P) molar ratios (Table 4.1, Appendix B) observed in the river and rain waters feeding the shelf ecosystem (Tuğrul *et al.*, 2004).

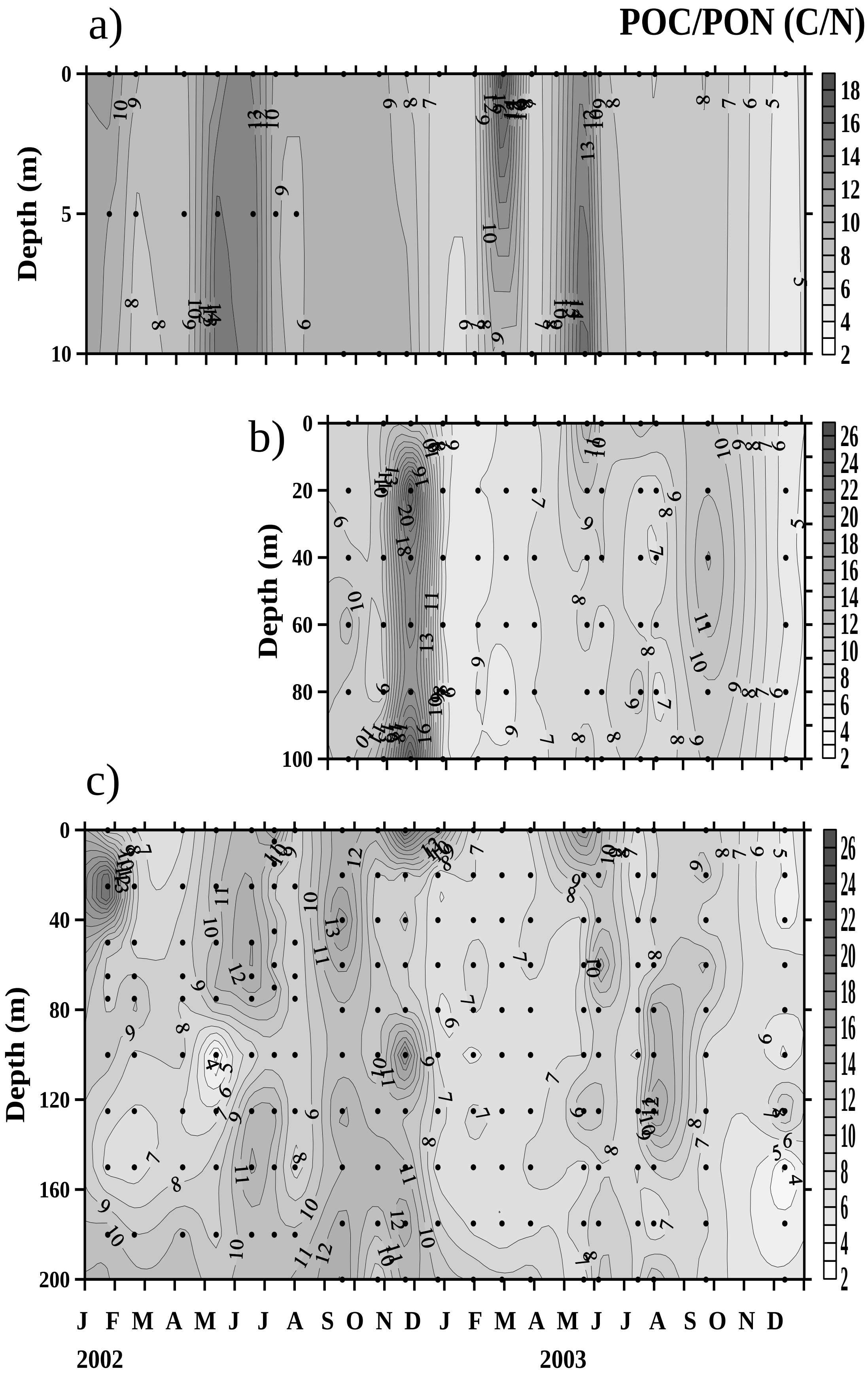


Figure 4.15 Contour plots of the vertical distribution of C/N at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

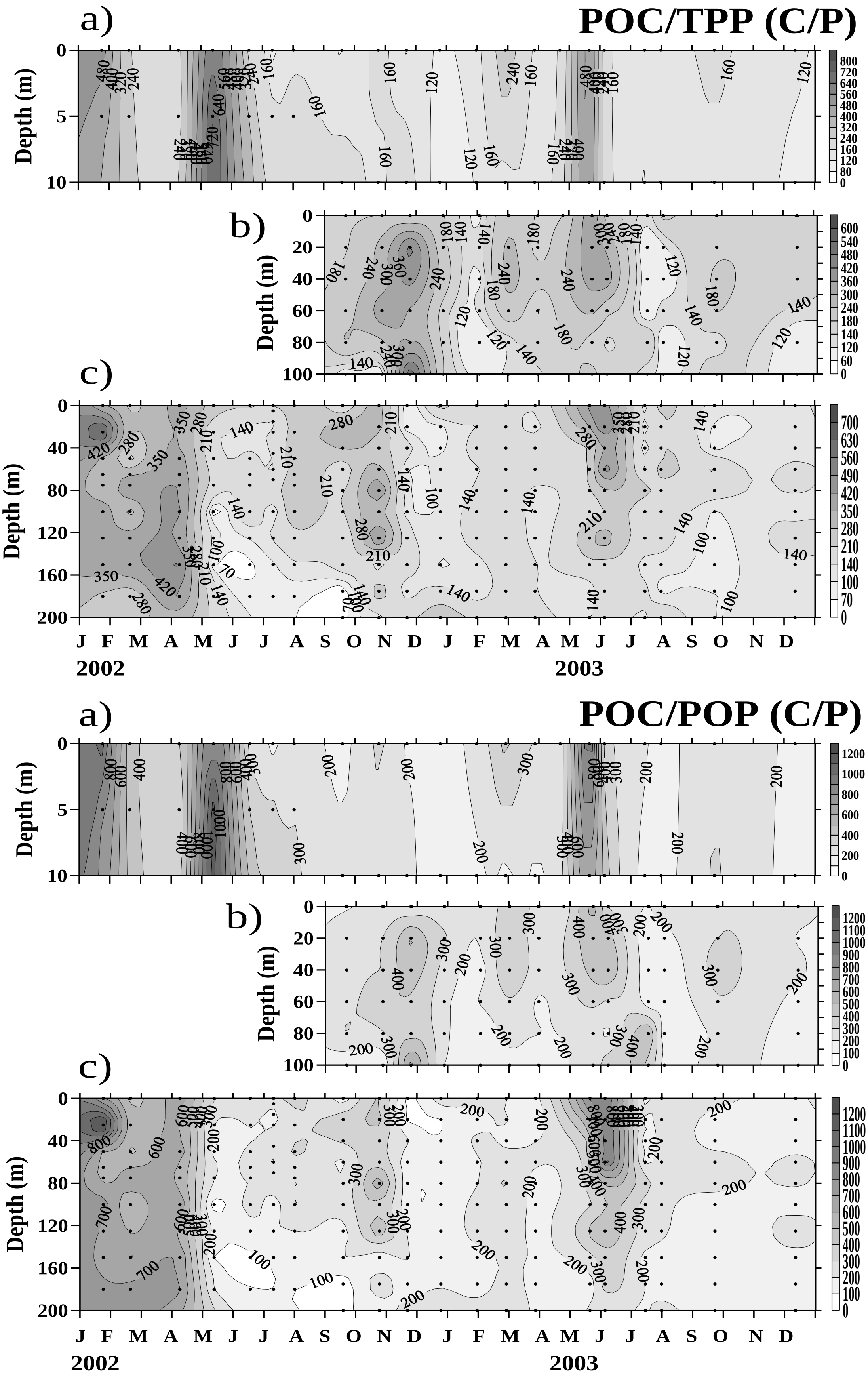
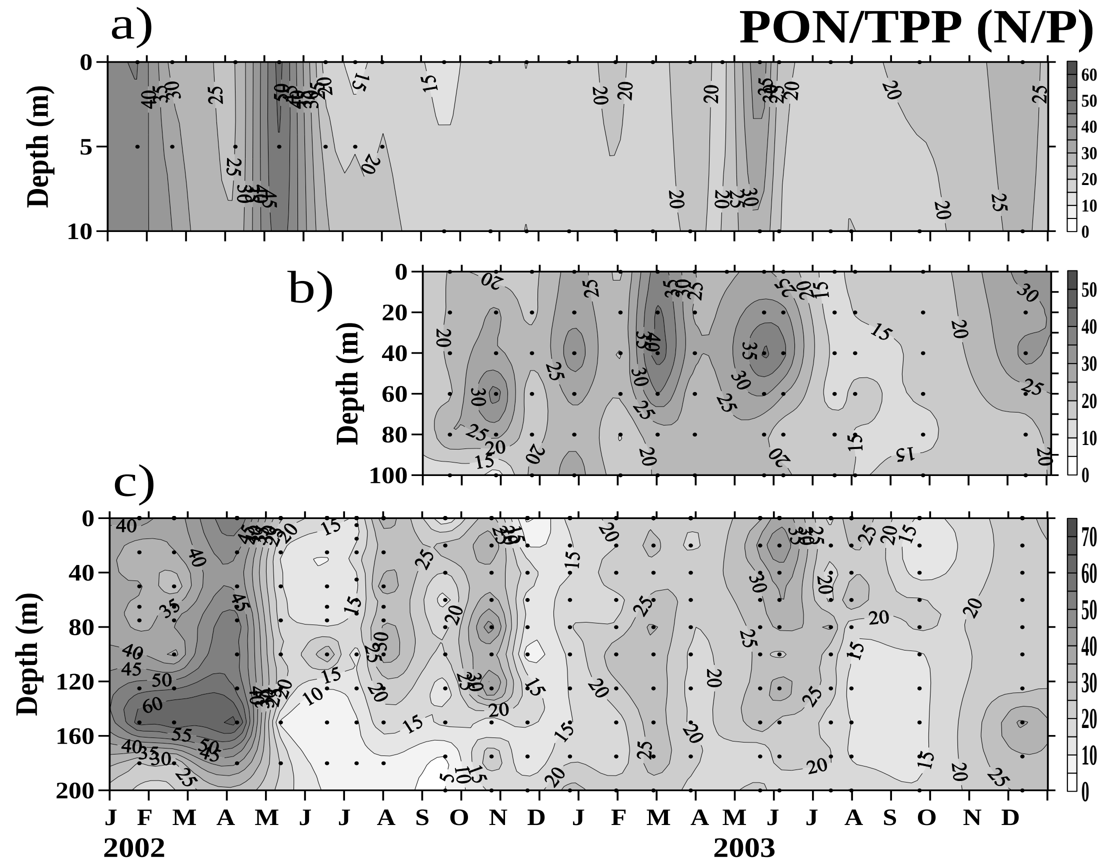


Figure 4.16 Contour plots of the vertical distribution of C/P at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

PON/TPP (N/P)



PON/POP (N/P)

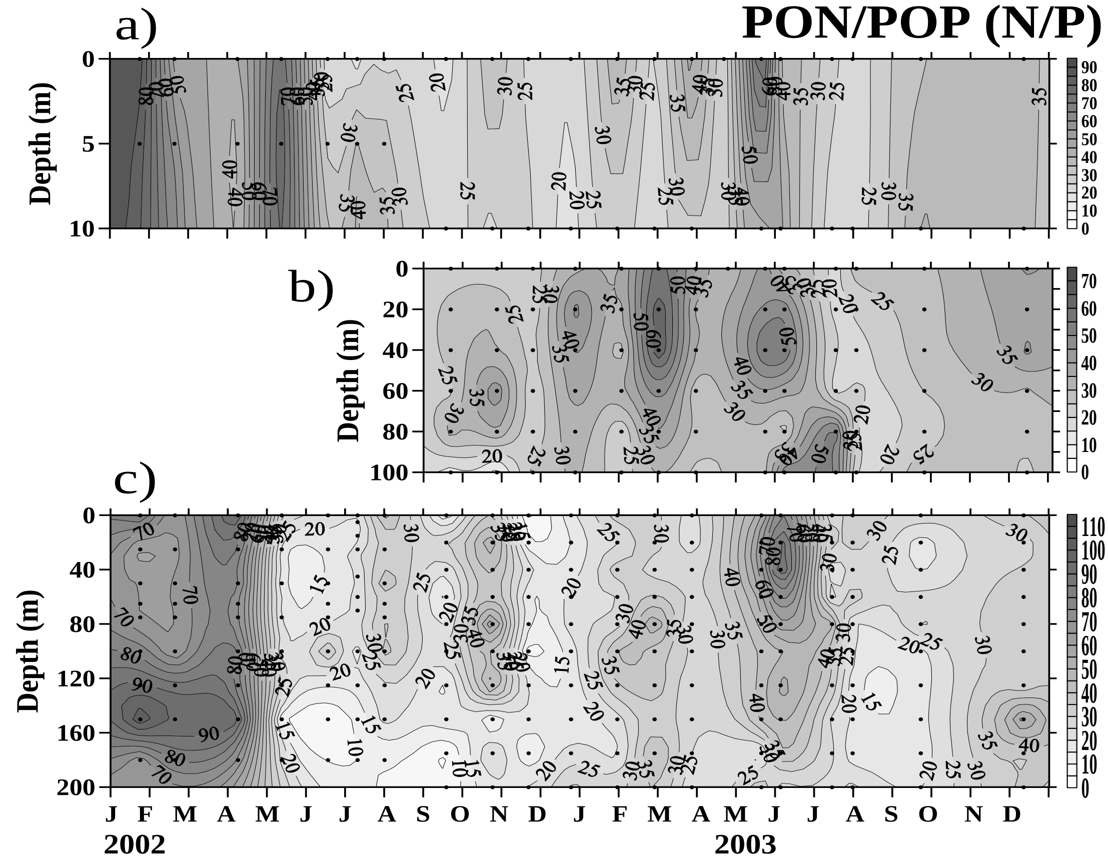


Figure 4.17 Contour plots of the vertical distribution of N/P at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

Chl-*a* concentrations (0.01-1.19 µgL^{-1}) in the shelfbreak station were in the range of oligotrophic waters (<1 µgL^{-1}) during the studied period. The vertical pattern of chl-*a* in winter showed a general decreasing trend from surface to the base of the EZ. Chl-*a* concentrations were low in the water column of the shelfbreak station and a weak deep chlorophyll maximum was observed around 100 m depth during summer of 2002 and 2003 (Yılmaz, 2006).

Differences in nutrient conditions and species composition between sampling periods could have affected the POC/Chl-*a* (C/Chl-*a*) ratios resulting in differences in productivity per unit chl-*a* (PI). When the C/Chl-*a* ratio ranges between 20 and 100; chlorophyll concentrations appear to be within the dynamic range of the grazing response of herbivorous copepods (Cullen and Eppley, 1981). C cell quotas of diatoms in the total algal biomass were much greater than the other microalgae. Phyto-C to Chl-*a* ratio estimated for the shelfbreak station (58) was higher than for the nearshore station (29); these values imply healthy population growth (Yılmaz, 2006). However, it was estimated to be 5 and 127 at the surface waters of the nearshore and shelfbreak stations, respectively, in July 2002 and March 2003, suggesting limitation of available nutrients (Yılmaz, 2006).

Elemental composition of planktonic POM, which dominates the abundance of bulk POM in the productive upper layer waters of NE Mediterranean shelf, may be assessed from linear regression analysis of POM (POC, PON, TPP and POP) data if the concentration changes are closely correlated with primary production and algal biomass increases in the water column. For this goal, all the POM data collected at 3 time-series stations on the shelf zone and reference station of the Cilician deep basin have been examined and the equations given in Table 4.2 and Figures 4.18 to 4.22 permit to estimate molar ratios of C:N:P of bulk POM of planktonic origin. Slopes of the regression lines of the regional POM data (POC vs. PON, POC vs. TPP, POC vs. POP, PON vs. TPP, and PON vs. POP) depicted in Figures 4.18 to 4.22, stand for the C/N, N/P and C/P ratios of bulk POM changing in the water column.

It appears that particulate carbon and nutrients (N, P) were significantly correlated (Table 4.2). The C/N ratio of the water column derived from the slope of C-N regression was 12.2 for the nearshore station, which was apparently higher than the classical Redfield ratio of 6.7 (106/16) for planktonic POM in the oceans (Redfield *et al.*, 1963). It was of 9.9 for the middle station, 8.8 for the shelfbreak station whereas a ratio of 7.5 was estimated for the reference station (Figure 4.18). POM increases in the nitrate-repleted nearshore waters appeared to occur with higher C/N ratios, implying direct influence of land-based more refractive POM input with high C/N ratios. Not unexpectedly, the C/N ratios at the reference station were comparable to the Redfield ratio, indicating plankton dominated POM increases in the EZ. Similarly, POC/TPP and PON/TPP ratios derived from the regression lines (Figures 4.19 and 4.21) were higher in the nearshore waters fed by the nitrate-repleted Lamas River. Likewise, a same pattern is found for POC/POP and PON/POP. The C/P ratio (as POC/TPP) of the POM ranged from 126 in the shelfbreak station to 453 in the nearshore station (Figure 4.19). Additionally, the temporal variation of C/P ratio (as POC/POP) was between 92 in the shelfbreak station and 566 in the nearshore station (Figure 4.20, Table 4.2). The N/P ratio of the POM from the middle station of the studied region was estimated to be 18 (as PON/TPP) and 21 (as PON/POP) (Figures 4.21 and 4.22). They are nearly similar to the planktonic ratio of 16, however, unexpectedly, the N/P ratio was anomalously low (9.6 for PON/TPP, 6.3 for PON/POP) at the shelfbreak station (Table 4.2 and Figures 4.21 and 4.22). Moreover, POM increases occurred with lower C/P and N/P ratios in the euphotic zone of the shelfbreak zone and open sea, implying more contribution of less degraded POM of planktonic origin to POM pool of NE Mediterranean. Put simply, the nutrient-depleted offshore waters of the NE Mediterranean are relatively poor in seston as compared to the nearshore waters; however, it contains more TPP in the shelf waters. Thus the POC/TPP and PON/TPP ratios derived from the regression analyses of the nearshore data are much above the open sea and the conventional Redfield ratios (Figures 4.18 to 4.22), due presumably to contribution of P-depleted POM of terrestrial origin.

Table 4.3 Linear regression analysis for organic carbon, nitrogen and phosphorus in POM from the time-series stations of the NE Mediterranean shelf

Stations	**Regression**	**r^2**	**n**	**Significance level**
Nearshore	$C = 12.2N - 4.07$	0.92	41	$p = 0.000$
	$C = 566P^* - 9.58$	0.40		$p = 0.000$
	$N = 48.6P^* - 0.56$	0.47		$p = 0.000$
Middle	$C = 9.99N - 0.69$	0.54	79	$p = 0.000$
	$C = 273P^* - 0.20$	0.43		$p = 0.000$
	$N = 21.2P^* + 0.17$	0.48		$p = 0.000$
Shelfbreak	$C = 8.80N - 0.05$	0.69	194	$p = 0.000$
	$C = 92.4P^* + 2.59$	0.07		$p = 0.001$
	$N = 6.28P^* + 0.37$	0.04		$p = 0.023$

P^* : POP

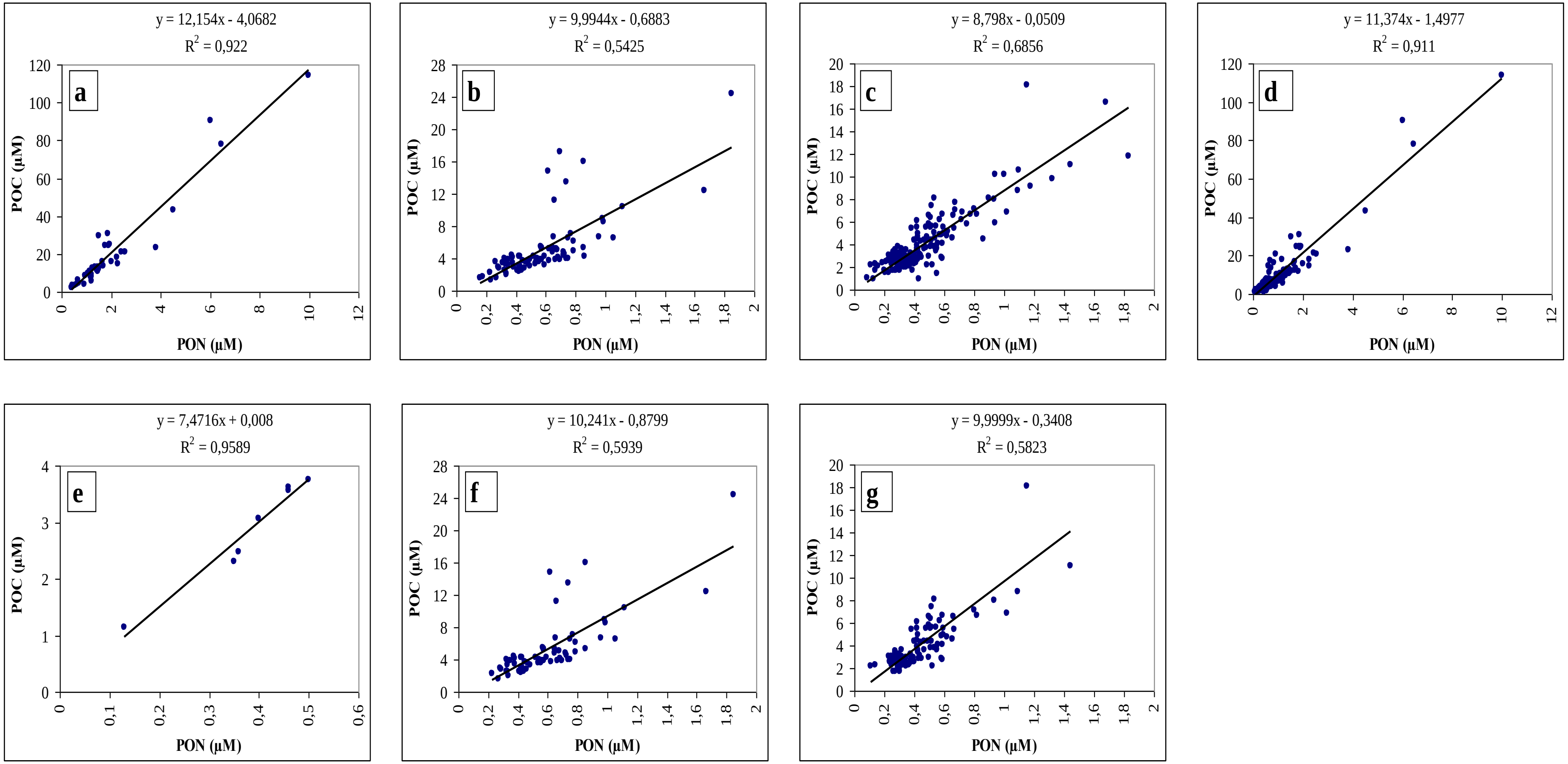


Figure 4.18 Relationship between POC and PON at the studied stations in the water column [Time series stations a: Nearshore, b: Middle, c: Shelfbreak, d: All data; Reference station e: R1] and in the EZ (f: Middle, g: Shelfbreak).

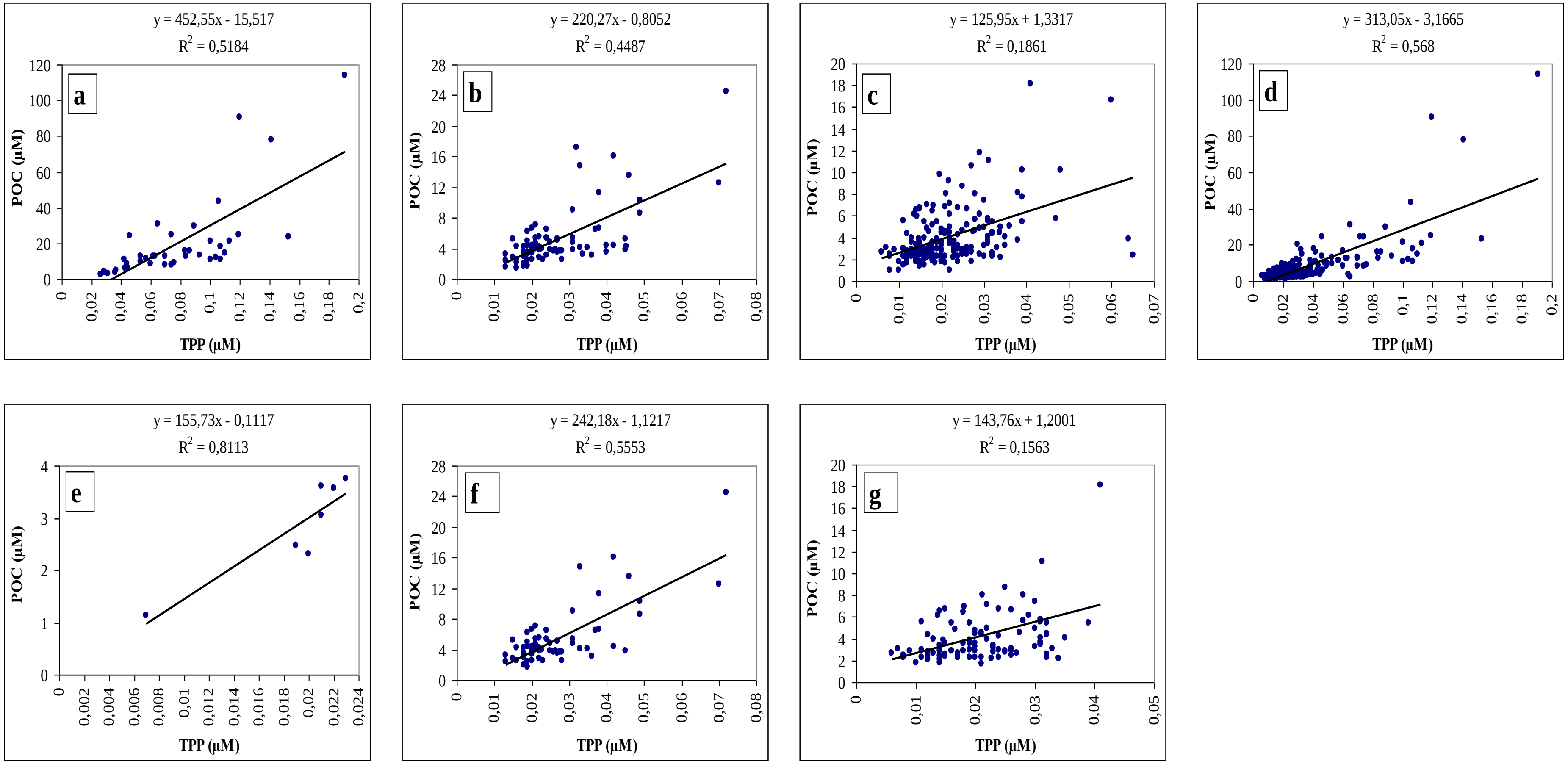


Figure 4.19 Relationship between POC and TPP at the studied stations in the water column [Time series stations a: Nearshore, b: Middle, c: Shelfbreak, d: All data; Reference station e: R1] and in the EZ (f: Middle, g: Shelfbreak).

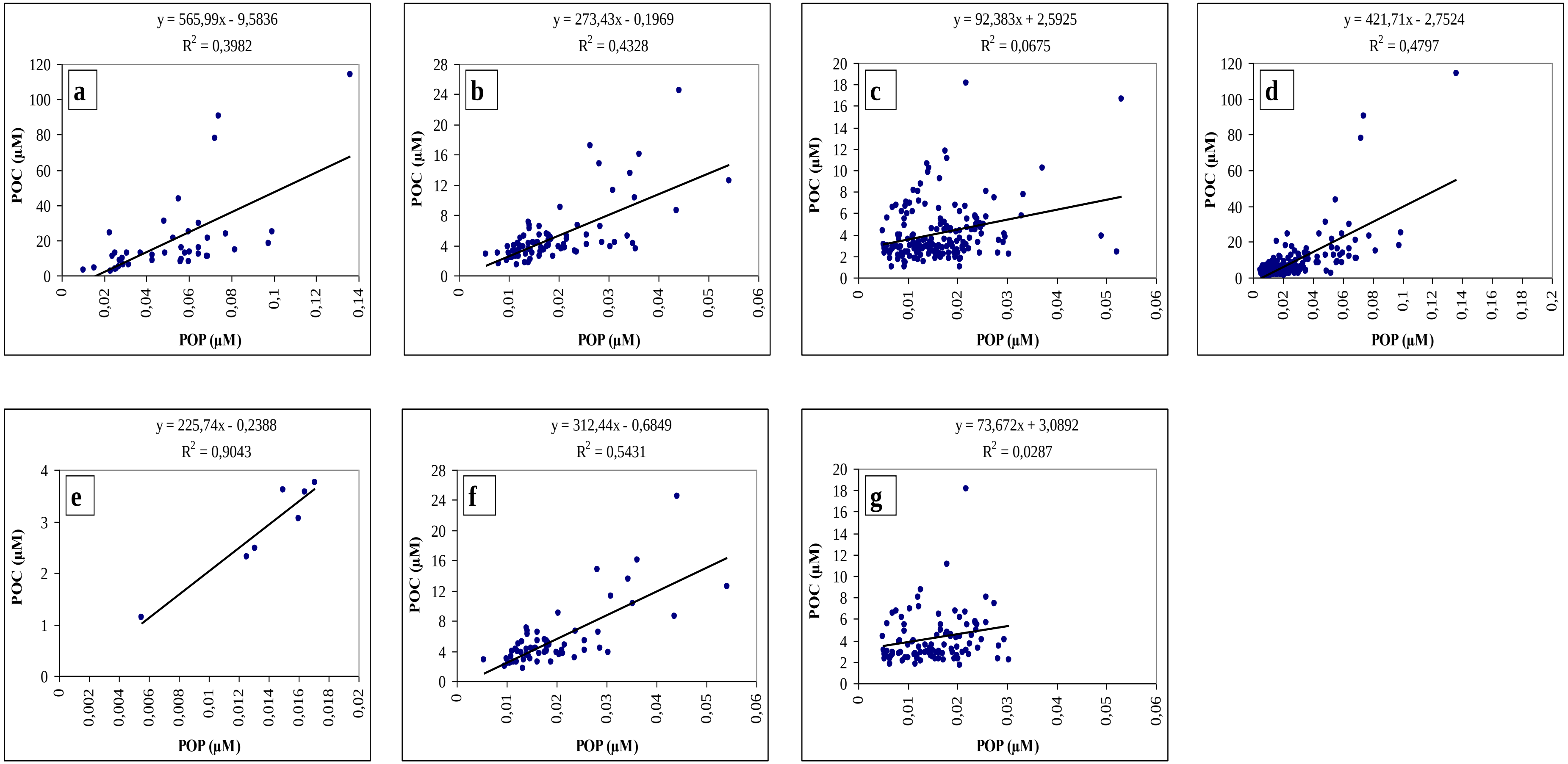


Figure 4.20 Relationship between POC and POP at the studied stations in the water column [Time series stations a: Nearshore, b: Middle, c: Shelfbreak, d: All data; Reference station e: R1] and in the EZ (f: Middle, g: Shelfbreak).

