DETERMINATION OF TOTAL NITROGEN AND TOTAL PHOSPHORUS IN THE NORTHEASTERN MEDITERRANEAN WATER COLUMN

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MUHAMMED FATİH SERT

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DETERMINATION OF TOTAL NITROGEN AND TOTAL PHOSPHORUS IN THE NORTHEASTERN MEDITERRANEAN WATER COLUMN

Submitted by **MUHAMMED FATİH SERT** in partial fulfillment of the requirements for the degree of **Master of Science in Department of Chemical Oceanography, Institute of Marine Science, Middle East Technical University** by

Prof. Dr. Ferit Bingel ------------------------------------
Director, Graduate School of **Marine Sciences**

Prof. Dr. Süleyman Tuğrul ------------------------------------
Head of Department, **Chemical Oceanography**

Prof. Dr. Süleyman Tuğrul ------------------------------------
Supervisor, **Chemical Oceanography Dept.**

Examining Committee Members:

Prof. Dr. Zahit Uysal ------------------------------------
Biological Oceanography Dept., METU

Prof. Dr. Süleyman Tuğrul ------------------------------------
Chemical Oceanography Dept., METU

Assist. Prof. Dr. Neslihan Doğan-Sağlamtimur ------------------------------------
Envionmental Engineering Dept., Niğde University

Date:---------------------------------

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Muhammed Fatih Sert

Signature :

ABSTRACT

DETERMINATION OF TOTAL NITROGEN AND TOTAL PHOSPHORUS IN THE NORTH EASTERN MEDITERRANEAN WATER COLUMN

Sert, Muhammed Fatih
M. Sc., Department of Chemical Oceanography
Supervisor: Prof. Dr. Süleyman Tuğrul

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Regional and temporal variations of principal hydrophysical (temperature, salinity, density) hydrochemical (nutrients, chl-a, dissolved oxygen) properties were examined at fifty selected stations on the shelf zone of the Northeastern Mediterranean between September 2008 and October 2009. In order to fill systematic gap on fractions of total phosphorus (TP) and total nitrogen (TN) in the region, collected samples were analysed by pH controlled Wet Chemical Oxidation (WCO) method. Accuracy tests of the WCO method reveal that the procedure is highly efficient for the determination of TP but needs some improvement to enhance the reliability of the TN analysis.

Seasonal and spatial distributions of the hydrophysical parameters in the NE Mediterranean water column are dominated by general circulation pattern of the basin. Thermohaline properties of the bay were highly influenced by the river discharges, surface water heating/cooling and wind-induced coastal processes.

Nutrient-replete Seyhan and Berdan discharges markedly enhanced the concentrations of nutrients and algal biomass (in terms of Chl-a) in the shallow zone (<15 m depth) of the bay. However, this regional effect appeared to weaken during the dry summer-autumn period due to significant decreases in flow regimes of the major rivers in the region.The mean concentration of TN varied regionally between 4.82 and 8.19 μM, having the greater values in the nearhore zone. TP concentrations were markedly high in the surface waters of the near-shore zone (0.20-0.70 μM); the offshore values were lower (0.10-0.12 μM) and displayed vertically uniform distribution in the euphotic zone and then increased slightly towards the bottom.

Keywords: Northeastern Mediterranean, total nitrogen, total phosphorus, nutrients.

ÖZ

KUZEYDOĞU AKDENİZ SU KOLONUNDA TOPLAM NİTROJEN VE TOPLAM FOSFOR TAYİNİ

Sert, Muhammed Fatih
Yüksek Lisans, Kimyasal Oşinografi Bölümü
Tez Yöneticisi: Prof. Dr. Süleyman Tuğrul

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Kuzeydoğu Akdeniz'in temel hidro-fiziksel (sıcaklık, tuzluluk, yoğunluk) ve hidro-kimyasal (besin elementleri, klorofil-a, çözünmüş oksijen) özelliklerinin, bölgesel ve dönemsel değişimleri, kıyı kesiminden seçilen elli istasyonda, Eylül 2008-Ekim 2009 aralığında incelenmiştir. Toplam fosfor (TP) ve toplam nitrojen (TN) fraksiyonları üzerine olan bilgi açığını doldurabilmek amacıyla, bölgeden toplanan örnekler "Yaş Kimyasal Oksidasyonu (WCO)" metodu ile analiz edilmiştir. WCO metodunun hassasiyet testlerinin ortaya çıkardığı üzere, kullanılan prosedür, TP ölçümleri için oldukça etkili bulunurken, TN ölçümlerinde verimliliği artırmak için daha ileri çalışmalara ihtiyaç olduğu görülmüştür.

Kuzey Doğu Akdeniz su kolonunda fiziksel parametrelerin mevsimsel ve dönemsel değişimleri tüm basende etkili olan genel akıntı sistemlerine bağlıdır. Bununla birlikte, nehir girdileri, yüzey suyu sıcaklık değişimleri ve rüzgar kaynaklı kıyı karışımları, sıcaklık ve tuzluluk özelliklerini etkilemektedir.

Besince zengin Seyhan ve Berdan ırmaklarının, körfezin sığ sularında (<15 m), besin elementleri ve klorofil-a konsantrasyonlarını arttırdığı gözlenmiştir. Fakat, yaz-sonbahar döneminde, nehirlerin akış hızlarının zayıflamasından dolayı, sözü edilen nehir etkisininde zayıfladığı izlenmiştir. Ortalama TN konsantrasyonları, en yüksek değerler kıyı kesiminde görülmek üzere, 4,82 ve 8,19 µM civarında bölgesel değişim göstermiştir. Kıyı kesimin yüzey sularında TP konsantrasyonları oldukça yüksek iken (0,20-0,70µM), açık sularda 0,10-0,12 µM seviyelerine düşmüştür. TP konsantrasyonlarının düşey profilleri ışıklı tabakada sabit iken, dip sulara doğru artış göstermiştir.

Anahtar Kelimeler: Kuzeydoğu Akdeniz, toplam nitrojen, toplam fosfor, besin elementleri.

To my parents

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CHAPTER 1

INTRODUCTION

1.1. Nitrogen and Phosphorus Cycling in the Marine Environments

Even though, they vary greatly in molecular weight and structure, the term “organic matter” is used to refer all kinds of organic compounds in sea water. Carbon, nitrogen, oxygen and phosphorus are the primary components of organic matters which synthesized by photosynthetic reactions as illustrated below:

$$106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4 \rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138\ O_2$$

Since the useable oceanic reservoir of the nitrogen and phosphorus are relatively small, their distributions in sea water are controlled by the biologically mediated redox processes which derive the biogeochemical cycle of organic matter as well (Libes, 1992). In marine environment nutrient elements have vital importance in every kind of chemical processes. Besides, their essential role in primary production and growth of organisms in water column, elevated inputs of phosphorus and nitrogen to the aquatic environments increase the risk of eutrophication and have serious impacts on water quality (Carpenter *et al.*, 1998; Pickney *et al.*, 2001; Pearl and Piehler, 2008).

1.1.1. Nitrogen cycling in marine environments

In marine environment, most abundant forms of nitrogen present in five relatively stable oxidation states with versatile reactivities. These are nitrate (+5), nitrite (+3), nitrous oxide (+1), molecular nitrogen (0) and ammonia and various organic compounds containing nitrogen as amino groups with an oxidation state of -3 (Gruber, 2005). Nitrogen species take place in many biotic and abiotic reactions in marine environment. Transformations between those species mostly mediated by biology and depend on redox conditions of that media (Gruber, 2005). Biotic reactions of nitrogen compounds are coupled with the marine cycling of oxygen, carbon and phosphorus and change the concentrations of nitrogen species either as a source of bioavailable inorganic components or as an assimilation of useable forms with demineralization processes. Main biotic reactions in marine environment were given in Figure 1.1.

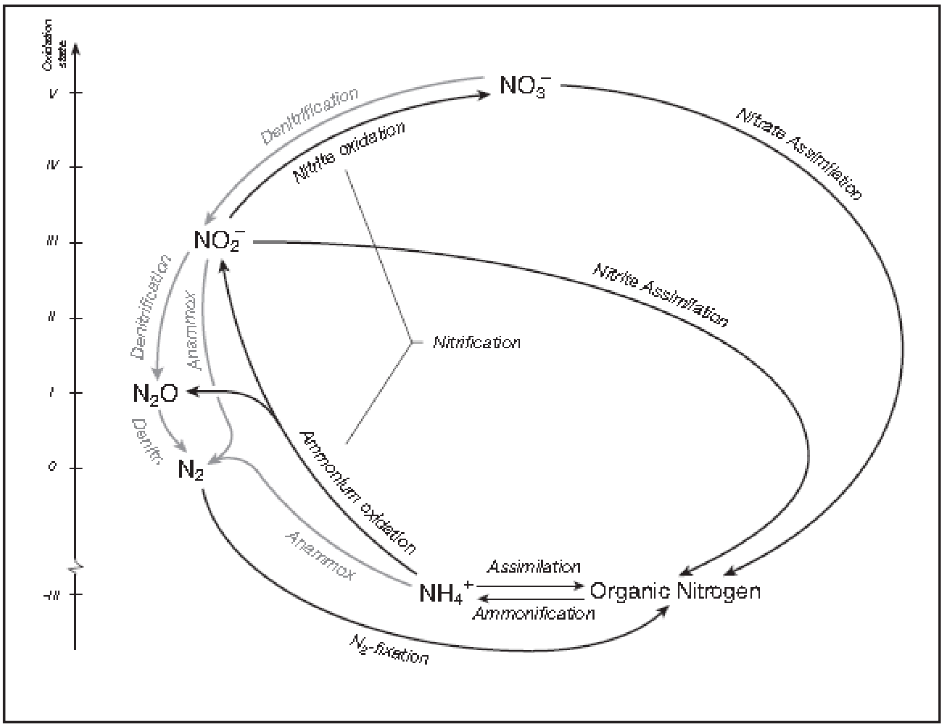


Figure 1.1: Major chemical forms and transformations of nitrogen in the marine environment. Processes shown in grey occur only in anoxic environments (Gruber, 2005).

By far the largest nitrogen inventory (94%) in the oceans is bio-unavailable N_2, and 88% of the remaining present as NO_3^- ion in the oceans. Dissolved organic nitrogen (DON) inventory makes up nearly all the remaining of 12%. Particulate organic nitrogen (PON), NO_2^-, NH_4^+ and N_2O altogether represent a minor fraction (<0.3%) of the total fixed nitrogen pool in the oceans (Gruber, 2005, see Table 1.1).

Global mean vertical profiles of NO_3, NH_4 and NO_2 have different features which are affected by biological pump and regeneration processes. Nitrate concentrations in the near-surface waters are generally low and increase with depth below the euphotic zone (EZ) (Gruber, 2005; Bronk and Ward, 2005). Nitrite and ammonium ions, on the other hand, reach maximum concentrations at the base of the EZ and then decrease rapidly under this boundary (Brzezinski, 1988; Hansell and Follows, 2008). Nitrite and ammonium concentrations accumulate appreciable levels only if, their production rate overwhelms their consumption rates (Dore and Karl, 1996; Gruber, 2005). For ammonium this occurs in the lower part of the euphotic layer where organic nitrogen rapidly remineralized and phytoplankton limited by light. Some part of this NH_4 is oxidized to NO_3 creating NO_2 alongside. Assimilation of NO_3 also creates NO_2 as an intermediary product which increase NO_2 concentrations in bottom of the euphotic layer. In the aphotic zone, neither NH_4 nor NO_2, are detectable levels due to nitrification process and utilizaton in photosynthesis (Christensen *et al.*, 1987; Zehr and Ward, 2002; Gruber, 2005).

In productive near-surface waters, NO_3^- concentrations are generally near or below detection levels over most of the oceans. However, in lower latitudes, where the upwelling is strong, the Equatorial Ocean and North Pacific surface waters have higher NO_3^- concentrations. Those regions are called HNLC (high nutrient low chlorophyll) regions where the nutrient concentrations are high but somehow the production is low (Libes, 1992; Wilson and Qui, 2008). NO_3^- concentrations in the interior ocean exhibits much more spatial variations than surface concentrations. Those variations are highly correlated with variations in PO_4^{3-}, dissolved inorganic carbon (DIC) and oxygen. While in the upper 500 m of the oceans, NO_3^- concentrations increase rapidly in tropics, but mid-latitude concentrations have much smaller gradients. And below 1000 m there exists a horizontal gradient which increases from the lower Atlantic concentrations to higher Pacific concentrations (Gruber, 2005).

Global mean concentration of DON for the surface ocean water is 5.8±2.0 μM averaged from a range between 0.8 to 13 μM (Bronk, 2002). Concentrations in the deep ocean are lower with the most measurements in 2 to 5 μM range (Jackson and Williams, 1985; Bronk, 2002). Concentrations tend to be progressively higher in coastal, then estuarine, and then riverine waters. In all environments, except the deep ocean, the bulk of total dissolved nitrogen (TDN) pool is in organic form, averaging 60-69% of the TDN pool (Bronk, 2002).

PON represents only about 0.5% of the total organic nitrogen pool. Its mean turnover time is only about 2 weeks (see Table 1.1), reflecting the rapid synthesis and degradation of PON (Gruber, 2005). In the euphotic zone, most of the POC is believed to be living matter, although the composition of PON is not well characterized. PON exists in size across several orders of magnitude, ranging from very fine suspended particles to large aggregates, such as marine snow or fecal pellets. In most cases, PON is highest near the surface and decreases quasiexponentially with depth (Gruber, 2005; see also Smith *et al.*, 2000). On a global mean, C:N ratios of marine sinking particles from the surface water amount to 7.1±0.1, and there is a systematic increase of C:N ratios with depth of 0.2±0.1 units per 1000 m (Schneider *et al.*, 2003).

Table 1.1: Oceanic inventory, turnover rates, and residence times for the major fixed nitrogen species in the ocean (adapted from Gruber (2005))

Species	Mean conc. euphotic zone (µM)	Mean conc. aphotic zone (µM)	Oceanic inventory (Tg N)	Turnover rate (Tg N/yr)	Turnover time (year)
Nitrate, NO_3^-	7	31	5.8×10^5	1570	370
Nitrite, NO_2^-	0.1	0.006	160		
Ammonium, NH_4^+	0.3	0.01	340	7000	0.05
Dissolved organic N, DON	6	4	7.7×10^4	3400	20
Particulate organic N, PON	0.4	0.01	400	8580	0.05
Nitrous oxide, N_2O	0.01	0.04	750	6	125
Fixed nitrogen*			6.6×10^5	200	3300
Nitrogen gas, N2	450	575	1×10^7	200	54000

**Sum of* NO_3^-, NO_2^-, NH_4^+, *DON, PON and* N_2O

1.1.2. Phosphorus cycling in marine environments

Compared to the much more comprehensive investigations of carbon and nitrogen dynamics in the sea, P pool inventories and fluxes and P dynamics in marine environment are less well documented though no less important (Benitez-Nelson, 2000; Karl and Björkman, 2002). With few exceptions, P in the sea is present in the pentavalent state (+5) as PO_4, whether as free orthophosphate or as P incorporated into either phosphate esters or phosphonate compounds. Phosphate has tetrahedral structure and does equilibrium reactions according to acidity of the existing media.

$$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+ \leftrightarrow HPO_4^{2-} + H^+ \leftrightarrow PO_4^{3-} + H^+$$

The oceanic pH is about 8.2 thus phosphate mainly exists as orthophosphate form (HPO_4^{2-}).

Instead of defining phosphorus compounds as a molecular formula basis, most of the studies identify P component operationally. That is; the differentiation is based on their reactivity with molybdate, ease of hydrolysis and particle size (Murphy and Riley, 1962; Strickland and Parsons, 1972). Dissolved inorganic P forms called as DIP (or SRP as soluble reactive forms) and generate molybdophosphoric acid complex under acidic conditions. Orthophosphate is the main component of DIP (87%) and most bioavailable form for planktonic organisms (Delaney, 1998; Benitez-Nelson, 2000; Baturin, 2002). Soluble P that does not form molybdophosphoric acid complex called as SNP (soluble non-reactive P). SNP is usually equated to dissolved organic P (DOP) however, this fraction may also includes inorganic forms, such as polyphosphates (Benitez-Nelson, 2000). Particulate fractions generally composed of biologically derived organic matters.

Phosphorus compounds are principally supplied into the ocean from continents mainly with river runoff via the weathering of crustal materials, which contain average of 0.1% P_2O_4 (Delaney, 1998; Benitez-Nelson, 2000). Phosphorus exists in the river runoff as solution and suspended matter in both inorganic and organic forms (see Table 1.2). Despite the fact that there is no significant stable gaseous form of phosphorus, importance of atmospheric input of phosphorus increases with increasing distance from coastal areas. Especially in oligotrophic waters, atmospheric deposition may be a significant source of P for the upper ocean. Atmospheric flux of P accounts for less than 1% of new production in the oceans. However short burst in fluxes, particularly on springs, could elevate biological productivity over brief periods. For example, discrete pulses of P to the oligotrophic, P limited regions increase plankton biomass and carbon export over short timescales (Jickells, 1995; Benitez-Nelson, 2000).

Table 1.2: Pre-anthropogenic marine P sources and sinks (Benitez-Nelson, 2000 reference therein)

SOURCES	
Riverine	TDP: 3-15x10^{10} mol P yr^{-1}
Atmospheric	Soluble reactive P: 1x10^{10} mol P yr^{-1}
Volcanic	Unknown, but most likely of only regional impact
Total	4-16x10^{10} mol P yr^{-1}
SINKS	
Organic matter burial	1.1-4.1x10^{10} mol P yr^{-1}
Precipication with oxohydroxides and clay adsorption	1.45-5.3x10^{10} molP yr^{-1}
Phosphorite burial	>8x10^{10} mol P yr^{-1}
Hydrothermal	0.4-0.65x10^{10} P yr^{-1}
Total	11-34.1x10^{10} mol P yr^{-1}
RESIDENCE TIME	Assuming a global P inventory of 3.2x10^{15} mol P
Maximum estimate	20,000-80,000 years (based on sources)
Minumum estimate	9300-29,100 years (based on sinks)

The primary net removal mechanism for P in the open ocean is via gravitational settling of particulate matter, downward diffusion and advection, and for selected regions of the world's ocean, horizontal transport (Delaney, 1998; Karl and Björkman, 2002).

Since riverine input is the major source for P, SRP concentrations tend to decrease with increasing distance from the continent. SRP concentration decreases with summer time stratification and increases with strong vertical winter mixing.

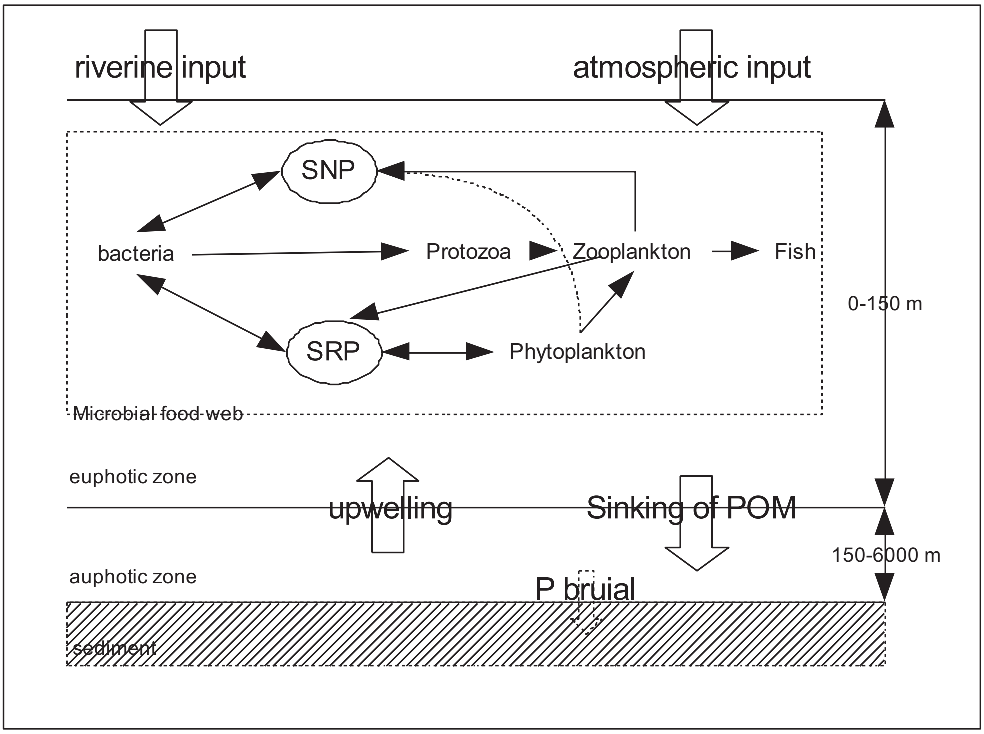


Figure 1.2: Pre-anthropogenic marine P cycle (Benitez-Nelson, 2000)

While, high nutrient input via rivers increases the P concentration on coastal oceans, it is also give rise to plankton blooms which decreases concentration of bioavailable P. SRP and nitrate maxima tend to coincide with the deep water oxygen minimum. Above that point, biological uptake depletes P concentration which results in decreasing P concentration with increasing depth. Below about 1000 m, SRP concentration tend to be constant at around 2-3 µM in the oceans (Benitez-Nelson, 2000, see Figure 1.3).

Biogeochemical cycles of C, N and P in the sea are ultimately sustained by solar energy via the process of photosynthesis. Consequently, DOP production is highly correlated with the primary formation of organic matter in the EZ. In surface waters, DOP concentrations range from less than 0.2 µM (North Atlantic, North Pacific) to 1.7 µM (Azov Sea) (Benitez-Nelson, 2000). DOP concentration may constitute even 75% of TDP pool in open surface waters. The contribution of DOP to the total phosphorus pool decreases with increasing depth with the increasing contribution of SRP. DOP concentrations at depths below 300 m are consistently less than 10% of the total TDP, indicating deep-P dominated by SRP (Karl *et al*., 2001; Karl and Björkman, 2002). In spite of these broad generalized patterns of DOP in the world ocean, local and regional variations are also evident. DOP is enriched by point or non-point sources of nutrient inputs in most coastal and estuarine habitats that have been investigated (Karl and Björkman, 2002).

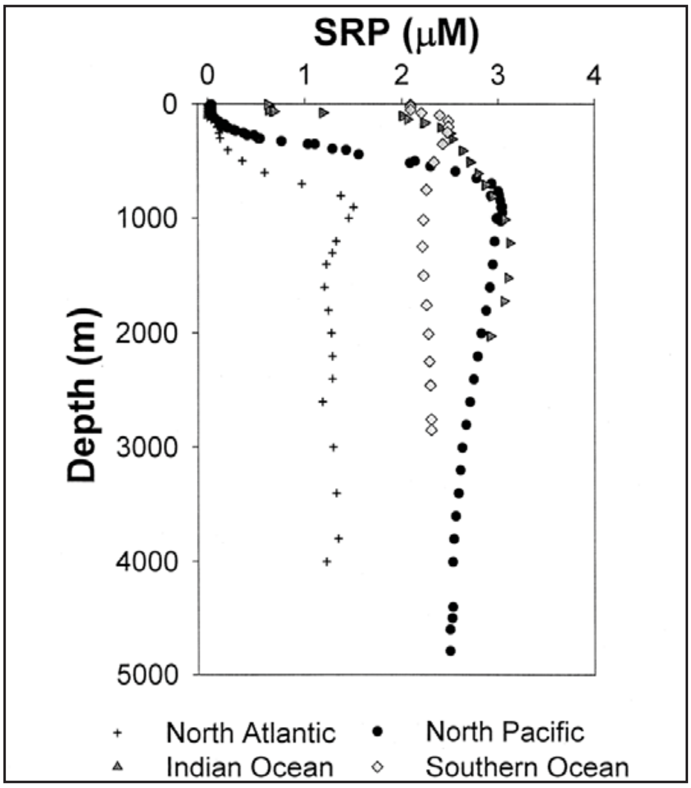


Figure 1.3: Typical distributions of SRP in the world's major oceans (Benitez-Nelson, 2000).

Though little is known about the distribution of P within the different fractions in marine particulate matter (Faul *et al*., 2005), several studies reveal that the particulate phosphorus (PP) is mainly composed of an organically bound form derived from biological materials (Clark *et al.*, 1998; Delaney, 1998; Suzumura and Ingall, 2004; Faul *et al.*, 2005). PP content in the studied samples from the wide range of oceanic regimes were analysed in the study of Faul et al. (2005). They reported that P in the sediment traps is typically composed of reactive P components including acid insoluble organic P (~40%), authigenic P (~25%), and oxide associated and/or labile P (21%), with lesser proportions of non-reactive detrital P depending on location (~13%). The concentrations and fluxes of all PP components decrease or remain constant with depth, indicating some regeneration of reactive P components (Faul *et al.*, 2005).

1.2. Principle Hydrochemical Properties of the Eastern Mediterranean Sea

The Levantine Sea in the NE Mediterranean is surrounded by the Turkish coasts on the north, and Israel, Lebanon and Syria on the east. Crete Island on the western side forms passages for the western Mediterranean and Aegean Sea: It has the biggest continental shelves of the NE Mediterranean (Fig. 1.4). The coastal shelves of the Levantine Sea are connected to the deep basin with 10-20 km decline belts (Oğuz and Tuğrul, 1998).

1.2.1. Hydrography and circulation patterns in the Eastern Mediterranean

The general circulation consists of three major elements; the cyclonic Rhodes gyre, a large feature with two eddy centers approximately located at the deep basin south of Rhodes, and a third one extending eastward toward Cyprus; the anti-cyclonic Mersa-Matruh gyre, the intense feature located to the south of the Rhodes gyre; and the anti-cyclonic Shikmona gyre, the large cell with three separate centers and which occupies the rest of the southern part of the Levantine basin (Özsoy *et al.*, 1991). Although their shapes may change to some degree those features are always recognized (Özsoy *et al.*, 1991; POEM Group, 1992; Souvermezoglou and Krasakopoulou, 1999). There is an eastward-flowing coherent jet, the Central Levantine Basin Current, which appears to be a continuation of the North-African Current, between the Rhodes gyre and the Mersa-Matruh and Shikmona gyres (Özsoy *et al.*, 1991).

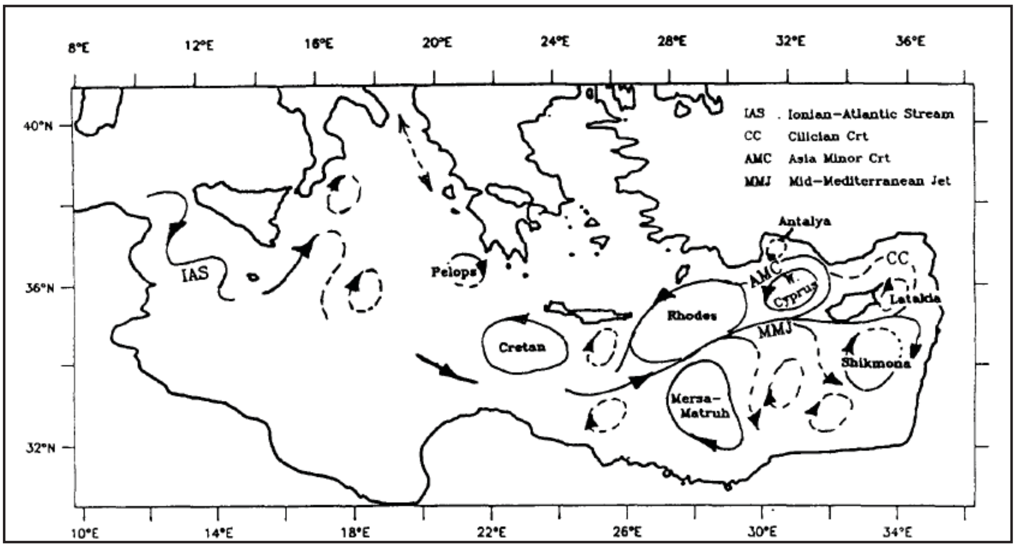


Figure 1.4: General circulation patterns in the Eastern Mediterranean (Özsoy *et al.*, 1991).

There are four main water masses in the water column of the Levantine Basin, which are distinguished by climatological salinity profiles (Özsoy *et al.*, 1991; Kress and Herut, 2001). According to salinity profiles, these water masses are; surface water (SW) with salinity ≥ 38.95 between 0-40 m, Atlantic water (AW) (enters to Mediterranean from the Straits of Gibraltar and afterwards sinks until 65-95m) ($S \leq 38.87$), Levantine intermediate water (LIW) which has a salinity of ≥ 38.94 and stands between 200-310 m, and deep water (DW) found below 700 m ($S < 38.74$) (Kress and Herut, 2001).

LIW affects not only the entire Mediterranean but the Atlantic Ocean as well. The northern Levantine Basin, specifically the Rhodes gyre (Souvermezoglou and Krasakopoulou, 1999), driven by surface buoyancy fluxes is identified as the main source region of LIW. On the other hand, the basin-wide heterogeneous distribution and year-around persistence of the LIW point to the role of interior dynamics in maintaining it (Özsoy *et al.*, 1993). The mechanism of the formation of LIW is not known exactly. However, as a general explanation, high evaporation and vertical mixing result in cooling and salinity increase in surface water during winter, then these water masses tend to sink convectively (Özsoy *et al.*, 1993, Souvermezoglou and Krasakopoulou, 1999), and reaching intermediate depths in late winter-early spring period (Özsoy *et al*., 1989).

AW enters Mediterranean through straits of Gibraltar then passes through Sicily channel into the Eastern Mediterranean. Its salinity is minimum among all the water masses in the region and salinity and the depth range increases as it flows eastward (Özsoy *et al*., 1989).

The origin and the formation of the eastern Mediterranean deep waters (EMDW) are poorly understood (Özsoy *et al*., 1989). There are two possible sources for EMDW. The Adriatic Sea is the main source region of the EMDW (Pollak, 1951; Zavatarelli *et al*., 1998; Souvermezoglou and Krasakopoulou, 1999). Winter winds that prevailing over the Northern Adriatic result in high surface heat loss which creates high amounts of water sinking through the Southern Adriatic. Then through the Otronto Channel, DW outflow into Levantine. Such flow is confirmed by the distribution of oxygen in the DW of the entire eastern Mediterranean Sea. DW of the eastern Mediterranean are formed primarily in the Adriatic, but recently Roether et al. (1996) and Klein et al. (1999) observed changes in the deep thermohaline circulation of the eastern Mediterranean, with the Aegean Sea contributes the major source of DW. This change in the thermohaline circulation was traced back to 1991 (Malanotte-Rizzoli *et al*., 1999).

1.2.2. Hydrochemistry of the Eastern Mediterranean

Eastern Mediterranean hydrophysical and hydrochemical features were analyzed within various detailed studies in recent decades. While these studies have given adequate answers for key points of the regime, there still exist a lot of unexplained cases like the exact reasons of P limitation of the system (Krom *et al*., 1991; Benitez-Nelson, 2000; Kress and Herut, 2001; Kress *et al.*, 2005;).

Vertical distributions of dissolved oxygen (DO) display a similar structure to salinity profiles, decreasing with depth in the eastern Mediterranean Sea. From the surface to 100 m depth DO concentrations range between 250-300 μM levels with almost 100% saturation. Euphotic layer depths are shallower in cyclonic regions; about 75-85 m thick whilst in anticyclonic regions the boundary of the euphotic layer is reached at 110-120 m (Yılmaz and Tuğrul, 1998). Under the euphotic layer DO concentrations tend to decrease with increasing depth until reaching constant deep water concentrations (180-200 µM). In the cyclonic regions, due to absence of LIW waters, the decline of DO concentrations is very steep, coinciding with the pycnocline. DO concentrations in the deep waters vary with depth and location; however, concentrations have similar density profiles which imply the rapid horizontal movement of deep water without creating significant regional differences (Oğuz and Tuğrul, 1998; Yılmaz and Tuğrul, 1998; Ediger *et al*., 2005).

The North Levantine Sea shows different spatial and seasonal features in terms of nutrient concentrations. In offshore areas receiving limited inputs from coastal waters, the upper 50-100 m layer has lower nutrient concentrations. Under the EZ, however, concentrations increase with increasing depth until reaching constant values of the deep layer. The N/P ratios are higher in deep waters, implying that phosphorus limitation controls primary production (Yılmaz and Tuğrul, 1998; Ediger *et al*., 2005). The shape of the nutricline in the Levantine is naturally dependent on the hydro-physical characteristic of the region. In cyclonic regions, such as the Rhodes gyre, the nutricline appears just under the boundary of the euphotic layer and forms a very sharp incline. The nutricline may even disappear in very severe winter conditions. In anticyclonic regions (Antalya, Cilician Basin), the nutricline is formed at greater depths and continues until depths of 500-600 meters (Oğuz and Tuğrul, 1998).

1.2.2.1. Distributions of total nitrogen and total phosphorus in the Eastern Mediterranean

Since total nitrogen (TN) and total phosphorus (TP) analyses require much effort, previous studies have mostly ignored these parameters. Early basin scale TP observations in the Eastern Mediterranean were conducted in the 60’s during the cruise of RV Atlantis and RV Chain (Miller *et al.* 1970). Those observations were limited to regions around the Rhodes gyre and Antalya bay; however, they gave a basic idea of TP distribution in the Eastern Mediterranean.