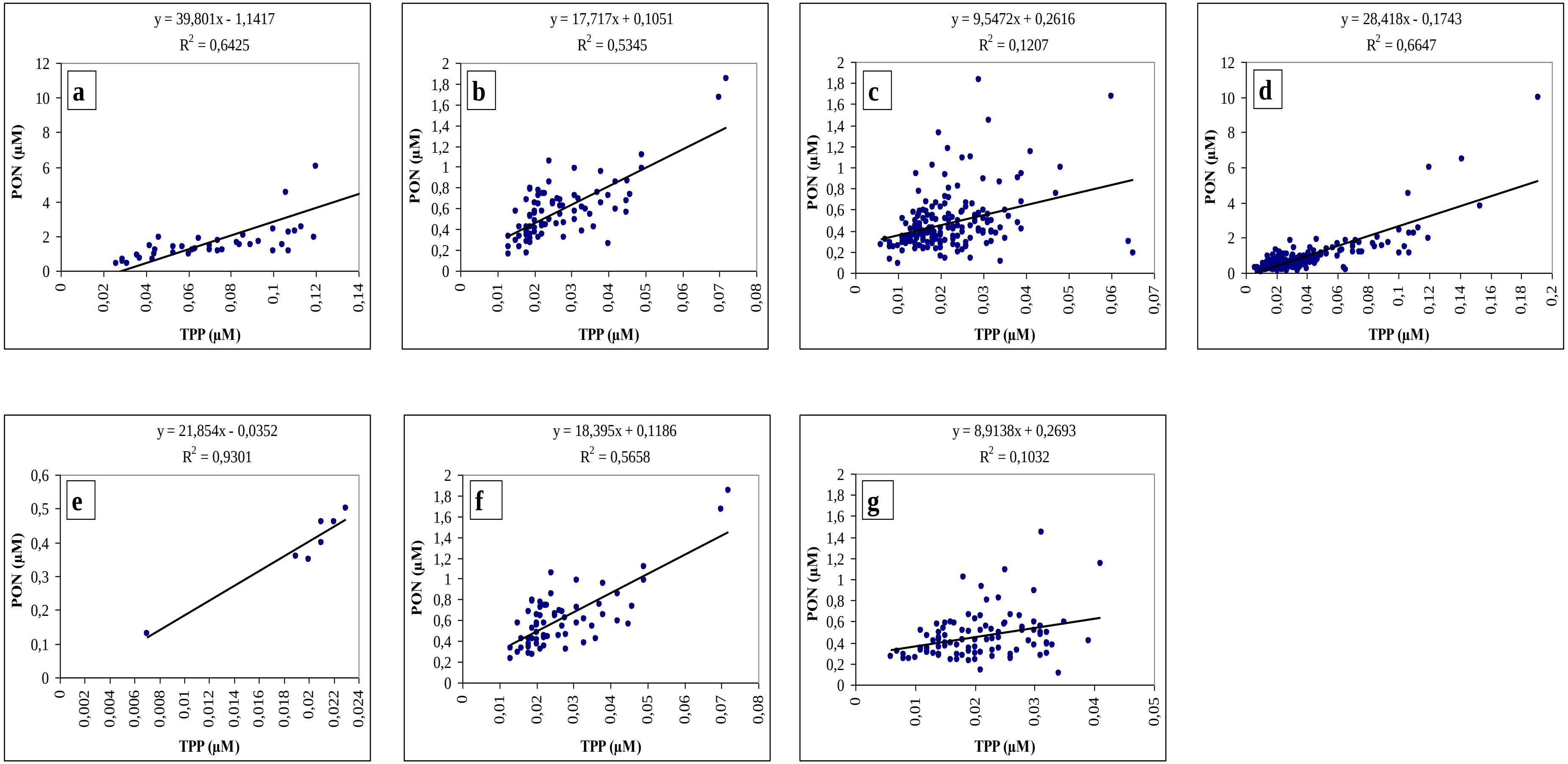


Figure 4.21 Relationship between PON and TPP at the studied stations in the water column [Time series stations a: Nearshore, b: Middle, c: Shelfbreak, d: All data; Reference station e: R1] and in the EZ (f: Middle, g: Shelfbreak).

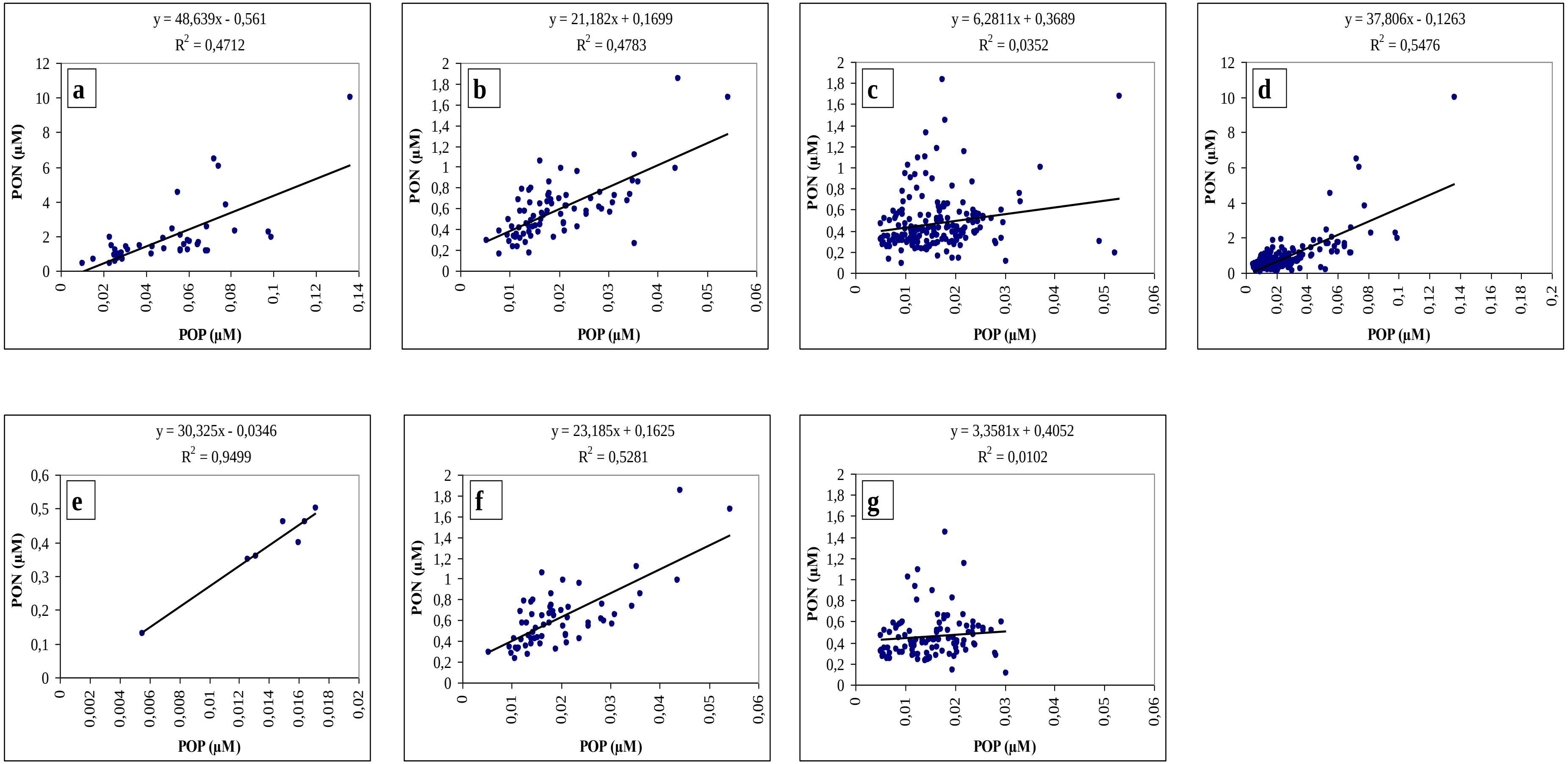


Figure 4.22 Relationship between PON and POP at the studied stations in the water column [Time series stations a: Nearshore, b: Middle, c: Shelfbreak, d: All data; Reference station e: R1] and in the EZ (f: Middle, g: Shelfbreak).

4.5 Interpretation of the Phosphorus Data

One of the major objectives of this study was to determine the different forms of phosphorus in the seawater to assess their relative contributions to phosphorus pool of the NE Mediterranean shelf ecosystem. In this context, spatial and temporal variations of P-fractions were studied in the shelf waters during 2002-2003. Temporal variations of total-phosphorus (TP) and its dissolved and particulate constituents at the three shelf stations and at deep (reference) station are discussed extensively in this section, based on time-series data of phosphorus fractions.

4.5.1 Spatial and temporal variations of phosphorus fractions in the Northeastern Mediterranean shelf water

Monthly variations of TP and, dissolved and particulate fractions of phosphorus in the water column from the three stations on the shelf are depicted in Figures 4.23 to 4.28 for 2002-2003. The geographic and temporal distribution pattern of the TP displayed a large variability during the investigation period. TP content of the shelf water was apparently higher in the shallow nearshore zone, varied seasonally between 0.20-0.43 (0.29±0.08) μM in 2002-2003 (Figure 4.23). In offshore waters, TP concentrations declined to levels of 0.11-0.32 (0.19±0.05) μM during the same period. The maximum values were obtained in spring of 2002-2003 in the nearshore waters as the increased riverine flow spread over the sampling area. However, water column distributions of TP displayed small variations with depth, which were less pronounced in the offshore water (Figure 4.23) due to the limited input from external sources. The TP content of the nearshore was higher in 2002, during which the river effect was more effective at the sampling site. TP concentrations were relatively low during spring-autumn period across the shelf, implying limited input from external sources. These values were comparable with those of (0.11-0.33 μM, 0.22±0.09 μM) determined at similar depths of the deep (reference) station off the shelf in December 2003.

Time-series data of TP and P-fractions in the surface water are given in Figure 4.24, demonstrating considerable variations depending on the season and region. The surface TP at the nearshore station reached the peak value of 0.430 μM in May 2002, whilst the surface salinity declined to 36.2 psu due to the increased river inflow with the associated chemical properties. Then the TP dropped to the background levels of 0.2-0.3 μM in late summer-autumn period of 2002. In 2003, a late winter maximum of 0.378-0.396 μM was recorded in the well mixed water column of the shallow station during February-March period, indicating a net input from the sediment layer, in addition to limited riverine input. In this period, the TP displayed a decreasing trend in the offshore waters, supporting the suggestion of limited input by the major rivers to the shelf. The surface TP concentrations exhibited a coherent minimum in April of 2003, followed by a peak in June whilst the river effect was still traced in the nearshore waters. The TP dropped to minimal levels of 0.171 μM in autumn months of 2003 (Figure 4.24), while the surface salinity displayed a maximum of 39.3 psu. As previously mentioned, the major river flows were at minimal levels during the dry autumn period. Temporal changes in the surface TP concentration, ranging between 0.198-0.430 μM, were less pronounced in the offshore zone which was occupied by the saltier waters that have almost similar hydro-chemical properties. Nevertheless, there was enrichment in TP content of the middle station in June 2003 when the surface salinity displayed a concurrent decrease due to river effect. These findings indicate that very limited influences of river runoff on the shelf ecosystem during the dry months of 2003. The present TP data are comparable to those of Giovanardi and Tromellini (1992) that ranged from 0.27 μM (oligotrophic) to 0.9 μM (mesotrophic) and 2.8 μM (eutrophic) seawaters.

Temporal variations in the total dissolved phosphorus (TDP) contents of the water column across the shelf were very similar to those of the vertical distribution of TP as expected (Figure 4.25). There was no close relationship between the salinity and concentration changes of TDP in the water column. That was because, the internal and external water sources refreshing the shelf water masses are principally poor in phosphorus compounds, except during the periods of heavy rains and increasing flows of the rivers due to surface runoff. TDP and TP concentrations displayed a similar increasing trend in winter 2003 because TDP is the major constituent of TP in the surface seawater (Figure 4.24) as indicated by Ormaza-González (1990) and Liu *et al.* (2003). The DOP with relatively long residence time in the upper layer (Scanlan and Wilson, 1999; Ammerman *et al.*, 2003) dominates the TP pool of the NE Mediterranean shelf. The present DOP data show apparent temporal changes as of similar to the other coastal seas that are influenced by riverine inputs (Liu *et al.*, 2003; Durrieu de Madron *et al.*, 2003; Van der Zee and Chou, 2005).

There were notable increases in the TP and TDP contents of the nearshore waters in May 2002 and March-April 2003. The dissolved and particulate phosphorus contents of the offshore waters did not exhibited any concurrent enrichment in the water column and were consistent with the lower POC concentrations at the deeper stations (Figure 4.10). This local difference was the result of the limited nutrient input by the river runoff towards the shelf water. Increases in nitrate and silicate concentrations of the phosphate-depleted nearshore waters (leading to high N/P ratios) however to lower POM values in summer-autumn period strongly suggests that P-limited organic matter production and algal biomass across the shelf (Eker-Develi, 2004; Yılmaz, 2006).

Dissolved organic phosphorus (DOP) has also been reported as a significant fraction of the TDP in the euphotic zone of the marine water, particularly where there is intensive biological activity. Phytoplankton are capable of assimilating P from the organic fractions of TP pool (e.g. Cembella *et al.*, 1984; Veldhuis and Admiraal, 1987; Veldhuis *et al.*, 1987; Suzumura and Ingall, 2004). DOP played an important role in biological and biogeochemical processes (e.g. Smith *et al.*, 1985; Smith *et al.*, 1986), which generally surpasses the DIP in the EZ (e.g. Romankevich, 1984; Orret and Karl, 1987; Sapozhnikov, 1988; Ormaza-González, 1990; Suzumura and Ingall, 2004). In this study, higher DOP concentrations in the shelf zone (0.058-0.256 μM) and in the open reference station (0.078-0.186 μM) (Figure 4.26) were consistent with the ranges previously reported for ocean waters (Romankevich, 1984; Suzumura and Ingall, 2004). Coastal water DOP concentrations are often found to be higher than DIP, even in pristine rivers and estuaries; DOP concentrations have been observed in some cases to exceed those of DIP concentrations (Ormaza-González and Statham, 1991; Monaghan and Ruttenberg, 1999). Similarly, the present nearshore data show higher concentrations of DOP (varying widely from 0.055 to

0.321 µM) than DIP values, fluctuating between 0.018-0.166 µM in the water column (Figures 4.7 and 4.26). Marchetti (1984) pointed out that, generally, the concentrations of DIP in the Mediterranean surface waters are extremely low (expressed as values for orthophosphate 0.03 µM or less), whereas the typical DIP concentrations for the eutrophic coastal waters are above 0.15 µM, exceeding to 0.3 µM in highly eutrophic system. The DIP results from this study are lower than the oligotrophic characteristics (0.12-0.14 µM) of the Red Sea coastal waters (Beltagi, 1984).

The time-series surface data in Figure 4.24, the nearshore water had higher concentrations of total particulate phosphorus (TPP) and TDP; however, they fluctuate significantly with season. On the other hand, DOP contents of the surface water across the shelf had displayed small regional differences, whereas considerable variations with season. Interestingly, the DOP data exhibited nearly similar temporal trends, increasing in winter of 2003 and then declining to minimal levels in March-May period (Figure 4.26). Though the trend was similar, the local differences in the surface DOP became evident during the winter of 2003; the DOP reached its maximum value of 0.321 µM in the nearshore water when the offshore values were as high as 0.104-0.187 µM. In this period, the surface water had both higher salinity and TP values as the TPP displayed a contrary view, suggesting TDP inputs both from sediment layer and by the river runoff.

TPP, particulate organic phosphorus (POP) and particulate inorganic phosphorus (PIP) contents of the nearshore waters were generally much higher than the offshore values; moreover, they exhibited significant variations with season (Figures 4.12, 4.13 and 4.27). These local features were very consistent with similar fluctuations in the POM concentrations from the shallow location fed by the Lamas River. However, at the offshore locations, particulate phosphorus varied slightly in the water column of deeper stations during the year, with greater variability in the time-dependent vertical distribution of POP (Figure 4.13).

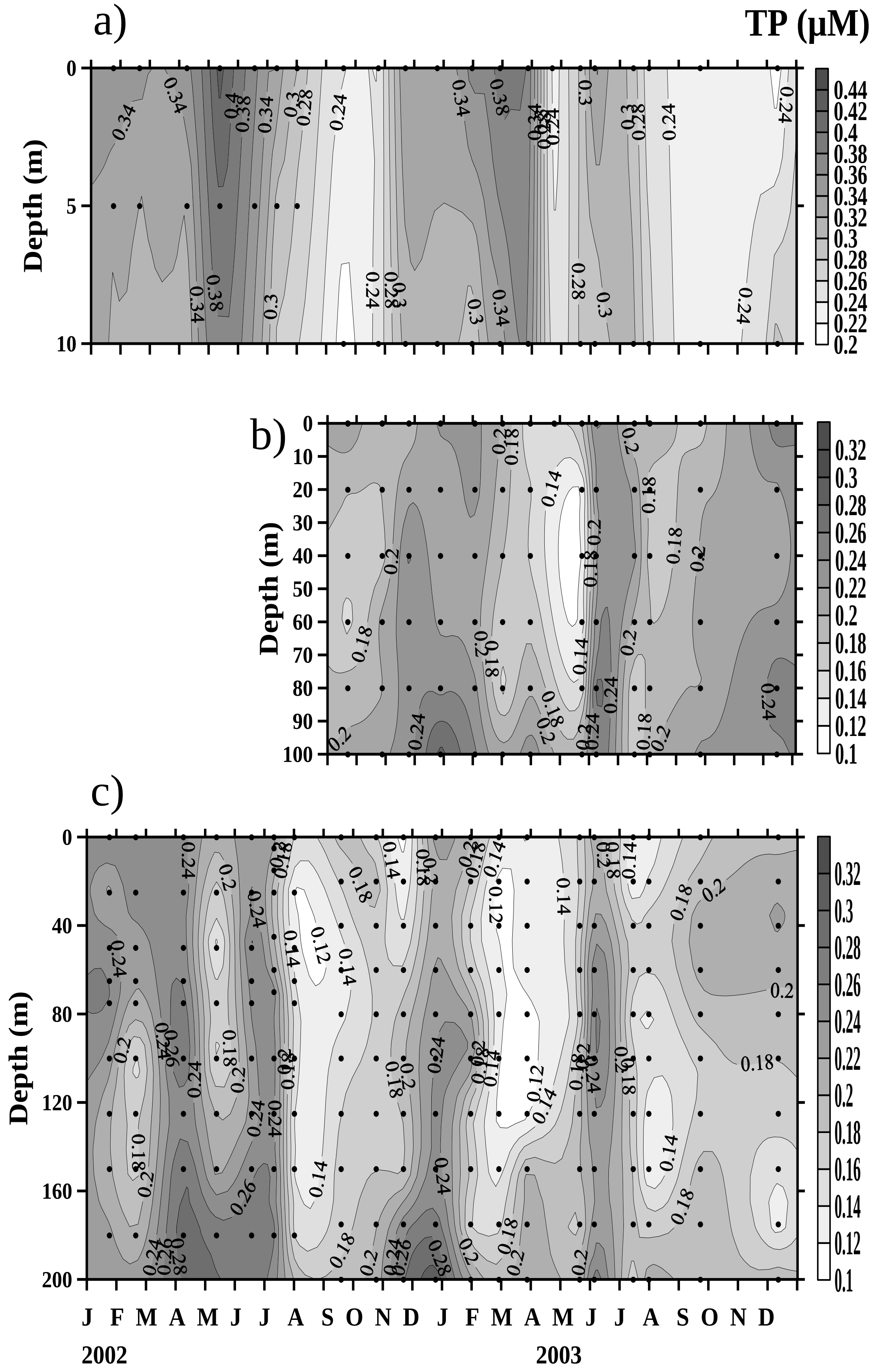


Figure 4.23 Contour plots of the vertical distribution of TP at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

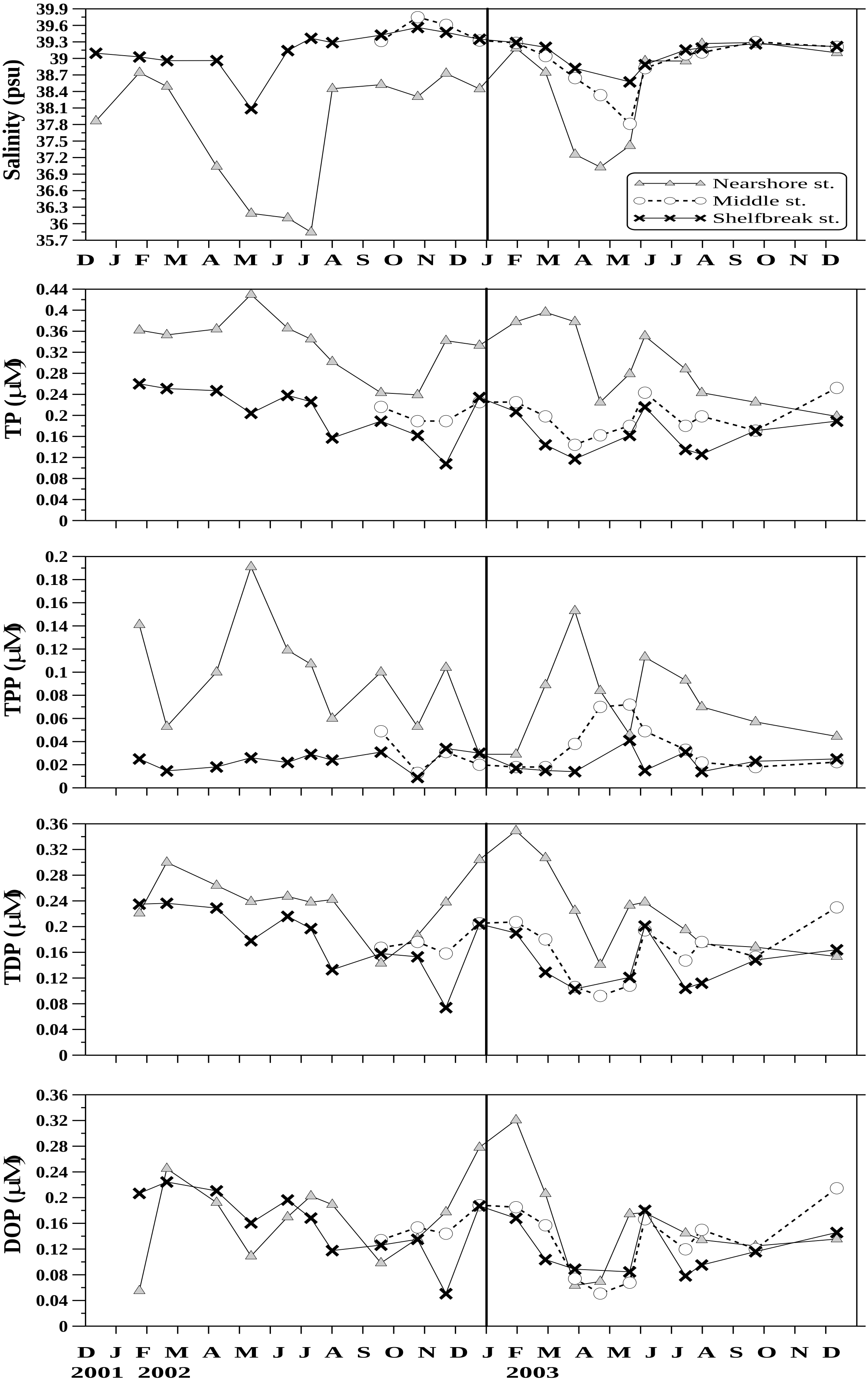


Figure 4.24 Time series distribution of salinity and P-fractions in the surface water of the stations.

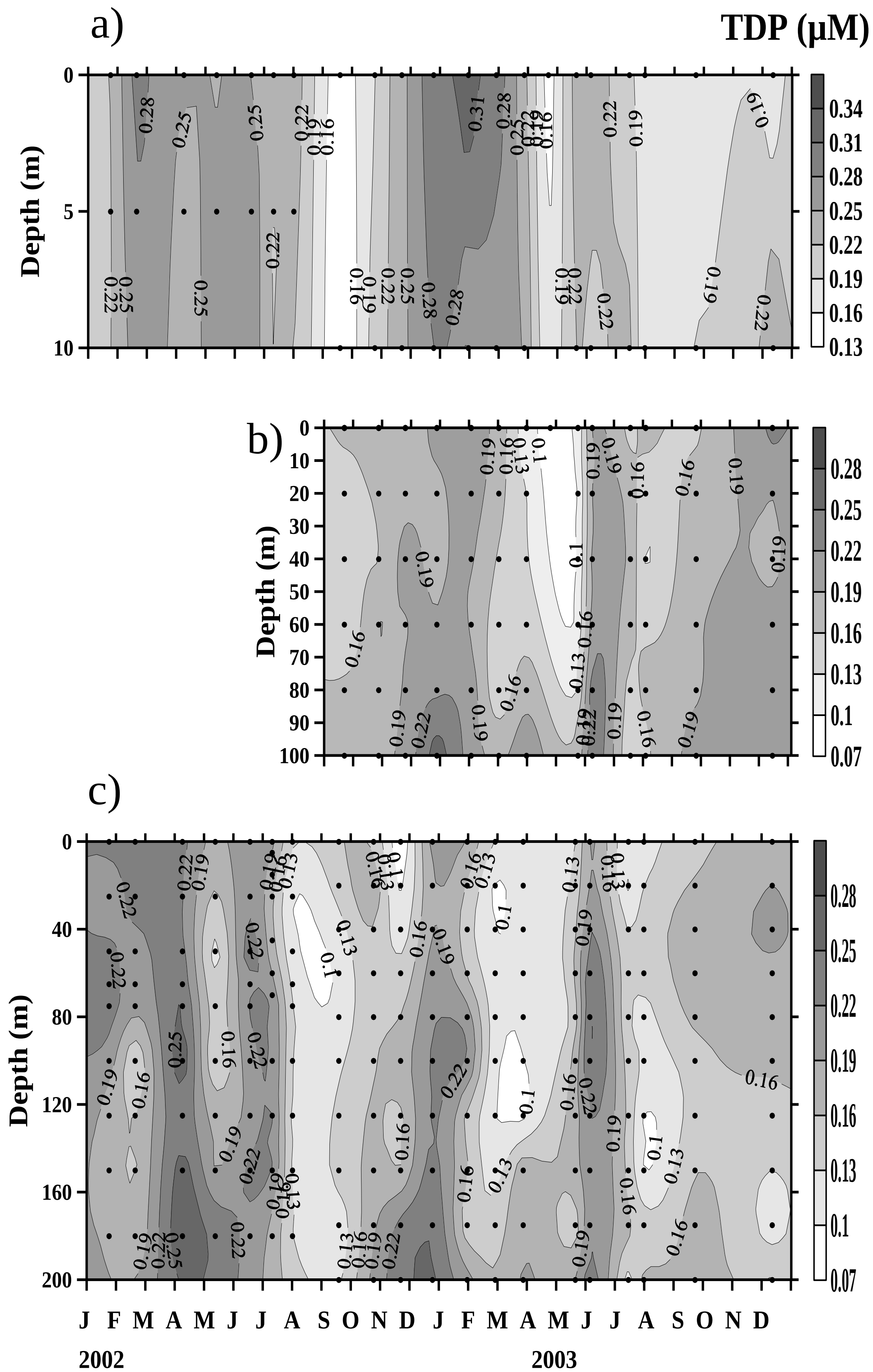


Figure 4.25 Contour plots of the vertical distribution of TDP at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

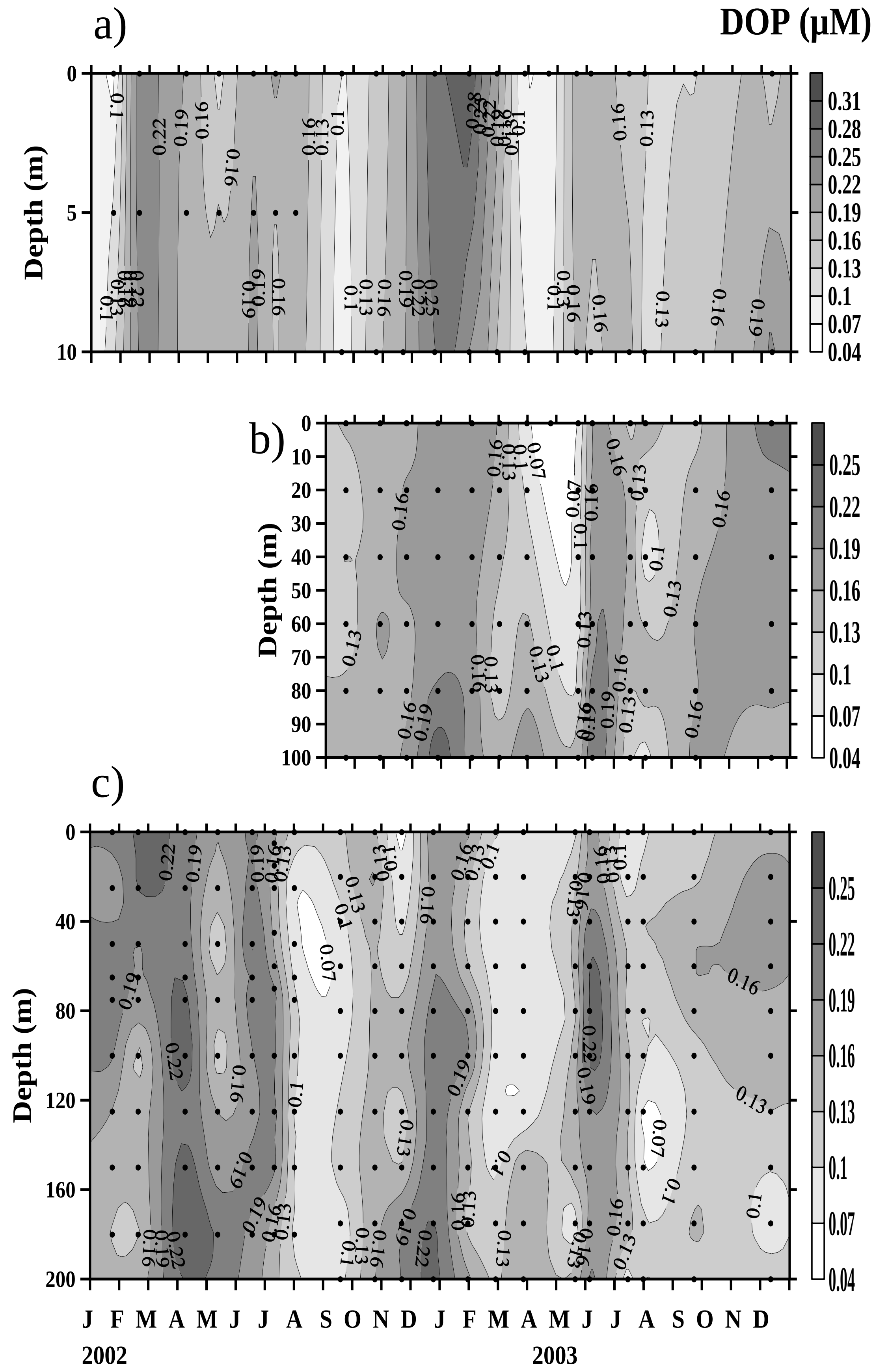


Figure 4.26 Contour plots of the vertical distribution of DOP at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

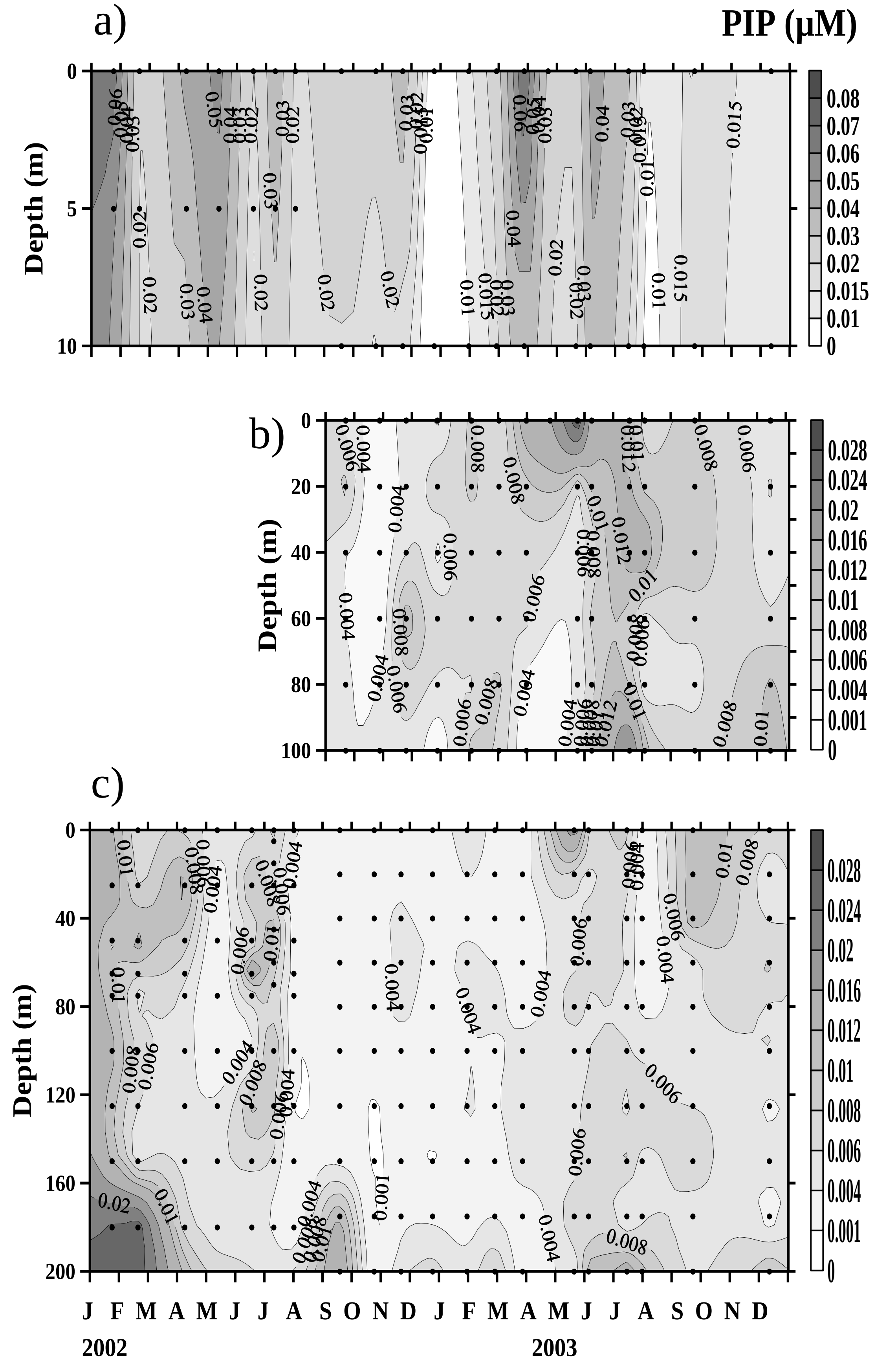


Figure 4.27 Contour plots of the vertical distribution of PIP at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

Figures 4.28a-b demonstrate the relative contributions of different P-forms to the total P content of the surface waters across the NE Mediterranean shelf off Erdemli. As previously mentioned, the TDP is the major constituent of the phosphorus pool in the shelf. TP was mainly composed of TDP (56-97%) in the shelf zone (Figure 4.28). Moreover, the DOP was the major constituent of TDP in the water column (Figures 4.26 and 4.27). However, this significant contribution at the coastal stations by the river shows a decreasing trend across the shelf zone due to PIP input from the sediment layer (see Figure 4.28 and Appendix D). The percentage of TDP in the TP ranged between 56-68% in May-June 2002 when the surface water salinity was at minimal levels (Figure 4.28.a). It ascended to levels of 85% to 91% in February and December 2002, when the surface salinity was relatively high. In summer-autumn 2003, the TDP fraction accounted almost 67% to 75% of the TP in the nearshore zone. The contribution of DOP appeared to be more pronounced at the shelfbreak station, constituting 38% to 90% of the TP in more productive periods of 2003 (Figure 4.27.b). Suzumura and Ingall (2004) have observed that the DOP was the major component of TP pool, constituting 70-98% of the TDP or 60-90% of the TP in the surface euphotic zone at oligotrophic ocean stations in the Pacific Ocean. Comparison of temporal and regional percentages of DOP and DIP contribution to TDP pool in the water column revealed that TP pool comprised relatively low DIP at the middle and the shelfbreak stations (see Appendix D). The DIP make up only 4% to 34% of the TP for 2002-2003 period, dropping to its minimal levels of 5-7 % in winter-spring of 2002. However, the DIP contribution to the TP pool increased in the nearshore zone fed by the river runoff that ranged between 7-69% of the TP. The largest percentage (69%) appeared in February 2002, when there was a net imbalance between sources and sink terms in the shelf. Similar results were reported for the rived-fed coastal zones (Liu *et al.*, 2003; references cited therein; Van der Zee and Chou, 2005).

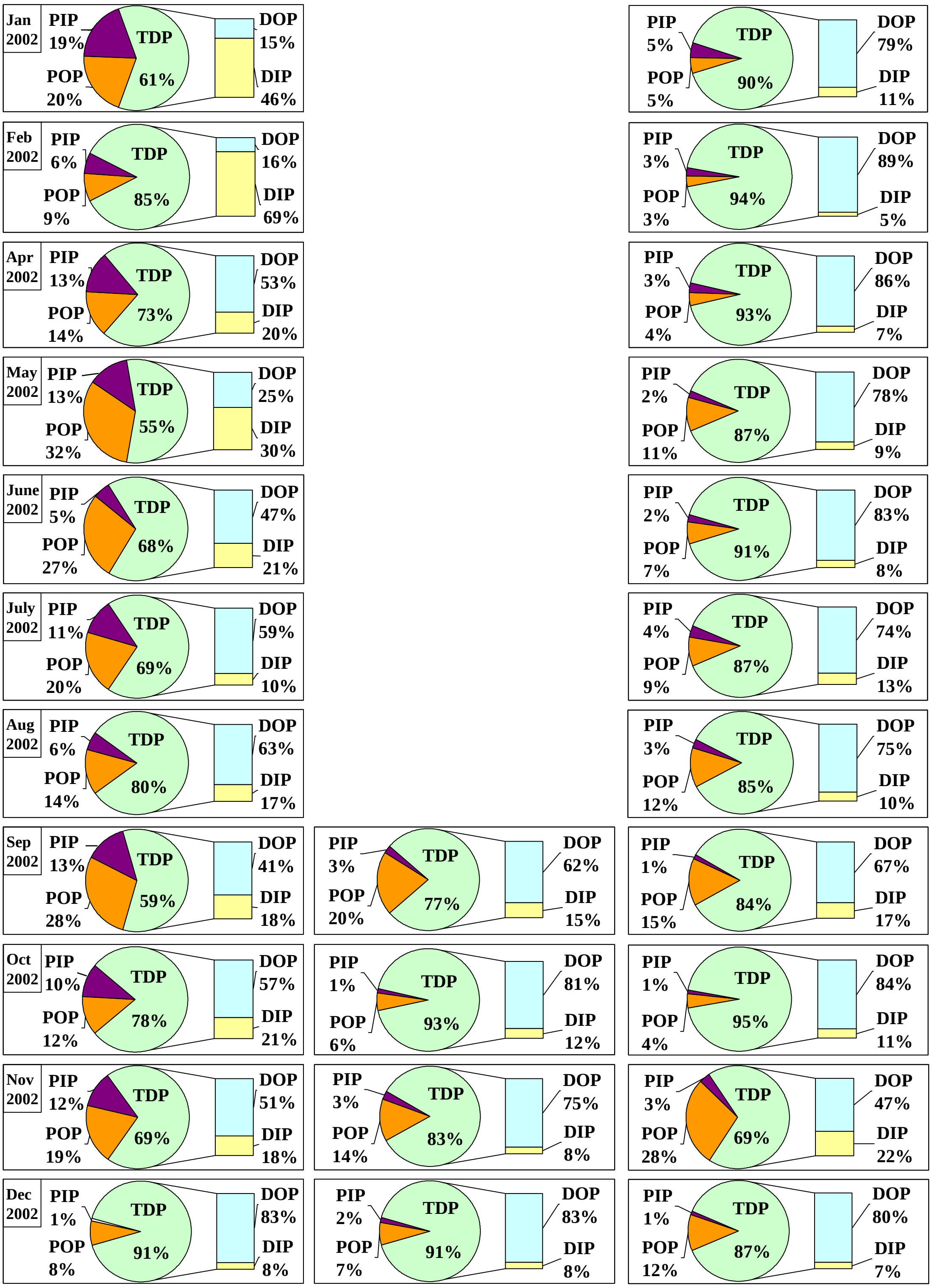


Figure 4.28.a Percentage pie graphs of phosphorus fractions in 2002 in the surface water of the studied stations (From left to right; Nearshore, Middle, Shelbreak).

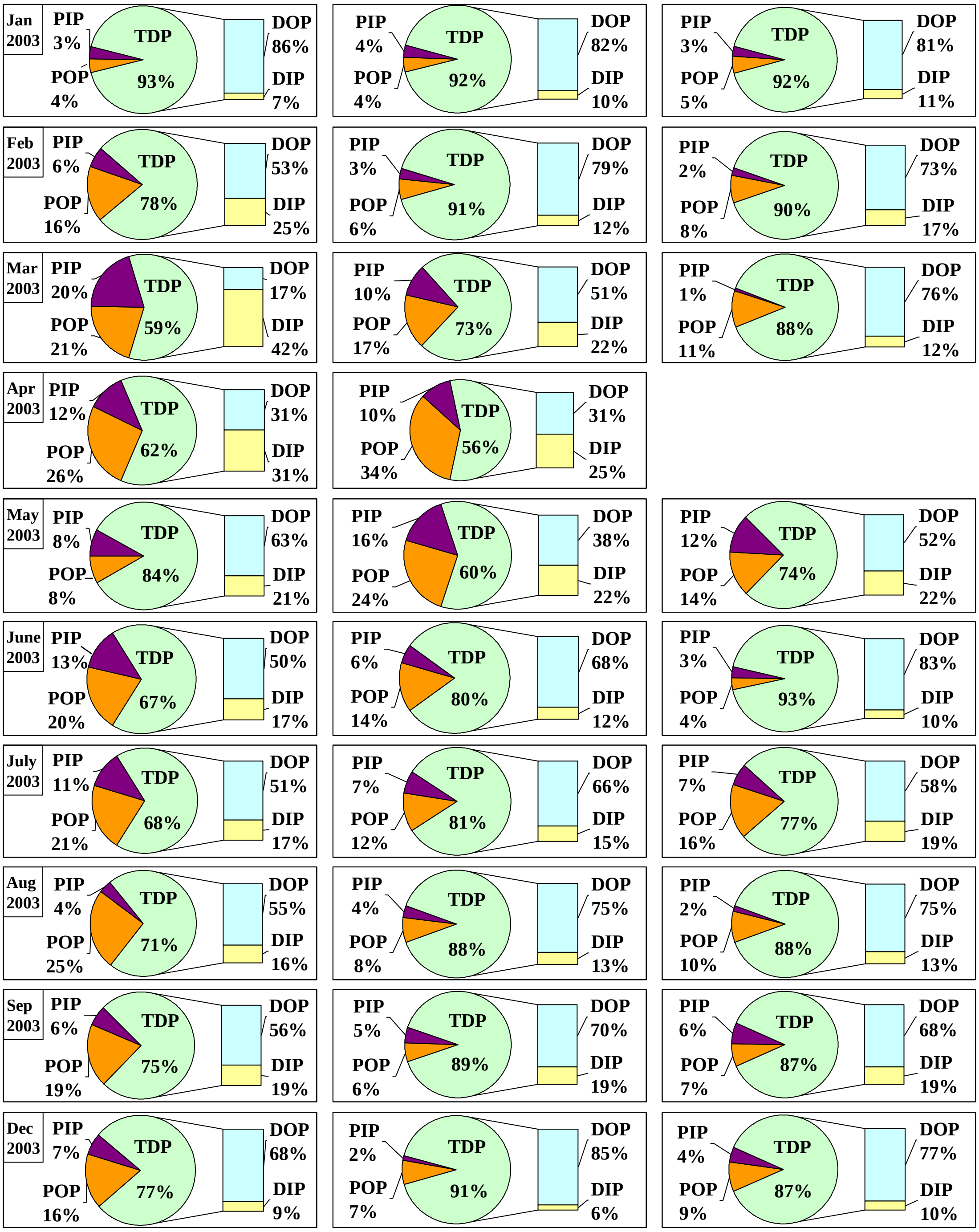


Figure 4.28.b Percentage pie graphs of phosphorus fractions in 2003 in the surface water of the studied stations (From left to right; Nearshore, Middle, Shelbreak).

The TPP concentrations were always lower than the TDP fraction of the TP in the shelf. The TPP displayed a decreasing trend towards the shelfbreak zone, constituting seasonal changes up to 8-44% of TP in the nearshore waters but slightly changed to 4% to 38% of the TP at the shelfbreak zone (see Appendix D). Moreover, percentages of the PIP and the POP fractions in the TP pool of the nearshore waters were approximately similar during the transitional and wet seasons. However, the

PIP% decreased in dry months, when the surface layer was thermally stratified and received limited input from the river runoff. Suzumura and Ingall (2004) reported that TPP was a minor component accounting 3-11% of the TP in the euphotic zone in the Pacific Ocean. A similar conclusion can be reached from the offshore P-fractionation data from this study. The TPP contributed a minor fraction (4-38%) of TP, which was principally composed of particulate organic phosphorus in dry seasons (Figure 4.28a-b).

In conclusion, TDP dominates TP pool in the deeper shelf zone receiving limited input from the river runoff. However, in winter and spring months, when the river inflow increases TPP appeared to constitute up to 8-44% of TP pool in the nearshore zone fed by river runoff and input from sediment layer via vertical mixing. Considerable decreases in DOP and TPP concentrations from the surface to deep waters suggest that a considerable fraction of the TP in surface waters is in biochemically labile forms.

4.5.2 N/P ratios of dissolved nutrients and particulate matter in the Northeastern Mediterranean shelf water

Nutrient pool in the shelf margin is determined by various biotic/abiotic complex processes in the water column and sediment layer. The wide shelf waters of the NE Mediterranean are fed by nutrient inputs by river runoff, atmospheric deposition (wet and dry) (Table 4.4), diffusion from sediment layer to overlying water and lateral intrusion from the open sea. The sink terms are biological uptake, geochemical processes and removal by POM sinking to depths and sediment layer. In order to evaluate the estimates of N/P ratios of dissolved nutrients and particulate matter (as NO_3/PO_4, PON/TPP and PON/POP) in the shelf waters, the relative importance of source and sink terms in the shelf ecosystem should be considered. Unfortunately no data from sediment traps exist, which would corroborate this close relationship between the N/P ratios of the surface seston and the subhalocline nutrient concentrations.

When the entire sampling period was taken into account, there was a positive correlation between dissolved nitrate/phosphate (N/P) molar ratios estimated from the data sets of both conventional (N/P^{AA}) and modified MAGIC methods (N/P^{MAGIC}) at the nearshore, middle and shelfbreak stations (Pearson correlation, $p<0.001$). Application of the t-test indicated that N/P ratios of the two measurement methods were consistent at the nearshore ($p >0.05$) and middle station ($p>0.05$) (see Appendix G.1). However, expectedly, they were not consistent at the shelfbreak station ($p<0.001$) because the DIP data of the MAGIC method were much more sensitive than the data by conventional method in the P-depleted shelfbreak waters.

As emphasized in the previous sections and the report of Tuğrul *et al.* (2004), the river waters of the region are relatively rich in NO_3 but very poor in DIP; thus N/P ratios are markedly high, ranging seasonally between 71 and 3100 (annual mean: 915) in the Lamas River waters. A similar conclusion has been reached for rain with very high N/P ratios (Tuğrul *et al.*, 2004). In other words, excess loads of nitrate are introduced by rivers and wet deposition to the coastal margins of the NE Mediterranean (Table 4.1 and 4.4). These results strongly suggest that the primary production especially in the nearshore waters are limited by phosphate as recently reported for the open waters of the eastern Mediterranean (Krom *et al.*, 1992; Yılmaz and Tuğrul, 1998; Ediger *et al.*, 2005; Herut *et al.*, 2005; Krom *et al.*, 2005). However, N/P ratios in the Lamas River waters have been observed to decline markedly to levels of 71-113 after heavy rains (Tuğrul *et al.*, 2004).

Table 4.4 Ranges and averages of nutrients via wet deposition (mmol m^{-2} yr^{-1}) in Erdemli for 1999-2004 period (data were provided by Prof. N. Kubilay).

Parameter	**Sampling period**		**Average**	
	1999-2004*	**2002-2003****	**1999-2004***	**2002-2003****
NO_3+NO_2-N	17-32	20-23	24.3	22
NH_4-N	22-36	25-26	26.6	26
PO_4-P	0.21-0.54	0.25-0.45	0.40	0.35

* Long term data, ** the same period as the present study

The NO_3/PO_4 (N/P) molar ratios were highly variable in the shelf waters. The ratio ranged between 1.2 and 189 in the nearshore water with higher values in the surface layer during late-summer and autumn 2002 and winter 2003 (Appendix A, Figure 4.29). It was in the ranges of 1.8-29 at the middle station, 1.7-109 at the shelfbreak station, reaching the peak values in winter and summer months. Moreover, it varied from 2.6 to 42 at the reference stations. Despite a broad range of the N/P ratios in the upper layer waters, average N/P values of the nearshore and reference stations comparable with the other regions across the Mediterranean Sea (Table 4.5).

In the P-depleted shelfbreak surface water, the N/P ratios (Figure 4.29) were estimated as high as 29-38 in September-October 2002, decreasing markedly to 7-9 in November-December 2002, indicating a net loss of NO_3 from the productive waters in autumn via regenerative production. The ratio increased again to levels of 21-22 in February-March 2003; then it declined to very low levels of 2.7-3.6 in May-June 2003, indicating more removal of nitrate to organic matter pool than phosphate ions. As reported by Çoban-Yıldız *et al.* (2000b) in the Mediterranean Sea, N/P ratios in the EZ of the shelf zone waters were low, especially in stratification periods whilst the ratio may be as high as 20 when the water column is vertically mixed and nutrient concentrations were relatively high. The N/P ratios exhibited less temporal variations due to the balance between source and sink terms in the aphotic zone. The highest N/P ratios (ca. 90) were encountered at 175-200 m depths due to relatively high nitrate content of deep water. This property can also be realized from the vertical distributions of DIP and NO_3 in Figures 4.7 and 4.8. This NO_3 enrichment is an inherent property of the intermediate waters of the Cilician basin rather than the dissociation of POM sinking from the euphotic zone of the shelf. It is well known that the intermediate layer of the eastern Mediterranean is relatively rich in nitrate but very poor in phosphate, leading to high N/P ratios (Krom *et al.*, 1991; Béthoux *et al.*, 1992; Yılmaz and Tuğrul, 1995; Krom *et al.*, 2005). Towards the nearshore zone of the shelf, the surface nitrate concentrations of the euphotic zone apparently increase, if the nitrate-enriched rivers with higher N/P ratios feed the region. These features were determined in the region when the riverine discharges are at maximal levels as was also observed by Çoban-Yıldız *et al.* (2000a).

Comparison of regional ratios in Figure 4.29 reveals that the NO_3/PO_4 molar ratio was relatively variable and occasionally very high in the nearshore waters due to riverine input. The ratio varied seasonally from 3 to 189 in 2002 and then ranged between 1-88 in 2003 in the nearshore water with higher salinity in 2003 (see Figure 4.28). The N/P ratio was between 29-38 in the shelfbreak waters during early autumn period of 2002, when the surface layer received limited input of nutrients with N/P ratios from external sources and from intermediate depths of the P-poor NE Mediterranean (N/P: 25-30) (Yılmaz and Tuğrul, 1998; Ediger *et al.*, 2005; Krom *et al.*, 2005). However, occasionally lower N/P ratios calculated for the EZ water strongly suggests that the phosphorus cycle is faster in the P-depleted waters than that in the nutrient repleted marine ecosystem (Krom *et al.*, 1991; Karafistan *et al.*, 2002; Ediger *et al.*, 2005; Slomp and Van Cappellen, 2007).

Table 4.5 The NO_3/PO_4 (N/P) molar ratios in the water column across the Mediterranean Sea.

Source	**Location**	**N/P ratio**
This study (December 2001-December 2003)	The NE Mediterranean, shelf zone (nearshore st., 0-20 m)	29 ± 27
This study (December 2001-December 2003)	The NE Mediterranean shelf zone (middle st., 0-100 m)	9 ± 7
This study (December 2001-December 2003)	The NE Mediterranean shelf zone (shelfbreak st., 0-200 m)	17 ± 15
This study (December 2003)	The NE Mediterranean, off Cyprus (reference st. R1, 0-800 m)	23 ± 10
This study (December 2003)	The NE Mediterranean, off Cyprus (reference st. R2, 0-950 m)	22 ± 11
This study (December 2003)	The NE Mediterranean, off Cyprus (reference st. R3, 0-750 m)	21 ± 10
This study (December 2003)	The NE Mediterranean, off Cyprus (reference st. R4, 0-1100 m)	20 ± 13
Krom *et al*. (1991)	The SE Levantine Basin (200-2000 m)	28 ± 3
Krom *et al*. (1991)	Cretan Strait (0-2000 m)	29 ± 5
Coste *et al*. (1984)	Alboran Sea (100-2800)	23 ± 2
Spencer (1983)	GEOSECS 404 (Sea of Crete, 100-4000 m)	24 ± 1

Phosphorus deficiency has led to higher N/P ratios in all of the inorganic and organic matter pools (both dissolved and particulate) in the EZ of the subtropical northwestern Atlantic (Gruber and Sarmiento, 1997; Wu *et al.*, 2000; Cavender-Bares *et al.*, 2001; Michaels *et al.*, 2001; Ammerman *et al.*, 2003), principally consistent with the present data in the NE Mediterranean shelf water. Thus, there is great potential for phosphorus limitation of phytoplankton and bacterial growth in the coastal region as reported for the open sea (e.g. Cotner *et al.*, 1997; Rivkin and Anderson, 1997; Ammerman *et al.*, 2003; Van Wambake *et al.*, 2002; Krom *et al.*, 2005).

The Eastern Mediterranean, particularly the Levantine Basin (Krom *et al*., 2003), has unusually high NO_3/PO_4 molar ratios (N/P: 25-27) in the deep water (McGill, 1965; McGill, 1969; Krom *et al*., 1991; Yılmaz and Tuğrul, 1998; Kress and Herut, 2001; Durrieu de Madron *et al*., 2003; Psarra *et al*., 2005). Therefore, there is growing evidence that the Eastern Mediterranean is phosphorus-limited (Krom *et al*., 1991, Zohary and Robarts, 1998) and that the Western Mediterranean is probably N-limited (Raimbault and Coste, 1990; Thingstad and Rassulzadegan, 1995), or that limitation shifts from nitrogen to phosphorus and vice versa, depending on the period of the year (Fiala *et al*., 1976; Dolan *et al*., 1995) or the area considered (Woodward and Owens, 1989). The uniquely high levels of N/P ratios in the eastern and western Mediterranean (20-27) deep layer waters, compared with other open ocean averages (15), are probably evidence of P limitation (Stirn, 1987; Coste *et al*., 1988; Béthoux *et al*., 1998; Guerzoni *et al*., 1999).

Though the DIP values of the deep layer are as low as 0.2 μM, it can be determined accurately by the classic colorimetric method, permitting to the reliable estimates of N/P ratios. However, the surface N/P ratios of the eastern Mediterranean could not evaluated reliably due to inadequate detection limit of the conventional method. In this study, N/P ratios in the water column (Table 4.3) were determined precisely by using high-sensitivity phosphate analysis methods (MAGIC). The estimated N/P ratios generally exceeded the canonical Redfield N/P ratio of 16 in the surface waters of the nearshore station and in the near-bottom layer of the deeper stations. The N/P ratios of the same locations calculated from the data of the conventional method also yielded high N/P ratios (>16:1). However, they were lower than those calculated from DIP data by MAGIC method because the DIP concentrations below 0.02 μM could not be detected by the conventional method.

The coastal surface waters possessed higher dissolved N/P ratios in some months than in the open stations, whereas, on the contrary the N/P ratio of the suspended particulate matter (bulk POM+inorganic particulate) was low. The N/P ratios of POM in the water column are expected to be closely related to the DIN and DIP contents of the EZ that are available for primary production, as well as the external inputs and degradation of shelf waters POM by heterotrophic activities in the water column (Çoban-Yıldız *et al.*, 2000b). In this context, the nearshore POM of the NE Mediterranean has naturally higher particulate N/P ratios than in the offshore water because more NO_3 is supplied by the river and rain to the sea, and thus N-replete POM is produced in the coastal waters. Slow turnover rates of nitrogenous compounds in the coastal waters of the sea cause to fast decrease in the NO_3 concentrations as compared to DIP content of the water. Moreover, total PP in NE Mediterranean shelf water was composed of particulate inorganic (PIP) and organic phosphorus (POP); the former had a marked contribution to suspended particulate matter in the nearshore waters. Considering this fact, the PON/POP ratio in NE Mediterranean has also been calculated to assess spatial and temporal variations of the PIP-corrected N/P ratio of bulk POM. Figure 4.17 shows time series vertical distributions of PON/POP ratios across the shelf. It appears that bulk POM in the shelf was much rich in nitrogenous organic compounds of biogenic origin. Moreover, POP deficiency in POM increased from the nearshore to the shelfbreak station. In other words, the synthesis, abundance, and composition of the particulate matter in the deeper shelf waters represent an active phosphorus cycle in the P-depleted upper layer water. Put simply, POM in the shelf zone was relatively poor in phosphorus, having higher N/P as compared to the classical Redfield ratio of 16 for planktonic organic matter. However, the estimates of PON/TPP (PIP uncorrected) and NO_3/PO_4 molar ratios are consistent with those reported in literature for the eastern Mediterranean (Krom *et al.*, 1991; Béthoux *et al.*, 1992; Ediger *et al.*, 1999; Çoban-Yıldız *et al.*, 2000b; Karafistan *et al.*, 2002). Supported to this assumption, it was reported by Letelier and Karl (1998) and Sanudo-Wilhelmy *et al.* (2001) that under oligotrophic conditions the N/P of POM tended to exceed the Redfield ratio of 16 and values of 40-50 N/P have been observed in *Trichodesmium* colonies. Similarly, high values of PON/TPP (>20) were found in oligotrophic regions of the equatorial Atlantic and Panama Basin (Bishop *et al.*, 1980).

Based on Pearson (2- tailed) correlation analysis, correlation was significant at the 0.001 level between PON/TPP and PON/POP in the nearshore, middle and shelfbreak stations (see Appendix L). It can concluded that, two particulate N/P ratios interact well with each other.