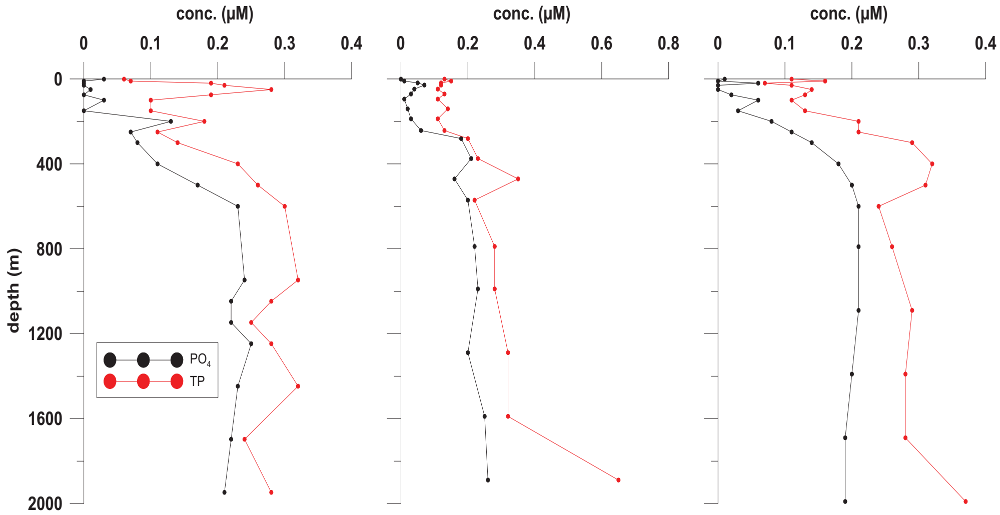


Figure 1.5: Depth profiles of PO_4 and TP from the data collected during expedition of RV Atlantis and RV Chain (Miller *et al.* 1970).

Despite the fact that TN and TP data are very limited in the Eastern Mediterranean, some studies at regional scales have illustrated the basic distributions of these properties in the water column. Due to the contribution of POM, TP concentrations tend to be higher than PO_4 concentrations in surface water. While PO_4 is depleted in the EZ with average concentrations of 0.02-0.03 µM, mean TP values were around 0.10-0.15 µM in the open waters. Under the EZ, TP concentrations increase with depth until reaching constant deep water values (0.30-0.40 µM). In the deep layer water of the NE Mediterranean, the TP pool is mostly dominated by PO_4.

Similar to the other nutrient elements, TP concentrations are high in coastal areas. Land based sources such as rivers and domestic discharges increase TP concentrations in the coastal sea to levels of 1.5-2.0 µM (Mersin Bay; Doğan-Sağlamtimur, 2007). Since the Eastern Mediterranean has a highly oligotrophic character, land-based nutrient fluxes increase primary production in coastal zone but their effect is very limited in the offshore waters of the NE Mediterranean (Eker-Develi, 2004; Ediger *et al*., 2005; Eker-Develi, 2006; Doğan-Sağlamtimur, 2007).

TN data from the Eastern Mediterranean are very sparse. Nevertheless, the distributions may be estimated from inorganic nitrogen concentrations plus very rare

DON data from previous studies. Krom et al. (2005) measured the DON in the southern Cyprus warm eddy during CYCLOPS P addition experiment. According to that study the surface DON concentrations change from between 4.5-11.5 µM concentrations in the upper 50 m depth to a constant level of ~2.0 µM below 350 m. The decrease of the DON concentrations below 350 m corresponds with an increase in NO_3 concentrations from 0.3-0.5 µM to 4.5-5.0 µM levels. Uncertainties in the TN pool in the Eastern Mediterranean are mostly due to uncertainties in DON distributions.

Unfortunately, TN distributions at regional scales in the Eastern Mediterranean were not reached in the literature. Nevertheless, it is well known that in the coastal areas, with the contribution of the land-based sources, dissolved inorganic nitrogen (DIN) are high, especially in the coastal zone of agricultural areas where ammonia concentrations may reach 4-5 µM levels. Thus, we expected to observe that the TN concentrations are to be high in the coastal regions due to large contribution of DON to the TN pool in the productive regions. Apparent decreases are expected in the surface TN values in the open sea.

1.2.2.2. Distributions of inorganic nutrients in the Eastern Mediterranean

As it is mentioned above, the Levantine basin circulation consists of a series of dynamically interacting cyclonic and anti-cyclonic eddies. Hydrographically it is possible to group whole area into three discrete regions which are the cyclonic Rhodes basin, the anti-cyclonic Cilician basin and transitional areas between the cyclonic and the anti-cyclonic basins (Özsoy *et al.*, 1991; Yılmaz and Tuğrul, 1998; Ediger *et al*., 2005). Different hydrophysical features of these regions dominate nutrient concentrations and vertical features in the upper 1000 m. In the Rhodes cyclonic gyre, where the vertical mixing is strong during the year, the concentrations of dissolved nutrients are almost constant through the whole water column under the EZ. In anti-cyclonic basins, however, vertical mixing keep the Levantine Deep Water (LDW) at much greater depths. The nutricline is thus formed between 300-500 m depth, depending on the location in the anticyclonic eddies (Yılmaz and Tuğrul, 1998).

In the Eastern Mediterranean, there are two important phenomena dominating seasonal variations of nutrient concentrations in the water column. In winter, surface waters mix with LDW with high nutrient concentrations in the cyclonic gyre. This winter mixing increases the EZ nutrient conentrations available for primary production. In this period, the nutricline can rise up to the base of the ephotic zone in the peripheries and even reaches the surface layer in the core of the cyclone (Yılmaz and Tuğrul, 1998; Ediger *et al*., 2005).

In winter, nutrient flux from LDW to the EZ through the nutrient-poor LIW is very limited in the anticylonic eddies. In the stratification seasons (spring to autumn) the LIW layer is stagnant and it receives a net input of labile particulate nutrient from the surface layer. During this period, dissolved inorganic nutrient content of the LIW is expected to increase slightly (Yılmaz and Tuğrul, 1998).

The eastern Mediterranean surface waters have relatively low PO_4 and NO_3 concentrations. Except the coastal regions, average surface concentrations are about 0.02-0.03 μM for phosphate and between 0.1-0.3 μM for nitrate (Yılmaz and Tuğrul, 1998) for most of the year. In the Rhodes cyconic gyre, the EZ (about 75-80 m), is also depleted in nutrients during spring-autumn period. In winter, upwelling of LDW supplies nutrients to the EZ (Ediger *et al*., 2005). Phosphate and nitrate concentrations thus increase to levels of 0.2-0.3 μM and 4-6 μM for phosphate and nitrate respectively, similar to the LDW values remaining almost constant with depth.

The NO_3/PO_4 (N/P) molar ratio of the Eastern Mediterranean has been studied extensively by Yılmaz and Tugrul (1998). According to that study; the N/P molar ratios in the Eastern Mediterranean water column vary substantially with depth. It has been estimated to be as low as 5-20 in the surface layer, with the assumption that phosphate concentration under the detection level were given as 0.02 μM (<0.02 μM). More reliable data were gathered as 25-29 in severe winters when the surface waters were enriched with nutrients by input from lower layers and the phosphate concentrations exceeded the detection level (>0.02 μM). Below the EZ, because of the shift between the onsets of the nitracline and phosphocline, N:P molar ratios exhibited anomalously high (40-120) values at the top of the nutricline. The maximum of N:P ratio appears at different depths over the basin (50-100 m in the Rhodes cyclonic region, 150-300 m in the anti-cyclonic region), corresponding to the depths of 39.1 psu salinity and sigma-t: 29.05 surface. The basin-wide average of the N:P ratio remained almost constant, ranging merely between 26-28 in the LDW.

1.3. Previous Works in Methodology

Nutrient determination in the sea water can be performed by colorimetric measurements methods developed for each parameter. In the manual method, each sample is treated individually and manually for each variable. However, automated versions of the manual methods have been applied to marine samples to provide simultaneous multivariable analyses (Koroleff, 1983). Here, it is aimed to summarize previous studies regarding the simultaneous treatment of total and organic nitrogen and total and organic phosphorus in sea water samples.

Determination methods of total and/or organic nitrogen and phosphorus in sea water samples were studied by many researchers in recent decades (Krogh and Keys, 1934; Armstrong *et al*., 1966; D'Elia *et al*., 1977; Solorzuno and Sharp, 1980; Valderemma 1981; Koroleff, 1983). It has been shown that the oxidation of phosphorus compounds in seawater by persulphate is achieved in both acidic and alkaline media, of which the latter one is superior at decomposing organically bounded phosphorus compounds (Grasshoff *et al.* 1983). The oxidation of nitrogen either with an oxidant aided by heating or UV light or high temperature catalytic oxidation are the prominent determination methods in the literature for total and organic nitrogen compounds.

Simultaneous digestion of TP and TN was firstly introduced by Koroleff in 1977 based on oxidation of the sample and the subsequent separation into portions to analyse TP as PO_4 and TN as NO_3 (Koroleff, 1983, reference therein). NO_3 and PO_4 analyses are performed by the conventional colorimetric methods (Strickland and Parsons, 1972; Grasshoff *et al.* 1983). Digestion with this method is done by autoclaving the sample with oxidants. Nearly 5 g of $K_2S_2O_8$ and 3 g of H_3BO_3 in 100 mL of 0.375 M NaOH are used as the oxidizing reagent. Then 5 mL of oxidating reagent is added into 50 mL of seawater sample of which 5 mL of the total amount is withdrawn for NO_3 analysis and the remaining used for the PO_4 after the completion of oxidation.

Solarzano and Sharp (1980) have introduced separate procedures for TDN, TDP and PP analyses. TDN procedure is presented for routine analysis using oxidation by potassium persulfate. Alkine conditions (pH 12.6-13.2) were adjusted by using NaOH solution. The method for TDP and PP procedures involves drying a sample with magnesium sulphate and baking the residue at a high temperature to decompose organic phosphorus compounds.

Valderemma (1981) applied different tests in order to determine characteristics of the persulphate oxidation method for the simultaneous determination of TN and TP in water. In that study, comparison tests with former methods for TP and TN were determined and analytical capabilities of the method were revealed.

Bronk et al. (2000) have made a comparison study on the persulphate, UV and high temperature combustion (HTC) methods for TDN analysis. They have concluded that the persulphate and high temperature oxidations can provide reproduciple results with consistency with each other; however, the standard UV method has been found to be highly unpredictable in practice.

In 2002, an inter-comparability of DON measurements was carried out within the study of Sharp *et al.*(2002). A set of 29 samples from five different marine environments were analysed using three groups of measurement techniques. Calculations of DON were done by subtracting DIN values from TDN values. This study has show that more uniformity in procedures is probably needed, since there is much scatter in each of the groups of the methods and for analysis when grouped. Another important unplanned observation is that the variability in DIN analysis is essentially as variable as in the TDN analyses.

The method that we used in this study was improved by Raimboult *et al*. (1999). The main contribution of this method is to allow the simultaneous determination of organic carbon, nitrogen and phosphorus in sea water samples. Different from the former methods, it permits us to provide direct measurements of the sample with the automated analysis from the same sample container, which is followed by autoclave digestion. High precision and accuracy were gathered within the comparisons with the former determination methods. The method is highly suitable for the routine analyses. Detailed information about the method will be introduced in the following chapters.

1.4. Previous Works in the Study Area

Nevertheless, DON and DOP have been ignored in most of the previous investigations in the study area, nutrient dynamics of the Eastern Mediterranean has been investigated extensively in many competent studies (see POEM Group, 1992; Zohary and Robarts, 1998; Yılmaz and Tuğrul, 1998; Kress and Herut, 2001; Eker-Develi, 2004; Ediger *et al*., 2005; Krom *et al*., 2005). Oligotrophic conditions and phosphorus deficiency have become a primary focus of interest in the Eastern Mediterranean Basin in this sense. In addition to that, many basin-scale projects have been carried out to monitor eutrophication levels and to assess pollution sources in the coastal shelves.

From 1985 to 1990 and from 1990 to 1995 the POEM program performed a series of cruises in the Eastern Mediterranean, which gathered valuable information about the current systems and hydrography of the large basin.

In order to further understand phosphorus cycling in the Eastern Mediterranean, CYCLOPS project has been carried out by the participation of several institutions in SE Mediterranean off Cyprus Island, between May 2001 and May 2002. Then a series of articles have been published, revealing the results of the experiments and hypotheses on possible reasons of P starvation in the system and the ecosystem dynamics dominating that situation. Within the project, Krom (2005) have presented a data set of dissolved and particulate nutrient elements (C, N, P) in the Eastern Mediterranean.

Yılmaz and Tuğrul (1998) have described the effects of cold and warm eddies on the distribution and stoichiometry of dissolved nutrient in NE Mediterranean. According to their study, nutrient distributions in the Levantine Sea are principally determined by the duration and the intensity of deep winter mixing in the quasi-permanent anti-cyclonic and cyclonic eddies. It has been investigated that the quasi-permanent nutriclines appeared at a specific density surface throughout the Levantine Basin even though their depths has been varying markedly with space and time. The upper boundary of the phosphate gradient zone was suited at a greater density surface which has resulted in the appearance of anonymously high N/P ratios in the upper nitracline depths. It has been concluded that the LDW have a relatively high N/P ratio (~26-28), greatly exceeding the classical Redfield ratio of 16 for the deep oceans. They have suggested that the sinking water, selectively enriched with labile, dissolved organic and inorganic nitrogen constituents, was the most probable source of the high N/P ratios in the LDW.

Dissolved organic nutrient dynamics in the Mediterranean Sea have been poorly investigated in recent decades. Some studies, however, have represented the distribution of DOM in the Western Mediterranean Basin. It is known that the Western Basin of the Mediterranean has quite different features as compared to the Eastern Mediterranean but these studies may give a rough picture of DOM cycling in oligotrophic waters. In this context; Doval *et al*. (1999) have demonstrated that the Catalan coastal waters of the NW Mediterranean in June 1995 during the stratified period were depleted inorganic nutrient, with well established deep chlorophyll-a maximum. They have observed that DOC and DON concentrations were 44-95 μM and 2.8-6.2 μM, respectively, with a DOC/DON molar ratio of 15.4 on average. Lucea (2003) have examined the distributions of nutrients in different layers (the upper, biogenic layer, the thermocline layer and the deeper, biolythic layer) of the stratified NW Mediterranean Sea. They have shown that DOM was highly depleted in N and in P relative to DOC. It was also concluded that the dissolved organic components dominated the pools of TN and TP in the biogenic layer, shifting to a dominance of dissolved inorganic nutrient pools below the thermocline. DOC, DON and DOP were measured in deep profiles of the NE Atlantic and NW Mediterranean during the period from 1984-2002 as described in the study of Aminot and Kerouel (2004).

In the scope of the Mediterranean Pollution Program (Tuğrul *et al.* 2009), compliance monitoring studies have been carried out at the discharges (rivers, municipal and industrial waste waters) of land based source along the Eastern Mediterranean and the Aegean coastal sites. This project aims to monitor and assess level of eutrophication in Mersin bay. During the program, the spatial and seasonal variations of nutrient concentrations have also been studied extensively in our study area.

1.5. Objectives of the Study

The main objectives of this study are:

- To introduce a practical analysis method which allows simultaneous measurement of TN and TP in seawater,
- To demonstrate the accuracy and precision of the selected method for TN, TP analysis in salty water,
- To compare the results of manual and automated methods for the determination of TP in seawater,
- To compare closed digestion and open digestion methods for the determination of TP,
- To show the spatial and regional distributions of the biochemical parameters obtained during the 2008-2009 period in the Cilician basin of the NE Mediterranean and to understand the dynamics of these parameters and their interrelations,
- To depict the spatial distributions of nitrogen and phosphorus fractions (total and dissolved organic forms) in the study region.

CHAPTER 2

EXPERIMENTAL

2.1. Sampling Locations and Strategy

In order to determine seasonal and spatial distributions of principal biochemical properties of the Cilician shelf zone, NE Mediterranean, 50 sampling locations were chosen in Mersin Bay (Fig 2.1) within the scope of TUBITAK-SINHA Project (No:107 G 066). The present station network will permit us to understand the extent of water exchanges between the inner bay waters and the open sea. The coordinates of the sampling locations are given in Table 2.1.

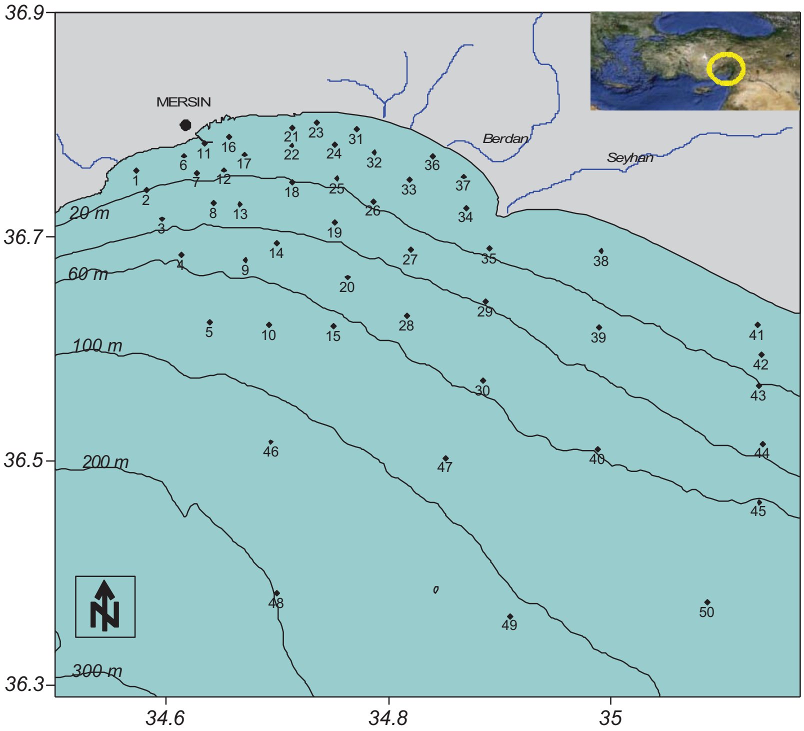


Figure 2.1: Station network visited in the Mersin Bay shelf zone.

The stations in Fig. 2.1 were visited 7 times in the period 2008-2009. In September 2008, the first cruise was carried out. Second, third and fourth cruises were made in January, February and March 2009 to examine the effect of winter cooling and vertical mixing on the shelf ecosystem. Fifth cruise was held in April 2009, representing spring condition in the region. The last two cruises were performed in August and October 2009.

2.2. Measurements of Physical Parameters

During field surveys, *in situ* measurements of physical parameters were carried out by a SEABIRD CTD probe fitted to a 12-bottle Rosette system. CTD data were gathered from downcasts. Sensitivities of salinity and temperature measurements were 0.001 psu and 0.0005 ^{o}C respectively.

2.3. Samplings for Biochemical Parameters

2.3.1. Sampling for dissolved oxygen

Sea water samples for biochemical measurements were taken at standard depths at the selected stations from the surface down to the near-bottom. DO sub-samples were collected in 100-ml Pyrex bottles. At least twice the volume of the bottle was overflowed with the sample in order to flush the bottles before it was finally filled. The transferring tube was then slowly withdrawn from the bottle while water was still flowing. Manganese (II) chloride and alkaline potassium iodide solutions were added immediately. Bottle stoppers were placed carefully to avoid the presence of any air bubbles. Samples were shaken vigorously to ensure the reagents were diffuse completely and stored in a dark media for at least 30 minutes to ensure completion of the reaction (APHA, 2005; Carpenter, 1965).

2.3.2. Sampling for dissolved inorganic nutrients

Samples of inorganic nutrients were collected in high density polyethylene (HDPE), 100 ml Nalgene containers. Before sampling, a pre-treatment procedure was applied. Sample bottles were flushed with diluted HCl and rinsed several times with double distilled water (DDW). Transfers of the samples were carried out using 15-20 cm silicone tubing. Sample bottles were washed several times with the sample itself before final filling. Analyses commenced as soon as possible after the sample collection, within 30 min-2 hours. If immediate analysis were not possible, the samples stored in a refrigerator at +4^{o}C and not warmed to room temperature until analysis (Strickland and Parsons, 1972; Grasshoff *et al.* 1983; Dore and Karl, 1996).

Table 2.1: Coordinates of the sampling locations visited in the Mersin Bay.

St.	***Degree, Minute, Second***		***Biochemistry***	
	Latitude	**Longitude**	***Profile***	***Surface***
1	36°45'32"N	34°34'24"E		**X**
2	36°44'30"N	34°34'59"E	**X**	
3	36°42'56"N	34°35'49"E		**X**
4	36°41'1"N	34°36'49"E	**X**	
5	36°37'25"N	34°38'22"E		**X**
6	36°46'20"N	34°36'59"E	**X**	
7	36°45'25"N	34°37'40"E	**X**	
8	36°43'47"N	34°38'35"E		**X**
9	36°40'44"N	34°40'17"E		**X**
10	36°37'16"N	34°41'34"E	**X**	
11	36°47'0"N	34°38'7"E	**X**	
12	36°45'34"N	34°39'7"E	**X**	
13	36°43'42"N	34°40'0"E	**X**	
14	36°41'38"N	34°42'0"E	**X**	
15	36°37'13"N	34°45'2"E		**X**
16	36°47'19"N	34°39'24"E	**X**	
17	36°46'24"N	34°40'13"E	**X**	
18	36°44'53"N	34°42'48"E	**X**	
19	36°42'45"N	34°45'5"E		**X**
20	36°39'49"N	34°45'48"E		**X**
21	36°47'51"N	34°42'48"E	**X**	
22	36°46'53"N	34°42'47"E	**X**	
23	36°48'6"N	34°44'7"E		**X**
24	36°46'56"N	34°45'8"E		**X**
25	36°45'7"N	34°45'13"E		**X**
26	36°43'54"N	34°47'11"E		**X**
27	36°41'17"N	34°49'12"E	**X**	
28	36°37'45"N	34°48'59"E	**X**	
29	36°38'32"N	34°53'16"E		**X**
30	36°34'18"N	34°53'5"E		**X**
31	36°47'45"N	34°46'16"E		**X**
32	36°46'31"N	34°47'14"E		**X**
33	36°45'3"N	34°49'9"E	**X**	
34	36°43'33"N	34°52'11"E	**X**	
35	36°41'23"N	34°53'28"E		**X**
36	36°46'19"N	34°50'23"E		**X**
37	36°45'13"N	34°52'5"E		**X**
38	36°41'14"N	34°59'28"E	**X**	
39	36°37'9"N	34°59'21"E	**X**	
40	36°30'36"N	34°59'19"E	**X**	
41	36°37'16.8"N	35°7'53.8"E		**X**
42	36°35'39.5"N	35°8'5.400"E		**X**
43	36°33'59.8"N	35°7'59.7"E	**X**	
44	36°30'55"N	35°8'11.46"E		**X**
45	36°27'47.4"N	35°8'0.72"E		**X**
46	36°31'0.2"N	34°41'40.2"E	**X**	
47	36°30'9.7"N	34°51'5.7"E	**X**	
48	36°22'55.4"N	34°42'0.4"E	**X**	
49	36°21'41.3"N	34°54'34.5"E		**X**
50	36°22'25.1"N	35°5'10.7"E		**X**

2.3.3. Sampling for total nitrogen and total phosphorus

Subsamples were taken into 125 ml of Schoot bottles, which were cleaned with dilute acid and were digested with DDW+mixed oxidation reagent before use. Teflon sealed taps were used with the bottles during storing and autoclaving. Pre-digested bottles were rinsed with seawater samples and then filled to near the bottle neck. Collected samples were stored frozen (-18°C) until analysis, without adding any chemicals for preservation. Mostly organic nitrogen compounds and ammonia are volatile and may contaminate the samples. Therefore, high care had been paid to minimize the risk of contaminations (Raimboult, *et al*. 1999).

When Schoot bottles were not available during the cruise, sub-sampling protocol for DIN could be followed for TN and TP. Generally, parallel samples were taken from selected depths.

2.3.4. Sampling for particulate organic matter and chlorophyll-a

Sampling of POC and PON were done by 25 mm GF/F filters on cruise. Suitable amounts of water were filtered through the GF/F filters with using 2 liter volumed Nalgene gaskets. Filters are pre-combusted at 450 °C for 4-5 hours and stored in aluminum foils which were also combusted with the filters. POC and PON sampling were performed in the same filter to enhance stability of the sampling. 2 or 3 parallel samplings were done to increase the precision of the measurement.

Chlorophyll-a samples were collected in dark colored Nalgene containers. Appropriate amount of water (1-2 liter) were filtered through the 47 mm GF/F filters and kept in a freezer until analysis.

2.4. Measurement Methods of Chemical Parameters

2.4.1. Dissolved oxygen analysis

Oxygen dissolved in sea water is almost exclusively determined by the chemical method first proposed by Winkler (1888) and modifications thereof. The Winkler method is an iodometric titration in which DO in sea water oxidize iodide ion to iodine with a multi-step oxidation, using manganese as a transfer medium (Grasshoff *et al.* 1983). Then liberated iodine titrated with 0.0125 N thiosulphate solution. Automated potentiometric titration was applied for the collected DO samples.

2.4.2. Dissolved inorganic nutrient analysis

A four-channel type Bran Luebbe auto analyser system equipped with AACE 6.04 software was used to determine dissolved inorganic nutrients in seawater samples. Analyses were mostly conducted onboard very soon after the sampling. Standard methods proposed in Bran Luebbe Auto Analyser Applications Booklet were applied for phosphate (method no: G-175-96, MT18), nitrate (G-172-96, MT 19), ammonia (G-171-96, MT19) and silicate (G-177-96, MT19). Samples were run against low nutrient seawater (LNSW) as a baseline in phosphate, ammonia and silicate and DDW in nitrate.

2.4.2.1. Dissolved inorganic phosphate (PO_4-P) analysis

Dissolved inorganic phosphate (DIP) analysis with the AA system is based on the formation of a blue colored complex with phosphate and acidified molybdate. To obtain rapid color development and avoid the interference of silicate, the final pH level was adjusted less than 1. The constant wavelength value of the detector is 880 nm. The detection limit of the automated analysis is given as 0.015 μM (Strickland and Parsons, 1972; Grasshoff *et al.* 1983; Koroleff, 1983).

2.4.2.2. Total oxidized nitrogen (NO_3+NO_2-N) analysis

The applied procedure for nitrite analysis is based on the formation of azo dye by aromatic amine reduction of the nitrite ion. The reddish product has the highest molar absorptivity at 540 nm. Nitrate is measured as nitrite after the reduction to nitrite via cadmium granules, then the formation of azo dye. A 10 cm long cadmium column is used as a reduction column. The analytical detection limits for nitrite and nitrate are 0.01 μM and 0.05 μM respectively (Grasshoff *et al.* 1983).

2.4.2.3. Ammonium (NH_4-N) analysis

In alkaline media (pH of between 9 and 11.5) ammonia reacts with hypochlorite to give monochloramine which, in the presence of phenol, catalytic amounts of nitroprusside ions and excess of hypochlorite, gives indophenol blue. The reaction called the Berthelot reaction in which a blue-green colored complex is formed and measured 660 nm. A complexing agent was used to prevent the precipitation of calcium and magnesium hydroxides. The detection limit of the method is 0.050 μM (Grasshoff *et al.* 1983).

2.4.2.4. Reactive silicate ($Si(OH)_4$-Si) analysis

An automated procedure for the determination of soluble silicates is based on the reduction of silico-molybdate 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 phosphates and to avoid reduction of the excess molybdate. Reactive silicate is determined by reduction of intensely blue colored complexes. The analytical detection limit of the method is 0.02 μM at 660 nm (Grasshoff *et al.* 1983).

2.4.3. Total nitrogen and total phosphorus analysis

TN and TP analysis were carried out after simultaneous digestion (see Figure 2.2). The digestion procedure, so-called Wet Chemical Oxidation (WCO), is based on the conversion of all nitrogen forms into nitrate and all phosphorus forms into phosphate (Raimboult, *et al*. 1999).

Digestion Procedure;

a. 40 ml of the sample is added into pre-digested Teflon screwed caped bottles.
b. 5 ml of oxidizing reagent is added (3 g of potassium peroxodisulfate and 6 g of sodium tetra borate are dissolved in 50 ml of double distilled water (DDW) in order to have 50 ml of oxidation reagent).
c. Samples are placed into autoclave and heated until 120 °C of temperature and 2 atm pressure which is approximately 40 minutes and let the autoclave cool for few hours. After cooling, inner pressure of the autoclave was stabilized with discharging valve.
d. Digested samples let to come room temperature and 5 ml of DDW added to make 50 ml of final volume.

e. 30 ml of sample is separated for phosphorus analysis and remaining 20 ml for nitrate analysis.

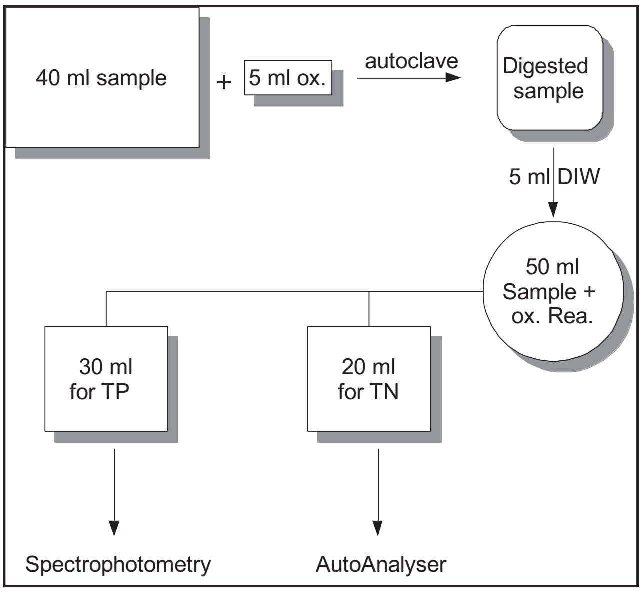


Figure 2.2: Schematic representation of WCO for TN and TP analysis in seawater.

2.4.3.1. Total nitrogen analysis

After the digestion procedure, the separated portions of the samples are measured as nitrate by automated analysis.

2.4.3.2. Total phosphorus analysis

The conventional determination method for phosphorus analysis by auto analyser was not preferred in the present study due to low precision for low concentrations of TP in oligotrophic open waters of the Mediterranean. The manual analysis method using spectrophotometry was used instead of automated analysis (Grasshoff *et al.* 1983; Koroleff, 1983). A detailed comparison between the manual and automated method is included in section 3.3.

Procedure for the manual method;

a. Ascorbic acid solution: 10 g of ascorbic acid dissolved in 50 ml of DDW and diluted to 100 ml by 4.5 M sulphuric acid solution. Resulting solution has a slightly yellowish color and it is stable for few days in dark colored glass bottle.
b. Mix reagent solution: 12.5 g of ammonium molybdate dissolved in 125 ml of DIW and added into 350 ml of 4.5 M sulphuric acid solution. 0.5 g of potassium antimony tartarate dissolved in 20 ml DDW added into previous solution and shaked vigorously. Resulting solution is stable for couple months.
c. A set of phosphate standards and blanks are prepared.
d. 1 ml of ascorbic acid solution is added into samples and standards. After couple minutes 1 ml of mix reagent added. Whole reaction requires 10 minutes.
e. Standards and samples are measured with spectrophotometer at 880 nm wavelength with 5 cm quartz cuvette.

2.4.4. Particulate organic matter and chlorophyll-a analysis

Particulate organic matter (POM) analyses were carried out with CHN Elemental Analyser. Parallel filters were measured with the dry combustion technique. To remove inorganic carbon, filters were treated with concentrated HCl fuming. Acetilanilide (71.09% C, 10.36% N) was used as standard material (Vario el cube manual booklet; Polat and Tuğrul, 1995; Çoban-Yıldız, 2003). Carbon results were gathered as Total Particulate Organic Carbon (TPOC). Total Particulate nitrogen was stated as particulate organic nitrogen (PON).

Chlorophyll-a measurements were carried out using the conventional fluorometric method (Grasshoff *et al.* 1983). Frozen samples were extracted in acetone and kept in a refrigerator overnight. Extracted samples were centrifuged and measured at the excitation wavelength of 420 nm and the emission wavelength of 669 nm with F-2500 type Hitachi spectrofluorometer.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Evaluation of Wet Chemical Oxidation Method for Total Nitrogen and Total Phosphorus Determinations

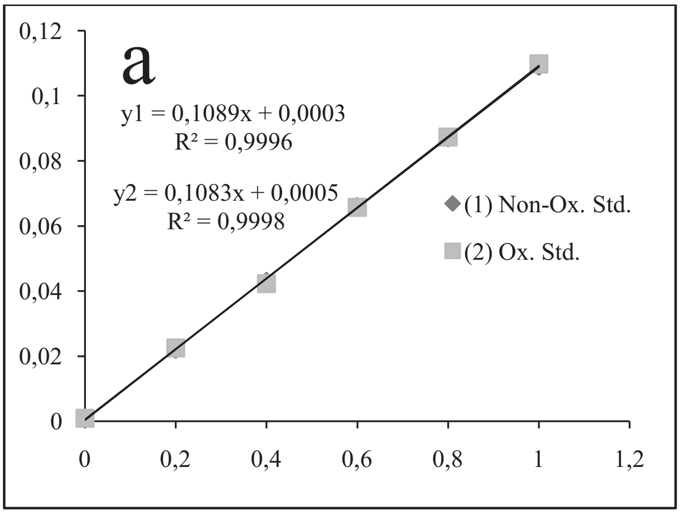
In order to evaluate the reliability of the conventional WCO method for TN and TP determination in the present study, followed procedures were tested. As it was mentioned in the previous sections, the automated measurement method of PO_4 is not suitable for seawater samples with low TP concentrations, due to high matrix effect of digested seawater samples on the baseline and peak shapes. Therefore, in order to minimize matrix effect, all the TP data given in this section were gathered from separate manual analyses of TP samples.

Calibration curves for TP analysis were obtained by preparing standards in DW and SW, separately (Table 3.1 and Figure 3.1). High correlations were gathered from oxidized and non-oxidized samples spiked with different concentration of PO_4 both in DW and SW. The slopes of the calibration curves obtained after the PO_4 oxidation were almost equivalent to those obtained with the non-oxidized standards, indicating that no significant interference originated from the oxidizing reagent in TP digests when the manual method was followed.

In contrary to very low blanks values of reagents used in TP analysis, distinctly high reagent blanks were determined for the wet TN measurement procedure, which was around 0.85 µM level. This blank value is about 20% of TN measured in oligotrophic NE Mediterranean water.