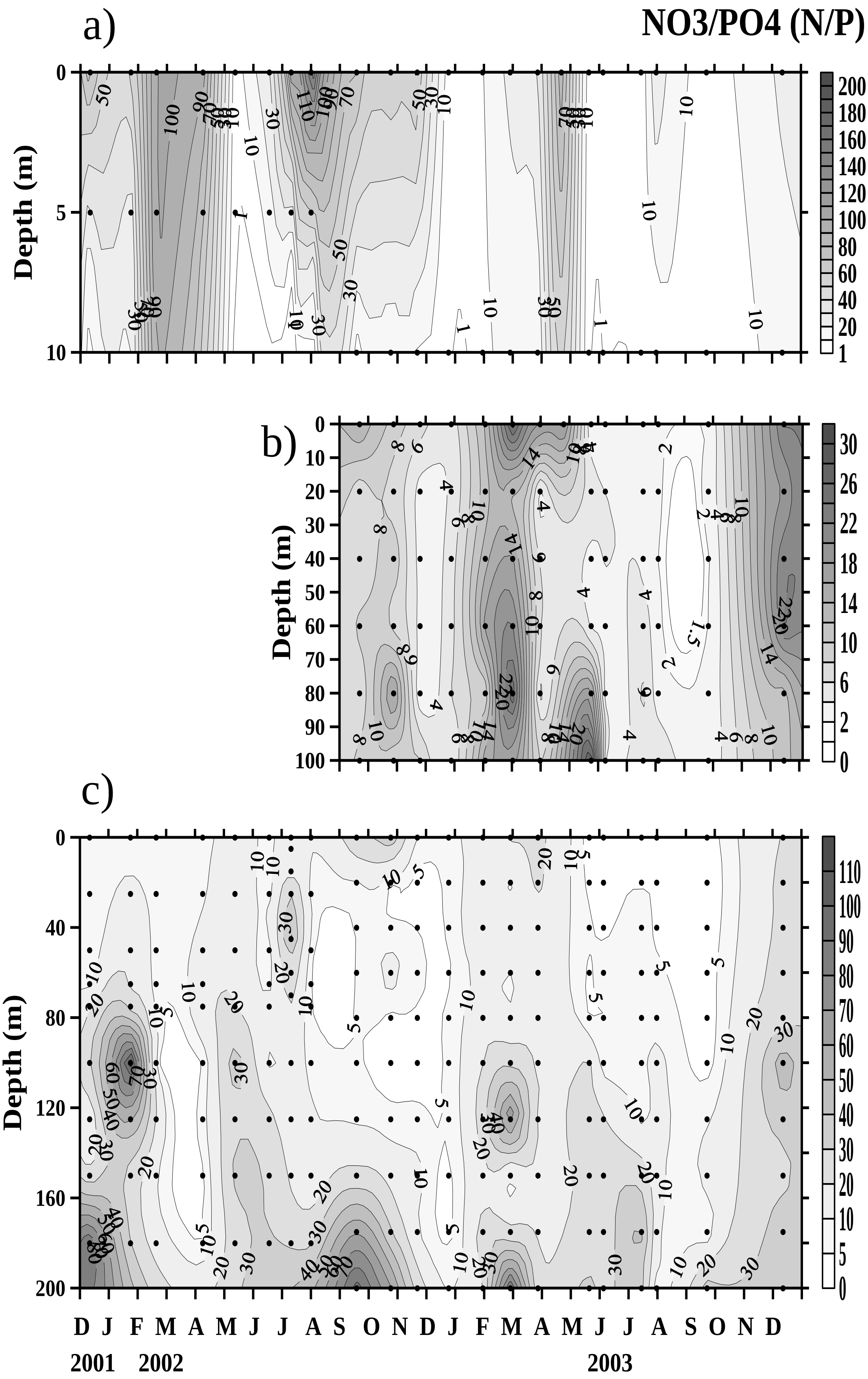


Figure 4.29 Contour plots of the vertical distribution of N/P at the time-series stations (a: Nearshore, b: Middle, c: Shelbreak). Dots indicate the sampling depths.

CHAPTER 5

CONCLUSION

Despite limited existing studies on spatial and temporal changes in hydrographic features, inorganic nutrients and abundance and elemental (C/N/P) composition of bulk suspended POM (Krom *et al.*, 1991; Yılmaz and Tuğrul, 1998; Çoban-Yıldız, 2000b; Eker-Develi *et al.*, 2006; Uysal, 2006), systematic information gap on fractions of total phosphorus, sensitive phosphate measurements and compound-specific studies on the composition of organic matter in the NE Mediterranean shelf water column remains to be filled. The aim of this study was to understand spatial and temporal variations of dissolved and particulate forms of nutrients, bulk POM and P-fractions in the largest shelf zone of the NE Mediterranean. For this goal, time-series hydro-chemical data were obtained monthly at the three stations across the shelf off Erdemli during 2002-2003.

Changes in principal hydro-chemical properties of the water masses at a given location are closely related to their sources and residence time (duration) on the shelf. The water circulations over the NE Mediterranean continental shelf zone are dominated by the general circulation character and wind-induced currents over the Cilician basin (Özsoy *et al.*, 1981; Hecht *et al.*, 1988; POEM Group, 1992; Pinardi *et al.*, 2005). The residence time of the near bottom waters on the shelf zone are very likely to range from week to month, depending on depth and location of water column interacting with the open sea system (Robinson and Golnaraghi, 1994; Béthoux and Gentili, 1999 and references therein).

Because the shelf waters are fed by a few major and small rivers and atmospheric input, the nutrient contents of both rivers and rainwaters in the region have been evaluated in the present study to determine their roles on the wide shelf ecosystem of the NE Mediterranean. These data are essential to assess roles of external sources on the nutrient cycling in the water column of the wide shelf ecosystem of the NE Mediterranean. Long-term data from the region (see Appendix B and Table 4.1) indicate that rain and river waters are highly rich in NO_3 and relatively poor in DIP, yielding high N/P ratios in freshwater runoff (Tuğrul *et al.*, 2004, Tuğrul *et al.*, 2005, Uysal *et al.*, 2007). In other words, large nitrate loads, supplied by the major rivers to the NE Mediterranean shelf (Tuğrul *et al.*, 2005), strongly suggest P-limited algal production in the shelf ecosystem (Tuğrul *et al.*, 2004) as recently experienced in the P-poor open waters of the eastern Mediterranean (Krom *et al.*, 1991; Herut *et al.*, 2005; Krom *et al.*, 2005). Annual averages of nutrient data depicted in Table 4.1 (Tuğrul *et al*, 2006) clearly show that fresh waters of the Seyhan, Ceyhan and Berdan rivers, feeding the nutrient pool of Mersin Bay, were poor in phosphate, but very rich in nitrate and reactive silicate, leading to markedly high N/P and Si/P molar ratios in Turkish river waters. Especially, the Lamas River waters have the lowest phosphate (0.02-0.81 μM), but high nitrate (79.3-114 μM) and silicate (62.2-124 μM) concentrations. Thus, estimates of the N/P ratio, ranging between 114-1358, are consistently the highest among the major rivers of the NE Mediterranean region and other rivers (Table 4.1). Moreover, the Lamas River, with the lowest chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total suspended solid (TSS) and ammonia (NH_4), represents the least contaminated fresh water properties in the NE Mediterranean region. Accordingly, its chemical concentrations can be used to assess levels of pollution in the regional rivers in recent decades. The present nutrient contents of the rivers permit us to distinguish the major origin of nutrients in the shelf waters off Erdemli.

Satellite pictures of the surface chlorophyll and temperature distributions in Figure 4.5 demonstrate that the NE Mediterranean coastal (shelf) margins can be highly influenced by the river inflows, as reported by Örek (2007). On the other hand, lateral and vertical circulations, resuspension from sediment on the coastal zone and water exchanges with the open sea are the internal source and sink terms of the coastal nutrient pool. However, the open waters of the NE Mediterranean are depleted in nutrients especially in phosphate (Krom *et al.*, 1991; Béthoux *et al.*, 1992; Yılmaz and Tuğrul, 1998, Krom *et al.,* 2005), becoming a limited nutrient source for the shelf ecosystem. Therefore, salinity changes in the shelf surface waters can be used as a natural tracer to understand the major sources of nutrient increases/decreases in the shelf from the surface to the bottom in space and time. Observations and satellite pictures both would lead to understand relative importance of compiled process on the shelf ecosystem.

Local and temporal variations of the surface salinity demonstrate that nutrient cycling, abundance and elemental composition of bulk POM in the nearshore ecosystem of the NE Mediterranean shelf are dominated by the small Lamas River runoff. Concentrations of dissolved inorganic nutrients and POM apparently increase in the shallow margin during the high flow period of the river. On the other hand, the near-surface layer of the deeper shelf zone off Erdemli are partly influenced by the NE Mediterranean general circulation system carrying discharges of the Ceyhan, Seyhan and Berdan Rivers as clearly seen from satellite pictures (Örek, 2007). This effect becomes more evident in spring due to increasing volume fluxes of the rivers with their associated bio-chemical properties.

The inorganic phosphate values of the near-shore waters were measured by a very sensitive MAGIC technique (sensitivity 1.0 nM) for the first time in the NE Mediterranean region. The DIP values are higher in the nearshore waters. This increase becomes pronounced in winter-spring period, when vertical mixing intensifies and the river inflow increases. Heavy rains can introduce large amounts of phosphorus from land via river runoff and partly by direct precipitation. The Lamas River and rain waters were observed to be selectively enriched in phosphorus when the Saharan dust reached as far as the region (Tuğrul *et al*., 2005). Kubilay *et al*. (2002) suggested short-term rainfall is necessary for wet deposition of dust minerals; longer duration rainfalls, as in the winter months, may lead to a complete washout of sulfate aerosol particles from the atmosphere. Observations in the region show that the April-May period is the most favorable periods for wet deposition of P-rich Saharan dust via spring rains. The river effect on the nearshore hydro-chemistry can be traced by apparent increases in nitrate and silicate concentrations in less saline surface waters as compared with the bottom water properties of the shallow zone and offshore surface waters (Tuğrul *et al*., 2004). From the comparison of the Si/NO_3

molar ratios of surface waters (0.02-0.9) with those of the Lamas River waters (0.67-1.38), it can be concluded that the NO_3 consumption in the nearshore waters much exceed the Si removal rate. Similarly, the NO_3/PO_4 (N/P) molar ratios were rather low in the nearshore waters as compared to the river ratios, strongly suggesting faster regeneration of phosphate in the coastal region fed by P-poor water masses. Possibility of overestimation of the DIP concentrations in the seawater due to positive chemical interferences from other forms of phosphorus in the upper layer is another factor for lower N/P ratios in the seawater, as suggested previously by Vitousek *et al.* (2002) and Moutin *et al.* (2002). This interference becomes less significant when DIP concentrations exceed 0.1 μM in the surface waters and in the deep waters having higher DIP than DOP. Therefore, pre-filtration of surface waters from productive regions helps to produce reliable DIP data though DOM still causes to positive interference. The deep waters of the open Mediterranean Sea have relatively high DIP (nearly 0.2 μM) but low DOP, which have been determined reliably by both the direct colorimetric and MAGIC methods. The agreement between the two methods indicates insignificant chemical interferences in DIP-replete waters of deep basins. In conclusion, the MAGIC data still is probably insufficient to determine only dissolved inorganic phosphate (DIP) ions in the surface waters and thus may partly overestimate the N/P ratio whereas the ratios could not be estimated by the standard method in the DIP-depleted surface waters.

Surface nutrient values of the nearshore and shelfbreak stations deplete and become identical during dry periods when the river effects weak and internal processes dominate the shelf system. However, winter vertical mixing also carries nutrients, especially phosphorus, from sediment layer to water column of the shallow zone. Present results show that the inorganic nutrient concentrations in the surface waters of the nearshore station increase in wet (winter and spring) seasons, when the internal and external inputs exceed the consumption rate of the nutrients. The nutrient concentrations of the nearshore zone are consistent with those reported from other coastal margins influenced by riverine inputs (Yılmaz *et al.*, 1992; Béthoux *et al.*, 1992; Justic *et al.*, 1995; Tugrul and Polat, 1995; Cociasu *et al.*, 1996; Laznik *et al.*, 1999; Monaghan and Ruttenberg, 1999; Stålnacke *et al.*, 1999; Çoban *et al.*, 2000a; Chen *et al.*, 2001; Giani *et al.*, 2003; Liu *et al.*, 2003; Durrieu de Madron *et al.*, 2003).

The bottom water of the shelfbreak zone contained high nitrates (0.17-3.61 μM); but it was poor in DIP, ranging merely between 0.02-0.07 μM, during 2002-2003. This feature is very similar to the inherent property of the eastern Mediterranean intermediate water (MIW) ventilating the bottom layer of the shelf. The MIW are well known to be depleted in DIP but relatively rich in nitrate, leading to high N/P ratios in the near-bottom waters of the shelf as experienced in the open sea (Béthoux *et al.*, 1992; Yılmaz and Tuğrul, 1998; Ediger *et al.*, 2005; Krom *et al.*, 2005). The upper water column down 125-150 m of the middle and the shelfbreak zones, however, had similar nutrient concentrations at similar depths. This feature indicates that the shelf zone was occupied by the water masses with similar hydro-chemical properties that change seasonally. Moreover, their residence time was not too long to be modified by POM sinking from the surface.

POM concentrations were more variable and higher in the nearshore zone under the direct influence of river discharges. This local difference becomes more coherent when the surface salinity was diluted by fresh waters having large nitrate and silicate concentrations (Tuğrul *et al.*, 2004). Temporal changes in POM content of the nearshore waters were much more variable and much greater in 2002, when the surface waters had lower salinity values due to freshwater inflow. However, in 2002, bulk POM in the nearshore waters was relatively rich in carbonaceous organic matter, leading to high C/N and C/P ratios. In other words, bulk POM pool of the nearshore waters are fed by remarkable input of terrestrial POM via the river water, which also has large concentrations of nitrate and silicate as experienced in other coastal seas (Rabitti *et al.*, 1994; Socal *et al.*, 1999; Laznik *et al.*, 1999; Rabalais *et al.*, 2002). However, nutrient inputs by the major rivers have less influence on the POM pool of the offshore zone. Therefore, temporal changes in PON content of the deeper shelf waters were closely correlated with POC abundance, dominated by internal processes. However, the TPP, which is composed of PIP and POP, displayed greater seasonal variations in phosphate depleted waters. The present POM data from the nearshore waters of the NE Mediterranean shelf zone are comparable to the measurements in the productive coastal waters of the other seas (Rabitti *et al*., 1994; Socal *et al*., 1999; Doval *et al*., 1999).

Briefly, the POM and nutrient concentrations of surface waters displayed an apparent declining trend from the river-fed nearshore to the shelfbreak station and to the open reference stations; a similar change appears from spring to summer-autumn months across the shelf. These features are principally controlled by inputs from the major rivers in the offshore zone as nutrient loads of the small Lamas River dominate the nearshore ecosystem within the river delta.

Comparison of temporal and spatial distributions of the abundance and elemental composition of bulk POM in the shelf margin, depicted in Figures 4.10 to 4.12, reveals that changes in POM abundance across the NE Mediterranean shelf occurred with similar C/N ratios. The higher C/N ratios (8-20) were observed in 2002 and spring-summer 2003, indicating the apparent influence of organic carbon-rich particles on the POM pool of the shelf. It was most probably the result of selective decay of nitrogenous constituents of POM as experienced in fast and slowly sinking particulate matter in the marine environments (Libes, 1992; Çoban-Yıldız *et al*., 2000b; Ediger *et al*., 2005). The decreased salinity and higher concentrations of nutrient in the nearshore surface waters show that (Tuğrul *et al*., 2004; Yılmaz, 2006) the increased river runoff introduces large loads of refractive POM with high C/N and N/P ratios to the sea, which expectedly influenced the chemical composition and abundance of bulk POM in the sea. However, in autumn 2002, the POM content of the saltier shelf waters declined to minimal levels, with higher C/N ratios, indicating that more labile fraction of bulk POM had been used by heterotrophic organisms. In summer-autumn 2003, the shelf ecosystem was still poor in POM but having lower C/N ratios (ranging between 5 and 9). This feature implies that: (i) the POM pool was dominated by autotrophic production fed by regenerated nutrients, (ii) the organic matter is essentially autochthonous origin from living organisms or from pysico-chemical transformations involving the colloids and (iii) state of decomposition of the organic matter (when organic matter is decomposing, the N is mineralized faster) as suggested by Frascari *et al*. (2002). These C/N values are consistent with the canonical Redfield ratio of approximately 6.7 estimated for the productive oceans (Geider and La Roche, 2002; Giani *et al.*, 2003).

Close examination of bulk POM data in the surface water across the shelf clearly show that the filtered particulate matter was depleted in phosphorus, leading to markedly high PON/TPP ratios in 2002. The lower C/N but higher N/P ratios of bulk POM across the shelf strongly suggest that DIP primarily limits POM production in the NE Mediterranean shelf water. This suggestion is corroborated by high NO_3/PO_4 ratios observed in the river and rain waters feeding the shelf ecosystem (Tuğrul *et al.*, 2004).

Regression analyses of the shelf POM data also indicate that the C/N/P ratios of the POM increase in the more productive nearshore waters. POM increases in the nitrate-repleted nearshore waters appeared to occur with higher C/N ratios, implying direct influence of land-based POM input with high C/N ratios. Not unexpectedly, the POM changes in the EZ of the deeper shelf zone took place with the C/N ratios comparable to the Redfield ratio. This feature strongly suggests plankton-dominated less degraded POM increase in the euphotic zone. POC/Chl-a ratio by regression analysis was estimated previously as 35-105 by Eker-Develi (2004) and cooperative of the present study as 25-56 (Yılmaz, 2006), strongly suggesting phytoplankton dominated POM changes in the shelfbreak zone. Phyto-C to Chl-a ratio estimated for the shelfbreak station (58) was higher than for nearshore station (29) (Yılmaz, 2006); these values imply healthy population growth across the shelf. Similarly, POC/TPP and PON/TPP ratios derived from the regression analysis were higher in the nearshore waters fed by the nitrate-repleted Lamas River, implying noticeable contribution of terrestrial particles to the POM pool in the nearshore zone; however, planktonic particles dominate bulk POM content of the deeper shelf. Briefly, N and P constituents of bulk POM increase from the nearshore to the shelfbreak zone and open sea. These results are comparable to those from the eastern Mediterranean coastal margins (Çoban-Yıldız *et al.*, 2000b; Yayla *et al.*, 2001; Ediger *et al.*, 2005).

Components (fractions) of total phosphorus measured in the shelf clearly demonstrate that the TDP dominates the phosphorus pool of the DIP-depleted shelf ecosystem. However, PIP has a remarkable contribution to the TPP pool (composed of POP and PIP) and thus to TP pool of the nearshore waters in winter-spring period when PIP inputs from sediment layer increased apparently via vertical mixing and by river runoff. This effect becomes more evident, especially during high flow and heavy rain periods. The PIP contribution to the TPP pool becomes insignificant in the open shelf waters; this change indicates high reactivity of phosphorus compounds in the water column. Accordingly, the PIP-corrected POC/POP and PON/POP ratios are much higher than the POC/TPP and PON/TPP ratios in the phosphate-depleted nearshore and open shelf waters. In conclusion, higher C/P and N/P ratios of bulk POM observed in the NE Mediterranean shelf water strongly suggest P-limited primary production as reported recently for the open sea ecosystem (Yılmaz and Tuğrul, 1998; Van Wambake *et al*., 2002; Giani *et al*., 2003; Herut *et al*., 2005; Krom *et al*., 2005). For further understanding of nutrient cycling and POM composition in the NE Mediterranean shelf, future studies are highly recommended to be performed in more productive and shallower regions of Mersin and Iskenderun bays because these margins of NE Mediterranean have limited water exchanges with the open sea but receives large nutrient inputs from urban wastewaters and major rivers in the region.

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APPENDICES

APPENDIX A. NUTRIENT CONCENTRATIONS AND N/P RATIOS AT THE STUDIED STATIONS

Date (dd/mm/yyyy)	Depth (m)	DIP (µM)		NO_3 (µM)	Si (µM)	N/P ^{AA}	N/P ^{MAGIC}
		AA	MAGIC*				
	NEARSHORE STATION						
11/12/2001	0	0.21	0.230	19.90	26.72	94.8	86.7
	5	0.12	0.151	1.59	18.90	13.3	10.5
23/01/2002	0	0.13	0.166	8.87	10.19	68.2	53.4
	5	0.10	0.105	2.08	2.38	20.8	19.8
19/02/2002	0	0.04	0.055	5.30	6.26	132.5	96.7
	5	0.02	0.033	3.59	4.50	179.5	107.5
09/04/2002	0	0.05	0.072	7.00	9.59	140.0	97.7
	5	0.07	0.057	3.87	8.35	55.3	68.4
13/05/2002	0	0.19	0.130	0.38	5.54	2.0	2.9
	5	0.13	0.103	0.38	9.23	2.9	3.7
18/06/2002	0	0.30	0.077	2.22	5.23	7.4	28.8
	5	0.23	0.073	1.21	2.96	5.3	16.5
11/07/2002	0	0.18	0.036	4.01	5.47	22.3	112.9
	5	0.49	0.066	0.66	3.24	1.3	10.0
01/08/2002	0	0.04	0.053	9.96	15.38	249.0	188.8
	5	0.02	0.043	0.87	3.70	43.5	20.1
18/09/2002	0	0.04	0.045	3.24	7.40	81.0	72.5
	10	0.02	0.042	0.15	1.85	7.5	3.5
24/10/2002	0	0.04	0.050	3.06	4.55	76.5	61.6
	10	0.05	0.052	0.38	1.88	7.6	7.4
21/11/2002	0	0.03	0.060	3.84	6.86	128.0	63.5
	10	0.04	0.057	0.24	2.27	6.0	4.2
24/12/2002	0	0.02	0.026	0.08	1.30	4.0	3.1
	10	0.03	0.030	0.11	1.39	3.7	3.6
29/01/2003	0	0.03	0.028	0.22	1.25	7.3	7.8
	10	0.03	0.027	0.25	1.36	8.3	9.1
27/02/2003	0	0.10	0.101	2.10	0.91	21.0	20.8
	10	0.10	0.097	1.77	1.01	17.7	18.2
28/03/2003	0	0.16	0.162	4.82	7.40	30.1	29.8
	10	0.14	0.142	1.40	8.48	10.0	9.8
22/04/2003	0	0.03	0.071	6.26	9.14	208.7	87.6
21/05/2003	0	0.03	0.058	0.07	4.41	2.3	1.2
	10	0.02	0.055	0.12	4.22	6.0	2.2
05/06/2003	0	0.03	0.061	0.44	1.44	14.7	7.2
	10	0.04	0.059	0.09	1.76	2.3	1.5
15/07/2003	0	0.06	0.050	0.13	1.55	2.2	2.6
	10	0.03	0.056	0.32	2.12	10.7	5.7
31/07/2003	0	0.03	0.039	1.10	2.70	36.7	28.4
	10	0.02	0.044	0.09	1.09	4.5	2.0
22/09/2003	0	0.02	0.043	0.08	1.76	4.0	1.9
	10	0.03	0.036	0.06	1.50	2.0	1.7
11/12/2003	0	0.03	0.018	0.40	1.76	13.3	22.2
	10	0.02	0.024	0.35	1.77	17.5	14.5

APPENDIX A (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	DIP (µM)		NO$_3$ (µM)	Si (µM)	N/P ^{AA}	N/P ^{MAGIC}
		AA	MAGIC*				
	MIDDLE STATION						
18/09/2002	0	0.03	0.033	0.47	1.85	15.7	14.2
	20	0.02	0.027	0.18	2.03	9.0	6.6
	40	0.02	0.021	0.13	1.83	6.5	6.2
	60	0.02	0.021	0.18	2.01	9.0	8.5
	80	0.02	0.031	0.19	1.49	9.5	6.2
	100	0.03	0.033	0.28	3.83	9.3	8.5
24/10/2002	0	0.03	0.022	0.21	1.39	7.0	9.4
	20	0.03	0.023	0.16	1.68	5.3	7.0
	40	0.05	0.025	0.24	1.44	4.8	9.8
	60	0.05	0.026	0.18	1.54	3.6	7.0
	80	0.06	0.022	0.38	1.29	6.3	17.1
	100	0.06	0.024	0.28	1.56	4.7	8.3
21/11/2002	0	0.02	0.014	0.10	1.44	5.0	7.0
	20	0.02	0.019	0.06	1.59	3.0	3.1
	40	0.02	0.027	0.09	2.21	4.5	3.4
	60	0.02	0.035	0.12	2.08	6.0	3.4
	80	0.02	0.041	0.09	1.98	4.5	2.2
	100	0.02	0.033	0.27	2.27	13.5	8.2
24/12/2002	0	0.04	0.017	0.08	1.52	2.0	4.7
	20	0.03	0.016	0.07	1.47	2.3	4.4
	40	0.03	0.017	0.09	1.43	3.0	5.2
	60	0.04	0.021	0.11	1.89	2.8	5.4
	80	0.05	0.020	0.12	1.46	2.4	6.2
	100	0.02	0.023	0.09	1.36	45	3.9
29/01/2003	0	0.02	0.022	0.27	1.50	13.5	12.3
	20	0.02	0.022	0.24	1.50	12.0	11.0
	40	0.02	0.020	0.26	1.53	13.0	13.2
	60	0.02	0.022	0.36	1.47	18.0	16.8
	80	0.02	0.024	0.19	1.38	9.5	8.0
	100	0.03	0.030	0.45	1.51	15.0	15.2
27/02/2003	0	0.02	0.023	0.63	0.84	31.5	27.2
	20	0.02	0.020	0.23	0.87	11.5	11.5
	40	0.02	0.023	0.38	0.79	19.0	16.4
	60	0.02	0.022	0.45	1.02	22.5	20.2
	80	0.03	0.025	0.66	1.67	22.0	26.0
	100	0.04	0.036	0.60	1.85	15.0	16.7
28/03/2003	0	0.03	0.032	0.58	1.33	19.3	18.1
	20	0.04	0.037	0.10	0.97	2.5	2.8
	40	0.02	0.019	0.11	0.85	5.5	5.8
	60	0.02	0.016	0.10	1.68	5.0	6.3
	80	0.03	0.025	0.08	2.82	2.7	3.2
	100	0.03	0.030	0.23	3.38	7.7	7.7
22/04/2003	0	0.03	0.041	0.78	1.73	26.0	18.9
21/05/2003	0	0.03	0.040	0.08	2.10	2.7	2.0
	20	0.02	0.019	0.10	0.85	5.0	5.4
	40	0.02	0.018	0.06	1.50	3.0	3.4
	60	0.03	0.024	0.08	2.75	2.7	3.3
	80	0.02	0.029	0.51	2.06	25.5	17.4
	100	0.02	0.031	0.88	2.02	44.0	28.7
05/06/2003	0	0.03	0.028	0.08	0.92	2.7	2.9
	20	0.04	0.020	0.08	0.89	2.0	4.1
	40	0.02	0.021	0.09	1.01	4.5	4.3
	60	0.03	0.025	0.08	1.02	2.7	3.2
	80	0.04	0.027	0.07	1.13	1.8	2.6
	100	0.04	0.025	0.10	2.54	2.5	4.0

APPENDIX A (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	DIP (µM)		NO$_3$ (µM)	Si (µM)	N/P ^{AA}	N/P ^{MAGIC}
		AA	MAGIC*				
	MIDDLE STATION						
15/07/2003	0	0.02	0.028	0.09	0.84	4.5	3.3
	20	0.03	0.028	0.11	1.21	3.7	3.9
	40	0.02	0.029	0.11	1.03	5.5	3.8
	60	0.04	0.021	0.11	1.05	2.8	5.3
	80	0.04	0.019	0.13	1.21	3.3	6.7
	100	0.04	0.028	0.14	1.71	3.5	4.9
31/07/2003	0	0.02	0.026	0.06	0.70	3.0	2.3
	20	0.03	0.030	0.07	0.83	2.3	2.3
	40	0.02	0.046	0.09	1.23	4.5	1.9
	60	0.02	0.025	0.06	0.84	3.0	2.4
	80	0.02	0.028	0.07	0.77	3.5	2.5
	100	0.03	0.066	0.40	1.59	13.3	6.1
22/09/2003	0	0.02	0.033	0.07	1.43	3.5	2.1
	20	0.02	0.035	0.10	1.48	5.0	2.9
	40	0.02	0.028	0.05	1.45	2.5	1.8
	60	0.02	0.025	0.05	1.71	2.5	2.0
	80	0.02	0.027	0.08	1.45	4.0	2.9
	100	0.02	0.037	0.09	1.65	4.5	2.4
11/12/2003	0	0.05	0.015	0.34	1.70	6.8	22.2
	20	0.03	0.018	0.33	1.68	11.0	17.9
	40	0.05	0.015	0.32	1.69	6.4	21.5
	60	0.04	0.016	0.36	1.69	9.0	22.2
	80	0.05	0.048	0.52	2.21	10.4	10.8
	100	0.06	0.059	0.67	2.38	11.2	11.3
	SHELFBREAK STATION						
11/12/2001	0	0.03	0.012	0.08	1.36	2.7	6.7
	25	0.03	0.010	0.06	1.39	2.0	6.0
	50	0.03	0.014	0.08	1.39	2.7	5.6
	65	0.03	0.018	0.14	1.35	4.7	7.8
	75	0.02	0.014	0.26	1.5	13.0	18.8
	100	0.03	0.006	0.16	1.39	5.3	28.9
	125	0.03	0.021	0.23	1.52	7.7	11.0
	150	0.03	0.012	0.24	1.43	8.0	19.8
	180	0.03	0.021	1.94	2.21	64.7	91.2
23/01/2002	0	0.05	0.028	0.24	1.07	4.8	8.4
	25	0.05	0.026	0.29	1.20	5.8	11.4
	50	0.10	0.023	0.46	1.41	4.6	19.7
	65	0.11		0.29	1.24	2.6	
	75	0.14	0.025	0.58	1.30	4.1	23.1
	100	0.15	0.009	0.97	1.33	6.5	108.5
	125	0.16		0.92	1.44	5.8	
	150	0.13	0.033	0.85	1.67	6.5	25.9
	180	0.16	0.058	1.72	2.69	10.8	29.6

APPENDIX A (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	DIP (µM)		NO$_3$ (µM)	Si (µM)	N/P ^{AA}	N/P ^{MAGIC}
		AA	MAGIC*				
	SHELFBREAK STATION						
19/02/2002	0	0.02	0.012	0.09	0.64	4.5	7.6
	25	0.02	0.017	0.14	0.75	7.0	8.4
	50	0.02	0.014	0.11	0.54	5.5	7.8
	65	0.04		0.11	0.62	2.8	
	75	0.02	0.018	0.14	0.55	7.0	7.6
	100	0.02	0.015	0.09	0.66	4.5	6.1
	125	0.05		0.46	0.69	9.2	
	150	0.02	0.017	0.17	0.59	8.5	10.2
	180	0.02	0.037	0.57	0.96	28.5	15.5
09/04/2002	0	0.03	0.018	0.13	0.84	4.3	7.1
	25	0.02	0.019	0.16	0.78	8.0	8.3
	50	0.02	0.020	0.26	0.71	13.0	13.1
	65	0.02		0.35	0.74	17.5	
	75	0.02	0.021	0.41	0.76	20.5	19.1
	100	0.03	0.021	0.09	0.81	3.0	4.3
	125	0.02		0.14	1.00	7.0	
	150	0.03	0.028	0.09	0.99	3.0	3.2
	180	0.02	0.025	0.11	1.00	5.5	4.5
13/05/2002	0	0.02	0.017	0.24	1.36	12.0	13.8
	25	0.02	0.012	0.25	0.91	12.5	20.3
	50	0.02	0.011	0.23	1.01	11.5	20.2
	75	0.02	0.011	0.21	0.89	10.5	19.7
	100	0.06	0.017	0.62	1.28	10.3	35.7
	125	0.08		0.59	1.85	7.4	
	150	0.04	0.017	0.55	0.93	13.8	33.3
	180	0.12	0.026	0.66	1.43	5.5	25.0
18/06/2002	0	0.04	0.020	0.17	0.97	4.3	8.7
	25	0.02	0.019	0.12	1.01	6.0	6.3
	50	0.05	0.020	0.12	1.18	2.4	6.1
	65	0.02	0.016	0.12	1.14	6.0	7.6
	75	0.02	0.017	0.22	1.15	11.0	13.1
	100	0.03	0.020	0.17	1.18	5.7	8.4
	125	0.04	0.025	0.57	1.34	14.3	22.8
	150	0.04	0.025	0.72	1.39	18.0	28.8
11/07/2002	0	0.07	0.029	0.40	0.82	5.7	13.9
	5	0.09	0.025	0.35	0.64	3.9	13.8
	15	0.08	0.030	0.40	0.67	5.0	13.2
	25	0.06	0.015	0.53	0.72	8.8	34.6
	45	0.11	0.015	0.61	0.79	5.5	41.9
	60	0.07	0.017	0.38	0.89	5.4	21.8
	70	0.12	0.016	0.39	1.18	3.3	24.6
	100		0.021				
	125		0.019				
	150		0.022				
	180		0.016				