Table 3.1: Absorbance readings of PO_4 standards spiked to DW and SW samples.

Added PO_4 concentration	**Standards in DW (absorbance)**		**Standards in SW (absorbance)**	
(µM)	**Non-ox.**	**Oxidized**	**Non-ox.**	**Oxidized**
blank	0.001	0.001	0.003	0.005
0.2	0.022	0.023	0.024	0.025
0.4	0.043	0.042	0.044	0.047
0.6	0.066	0.066	0.065	0.064
0.8	0.087	0.087	0.087	0.089
1.0	0.109	0.110	0.108	0.109



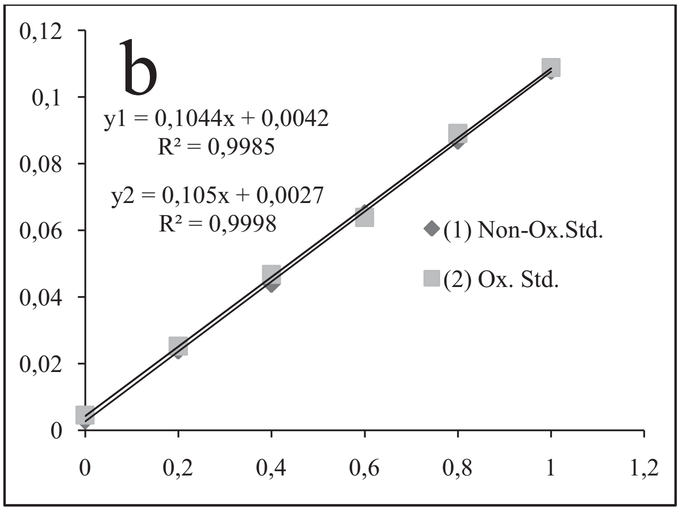


Figure 3.1: Calibration curves of PO_4 standards (a) in DW, (b) in SW.

Table 3.2: Measured concentrations of NO_3 added samples in DW and SW.

NO_3 addition in DW samples				
Non-oxidized NO_3		**Oxidized NO_3**		
Added (µM)	**Measured (µM)**	**Added (µM)**	**Measured (µM)**	**Rec.%**
Blank	0	Blank	0.83	
2	2.18	3	3.76	98
4	4.23	6	6.58	96
8	8.16	9	9.56	97
12	12.19			

NO_3 addition in SW samples				
Non-oxidized NO_3		**Oxidized NO_3**		
Added (µM)	**Measured (µM)**	**Added (µM)**	**Measured (µM)**	**Rec.%**
Blank	1.6	Blank	4.34	
2	3.7	3	7.59	88
4	5.77	6	10.34	90
8	9.78	9	12.83	88
12	13.71			

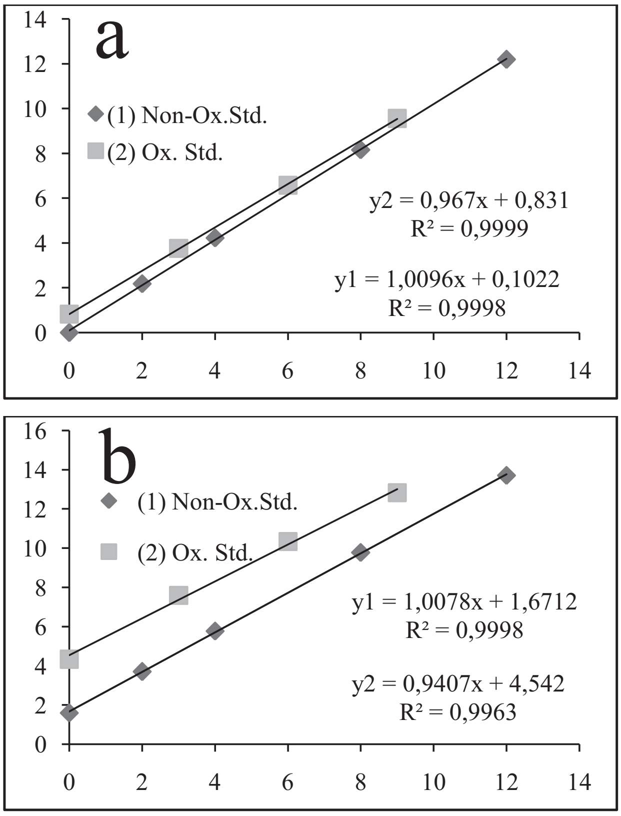


Figure 3.2: Calibration curves of NO_3 standards (a) in DW, (b) in SW.

Table 3.3: Measured concentrations of NH$_4$ and urea added samples in DW and SW.

NH4 addition in DW samples			**NH4 addition in SW samples**		
Added (µM)	**Measured (µM)**	**Rec.%**	**Added (µM)**	**Measured (µM)**	**Rec.%**
Blank	0.83		Blank	4.34	
3	3.82	100	3	7.77	94
6	6.74	99	6	10.39	91
9	9.7	99	9	12.95	89

urea addition in DW samples			**urea addition in SW samples**		
Added (µM)	**Measured (µM)**	**Rec.%**	**Added (µM)**	**Measured (µM)**	**Rec.%**
Blank	0.83		Blank	4.34	
3	3.8	99	3	7.58	88
6	6.86	101	6	9.88	82
9	9.44	96	9	12.24	81

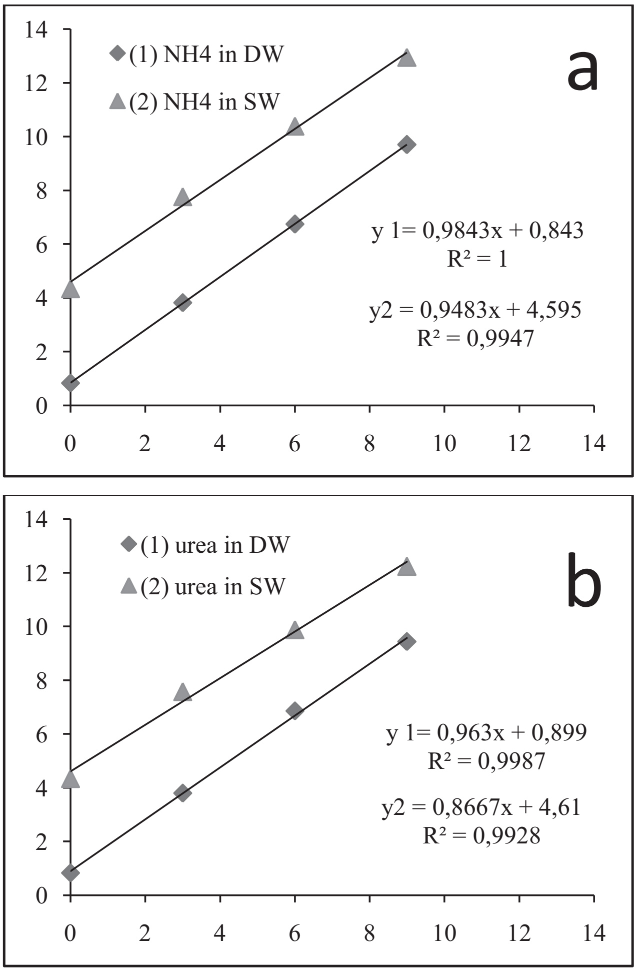


Figure 3.3: Calibration curves of (a) NH$_4$-N and, (b) urea-N standards

In contrary to very low blanks values of reagents used in TP analysis, distinctly high reagent blanks were determined for the wet TN measurement procedure, which was around 0.85 μM level. This blank value is about 20% of TN measured in oligotrophic NE Mediterranean water.

Recovery tests reveal that NO_3 recovery is as high as 97% in DW digests. On the other hand, NO_3 recoveries in natural SW matrix decreased slightly to the level of 89%, implying about 10% loss of NO3 standards added to SW + oxidative reagent as compared to the standards prepared in natural SW and measured directly (Table 3.2 and Figure 3.2).

In addition to nitrate recovery tests, several tests of reproducibility were made in DW and SW spiked with different concentrations of NH_4 and urea (Table 3.3 and Figure 3.3). In DW, ~100% recoveries were obtained whilst the recoveries were around 90% and 85% for natural SW (NE Mediterranean surface water) matrix spiked with NH_4 and urea standards, respectively (Figure 3.3). Comparison of recovery tests reveals that the recovery of reduced nitrogen compounds in SW is nearly similar to that of NO3 in SW. This indicates that their recoveries are principally affected by the matrix of sea water itself rather than the chemical forms of nitrogen in SW and oxidation efficiency.

In order to further understand the matrix effect on TN recovery by WCO method, synthetic sea water (SSW; salinity: 35 ppt) solution was prepared using ultrapure NaCl and $NaHCO_3$ (0.2 g/L) chemicals. Standard addition experiments were performed using inorganic nitrogen standards; first, the oxidized SSW blank was 0.90 μM and consistent with that observed in DW digests.

Recoveries of NO_3 and NH_4 standards spiked to SSW and then oxidized with WCO method (Table 3.4 and Figure 3.4) reached 95-100% of the direct measurements of standards in SSW. As stated in the Methods of Sea Water Analysis (Grasshoff *et al.* 1983); sodium chloride solution at ppt level (30-40 ppt), similar to ionic strength of the sea water but has no buffer capacity in SW, has insignificant effect on the recovery of TN in SW samples. The lower recovery of TN in natural SW by WCO method relative standards in SSW strongly suggests that other chemicals present in

SW and pH changes (insufficient buffer capacity of NH_4Cl for digested SW samples) during the measurements could have noticeable suppressive effect on the colored complex formation of oxidized-N in the digested SW.

In order to see the total buffer capacity of NH_4Cl in the oxidized DW/SW matrix during the colorimetric analysis, the pH values of the N-spiked and digested DW/SW samples were measured before and after the analysis. It was observed that the pH of the oxidized SW samples were slightly lower (7.80) than the samples prepared with DW (8.09) before the analysis. Though the initial pH's of the oxidized samples were slightly different, the final pH measured in samples from the exit line of the auto-analyzer ranged merely between 1.59-1.61 in both media. The concentrations of NH_4Cl pumped to the sample line of the automated system were increased from 10 g/l to 60 g/l. This change, however, increased the exit pH of the solution slightly from 1.55 to 1.65. This change in ammonium chloride concentration and consequent pH increase enhanced the recovery of TN in the oxidized SW samples markedly. However; it also creates an artificial increase in the N concentration of the oxidized samples and the reagent blanks (Figure 3.2), as compared to standard calibration curves prepared in DW.

The recovery of standards in SW matrix was estimated as 88%, less than in DW, though NH_4Cl concentration was increased (Table 3.5). Thus, the optimum concentration of ammonium chloride was chosen as 40 g/l for the automated analysis of TN in SW digests.

It can be concluded that the WCO method is highly efficient for the determination of TP; however it needs some improvement to enhance the reliability of TN analysis by the automated colorimetric method. It should be noticed that the reagent blank is significantly high even though ultrapure chemicals are used for oxidative agent. Different concentrations of complexing agents should be tested to increase the TN recovery over 90% and make it reliable in sea water digests. In the present study, pumping rates of sample and NH_4Cl lines tested and the recovery approached 90% level for SW samples. The reduction of blank values is essential especially for highly oligotrophic marine environments that have low total/organic nitrogen concentrations in the water columns.

Table 3.4: Measured concentrations of NO_3 and NH_4 standards added to SSW samples.

Standard addition in SSW Matrix						
Non-oxidized NO_3 addition in SSW		**Oxidized**				
Added (µM)	**Measured (µM)**	**Added (µM)**	**NO_3 addition**		**NH_4 addition**	
			Mea. (µM)	**rec.%**	**Mea. (µM)**	**rec.%**
Blank	0.13	Blank	0.90		0.9	
2	2.21	3	3.79	97	3.9	100
4	4.28	6	6.55	94	6.87	100
8	8.14	9	9.35	94	9.74	98
10	10.23					

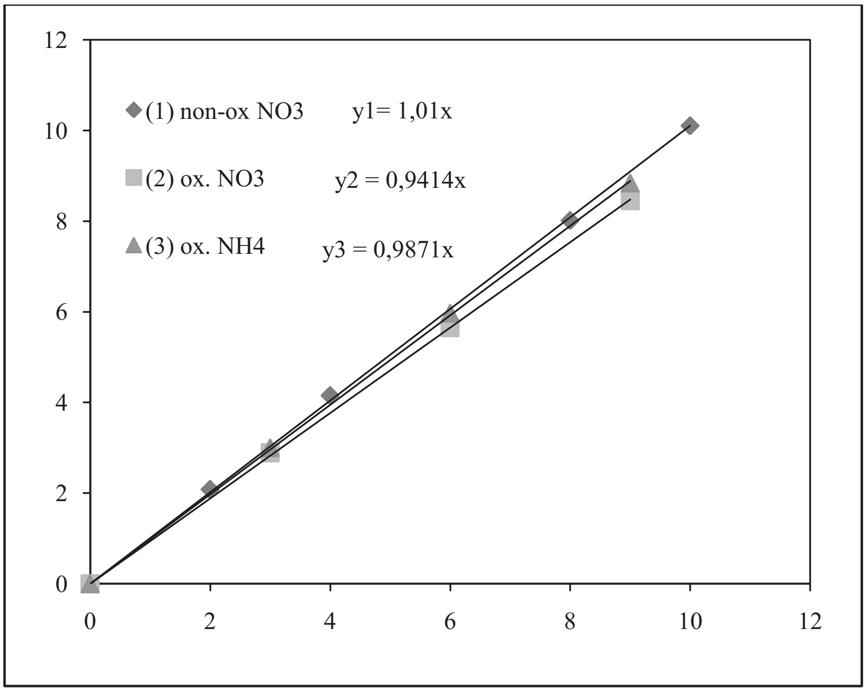


Figure 3.4: Calibration curves of NO_3 and NH_4 standards in SSW matrix.

In the present study, the raw TN data obtained by the automated method were then corrected by a factor of 0.8-0.9 (see Appendix C) to compensate the recovery loss during the measurements. The recovery results were derived from the NH_4 standards spiked to SW samples and then treated with exactly same procedure that was applied to the SW samples.

Table 3.5: Recoveries of NO_3 standards in DW and SW with changing NH_4Cl concentrations and corresponding pH values.

NO$_3$ standard addition in DW								
Added conc. (µM)	**10 g/l**		**20 g/l**		**40 g/l**		**60 g/l**	
	meas.	**rec%**	**meas.**	**rec%**	**meas.**	**rec%**	**meas.**	**rec%**
Blank	1.44		1.51		1.72		1.81	
3	4.21	92	4.43	97	4.81	103	4.96	105
6	7.06	94	7.41	98	7.94	104	8.12	105
9	9.84	93	10.36	98	11.01	103	11.23	105
pH	**1.54**		**1.59**		**1.64**		**1.65**	

NO$_3$ standard addition in SW Matrix								
Added conc. (µM)	**10 g/l**		**20 g/l**		**40 g/l**		**60 g/l**	
	meas.	**rec%**	**meas.**	**rec%**	**meas.**	**Rec%**	**meas.**	**rec%**
Blank	4.91		5.32		6.02		6.12	
3	7.06	72	7.63	77	8.67	88	8.82	90
6	9.21	72	9.96	77	11.32	88	11.52	90
9	11.38	72	12.28	77	13.91	88	14.03	88
pH	**1.55**		**1.59**		**1.62**		**1.65**	

3.2. Comparison of the Closed Digestion and Open Digestion Methods for Determination of Total Phosphorus

Determination of phosphorus via the open digestion procedure is widely used in manual analysis (Koroleff, 1983). It is practical to perform the technique for a limited number of samples which do not require further nitrogen analysis. It is reliable, robust and proven within numerous studies (Murphy and Riley, 1962; Solorzuno and Sharp, 1980; Koroleff, 1983). Nevertheless, it is susceptible to additional biases. Firstly, it requires high effort and time to be able to gather reliable results. Since the technique has to be carried out in open vessels which increase risks of contamination and sample losses. Moreover, it requires pH adjustment via additives and/or pH meters, which affects the precision of measurements. Lastly, final volume adjustments of the pH-adjusted samples are performed in new containers, which may cause contamination or subsample losses during this protocol.

Despite the above discussed weaknesses of the open digestion method, it was used as a reference procedure to test the reliability of closed digestion (WCO) for TP determination. Comparable results were obtained in the samples measured by the spectrophotometric method. Calibration curves were plotted for both open and closed digestion methods with the samples spiked with oxidized and non-oxidized PO_4 standards (Figure 3.5). Lower reagent blanks were obtained with the WCO method as the open digestion. Recoveries were slightly higher in the WCO method (slope: 0.104) due presumably to potential sample loss and incomplete oxidation by the open digestion (slope: 0.102) of some fractions of dissolved organic-P compound in SW. Oxidized and non-oxidized standards were prepared in DW, SW and SSW. Absorbance readings are given in Table 3.6 and depicted in Figure 3.5.

Table 3.6: Absorbance readings of blank and standards in DW, SW and SSW with closed and open digestion methods.

	Standard addition in DW samples			**Standard addition in SW samples**			**Standard addition in SSW samples**		
Added conc. (µM)	**Absorbance**			**Absorbance**			**Absorbance**		
	Non-ox.	**Closed**	**Open**	**Non-ox.**	**Closed**	**Open**	**Non-ox.**	**Closed**	**Open**
Blank	0.001	0.001	0.005	0.003	0.005	0.011	0.002	0.003	0.005
0.2	0.022	0.023	0.021	0.024	0.025	0.032	0.021	0.023	0.026
0.4	0.043	0.042	0.043	0.044	0.047	0.054	0.044	0.044	0.045
0.6	0.066	0.066	0.067	0.065	0.064	0.071	0.064	0.064	0.066
0.8	0.087	0.087	0.092	0.087	0.089	0.093	0.084	0.090	0.087
1	0.109	0.110	0.112	0.108	0.109	0.114	0.103	0.110	0.105

Table 3.7: Comparison of TP concentration measured in the Harbor sea water by closed and open digestion methods.

SW Samples from Institute Harbor		
Sample	**Concentrations (µM)**	
	Open digestion	**Closed digestion**
H1	0.22	0.24
H2	0.22	0.26
H3	0.22	0.23
H4	0.23	0.25
H5	0.34	0.23

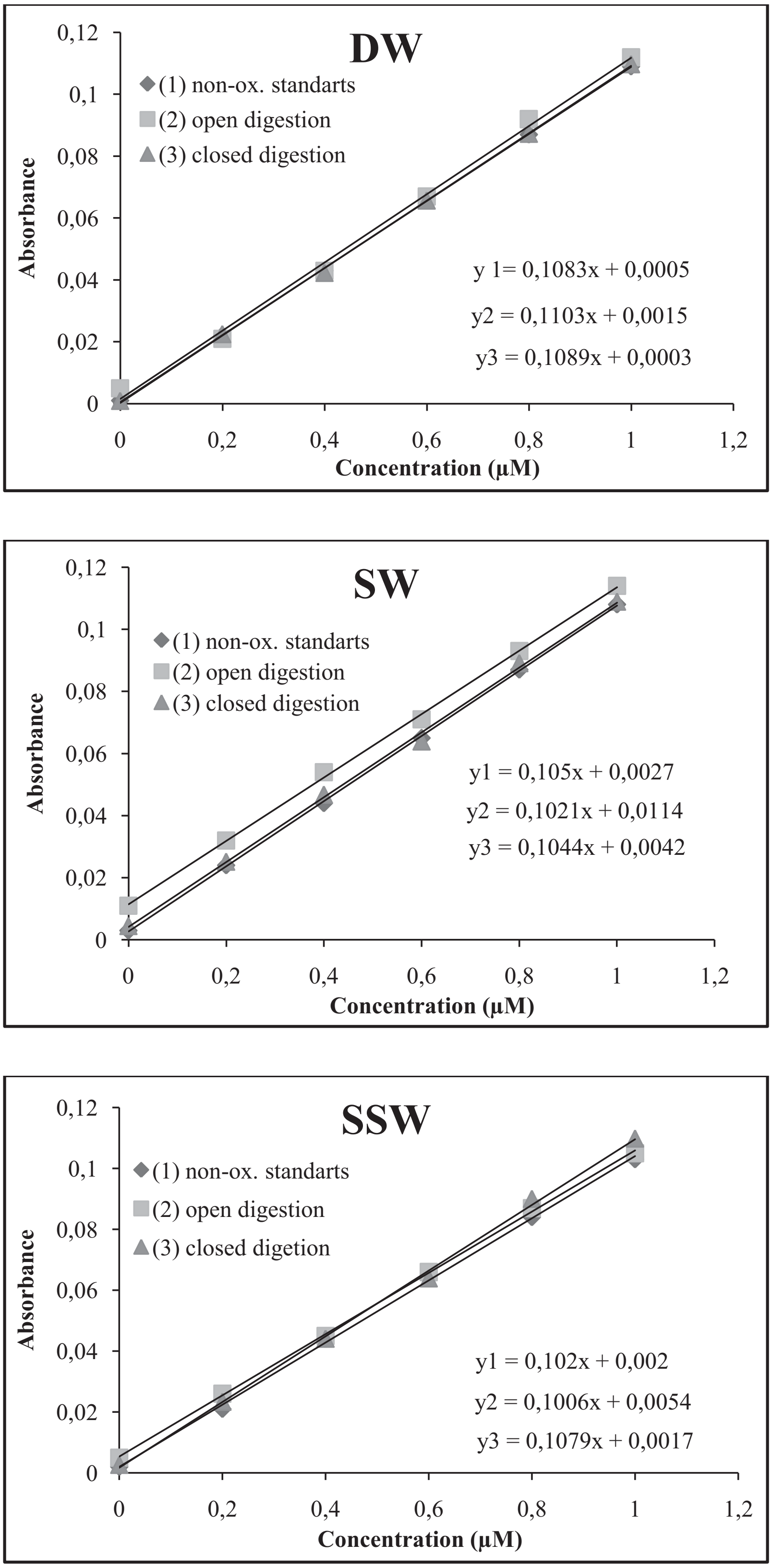


Figure 3.5: Calibration curves of PO_4 standards in DW, SW and SSW.

In order to show comparability of both methods, seawater samples from the Institute harbor were analyzed with open and closed digestion methods. The blank-corrected TP results are shown in Table 3.7. Comparison of the results demonstrates that the TP measured by the closed digestion method are slightly higher than those by the open digestion. Besides, the closed digestion method has lower blank values; it is fast, robust and less susceptible to contamination.

3.3. Comparison of Manual and Automated Determination of Total Phosphorus by Colorimetric Methods

As it was discussed in the previous section, in this study, the manual colorimetric method for TP analysis in digested seawater samples was preferred to the automated method. To show the analytical limitations, precision of the automated method, many samples were measured by both methods. January, February, March and April samples from the study site and Quasimeme reference samples (Quasimeme Laboratory Performance Studies) were analyzed using the manual and automated methods. A high correlation was obtained in the samples with TP concentrations over 0.20 μM (Figure 3.6). Though the automated method be as sensitive as the manual method, the precision and blank reading of the method under the present analytical conditions were not good enough to apply to oligotrophic seas having low TP values (<0.2 μM).

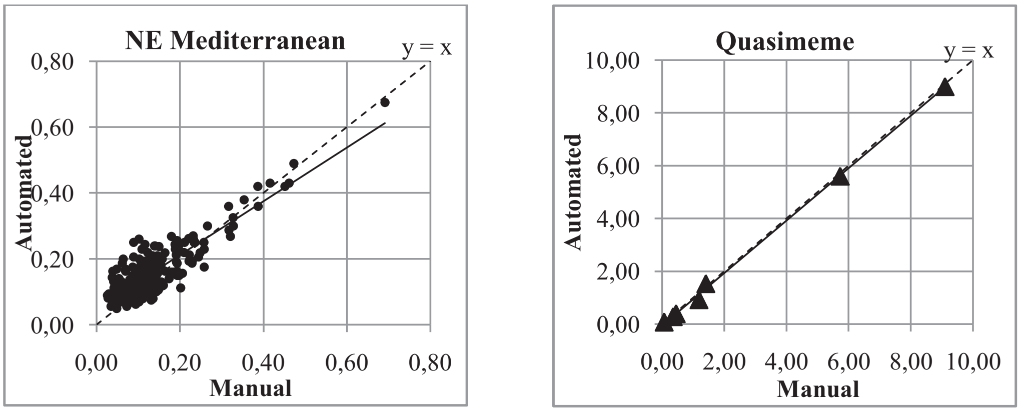


Figure 3.6: Comparison of manual and automated procedures with studied samples and Quasimeme reference samples.

Since matrix changes highly influence the baseline in the automated method, the reagent blank absorbance was as high as 0.08-0.12 µM relative to P-depleted SW baseline. However, it was merely 0.02 µM for the manual method. In other words, the blank of the automated method was higher than or at comparable levels with the TP content of NE Mediterranean upper layer water. This highly limits the reliability of low TP data obtained by the automated method. Lowering the pumping rate of samples to minimize matrix effect leads to decreases in sensitivity of the automated method. Therefore, the automated analysis can only be used for TP concentrations exceeding 0.20 µM. However; manual analysis with 5-10 cm optical cell is more convenient for SW samples with lower TP concentrations as in the NE Mediterranean waters.

3.4. Hydrographic Properties of the Study Area during September 2008-October 2009 Period

3.4.1. Surface distributions and depth profiles of hydrophysical parameters

Hydrophysical parameters were measured during 2008-2009 period at all stations in the study area. Continuous type SeaBird CTD profiler was used for CTD measurements (Section 2.2). CTD data obtained in January, April, August and October were used to represent winter, spring, summer and autumn seasons, respectively. Surface water distributions of salinity and temperature for different seasons are displayed in Figure 3.8. In order to examine spatial and seasonal changes of hydrophysical parameters, depth profiles of T, S at selected stations on the nearshore (St 2), middle (St 4, St 10), and offshore (St 46, St 48) zones are depicted in Figures 3.9a and 3.9b.

In September 2008, surface water temperatures were observed to range between 28.9 and 30.1 ^{o}C in the study area. Coastal waters of the Mersin bay were slightly warmer than the offshore waters (Figure 3.8). High evaporation rates in the dry season appeared to increase surface salinity values up to 39.5 psu in the Bay. Depth profiles of salinity and temperature display a clear decline at 30-40 m. Values under this depth continued to decrease until 100 m levels and then stayed constant below this depth in the offshore zone. The vertical profiles were almost vertically uniform in the shallow zone (<30 m in depth), where salinity, temperature and density values were 29.2 °C, 39.4 psu, and about 26.0 (sigma-t unit), respectively. Seasonal thermocline and halocline were formed at 30-40 m depths.

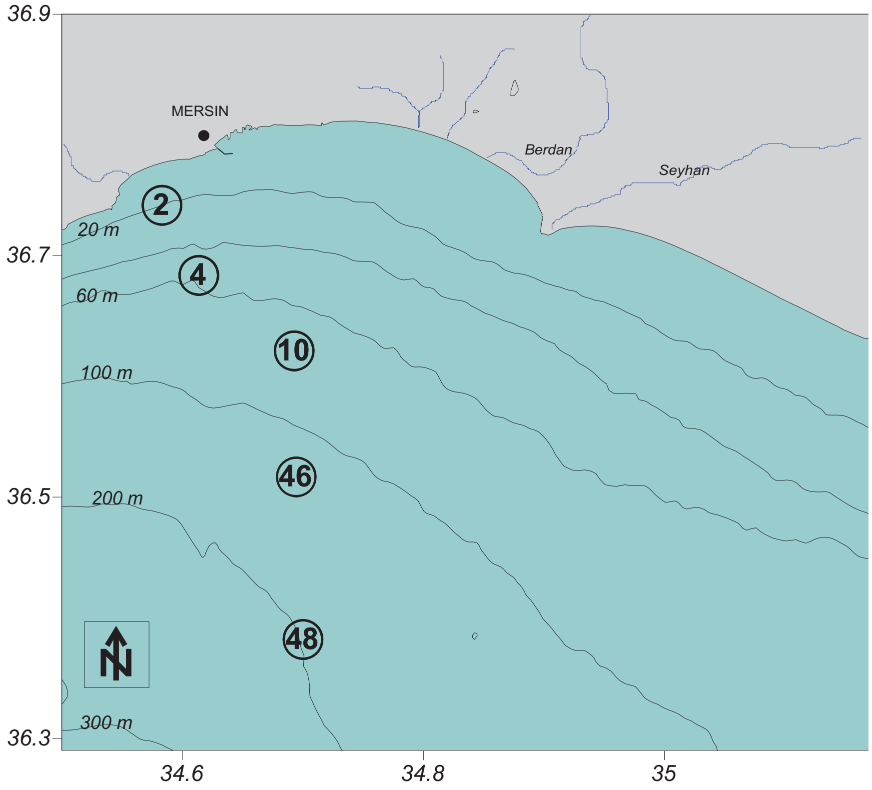


Figure 3.7: The Locations of the transect stations on the shelf zone of the Mersin Bay.

In January 2009, general vertical features of the depth profiles of T, S at the selected stations displayed vertically uniform distributions due to intensive vertical mixing in winter (Figures 3.9a and 3.9b). The seasonal features were almost disappeared over the bay. Average value of temperature, salinity and density were observed as 18.4 °C, 39.4 psu and 28.6, respectively. The coastal zone was occupied by less saline and colder surface waters due to high river discharges in wet season, leading to apparent spatial changes.

From January to February, near-surface temperature decreased by 1-2 °C, to levels of 15.3 ^{o}C in shallow coastal zone. Middle stations of the bay, however, were not exposed to such decrease in temperature, implying limited effect of river discharges on the offshore zone. In the deep zone, the seasonal thermocline, halocline and pycnocline disappeared completely. Temperature values were constant through the whole water column and decreased about 2 ^{o}C as compared to in January. In February, the average values of temperature, salinity and density were recorded as 17.9 C, 39.4 psu and 28.7 (sigma-t), respectively, at St. 48 (20 m depth) on shelfbreak zone.

In March 2009, the winter conditions were observed to persist over the bay (Figure 3.8); temperature, salinity and density profiles remained almost vertical uniform down to sea bottom (200 m depth) as experienced in February. However, lower surface salinity values were recorded in the coastal region due to river inputs.

In April 2009, rise in the air temperature caused increased surface water temperature values throughout the Cilician basin (Figure 3.8). A steep halocline was observed at around 5 m in the coastal zone due river inflows. Sea water temperature at St. 48 decreased from 19.4 ^{o}C in the surface to levels of 16.7 ^{o}C in the near bottom water. Broader thermocline and halocline were formed in the offshore zone (Figure 3.9b).

In August 2009, surface temperature of the coastal waters reached 30.5-31.0 ^{o}C levels. In the coastal zone, vertically uniform temperature profiles were observed (Figures 3.8, 3.9a and 3.9b). However, at the deeper locations (>50 m) a sharp thermocline was formed between 40-50 m, coinciding with seasonal halocline and pycnocline. Temperature, salinity and density values were recorded as 29.7 ^{o}C, 39.5 psu and 25.2 in surface waters of St 48, decreasing to 16.6 ^{o}C, 39.3 psu and 28.9, respectively, in the offshore bottom water (200 m).

The last field survey was carried out in October 2009. Upper layer temperature was uniform (26.5 ^{o}C) down the thermocline depth (40 m) in the open sea. A steep thermocline was formed between 40-50 m. Greater salinity values were recorded in the surface waters due to high evaporation during the summer months. The halocline coincided with the thermocline at around 40 m depth.

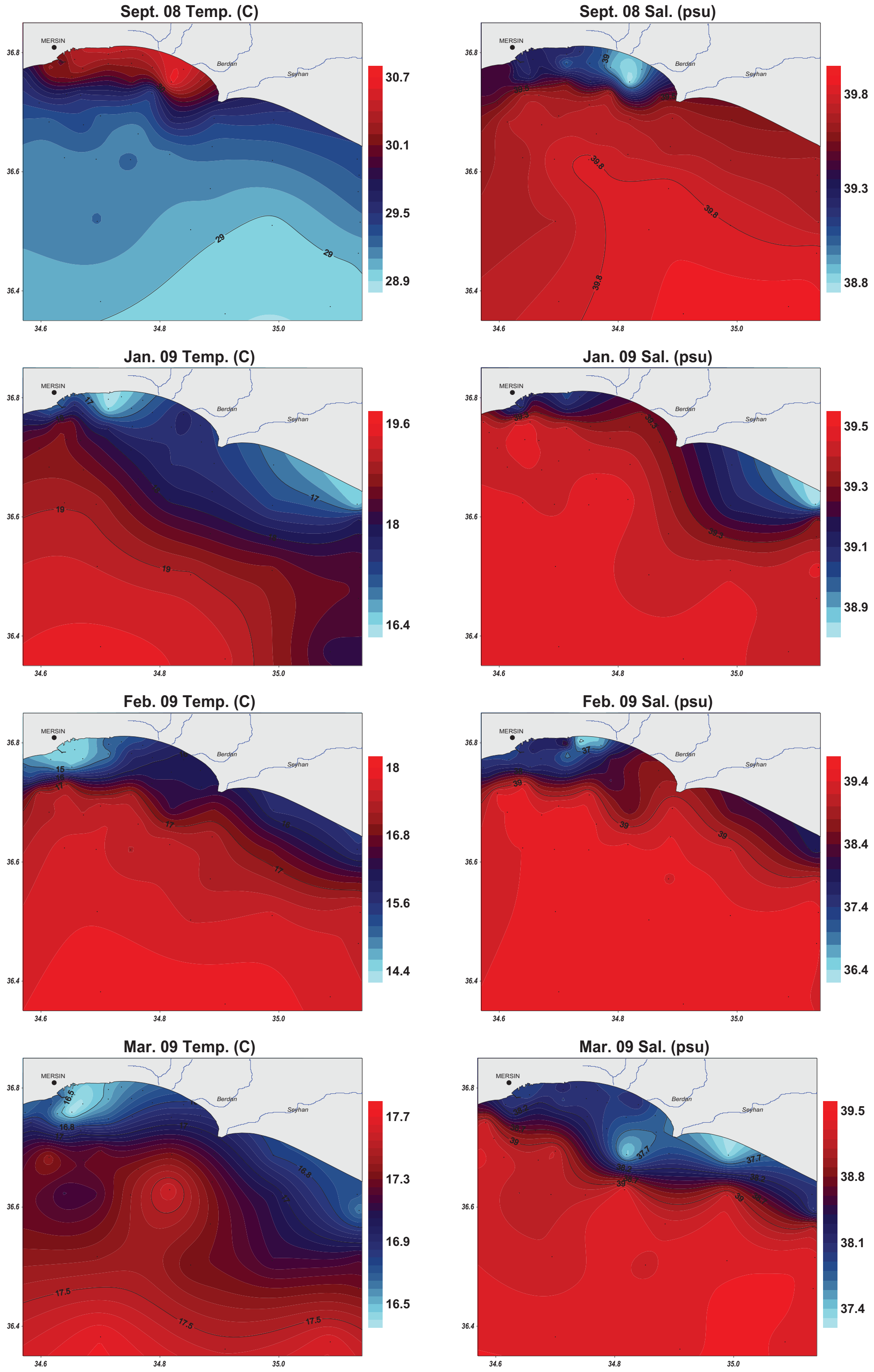


Figure 3.8: Surface distributions of temperature and salinity throughout the study region.

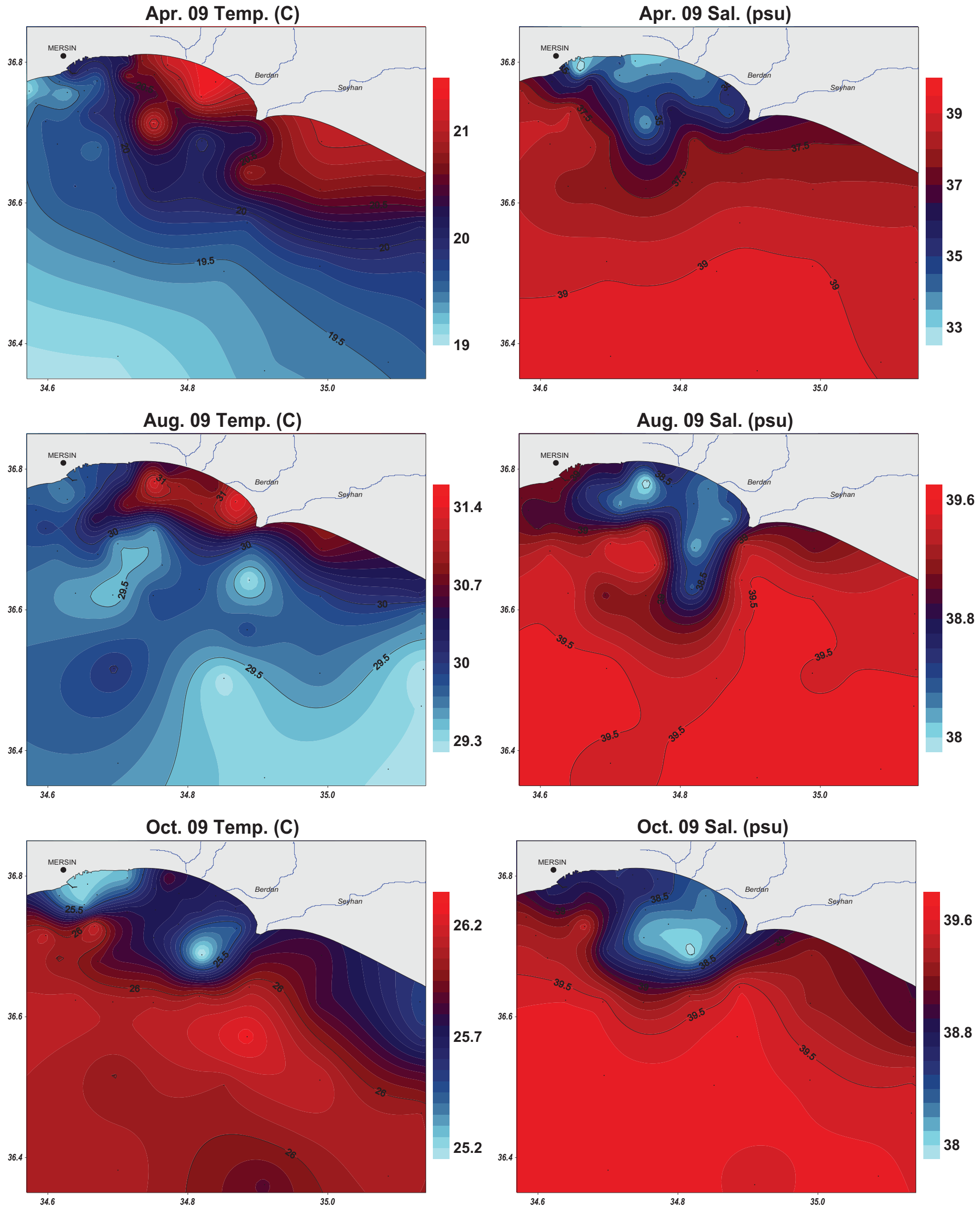


Figure 3.8: Continued.

Seasonal and spatial distributions of the hydrophysical parameters in the NE Mediterranean water column are dominated by general circulation pattern of the basin. However, in semi-enclosed coastal regions, river discharges, surface water heating/cooling and wind-induced coastal processes highly influence the coastal water properties (Özsoy *et al.*, 1991; Zavatarelli *et al.*, 1998), as experienced in the

Mersin Bay. In period of 2008-2009, it was observed that the strong vertical mixing in winter created vertically uniform profiles of temperature, salinity and water density in the bay. After the winter cooling period, volume fluxes of the river discharges to the sea increased with the contribution of melted snow waters, which decreased surface temperature and salinity markedly in the shallow coastal zone as observed in the bay. During the summer-early autumn period, salinity and temperature stratifications developed in the deeper part of the bay. Warmer and saltier waters occupied the upper layer down to 40 m in the offshore zone in autumn. A steep gradient zone was formed in between.

At St 2, when the surface layer is seasonally stratified during the spring (April 2009) and summer (August 2009) period, the saline water occupied the upper 10 m; it was separated from the less saline upper layer by a well-defined pycnocline (Figure 3.9a). During the prolonged period of cooling in winter and autumn, denser surface waters led to occur deep convective mixing processes; thus a well-mixed (isohaline and isothermal) water mass was formed from the surface to at least down to 20-m depth in January and October 2009 (see Fig. 3.9a; temperature: ~29 °C and sal.: ~39.5 psu).

At St 4, convective winter mixing in 2009 homogenized the upper layer of the basin down to 50 m, leading to the formation water column with vertically almost isohaline (39.5) and isothermal (29 °C) properties (Figure 3.9a). Surface water occupied less saline water in spring (April 2009) and it disappeared in summer (August 2009). And then the seasonal thermocline was observed in autumn (October 2009).

In St 10, deep water mixed thoroughly with the surface waters in winter to form a vertically homogenous upper layer down to 60 m (Figure 3.9a). The new water source was observed between 60-70 m. Less saline water was observed upper 20 m in spring and disappeared in summer. The seasonal thermocline is established in autumn as experienced in St 4.

The offshore stations (St 46 and St 48) have same characteristics. Water column was well mixed in winter months (February 2009 in St 46, January 2009 in St 48). The surface water became more saline during August and October 2009 (38 – 39.6 psu) due to the excessive evaporation (Figure 3.9b).

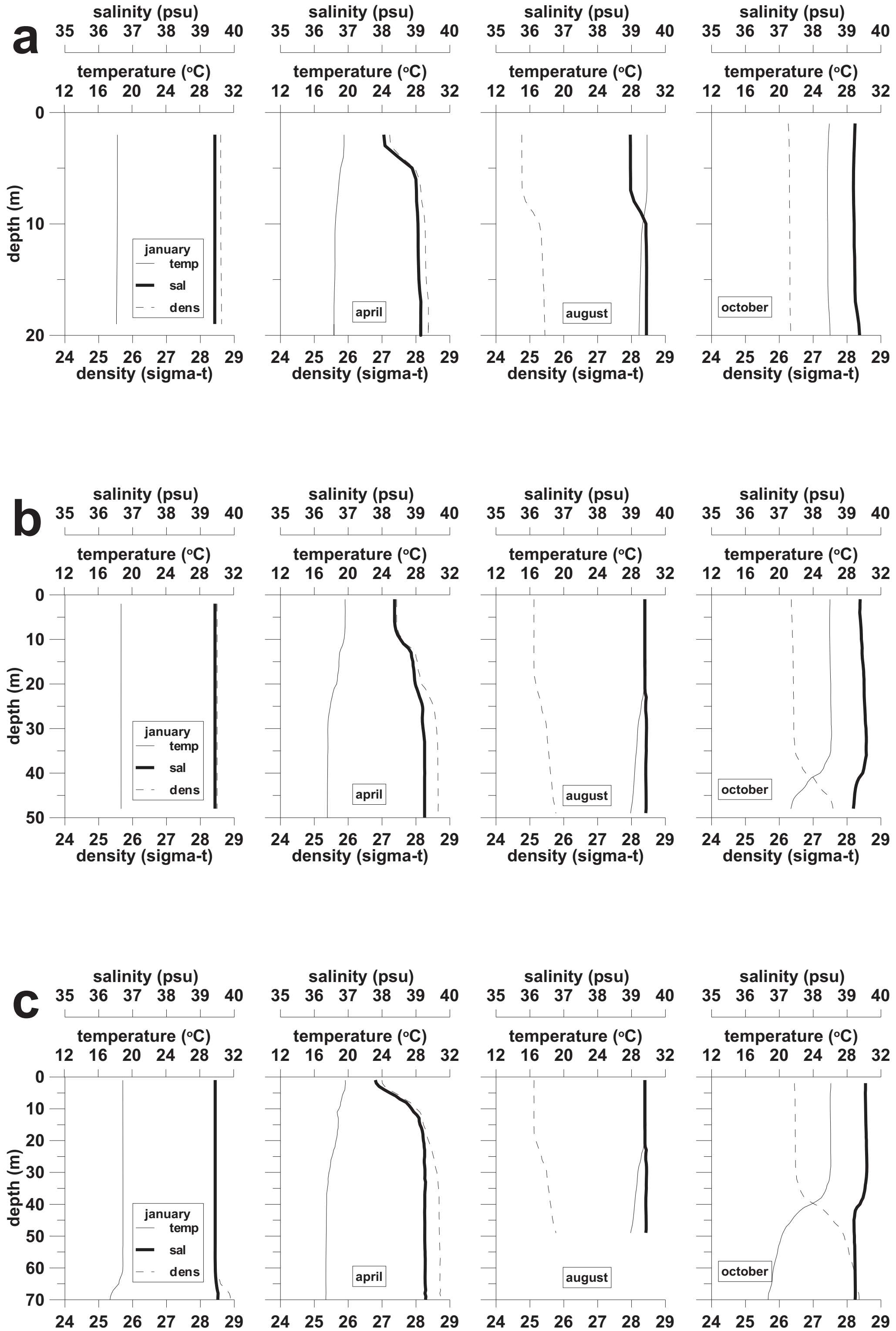


Figure 3.9a: Depth profiles of temperature, salinity and density from selected stations and seasons (a: St. 2, b: St. 4, c: St. 10; January, April, August and October)

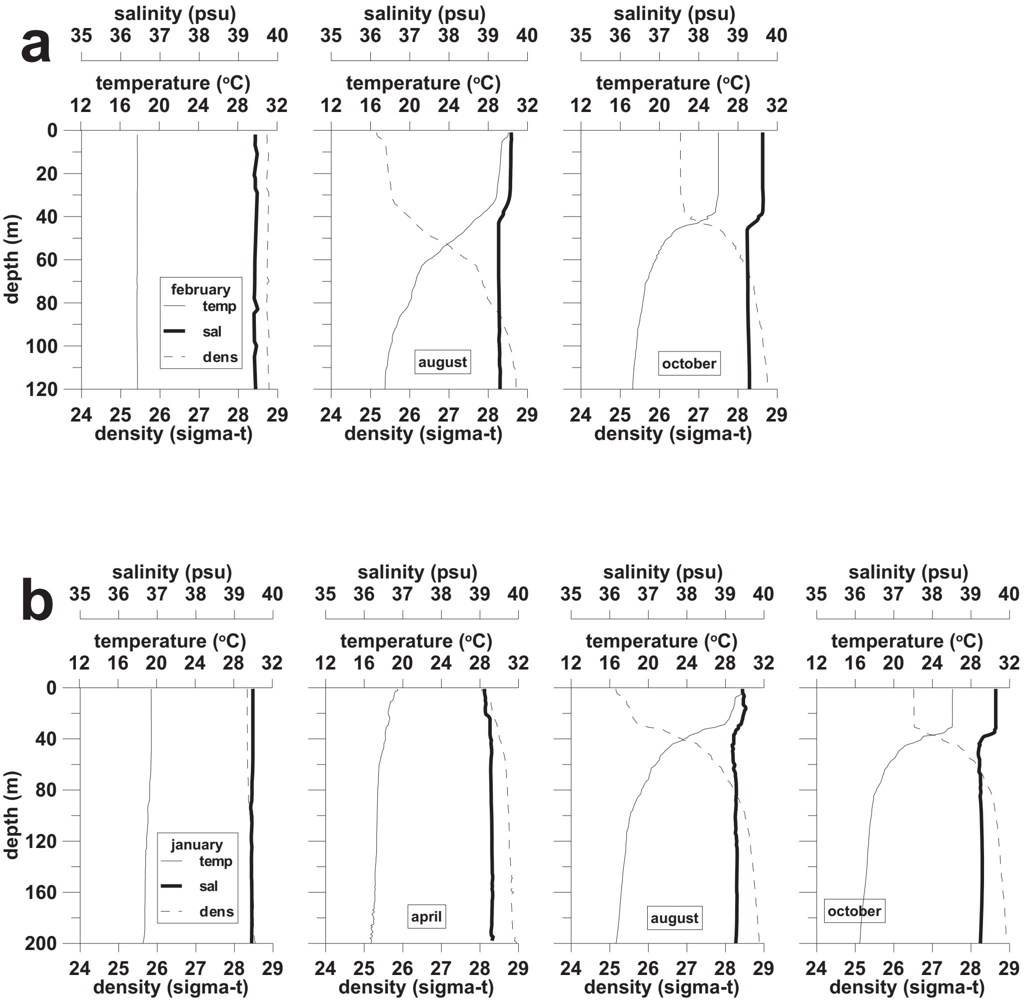


Figure 3.9b: Depth profiles of temperature, salinity and density from selected stations and seasons (a: St. 46, b: St. 48; January, April, August and October)

3.4.2. Evaluation of hydrophysical parameters along the selected transect

Depth distributions of temperature and salinity are also depicted on a selected transect extending from nearshore to offshore zone for different seasons (Figure 3.11). The transect figures were produced from the measurement at St. 2, 4, 10, 46, 48 on the Bay (Figure 3.10). The transect plots demonstrate spatial and temporal variations of termohaline features in the Bay.

In September 2008, St. 48 was not visited. Figure 3.11 shows that temperature and salinity were uniformly distributed in the upper 20 m over the basin. Below this depth, seasonal halocline and thermocline were formed. Coastal surface waters had lower salinity values due to river inflows.

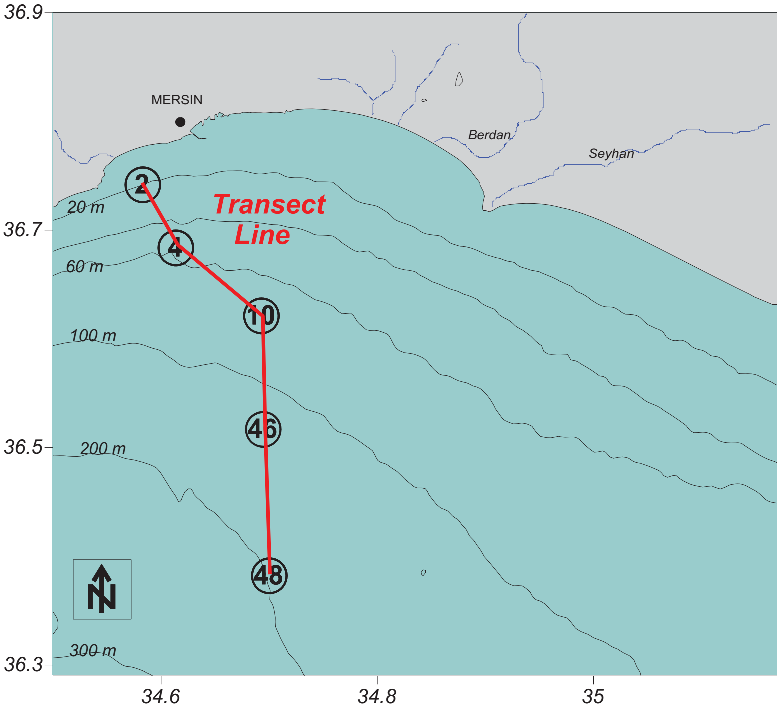


Figure 3.10: The locations of stations on the selected transect.

In January 2009, the seasonal stratifications formed in the water column almost disappeared due to surface water cooling and intensive vertical mixing. The coastal zone waters were flushed by the open sea via general circulations. However, colder and less saline waters occupied the nearshore zone, indicating weak interactions with the open sea. Vertically uniform features along the transect persisted in February and March due to winter mixing and cooling of the surface waters.

The transect in April 2009 shows development of a weak density gradient zone in the upper layer. Less saline water masses still exist on the nearshore zone due to river discharges (Figure 3.11).

In August 2009, because of very high evaporation rates, the surface salinity increased to levels of 39.5 psu throughout the study area (see Figure 3.11.). The river effect became less detectable on the coastal zone due to the lowering discharges of the regional rivers. Vertically stratified water column was clearly observed over the basin.

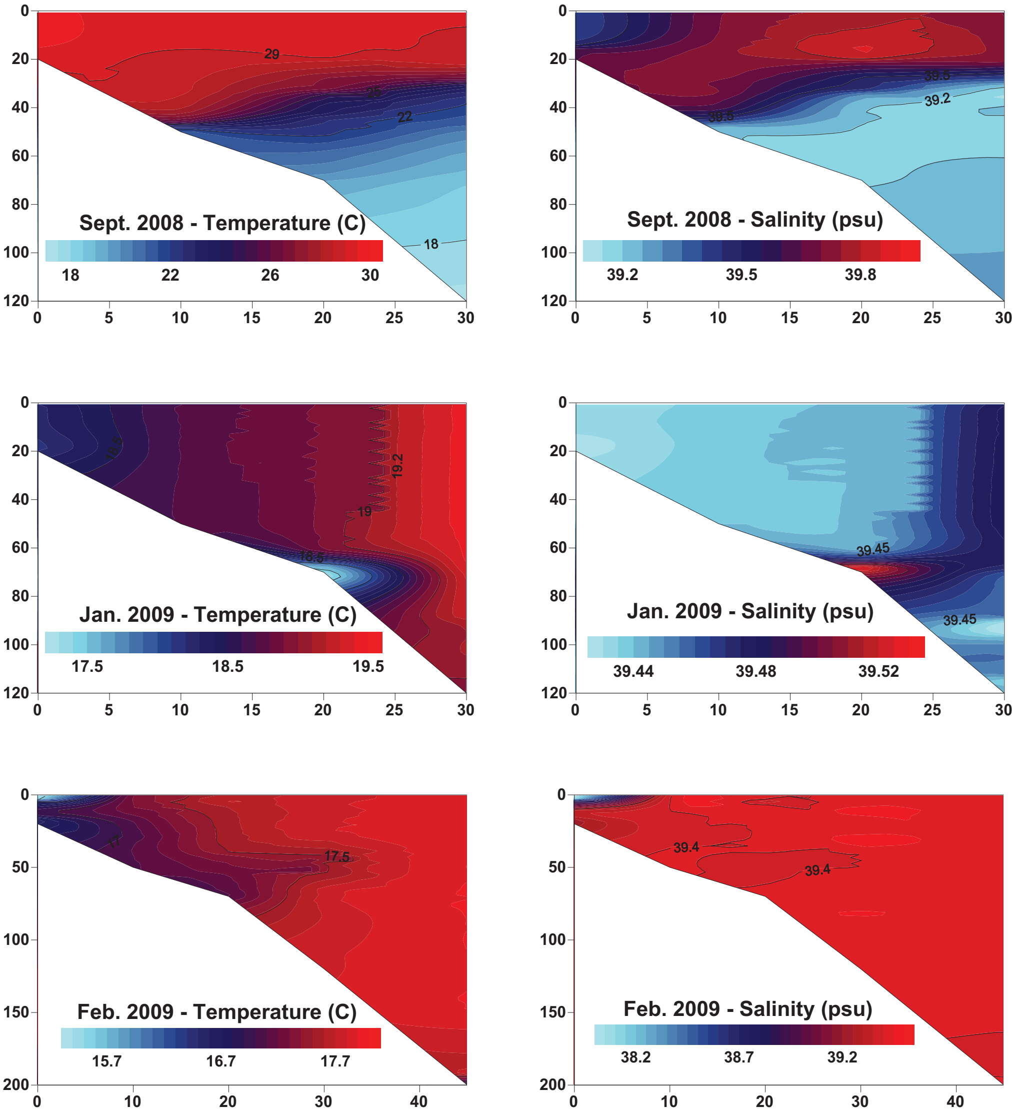


Figure 3.11: Transects plots of temperature and salinity along the selected line

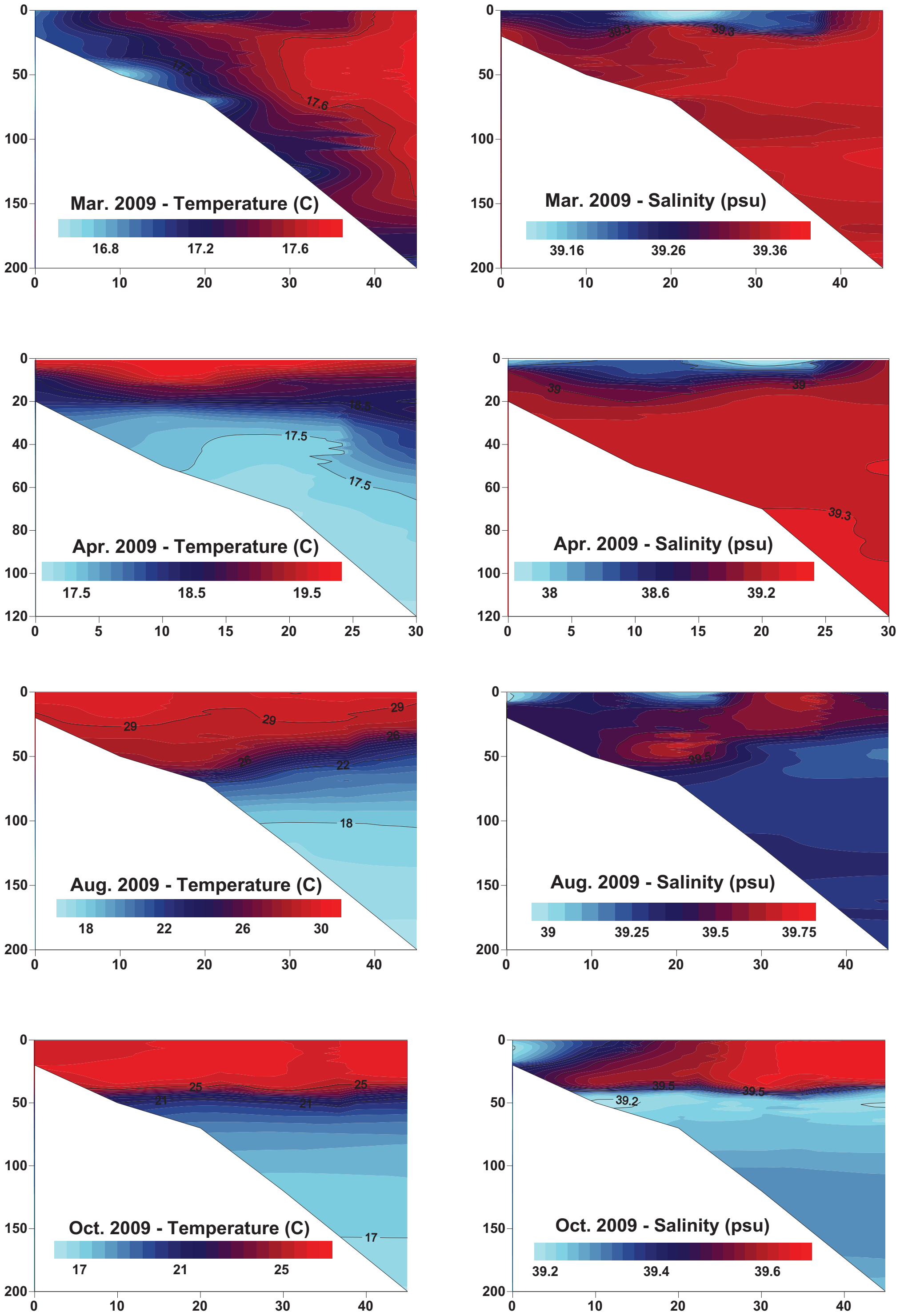


Figure 3.11: Continued.

Simply put, thermohaline features in the Mersin Bay of the Cilician basin displayed drastic seasonal changes as experienced over the Cilician Basin. However, temporal variations were more pronounced in the nearshore waters due to wind-induced circulations, mixing and river inflows increasing winter-spring period. In winter the shelf waters are mixed thoroughly, displaying vertically uniform profiles. During spring and summer months, a thermohaline stratification starts to develop in the water column and progresses vertically by late October.

3.5. Spatial and Temporal Variations of Biochemical Parameters during September 2008-October 2009 Period

3.5.1. Surface distributions of nutrients, dissolved oxygen and chlorophyll-a along the study region

For sound understanding effects of land-based inputs on the Mersin Bay ecosystem, surface distributions of the nutrients, DO and chl-a concentrations are depicted in Figures 3.12a-g for the seven field surveys carried between September 2008 and October 2009. In polluted nearshore zone, the concentrations were much higher than in the offshore zone. Such large spatial differences limit to easily examine small-scale variations in the pollution parameters in the surface waters of the Bay. In order to illustrate the nutrient gradients between river-fed coastal regions and offshore waters, high value data points that were excessively higher than the rest of the region, were adjusted down to comparable levels. For instance; the nitrate concentration was recorded as 3.50 µM at St 16 in September 2008; however, the rest of the measurements were below 1.0 µM. To use such a large concentration at a single coastal point caused to disappear of scaling between river-fed zone and offshore site. Therefore, NO_3 concentration in this station was artificially lowered to 1.0 µM. However, all the raw data used in the surface distributions are also given correctly in Appendix A to further understand the magnitude of spatial changes/increases in the river-fed polluted zones in different seasons.

In autumn of 2008, the first field survey was conducted in September. Maximum surface concentrations of PO_4 and NO_3 were measured at stations 33 and 16, as 0.26 µM and 3.50 µM, respectively. TP concentrations exceeded 1.0 µM at St. 16 where

TN concentration reached 24.3 µM levels. NH_4 concentrations ranged between 0.08 and 6.62 µM, with the maximum value at St. 11. NO_3/PO_4 ratios were as high as 40-45 in the river-fed coastal zone. DIN/TP ratio ranged from 0.5 to 33; whereas TN/TP ratios varied between 13 and 90 in the surface waters of the bay. Silicate rich coastal waters were found to exist along the western nearshore zone of the studied area; the concentrations ranged between 0.6 and 6.20 µM, with lowest values in the offshore waters. DO concentrations varied from 6.0 mg/l to 8.0 mg/l. Chl-a concentrations ranged between 0.02 and 4.20 µg/l and reached the peak value in the western coastal waters fed by river discharges (Figure 3.12a).

In winter months of 2009, surface nutrient concentrations increased markedly, due to the effective winter mixing and river inflow into the region during January-February (Figure 3.12b). Concentrations of PO_4 ranged between 0.02-0.24 µM in January and 0.02-0.26 µM in February with the peak values in the polluted sites. NO_3 and NH_4 were close to detection limits in offshore waters, whereas the concentrations increased to the peak values of 21.3 and 22.7 µM, respectively at St. 11 in January. Surface concentrations of TP and TN ranged between 0.05-0.74 µM and 4.74-12.90 µM respectively in January 2009. The lowest TP was recorded at St 28. TN concentrations increased considerably in the nearshore zone in February and the highest silicate concentration was recorded at St. 18 with 5.19 µM. N/P elemental ratios considerably varied with region in winter months. In January NO_3/PO_4 ratio ranged from 3 to 53, whilst it increased up to 180 in February. On the contrary, the maximum DIN/TP ratio decreased from 108 in January to 65 in February. TN/TP ratio ranged between 24-126 and 44-130 in January and February, respectively. DO concentrations were high in the river-fed coastal waters, ranging between 7.22-7.78 mg/l in January and 7.5-9.3 mg/l in February. A similar feature was observed in the Chl-a concentrations, which varied regionally between 0.05-0.66 µg/l in January and between 0.09 and 6.69 µg/l in February, with highest values in the polluted zone.

In March, which represents late-winter early-spring period in the region, surface nutrient concentrations slightly decreased as compared to the winter values (Figure 3.12c). River-fed coastal waters had remarkably greater nutrient concentrations; PO_4 values reached 0.5 µM level at St. 11 and decreased to hardly detectable levels (0.02 µM) in offshore waters of the Bay. NO_3 concentrations ranged locally from 0.23 to

7.96 µM. In the site polluted by Mersin domestic effluents, NH_4 concentrations were higher than NO_3 values (Tuğrul *et al.* 2009). NH_4-N concentrations were recorded as high as 15.7 µM in polluted surface waters of the discharge zone. In spatial distributions of all the monitored parameters, distinct decreasing gradients were evident from the nearshore to the offshore area of the Bay. TP and TN concentrations declined down to 0.10 and 4.70 µM levels respectively in offshore region whereas it was observed high levels of concentrations with 1.14 and 15 µM in river-fed coastal site. NO_3/PO_4 and DIN/TP ratios were high on the coastal waters of the bay reached 72 and 25 levels respectively. TN/TP ratio ranged from 25 to 68 and maximum values were observed in the middle region of the Bay. Surface Si concentrations ranged between 0.83-5.36 µM in this period. DO and Chl-a concentrations were high (8.66 mg/l and 2.38 µg/l) in the river-fed coastal water with high nutrient values.

In April 2009, nutrient concentrations were markedly high between the Mersin Harbor and Seyhan Delta, exhibiting similar spatial distributions to those observed in March (Figure 3.12d). The surface NO_3 concentrations exceeded 5.0 µM at St. 16 and then decreased down to 0.06-0.09 µM in the offshore waters. PO_4 concentrations showed a similar spatial pattern with a value of 0.31 µM recorded at St 23, decreasing to 0.02-0.03 µM in the offshore site. TN concentrations ranged between 3.36 and 18.43 µM and maximum value was observed in St 33. TP concentrations exceeded 0.40 µM levels in polluted coastal waters whilst, it declined to 0.04 µM in St 48. In April, Berdan and Seyhan river discharges highly influenced surface distributions of nutrients in nearshore waters, due to their increased flow regimes in spring. NO_3/PO_4 molar ratios ranged markedly between 0.8 and 52 in the Bay, locally lower than the March N/P ratios (8-72). DIN/TP and TN/TP ratios varied locally between 2-14 and 40-97 respectively. DO concentration reached a peak value of 9.73 mg/l at St. 16 and exhibited similar spatial distribution to the other related parameters. Chl-a concentrations varied with region, increasing from 0.06 µg/l in the offshore to 1.55 µg/l in the coastal zone fed by the river discharges (Figure 3.12e).

Summer field survey was carried out in August 2009. Except NH_4 in the nearshore zone, surface nutrient concentrations decreased remarkably in the bay, consistent with declines in the river flows (Figure 3.12f). PO_4 and NO_3 concentrations were recorded to decrease below 0.10 and 1.0 µM in the shallow waters, respectively.

However, NH_4 concentration reached a maximum value of 4.24 µM at St. 16 on the nearshore zone where untreated domestic wastes were discharged. Surface TP concentrations ranged between 0.05 µM and 0.61 µM, reaching the peak values in the polluted nearshore waters having high NH_4-N. The maximum TN concentration (15.2 µM) was recorded at St. 36 on the river-fed zone. NO_3/PO_4 ratios was as high as 38 at St. 31, then decreased to level of 1-2 in the coastal zone, indicating NO_3 deficiency in the surface water outside direct effect of the river discharges. DIN/TP ratios increased from 2 to 30 at St. 4 due to relatively higher contribution of NH_4 (1.22 µM) at this station. TN/TP ratio ranged between 20 and 93, indicating significant regional changes as experienced in April (40-97). Si concentrations were markedly high, exceeding 7.8 µM in the river-fed coastal zone and declined to 0.7 µM level in the offshore surface water. DO was markedly high (7.74 µM) in the nutrient-replete coastal zone, decreased to 6.2 µM levels in more saline offshore waters. Surface Chl-a values varied regionally between 0.02 µg/l and 2.11 µg/l, exhibiting a similar spatial pattern to those of nutrients in the Bay.

The last field survey was conducted in October 2009, representing the dry autumn condition in the Bay. Relatively low nutrient concentrations were observed in the Bay (Figure 3.12g). Surface PO_4 concentrations were around 0.20 µM levels in the polluted coastal zone and declined to 0.02 µM levels in the offshore waters. NO_3 concentrations were as high as 8.34 and 5.01 µM at St. 16 and St. 11 polluted by domestic effluent discharges, and then rapidly decreased to 0.50 µM levels in the deeper locations of the bay. The highest NH_4 concentration was also measured at St 16 as 4.91 µM. TP and TN concentrations ranged between 0.05-0.61 µM and 3.3-15.2 µM, respectively, with greater values in the polluted coastal locations. Estimates of N/P molar ratios varied markedly between 0.86-100 for NO_3/PO_4, 0.6-26 for DIN/TP and 14-47 for TN/TP. The lowest ratios were reported for the offshore region of the Bay. The reactive Si concentrations ranged between 1.08 and 5.33 µM in the surface waters, with the highest values in the near shore waters as experienced in the previous field surveys. DO concentrations increased from 6.42 mg/l in the offshore waters to 7.50 mg/l levels in the coastal zone. Chl-a concentrations varied regionally between 0.03 and 2.34 µg/l with the highest concentration at St. 11 fed by river discharges.