APPENDIX A (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	DIP (µM)		NO$_3$ (µM)	Si (µM)	N/P ^{AA}	N/P ^{MAGIC}
		AA	MAGIC*				
	SHELFBREAK STATION						
01/08/2002	0	0.02	0.015	0.16	1.61	8.0	10.4
	25	0.05	0.029	0.20	1.73	4.0	6.9
	50	0.03	0.029	0.16	1.49	5.3	5.4
	65	0.02	0.030	0.15	1.46	7.5	5.0
	75	0.02	0.024	0.12	2.57	6.0	5.0
	100	0.02	0.023	0.21	1.48	10.5	9.2
	125	0.02	0.026	0.29	1.55	14.5	11.0
	150	0.02	0.026	0.27	1.59	13.5	10.3
	180	0.02	0.038	1.04	1.96	52.0	27.3
18/09/2002	0	0.06	0.032	0.94	2.88	15.7	29.5
	20	0.06	0.030	0.23	1.92	3.8	7.7
	40	0.06	0.028	0.15	1.98	2.5	5.3
	60	0.04	0.026	0.14	1.85	3.5	5.3
	80	0.02	0.030	0.16	1.86	8.0	5.4
	100	0.03	0.033	0.18	1.60	6.0	5.5
	125	0.05	0.034	0.29	1.61	5.8	8.6
	150	0.03	0.030	0.68	1.83	22.7	23.0
	175	0.03	0.030	1.83	2.94	61.0	60.1
	200	0.06	0.033	3.11	4.73	51.8	95.5
24/10/2002	0	0.03	0.018	0.69	1.51	23.0	38.8
	20	0.06	0.021	0.07	1.37	1.2	3.3
	40	0.04	0.019	0.11	1.37	2.8	5.8
	60	0.04	0.019	0.27	1.48	6.8	14.5
	80	0.07	0.017	0.06	1.38	0.9	3.5
	100	0.03	0.022	0.06	1.34	2.0	2.7
	125	0.03	0.025	0.16	1.55	5.3	6.4
	150	0.05	0.025	0.41	1.48	8.2	16.7
	175	0.07	0.034	1.01	1.73	14.4	29.9
	200	0.1	0.038	2.38	2.49	23.8	62.3
21/11/2002	0	0.07	0.023	0.22	1.89	3.1	9.4
	20	0.02	0.020	0.06	2.35	3.0	2.9
	40	0.04	0.021	0.11	1.91	2.8	5.1
	60	0.04	0.026	0.17	2.14	4.3	6.5
	80	0.02	0.023	0.10	2.01	5.0	4.3
	100	0.03	0.021	0.07	1.36	2.3	3.3
	125	0.02	0.047	0.30	2.37	15.0	6.4
	150	0.02	0.030	0.39	2.04	19.5	13.1
	175	0.02	0.042	0.42	2.57	21.0	9.9
	200	0.06	0.049	1.29	5.04	21.5	26.1

APPENDIX A (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	DIP (µM)		NO_3 (µM)	Si (µM)	N/P ^{AA}	N/P ^{MAGIC}
		AA	MAGIC*				
	SHELFBREAK STATION						
24/12/2002	0	0.06	0.017	0.12	2.10	2.0	7.1
	20	0.04	0.013	0.08	1.80	2.0	6.2
	40	0.03	0.016	0.09	1.62	3.0	5.8
	60	0.02	0.016	0.06	1.51	3.0	3.8
	80	0.04	0.017	0.10	1.66	2.5	6.1
	100	0.04	0.017	0.10	1.67	2.5	5.9
	125	0.02	0.017	0.09	1.48	4.5	5.4
	150	0.02	0.019	0.07	1.40	3.5	3.7
	175	0.02	0.022	0.08	1.43	4.0	3.7
	200	0.08	0.022	0.19	2.08	2.4	8.5
29/01/2003	0	0.02	0.022	0.32	1.22	16.0	14.5
	20	0.02	0.021	0.28	1.31	14.0	13.5
	40	0.02	0.020	0.44	1.20	22.0	21.8
	60	0.03	0.028	0.25	1.20	8.3	9.0
	80	0.03	0.025	0.45	1.15	15.0	17.9
	100	0.03	0.026	0.51	1.31	17.0	19.3
	125	0.02	0.023	0.60	1.38	30.0	25.7
	150	0.02	0.023	0.38	1.37	19.0	16.6
	175	0.02	0.022	0.59	1.14	29.5	26.3
	200	0.03	0.035	0.63	1.19	21.0	18.0
27/02/2003	0	0.03	0.025	0.54	1.77	18.0	21.3
	20	0.02	0.023	0.17	1.78	8.5	7.3
	40	0.02	0.020	0.42	1.85	21.0	20.5
	60	0.02	0.022	0.17	1.86	8.5	7.6
	80	0.02	0.025	0.27	1.83	13.5	11.0
	100	0.02	0.023	0.62	1.90	31.0	27.3
	125	0.03	0.028	0.37	0.82	12.3	13.2
	150	0.02	0.024	0.13	0.87	6.5	5.4
	175	0.03	0.029	0.58	1.83	19.3	20.0
	200	0.04	0.039	3.61	1.65	90.3	92.0
28/03/2003	0	0.01	0.014	0.32	1.69	32.0	22.4
	20	0.01	0.014	0.31	2.17	31.0	21.7
	40	0.02	0.017	0.27	2.21	13.5	16.3
	60	0.02	0.015	0.30	2.25	15.0	19.8
	80	0.02	0.017	0.30	1.39	15.0	18.2
	100	0.02	0.018	0.32	2.92	16.0	17.5
	125	0.02	0.021	0.36	3.75	18.0	17.2
	150	0.02	0.025	0.46	3.27	23.0	18.7
	175	0.03	0.026	0.49	2.77	16.3	18.6
	200	0.04	0.040	0.84	1.77	21.0	21.1
21/05/2003	0	0.05	0.036	0.10	2.12	2.0	2.7
	20	0.03	0.019	0.07	1.48	2.3	3.8
	40	0.04	0.017	0.10	0.96	2.5	5.9
	60	0.03	0.020	0.07	0.96	2.3	3.4
	80	0.03	0.026	0.11	1.38	3.7	4.2
	100	0.04	0.028	0.60	1.17	15.0	21.8
	125	0.02	0.027	0.70	1.24	35.0	25.8
	150	0.02	0.033	0.72	1.28	36.0	21.6
	175	0.04	0.047	1.09	1.47	27.3	23.3
	200	0.08	0.068	2.28	5.79	28.5	33.4

APPENDIX A (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	DIP (µM)		NO_3 (µM)	Si (µM)	N/P ^{AA}	N/P ^{MAGIC}
		AA	MAGIC*				
	SHELFBREAK STATION						
05/06/2003	0	0.02	0.021	0.08	1.03	4.0	3.9
	20	0.03	0.018	0.06	1.26	2.0	3.3
	40	0.02	0.015	0.05	1.16	2.5	3.3
	60	0.03	0.014	0.13	1.32	4.3	9.6
	80	0.03	0.014	0.07	0.99	2.3	4.8
	100	0.03	0.017	0.09	1.45	3.0	5.4
	125	0.04	0.033	0.68	2.06	17.0	20.8
	150	0.04	0.038	1.03	2.55	25.8	27.3
	175	0.03	0.035	0.80	1.64	26.7	22.6
	200	0.04	0.039	1.03	1.89	25.8	26.1
15/07/2003	0	0.03	0.026	0.09	0.84	3.0	3.5
	20	0.02	0.019	0.09	0.89	4.5	4.6
	40	0.02	0.014	0.12	1.19	6.0	8.5
	60	0.03	0.014	0.09	1.14	3.0	6.6
	80	0.03	0.012	0.10	0.94	3.3	8.4
	100	0.02	0.012	0.11	1.30	5.5	8.9
	125	0.02	0.021	0.36	3.75	18.0	17.2
	150	0.03	0.020	0.54	1.28	18.0	27.1
	175	0.03	0.018	0.79	1.82	26.3	44.7
	200	0.04	0.036	1.19	2.81	29.8	32.7
31/07/2003	0	0.02	0.017	0.07	0.67	3.5	4.2
	20	0.02	0.016	0.08	0.66	4.0	4.9
	40	0.02	0.019	0.06	0.70	3.0	3.2
	60	0.02	0.019	0.12	0.70	6.0	6.4
	80	0.02	0.023	0.19	0.68	9.5	8.2
	100	0.02	0.022	0.27	1.30	13.5	12.2
	125	0.03	0.036	0.45	1.45	15.0	12.6
	150	0.03	0.029	0.36	1.02	12.0	12.5
	175	0.03	0.040	0.46	1.20	15.3	11.4
	200	0.02	0.032	0.17	1.07	8.5	5.2
22/09/2003	0	0.02	0.032	0.07	1.47	3.5	2.2
	20	0.02	0.041	0.07	1.54	3.5	1.7
	40	0.02	0.031	0.07	1.52	3.5	2.2
	60	0.02	0.024	0.08	1.23	4.0	3.3
	80	0.02	0.024	0.06	1.33	3.0	2.5
	100	0.02	0.027	0.07	1.35	3.5	2.6
	125			0.33	1.47		
	150	0.03	0.040	0.53	1.51	17.7	13.1
	175	0.03	0.038	0.17	1.43	5.7	4.4
	200	0.04	0.044	1.53	2.02	38.3	34.7
11/12/2003	0	0.06	0.018	0.37	1.67	6.2	20.3
	20	0.05	0.014	0.34	1.65	6.8	23.6
	40	0.04	0.017	0.36	1.66	9.0	21.6
	60	0.03	0.015	0.39	1.65	13.0	25.5
	80	0.04	0.016	0.34	1.64	8.5	21.6
	100	0.03	0.021	1.03	1.72	34.3	48.3
	125	0.03	0.025	0.81	1.79	27.0	32.2
	150	0.03	0.029	0.81	1.79	27.0	28.2
	175	0.03	0.030	1.01	1.91	33.7	34.1
	200	0.05	0.048	1.59	2.51	31.8	32.9

APPENDIX A (CONTINUED)

Date (dd/mm/yyyy)	**Depth (m)**	**DIP (µM)**		**NO$_3$ (µM)**	**Si (µM)**	**N/P ^{AA}**	**N/P ^{MAGIC}**
		AA	**MAGIC***				
	REFERENCE STATION (R1)						
29/12/2003	0	0.03	0.020	0.29	1.69	9.7	14.5
	25	0.02	0.018	0.16	1.91	8.0	8.9
	50	0.02	0.014	0.10	1.69	5.0	7.1
	100	0.02	0.020	0.15	1.83	7.5	7.5
	125	0.03	0.011	0.30	1.51	5.0	27.3
	150	0.03	0.010	0.26	1.59	8.7	26.0
	175	0.05	0.018	0.38	1.66	7.6	21.1
	200	0.02	0.020	0.70	1.77	35.0	35.0
	250	0.04	0.053	1.77	2.87	44.3	33.4
	275	0.05	0.072	3.04	3.65	60.8	42.2
	300	0.08	0.110	2.89	4.62	36.1	26.3
	350	0.14	0.134	3.84	6.57	27.4	28.7
	400	0.18	0.189	4.56	8.30	25.3	24.1
	500	0.22	0.208	5.30	10.48	24.1	25.5
	600	0.21	0.200	4.88	10.69	23.2	24.4
	800	0.21	0.199	4.25	11.20	20.2	21.4
	REFERENCE STATION (R2)						
29/12/2003	2	0.02	0.017	0.08	1.95	4.0	4.7
	20	0.02		0.06	2.05	3.0	
	35	0.02	0.009	0.09	1.94	4.5	10.0
	40	0.02	0.025	0.08	2.03	4.0	3.2
	106	0.03	0.024	0.50	1.86	16.7	20.8
	145	0.03	0.027	0.49	1.90	16.3	18.1
	195	0.03		0.99	2.18	33.0	
	245	0.11	0.097	3.30	4.33	30.0	34.0
	296		0.162	4.82	7.18		29.8
	396		0.175	5.58	9.58		31.9
	491		0.192	5.67	10.35		29.5
	736		0.198	5.22	11.45		26.4
	964		0.168	5.20	13.78		31.0
	REFERENCE STATION (R3)						
29/12/2003	5	0.02		0.06	1.73	3.0	
	25	0.03	0.017	0.11	1.85	3.7	6.5
	50	0.02	0.017	0.10	2.16	5.0	5.9
	96	0.02	0.023	0.37	1.70	18.5	16.1
	125	0.02	0.020	0.38	1.78	19.0	19.0
	150	0.02	0.041	1.01	2.22	50.5	24.6
	200	0.03	0.035	1.38	2.42	46.0	39.4
	222	0.07	0.064	0.40	3.63	5.7	6.3
	250	0.10	0.100	3.37	4.56	33.7	33.7
	300	0.19	0.202	4.95	7.82	26.1	24.5
	350		0.207	5.35	9.00		25.8
	399		0.208	5.38	10.07		25.9
	499		0.225	5.70	11.05		25.3
	749		0.214	5.52	12.21		25.8
	REFERENCE STATION (R4)						
29/12/2003	1	0.02	0.023	0.06	1.89	3.0	2.6
	25	0.02	0.021	0.07	1.86	3.5	3.3
	51	0.02	0.017	0.05	1.74	2.5	2.9
	100	0.03	0.015	0.07	1.62	2.3	4.7
	127	0.02	0.023	0.35	1.71	17.5	15.2
	150	0.02	0.029	0.95	2.03	47.5	32.8
	200	0.04	0.058	2.30	3.58	57.5	39.7
	250	0.10	0.113	3.68	5.01	36.8	32.6
	300	0.17	0.169	5.02	7.11	29.5	29.7
	400	0.23	0.204	5.82	9.76	25.3	28.5
	500	0.23	0.222	5.55	10.87	24.1	25.0
	751	0.22	0.221	5.20	11.56	23.6	23.5
	1102	0.20	0.214	4.86	12.02	24.3	22.7

APPENDIX B. NUTRIENT CONCENTRATIONS AND, N/P AND Si/N RATIOS IN THE RAINWATER COLLECTED IN THE STUDY REGION (after Tuğrul *et al.*, 2004 and unpublished data of the IMS-METU Chemical Oceanography department)

Date (dd/mm/yyyy)	PO$_4$ (µM) ^{AA}	NO$_3$ (µM)	Si (µM)	N/P ^{AA}	Si/N
12/04/2002	0.97	109.43	5.84	112.8	0.053
12/07/2002	0.61	83.08	1.07	136.2	0.013
12/09/2002	0.29	28.3	0.49	97.6	0.017
19/12/2002	0.78	156.24	0.85	200.3	0.005
20/12/2002	0.23	25.82	0.63	112.3	0.024
29/12/2002	0.68	103.45	0.93	152.1	0.009
30/12/2002	0.40	35.79	0.32	89.5	0.009
02/01/2003	0.85	60.39	0.45	71.0	0.007
03/01/2003	0.21	17.65	0.17	84.0	0.010
05/01/2003	9.00	84.14	2.29	9.3	0.027
06/01/2003	2.70	61.96	1.04	22.9	0.017
24/01/2003	1.05	105.4	5.31	100.4	0.050
28/01/2003	1.75	69.6	0.53	39.8	0.008
31/01/2003	1.24	40.49	0.06	32.7	0.001
02/02/2003	1.21	64.39	0.47	53.2	0.007
03/02/2003	1.46	50.32	1	34.5	0.020
06/02/2003	1.00	39.96	0.31	40.0	0.008
07/02/2003	1.45	37.95	1.67	26.2	0.044
08/02/2003	0.94	18.4	0.19	19.6	0.010
13/02/2003	0.90	17.36	2.24	19.3	0.129
14/02/2003	1.97	20.99	1.1	10.7	0.052
18/02/2003	0.83	65.99	8.63	79.5	0.131
19/02/2003	1.00	32.47	0.45	32.5	0.014
23/02/2003	0.95	29.48	0.1	31.0	0.003
25/02/2003	0.94	39.16	0.19	41.7	0.005
05/03/2003	1.63	62.13	5.14	38.1	0.083
08/03/2003	1.07	34.25	0.31	32.0	0.009
18/03/2003	0.86	34.58	0.93	40.2	0.027
23/03/2003	1.63	48.42	0.77	29.7	0.016
14/04/2003	1.64	61.41	3.06	37.4	0.050
15/04/2003	0.80	35.45	28	44.3	0.790
18/04/2003	1.16	94.78	1.68	81.7	0.018
24/04/2003	1.35	96.01	6.6	71.1	0.069
25/04/2003	0.95	28.77	1.42	30.3	0.049
26/04/2003	1.24	31.42	0.78	25.3	0.025
30/05/2003	1.23	93.36	10.44	75.9	0.112
31/05/2003	1.65	77.94	0.96	47.2	0.012
02/06/2003	1.31	209.05	1	159.6	0.005
13/06/2003	1.56	86.39	0.84	55.4	0.010
31/10/2003	2.04	197.5	3.16	96.8	0.016
11/11/2003	0.43	200	2.31	465.1	0.012
04/12/2003	1.09	469.5	4.54	430.7	0.010
05/12/2003	0.48	81.76	5.51	170.3	0.067
09/12/2003	0.42	85.09	1.2	202.6	0.014
17/12/2003	0.22	28.79	0.67	130.9	0.023
18/12/2003	0.17	16.55	1.16	97.4	0.070
26/12/2003	0.57	69.12	2.13	121.3	0.031
27/12/2003	0.38	28.72	2.13	75.6	0.074

APPENDIX C. PARTICULATE MATTER CONCENTRATIONS AND, C/P, C/N AND N/P RATIOS AT THE STUDIED STATIONS

Date (dd/mm/yyyy)	**Depth (m)**	**POC (µM)**	**PON (µM)**	**TPP (µM)**	**C/P**		**C/N (POC/PON)**	**N/P**	
					(POC/TPP)	**(POC/POP)**		**(PON/TPP)**	**(PON/POP)**
	NEARSHORE STATION								
23/01/2002	0	77.73	6.47	0.141	551.3	1075.9	12.0	45.9	89.5
	5	43.30	4.51	0.106	408.5	785.7	9.6	42.6	81.9
19/02/2002	0	12.91	1.37	0.053	243.7	421.0	9.4	25.9	44.7
	5	10.81	1.45	0.042	257.4	451.0	7.4	34.6	60.6
09/04/2002	0	21.28	2.43	0.100	212.8	404.0	8.8	24.3	46.1
	5	15.98	2.02	0.086	185.8	282.6	7.9	23.5	35.8
13/05/2002	0	114.06	9.99	0.191	597.2	836.5	11.4	52.3	73.3
	5	90.38	6.00	0.120	753.2	1216.8	15.1	50.0	80.8
18/06/2002	0	24.83	1.95	0.119	208.7	250.4	12.7	16.4	19.6
	5	24.60	1.74	0.074	332.5	411.9	14.1	23.6	29.2
11/07/2002	0	10.83	1.12	0.107	101.2	156.7	9.6	10.5	16.3
	5	12.94	1.46	0.070	184.8	348.3	8.8	20.9	39.4
01/08/2002	0	8.59	0.94	0.060	143.2	201.4	9.1	15.7	22.1
	5	8.29	0.94	0.044	188.4	301.8	8.8	21.4	34.3
18/09/2002	0	10.70	1.16	0.100	107.0	156.4	9.3	11.6	16.9
	10	15.97	1.63	0.083	192.4	246.7	9.8	19.7	25.2
24/10/2002	0	9.71	1.05	0.053	183.1	339.6	9.2	19.8	36.7
	10	6.08	0.66	0.043	141.4	209.2	9.2	15.3	22.7
21/11/2002	0	11.88	1.51	0.104	114.2	183.8	7.8	14.6	23.4
	10	12.57	1.29	0.063	199.4	258.0	9.8	20.5	26.5
24/12/2002	0	3.47	0.54	0.029	119.6	134.9	6.4	18.7	21.0
	10	2.51	0.41	0.026	96.7	108.5	6.1	15.9	17.9
29/01/2003	0	4.03	0.63	0.029	139.0	258.8	6.4	21.9	40.7
	10	4.56	0.70	0.037	123.2	169.0	6.5	18.8	25.8
27/02/2003	0	29.73	1.52	0.089	334.0	460.3	19.6	17.1	23.5
	10	8.13	1.16	0.074	109.9	144.7	7.0	15.7	20.7
28/03/2003	0	23.22	3.82	0.153	151.8	299.4	6.1	25.0	49.3
	10	14.76	2.27	0.110	134.2	180.4	6.5	20.6	27.7
22/04/2003	0	12.53	1.49	0.084	149.1	215.4	8.4	17.8	25.7
21/05/2003	0	24.25	1.91	0.046	527.1	1060.0	12.7	41.6	83.6
	10	30.77	1.86	0.065	473.3	635.8	16.5	28.6	38.4
05/06/2003	0	20.91	2.55	0.113	185.1	303.4	8.2	22.6	37.1
	10	12.45	1.23	0.062	200.8	489.7	10.1	19.9	48.4
15/07/2003	0	13.43	1.70	0.093	144.4	222.3	7.9	18.3	28.1
	10	8.83	1.21	0.076	116.2	156.2	7.3	15.9	21.3
31/07/2003	0	8.13	1.21	0.070	116.1	136.0	6.7	17.2	20.2
	10	18.03	2.25	0.107	168.5	184.4	8.0	21.0	23.0
22/09/2003	0	11.49	1.41	0.057	201.6	267.8	8.1	24.8	33.0
	10	3.30	0.43	0.031	106.4	319.1	7.6	14.0	41.9
11/12/2003	0	5.76	1.22	0.044	129.5	182.4	4.7	27.4	38.6
	10	3.85	0.93	0.036	107.5	153.5	4.2	25.8	36.9

APPENDIX C (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	POC (µM)	PON (µM)	TPP (µM)	C/P		C/N	N/P	
					(POC/TPP)	(POC/POP)	(POC/PON)	(PON/TPP)	(PON/POP)
	MIDDLE STATION								
18/09/2002	0	8.53	0.99	0.049	174.1	195.8	8.6	20.2	22.7
	20	6.50	0.75	0.037	175.7	229.4	8.7	20.3	26.5
	40	3.45	0.38	0.018	191.7	246.1	9.2	20.9	26.8
	60	4.37	0.37	0.020	218.6	276.7	11.8	18.6	23.5
	80	5.45	0.57	0.022	247.8	309.0	9.6	25.9	32.2
	100	1.69	0.17	0.018	93.8	120.8	9.7	9.7	12.5
24/10/2002	0	2.33	0.23	0.013	179.3	217.2	10.2	17.6	21.3
	20	4.25	0.42	0.016	265.4	302.1	10.0	26.5	30.1
	40	3.28	0.33	0.013	251.9	299.5	10.0	25.2	29.9
	60	5.23	0.57	0.015	349.0	399.7	9.1	38.3	43.8
	80	4.32	0.52	0.019	227.1	290.4	8.3	27.3	34.9
	100	3.56	0.26	0.040	88.9	100.4	13.7	6.5	7.3
21/11/2002	0	5.31	0.57	0.031	171.2	206.9	9.2	18.5	22.4
	20	14.79	0.61	0.033	448.3	524.1	24.1	18.6	21.7
	40	16.02	0.85	0.042	381.5	443.8	18.8	20.3	23.6
	60	13.49	0.74	0.046	293.3	391.9	18.3	16.0	21.4
	80	11.26	0.66	0.038	296.4	364.2	17.2	17.3	21.2
	100	17.15	0.69	0.032	535.9	649.1	24.7	21.7	26.2
24/12/2002	0	3.66	0.55	0.020	183.2	222.3	6.6	27.7	33.6
	20	3.92	0.57	0.020	195.9	322.1	6.8	28.7	47.3
	40	4.59	0.73	0.021	218.7	256.4	6.3	34.6	40.6
	60	3.85	0.66	0.025	153.9	218.1	5.8	26.6	37.7
	80	3.31	0.48	0.020	165.4	229.0	6.9	24.0	33.2
	100	3.38	0.53	0.019	177.9	198.6	6.3	28.1	31.3
29/01/2003	0	1.99	0.34	0.018	110.6	207.5	5.9	18.8	35.2
	20	2.75	0.46	0.022	125.0	204.0	6.0	20.7	33.8
	40	2.50	0.44	0.023	108.7	155.2	5.7	19.2	27.4
	60	2.50	0.41	0.020	125.0	209.0	6.1	20.4	34.1
	80	1.65	0.27	0.019	86.8	123.8	6.2	14.1	20.1
	100	4.40	0.72	0.040	110.0	140.5	6.1	18.0	23.0
27/02/2003	0	4.16	0.69	0.018	231.2	351.9	6.1	38.1	57.9
	20	4.87	0.79	0.019	256.5	391.8	6.2	41.5	63.4
	40	6.52	1.05	0.024	271.7	403.4	6.2	43.9	65.1
	60	5.29	0.85	0.024	220.2	293.3	6.2	35.5	47.3
	80	2.33	0.42	0.019	122.9	224.4	5.5	22.2	40.5
	100	3.05	0.50	0.024	127.0	186.5	6.1	20.7	30.4
28/03/2003	0	6.62	0.95	0.038	174.3	278.4	6.9	25.1	40.1
	20	4.83	0.72	0.031	155.7	223.7	6.7	23.3	33.5
	40	4.81	0.65	0.025	192.5	258.6	7.4	25.9	34.8
	60	3.59	0.54	0.027	132.8	175.0	6.7	19.9	26.2
	80	3.01	0.43	0.018	167.5	204.4	7.1	23.7	28.9
	100	2.11	0.33	0.016	131.6	147.3	6.3	20.9	23.4

APPENDIX C (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	POC (µM)	PON (µM)	TPP (µM)	C/P		C/N (POC/PON)	N/P	
					(POC/TPP)	(POC/POP)		(PON/TPP)	(PON/POP)
	MIDDLE STATION								
22/04/2003	0	12.46	1.67	0.070	178.1	229.9	7.5	23.8	30.7
21/05/2003	0	24.41	1.85	0.072	339.1	552.0	13.2	25.7	41.8
	20	6.64	0.65	0.020	332.1	467.0	10.2	32.6	45.8
	40	6.19	0.79	0.019	325.7	433.8	7.8	41.5	55.3
	60	5.39	0.65	0.021	256.8	331.8	8.3	30.8	39.8
	80	2.56	0.33	0.016	160.1	223.0	7.7	20.7	28.8
	100	5.23	0.62	0.027	193.8	242.5	8.4	22.9	28.7
05/06/2003	0	10.34	1.11	0.049	211.0	293.2	9.3	22.7	31.6
	20	8.94	0.98	0.031	288.3	438.4	9.1	31.8	48.3
	40	7.09	0.77	0.021	337.5	504.6	9.2	36.7	54.9
	60	5.13	0.68	0.027	189.9	279.2	7.6	25.1	36.9
	80	3.66	0.46	0.028	130.8	174.8	8.0	16.4	22.0
	100	2.93	0.39	0.018	162.7	373.8	7.6	21.5	49.4
15/07/2003	0	4.07	0.38	0.033	123.4	192.7	10.8	11.5	17.9
	20	3.10	0.42	0.036	86.2	130.9	7.3	11.7	17.8
	40	4.31	0.59	0.042	102.6	149.9	7.3	14.0	20.5
	60	2.48	0.32	0.028	88.7	131.2	7.7	11.5	17.0
	80	2.85	0.29	0.015	190.1	530.4	9.9	19.2	53.6
	100	3.81	0.49	0.031	122.8	387.0	7.8	15.8	49.9
31/07/2003	0	4.28	0.43	0.022	194.6	281.8	10.0	19.5	28.2
	20	4.02	0.54	0.035	114.7	156.5	7.4	15.5	21.2
	40	3.83	0.56	0.045	85.2	126.1	6.8	12.5	18.4
	60	3.73	0.45	0.026	143.4	178.0	8.3	17.2	21.4
	80	1.40	0.23	0.016	87.3	119.7	6.0	14.5	19.9
	100	5.17	0.67	0.045	114.9	153.0	7.7	14.9	19.8
22/09/2003	0	2.90	0.28	0.018	160.9	291.4	10.2	15.8	28.5
	20	3.83	0.35	0.022	174.1	298.6	10.9	15.9	27.3
	40	3.95	0.32	0.021	188.1	354.2	12.2	15.4	29.0
	60	3.52	0.31	0.019	185.2	287.9	11.4	16.3	25.3
	80	1.57	0.16	0.013	120.5	196.1	9.8	12.4	20.1
	100	3.23	0.35	0.019	169.8	281.8	9.2	18.4	30.5
11/12/2003	0	4.06	0.74	0.022	182.1	225.0	5.5	33.2	41.0
	20	3.85	0.70	0.026	146.2	191.7	5.5	26.5	34.7
	40	3.95	0.75	0.023	173.9	219.6	5.3	32.9	41.5
	60	3.68	0.62	0.028	133.5	172.8	5.9	22.5	29.1
	80	3.19	0.59	0.034	94.5	137.4	5.4	17.6	25.6
	100	4.21	0.86	0.045	93.1	120.5	4.9	19.1	24.6

APPENDIX C (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	POC (µM)	PON (µM)	TPP (µM)	C/P		C/N	N/P	
					(POC/TPP)	(POC/POP)	(POC/PON)	(PON/TPP)	(PON/POP)
	SHELFBREAK STATION								
23/01/2002	0	8.75	1.09	0.025	350.2	692.1	8.0	43.7	86.4
	25	20.49	0.89	0.030	683.1	1316.5	22.9	29.8	57.5
	50	7.17	0.80	0.022	326.0	581.8	9.0	36.3	64.8
	75	6.17	0.72	0.022	280.3	559.0	8.6	32.6	65.0
	100	10.58	1.10	0.027	392.0	756.6	9.6	40.6	78.4
	150	11.79	1.33	0.029	406.4	672.7	8.8	46.0	76.1
	180	10.21	0.94	0.039	261.7	716.1	10.8	24.1	66.0
19/02/2002	0	3.82	0.54	0.015	260.0	460.8	7.1	36.5	64.7
	25	4.83	0.58	0.017	290.8	518.5	8.3	35.0	62.5
	50	3.94	0.55	0.022	179.9	470.7	7.2	25.1	65.7
	75	6.16	0.57	0.014	449.2	694.7	10.8	41.7	64.5
	100	3.95	0.51	0.016	247.9	492.5	7.7	32.3	64.2
	150	5.90	0.74	0.014	412.4	591.8	8.0	51.7	74.3
	180	8.12	0.90	0.038	213.7	724.0	9.0	23.7	80.2
09/04/2002	0	6.90	1.02	0.018	381.6	657.6	6.8	56.2	96.8
	25	11.06	1.44	0.031	354.3	615.3	7.7	46.2	80.3
	50	8.05	0.93	0.021	380.2	665.7	8.6	44.0	77.1
	75	9.18	1.18	0.022	422.3	560.3	7.8	54.1	71.8
	100	6.63	0.78	0.015	445.0	694.9	8.5	52.2	81.5
	150	9.78	1.32	0.020	500.7	689.9	7.4	67.8	93.4
	180	7.01	0.67	0.017	424.1	726.6	10.5	40.5	69.4
13/05/2002	0	6.60	0.66	0.026	253.8	305.2	10.0	25.5	30.6
	25	2.53	0.23	0.017	148.6	173.5	10.8	13.8	16.1
	50	2.83	0.28	0.018	157.5	173.8	10.1	15.6	17.2
	75	3.57	0.32	0.019	188.1	204.8	11.3	16.7	18.2
	100	1.00	0.43	0.022	45.3	48.7	2.3	19.7	21.1
	150	1.74	0.20	0.024	72.5	94.9	8.6	8.4	11.0
	180	4.87	0.57	0.029	167.8	200.2	8.6	19.6	23.3
18/06/2002	0	4.93	0.42	0.022	223.9	294.4	11.6	19.2	25.3
	25	3.05	0.25	0.026	117.3	203.5	12.3	9.6	16.6
	50	3.01	0.23	0.019	158.6	215.8	13.1	12.1	16.5
	65	5.49	0.42	0.039	140.8	251.1	13.2	10.7	19.1
	75	2.89	0.24	0.020	144.3	203.6	11.9	12.1	17.1
	100	4.58	0.66	0.021	218.0	257.2	7.0	31.2	36.8
	125	2.49	0.21	0.025	99.6	171.8	11.7	8.5	14.7
	150	1.74	0.14	0.027	64.6	84.1	12.3	5.2	6.8
11/07/2002	0	6.11	0.42	0.029	210.7	298.6	14.6	14.5	20.5
	5	5.50	0.48	0.031	177.5	232.0	11.5	15.4	20.1
	15	2.88	0.29	0.026	110.7	151.9	10.1	11.0	15.1
	25	4.93	0.59	0.030	164.3	207.5	8.3	19.8	25.0
	45	4.35	0.40	0.032	135.9	212.4	10.9	12.4	19.4
	60	4.42	0.49	0.032	138.1	193.9	9.0	15.4	21.6
	70	5.79	0.49	0.031	186.6	245.4	11.7	16.0	21.0
	100	3.11	0.38	0.033	94.2	143.0	8.3	11.4	17.3
	125	4.99	0.43	0.034	146.7	197.8	11.7	12.5	16.9
	150	3.29	0.32	0.035	94.0	112.2	10.2	9.2	11.0

APPENDIX C (CONTINUED)

Date	Depth	POC	PON	TPP	C/P		C/N	N/P	
(dd/mm/yyyy)	(m)	(µM)	(µM)	(µM)	(POC/TPP)	(POC/POP)	(POC/PON)	(PON/TPP)	(PON/POP)
	SHELFBREAK STATION								
01/08/2002	0	6.70	0.82	0.024	279.3	343.5	8.2	34.2	42.0
	25			0.020					
	50	5.42	0.67	0.019	285.4	325.9	8.1	35.1	40.1
	65	3.60	0.43	0.018	200.2	244.4	8.5	23.6	28.8
	75	4.60	0.54	0.017	270.8	310.7	8.5	31.8	36.5
	100	5.13	0.63	0.018	285.0	305.9	8.2	34.8	37.4
	125	2.40	0.30	0.013	184.5	197.4	8.1	22.9	24.5
	150	1.50	0.21	0.011	136.3	160.4	7.2	18.8	22.1
	180			0.019					
18/09/2002	0	3.51	0.27	0.031	113.6	123.9	12.8	8.9	9.7
	20	6.41	0.51	0.018	356.4	392.0	12.6	28.3	31.2
	40	8.07	0.53	0.028	288.2	313.3	15.1	19.1	20.7
	60	3.36	0.27	0.023	146.1	168.7	12.4	11.8	13.6
	80	5.62	0.52	0.028	200.7	218.1	10.9	18.5	20.1
	100	5.65	0.54	0.028	201.8	239.2	10.4	19.4	23.0
	125	3.29	0.26	0.024	137.0	155.4	12.7	10.8	12.3
	150	4.63	0.43	0.025	185.1	210.1	10.8	17.1	19.4
	175	2.39	0.19	0.065	36.8	45.8	12.6	2.9	3.6
	200	3.85	0.29	0.064	60.2	78.5	13.2	4.6	6.0
24/10/2002	0	2.88	0.25	0.009	319.5	412.2	11.6	27.6	35.7
	20	2.47	0.28	0.008	308.5	436.2	8.7	35.6	50.3
	40	2.74	0.34	0.012	228.3	334.3	8.1	28.2	41.3
	60	3.93	0.42	0.013	302.5	355.1	9.4	32.0	37.6
	80	3.06	0.32	0.007	437.6	589.7	9.7	45.0	60.6
	100	2.28	0.25	0.008	284.7	359.6	9.2	31.1	39.3
	125	2.69	0.27	0.006	448.8	500.1	10.1	44.7	49.8
	150	1.02	0.08	0.010	101.9	108.7	12.0	8.5	9.0
	175	2.93	0.29	0.011	266.0	279.6	10.1	26.2	27.6
	200	0.98	0.13	0.008	122.5	144.9	7.8	15.7	18.6
21/11/2002	0	2.16	0.11	0.034	63.5	71.3	20.1	3.2	3.6
	20	2.31	0.30	0.032	72.3	82.2	7.8	9.3	10.6
	40	4.24	0.44	0.024	176.6	215.3	9.5	18.5	22.6
	60	2.65	0.33	0.027	98.2	119.0	8.1	12.1	14.7
	80	3.27	0.38	0.030	109.0	135.4	8.7	12.6	15.6
	100	2.32	0.14	0.021	110.4	119.0	16.8	6.6	7.1
	125	4.66	0.49	0.028	166.4	188.9	9.6	17.3	19.7
	150	2.54	0.23	0.014	181.2	211.6	11.2	16.1	18.8
	175	2.09	0.16	0.020	104.6	125.9	13.0	8.0	9.7
	200	7.71	0.67	0.039	197.6	231.7	11.5	17.2	20.2
24/12/2002	0	7.40	0.51	0.030	246.7	269.6	14.4	17.1	18.7
	20	1.73	0.30	0.021	82.2	84.4	5.7	14.4	14.8
	40	2.23	0.35	0.024	92.9	110.4	6.4	14.5	17.2
	60	2.31	0.36	0.020	115.7	141.4	6.4	18.1	22.1
	80	2.09	0.37	0.018	116.2	130.1	5.7	20.4	22.9
	100	1.89	0.29	0.018	105.0	113.5	6.6	16.0	17.3
	125	2.65	0.35	0.023	115.2	125.7	7.6	15.1	16.5
	150	1.84	0.30	0.020	91.8	94.2	6.2	14.8	15.2
	175	3.43	0.42	0.022	155.8	185.8	8.1	19.1	22.8
	200	16.59	1.68	0.060	276.5	312.8	9.9	27.9	31.6

APPENDIX C (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	POC (µM)	PON (µM)	TPP (µM)	C/P		C/N	N/P	
					(POC/TPP)	(POC/POP)	(POC/PON)	(PON/TPP)	(PON/POP)
	SHELFBREAK STATION								
29/01/2003	0	2.67	0.37	0.017	157.1	235.7	7.1	22.0	33.0
	20	3.14	0.44	0.023	136.5	166.9	7.2	19.0	23.3
	40	2.04	0.31	0.012	170.0	226.4	6.7	25.5	33.9
	60	2.23	0.29	0.017	131.2	187.4	7.7	17.1	24.5
	80	2.35	0.32	0.016	146.9	190.8	7.2	20.3	26.3
	100	2.34	0.41	0.014	167.1	235.1	5.7	29.5	41.4
	125	2.25	0.31	0.013	173.1	258.2	7.4	23.5	35.0
	150	1.75	0.26	0.015	116.7	153.5	6.8	17.1	22.5
	175	1.51	0.23	0.016	94.4	114.0	6.5	14.5	17.5
	200	4.45	0.49	0.022	202.3	256.9	9.1	22.3	28.3
27/02/2003	0	2.37	0.37	0.015	157.7	200.3	6.4	24.7	31.4
	20	2.53	0.40	0.015	168.4	211.6	6.4	26.5	33.3
	40	2.83	0.43	0.018	157.3	180.2	6.6	23.9	27.4
	60	2.36	0.36	0.014	168.8	236.2	6.6	25.7	36.0
	80	2.84	0.45	0.014	202.8	326.8	6.4	31.9	51.4
	100	1.97	0.33	0.012	164.5	220.8	6.0	27.6	37.1
	125	3.07	0.44	0.015	204.5	273.2	7.0	29.2	39.0
	150	2.63	0.41	0.015	175.1	207.9	6.5	27.1	32.2
	175	2.04	0.35	0.012	169.7	250.2	5.9	28.9	42.6
	200	5.15	0.62	0.026	198.0	295.0	8.3	23.9	35.5
28/03/2003	0	2.07	0.29	0.014	147.5	163.4	7.1	20.7	22.9
	20	2.25	0.35	0.019	118.3	144.2	6.5	18.2	22.1
	40	2.86	0.39	0.016	178.6	201.0	7.3	24.5	27.6
	60	2.91	0.39	0.016	181.8	216.2	7.4	24.5	29.1
	80	1.75	0.27	0.014	125.0	151.6	6.4	19.6	23.7
	100	1.98	0.31	0.016	123.6	188.1	6.4	19.2	29.3
	125	2.12	0.32	0.018	117.6	167.1	6.6	17.9	25.5
	150	2.81	0.38	0.020	140.4	195.5	7.4	19.0	26.5
	175	2.52	0.38	0.018	140.0	159.1	6.6	21.3	24.2
	200	3.64	0.42	0.023	158.1	177.6	8.7	18.1	20.4
21/05/2003	0	18.07	1.15	0.041	440.8	829.0	15.7	28.0	52.7
	20	5.48	0.59	0.016	342.7	583.8	9.3	36.9	62.9
	40	2.24	0.33	0.011	203.7	419.6	6.8	30.0	61.8
	60	2.46	0.34	0.012	205.3	373.9	7.2	28.7	52.3
	80	3.82	0.51	0.019	200.9	350.0	7.5	26.7	46.5
	100	1.75	0.26	0.010	175.0	276.6	6.8	25.9	40.9
	125	3.55	0.34	0.013	273.0	426.4	10.3	26.5	41.4
	150	3.44	0.55	0.018	190.9	260.7	6.3	30.4	41.5
	175	3.72	0.48	0.020	185.8	317.8	7.8	23.9	40.9
	200	1.70	0.28	0.012	141.6	212.3	6.1	23.1	34.7
05/06/2003	0	6.70	0.59	0.015	446.6	880.5	11.4	39.0	76.9
	20	5.55	0.51	0.011	504.8	955.9	10.9	46.5	88.0
	40	4.35	0.46	0.012	362.6	866.1	9.4	38.7	92.4
	60	6.57	0.50	0.014	469.5	956.8	13.2	35.7	72.7
	80	2.96	0.35	0.011	269.3	509.9	8.5	31.5	59.7
	100	2.67	0.30	0.013	205.5	387.7	8.9	23.1	43.6
	125	6.87	0.72	0.021	327.2	506.5	9.5	34.3	53.1
	150	2.83	0.36	0.016	177.1	362.1	7.9	22.5	46.1
	175	2.88	0.32	0.013	221.4	379.7	9.1	24.5	41.9
	200	5.02	0.53	0.036	139.5	204.9	9.4	14.8	21.7

APPENDIX C (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	POC (µM)	PON (µM)	TPP (µM)	C/P		C/N (POC/PON)	N/P	
					(POC/TPP)	(POC/POP)		(PON/TPP)	(PON/POP)
	SHELFBREAK STATION								
15/07/2003	0	3.63	0.55	0.031	117.0	161.9	6.6	17.9	24.7
	20	2.96	0.50	0.024	123.1	180.7	6.0	20.7	30.3
	40	4.10	0.59	0.035	117.0	139.2	6.9	16.9	20.1
	60	4.08	0.56	0.031	131.5	164.2	7.3	17.9	22.4
	80	3.57	0.47	0.015	238.2	358.0	7.6	31.2	46.8
	100	2.41	0.36	0.016	150.3	252.5	6.7	22.4	37.6
	125	3.08	0.40	0.017	181.2	263.2	7.7	23.7	34.4
	150	3.03	0.44	0.027	112.4	163.7	6.8	16.4	23.9
	175	2.65	0.34	0.016	165.5	203.5	7.7	21.4	26.4
	200	5.77	0.75	0.047	122.7	175.0	7.7	15.9	22.7
31/07/2003	0	3.41	0.43	0.014	243.7	278.2	8.0	30.5	34.8
	20	2.42	0.31	0.012	201.6	255.6	7.9	25.7	32.5
	40	4.37	0.52	0.021	208.2	234.3	8.4	24.7	27.7
	60	4.73	0.62	0.020	236.6	263.9	7.6	31.0	34.5
	80	2.92	0.24	0.016	182.5	232.3	12.1	15.1	19.2
	100	3.26	0.29	0.020	163.1	225.3	11.1	14.7	20.3
	125	5.41	0.38	0.032	169.2	226.1	14.1	12.0	16.1
	150	2.87	0.35	0.023	124.6	160.6	8.2	15.2	19.5
	175	2.24	0.40	0.030	74.8	91.5	5.6	13.3	16.3
	200	10.18	1.00	0.048	212.0	273.5	10.2	20.8	26.8
22/09/2003	0	2.76	0.33	0.023	120.2	240.0	8.4	14.3	28.6
	20	2.44	0.25	0.026	93.7	162.2	9.6	9.7	16.8
	40	2.61	0.39	0.032	81.7	131.5	6.8	12.1	19.5
	60	4.44	0.42	0.020	221.9	280.2	10.5	21.0	26.6
	80	3.53	0.43	0.020	176.6	260.7	8.3	21.4	31.5
	100	1.82	0.28	0.020	90.8	116.4	6.5	14.0	18.0
	150	2.50	0.40	0.029	86.2	116.8	6.3	13.8	18.7
	175	2.32	0.32	0.023	101.0	127.0	7.4	13.7	17.3
	200	2.45	0.38	0.025	97.8	125.5	6.4	15.4	19.7
11/12/2003	0	2.80	0.59	0.025	111.8	164.1	4.8	23.4	34.4
	20	2.89	0.58	0.025	115.7	137.5	5.0	23.2	27.5
	40	2.22	0.52	0.023	97.5	129.7	4.3	22.9	30.5
	60	4.57	0.65	0.027	166.5	245.8	7.0	23.8	35.1
	80	2.63	0.43	0.017	150.6	214.3	6.2	24.4	34.7
	100	1.71	0.39	0.019	92.2	141.0	4.4	20.8	31.8
	125	3.23	0.33	0.014	222.8	290.0	9.8	22.8	29.7
	150	1.41	0.55	0.015	94.6	149.0	2.6	37.1	58.4
	175	2.15	0.49	0.017	129.3	151.1	4.4	29.2	34.2
	200	4.45	0.86	0.034	131.9	188.6	5.2	25.5	36.4
	REFERENCE STATION (R1)								
29/12/2003	0	3.06	0.4	0.021	145.7	191.2	7.7	19.0	25.0
	25	3.76	0.50	0.023	163.5	219.7	7.5	21.7	29.2
	50	2.48	0.36	0.019	130.5	189.3	6.9	18.9	27.5
	75	3.57	0.46	0.022	162.3	217.2	7.8	20.9	28.0
	100	3.61	0.46	0.021	171.9	241.5	7.8	21.9	30.8
	150	2.31	0.35	0.02	115.5	183.9	6.6	17.5	27.9
	250	1.14	0.13	0.007	162.9	206.2	8.8	18.6	23.5
	500	1.06	0.10	0.006	176.7	219.0	10.6	16.7	20.7
	800	1.19	0.12	0.007	170.0	215.4	9.9	17.1	21.7

APPENDIX D. CONCENTRATIONS AND PERCENTAGES OF PHOSPHORUS FRACTIONS AT THE STUDIED STATIONS

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP $^{\text{MAGIC}}$		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	NEARSHORE STATION													
23/01/02	0	0.362	0.221	61.0	0.166	45.8	0.055	15.2	0.141	39.0	0.069	19.0	0.072	20.0
	5	0.323	0.217	67.2	0.105	32.4	0.112	34.7	0.106	32.8	0.051	15.8	0.055	17.1
19/02/02	0	0.353	0.300	85.0	0.055	15.5	0.245	69.5	0.053	15.0	0.022	6.3	0.031	8.7
	5	0.311	0.269	86.5	0.033	10.7	0.236	75.8	0.042	13.5	0.018	5.8	0.024	7.7
09/04/02	0	0.364	0.264	72.5	0.072	19.7	0.192	52.8	0.100	27.5	0.047	13.0	0.053	14.5
	5	0.311	0.225	72.3	0.057	18.2	0.168	54.2	0.086	27.7	0.029	9.5	0.057	18.2
13/05/02	0	0.430	0.239	55.6	0.130	30.2	0.109	25.4	0.191	44.4	0.055	12.7	0.136	31.7
	5	0.396	0.276	69.7	0.103	26.1	0.173	43.6	0.120	30.3	0.046	11.6	0.074	18.8
18/06/02	0	0.366	0.247	67.5	0.077	21.1	0.170	46.4	0.119	32.5	0.020	5.4	0.099	27.1
	5	0.349	0.275	78.8	0.073	21.0	0.202	57.8	0.074	21.2	0.014	4.1	0.060	17.1
11/07/02	0	0.345	0.238	69.0	0.036	10.3	0.202	58.7	0.107	31.0	0.038	11.0	0.069	20.0
	5	0.285	0.215	75.4	0.066	23.2	0.149	52.3	0.070	24.6	0.033	11.5	0.037	13.0
01/08/02	0	0.302	0.242	80.1	0.053	17.5	0.189	62.7	0.060	19.9	0.017	5.7	0.043	14.1
	5	0.272	0.228	83.8	0.043	15.9	0.185	67.9	0.044	16.2	0.017	6.1	0.027	10.1
18/09/02	0	0.243	0.143	58.8	0.045	18.4	0.098	40.5	0.100	41.2	0.032	13.0	0.068	28.2
	10	0.207	0.124	59.9	0.042	20.5	0.082	39.4	0.083	40.1	0.018	8.8	0.065	31.3
24/10/02	0	0.239	0.186	77.8	0.050	20.8	0.136	57.0	0.053	22.2	0.024	10.2	0.029	12.0
	10	0.252	0.209	82.9	0.052	20.5	0.157	62.5	0.043	17.1	0.014	5.5	0.029	11.5
21/11/02	0	0.342	0.238	69.6	0.060	17.7	0.178	51.9	0.104	30.4	0.039	11.5	0.065	18.9
	10	0.306	0.243	79.4	0.057	18.8	0.186	60.6	0.063	20.6	0.014	4.7	0.049	15.9
24/12/02	0	0.333	0.304	91.3	0.026	7.8	0.278	83.5	0.029	8.7	0.003	1.0	0.026	7.7
	10	0.306	0.280	91.5	0.030	9.9	0.250	81.6	0.026	8.5	0.003	0.9	0.023	7.6
29/01/03	0	0.378	0.349	92.3	0.028	7.5	0.321	84.9	0.029	7.7	0.013	3.6	0.016	4.1
	10	0.270	0.233	86.3	0.027	10.1	0.206	76.2	0.037	13.7	0.010	3.7	0.027	10.0

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP ^{MAGIC}		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	NEARSHORE STATION													
27/02/03	0	0.396	0.307	77.5	0.101	25.5	0.206	52.1	0.089	22.5	0.024	6.2	0.065	16.3
	10	0.324	0.250	77.2	0.097	30.0	0.153	47.1	0.074	22.8	0.018	5.5	0.056	17.3
28/03/03	0	0.378	0.225	59.5	0.162	42.8	0.063	16.8	0.153	40.5	0.075	20.0	0.078	20.5
	10	0.360	0.250	69.4	0.142	39.6	0.108	29.9	0.110	30.6	0.028	7.8	0.082	22.7
22/04/03	0	0.225	0.141	62.7	0.071	31.8	0.070	30.9	0.084	37.3	0.026	11.5	0.058	25.8
21/05/03	0	0.279	0.233	83.5	0.058	20.9	0.175	62.6	0.046	16.5	0.023	8.3	0.023	8.2
	10	0.288	0.223	77.4	0.055	19.2	0.168	58.3	0.065	22.6	0.017	5.8	0.048	16.8
05/06/03	0	0.351	0.238	67.8	0.061	17.5	0.177	50.3	0.113	32.2	0.044	12.6	0.069	19.6
	10	0.270	0.208	77.0	0.059	21.7	0.149	55.3	0.062	23.0	0.037	13.5	0.025	9.4
15/07/03	0	0.288	0.195	67.7	0.050	17.5	0.145	50.3	0.093	32.3	0.033	11.3	0.060	21.0
	10	0.306	0.230	75.2	0.056	18.3	0.174	56.8	0.076	24.8	0.019	6.4	0.057	18.5
31/07/03	0	0.243	0.173	71.2	0.039	15.9	0.134	55.3	0.070	28.8	0.010	4.2	0.060	24.6
	10	0.270	0.163	60.4	0.044	16.3	0.119	44.1	0.107	39.6	0.009	3.4	0.098	36.2
22/09/03	0	0.225	0.168	74.7	0.043	19.2	0.125	55.5	0.057	25.3	0.014	6.3	0.043	19.1
	10	0.225	0.194	86.2	0.036	16.0	0.158	70.2	0.031	13.8	0.021	9.2	0.010	4.6
11/12/03	0	0.198	0.154	77.5	0.018	9.1	0.136	68.5	0.044	22.5	0.013	6.5	0.032	15.9
	10	0.297	0.261	87.9	0.024	8.1	0.237	79.8	0.036	12.1	0.011	3.6	0.025	8.4
	MIDDLE STATION													
18/09/02	0	0.216	0.167	77.3	0.033	15.4	0.134	62.0	0.049	22.7	0.005	2.5	0.044	20.2
	20	0.180	0.143	79.5	0.027	15.2	0.116	64.2	0.037	20.5	0.009	4.8	0.028	15.7
	40	0.171	0.153	89.5	0.021	12.3	0.132	77.2	0.018	10.5	0.004	2.3	0.014	8.2
	60	0.153	0.133	86.9	0.021	13.9	0.112	73.0	0.020	13.1	0.004	2.7	0.016	10.3
	80	0.189	0.167	88.4	0.031	16.2	0.137	72.2	0.022	11.6	0.004	2.3	0.018	9.3
	100	0.207	0.189	91.3	0.033	15.9	0.156	75.4	0.018	8.7	0.004	1.9	0.014	6.7
24/10/02	0	0.189	0.176	93.1	0.022	11.9	0.154	81.3	0.013	6.9	0.002	1.2	0.011	5.7
	20	0.180	0.164	91.1	0.023	12.7	0.141	78.4	0.016	8.9	0.002	1.1	0.014	7.8
	40	0.171	0.158	92.4	0.025	14.4	0.134	78.0	0.013	7.6	0.002	1.2	0.011	6.4
	60	0.207	0.192	92.8	0.026	12.4	0.167	80.4	0.015	7.2	0.002	0.9	0.013	6.3
	80	0.198	0.179	90.4	0.022	11.2	0.157	79.2	0.019	9.6	0.004	2.1	0.015	7.5
	100	0.216	0.176	81.5	0.024	15.6	0.142	65.9	0.040	18.5	0.005	2.1	0.035	16.4

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP ^{MAGIC}		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	MIDDLE STATION													
21/11/02	0	0.189	0.158	83.6	0.014	7.5	0.144	76.1	0.031	16.4	0.005	2.8	0.026	13.6
	20	0.216	0.183	84.7	0.019	9.0	0.164	75.8	0.033	15.3	0.005	2.2	0.028	13.1
	40	0.243	0.201	82.7	0.027	10.9	0.175	71.8	0.042	17.3	0.006	2.4	0.036	14.8
	60	0.234	0.188	80.4	0.035	15.1	0.153	65.3	0.046	19.6	0.012	4.9	0.034	14.7
	80	0.230	0.192	83.5	0.041	18.1	0.150	65.4	0.038	16.5	0.007	3.1	0.031	13.5
	100	0.232	0.200	86.2	0.033	14.2	0.167	72.0	0.032	13.8	0.006	2.4	0.026	11.4
24/12/02	0	0.225	0.205	91.1	0.017	7.5	0.188	83.6	0.020	8.9	0.004	1.6	0.016	7.3
	20	0.198	0.178	89.9	0.016	8.1	0.162	81.8	0.020	10.1	0.008	4.0	0.012	6.1
	40	0.207	0.186	89.9	0.017	8.4	0.169	81.4	0.021	10.1	0.003	1.5	0.018	8.7
	60	0.216	0.191	88.4	0.021	9.5	0.171	78.9	0.025	11.6	0.007	3.4	0.018	8.2
	80	0.234	0.214	91.5	0.020	8.4	0.195	83.1	0.020	8.5	0.006	2.4	0.014	6.2
	100	0.288	0.269	93.4	0.023	8.1	0.246	85.4	0.019	6.6	0.002	0.7	0.017	5.9
29/01/03	0	0.225	0.207	92.0	0.022	9.8	0.185	82.2	0.018	8.0	0.008	3.7	0.010	4.3
	20	0.225	0.203	90.2	0.022	9.8	0.181	80.5	0.022	9.8	0.009	3.8	0.013	6.0
	40	0.216	0.193	89.4	0.020	9.1	0.173	80.2	0.023	10.6	0.007	3.2	0.016	7.4
	60	0.207	0.187	90.3	0.022	10.4	0.166	79.9	0.020	9.7	0.008	3.9	0.012	5.8
	80	0.225	0.206	91.6	0.024	10.6	0.182	81.0	0.019	8.4	0.006	2.5	0.013	5.9
	100	0.243	0.203	83.6	0.030	12.2	0.174	71.4	0.040	16.4	0.009	3.6	0.031	12.9
27/02/03	0	0.198	0.180	90.9	0.023	11.7	0.157	79.2	0.018	9.1	0.006	3.1	0.012	6.0
	20	0.189	0.170	89.9	0.020	10.6	0.150	79.3	0.019	10.1	0.007	3.5	0.012	6.6
	40	0.180	0.156	86.7	0.023	12.9	0.133	73.8	0.024	13.3	0.008	4.3	0.016	9.0
	60	0.166	0.142	85.5	0.022	13.4	0.120	72.1	0.024	14.5	0.006	3.6	0.018	10.9
	80	0.153	0.134	87.6	0.025	16.6	0.109	71.0	0.019	12.4	0.009	5.6	0.010	6.8
	100	0.207	0.183	88.4	0.036	17.4	0.147	71.0	0.024	11.6	0.008	3.7	0.016	7.9
28/03/03	0	0.144	0.106	73.6	0.032	22.3	0.074	51.3	0.038	26.4	0.014	9.9	0.024	16.5
	20	0.162	0.131	80.9	0.037	22.6	0.095	58.3	0.031	19.1	0.009	5.8	0.022	13.3
	40	0.158	0.133	84.2	0.019	12.1	0.114	72.0	0.025	15.8	0.006	4.0	0.019	11.8
	60	0.178	0.151	84.8	0.016	9.0	0.135	75.8	0.027	15.2	0.007	3.7	0.021	11.5
	80	0.198	0.180	90.9	0.025	12.8	0.155	78.1	0.018	9.1	0.003	1.6	0.015	7.4
	100	0.234	0.218	93.2	0.030	12.8	0.188	80.4	0.016	6.8	0.002	0.7	0.014	6.1

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP ^{MAGIC}		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	MIDDLE STATION													
22/04/03	0	0.162	0.092	56.8	0.041	25.5	0.051	31.3	0.070	43.2	0.016	9.7	0.054	33.4
21/05/03	0	0.180	0.108	60.0	0.040	22.5	0.068	37.6	0.072	40.0	0.028	15.4	0.044	24.5
	20	0.117	0.097	82.9	0.019	15.9	0.079	67.0	0.020	17.1	0.006	4.9	0.014	12.1
	40	0.117	0.098	83.8	0.018	15.1	0.080	68.6	0.019	16.2	0.005	4.0	0.014	12.2
	60	0.126	0.105	83.4	0.024	19.0	0.081	64.3	0.021	16.7	0.005	3.8	0.016	12.9
	80	0.144	0.128	88.9	0.029	20.3	0.099	68.6	0.016	11.1	0.005	3.1	0.011	8.0
	100	0.198	0.171	86.4	0.031	15.5	0.141	70.9	0.027	13.6	0.005	2.7	0.022	10.9
05/06/03	0	0.243	0.194	79.9	0.028	11.5	0.166	68.4	0.049	20.1	0.014	5.6	0.035	14.5
	20	0.225	0.194	86.2	0.020	8.8	0.174	77.4	0.031	13.8	0.011	4.7	0.020	9.1
	40	0.221	0.200	90.5	0.021	9.6	0.179	80.9	0.021	9.5	0.007	3.1	0.014	6.4
	60	0.234	0.207	88.5	0.025	10.7	0.182	77.7	0.027	11.5	0.009	3.7	0.018	7.8
	80	0.270	0.242	89.6	0.027	10.1	0.215	79.5	0.028	10.4	0.007	2.6	0.021	7.8
	100	0.261	0.243	93.1	0.025	9.5	0.219	83.6	0.018	6.9	0.010	3.9	0.008	3.0
15/07/03	0	0.180	0.147	81.7	0.028	15.3	0.120	66.4	0.033	18.3	0.012	6.6	0.021	11.7
	20	0.216	0.180	83.4	0.028	12.9	0.152	70.4	0.036	16.7	0.012	5.7	0.024	11.0
	40	0.225	0.183	81.4	0.029	13.0	0.154	68.3	0.042	18.6	0.013	5.9	0.029	12.8
	60	0.194	0.166	85.6	0.021	10.7	0.145	74.8	0.028	14.4	0.009	4.7	0.019	9.8
	80	0.162	0.147	90.8	0.019	12.0	0.128	78.7	0.015	9.3	0.010	5.9	0.005	3.3
	100	0.162	0.131	80.9	0.028	17.5	0.103	63.4	0.031	19.1	0.021	13.0	0.010	6.1
31/07/03	0	0.198	0.176	88.9	0.026	13.2	0.150	75.7	0.022	11.1	0.007	3.4	0.015	7.7
	20	0.171	0.136	79.6	0.030	17.7	0.106	61.9	0.035	20.4	0.009	5.5	0.026	15.0
	40	0.171	0.126	73.7	0.046	27.0	0.080	46.7	0.045	26.3	0.015	8.5	0.030	17.8
	60	0.180	0.154	85.6	0.025	14.1	0.129	71.5	0.026	14.4	0.005	2.8	0.021	11.6
	80	0.189	0.173	91.5	0.028	14.6	0.146	77.0	0.016	8.5	0.004	2.3	0.012	6.2
	100	0.198	0.153	77.3	0.066	33.3	0.087	44.0	0.045	22.7	0.011	5.7	0.034	17.1
22/09/03	0	0.171	0.153	89.5	0.033	19.2	0.120	70.3	0.018	10.5	0.008	4.7	0.010	5.8
	20	0.198	0.176	88.9	0.035	17.7	0.141	71.2	0.022	11.1	0.009	4.6	0.013	6.5
	40	0.202	0.181	89.6	0.028	13.6	0.153	76.0	0.021	10.4	0.010	4.9	0.011	5.5
	60	0.207	0.188	90.8	0.025	12.2	0.163	78.6	0.019	9.2	0.007	3.3	0.012	5.9
	80	0.198	0.185	93.4	0.027	13.8	0.158	79.7	0.013	6.6	0.005	2.5	0.008	4.0
	100	0.225	0.206	91.6	0.037	16.4	0.169	75.2	0.019	8.4	0.008	3.4	0.011	5.1