Close examination of surface distributions of chemical parameters in Figures 3.12a-g demonstrate that the nutrient concentrations in the studies area of the Bay were drastically affected by inputs from domestic and river discharges. Oxygenated nutrient-replete Seyhan and Berdan discharges markedly enhanced the concentrations of nutrients and algal biomass (in terms of Chl-a) in the shallow zone (<15 m depth) of the Bay. However, this regional effect appeared to weaken during the dry summer-autumn period due to significant decreases in flow regimes of the major rivers in the region. Another nutrient source for the nearhore zone of the region was domestic effluents from Mersin city, which have been discharged for years at 10 m depth off the Mersin Harbor without any biochemical treatment. Therefore, pronounced levels of NH_4 and TP were measured in the discharge point and nearby locations. This effect was consistently monitored at St. 16 and St. 11, where large concentrations of nutrients were determined during the study period. In addition to external pressures, intensive winter mixing also supply nutrients from bottom to the surface layer but also enhance ventilation of the Bay by the offshore water via general circulation patterns of the Cilician basin (Özsoy *et al*., 1989; Oğuz and Tuğrul, 1998; Tuğrul *et al.* 2009). It was observed that local concentration differences became less pronounced and the surface nutrient concentrations generally increased over the Bay in winter months when the water column being well-mixed. However, PO_4 values remained almost constant and low over the Bay because NE Mediterranean upper layer water is always depleted in phosphate (Yılmaz and Tuğrul, 1998; Krom *et al*., 2005). Moreover ventilated coastal waters increased the area of influence via lateral intrusion associated with coastal upwelling. Therefore, five to ten fold higher nutrient concentrations were observed in winter period.

N/P molar ratios were calculated for different fractions of nitrogen and phosphorus pools in the bay. The highest TN/TP ratios (126 in January, 127 in February) were observed during winter months in the coastal zone due to increasing discharges of TN and DIN-replete rivers in the region. Low ratios of NO_3/PO_4 (0.8-10) and DIN/TP (0.5-10) were recorded in the offshore, indicating rapid consumption of bio-available inorganic nitrogen compounds but rapid recycling of PO_4 in the productive surface waters. The surface TN/TP ratios were much greater than the Redfield ratio of 16, due to low bio-availability of DON in productive marine environments, as experienced in most surface oceans and coastal zones of the world (Guilford and

Hecky, 2000; Jickells *et al*., 1998; Jackson and Williams, 1985). Similar results have been obtained by Bergström (2010) in oligotrophic lakes where a significant fraction of TN being in refractory DON form. Therefore, variations in the ratio of DIN to TP have been shown to be a better indicator than TN/TP ratio for discriminating between N and P limitation of phytoplankton in oligotrophic waters (Bergström, 2010; Downing, 1997).

Average concentrations of nutrients and their molar ratios were calculated from the seasonal data obtained during TÜBİTAK-SINHA (Project no: 107 G 066) cruises in the Mersin Bay between September 2008 and April 2010 (Figure 3.12h). Expectedly, annual average concentrations of nutrients imply the similar regional features that obtained during the course of the study. The highest values were always detected in the shallow nearshore waters between Mersin harbor and Seyhan river delta, where water circulations were very limited. DIN/PO4 ratios ranged from 14 to 108, with the highest values in the DIN-polluted nearshore waters between Mersin harbor and Berdan river delta. Since the regional river waters are relatively rich in DIN and thus have high DIN/PO4 ratios (Tuğrul *et al*., 2009), the river-fed coastal waters have higher DIN/PO4 ratios. TN/TP ratios varied between 29 and 95, with the lowest values in the nearhore zone fed by TP-rich domestic waters. DIN/TP ratios ranged between 2.9 and 21.9. As is stated in previous sections DIN/TP ratios varied seasonally in the coastal waters of the bay. These variations were mostly dominated by fluctuations of DIN concentrations rather than TP values, due to larger fluctuations in DIN inputs by river and domestic discharges.

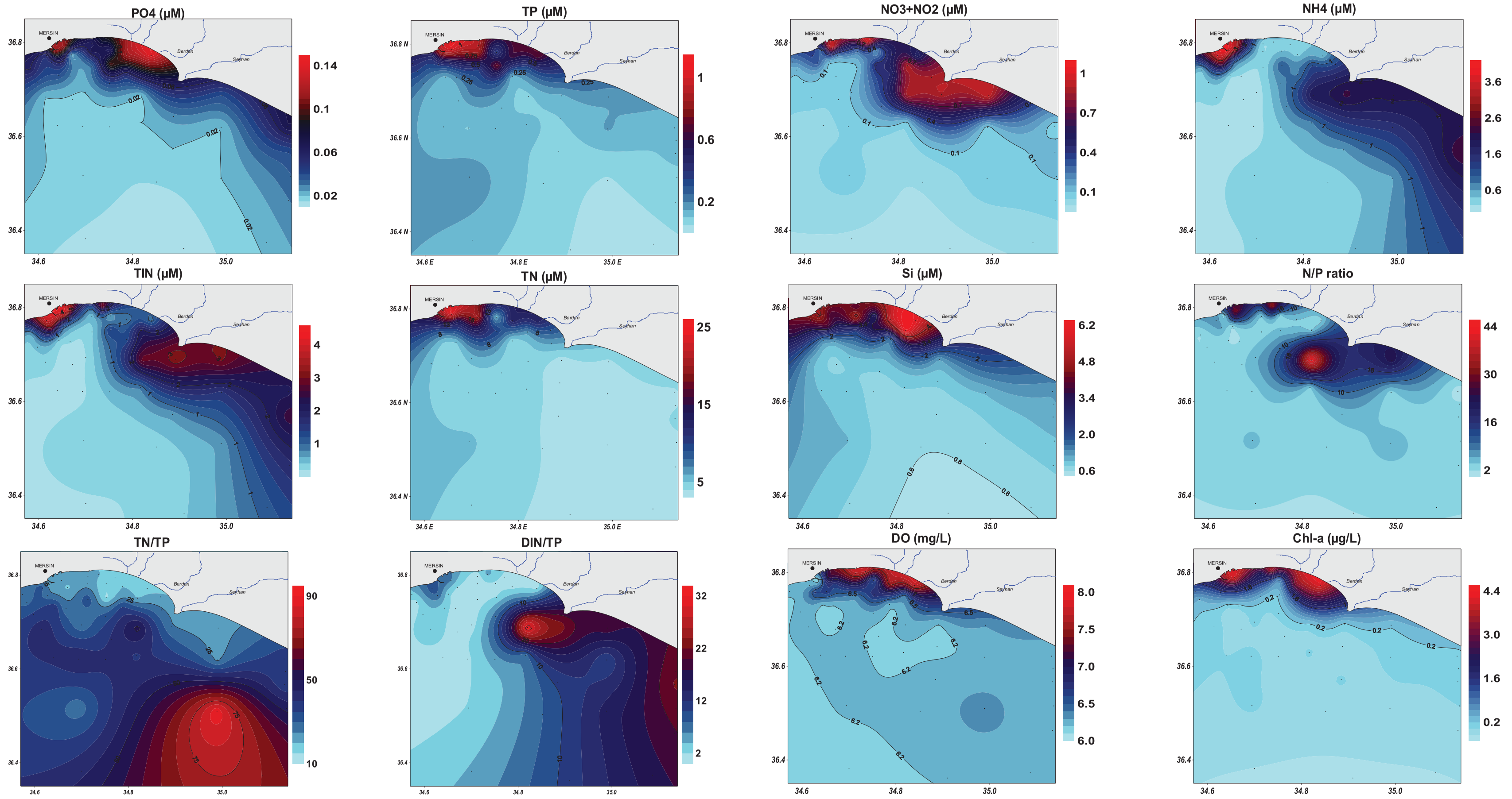


Figure 3.12a: September 2008-Surface distribution of nutrients.

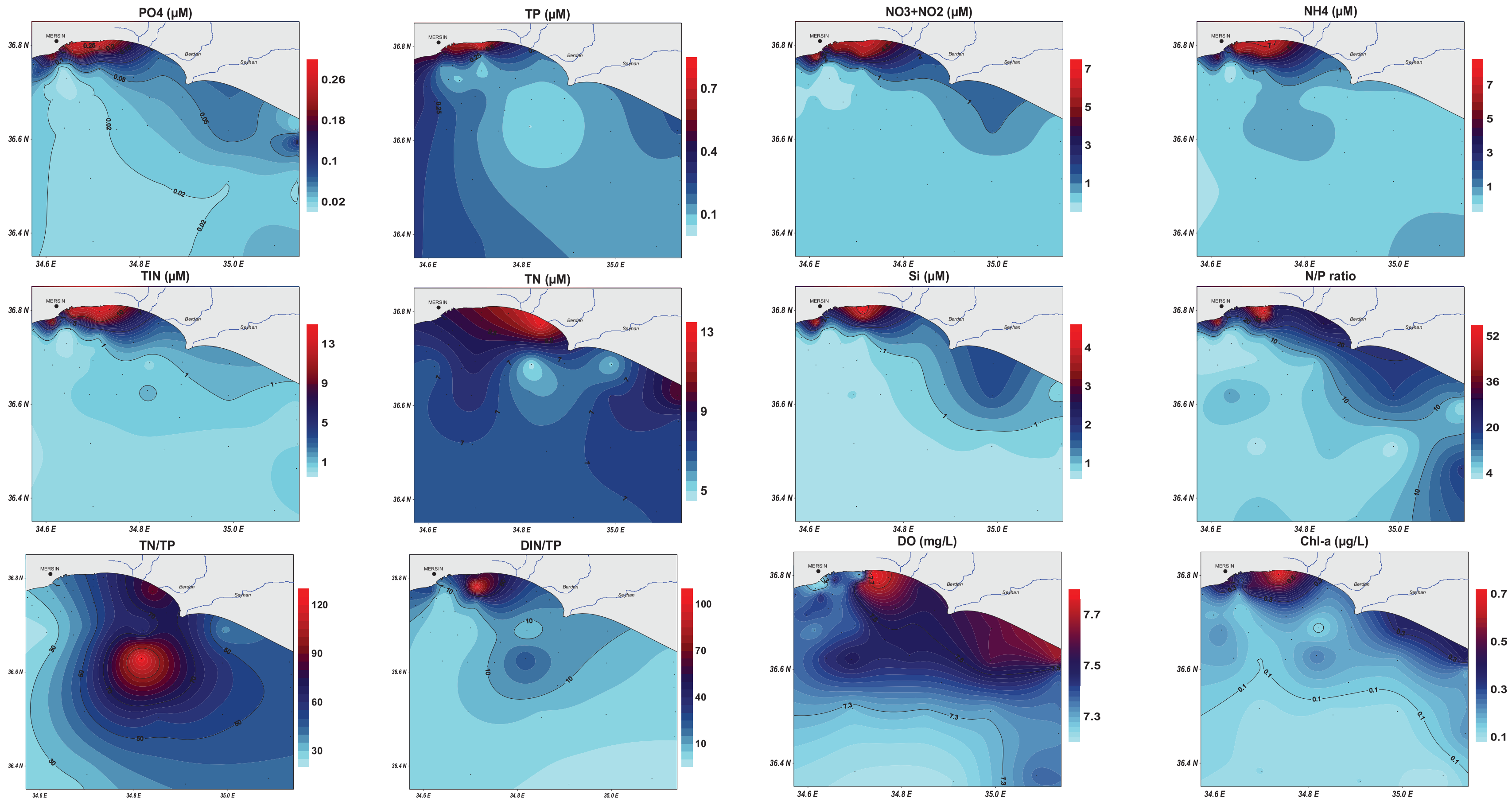
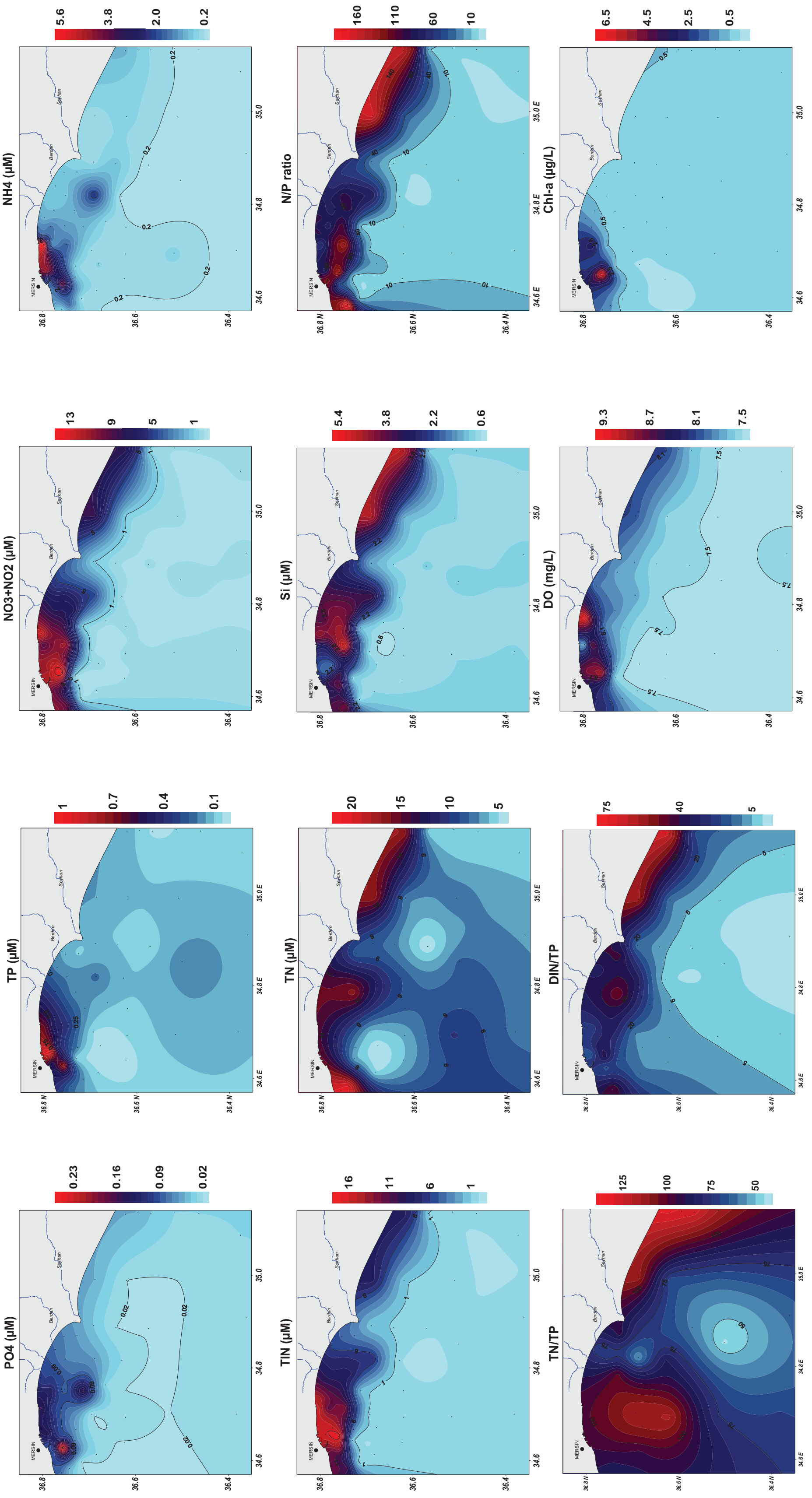


Figure3.12b: January 2009-Surface distribution of nutrients.



PO4 (µM)

TIN (µM)

TN/TP

TP (µM)

TN (µM)

DIN/TP

NO3+NO2 (µM)

Si (µM)

DO (mg/L)

NH4 (µM)

N/P ratio

Chl-a (µg/L)

Figure 3.12c: February 2009-Surface distributions of nutrients.

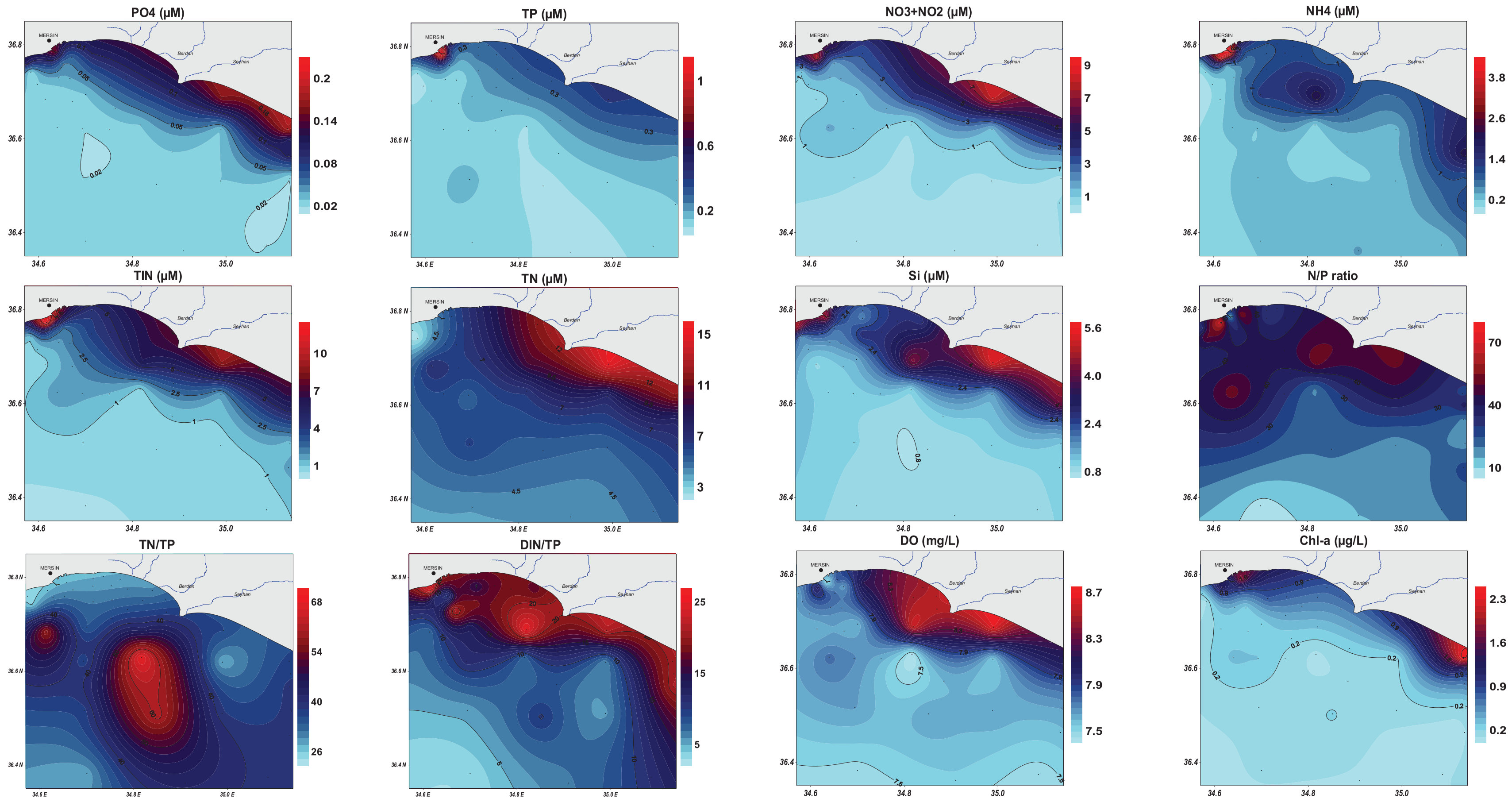


Figure 3.12d: March 2009-Surface distribution of nutrients.

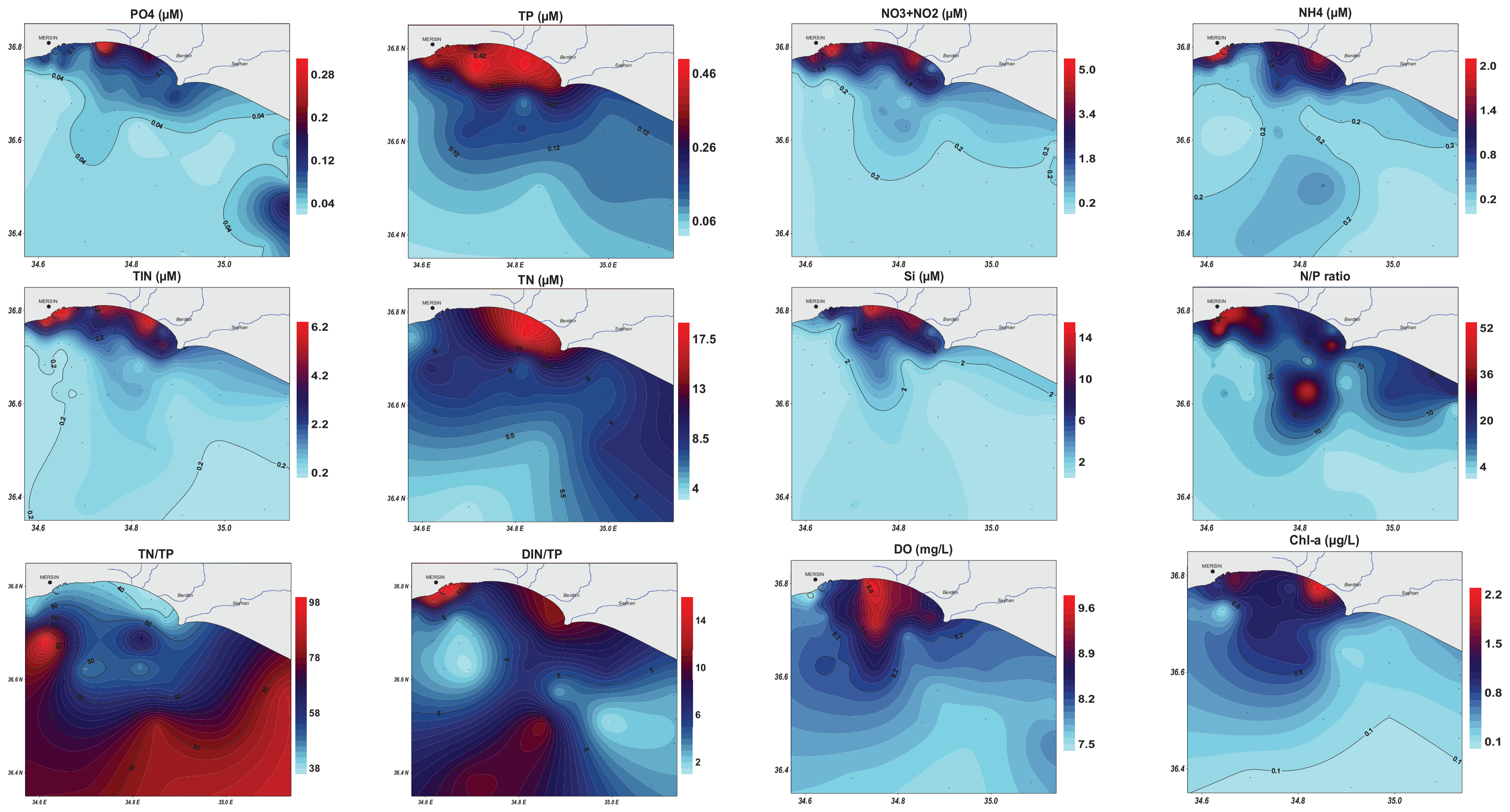


Figure 3.12e: April 2009-Surface distribution of nutrients

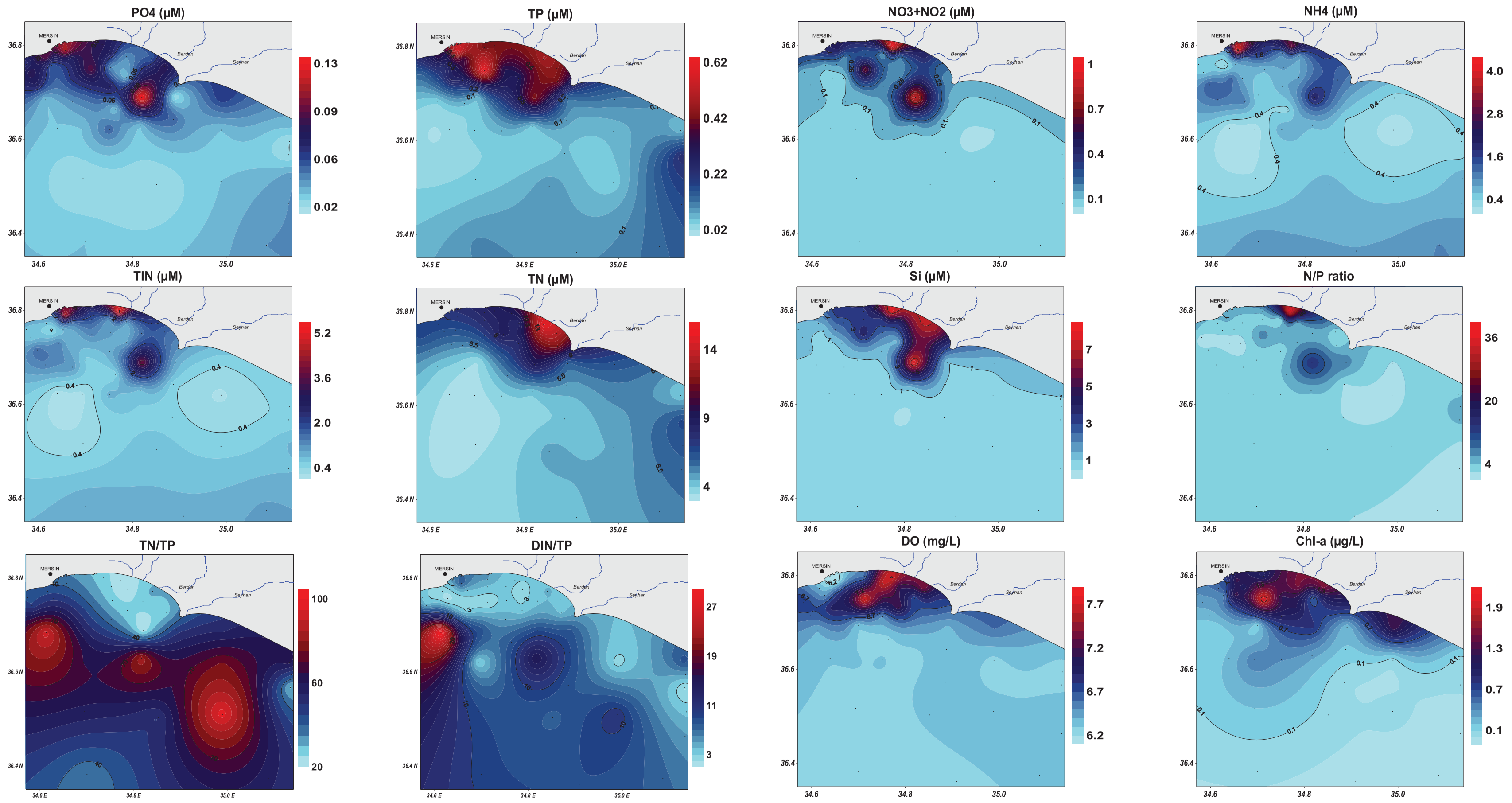


Figure 3.12f: August 2009-Surface distribution of nutrients

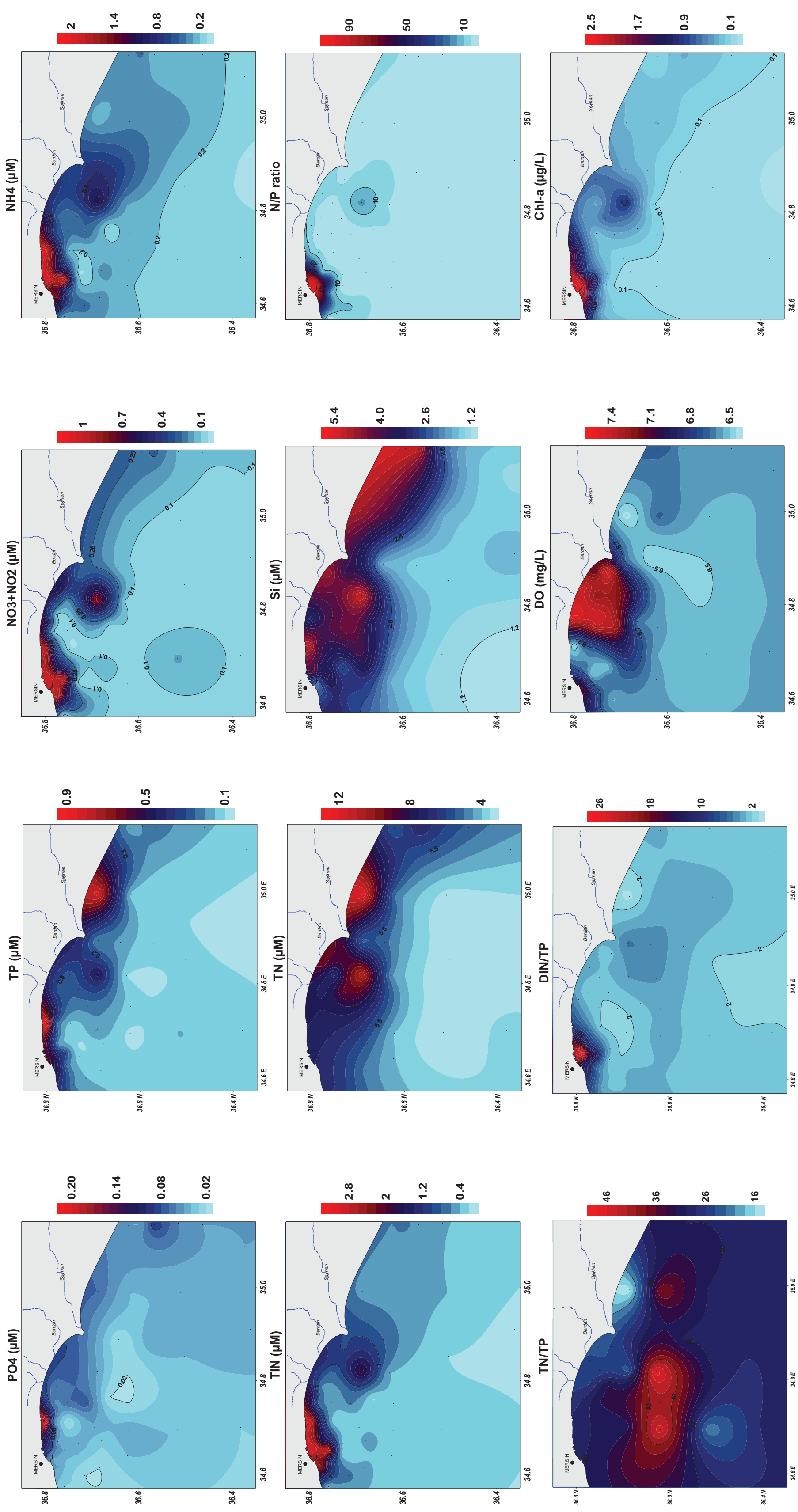


Figure 3.12g: October 2009-Surface distribution of nutrients.

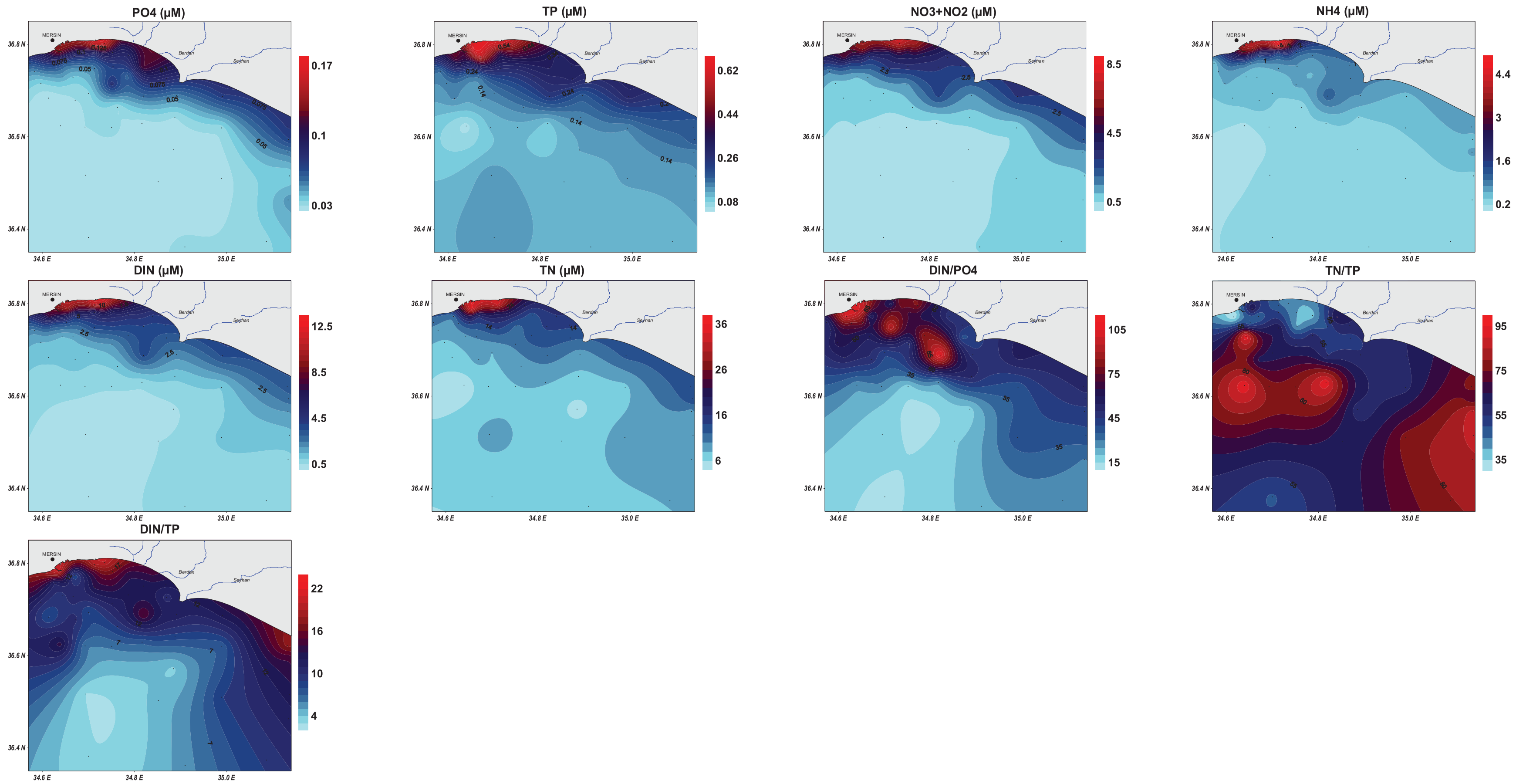


Figure 3.12h: Surface distributions of average concentrations of nutrients and ratios in Mersin Bay for the period of September 2008-April 2010.

3.5.2. Vertical distributions of nutrients and related parameters in the study region

Vertical profiles of nutrients and related parameters from selected stations and seasons from the study area are depicted Figures 3.13a-3.13b. Data obtained in February, April, August and October represent winter, spring, summer and autumn seasons respectively and entire data set is provided in Appendix A.

Measurements at St 2 (20 m) stand for nearshore water properties of the bay. In February, the highest DIN concentration (10 μM) was observed in the surface water and then rapidly decreased to 2 μM at 10 m depth. Near bottom water had slightly higher DIN concentrations in spring, summer and autumn periods (Figure 3.13a). Very low DIP concentrations were observed in the water column and concentrations merely exceeded 0.08 μM level. In winter, TN concentrations were as high as 20.3 μM in the coastal surface waters and decreased to 7.0 μM in the coastal bottom waters. TN concentrations ranged between 6.0 and 6.5 μM in the near surface waters in summer and autumn period. In winter, spring and summer seasons, TP concentrations varied from 0.11 μM to 0.23 μM in the near surface water and declined down to 0.07 μM at 10 m depth; it remained constant at 0.20 μM level in autumn season.

The NO_3/PO_4 molar ratio ranged between 43 and 180, with high values in the surface water of St 2, where TN/TP ratios ranged from 30 to 106 with the maximum value observed in spring at 10 m depth. Fresh water input during winter-spring season led to high DO concentrations in the well mixed water column (7.69-8.17 mg/l); whereas concentrations decreased to 6.0-6.5 mg/l levels during summer and autumn. Chl-a concentrations ranged between 0.20 and 0.51 μg/l, with the exception of the maximum value of 1.2 μg/l observed in the surface water in February.

At the coastal station (St 4, depth; 50 m), DIN concentrations ranged between 0.24-2.71 μM, higher values were measured in August due to high contribution of NH_4 concentrations (mean: 1.47 μM) from domestic discharges of Mersin city (Figure 3.13a). NO_3 concentrations varied seasonally between 0.06 and 2.2 μM, with the maximum value observed in October in the bottom water. DIP concentrations were very low throughout the water column, ranging merely from 0.02 to 0.06 µM. TP concentrations varied between 0.05 and 0.10 µM in winter, spring and summer, and increased slightly in autumn to the levels of 0.10-0.15 µM. TN profiles were almost uniform, and merely ranged between 4 and 6 µM. TN/TP ratios were in the range of 45-117, with the peak values observed in February, indicating large amounts of land-based TN input. NO_3/PO_4 ratios were lower in the upper layer water than in the near bottom waters (38-111) in April and October. The highest concentrations of DO and Chl-a were observed during winter and spring. DO concentrations decreased from 7.43-8.12 mg/l in February and April to levels of 6.25-6.61 mg/l in August and October. Chl-a concentrations ranged between 0.06 and 0.35 µg/l in February, August and October; in April; concentrations increased to 0.60 µg/l in near surface and reached 0.75 µg/l in the near bottom waters.

Station 10 was selected at a depth of 70 m, as the middle station of the study area. DIN concentrations varied seasonally between 0.14 and 2.47 µM, with the maximum values observed in March (Figure 3.13b).Vertically uniform profile of DIN was observed in February due to effective winter mixing. The onset of the nitracline situated at 30 m depth in April and deepens down to 50 m depth in summer. DIP concentrations were consistently low, ranging from 0.02 to 0.08 µM. TP and TN concentrations ranged seasonally between 0.04 and 0.17 µM and, between 3.33 and 8.21 µM, respectively. During the study period, NO_3/PO_4 and TN/TP ratios ranged between 2-54 and 30-144 respectively at St 10. TN/TP ratios exceeded NO_3/PO_4 ratios, due to large TN input by the river discharges and thus large DON in the TN pool of the region. NO_3/PO_4 ratios were low in upper layers and then increased within the nutricline depths, where PO_4 changed slightly. The highest DO concentrations were observed in April when at mean value of 7.73 mg/l was recorded. In August and October, DO concentrations varied between 6.31 and 7.61 mg/l whilst concentrations ranged between 7.30 and 7.71 mg/l during winter and early spring. Chl-a concentrations varied between 0.06 and 0.79 µg/l, with maximum values observed in April. Chl-a concentrations decreased sharply in summer within the upper 20 m layer.

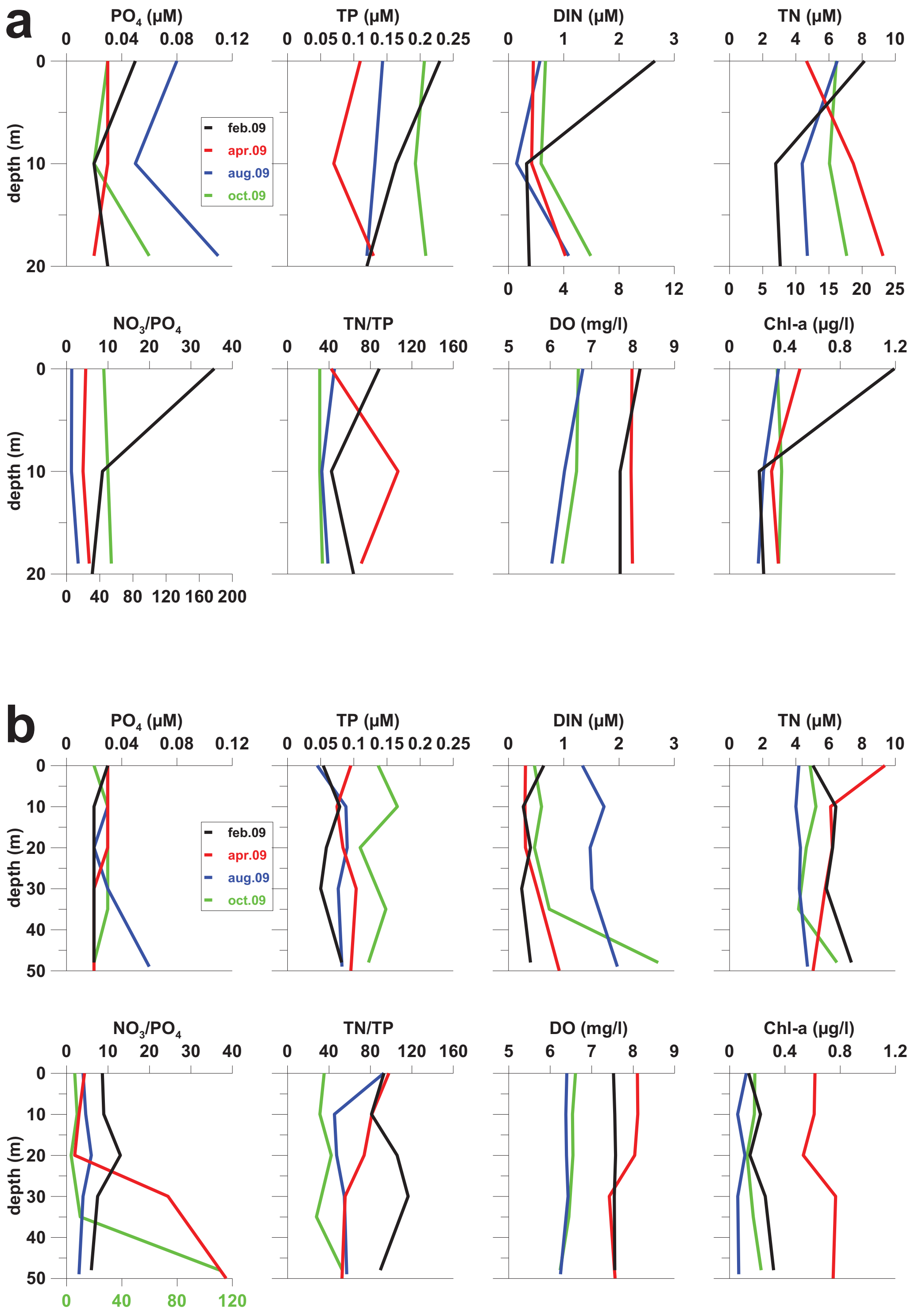


Figure 3.13a: Vertical profiles of nutrients at St 2 (a) and St 4 (b) representing winter, spring, summer and autumn periods.

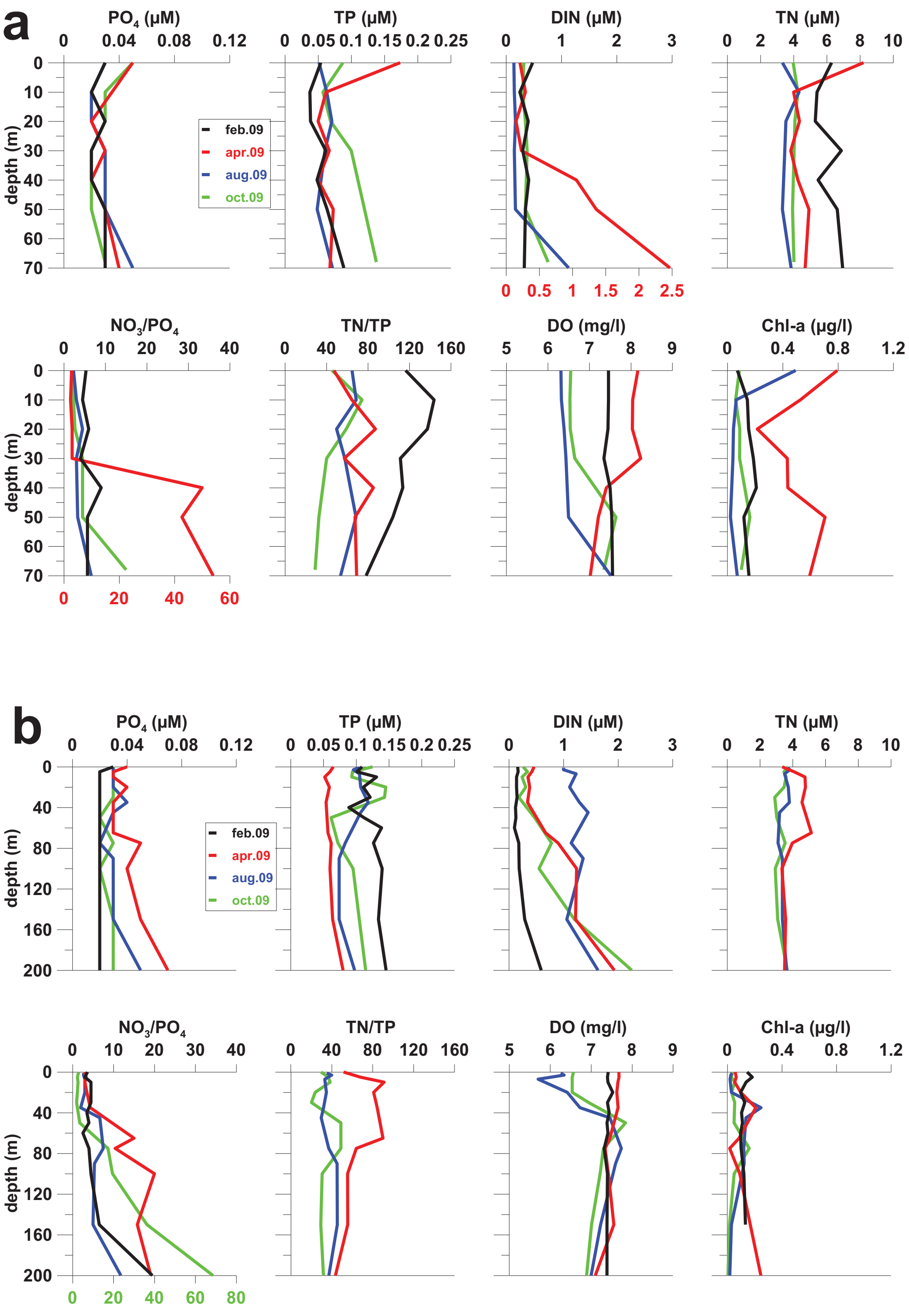


Figure 3.13b: Vertical profiles of nutrients at St 10 (a) and St 48 (b) representing winter, spring, summer and autumn periods.

St 48 (200 m depth) was selected on the shelf break zone, representing offshore water properties of the bay. DIN concentrations varied seasonally between 0.10 and 2.23 μM in the water column (Figure 3.13b). Maximum DIN values were observed in the near bottom waters in October 2009. DIP concentrations were low and ranged merely between 0.02 and 0.07 μM. TN concentrations, not measured in February, ranged between 1.98 and 9.90 μM during the study period, with higher concentrations in the upper 80 m. In April, at 80 m depth, TN concentrations decreased sharply to 3.0 μM level and remained constant below this depth. In August and October, TN concentrations varied slightly, ranging between 3.0 and 4.0 μM. Throughout the period of the study, TP concentrations were consistently low, ranging between 0.03 and 0.35 μM. NO_3/PO_4 ratios were low in upper waters and steadily increased through the water column, reaching peak values in near bottom waters. NO_3/PO_4 ratios ranged between 3-20 in February and April 2-12 in August and 2-70 in October. TN/TP ratios varied from 20 to 85, with greater values in April. In summer and autumn vertical profiles of TN/TP ratios were approximately uniform with slight variations at intermediate depths. In August and October, DO profiles displayed an increasing trend in the seasonal thermocline formed in the upper layer (Figure 3.13b). DO concentrations ranged between 5.90 and 6.50 mg/l above the thermocline and reached 7.01-7.84 mg/l levels in bottom waters. Due to effective winter mixing, DO concentrations exhibited vertically uniform profiles with the mean value of 7.40 mg/l in February. Chl-a concentrations ranged between 0.02 and 0.21 μg/l with sharp fluctuations through the water column.

During the course of the study, vertical distributions of nutrients and Chl-a demonstrated the oligotrophic conditions in the middle and offshore zones of the Bay (>50m depth), due to limited influence of river discharges. Throughout the study period, DIP and TP concentrations were low in the deeper parts of the Bay. PO4 concentrations were as low as 0.02-0.04 μM in the productive upper layer waters and increased slightly to 0.05-0.06 μM levels in the bottom waters below the euphotic zone (EZ). TP concentrations were found to be higher in the surface waters of the near-shore zone; however, the offshore TP values were lower and displayed vertically almost uniform distribution in the upper layer and then varied slightly below the EZ.

From the seasonal observations and examination of all the data, it can be conclude that temporal variations of NO_3 and NH_4 in the upper layer of the Bay appeared to be strongly dominated by river and domestic discharges in the region. The nearshore water concentrations ranged between 0.10-25 μM for NO_3, 0.10-27 μM for NH_4 and 0.25-52 μM for DIN during the study period. Their offshore values decreased to levels of 0.06, 0.05 and 0.10 μM for NO_3, NH_4 and DIN, respectively. Primary productivity studies have shown that NH_4 is more readily used by marine microorganisms in photosynthesis (Brzezinski, 1988; Gruber and Sarmiento, 1997) as compared to NO_3. In addition to land-based inputs, NH_4 is regenerated via respiration in the EZ. Therefore, it comprised a significant fraction of DIN in the EZ of the Bay, depending on the rates of source and sink terms. For example, NH_4 concentrations exceeded NO_3 values in the nearshore waters of the bay receiving NH_4 inputs from domestic wastewater and polluted river discharges of the region.

TN vs. TP plots in Figure 3.14 demonstrate that the slopes of the scattered TN and TP values were comparable during summer-autumn period but different from the slopes of winter and spring data. Higher correlations were observed in nutrient enriched waters. More specifically, the highest slopes (TN/TP ratio) were obtained from the data collected during January and February, from which gradients of 50.6 and 78.0 were calculated respectively and decreased to 37.0 in March and 41.4 in April; finally, September, August and October slopes were calculated as 23.2, 30.7 and 24.9, respectively. The distribution of data points on the graph, which display large scattering at lower concentration ranges, indicates that the TN/TP ratios decreased from winter to summer seasons as observed from their vertical profiles.

As is mentioned above, DIN to TP ratios were found to be a better indicator than TN to TP ratio in terms of representing N and P limitation of phytoplankton in oligotrophic marine environments (Bergström, 2010). Therefore, the scattered DIN and TP values was illustrated in Figure 3.15, in which slopes of the data represent mean value of DIN/TP ratios in that season. As is shown in the figure, highest slopes were obtained in January and February with 20.1 and 19.0 respectively. In March, the gradient decreased to 14.2, indicating relative decrease in DIN/TP ratios. The rest of the slope values changed merely between 5.5 and 7.4.

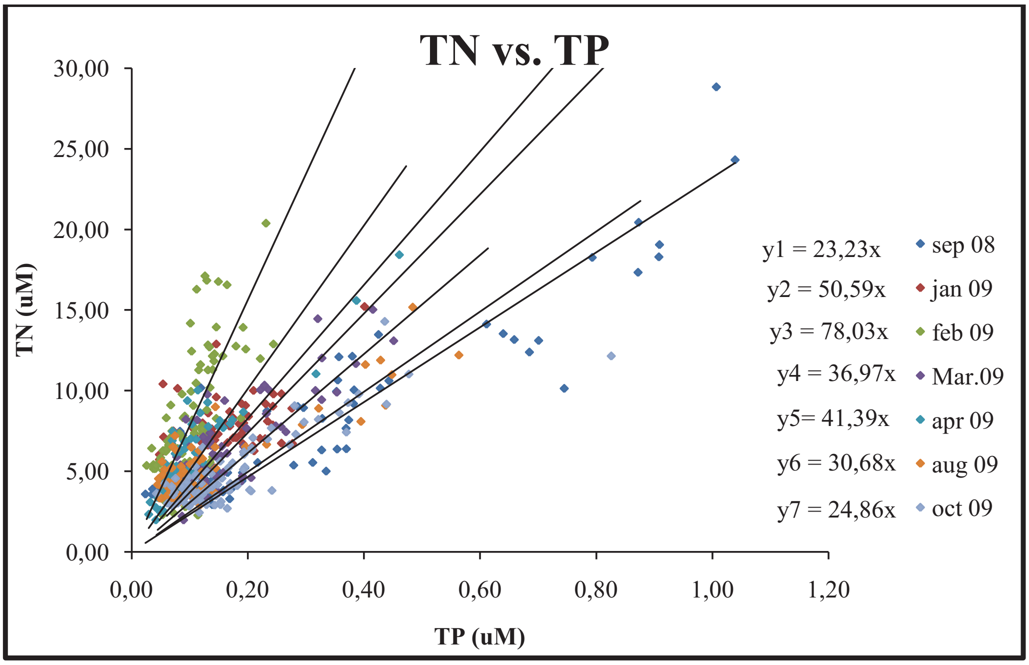


Figure3.14: TP vs. TN plot of the data measured from the study region in Sept. 2008-Oct. 2009 period.

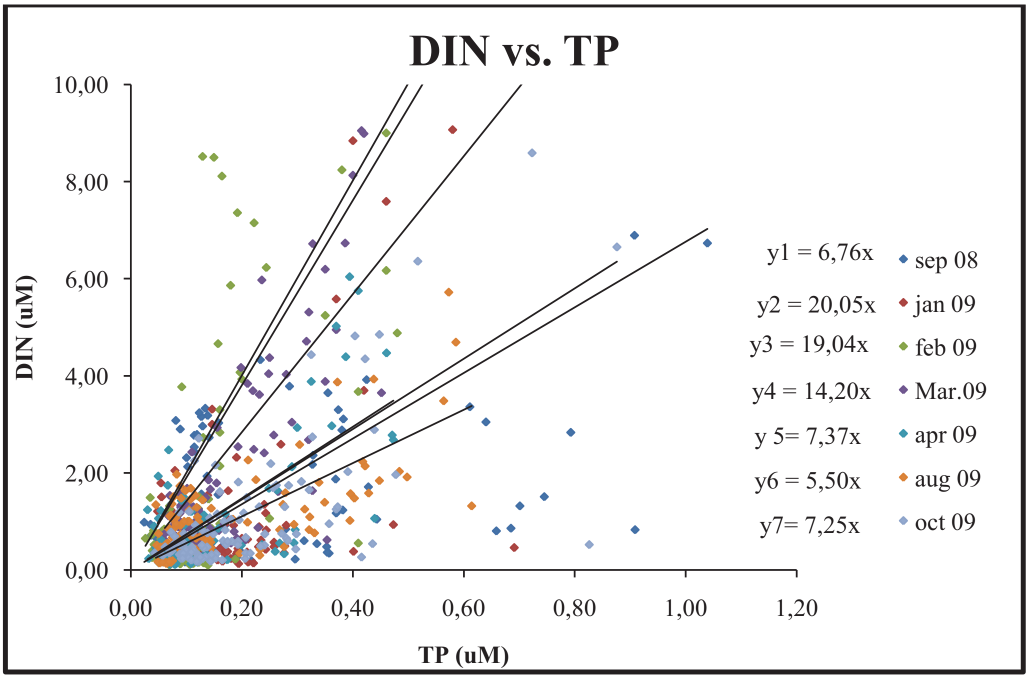


Figure 3.15: TP vs. DIN plot of the data measured from the study region in Sept. 2008-Oct. 2009 period.

Mean values of TN and TP measurements from coastal, middle and offshore sites were compared with previous observations from the different seas (see Table 3.8). In the NE Mediterranean, TN and TP values are much lower than in the more productive oceanic environments; they are only comparable with the NW Mediterranean Provencal Basin. The data compiled in Table 3.8 imply significant differences among different areas of the Mediterranean Basin. For instance, Atlantic inflow enters the western Mediterranean with lower TN/TP ratios. Then it increases to higher levels as the Eastern Basin has been reached via general circulation of basin. TN/TP ratios varied between 36 and 43 in the Mersin Bay, much lower than in the TN-replete Northern Adriatic waters. It appears that land-based nutrient inputs and chemical properties of upwelling water dominate the N/P ratio in the coastal waters and open seas.

Table3.8: Comparison of TN, TP and TN/TP ratio with previous observations from the different seas.

location	**TN**	**TP**	**TN/TP**	**Reference**
NE Mediterranean (coastal 0-20 m)	8.2	0.19	43	This study
NE Mediterranean (middle 50-120 m)	5.4	0.15	36	This study
NE Mediterranean (shelfbreak 200 m)	4.9	0.12	41	This study
NW Mediterranean (Spain)*	5-6	0.05		Lucea *et al*. 2003
Provencal Basin (NW Mediterranean)	8.2	0.44	19	Bethoux *et al.* 1992
Gulf of Lion (NW Mediterranean)*	5.8-6.1	0.12-0.14		Aminot and Kerouel 2004
Marmara Sea	12.7	1.05	12	Polat and Tugrul 1995
Black Sea	20.1	0.33	61	Polat and Tugrul 1995
Northern Adriatic	29	0.18	161	Lipizer *et al.* 1999
Baltic Sea	19.7	0.32	62	Valderrama 1981
Gilbaltar Strait (Mediterranean)	11.6	0.45	26	Coste *et al.* 1988
Gilbaltar Strait (Atlantic)	9.5	0.33	29	Coste *et al.* 1988
UK (Scotish shelf)	32.4	1.3	25	Guilford and Hecky 2000
Sargasso Sea (Atlantic)	30.5	0.6	51	Guilford and Hecky 2000
N. Atlantic cont. slope	33.3	1	33	Guilford and Hecky 2000
Arctic coasts (Canada)	31.1	1.6	19	Guilford and Hecky 2000

**DON and DOP data were gathered instead of TN and TP.*

3.5.3. Contributions of dissolved inorganic nitrogen and dissolved inorganic phosphorus to total nitrogen and total phosphorus pools of the bay

DIN and DIP data were evaluated though analysis of basin wide surface distributions and vertical transects along selected lines (Figure 3.16 and 3.18). Spatial and vertical distributions of TN and TP are depicted in Figure xxx. In addition DIN, dissolved organic and particulate fractions of N (DON, PN) and P (DOP, PP) have significant contributions to TN and TP pools in the productive upper layer of the marine environments (Coste *et al*., 1988; Bronk and Ward, 1999; Bronk, 2002). In the present study, limited PN and PP were measured at selected stations. Therefore, in the present study, the total of DON+PON (referred to as DON in the text and figures) and DOP+PP (thereafter, referred to as DON in the text and figures) were calculated by subtracting DIN and DIP from TN and TP, respectively. According to limited data in the Bay, PN concentrations ranged from 0.75-10.10 μM in nearshore zone to 0.19-1.28 μM in the offshore waters; their levels were comparable with DIN from the same depths. Similar conclusion could be reached for PP values, varying between 0.01 and 0.70 μM in the water of the Bay and at similar levels with DIP results.

Relative importance of DON and DOP in the TN and TP pool of the Bay are evaluated in the present study.

In September 2008, higher DON concentrations were observed in river-fed coastal waters (Figure 3.16). Surface concentrations of DON ranged between 0.80 and 18.23 μM and lower concentrations were observed in the eastern part of the basin. Along the transect in Figure 3.18 DON concentrations were higher in the coastal shelf, decreasing with increasing distance from the shore as experienced in the surface distribution. Surface DOP concentrations ranged between 0.03 and 0.93 μM in September 2008. The highest concentration was observed at St 16 which was located close to the city harbor. Relatively higher DOP concentrations were observed in the upper 20 m along the transect, whilst rest of the water column had moderately uniform distributions, with lower concentrations.

During the winter months of the study period, surface waters with higher DON content spread over a wider area of the basin. DON concentrations ranged between

3.77-9.59 µM and 4.05-9.79 µM in January and February respectively. In January, higher DON concentrations were observed in the upper 50 m on the coastal shelf. In February, DON concentrations were almost uniform throughout the entire water column in the offshore regions. Surface DOP concentrations were higher in February, decreasing from 0.85 to 0.02 µM in the offshore. Maximum values were detected at St 16 in winter. In February, DOP distributions were similar to DON, with DOP rich waters observed at offshore waters, implying local changes in flow patterns of the major river in the region.

Spring cruises were carried out in March and April 2009. During this period, surface DON concentrations varied within the range of 1.07-6.24 µM and 2.90-13.96 µM in March and April, respectively (Figure 3.16). The surface distribution of DON in March was similar to that observed in February, with higher concentrations spreading over a wider area, rather than accumulation in the coastal region. In March, maximum DON concentrations were observed in near bottom water and intermediate depths. In April, vertical stratification was formed again, resulting in higher values in the upper waters and a decreasing trend with increasing depth. Surface DOP concentrations ranged between 0.07-0.65 µM and 0.01-0.40 µM in March and April respectively. DOP transects were similar to DON during in this period. Maximum values were observed at intermediate depths in both transects in March whereas in April DOP rich waters were detected in the upper 50 m of the coastal shelf within vertically stratified water column.

According to data collected in August 2009, surface DON and DOP concentrations varied within the ranges of 2.70-13.15 µM and 0.02-0.52 µM respectively (Figure 3.16). For both parameters concentrations were higher in the coastal regions. Relatively low concentrations were observed in the water column, compared to winter and spring seasons (Figure 3.18).

The last field survey was carried out in October 2009. Higher DON concentrations were observed on the Eastern coast of the basin where highly affected by the Seyhan river influx. DON concentrations ranged between 2.80-11.63 µM in the surface waters. DON values were highest in the upper 20-30 m layer (Figure 3.18). Surface DOP concentrations varied within the range of 0.04-0.76 µM. Maximum concentrations were observed in the Seyhan river plume and Mersin city coasts. The same vertical features were obtained along the transect. A secondary DOP maximum was observed in near bottom water on the coastal zone.

As is illustrated in Figure 3.16, surface distributions of DON demonstrated different features than DIN, due to background concentrations of TN in the seawater. More uniform spatial distributions were observed across the study region especially in February and March, when the lateral and vertical mixing and ventilation of the Bay at maximal levels. Nevertheless, as is shown in Figure 3.16, DON and DOP concentrations were consistently higher in the river-fed nearshore zone throughout the course of the study.

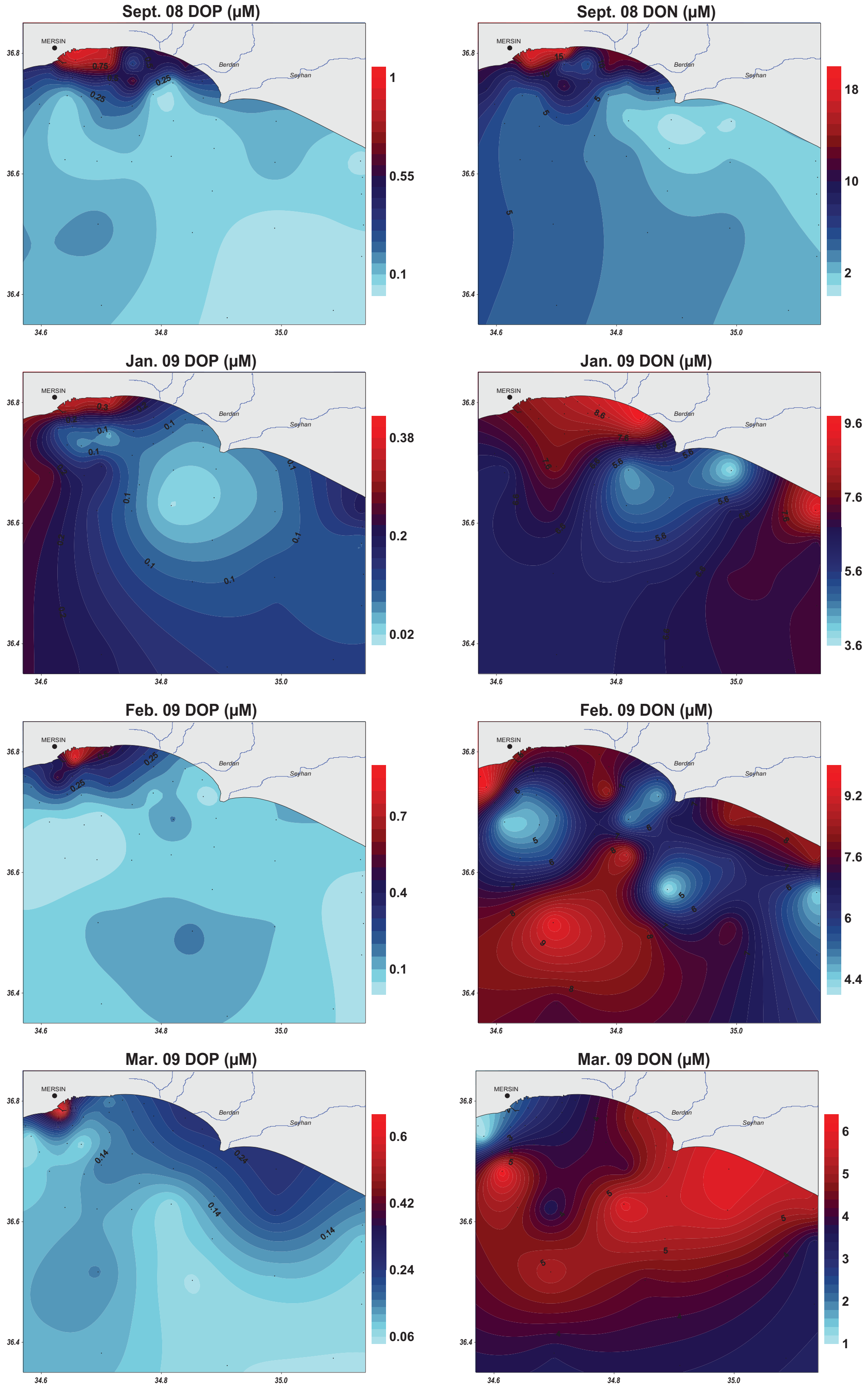
Close examination of seasonal DIN, TN, DIP and TP data reveals that spatial and temporal changes in TN and its constituents (DIN, PN, DON) were much greater than those in TP, due to large TN input by the regional rivers as compared to their TP loads.

Previous DON and DOP observations from the Mediterranean Sea have been evaluated Section 1.4. Limited data from Mediterranean Sea are compiled Table 3.9. In 2005, Krom *et al*. published their DOM data which were obtained in the vicinity of a warm core eddy of Cyprus and its frontal region. According to their data, outside of the eddy, DON decreased from 4.5-11.5 μM in the upper 50 m to a constant value of ~2 μM below 350 m depth. At the same location, DOP demonstrated a small decrease in the upper water column (>350 m) and then maintained a relatively constant of ~50 nM below that depth. In the core of the eddy, DON values decreased rapidly from 5-10 μM in the uppermost layers to ~2 μM below 300 m, DOP decreased by a relatively small amount from 50-60 nM in the uppermost photic zone to ~40 nM at depth.