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP $^{\text{MAGIC}}$		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	MIDDLE STATION													
11/12/03	0	0.252	0.230	91.2	0.015	6.1	0.215	85.1	0.022	8.8	0.004	1.7	0.018	7.1
	20	0.216	0.190	87.8	0.018	8.5	0.171	79.3	0.026	12.2	0.006	2.9	0.020	9.3
	40	0.207	0.184	89.0	0.015	7.2	0.170	81.9	0.023	11.0	0.005	2.3	0.018	8.7
	60	0.225	0.198	87.7	0.016	7.2	0.181	80.5	0.028	12.3	0.006	2.8	0.021	9.5
	80	0.252	0.219	86.6	0.048	19.1	0.170	67.5	0.034	13.4	0.011	4.2	0.023	9.2
	100	0.234	0.189	80.7	0.059	25.2	0.130	55.5	0.045	19.3	0.010	4.4	0.035	14.9
	SHELFBREAK STATION													
23/01/02	0	0.260	0.235	90.4	0.028	10.9	0.207	79.5	0.025	9.6	0.012	4.8	0.013	4.9
	25	0.213	0.183	85.9	0.026	12.0	0.157	73.9	0.030	14.1	0.014	6.8	0.016	7.3
	50	0.255	0.233	91.4	0.023	9.1	0.210	82.2	0.022	8.6	0.010	3.8	0.012	4.8
	75	0.264	0.242	91.7	0.025	9.5	0.217	82.2	0.022	8.3	0.011	4.2	0.011	4.2
	100	0.234	0.207	88.5	0.009	3.8	0.198	84.6	0.027	11.5	0.013	5.6	0.014	6.0
	150	0.204	0.175	85.8	0.033	16.1	0.142	69.7	0.029	14.2	0.011	5.6	0.018	8.6
	180	0.226	0.187	82.7	0.058	25.7	0.129	57.0	0.039	17.3	0.025	10.9	0.014	6.3
19/02/02	0	0.251	0.236	94.2	0.012	4.7	0.224	89.4	0.015	5.8	0.006	2.5	0.008	3.3
	25	0.260	0.243	93.6	0.017	6.4	0.227	87.2	0.017	6.4	0.007	2.8	0.009	3.6
	50	0.221	0.199	90.1	0.014	6.4	0.185	83.7	0.022	9.9	0.014	6.1	0.008	3.8
	75	0.213	0.199	93.6	0.018	8.6	0.181	84.9	0.014	6.4	0.005	2.3	0.009	4.2
	100	0.140	0.124	88.6	0.015	10.5	0.109	78.1	0.016	11.4	0.008	5.6	0.008	5.7
	150	0.170	0.156	91.6	0.017	9.8	0.139	81.8	0.014	8.4	0.004	2.6	0.010	5.9
	180	0.200	0.162	81.0	0.037	18.4	0.125	62.6	0.038	19.0	0.027	13.4	0.011	5.6
09/04/02	0	0.247	0.229	92.7	0.018	7.4	0.211	85.2	0.018	7.3	0.008	3.1	0.010	4.2
	25	0.255	0.224	87.8	0.019	7.6	0.204	80.2	0.031	12.2	0.013	5.2	0.018	7.1
	50	0.251	0.230	91.6	0.020	7.9	0.210	83.7	0.021	8.4	0.009	3.6	0.012	4.8
	75	0.274	0.252	92.1	0.021	7.8	0.231	84.2	0.022	7.9	0.005	2.0	0.016	6.0
	100	0.289	0.274	94.8	0.021	7.3	0.253	87.6	0.015	5.2	0.005	1.9	0.010	3.3
	150	0.285	0.265	93.1	0.028	10.0	0.237	83.2	0.020	6.9	0.005	1.9	0.014	5.0
	180	0.294	0.277	94.4	0.025	8.3	0.253	86.0	0.017	5.6	0.007	2.3	0.010	3.3

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP ^{MAGIC}		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	SHELFBREAK STATION													
13/05/02	0	0.204	0.178	87.3	0.017	8.5	0.161	78.8	0.026	12.7	0.004	2.1	0.022	10.6
	25	0.170	0.153	90.0	0.012	7.3	0.141	82.7	0.017	10.0	0.002	1.4	0.015	8.6
	50	0.128	0.110	85.9	0.011	8.9	0.099	77.0	0.018	14.1	0.002	1.3	0.016	12.7
	75	0.166	0.147	88.6	0.011	6.4	0.136	82.1	0.019	11.4	0.002	0.9	0.017	10.5
	100	0.145	0.123	84.8	0.017	12.0	0.106	72.8	0.022	15.2	0.002	1.1	0.020	14.1
	150	0.209	0.185	88.5	0.017	7.9	0.168	80.6	0.024	11.5	0.006	2.7	0.018	8.8
	180	0.272	0.243	89.3	0.026	9.7	0.217	79.6	0.029	10.7	0.005	1.7	0.024	8.9
18/06/02	0	0.238	0.216	90.8	0.020	8.2	0.196	82.5	0.022	9.2	0.005	2.2	0.017	7.0
	25	0.243	0.217	89.3	0.019	7.8	0.198	81.5	0.026	10.7	0.011	4.5	0.015	6.2
	50	0.268	0.249	92.9	0.020	7.4	0.229	85.5	0.019	7.1	0.005	1.9	0.014	5.2
	65	0.243	0.204	84.0	0.016	6.5	0.188	77.5	0.039	16.0	0.017	7.0	0.022	9.0
	75	0.247	0.227	91.9	0.017	6.8	0.210	85.1	0.020	8.1	0.006	2.4	0.014	5.7
	100	0.230	0.209	90.9	0.020	8.8	0.189	82.0	0.021	9.1	0.003	1.4	0.018	7.7
	125	0.221	0.196	88.7	0.025	11.3	0.171	77.4	0.025	11.3	0.011	4.8	0.014	6.6
	150	0.255	0.228	89.4	0.025	9.8	0.203	79.6	0.027	10.6	0.006	2.5	0.021	8.1
11/07/02	0	0.226	0.197	87.2	0.029	12.7	0.168	74.5	0.029	12.8	0.009	3.8	0.020	9.1
	5	0.215	0.184	85.6	0.025	11.8	0.159	73.8	0.031	14.4	0.007	3.4	0.024	11.0
	15	0.207	0.181	87.4	0.030	14.6	0.151	72.8	0.026	12.6	0.007	3.4	0.019	9.2
	25	0.191	0.161	84.3	0.015	8.0	0.146	76.3	0.030	15.7	0.006	3.3	0.024	12.4
	45	0.200	0.168	84.0	0.015	7.3	0.153	76.7	0.032	16.0	0.012	5.8	0.020	10.2
	60	0.217	0.185	85.3	0.017	8.0	0.168	77.2	0.032	14.7	0.009	4.2	0.023	10.5
	70	0.251	0.220	87.6	0.016	6.3	0.204	81.3	0.031	12.4	0.007	3.0	0.024	9.4
	100	0.255	0.222	87.1	0.021	8.4	0.201	78.6	0.033	12.9	0.011	4.4	0.022	8.5
	125	0.258	0.224	86.8	0.019	7.4	0.205	79.4	0.034	13.2	0.009	3.4	0.025	9.8
	150	0.260	0.225	86.5	0.022	8.4	0.203	78.1	0.035	13.5	0.006	2.2	0.029	11.3
	180	0.272	0.272		0.016		0.256							

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP ^{MAGIC}		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	SHELFBREAK STATION													
01/08/02	0	0.157	0.133	84.7	0.015	9.8	0.118	75.0	0.024	15.3	0.004	2.9	0.020	12.4
	25	0.115	0.095	82.6	0.029	25.3	0.066	57.3	0.020	17.4	0.002	1.9	0.018	15.5
	50	0.128	0.109	85.2	0.029	22.9	0.080	62.2	0.019	14.8	0.002	1.8	0.017	13.0
	65	0.140	0.122	87.1	0.030	21.3	0.092	65.9	0.018	12.9	0.003	2.3	0.015	10.5
	75	0.149	0.132	88.6	0.024	16.0	0.108	72.6	0.017	11.4	0.002	1.5	0.015	9.9
	100	0.145	0.127	87.6	0.023	15.7	0.104	71.9	0.018	12.4	0.001	0.8	0.017	11.6
	125	0.132	0.119	90.2	0.026	20.0	0.093	70.2	0.013	9.8	0.001	0.6	0.012	9.2
	150	0.132	0.121	91.7	0.026	19.8	0.095	71.8	0.011	8.3	0.002	1.3	0.009	7.1
	180	0.149	0.130	87.2	0.038	25.6	0.092	61.7	0.019	12.8	0.002	1.1	0.017	11.6
18/09/02	0	0.189	0.158	83.6	0.032	16.9	0.126	66.7	0.031	16.4	0.003	1.4	0.028	15.0
	20	0.162	0.144	88.9	0.030	18.4	0.114	70.5	0.018	11.1	0.002	1.0	0.016	10.1
	40	0.144	0.116	80.6	0.028	19.7	0.088	60.9	0.028	19.4	0.002	1.6	0.026	17.9
	60	0.126	0.103	81.7	0.026	20.8	0.077	61.0	0.023	18.3	0.003	2.4	0.020	15.8
	80	0.135	0.107	79.3	0.030	21.9	0.077	57.4	0.028	20.7	0.002	1.7	0.026	19.1
	100	0.153	0.125	81.7	0.033	21.5	0.092	60.2	0.028	18.3	0.004	2.9	0.024	15.4
	125	0.162	0.138	85.2	0.034	20.8	0.104	64.4	0.024	14.8	0.003	1.8	0.021	13.1
	150	0.171	0.146	85.4	0.030	17.3	0.116	68.1	0.025	14.6	0.003	1.7	0.022	12.9
	175	0.171	0.106	62.0	0.030	17.8	0.076	44.2	0.065	38.0	0.013	7.5	0.052	30.5
	200	0.189	0.125	66.1	0.033	17.2	0.092	48.9	0.064	33.9	0.015	7.9	0.049	26.0
24/10/02	0	0.162	0.153	94.4	0.018	11.0	0.135	83.5	0.009	5.6	0.002	1.2	0.007	4.3
	20	0.198	0.190	96.0	0.021	10.8	0.169	85.1	0.008	4.0	0.002	1.2	0.006	2.9
	40	0.171	0.159	93.0	0.019	11.1	0.140	81.8	0.012	7.0	0.004	2.2	0.008	4.8
	60	0.166	0.153	92.2	0.019	11.2	0.134	80.9	0.013	7.8	0.002	1.2	0.011	6.7
	80	0.162	0.155	95.7	0.017	10.7	0.138	85.0	0.007	4.3	0.002	1.1	0.005	3.2
	100	0.167	0.159	95.2	0.022	13.3	0.137	81.9	0.008	4.8	0.002	1.0	0.006	3.8
	125	0.171	0.165	96.5	0.025	14.6	0.140	81.9	0.006	3.5	0.001	0.4	0.005	3.1
	150	0.180	0.170	94.4	0.025	13.7	0.145	80.8	0.010	5.6	0.001	0.4	0.009	5.2
	175	0.198	0.187	94.4	0.034	17.0	0.153	77.4	0.011	5.6	0.001	0.3	0.010	5.3
	200	0.207	0.199	96.1	0.038	18.5	0.161	77.7	0.008	3.9	0.001	0.6	0.007	3.3

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP $^{\text{MAGIC}}$		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	SHELFBREAK STATION													
21/11/02	0	0.108	0.074	68.5	0.023	21.7	0.051	46.8	0.034	31.5	0.004	3.4	0.030	28.0
	20	0.126	0.094	74.6	0.020	16.2	0.074	58.4	0.032	25.4	0.004	3.0	0.028	22.4
	40	0.135	0.111	82.2	0.021	15.9	0.090	66.3	0.024	17.8	0.004	3.2	0.020	14.6
	60	0.162	0.135	83.3	0.026	16.2	0.109	67.2	0.027	16.7	0.005	2.9	0.022	13.8
	80	0.189	0.159	84.1	0.023	12.4	0.136	71.7	0.030	15.9	0.006	3.1	0.024	12.8
	100	0.198	0.177	89.4	0.021	10.9	0.156	78.5	0.021	10.6	0.002	0.8	0.019	9.8
	125	0.180	0.152	84.4	0.047	26.0	0.105	58.4	0.028	15.6	0.003	1.9	0.025	13.7
	150	0.171	0.157	91.8	0.030	17.4	0.127	74.4	0.014	8.2	0.002	1.2	0.012	7.0
	175	0.252	0.232	92.1	0.042	16.8	0.190	75.3	0.020	7.9	0.003	1.3	0.017	6.6
	200	0.279	0.240	86.0	0.049	17.7	0.191	68.3	0.039	14.0	0.006	2.1	0.033	11.9
24/12/2002	0	0.234	0.204	87.2	0.017	7.2	0.187	79.9	0.030	12.8	0.003	1.1	0.027	11.7
	20	0.207	0.186	89.9	0.013	6.3	0.173	83.6	0.021	10.1	0.001	0.3	0.020	9.9
	40	0.216	0.192	88.9	0.016	7.2	0.176	81.7	0.024	11.1	0.004	1.8	0.020	9.3
	60	0.225	0.205	91.1	0.016	6.9	0.189	84.2	0.020	8.9	0.004	1.6	0.016	7.3
	80	0.234	0.216	92.3	0.017	7.1	0.199	85.2	0.018	7.7	0.002	0.8	0.016	6.9
	100	0.243	0.225	92.6	0.017	7.0	0.208	85.6	0.018	7.4	0.001	0.6	0.017	6.8
	125	0.248	0.225	90.7	0.017	6.7	0.208	84.1	0.023	9.3	0.002	0.8	0.021	8.5
	150	0.252	0.232	92.1	0.019	7.4	0.213	84.6	0.020	7.9	0.001	0.2	0.019	7.7
	175	0.270	0.248	91.9	0.022	8.1	0.226	83.8	0.022	8.1	0.004	1.3	0.018	6.8
	200	0.315	0.255	81.0	0.022	7.1	0.233	73.9	0.060	19.0	0.007	2.2	0.053	16.8
29/01/03	0	0.207	0.190	91.8	0.022	10.6	0.168	81.2	0.017	8.2	0.006	2.7	0.011	5.5
	20	0.180	0.157	87.2	0.021	11.5	0.136	75.7	0.023	12.8	0.004	2.3	0.019	10.5
	40	0.153	0.141	92.2	0.020	13.2	0.121	78.9	0.012	7.8	0.003	2.0	0.009	5.9
	60	0.171	0.154	90.1	0.028	16.3	0.126	73.8	0.017	9.9	0.005	3.0	0.012	7.0
	80	0.225	0.209	92.9	0.025	11.2	0.184	81.7	0.016	7.1	0.004	1.6	0.012	5.5
	100	0.243	0.229	94.2	0.026	10.9	0.203	83.3	0.014	5.8	0.004	1.7	0.010	4.1
	125	0.162	0.149	92.0	0.023	14.4	0.126	77.6	0.013	8.0	0.004	2.6	0.009	5.4
	150	0.180	0.165	91.7	0.023	12.7	0.142	78.9	0.015	8.3	0.004	2.0	0.011	6.3
	175	0.153	0.137	89.5	0.022	14.7	0.115	74.9	0.016	10.5	0.003	1.8	0.013	8.7
	200	0.225	0.203	90.2	0.035	15.5	0.168	74.7	0.022	9.8	0.005	2.1	0.017	7.7

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	**Depth (m)**	**TP µM**	**TDP**		**DIP $^{\text{MAGIC}}$**		**DOP**		**TPP**		**PIP**		**POP**	
			µM	**%**	**µM**	**%**	**µM**	**%**	**µM**	**%**	**µM**	**%**	**µM**	**%**
	SHELFBREAK STATION													
27/02/03	0	0.144	0.129	89.6	0.025	17.6	0.104	71.9	0.015	10.4	0.003	2.2	0.012	8.2
	20	0.108	0.093	86.1	0.023	21.5	0.070	64.7	0.015	13.9	0.003	2.8	0.012	11.1
	40	0.117	0.099	84.6	0.020	17.5	0.079	67.1	0.018	15.4	0.002	2.0	0.016	13.4
	60	0.122	0.108	88.5	0.022	18.3	0.086	70.3	0.014	11.5	0.004	3.3	0.010	8.2
	80	0.126	0.112	88.9	0.025	19.5	0.087	69.4	0.014	11.1	0.005	4.2	0.009	6.9
	100	0.117	0.105	89.7	0.023	19.4	0.082	70.3	0.012	10.3	0.003	2.6	0.009	7.6
	125	0.113	0.098	86.7	0.028	24.8	0.070	61.9	0.015	13.3	0.004	3.3	0.011	9.9
	150	0.131	0.116	88.5	0.024	18.4	0.092	70.2	0.015	11.5	0.002	1.8	0.013	9.6
	175	0.153	0.141	92.2	0.029	18.9	0.112	73.2	0.012	7.8	0.004	2.5	0.008	5.3
	200	0.189	0.163	86.2	0.039	20.8	0.124	65.5	0.026	13.8	0.009	4.5	0.017	9.2
28/03/03	0	0.117	0.103	88.0	0.014	12.2	0.089	75.8	0.014	12.0	0.001	1.2	0.013	10.8
	20	0.135	0.116	85.9	0.014	10.6	0.102	75.3	0.019	14.1	0.003	2.5	0.016	11.5
	40	0.131	0.115	87.8	0.017	12.6	0.098	75.2	0.016	12.2	0.002	1.4	0.014	10.9
	60	0.126	0.110	87.3	0.015	12.0	0.095	75.3	0.016	12.7	0.003	2.0	0.013	10.7
	80	0.117	0.103	88.0	0.017	14.1	0.086	73.9	0.014	12.0	0.002	2.1	0.012	9.9
	100	0.117	0.101	86.3	0.018	15.6	0.083	70.7	0.016	13.7	0.005	4.7	0.011	9.0
	125	0.108	0.090	83.3	0.021	19.4	0.069	63.9	0.018	16.7	0.005	4.9	0.013	11.7
	150	0.207	0.187	90.3	0.025	11.9	0.162	78.5	0.020	9.7	0.006	2.7	0.014	6.9
	175	0.210	0.192	91.4	0.026	12.5	0.166	78.9	0.018	8.6	0.002	1.0	0.016	7.5
	200	0.216	0.193	89.4	0.040	18.4	0.153	71.0	0.023	10.6	0.003	1.2	0.020	9.5
21/05/03	0	0.162	0.121	74.7	0.036	22.5	0.085	52.2	0.041	25.3	0.019	11.8	0.022	13.5
	20	0.156	0.140	89.7	0.019	11.9	0.121	77.8	0.016	10.3	0.007	4.2	0.009	6.0
	40	0.162	0.151	93.2	0.017	10.4	0.134	82.8	0.011	6.8	0.006	3.5	0.005	3.3
	60	0.171	0.159	93.0	0.020	11.9	0.139	81.1	0.012	7.0	0.005	3.2	0.007	3.9
	80	0.153	0.134	87.6	0.026	17.1	0.108	70.5	0.019	12.4	0.008	5.3	0.011	7.1
	100	0.180	0.170	94.4	0.028	15.3	0.142	79.1	0.010	5.6	0.004	2.0	0.006	3.5
	125	0.189	0.176	93.1	0.027	14.3	0.149	78.8	0.013	6.9	0.005	2.5	0.008	4.4
	150	0.198	0.180	90.9	0.033	16.8	0.147	74.1	0.018	9.1	0.005	2.4	0.013	6.7
	175	0.171	0.151	88.3	0.047	27.3	0.083	48.4	0.038	11.7	0.008	4.9	0.012	6.8
	200	0.198	0.186	93.9	0.068	34.4	0.139	70.3	0.012	6.1	0.004	2.0	0.008	4.0

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP $^{\text{MAGIC}}$		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	SHELFBREAK STATION													
05/06/03	0	0.216	0.201	93.1	0.021	9.6	0.180	83.5	0.015	6.9	0.007	3.4	0.008	3.5
	20	0.207	0.196	94.7	0.018	8.7	0.178	86.0	0.011	5.3	0.005	2.5	0.006	2.8
	40	0.234	0.222	94.9	0.015	6.6	0.207	88.3	0.012	5.1	0.007	3.0	0.005	2.1
	60	0.261	0.247	94.6	0.014	5.2	0.233	89.4	0.014	5.4	0.007	2.7	0.007	2.6
	80	0.266	0.255	95.9	0.014	5.4	0.241	90.4	0.011	4.1	0.005	2.0	0.006	2.2
	100	0.270	0.257	95.2	0.017	6.2	0.240	89.0	0.013	4.8	0.006	2.3	0.007	2.6
	125	0.243	0.222	91.4	0.033	13.5	0.189	77.9	0.021	8.6	0.007	3.1	0.014	5.6
	150	0.225	0.209	92.9	0.038	16.7	0.171	76.1	0.016	7.1	0.008	3.6	0.008	3.5
	175	0.234	0.221	94.4	0.035	15.1	0.186	79.3	0.013	5.6	0.005	2.3	0.008	3.2
	200	0.279	0.243	87.1	0.039	14.1	0.204	73.0	0.036	12.9	0.011	4.1	0.025	8.8
15/07/03	0	0.135	0.104	77.0	0.026	19.0	0.078	58.0	0.031	23.0	0.009	6.4	0.022	16.6
	20	0.117	0.093	79.5	0.019	16.6	0.074	62.9	0.024	20.5	0.008	6.5	0.016	14.0
	40	0.162	0.127	78.4	0.014	8.7	0.113	69.7	0.035	21.6	0.006	3.4	0.029	18.2
	60	0.170	0.139	81.8	0.014	8.0	0.125	73.7	0.031	18.2	0.006	3.6	0.025	14.6
	80	0.144	0.129	89.6	0.012	8.2	0.117	81.3	0.015	10.4	0.005	3.5	0.010	6.9
	100	0.162	0.146	90.1	0.012	7.6	0.134	82.5	0.016	9.9	0.006	4.0	0.010	5.9
	125	0.171	0.154	90.1	0.021	8.5	0.139	81.5	0.017	9.9	0.005	3.1	0.012	6.8
	150	0.180	0.153	85.0	0.020	11.1	0.133	73.9	0.027	15.0	0.008	4.7	0.019	10.3
	175	0.185	0.169	91.4	0.018	9.6	0.151	81.8	0.016	8.6	0.003	1.6	0.013	7.0
	200	0.162	0.115	71.0	0.036	22.5	0.079	48.5	0.047	29.0	0.014	8.7	0.033	20.3
31/07/03	0	0.126	0.112	88.9	0.017	13.4	0.095	75.5	0.014	11.1	0.002	1.4	0.012	9.7
	20	0.144	0.132	91.7	0.016	11.4	0.116	80.3	0.012	8.3	0.003	1.8	0.009	6.6
	40	0.171	0.150	87.7	0.019	10.9	0.131	76.8	0.021	12.3	0.002	1.4	0.019	10.9
	60	0.162	0.142	87.7	0.019	11.5	0.123	76.2	0.020	12.3	0.002	1.3	0.018	11.1
	80	0.135	0.119	88.1	0.023	17.1	0.096	71.1	0.016	11.9	0.003	2.5	0.013	9.3
	100	0.149	0.129	86.6	0.022	14.9	0.107	71.7	0.020	13.4	0.006	3.7	0.014	9.7
	125	0.126	0.094	74.6	0.036	28.2	0.058	46.4	0.032	25.4	0.008	6.4	0.024	19.0
	150	0.117	0.094	80.3	0.029	24.7	0.065	55.7	0.023	19.7	0.005	4.4	0.018	15.3
	175	0.171	0.141	82.5	0.040	23.7	0.101	58.8	0.030	17.5	0.005	3.2	0.025	14.3
	200	0.216	0.168	77.8	0.032	15.0	0.136	62.8	0.048	22.2	0.011	5.0	0.037	17.2

APPENDIX D (CONTINUED)

Date (dd/mm/yy)	Depth (m)	TP µM	TDP		DIP ^{MAGIC}		DOP		TPP		PIP		POP	
			µM	%	µM	%	µM	%	µM	%	µM	%	µM	%
	SHELFBREAK STATION													
22/09/03	0	0.171	0.148	86.5	0.032	18.7	0.116	67.8	0.023	13.5	0.011	6.7	0.012	6.7
	20	0.189	0.163	86.2	0.041	21.8	0.122	64.5	0.026	13.8	0.011	5.8	0.015	8.0
	40	0.216	0.184	85.2	0.031	14.4	0.153	70.8	0.032	14.8	0.012	5.6	0.020	9.2
	60	0.207	0.187	90.3	0.024	11.6	0.163	78.8	0.020	9.7	0.004	2.0	0.016	7.7
	80	0.189	0.169	89.4	0.024	12.9	0.145	76.5	0.020	10.6	0.006	3.4	0.014	7.2
	100	0.162	0.142	87.7	0.027	16.7	0.115	70.9	0.020	12.3	0.004	2.7	0.016	9.6
	150	0.189	0.160		0.040		0.120		0.029		0.008		0.021	
	175	0.198	0.175	84.7	0.038	21.4	0.137	63.2	0.023	15.3	0.005	4.0	0.018	11.3
	200	0.189	0.164	88.4	0.044	19.3	0.120	69.1	0.025	11.6	0.006	2.4	0.019	9.2
11/12/03	0	0.189	0.164	86.8	0.018	23.3	0.146	63.5	0.025	13.2	0.008	2.9	0.017	10.3
	20	0.216	0.191	86.8	0.014	9.6	0.177	77.1	0.025	13.2	0.004	4.2	0.021	9.0
	40	0.225	0.202	88.4	0.017	6.7	0.186	81.8	0.023	11.6	0.006	1.8	0.017	9.7
	60	0.207	0.180	89.9	0.015	7.4	0.164	82.5	0.027	10.1	0.009	2.5	0.019	7.6
	80	0.189	0.172	86.7	0.016	7.4	0.156	79.3	0.017	13.3	0.005	4.3	0.012	9.0
	100	0.180	0.161	90.8	0.021	8.3	0.140	82.4	0.019	9.2	0.006	2.7	0.012	6.5
	125	0.171	0.157	89.7	0.025	11.9	0.131	77.8	0.014	10.3	0.003	3.6	0.011	6.7
	150	0.144	0.129	91.5	0.029	14.7	0.100	76.8	0.015	8.5	0.005	2.0	0.009	6.5
	175	0.126	0.109	89.7	0.030	19.9	0.080	69.8	0.017	10.3	0.002	3.8	0.014	6.5
	200	0.198	0.164	86.8	0.048	23.5	0.116	63.3	0.034	13.2	0.010	1.9	0.024	11.3
	REFERENCE STATION (R1)													
29/12/03	0	0.180	0.159	88.3	0.020	11.0	0.139	77.2	0.021	11.7	0.005	2.8	0.016	8.9
	25	0.162	0.139	85.8	0.018	11.1	0.121	74.7	0.023	14.2	0.006	3.6	0.017	10.6
	50	0.144	0.125	86.8	0.014	9.7	0.111	77.1	0.019	13.2	0.006	4.1	0.013	9.1
	100	0.180	0.159	88.3	0.020	11.1	0.139	77.2	0.021	11.7	0.006	3.4	0.015	8.3
	150	0.108	0.088	81.5	0.010	9.3	0.078	72.2	0.02	18.5	0.007	6.9	0.013	11.6
	250	0.234	0.227	97.0	0.053	22.6	0.174	74.4	0.007	3.0	0.001	0.6	0.006	2.4
	500	0.333	0.327	98.2	0.208	62.4	0.119	35.8	0.006	1.8	0.001	0.3	0.005	1.5
	800	0.315	0.308	97.8	0.199	63.1	0.109	34.7	0.007	2.2	0.001	0.5	0.006	1.8

APPENDIX E. DISSOLVED OXYGEN (DO) CONCENTRATIONS AT THE TIME-SERIES STATIONS (after Tuğrul *et al*., 2004 and unpublished data of the IMS-METU Chemical Oceanography department)

Date (dd/mm/yyyy)	Depth (m)	DO (µM)	Date (dd/mm/yyyy)	Depth (m)	DO (µM)
	NEARSHORE STATION				
18/09/2002	0	202.3	28/03/2003	0	259.2
	10	203.4		10	250.6
24/10/2002	0	211.5	21/05/2003	0	244.8
	10	215.0		10	261.9
21/11/2002	0	234.0	05/06/2003	0	221.2
	10	224.6		10	222.0
24/12/2002	0	223.7	31/07/2003	0	203.2
	10	224.1		10	202.3
29/01/2002	0	228.1	11/12/2003	0	229.7
	10	227.7		10	227.6
27/02/2003	0	241.8			
	10	239.3			
	MIDDLE STATION				
18/09/2002	0	202.9	28/03/2003	0	238.1
	20	183.3		20	234.8
	40	198.8		40	233.2
	60	247.2		60	231.7
	80	237.1		80	232.2
	100	231.9		100	233.4
24/10/2002	0	212.1	21/05/2003	0	227.3
	20	211.1		20	244.4
	40	212.0		40	238.7
	60	250.1		60	235.7
	80	245.2		80	221.7
21/11/2002	0	220.0		100	221.2
	20	222.7	05/06/2003	0	215.3
	40	221.3		20	215.9
	60	218.9		40	236.2
	80	218.8		60	235.5
	100	248.0		80	240.2
24/12/2002	0	225.8		100	233.8
	20	225.3	31/07/2003	0	213.0
	40	224.7		20	205.5
	60	225.2		40	223.2
	80	225.7		60	248.7
	100	226.6		80	255.8
29/01/2003	0	227.5		100	239.6
	20	227.6	11/12/2003	0	225.0
	40	227.2		20	229.4
	60	227.7		40	230.3
	80	227.5		60	229.5
	100	227.9		80	226.0
27/02/2003	0	235.0		100	226.7
	20	234.8			
	40	235.7			
	60	234.4			
	80	234.7			
	100	227.9			