Raimboult *et al*. (1999) estimated DOC, DON and DOP concentrations in the Northwestern Mediterranean using the wet oxidation method in November 97 and January 98 at coastal and offshore zones. Mean values of DON and DOP were recorded as 5.4 and 0.09 μM at the coastal station (160 m) and 5.0 and 0.057 μM. At the offshore station (400 m) mean values of DON and DOP were given as 4.8 and 0.11 µM respectively.

Table 3.9: Comparison of DON and DOP concentrations with previous observations from the different regions of Mediterranean Sea.

Location/date	**Depth (m)**	**DON (µM)**	**DOP (µM)**	**Reference**
NE Med. (Sept. 2008 - Oct. 2009)	(St 2) 20 m	5.70	0.11	This study
	(St 4) 50 m	4.94	0.09	
	(St 10) 70 m	4.70	0.07	
	(St 48) 200 m	5.07	0.09	
SE Med., Cyprus warm core Eddy (summer 2002)	photic zone	3 -11	0.05	Krom *et al*. 2005
	500 -1200	1 - 2	0.04	
NW Med. (March 98)	0 - 400	5	0.13	Raimboult *et al*. 1999
NW Med., Spain (September 96)	0-150	5-6	0.05	Anna Lucea *et al*. 2003
NW Med., France (September 84)	0-200	4.0	0.08	Aminot and Kerouel 2004
	200-600	3.0	0.04	
	800-1500	2.7	0.03	


Sept. 08 DOP (μM)

Sept. 08 DON (μM)

Jan. 09 DOP (μM)

Jan. 09 DON (μM)

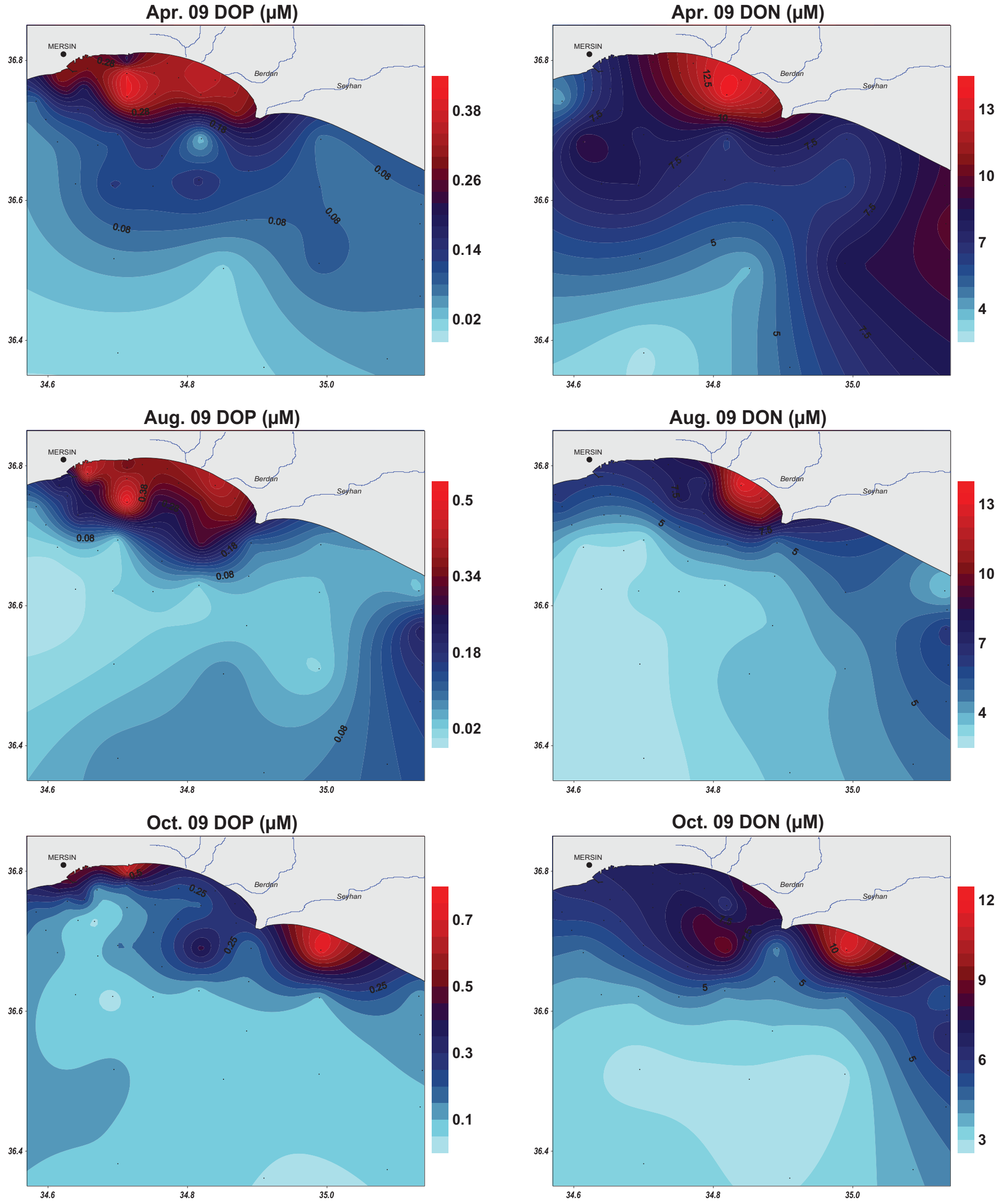
Feb. 09 DOP (μM)

Feb. 09 DON (μM)

Mar. 09 DOP (μM)

Mar. 09 DON (μM)

Figure 3.16: Surface distributions of DON and DOP



Apr. 09 DOP (µM)

Apr. 09 DON (µM)

Aug. 09 DOP (µM)

Aug. 09 DON (µM)

Oct. 09 DOP (µM)

Oct. 09 DON (µM)

Figure 3.16: Continued

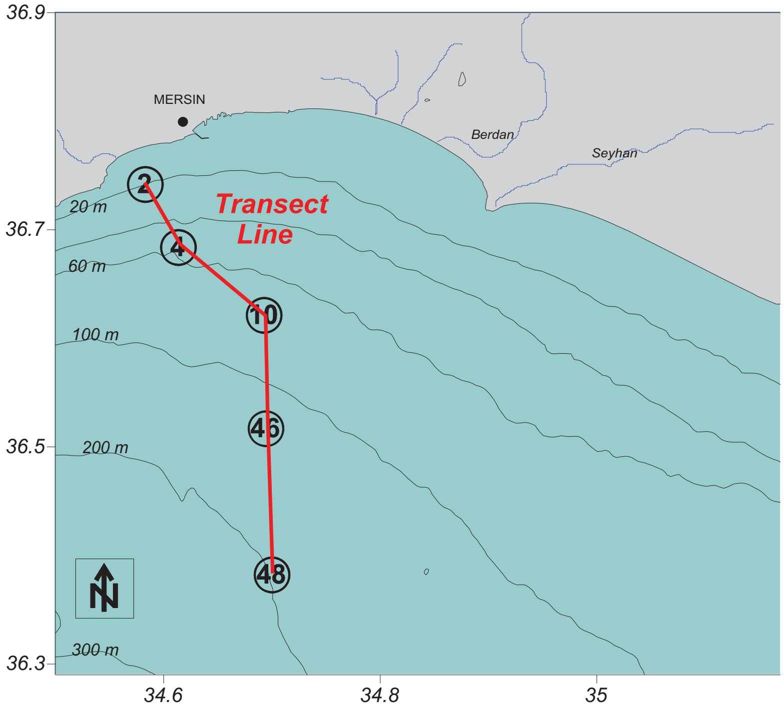


Figure 3.17: The sampling locations on the selected transect

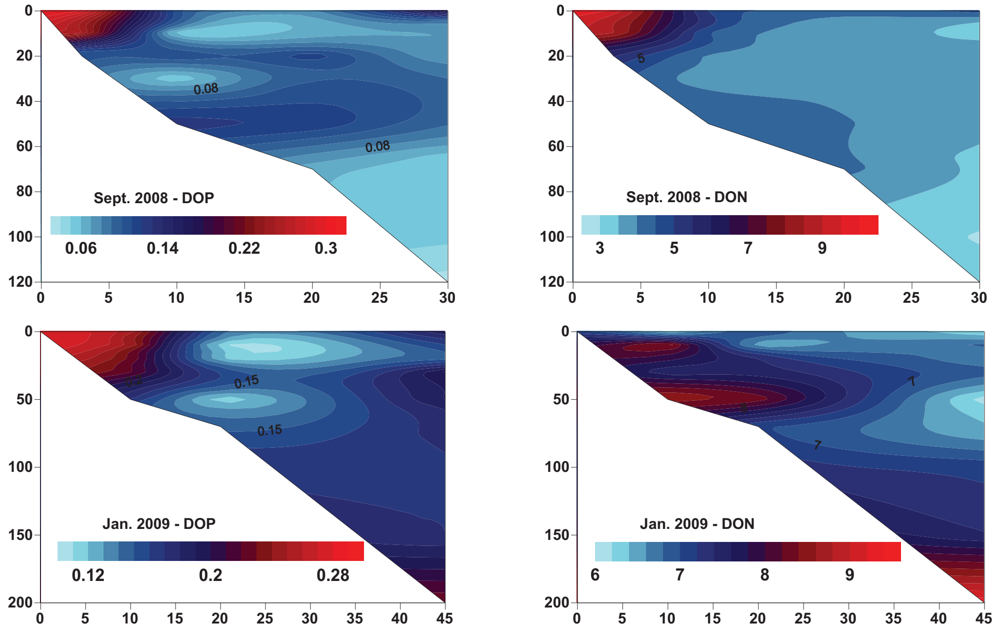


Figure 3.18: Transects plots of DON and DOP along the selected line

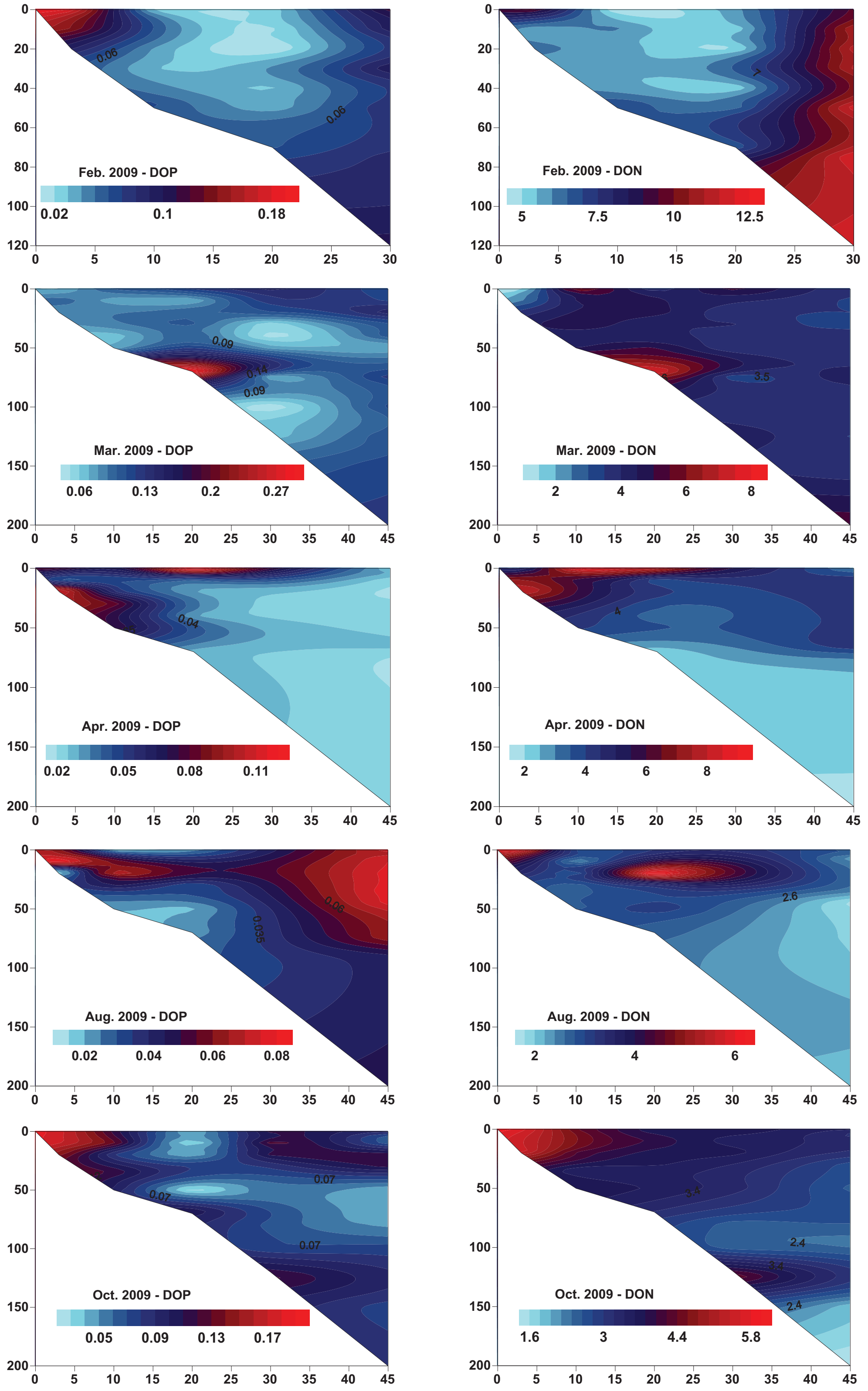


Figure 3.18: continued

CHAPTER 4

CONCLUSION

Beside the fact that, the organic and total N and P pools are essential to our understanding of N and P cycling in marine environment, global data on organic forms of nitrogen and phosphorus or TN and TP for the world's seas are still relatively sparse (Guilford and Hecky, 2000; Downing, 1997; Vidal *et al*., 1999). On the other hand, it should be considered that the measurements of the size of these pools and their dynamics have been beyond the reach of standard marine chemical methodology (Downing, 1997; Sharp *et al*., 2002).

In order to fill the systematic gap on this issue, TN and TP contents of the water column were determined in the Mersin Bay of Cilician Basin, NE Mediterranean, in the period of September 2008-October 2009, together with related hydro-chemical and hydro-physical parameters. In compliance with the main aim, inorganic nutrient measurements were also performed in order to depict more comprehensive picture of the spatial and temporal variations of nitrogen and phosphorus fractions in the area.

The method of Wet Chemical Oxidation (WCO) in closed bottles (pH controlled oxidation) was applied for TN and TP analyses as introduced in the study of Raimboult *et al.* (1999). Accuracy of the selected measurement methods was tested and the results were given in related sections. The WCO procedure was found simple, robust and less susceptible to contamination problems. On the other hand, unexpected reagent blank values were obtained in TN measurements, which corresponds nearly 20% of measured TN concentrations in oligotrophic NE Mediterranean. Furthermore, slightly lower oxidized-N recoveries (90%) were obtained in sea water (SW) samples due to suppressive coloring effect of other chemicals that naturally present in SW. Nevertheless, WCO was applied efficiently for the determination of TP and comparable results were obtained from the spectrophotometric measurements of studied samples. After all, it can be concluded that the WCO method was found appropriate for the determination of TP. However, it needs some improvement to enhance the reliability of the TN analysis, especially oriented to reduce suppressive matrix effect in SW digests.

Seasonal and spatial distributions of the hydro-physical parameters in the NE Mediterranean water column are dominated by general circulation pattern of the basin. Furthermore, thermohaline properties of the Mersin Bay were highly influenced by the river discharges, surface water heating/cooling and wind-induced coastal processes. In period of 2008-2009, it was observed that the strong vertical mixing in winter created vertically uniform profiles of temperature (~17.8 °C), salinity (~39.4 psu) and water density (~28.6) in the Bay. After the winter cooling period, volume fluxes of the river discharges to the sea increased with the contribution of melted snow waters, which decreased surface temperature (16.9 ^{o}C) and salinity (38.1 psu) markedly in the shallow coastal zone as observed in the bay. During the summer-early autumn period, warmer and saltier waters (~26.1 ^{o}C and ~39.6 psu) occupied the upper layer down to 40 m in the offshore zone.

A number of studies implied that the nutrient cycling in the NE Mediterranean is subject to seasonal and regional variations. River and atmospheric inputs of nutrients have effect upon not only coastal sites of the basin but also Cilician open waters via internal mixing processes which lead to less pronounced local concentration differences especially in winter months. Nevertheless, a distinct decreasing gradient is evident in nutrient and Chl-a concentrations from the nearshore to the offshore area of the Bay. Nutrient-replete Seyhan and Berdan discharges markedly enhanced the concentrations of nutrients and algal biomass (in terms of Chl-a) in the shallow zone (<15 m depth) of the bay. However, this regional effect appeared to weaken markedly during the dry summer-autumn period due to significant decreases in flow regimes of the major rivers in the region.

Surface PO_4 concentrations ranged from 0.20-0.50 µM levels in the polluted coastal zone to 0.02-0.04 µM in the offshore where the concentrations remained almost constant at 0.05-0.06 µM levels the bottom water below the EZ. The near shore water concentrations varied seasonally and locally between 0.10-25 µM for NO_3, 0.10-27 µM for NH_4 and 0.25-52 µM for DIN during the study period. However, the offshore values were as low as 0.06, 0.05 and 0.10 µM for NO_3, NH_4 and DIN, respectively.

As can be seen in the Table 4.1, the mean concentration of TN varied regionally between 4.82 and 8.19 µM, having the greater values in the nearhore zone. Similar spatial trend were observed in the other nutrient parameters measured in the Bay. TP concentrations were markedly high in the surface waters of the near-shore zone; the offshore values were lower and displayed vertically almost uniform distribution in the EZ and then increased slightly towards the bottom.

Close examination of the fractions of TN and TP reveals that dissolved and particulate organic nitrogen (DON+PON) and dissolved organic and particulate phosphorus (DOP+PP) dominate the TN and TP pools in the study area.

Table 4.1: Surface concentrations of TN, TP, DIN and their N/P ratios in the studied region

Sampling station		**TN**	**TP**	**DIN**	**DIN/TP**	**TN/TP**
Nearshore	(St. 2)	8.19	0.19	2.06	10.8	43.1
Middle	(St. 4)	6.08	0.12	0.65	5.4	50.7
	(St. 10)	5.62	0.11	0.56	5.1	51.1
Offshore	(St. 46)	4.82	0.16	0.44	2.8	30.1
	(St. 48)	4.85	0.12	0.45	3.8	40.4

Measured concentrations of nutrients are consistent with previous observations, carried out in our study area. Recently, seasonal variations of particulate and dissolved fractions of phosphorus were studied by Doğan-Sağlamtimur (2007) off Erdemli (Mersin), showing significant regional and seasonal changes in concentrations and molar ratios, with higher values in the river fed nearshore waters.

Long-term river data from the region indicate that large nitrogen loads by the major rivers with high N/P ratios (Tuğrul *et al*., 2009), lead to P-limited primary production in the coastal shelf, as experienced in the P-starved open waters of the Eastern Mediterranean (Yılmaz and Tuğrul, 1998; Kress and Herut, 2000; Krom *et al*., 2005).

Bioassay experiments carried out in the coastal zone of the Bay clearly indicate P-limitations. In addition to bioassays, NO_3/PO_4, TN/TP and DIN/TP, PON/PP ratios are commonly used to discriminate between N and P limitation on photosynthetic production (Guilford and Hecky, 2000; Bergström, 2010). The highest NO_3/PO_4 ratios were observed in the coastal zone due to large DIN inputs by the N-replete rivers (see Table 4.1), consistent with the results of bioassay experiments (TUBITAK-SINHA progress report, 2009). However, the N/P molar ratios were low in the offshore during spring-autumn period, indicating slower recycling of DIN than PO_4 in the productive upper layer waters. This rate difference leads to greater TN/TP ratios in the surface water than the conventional Redfield ratio of 16, due to low bio-availability of DON in productive marine environments, as experienced in most surface oceans and coastal zones of the world (Guilford and Hecky, 2000; Jickells *et al*., 1998).

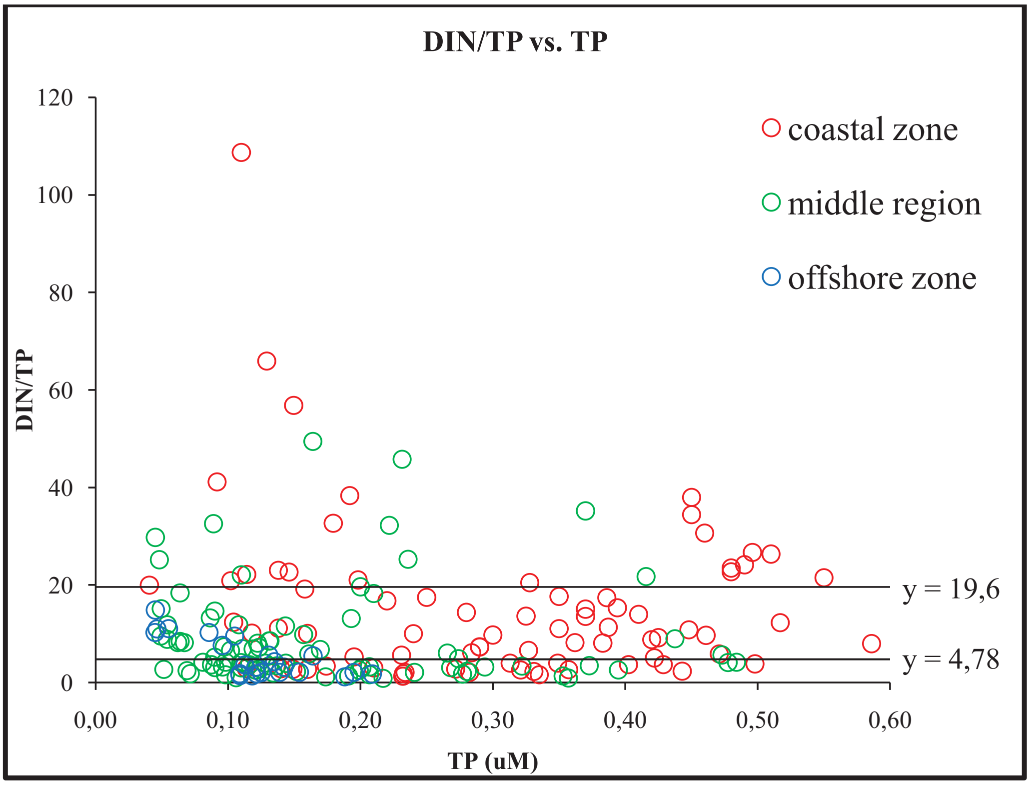


Figure 4.1: TP vs. DIN/TP ratio plot of the surface data measured from the study region in Sept. 2008-Oct. 2009 period.

DIN/TP ratio in the Bay ranged regionally from about 3 in the offshore to 5 in the coastal zone and to 11 in the polluted nearshore waters. Evaluation of the present nutrient results with bio-assay experiments (TUBITAK-SINHA progress report, 2009) shows that DIN/TP ratios exceeds 5 in P-limited coastal surface waters of the Mersin Bay.

Relationship between DIN/TP and TP concentrations from selected data is shown in Figure 4.1. The ratio apparently decreases from the polluted nearshore waters to offshore/shelfbreak zone of the bay (Tugrul et al, 2009; TUBITAK-SINHA progress report, 2009). The lower ratios with greater TP values were merely obtained in the nearshore zone polluted heavily by TP-rich wastewater discharges. The coastal sites with higher DIN/TP ratios and concentration values are the regions fed by nitrate-replete river discharges. The solid lines in the figure stand for the average ratios for the nearshore zone (19.6) and the middle part of the bay (4.78), where the bioassay experiment results from different seasons indicate P-limited primary production during the year. It can be concluded that the bay coastal ecosystem of the Bay, fed by DIN-replete river and domestic discharges, will have been P-limited when DIN/TP ratio remains above 4.5 but TP of domestic waters origin being reduced in the receiving water.

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APPENDICES

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

St.	Dep.	TP	DIP	DOP	TN	DON	NO3	NO2	NH4	DIN	NO3/ PO4	DIN/ TP	TN/ TP	Si	DO	chl-a
no	(m)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)				(µM)	(mg/L)	(µg/L)
1. CRUISE - SEPTEMBER 2008																
2	0	0.35	0.06	0.29	9.96	9.48	0.11	0.04	0.37	0.48	1.83	1.36	28.22	3.54	6.19	0.40
	10	0.30	0.04	0.26	8.95	8.73	0.11	0.05	0.11	0.22	2.75	0.74	30.24	3.51	6.14	0.06
	18	0.33	0.22	0.11	8.27	5.91	1.22	0.36	1.14	2.36	5.55	7.20	25.21	5.44	4.99	0.37
4	0	0.12	0.02	0.10	5.20	4.82	0.07	0.03	0.31	0.38	3.50	3.14	42.98	1.18	6.25	0.14
	10	0.08	0.03	0.05	4.85	4.45	0.08	0.02	0.32	0.40	2.67	5.00	60.63	1.11	6.27	0.06
	20	0.13	0.02	0.11	4.23	3.93	0.06	0.01	0.24	0.30	3.00	2.31	32.54	0.96	6.32	0.00
	30	0.08	0.03	0.05	4.15	3.67	0.15	0.01	0.33	0.48	5.00	5.93	51.23	1.02	6.36	0.06
	50	0.17	0.04	0.13	4.91	4.42	0.32	0.11	0.17	0.49	8.00	2.97	29.76	2.29	7.14	0.06
6	0	0.43	0.05	0.38	13.48	9.56	0.37	0.04	3.55	3.92	7.40	9.22	31.72	4.23	6.25	1.84
	8	0.36	0.07	0.29	10.66	7.01	0.35	0.04	3.30	3.65	5.00	10.28	30.03	4.34	6.08	1.45
7	0	0.38	0.05	0.33	10.05	6.94	0.34	0.03	2.77	3.11	6.80	8.12	26.24	3.65	6.65	1.35
	10	0.29	0.03	0.26	9.02	5.24	0.35	0.02	3.43	3.78	11.67	13.22	31.54	3.67	6.24	1.39
	15	0.23	0.06	0.17	8.74	4.41	0.57	0.05	3.76	4.33	9.50	18.58	37.51	3.81	5.98	1.42
8	0	0.12	0.04	0.08	4.92	4.57	0.08	0.05	0.27	0.35	2.00	2.82	39.68	1.37	6.18	0.08
10	0	0.10	0.02	0.08	4.36	4.20	0.06	0.02	0.10	0.16	3.00	1.63	44.49	0.97	6.25	0.06
	10	0.09	0.02	0.07	4.10	3.83	0.05	0.02	0.22	0.27	2.50	3.18	48.24	0.89	6.18	0.02
	20	0.14	0.02	0.12	4.29	4.01	0.11	0.01	0.17	0.28	5.50	2.04	31.31	0.87	6.29	0.10
	35	0.14	0.03	0.11	4.30	3.96	0.11	0.01	0.23	0.34	3.67	2.45	30.94	0.92	7.26	0.13
	50	0.14	0.02	0.12	4.48	4.04	0.13	0.01	0.31	0.44	6.50	3.17	32.23	0.94	7.66	0.07
	70	0.08	0.02	0.06	4.63	4.13	0.11	0.01	0.39	0.50	5.50	5.88	54.47	1.36	7.78	0.11
11	0	0.91	0.12	0.79	18.31	11.42	0.27	0.07	6.62	6.89	2.25	7.59	20.17	4.97	6.07	3.28
	10	0.43	0.06	0.37	10.16	8.45	0.09	0.05	1.62	1.71	1.50	4.00	23.74	4.32	6.09	2.89
12	0	0.44	0.06	0.38	10.62	9.58	0.10	0.08	0.94	1.04	1.67	2.35	23.97	4.01	6.73	1.66
	10	0.38	0.03	0.35	9.20	7.97	0.33	0.09	0.90	1.23	11.00	3.22	24.08	3.91	6.16	1.54
	16	0.37	0.09	0.28	8.19	4.89	1.69	0.20	1.61	3.30	18.78	8.82	21.90	5.78	4.86	0.90
13	0	0.19	0.03	0.16	4.91	4.65	0.06	0.04	0.20	0.26	2.00	1.36	25.71	1.21	6.19	0.10
	10	0.19	0.03	0.16	4.47	4.18	0.08	0.04	0.21	0.29	2.67	1.53	23.53	1.23	6.19	0.08
	20	0.15	0.03	0.12	4.71	4.38	0.07	0.04	0.26	0.33	2.33	2.23	31.82	1.33	6.11	0.18
	29	0.28	0.11	0.17	5.38	4.54	0.36	0.10	0.48	0.84	3.27	3.01	19.28	1.93	5.90	0.19
14	0	0.22	0.02	0.20	5.55	5.36	0.11	0.09	0.08	0.19	5.50	0.88	25.58	0.97	6.24	0.06
	10		0.02				0.08	0.05	0.04	0.12	4.00			0.94	6.30	0.06
	20	0.15	0.02	0.13	5.07	4.84	0.06	0.04	0.17	0.23	3.00	1.56	34.49	0.88	6.22	0.06
	30	0.19	0.02	0.17	4.41	4.23	0.07	0.04	0.11	0.18	3.50	0.95	23.21	0.96	6.22	0.10
	40	0.17	0.03	0.14	3.89	3.53	0.08	0.06	0.28	0.36	2.67	2.11	22.75	0.95	6.17	0.15
16	0	1.04	0.11	0.93	24.32	17.59	3.50	0.14	3.23	6.73	31.82	6.48	23.41	3.92	7.20	4.20
	6	1.01	0.12	0.89	28.85	17.07	6.09	0.18	5.69	11.78	50.75	11.70	28.65	3.93	7.17	4.11
17	0	0.70	0.02	0.68	13.12	11.80	0.22	0.05	1.10	1.32	11.00	1.88	18.72	3.67	6.62	2.33
	13	0.38	0.08	0.30	12.13	9.25	1.69	0.13	1.19	2.88	21.13	7.58	31.92	3.41	5.89	1.88
18	0	0.36	0.03	0.33	12.10	11.76	0.10	0.06	0.24	0.34	3.33	0.95	33.89	2.17	6.33	0.43
	10	0.35	0.03	0.32	6.37	6.01	0.07	0.04	0.29	0.36	2.33	1.02	17.99	2.24	6.35	0.30
	18	0.37	0.14	0.23	6.39	5.22	0.82	0.18	0.35	1.17	5.86	3.16	17.27	1.01	5.59	1.17
21	0	0.91	0.06	0.85	19.06	18.23	0.63	0.13	0.20	0.83	10.50	0.91	20.97	3.93	7.73	2.11
	7	0.79	0.06	0.73	18.27	15.44	2.42	0.15	0.41	2.83	40.33	3.57	23.04	4.26	7.32	3.90
22	0	0.87	0.07	0.80	20.45	4.90	15.34	0.07	0.21	15.55	219.14	17.81	23.42	5.16	7.21	1.74
	10	0.87	0.04	0.83	17.35	4.09	13.02	0.08	0.24	13.26	325.50	15.21	19.90	4.11	6.64	1.41
23	0	0.64	0.08	0.56	13.53	10.48	2.70	0.13	0.35	3.05	33.75	4.77	21.14	4.36	7.73	3.46
	6	0.61	0.10	0.51	14.13	10.77	2.73	0.12	0.63	3.36	27.30	5.50	23.13	4.38	7.67	2.59