APPENDIX E (CONTINUED)

Date (dd/mm/yyyy)	Depth (m)	DO (µM)	Date (dd/mm/yyyy)	Depth (m)	DO (µM)
	SHELFBREAK STATION				
18/09/2002	0	191.5	28/03/2003	0	232.3
	20	194.2		20	230.1
	40	194.6		40	231.2
	60	215.8		60	231.6
	80	232.9		80	232.4
	100	230.4		100	230.9
	125	223.4		125	229.8
	150	211.8		150	228.6
	175	204.3		175	233.3
	200	190.7		200	227.8
24/10/2002	0	214.9	21/05/2003	0	224.7
	20	212.3		20	243.2
	40	214.9		40	233.7
	60	248.6		60	232.4
	80	243.9		80	229.5
	100	234.8		100	223.8
	125	226.9		125	224.7
	150	222.8		150	223.2
	175	216.9		175	221.9
	200	211.7		200	208.8
21/11/2002	0	221.0	05/06/2003	0	220.5
	20	221.4		20	227.6
	40	220.7		40	237.5
	60	222.0		60	237.9
	80	228.4		80	235.8
	100	256.6		100	233.9
	125	246.1		125	222.6
	150	239.8		150	214.8
	175	237.3		175	222.4
	200	216.8		200	213.4
24/12/2002	0	225.5	31/07/2003	0	227.1
	20	224.3		20	224.5
	40	220.6		40	235.3
	60	224.9		60	256.0
	80	225.9		80	263.8
	100	227.1		100	242.3
	125	226.6		125	239.5
	150	221.5		150	228.9
	175	225.3		175	238.8
	200	223.2		200	236.7
29/01/2003	0	229.5	11/12/2003	0	239.3
	20	228.3		20	235.1
	40	225.7		40	232.8
	60	229.4		60	229.2
	80	226.7		80	229.6
	100	226.8		100	239.6
	125	226.1		125	222.2
	150	224.8		150	227.5
	175	227.0		175	225.0
	200	227.8		200	232.2
27/02/2003	0	236.9			
	20	231.8			
	40	231.2			
	60	232.8			
	80	235.4			
	100	238.9			
	125	235.7			
	150	230.7			
	175	236.3			
	200	232.9			

APPENDIX F. DESCRIPTIVE STATISTICS FOR THE HYDROGRAPHIC AND BIO-CHEMICAL PARAMETERS AT THE TIME-SERIES STATIONS

Parameters	Mean	Std. Deviation	N
	NEARSHORE STATION		
Salinity (psu)	38.39	1.007	43
Temperature (°C)	22.57	4.928	43
Density	26.51	1.679	43
DO (µM)	229	19.84	30
DIP^{AA} (µM)	0.078	0.017	56
$\text{DIP}^{\text{MAGIC}}$ (µM)	0.063	0.043	53
DOP^{AA} (µM)	0.142	0.094	53
$\text{DOP}^{\text{MAGIC}}$ (µM)	0.157	0.062	50
NO_3 (µM)	2.081	1.368	56
Si (µM)	4.421	3.792	56
N/P ($\text{DIN/DIP}^{\text{AA}}$)	37	57	52
N/P ($\text{DIN/DIP}^{\text{MAGIC}}$)	29	39	52
POC (µM)	18.58	22.12	46
PON (µM)	1.864	1.751	46
TP (µM)	0.289	0.083	53
TDP (µM)	0.217	0.066	53
TPP (µM)	0.076	0.039	50
PIP (µM)	0.024	0.017	50
POP (µM)	0.052	0.028	50
C/N (POC/PON)	9.1	2.9	46
C/P (POC/POP)	331	268	46
C/P (POC/PP)	208	152	46
N/P (PON/POP)	35	20	46
N/P (PON/PP)	22	10	46
	MIDDLE STATION		
Salinity (psu)	39.12	0.262	77
Temperature (°C)	20.76	3.784	77
Density	27.64	1.088	77
DO (µM)	228	12.50	65
DIP^{AA} (µM)	0.029	0.011	79
$\text{DIP}^{\text{MAGIC}}$ (µM)	0.027	0.009	79
DOP^{AA} (µM)	0.144	0.034	79
$\text{DOP}^{\text{MAGIC}}$ (µM)	0.147	0.037	79
NO_3 (µM)	0.222	0.192	79
Si (µM)	1.565	0.574	79
N/P ($\text{DIN/DIP}^{\text{AA}}$)	8.2	7.6	79
N/P ($\text{DIN/DIP}^{\text{MAGIC}}$)	8.5	6.8	79
POC (µM)	5.147	3.857	79
PON (µM)	0.584	0.284	79
TP (µM)	0.200	0.034	79
TDP (µM)	0.173	0.035	79
TPP (µM)	0.027	0.012	79
PIP (µM)	0.007	0.004	79
POP (µM)	0.019	0.009	79
C/N (POC/PON)	8.7	3.7	79
C/P (POC/POP)	266	116	79
C/P (POC/PP)	189	86	79
N/P (PON/POP)	32	12	79
N/P (PON/PP)	22	8	79

APPENDIX F (CONTINUED)

Parameters	**Mean**	**Std. Deviation**	**N**
	SHELFBREAK STATION		
Salinity (psu)	39.09	0.168	202
Temperature (°C)	19.10	3.070	200
Density	28.09	0.850	200
DO (µM)	229	14.58	141
DIP^{AA} (µM)	0.038	0.028	237
DIP^{MAGIC} (µM)	0.024	0.010	219
DOP^{AA} (µM)	0.130	0.054	210
DOP^{MAGIC} (µM)	0.141	0.051	210
NO_3 (µM)	0.429	0.252	238
Si (µM)	1.516	0.711	238
N/P (DIN/DIP^{AA})	13.15	14.71	215
N/P (DIN/DIP^{MAGIC})	16.76	17.22	215
POC (µM)	4.106	2.750	197
PON (µM)	0.473	0.264	197
TP (µM)	0.186	0.052	217
TDP (µM)	0.166	0.050	210
TPP (µM)	0.022	0.009	209
PIP (µM)	0.006	0.004	209
POP (µM)	0.016	0.008	209
C/N (POC/PON)	8.8	2.8	197
C/P (POC/POP)	287	203	197
C/P (POC/PP)	195	106	197
N/P (PON/POP)	34	21	197
N/P (PON/PP)	23	11	197

APPENDIX G.1. T-TEST FOR PAIRED SAMPLES AT THE TIME-SERIES STATIONS

Parameters	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
	NEARSHORE STATION							
DIP^{AA} - DIP^{MAGIC}	0,012	0,076	0,011	-0,009	0,033	1,126	51	0,265
N/P^{AA} - N/P^{MAGIC}	7.169	27.77	3.851	-0.562	14.90	1.862	51	0.068
	MIDDLE STATION							
DIP^{AA} - DIP^{MAGIC}	0,002	0,014	0,002	-0,001	0,005	1,406	78	0,164
N/P^{AA} - N/P^{MAGIC}	-0.307	4.347	0.489	-1.281	0.667	-0.63	78	0.532
	SHELFBREAK STATION							
DIP^{AA} - DIP^{MAGIC}	0,012	0,025	0,002	0,009	0,016	7,174	214	0,000
N/P^{AA} - N/P^{MAGIC}	-3.609	10.664	0.727	-5.043	-2.176	-4.963	214	0.000

APPENDIX G.2. CORRELATIONS BETWEEN PAIRED SAMPLES AT THE TIME-SERIES STATIONS

Parameters	N	Correlation	Significance (p)
	NEARSHORE STATION		
DIP^{AA} - DIP^{MAGIC}	52	0.478	0.000
N/P^{AA} - N/P^{MAGIC}	52	0.896	0.000
	MIDDLE STATION		
DIP^{AA} - DIP^{MAGIC}	79	0.108	0.343
N/P^{AA} - N/P^{MAGIC}	79	0.824	0.000
	SHELFBREAK STATION		
DIP^{AA} - DIP^{MAGIC}	215	0.255	0.000
N/P^{AA} - N/P^{MAGIC}	215	0.788	0.000

APPENDIX H. CORRELATIONS BETWEEN THE HYDROGRAPHIC AND BIO-CHEMICAL DATA AT THE TIME-SERIES STATIONS

Parameters		**Depth**	**Salinity**	**Temperature**	**Density**
		NEARSHORE STATION			
Depth	Pearson Correlation	1.000	0.402(**)	-0.011	0.216
	Sig. (2-tailed)	.	0.007	0.944	0.165
	N	58	43	43	43
Salinity (psu)	Pearson Correlation	0.402(**)	1.000	-0.002	0.436(**)
	Sig. (2-tailed)	0.007	.	0.990	0.003
	N	43	43	43	43
Temperature (°C)	Pearson Correlation	-0.011	-0.002	1.000	-0.889(**)
	Sig. (2-tailed)	0.944	0.990	.	0.000
	N	43	43	43	43
Density	Pearson Correlation	0.216	0.436(**)	-0.889(**)	1.000
	Sig. (2-tailed)	0.165	0.003	0.000	.
	N	43	43	43	43
DO (μM)	Pearson Correlation	-0.015	-0.588(**)	-0.778(**)	0.595(**)
	Sig. (2-tailed)	0.936	0.004	0.000	0.003
	N	30	22	22	22
DIP^{AA} (μM)	Pearson Correlation	-0.138	-0.448(**)	0.078	-0.261
	Sig. (2-tailed)	0.312	0.003	0.617	0.091
	N	56	43	43	43
DIP^{MAGIC} (μM)	Pearson Correlation	-0.201	-0.361(*)	-0.376(*)	0.168
	Sig. (2-tailed)	0.150	0.017	0.013	0.282
	N	53	43	43	43
DOP^{AA} (μM)	Pearson Correlation	0.030	0.332(*)	-0.323(*)	0.431(**)
	Sig. (2-tailed)	0.830	0.034	0.039	0.005
	N	53	41	41	41
DOP^{MAGIC} (μM)	Pearson Correlation	0.042	0.110	-0.145	0.190
	Sig. (2-tailed)	0.770	0.495	0.366	0.233
	N	50	41	41	41
NO_3 (μM)	Pearson Correlation	-0.405(**)	-0.245	-0.221	0.076
	Sig. (2-tailed)	0.002	0.113	0.155	0.628
	N	56	43	43	43
Si (μM)	Pearson Correlation	-0.304(*)	-0.372(*)	-0.177	-0.010
	Sig. (2-tailed)	0.023	0.014	0.256	0.947
	N	56	43	43	43
POC (μM)	Pearson Correlation	-0.177	-0.517(**)	-0.115	-0.118
	Sig. (2-tailed)	0.239	0.001	0.475	0.462
	N	46	41	41	41
PON (μM)	Pearson Correlation	-0.203	-0.476(**)	-0.158	-0.067
	Sig. (2-tailed)	0.176	0.002	0.322	0.677
	N	46	41	41	41
TP (μM)	Pearson Correlation	-0.185	-0.509(**)	-0.396(*)	0.126
	Sig. (2-tailed)	0.184	0.001	0.010	0.432
	N	53	41	41	41
TDP (μM)	Pearson Correlation	-0.110	-0.169	-0.441(**)	0.322(*)
	Sig. (2-tailed)	0.433	0.290	0.004	0.040
	N	53	41	41	41
TPP (μM)	Pearson Correlation	-0.237	-0.561(**)	-0.035	-0.226
	Sig. (2-tailed)	0.098	0.000	0.830	0.155
	N	50	41	41	41
PIP (μM)	Pearson Correlation	-0.292(*)	-0.424(**)	-0.223	0.018
	Sig. (2-tailed)	0.040	0.006	0.161	0.911
	N	50	41	41	41
POP (μM)	Pearson Correlation	-0.158	-0.528(**)	0.094	-0.334(*)
	Sig. (2-tailed)	0.273	0.000	0.561	0.033
	N	50	41	41	41

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX H (CONTINUED)

Parameters		**Depth**	**Salinity**	**Temperature**	**Density**
		MIDDLE STATION			
Depth	Pearson Correlation	1.000	-0.015	-0.511(**)	0.519(**)
	Sig. (2-tailed)	.	0.898	0.000	0.000
	N	79	77	77	77
Salinity (psu)	Pearson Correlation	-0.015	1.000	0.140	0.028
	Sig. (2-tailed)	0.898	.	0.225	0.810
	N	77	77	77	77
Temperature (°C)	Pearson Correlation	-0.511(**)	0.140	1.000	-0.984(**)
	Sig. (2-tailed)	0.000	0.225	.	0.000
	N	77	77	77	77
Density	Pearson Correlation	0.519(**)	0.028	-0.984(**)	1.000
	Sig. (2-tailed)	0.000	0.810	0.000	.
	N	77	77	77	77
DO (μM)	Pearson Correlation	0.370(**)	-0.421(**)	-0.721(**)	0.652(**)
	Sig. (2-tailed)	0.002	0.000	0.000	0.000
	N	65	65	65	65
DIP^{AA} (μM)	Pearson Correlation	0.211	-0.042	-0.164	0.165
	Sig. (2-tailed)	0.062	0.715	0.154	0.153
	N	79	77	77	77
$\text{DIP}^{\text{MAGIC}}$ (μM)	Pearson Correlation	0.294(**)	-0.299(**)	0.081	-0.137
	Sig. (2-tailed)	0.008	0.008	0.481	0.236
	N	79	77	77	77
DOP^{AA} (μM)	Pearson Correlation	0.226(*)	0.412(**)	-0.021	0.102
	Sig. (2-tailed)	0.045	0.000	0.853	0.378
	N	79	77	77	77
$\text{DOP}^{\text{MAGIC}}$ (μM)	Pearson Correlation	0.202	0.443(**)	-0.091	0.179
	Sig. (2-tailed)	0.074	0.000	0.429	0.118
	N	79	77	77	77
NO_3 (μM)	Pearson Correlation	0.160	-0.095	-0.382(**)	0.361(**)
	Sig. (2-tailed)	0.158	0.414	0.001	0.001
	N	79	77	77	77
Si (μM)	Pearson Correlation	0.413(**)	0.027	-0.200	0.212
	Sig. (2-tailed)	0.000	0.816	0.081	0.064
	N	79	77	77	77
POC (μM)	Pearson Correlation	-0.226(*)	-0.386(**)	0.174	-0.217
	Sig. (2-tailed)	0.045	0.001	0.129	0.058
	N	79	77	77	77
PON (μM)	Pearson Correlation	-0.349(**)	-0.493(**)	-0.034	-0.035
	Sig. (2-tailed)	0.002	0.000	0.766	0.765
	N	79	77	77	77
TP (μM)	Pearson Correlation	0.236(*)	0.245(*)	0.008	0.051
	Sig. (2-tailed)	0.036	0.032	0.947	0.660
	N	79	77	77	77
TDP (μM)	Pearson Correlation	0.292(**)	0.391(**)	-0.075	0.154
	Sig. (2-tailed)	0.009	0.000	0.520	0.182
	N	79	77	77	77
TPP (μM)	Pearson Correlation	-0.184	-0.453(**)	0.244(*)	-0.309(**)
	Sig. (2-tailed)	0.104	0.000	0.032	0.006
	N	79	77	77	77
PIP (μM)	Pearson Correlation	-0.165	-0.588(**)	0.195	-0.288(*)
	Sig. (2-tailed)	0.145	0.000	0.089	0.011
	N	79	77	77	77
POP (μM)	Pearson Correlation	-0.157	-0.303(**)	0.218	-0.258(*)
	Sig. (2-tailed)	0.166	0.007	0.057	0.024
	N	79	77	77	77

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX H (CONTINUED)

Parameters		**Depth**	**Salinity**	**Temperature**	**Density**
		SHELFBREAK STATION			
Depth	Pearson Correlation	1.000	-0.107	-0.615(**)	0.607(**)
	Sig. (2-tailed)	.	0.129	0.000	0.000
	N	243	202	200	200
Salinity (psu)	Pearson Correlation	-0.107	1.000	0.304(**)	-0.178(*)
	Sig. (2-tailed)	0.129	.	0.000	0.011
	N	202	202	200	200
Temperature (°C)	Pearson Correlation	-0.615(**)	0.304(**)	1.000	-0.985(**)
	Sig. (2-tailed)	0.000	0.000	.	0.000
	N	200	200	200	200
Density	Pearson Correlation	0.607(**)	-0.178(*)	-0.985(**)	1.000
	Sig. (2-tailed)	0.000	0.011	0.000	.
	N	200	200	200	200
DO (μM)	Pearson Correlation	-0.072	-0.287(**)	-0.304(**)	0.277(**)
	Sig. (2-tailed)	0.399	0.002	0.001	0.004
	N	141	109	109	109
DIP^{AA} (μM)	Pearson Correlation	0.071	0.032	0.037	-0.043
	Sig. (2-tailed)	0.276	0.655	0.609	0.555
	N	237	196	194	194
DIP^{MAGIC} (μM)	Pearson Correlation	0.484(**)	-0.062	-0.131	0.095
	Sig. (2-tailed)	0.000	0.392	0.071	0.193
	N	219	193	191	191
DOP^{AA} (μM)	Pearson Correlation	0.053	-0.016	-0.188(*)	0.208(**)
	Sig. (2-tailed)	0.444	0.826	0.011	0.005
	N	210	184	182	182
DOP^{MAGIC} (μM)	Pearson Correlation	-0.008	0.022	-0.127	0.151(*)
	Sig. (2-tailed)	0.907	0.769	0.088	0.042
	N	210	184	182	182
NO_3 (μM)	Pearson Correlation	0.501(**)	-0.018	-0.316(**)	0.303(**)
	Sig. (2-tailed)	0.000	0.804	0.000	0.000
	N	238	197	195	195
Si (μM)	Pearson Correlation	0.327(**)	0.083	-0.174(*)	0.165(*)
	Sig. (2-tailed)	0.000	0.247	0.015	0.021
	N	238	197	195	195
POC (μM)	Pearson Correlation	-0.099	-0.248(**)	0.067	-0.110
	Sig. (2-tailed)	0.166	0.001	0.371	0.144
	N	197	181	179	179
PON (μM)	Pearson Correlation	-0.041	-0.223(**)	-0.021	-0.005
	Sig. (2-tailed)	0.564	0.003	0.783	0.951
	N	197	181	179	179
TP (μM)	Pearson Correlation	0.111	0.002	-0.130	0.144
	Sig. (2-tailed)	0.104	0.979	0.080	0.052
	N	217	184	182	182
TDP (μM)	Pearson Correlation	0.094	0.010	-0.155(*)	0.173(*)
	Sig. (2-tailed)	0.175	0.898	0.037	0.019
	N	210	184	182	182
TPP (μM)	Pearson Correlation	0.124	-0.038	0.104	-0.123
	Sig. (2-tailed)	0.075	0.607	0.162	0.098
	N	209	183	181	181
PIP (μM)	Pearson Correlation	0.041	-0.196(**)	-0.016	-0.017
	Sig. (2-tailed)	0.557	0.008	0.831	0.816
	N	209	183	181	181
POP (μM)	Pearson Correlation	0.127	0.060	0.139	-0.144
	Sig. (2-tailed)	0.066	0.421	0.063	0.054
	N	209	183	181	181

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed)

APPENDIX I. CORRELATIONS BETWEEN THE NUTRIENT DATA AND DISSOLVED ORGANIC PHOSPHORUS (DOP) AT THE TIME-SERIES STATIONS

Parameters		**DIP^{AA}**	**DOP^{AA}**	**DIP^{MAGIC}**	**DOP^{MAGIC}**	**NO_3**	**Si**
		NEARSHORE STATION					
DIP^{AA}	Pearson Correlation	1.000	-0.738(**)	0.478(**)		0.247	0.293(*)
	Sig. (2-tailed)		0.000	0.000		0.066	0.029
	N	56	53	52		56	56
DOP^{AA}	Pearson Correlation	-0.738(**)	1.000			0.026	-0.053
	Sig. (2-tailed)	0.000				0.852	0.709
	N	53	53			53	53
DIP^{MAGIC}	Pearson Correlation	0.478(**)		1.000	-0.300(*)	0.613(**)	0.717(**)
	Sig. (2-tailed)	0.000		.	0.034	0.000	0.000
	N	52		53	50	52	52
DOP^{MAGIC}	Pearson Correlation			-0.300(*)	1.000	-0.081	-0.126
	Sig. (2-tailed)			0.034	.	0.578	0.383
	N			50	50	50	50
NO_3	Pearson Correlation	0.247	0.026	0.613(**)	-0.081	1.000	0.828(**)
	Sig. (2-tailed)	0.066	0.852	0.000	0.578		0.000
	N	56	53	52	50	56	56
Si	Pearson Correlation	0.293(*)	-0.053	0.717(**)	-0.126	0.828(**)	1.000
	Sig. (2-tailed)	0.029	0.709	0.000	0.383	0.000	
	N	56	53	52	50	56	56

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX I (CONTINUED)

Parameters		**DIP^{AA}**	**DOP^{AA}**	**DIP^{MAGIC}**	**DOP^{MAGIC}**	**NO_3**	**Si**
		MIDDLE STATION					
DIP^{AA}	Pearson Correlation	1.000	-0.128			0.211	0.146
	Sig. (2-tailed)		0.259			0.062	0.198
	N	79	79			79	79
DOP^{AA}	Pearson Correlation	-0.128	1.000			-0.179	0.092
	Sig. (2-tailed)	0.259				0.115	0.420
	N	79	79			79	79
DIP^{MAGIC}	Pearson Correlation			1.000	-0.350(**)	0.309(**)	0.244(*)
	Sig. (2-tailed)			.	0.002	0.006	0.030
	N			79	79	79	79
DOP^{MAGIC}	Pearson Correlation			-0.350(**)	1.000	-0.180	0.068
	Sig. (2-tailed)			0.002	.	0.113	0.550
	N			79	79	79	79
NO_3	Pearson Correlation	0.211	-0.179	0.309(**)	-0.180	1.000	0.185
	Sig. (2-tailed)	0.062	0.115	0.006	0.113	.	0.103
	N	79	79	79	79	79	79
Si	Pearson Correlation	0.146	0.092	0.244(*)	0.068	0.185	1.000
	Sig. (2-tailed)	0.198	0.420	0.030	0.550	0.103	.
	N	79	79	79	79	79	79

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX I (CONTINUED)

Parameters		**DIP^{AA}**	**DOP^{AA}**	**DIP^{MAGIC}**	**DOP^{MAGIC}**	**NO_3**	**Si**
		SHELFBREAK STATION					
DIP^{AA}	Pearson Correlation	1.000	-0.370(**)			0.281(**)	0.142(*)
	Sig. (2-tailed)		0.000			0.000	0.029
	N	237	206			237	237
DOP^{AA}	Pearson Correlation	-0.370(**)	1.000			-0.231(**)	-0.203(**)
	Sig. (2-tailed)	0.000				0.001	0.003
	N	206	210			206	206
DIP^{MAGIC}	Pearson Correlation			1.000	-0.260(**)	0.576(**)	0.500(**)
	Sig. (2-tailed)			.	0.000	0.000	0.000
	N			219	210	215	215
DOP^{MAGIC}	Pearson Correlation			-0.260(**)	1.000	-0.192(**)	-0.213(**)
	Sig. (2-tailed)			0.000	.	0.006	0.002
	N			210	210	206	206
NO_3	Pearson Correlation	0.281(**)	-0.231(**)	0.576(**)	-0.192(**)	1.000	0.573(**)
	Sig. (2-tailed)	0.000	0.001	0.000	0.006		0.000
	N	237	206	215	206	238	238
Si	Pearson Correlation	0.142(*)	-0.203(**)	0.500(**)	-0.213(**)	0.573(**)	1.000
	Sig. (2-tailed)	0.029	0.003	0.000	0.002	0.000	
	N	237	206	215	206	238	238

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX J. CORRELATIONS BETWEEN PARTICULATE ORGANIC MATTER (POM) DATA AT THE TIME-SERIES STATIONS

Parameters		POC	PON	POP
		NEARSHORE STATION		
POC	Pearson Correlation	1.000	0.961(**)	0.515(**)
	Sig. (2-tailed)		0.000	0.000
	N	46	46	46
PON	Pearson Correlation	0.961(**)	1.000	0.568(**)
	Sig. (2-tailed)	0.000		0.000
	N	46	46	46
POP	Pearson Correlation	0.515(**)	0.568(**)	1.000
	Sig. (2-tailed)	0.000	0.000	
	N	46	46	50
		MIDDLE STATION		
POC	Pearson Correlation	1.000	0.736(**)	0.653(**)
	Sig. (2-tailed)		0.000	0.000
	N	79	79	79
PON	Pearson Correlation	0.736(**)	1.000	0.689(**)
	Sig. (2-tailed)	0.000		0.000
	N	79	79	79
POP	Pearson Correlation	0.653(**)	0.689(**)	1.000
	Sig. (2-tailed)	0.000	0.000	
	N	79	79	79
		SHELFBREAK STATION		
POC	Pearson Correlation	1.000	0.832(**)	0.238(**)
	Sig. (2-tailed)		0.000	0.001
	N	197	197	197
PON	Pearson Correlation	0.832(**)	1.000	0.162(*)
	Sig. (2-tailed)	0.000		0.023
	N	197	197	197
POP	Pearson Correlation	0.238(**)	0.162(*)	1.000
	Sig. (2-tailed)	0.001	0.023	
	N	197	197	209

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX K. CORRELATIONS BETWEEN PHOSPHORUS FRACTIONS DATA AT THE TIME-SERIES STATIONS

Parameters		**TP**	**TDP**	**TPP**	**PIP**	**POP**
		NEARSHORE STATION				
TP	Pearson Correlation	1.000	0.863(**)	0.662(**)		
	Sig. (2-tailed)	.	0.000	0.000		
	N	53	53	50		
TDP	Pearson Correlation	0.863(**)	1.000	0.221		
	Sig. (2-tailed)	0.000	.	0.123		
	N	53	53	50		
TPP	Pearson Correlation	0.662(**)	0.221	1.000	0.784(**)	0.930(**)
	Sig. (2-tailed)	0.000	0.123	.	0.000	0.000
	N	50	50	50	50	50
PIP	Pearson Correlation				1.000	0.501(**)
	Sig. (2-tailed)					0.000
	N				50	50
POP	Pearson Correlation				0.501(**)	1.000
	Sig. (2-tailed)				0.000	
	N				50	50
		MIDDLE STATION				
TP	Pearson Correlation	1.000	0.942(**)	0.090		
	Sig. (2-tailed)	.	0.000	0.429		
	N	79	79	79		
TDP	Pearson Correlation	0.942(**)	1.000	-0.250(*)		
	Sig. (2-tailed)	0.000	.	0.027		
	N	79	79	79		
TPP	Pearson Correlation	0.090	-0.250(*)	1.000	0.698(**)	0.945(**)
	Sig. (2-tailed)	0.429	0.027	.	0.000	0.000
	N	79	79	79	79	79
PIP	Pearson Correlation				1.000	0.425(**)
	Sig. (2-tailed)					0.000
	N				79	79
POP	Pearson Correlation				0.425(**)	1.000
	Sig. (2-tailed)				0.000	
	N				79	79
		SHELFBREAK STATION				
TP	Pearson Correlation	1.000	0.983(**)	0.031(**)		
	Sig. (2-tailed)	.	0.000	0.000		
	N	217	210	209		
TDP	Pearson Correlation	0.983(**)	1.000	0.133		
	Sig. (2-tailed)	0.000	.	0.054		
	N	210	210	209		
TPP	Pearson Correlation	0.313(**)	0.133	1.000		
	Sig. (2-tailed)	0.000	0.054	.		
	N	209	209	209		
PIP	Pearson Correlation				1.000	0.204(**)
	Sig. (2-tailed)					0.003
	N				209	209
POP	Pearson Correlation				0.204(**)	1.000
	Sig. (2-tailed)				0.003	
	N				209	209

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX L. CORRELATIONS BETWEEN C/N/P MOLAR RATIOS AT THE TIME-SERIES STATIONS

Parameters		**C/P (POC/POP)**	**C/P (POC/TPP)**	**N/P (PON/POP)**	**N/P (PON/TPP)**
		NEARSHORE STATION			
C/P (POC/POP)	Pearson Correlation	1.000	0.960(**)		
	Sig. (2-tailed)	.	0.000		
	N	46	46		
C/P (POC/TPP)	Pearson Correlation	0.960(**)	1.000		
	Sig. (2-tailed)	0.000	.		
	N	46	46		
N/P (PON/POP)	Pearson Correlation			1.000	0.931(**)
	Sig. (2-tailed)			.	0.000
	N			46	46
N/P (PON/TPP)	Pearson Correlation			0.931(**)	1.000
	Sig. (2-tailed)			0.000	.
	N			46	46
		MIDDLE STATION			
C/P (POC/POP)	Pearson Correlation	1.000	0.887(**)		
	Sig. (2-tailed)	.	0.000		
	N	79	79		
C/P (POC/TPP)	Pearson Correlation	0.887(**)	1.000		
	Sig. (2-tailed)	0.000	.		
	N	79	79		
N/P (PON/POP)	Pearson Correlation			1.000	0.848(**)
	Sig. (2-tailed)			.	0.000
	N			79	79
N/P (PON/TPP)	Pearson Correlation			0.848(**)	1.000
	Sig. (2-tailed)			0.000	.
	N			79	79
		SHELFBREAK STATION			
C/P (POC/POP)	Pearson Correlation	1.000	0.930(**)		
	Sig. (2-tailed)	.	0.000		
	N	197	197		
C/P (POC/TPP)	Pearson Correlation	0.930(**)	1.000		
	Sig. (2-tailed)	0.000	.		
	N	197	197		
N/P (PON/POP)	Pearson Correlation			1.000	0.920(**)
	Sig. (2-tailed)			.	0.000
	N			197	197
N/P (PON/TPP)	Pearson Correlation			0.920(**)	1.000
	Sig. (2-tailed)			0.000	.
	N			197	197

** Correlation is significant at the 0.01 level (2-tailed).

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PUBLICATIONS

Thesis

Doğan, N. (1997) Mersin (İçel)'de Balıkta ve Bölgede Yaşayan İnsanların Saçında Cıva Düzeyinin Araştırılması. M.S. Thesis, Mersin University, 125 p.

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