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
25	0	0.75	0.10	0.65	10.14	8.63	0.47	0.40	1.04	1.51	4.70	2.03	13.61	3.55	6.79	0.25
26	0	0.12	0.05	0.07	4.25	3.05	0.45	0.37	0.75	1.20	9.00	10.17	36.02	1.42	6.23	0.99
27	0	0.09	0.02	0.07	4.65	1.75	0.89	0.04	2.01	2.90	44.50	32.58	52.25	1.50	6.29	0.11
	4	0.13	0.02	0.11	3.53	0.57	0.71	0.03	2.25	2.96	35.50	22.95	27.36	1.24	6.27	0.10
	7	0.14	0.02	0.12	3.67	0.94	0.84	0.03	1.89	2.73	42.00	19.36	26.03	1.21	6.24	0.09
	10	0.13	0.02	0.11	3.61	0.45	0.87	0.01	2.29	3.16	43.50	24.88	28.43	1.21	6.32	0.20
	12	0.13	0.03	0.10	3.75	0.42	0.90	0.09	2.43	3.33	30.00	24.85	27.99	1.23	6.25	0.36
	21	0.12	0.03	0.09	4.43	1.19	0.94	0.13	2.30	3.24	31.33	26.34	36.02	1.34	6.21	0.17
	24	0.11	0.02	0.09	3.77	1.00	0.88	0.11	1.89	2.77	44.00	24.30	33.07	1.08	6.23	0.15
	30	0.08	0.02	0.06	3.70	0.62	0.85	0.12	2.23	3.08	42.50	38.02	45.68	1.05	6.24	
28	0	0.12	0.02	0.10	4.67	3.85	0.07	0.02	0.75	0.82	3.50	6.89	39.24	0.82	6.18	0.03
	10	0.09	0.02	0.07	7.24	6.78	0.06	0.04	0.40	0.46	3.00	5.23	82.27	0.78	6.21	0.03
	20	0.07	0.02	0.05	6.70	6.30	0.07	0.04	0.33	0.40	3.50	5.80	97.10	0.73	6.21	0.03
	30	0.08	0.03	0.05	7.49	6.95	0.10	0.07	0.44	0.54	3.33	6.51	90.24	0.92	6.59	0.09
	50	0.12	0.03	0.09	10.17	9.24	0.15	0.12	0.78	0.93	5.00	7.82	85.46	1.20	7.42	0.14
30	0		0.02				0.10	0.06	0.59	0.69	5.00			0.73	6.27	0.02
32	0	0.66	0.12	0.54	13.17	12.37	0.51	0.47	0.29	0.80	4.25	1.21	19.98	5.42	7.62	3.32
33	0	0.33	0.26	0.07	6.33	4.16	0.91	0.67	1.26	2.17	3.50	6.64	19.36	6.24	6.38	2.97
	10	0.37	0.24	0.13	7.67	5.80	0.76	0.68	1.11	1.87	3.17	5.07	20.79	5.96	6.28	2.22
34	0	0.34	0.06	0.28	5.01	4.47	0.15	0.11	0.39	0.54	2.50	1.61	14.96	2.93	6.46	0.44
	8	0.31	0.08	0.23	5.54	4.94	0.17	0.12	0.43	0.60	2.13	1.92	17.76	2.56	6.40	0.69
35	0	0.14	0.05	0.09	3.53	0.35	0.90	0.04	2.28	3.18	18.00	23.04	25.58	1.19	6.19	0.11
36	0	0.69	0.14	0.55	12.40	11.54	0.45	0.41	0.41	0.86	3.21	1.26	18.10	5.92	7.78	4.19
38	0	0.16	0.04	0.12	3.83	0.80	0.95	0.04	2.08	3.03	23.75	19.18	24.24	2.05	6.31	0.23
	10	0.11	0.02	0.09	3.21	0.77	0.94	0.03	1.50	2.44	47.00	21.40	28.16	1.40	6.32	0.19
39	0	0.16	0.02	0.14	3.72	2.17	0.06	0.01	1.49	1.55	3.00	9.87	23.69	1.03	6.23	0.06
	10	0.14	0.02	0.12	3.36	1.43	0.06	0.02	1.87	1.93	3.00	14.09	24.53	1.05	6.25	0.10
	24	0.12	0.02	0.10	3.84	1.05	1.15	0.02	1.64	2.79	57.50	23.45	32.27	1.05	6.26	0.11
40	0	0.05	0.02	0.03	4.00	3.33	0.10	0.06	0.57	0.67	5.00	14.89	88.89	0.73	6.35	0.00
	10	0.04	0.03	0.01	3.57	2.63	0.09	0.05	0.85	0.94	3.00	26.86	102.00	0.71	6.37	0.02
	20	0.04	0.03	0.01	3.58	2.60	0.09	0.07	0.89	0.98	3.00	24.50	89.50	0.70	6.44	0.01
	30	0.04	0.03	0.01	3.91	3.20	0.13	0.11	0.58	0.71	4.33	19.72	108.61	0.64	7.39	0.02
	40	0.14	0.02	0.12	2.92	2.08	0.09	0.07	0.75	0.84	4.50	6.04	21.01	0.71	7.87	0.03
	55	0.17	0.03	0.14	3.29	2.38	0.13	0.09	0.78	0.91	4.33	5.38	19.47	1.07	7.71	0.15
41	0	0.10	0.07	0.03	3.88	1.75	0.06	0.05	2.07	2.13	0.86	20.88	38.04	1.23	6.21	0.10
43	0	0.11	0.04	0.07	4.08	1.55	0.15	0.02	2.38	2.53	3.75	22.19	35.79	1.15	6.25	0.08
	10	0.13	0.02	0.11	4.52	2.96	0.06	0.01	1.50	1.56	3.00	12.28	35.59	1.12	6.25	0.06
	18	0.10	0.03	0.07	3.65	1.34	0.10	0.02	2.21	2.31	3.33	23.10	36.50	1.12	6.24	0.07
46	0	0.20	0.02	0.18	5.21	4.80	0.09	0.02	0.32	0.41	4.50	2.10	26.72	1.02	6.22	0.03
	5	0.10	0.02	0.08	3.82	3.49	0.10	0.03	0.23	0.33	5.00	3.20	37.09	0.95	6.21	0.04
	10	0.09	0.02	0.07	3.68	3.35	0.11	0.01	0.22	0.33	5.50	3.63	40.44	0.83	6.26	0.03
	20	0.09	0.02	0.07	4.20	3.84	0.13	0.01	0.23	0.36	6.50	4.00	46.67	0.82	6.44	0.03
	65	0.08	0.02	0.06	3.68	3.37	0.10	0.01	0.21	0.31	5.00	4.13	49.07	0.91	7.81	0.05
	85	0.07	0.02	0.05	3.59	3.21	0.09	0.04	0.29	0.38	4.50	5.43	51.29	1.00	7.53	0.11
	100	0.07	0.02	0.05	3.47	2.96	0.18	0.02	0.33	0.51	9.00	6.99	47.53	1.08	7.39	0.14
	120	0.06	0.02	0.04	3.97	3.17	0.49	0.10	0.31	0.80	24.50	14.29	70.89	1.21	7.22	0.13
2. CRUISE - JANUARY 2009																
1	0		0.06				0.70	0.34	0.30	1.00	11.67			0.97	7.39	0.18
2	0		0.09				0.34	0.02	0.19	0.53	3.78			0.87	7.36	0.16
	10		0.07				0.25	0.09	0.28	0.53	3.57			0.89	7.35	0.18
	19		0.08				0.28	0.26	0.29	0.57	3.50			0.96	7.36	0.18
3	0		0.02				0.07	0.05	0.35	0.42	3.50			0.73	7.41	0.13
4	0	0.28	0.02	0.26	6.73	6.24	0.06	0.03	0.43	0.49	3.00	1.77	24.30	0.66	7.33	0.18
	10	0.28	0.02	0.26	8.90	8.55	0.09	0.05	0.26	0.35	4.50	1.27	32.25	0.66	7.34	0.13

APPENDIX A. CONTINUED

St.	Dep.	TP	DIP	DOP	TN	DON	NO3	NO2	NH4	DIN	NO3/ PO4	DIN/ TP	TN/ TP	Si	DO	chl-a
no	(m)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)	(μM)				(μM)	(mg/L)	(μg/L)
4	20	0.26	0.03	0.23			0.09	0.06	0.37	0.46	3.00	1.80	0.00	0.65	7.34	0.10
	30	0.24	0.02	0.22	7.87	7.45	0.06	0.03	0.36	0.42	3.00	1.73	32.39	0.67	7.32	0.12
	48	0.20	0.02	0.18	9.09	8.54	0.06	0.02	0.49	0.55	3.00	2.81	46.38	0.67	7.32	0.10
5	0		0.02				0.18	0.08	0.22	0.40	9.00			0.80	7.45	0.15
6	0	0.46	0.21	0.25			8.92	0.73	5.19	14.11	42.48	30.67		3.85	7.26	0.37
	9	0.40	0.14	0.26			5.50	0.61	3.34	8.84	39.29	22.10		1.98	7.24	0.33
7	0	0.14	0.02	0.12			0.12	0.08	0.28	0.40	6.00	2.86		0.80	7.45	0.23
	10	0.19	0.03	0.16			0.08	0.06	0.25	0.33	2.67	1.74		0.81	7.37	0.10
	16	0.07	0.04	0.03			0.15	0.07	0.33	0.48	3.75	6.86		0.88	7.42	0.29
10	0	0.16	0.02	0.14	7.99	7.04	0.15	0.13	0.80	0.95	7.50	5.90	49.63	0.81	7.50	0.10
	10	0.13	0.02	0.11	6.62	6.39	0.12	0.11	0.11	0.23	6.00	1.76	50.53	0.79	7.53	0.07
	20	0.14	0.02	0.12	7.64	7.41	0.12	0.09	0.11	0.23	6.00	1.67	55.36	0.80	7.32	0.05
	50	0.13	0.02	0.11	8.61	8.33	0.12	0.09	0.16	0.28	6.00	2.12	65.23	0.78	7.30	0.07
	70	0.19	0.04	0.15	7.95	7.03	0.37	0.20	0.55	0.92	9.25	4.97	42.97	1.11	7.54	0.38
11	0	0.42	0.13	0.29			2.41	0.55	1.29	3.70	18.54	8.81		1.58	7.22	0.43
	9	0.37	0.21	0.16			7.81	0.64	5.91	13.72	37.19	37.08		2.64	7.39	0.38
12	0	0.16	0.04	0.12			0.28	0.09	0.16	0.44	7.00	2.75		0.86	7.36	0.13
	10	0.15	0.04	0.11			0.36	0.11	0.14	0.50	9.00	3.33		0.95	7.42	0.19
	18	0.24	0.11	0.13			0.94	0.17	0.41	1.35	8.55	5.63		1.49	7.31	0.22
13	0	0.09	0.02	0.07			0.10	0.07	0.37	0.47	5.00	5.22		0.8	7.37	0.10
	10	0.12	0.03	0.09			0.06	0.04	0.17	0.23	2.00	1.92		0.82	7.48	0.22
	20	0.12	0.04	0.08			0.29	0.09	0.45	0.74	7.25	6.17		0.92	7.43	0.24
	29	0.28	0.10	0.18			0.52	0.17	0.40	0.92	5.20	3.29		1.08	7.51	0.26
14	0	0.20	0.02	0.18	8.41	7.80	0.08	0.07	0.53	0.61	4.00	3.03	41.84	0.81	7.39	0.12
	10	0.19	0.02	0.17	8.00	7.46	0.11	0.09	0.43	0.54	5.50	2.80	41.45	0.83	7.38	0.17
	20	0.19	0.03	0.16	7.56	7.12	0.08	0.07	0.36	0.44	2.67	2.28	39.17	0.81	7.37	0.15
	40	0.24	0.04	0.20	9.03	7.86	0.35	0.17	0.82	1.17	8.75	4.81	37.16	0.96	7.48	0.18
16	0	0.55	0.24	0.31			5.08	0.13	6.74	11.82	21.17	21.49		2.26	7.48	0.24
	7	0.58	0.25	0.33			3.69	0.30	5.38	9.07	14.76	15.64		2.51	7.18	0.47
17	0	0.37	0.18	0.19			2.36	0.11	3.22	5.58	13.11	15.08		1.81	7.33	0.44
	14	0.46	0.24	0.22			3.86	0.25	3.73	7.59	16.08	16.50		2.94	7.42	0.33
18	0	0.09	0.04	0.05			0.37	0.07	0.95	1.32	9.25	14.67		0.82	7.52	0.28
	10	0.08	0.03	0.05			0.28	0.08	0.85	1.13	9.33	14.13		0.84	7.52	0.28
	19	0.27	0.12	0.15			0.78	0.14	1.81	2.59	6.50	9.59		1.37	7.59	0.64
21	0	0.74	0.40	0.34			21.30	1.86	22.76	44.06	53.25	59.54		4.42	7.25	0.51
	7	0.68	0.30	0.38			24.29	1.87	27.12	51.41	80.97	75.60		4.37	7.27	0.49
22	0	0.11	0.15	-0.04			5.74	1.22	6.22	11.96	38.27	108.73		3.31	7.66	0.49
	9	0.40	0.25	0.15			4.82	1.49	7.21	12.03	19.28	30.08		2.93	7.49	0.63
23	0		0.23				6.00	2.01	13.22	19.22	26.09			3.56	7.78	0.66
	6		0.32				6.37	2.30	17.68	24.05	19.91			4.25	7.82	0.97
27	2	0.08	0.04	0.04	4.74	4.40	0.24	0.13	0.10	0.34	6.00	4.20	58.52	0.94	7.49	0.08
	4	0.05	0.04	0.01	5.73	5.42	0.19	0.14	0.12	0.31	4.75	6.46	119.38	0.92	7.53	
	8	0.16	0.04	0.12			0.16	0.14	0.04	0.20	4.00	1.28		0.92	7.52	0.14
	13	0.17	0.06	0.11	8.70	8.34	0.20	0.17	0.16	0.36	3.33	2.13	51.48	0.99	7.52	
	18	0.20	0.04	0.16			0.18	0.17	0.47	0.65	4.50	3.25		0.93	7.53	0.16
	27	0.24	0.06	0.18	9.80	8.98	0.21	0.17	0.61	0.82	3.50	3.36	40.16	0.97	7.53	
	29	0.23	0.07	0.16	9.19	8.30	0.22	0.16	0.67	0.89	3.14	3.85	39.78	0.98	7.55	0.24
28	0	0.05	0.03	0.02	6.05	4.84	0.21	0.13	1.00	1.21	7.00	25.21	126.04	0.89	7.48	0.20
	10	0.07	0.04	0.03	7.51	6.28	0.15	0.13	1.08	1.23	3.75	17.08	104.31	0.89	7.49	0.14
	20	0.06	0.03	0.03	7.13	5.63	0.19	0.13	1.31	1.50	6.33	27.27	129.64	0.88	7.49	0.10
	30	0.05	0.03	0.02	10.41	8.62	0.22	0.17	1.57	1.79	7.33	33.15	192.78	0.87	7.48	0.20
	50	0.08	0.05	0.03	10.14	8.09	0.24	0.16	1.81	2.05	4.80	25.95	128.35	0.89	7.46	0.16
36	0	0.15	0.06	0.09	12.90	9.59	1.75	0.09	1.56	3.31	29.17	22.67	88.36	1.41	7.53	0.20
	8	0.15	0.06	0.09	9.61	6.61	1.42	0.10	1.58	3.00	23.67	20.55	65.82	1.32	7.52	0.19

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
38	0	0.14	0.06	0.08	5.31	3.77	1.18	0.11	0.36	1.54	19.67	11.16	38.48	1.79	7.58	0.32
	10	0.18	0.05	0.13	7.08	5.45	1.28	0.15	0.35	1.63	25.60	9.31	40.46	1.78	7.60	0.27
39	0	0.13	0.06	0.07	7.59	6.47	1.08	0.11	0.04	1.12	18.00	8.55	57.94	1.68	7.58	0.15
	10	0.18	0.07	0.11	8.32	7.28	1.00	0.09	0.04	1.04	14.29	5.94	47.54	1.59	7.48	0.24
	24	0.17	0.08	0.09	4.03	3.09	0.90	0.08	0.04	0.94	11.25	5.56	23.85	1.48	7.45	0.23
40	0	0.14	0.02	0.12	7.32	7.03	0.06	0.02	0.23	0.29	3.00	2.09	52.66	0.76	7.31	0.07
	10	0.11	0.02	0.09	7.20	6.96	0.08	0.02	0.16	0.24	4.00	2.22	66.67	0.76	7.32	0.11
	20	0.12	0.02	0.10	8.01	7.65	0.09	0.07	0.27	0.36	4.50	2.95	65.66	0.76	7.34	0.05
	30	0.14	0.02	0.12	6.95	6.64	0.10	0.05	0.21	0.31	5.00	2.17	48.60	0.78	7.37	0.20
	50	0.14	0.03	0.11	7.30	7.01	0.12	0.03	0.17	0.29	4.00	2.06	51.77	0.79	7.42	0.15
41	0	0.21	0.02	0.19	10.02	9.39	0.24	0.02	0.39	0.63	12.00	3.00	47.71	0.81	7.67	0.36
	12	0.19	0.03	0.16	9.19	6.87	1.73	0.03	0.59	2.32	57.67	12.21	48.37	1.86	7.54	0.29
42	0		0.11				0.37	0.20	0.04		3.36			1.13	7.41	0.15
43	0	0.15	0.05	0.10	7.31	6.90	0.37	0.09	0.04	0.41	7.40	2.75	49.06	0.96	7.37	0.17
	10	0.17	0.04	0.13	7.79	7.46	0.29	0.09	0.04	0.33	7.25	1.95	46.09	0.96	7.39	0.17
	20	0.40	0.05	0.35	15.21	14.83	0.34	0.11	0.04	0.38	6.80	0.95	37.93	1.07	7.42	0.15
44	0		0.02				0.24	0.02	0.24	0.48	12.00			0.80	7.36	0.16
45	0		0.02				0.38	0.04	0.36	0.74	19.00			0.80	7.33	0.17
46	0		0.02				0.07	0.03	0.07	0.14	3.50			0.73	7.28	0.07
47	0	0.12	0.02	0.10	6.76	6.38	0.13	0.03	0.25	0.38	6.50	3.14	55.87	0.74	7.28	0.07
	10	0.17	0.02	0.15	8.19	7.81	0.13	0.02	0.25	0.38	6.50	2.18	47.07	0.73	7.28	
	20	0.20	0.02	0.18			0.12	0.02	0.81	0.93	6.00	4.65		0.74	7.27	0.12
	30	0.26	0.02	0.24	6.74	6.17	0.10	0.05	0.47	0.57	5.00	2.21	26.12	0.74	7.31	0.11
	50	0.23	0.02	0.21	6.73	6.12	0.18	0.08	0.43	0.61	9.00	2.61	28.76	0.77	7.21	0.09
	75	0.23	0.02	0.21	6.71	6.34	0.16	0.10	0.21	0.37	8.00	1.59	28.92	0.78	7.23	0.06
	83	0.23	0.02	0.21	7.03	6.55	0.18	0.06	0.30	0.48	9.00	2.09	30.57	0.85	7.31	0.06
48	0	0.21	0.02	0.19	6.58	6.21	0.13	0.04	0.24	0.37	6.50	1.77	31.48	0.79	7.22	0.08
	10	0.18	0.02	0.16	7.08	6.85	0.13	0.05	0.10	0.23	6.50	1.28	39.33	0.80	7.19	0.07
	20	0.17	0.02	0.15	6.79	6.61	0.13	0.05	0.05	0.18	6.50	1.09	41.15	0.78	7.30	0.08
	30	0.22	0.02	0.20	7.05	6.91	0.09	0.04	0.05	0.14	4.50	0.63	31.90	0.78	7.23	0.08
	50	0.21	0.02	0.19	6.26	6.10	0.12	0.06	0.04	0.16	6.00	0.76	29.67	0.78	7.18	0.10
	75	0.19	0.02	0.17	6.60	6.47	0.09	0.04	0.04	0.13	4.50	0.67	34.02	0.75	7.13	0.06
	100	0.19	0.02	0.17	7.32	7.13	0.13	0.08	0.06	0.19	6.50	1.01	38.73	0.74	7.11	0.05
	150	0.20	0.03	0.17	7.64	7.41	0.19	0.09	0.04	0.23	6.33	1.15	38.20	0.80	7.09	
	200	0.26	0.03	0.23	9.81	9.33	0.26	0.12	0.22	0.48	8.67	1.86	38.02	0.84	7.28	
49	0		0.02				0.12	0.03	0.29	0.41	6.00			0.78	7.22	0.08
50	0		0.04				3.50	0.24	0.94	4.44	87.50			2.86	7.37	0.05
3. CRUISE - FEBRUARY 2009																
1	0		0.08				10.38	0.44	0.52	10.90	129.75			3.77		
2	0	0.23	0.05	0.18	20.39	9.79	8.91	0.47	1.69	10.60	178.20	45.79	88.08	4.02	8.17	1.19
	10	0.16	0.02	0.14	6.97	5.65	0.87	0.14	0.45	1.32	43.50	8.05	42.50	1.12	7.69	0.21
	20	0.12	0.03	0.09	7.66	6.15	0.93	0.16	0.58	1.51	31.00	12.33	62.53	1.32	7.69	0.25
3	0		0.02				0.10	0.09	0.26	0.36	5.00			0.80		0.10
4	0	0.05	0.03	0.02	5.04	4.40	0.26	0.09	0.38	0.64	8.67	11.85	93.31	0.82	7.53	0.14
	10	0.08	0.02	0.06	6.42	6.15	0.18	0.10	0.09	0.27	9.00	3.41	81.17	0.84	7.56	0.22
	20	0.06	0.02	0.04	6.23	5.83	0.26	0.09	0.14	0.40	13.00	6.80	105.89	0.85	7.58	0.15
	30	0.05	0.02	0.03	5.85	5.61	0.15	0.08	0.09	0.24	7.50	4.79	116.64	0.85	7.55	0.26
	48	0.08	0.02	0.06	7.36	6.96	0.12	0.10	0.28	0.40	6.00	4.88	89.77	0.86	7.56	0.32
6	0	0.48	0.10	0.38			9.34	0.48	1.58	10.92	93.40	22.75		3.09	8.35	2.47
	8	0.46	0.09	0.37			7.38	0.42	1.62	9.00	82.00	19.57		2.57	8.06	2.39
7	0	0.78	0.26	0.52			9.62	0.57	4.16	13.78	37.00	17.67		3.92	8.29	2.73
	10	0.14	0.04	0.10			0.83	0.08	0.63	1.46	20.75	10.43		1.24	7.65	0.30
	16	0.16	0.10	0.06			1.67	0.14	1.16	2.83	16.70	17.69		1.6	7.70	0.34
8	0		0.07		6.45	5.28	0.29	0.07	0.88	1.17	4.14			0.87	7.58	

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (μM)	DIP (μM)	DOP (μM)	TN (μM)	DON (μM)	NO3 (μM)	NO2 (μM)	NH4 (μM)	DIN (μM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (μM)	DO (mg/L)	chl-a (μg/L)
9	0		0.02				0.40	0.06	0.45	0.85	20.00			0.84		
10	0	0.05	0.03	0.02	6.29	5.81	0.16	0.10	0.32	0.48	5.33	8.89	116.45	0.73	7.46	0.07
	10	0.04	0.02	0.02	5.41	5.16	0.09	0.07	0.16	0.25	4.50	6.65	143.82	0.71	7.46	0.14
	20	0.04	0.03	0.01	5.30	4.90	0.18	0.05	0.22	0.40	6.00	10.37	137.38	0.71	7.45	0.15
	30	0.06	0.02	0.04	6.88	6.58	0.08	0.12	0.22	0.30	4.00	4.86	111.46	0.72	7.35	0.19
	40	0.05	0.02	0.03	5.48	5.07	0.18	0.15	0.23	0.41	9.00	8.50	113.63	0.77	7.50	0.21
	50	0.06	0.03	0.03	6.63	6.28	0.17	0.16	0.18	0.35	5.67	5.50	104.15	0.77	7.54	0.12
	70	0.09	0.03	0.06	6.95	6.62	0.17	0.15	0.16	0.33	5.67	3.72	78.32	0.79	7.56	0.16
11	0	0.51	0.09	0.42			11.69	0.57	1.75	13.44	129.89	26.35		3.4	8.51	3.61
	10	0.38	0.10	0.28			6.36	0.38	1.88	8.24	63.60	21.68		2.7	7.85	2.32
12	0	0.45	0.10	0.35			14.39	0.63	2.71	17.10	143.90	38.00		3.64	9.03	6.69
	10	0.16	0.05	0.11			1.09	0.16	1.05	2.14	21.80	13.38		1.28	8.97	0.55
	18	0.16	0.03	0.13			2.01	0.15	1.29	3.30	67.00	20.63		1.47	7.75	0.49
13	0	0.20	0.06	0.14			3.43	0.14	0.50	3.93	57.17	19.65		2.23	7.75	0.24
	10	0.16	0.04	0.12			0.50	0.04	0.45	0.95	12.50	5.94		0.97	7.71	0.26
	20	0.20	0.06	0.14			0.34	0.07	0.21	0.55	5.67	2.75		1.09	7.56	0.30
	27	0.25	0.10	0.15			0.36	0.09	0.70	1.06	3.60	4.24		1.12	7.59	0.33
14	0	0.05	0.02	0.03	5.66	5.19	0.18	0.15	0.29	0.47	9.00	9.55	115.06	0.76	7.51	0.14
	10	0.04	0.02	0.02	5.16	4.43	0.22	0.19	0.51	0.73	11.00	19.41	137.18	0.76	7.49	0.19
	20	0.06	0.02	0.04	5.20	4.36	0.23	0.20	0.61	0.84	11.50	14.05	86.96	0.77	7.48	0.23
	30	0.03	0.02	0.01	5.36	4.71	0.26	0.17	0.39	0.65	13.00	24.96	205.82	0.78	7.55	0.16
	40		0.02				0.26	0.18	0.43	0.69	13.00			0.77	7.52	0.23
15	0		0.02				0.18	0.11	0.26	0.44	9.00			0.76	7.53	
16	0	1.00	0.15	0.85			11.35	0.63	4.52	15.87	75.67	15.87		1.83	8.87	2.56
	5	0.87	0.17	0.70			11.70	0.67	4.76	16.46	68.82	18.92		1.85	8.93	3.47
17	0	0.45	0.11	0.34			12.42	0.56	3.09	15.51	112.91	34.47		1.83	8.77	2.27
	12.5	0.35	0.08	0.27			3.49	0.26	1.75	5.24	43.63	14.97		1.85	9.19	1.31
18	0	0.37	0.08	0.29			11.23	0.43	1.80	13.03	140.38	35.22		5.19	8.02	0.51
	10	0.48	0.08	0.40			3.80	0.31	1.08	4.88	47.50	10.17		1.92	7.89	1.20
	17	0.41	0.10	0.31			2.73	0.22	0.94	3.67	27.30	8.95		2.12	7.67	0.95
19	0		0.16				0.69	0.07	0.91	1.60	4.31			1.00		
20	0		0.03				0.23	0.18	0.40	0.63	7.67			0.78	7.51	
21	0	0.65	0.15	0.50			8.89	1.29	5.93	14.82	59.27	22.80		2.94	7.66	2.78
	6	0.23	0.15	0.08			9.51	1.28	6.00	15.51	63.40	67.43		3.19	7.75	2.60
22	0	0.48	0.11	0.37			10.08	0.46	1.20	11.28	91.64	23.50		3.10	8.79	3.46
	9	0.46	0.08	0.38			5.16	0.30	1.01	6.17	64.50	13.41		2.38	8.03	2.23
23	0		0.14				13.01	0.70	1.53	14.54	92.93			4.42		
24	0		0.13				9.47	0.52	1.55	11.02	72.85			4.14		
25	0		0.08				8.47	0.38	1.10	9.57	105.88			4.46	7.87	0.41
26	0	0.16	0.08	0.08	16.57	8.46	7.17	0.28	0.94	8.11	89.63	49.45	101.04	3.86	7.9	0.35
27	2	0.22	0.06	0.16	11.98	4.83	4.86	0.42	2.29	7.15	81.00	32.23	54.00	3.56	7.76	0.11
	5	0.24	0.05	0.19	12.90	6.67	4.12	0.36	2.11	6.23	82.40	25.53	52.86	3.08	7.73	0.24
	10	0.10	0.02	0.08	10.20	8.84	0.44	0.06	0.92	1.36	22.00	13.56	101.69	0.93	7.57	0.20
	15	0.10	0.02	0.08	9.95	8.95	0.18	0.04	0.82	1.00	9.00	9.78	97.32	0.85	7.57	0.21
	20	0.15	0.02	0.13	8.27	7.42	0.12	0.04	0.73	0.85	6.00	5.84	56.78	0.81	7.59	0.19
	30	0.12	0.03	0.09	7.34	6.08	0.27	0.07	0.99	1.26	9.00	10.37	60.40	0.93	7.62	0.22
28	0	0.11	0.03	0.08	9.08	8.97	0.06	0.03	0.05	0.11	2.00	1.04	85.58	0.84	7.50	0.11
	10	0.07	0.02	0.05	5.38	5.28	0.05	0.01	0.05	0.10	2.50	1.44	77.47	0.83	7.51	0.12
	20	0.06	0.02	0.04	5.92	5.74	0.12	0.02	0.06	0.18	6.00	3.16	104.03	0.83	7.51	0.13
	30	0.08	0.02	0.06	6.45	6.29	0.10	0.02	0.06	0.16	5.00	2.13	85.74	0.83	7.46	0.12
	40	0.07	0.03	0.04	7.18	7.05	0.07	0.02	0.06	0.13	2.33	1.87	103.39	0.84	7.49	0.15
	50	0.07	0.03	0.04	9.10	8.93	0.11	0.03	0.06	0.17	3.67	2.52	134.78	0.84	7.50	0.12
29	0		0.02				0.06	0.02	0.74	0.80	3.00			0.79	7.53	
30	0	0.07	0.02	0.05	4.18	4.05	0.06	0.04	0.07	0.13	3.00	1.82	58.57	0.83	7.57	0.15

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
31	0		0.10				9.17	0.52	0.86	10.03	91.70			3.58	9.30	
32	0		0.10				7.39	0.45	0.82	8.21	73.90			4.13	8.25	0.57
33	0	0.19	0.07	0.12	13.92	6.56	6.66	0.39	0.70	7.36	95.14	38.35	72.52	3.63	7.92	0.49
	8	0.20	0.11	0.09	12.58	8.51	3.60	0.30	0.47	4.07	32.73	20.69	63.94	3.19	7.8	0.33
34	0	0.09	0.06	0.03	8.42	4.65	3.13	0.25	0.64	3.77	52.17	41.14	91.89	2.49	7.76	0.27
	8	0.13	0.06	0.07	7.41	4.68	2.06	0.22	0.67	2.73	34.33	20.97	56.91	1.89	7.93	0.24
35	0	0.10	0.04	0.06	8.18	6.89	0.99	0.09	0.30	1.29	24.75	12.38	78.53	1.22	7.75	0.11
36	0	0.18	0.08	0.10	12.76	6.90	5.23	0.35	0.63	5.86	65.38	32.66	71.13	3.35	7.92	0.20
37	0		0.07				4.12	0.32	0.71	4.83	58.86			2.84	7.96	
38	0	0.15	0.05	0.10	16.77	8.27	8.19	0.30	0.31	8.50	163.80	56.86	112.18	4.64	8.06	0.40
	10	0.16	0.06	0.10	12.16	7.50	4.34	0.26	0.32	4.66	72.33	29.64	77.35	3.45	7.88	0.24
39	0	0.11	0.02	0.09	7.38	6.10	0.79	0.06	0.49	1.28	39.50	11.85	68.32	1.18	7.58	0.19
	10	0.09	0.02	0.07	6.10	4.94	0.81	0.05	0.35	1.16	40.50	13.36	70.27	1.17	7.56	0.30
	20	0.07	0.02	0.05	6.30	5.05	0.82	0.05	0.43	1.25	41.00	18.00	90.72	1.17	7.59	0.29
	25	0.03	0.03	0.00	6.44	4.95	0.82	0.05	0.67	1.49	27.33	42.91	185.47	1.16	7.74	0.24
40	0	0.12	0.02	0.10	7.84	7.62	0.12	0.05	0.10	0.22	6.00	1.81	64.51	0.82	7.47	0.17
	10	0.14	0.03	0.11	8.12	7.63	0.11	0.06	0.38	0.49	3.67	3.43	56.88	0.83	7.47	0.21
	20	0.13	0.02	0.11	8.81	8.36	0.11	0.04	0.34	0.45	5.50	3.48	68.17	0.81	7.48	0.20
	30	0.09	0.03	0.06	8.31	7.84	0.18	0.05	0.29	0.47	6.00	5.30	93.65	0.83	7.58	0.23
	40	0.13	0.02	0.11	7.43	7.11	0.21	0.05	0.11	0.32	10.50	2.44	56.64	0.80	7.47	0.18
	58	0.06	0.03	0.03	6.32	5.72	0.14	0.07	0.46	0.60	4.67	9.87	104.01	0.81	7.46	0.21
41	0	0.13	0.05	0.08	16.84	8.32	7.65	0.28	0.87	8.52	153.00	65.92	130.30	4.76	8.11	0.53
42	0		0.05				5.70	0.20	0.58	6.28	114.00			3.74	7.89	
43	0	0.04	0.04	0.00	5.16	4.35	0.43	0.03	0.38	0.81	10.75	20.00	127.38	0.99	7.67	0.15
	10	0.06	0.02	0.04	5.23	4.70	0.21	0.02	0.32	0.53	10.50	8.86	87.46	0.97	7.67	0.19
	20	0.04	0.02	0.02	5.37	4.85	0.22	0.05	0.30	0.52	11.00	12.54	129.48	0.96	7.70	0.15
44	0		0.03				0.06	0.02	0.18	0.24	2.00			0.85	7.51	
45	0		0.03				0.09	0.03	0.15	0.24	3.00			0.86	7.47	
46	0	0.14	0.02	0.12	10.20	9.62	0.12	0.03	0.46	0.58	6.00	4.30	75.54	0.80	7.43	0.10
	10	0.12	0.02	0.10	11.29	10.96	0.12	0.03	0.21	0.33	6.15	2.88	97.55	0.81	7.43	0.10
	20	0.09	0.02	0.07	11.50	11.25	0.11	0.03	0.14	0.25	5.50	2.70	124.20	0.81	7.43	0.14
	30	0.12	0.02	0.10	11.61	11.11	0.12	0.03	0.38	0.50	6.00	4.21	97.86	0.81	7.43	0.13
	40	0.09	0.02	0.07			0.11	0.03	0.11	0.22	5.50	2.40		0.80	7.42	0.13
	50	0.10	0.02	0.08	12.30	11.79	0.13	0.04	0.38	0.51	6.50	5.10	123.00	0.78	7.43	0.07
	75	0.10	0.02	0.08	12.45	12.02	0.14	0.04	0.29	0.43	7.00	4.17	120.64	0.80	7.43	0.11
	100	0.12	0.03	0.09	11.80	11.40	0.22	0.04	0.18	0.40	7.33	3.28	96.72	0.76	7.47	0.12
	120	0.13	0.03	0.10	12.71	11.91	0.59	0.12	0.21	0.80	19.67	5.97	94.80	1.12	7.36	0.04
47	0	0.19	0.02	0.17	8.29	8.07	0.14	0.04	0.08	0.22	7.00	1.17	44.08	0.86	7.45	0.09
	10	0.11	0.03	0.08	7.28	7.01	0.13	0.04	0.14	0.27	4.33	2.37	63.97	0.87	7.47	0.13
	20	0.14	0.04	0.10	5.56	4.89	0.29	0.04	0.38	0.67	7.25	4.96	41.18	0.90	7.48	0.15
	30	0.14	0.02	0.12	5.89	5.63	0.12	0.04	0.14	0.26	6.00	1.86	42.12	0.87	7.45	0.18
	40	0.13	0.02	0.11	6.41	6.00	0.14	0.03	0.27	0.41	7.00	3.11	48.56	0.89	7.34	0.11
	50	0.12	0.05	0.07	7.52	7.06	0.20	0.04	0.26	0.46	4.00	3.79	61.88	0.92	7.47	0.10
	85	0.14	0.02	0.12	11.84	11.38	0.16	0.04	0.30	0.46	8.00	3.24	83.51	0.93	7.55	0.09
48	0	0.11	0.03	0.08			0.11	0.05	0.05	0.16	3.67	1.47		0.81	7.42	0.15
	5	0.10	0.02	0.08			0.06	0.03	0.11	0.17	3.00	1.68		0.80	7.40	0.18
	10	0.13	0.02	0.11			0.09	0.04	0.05	0.14	4.50	1.07		0.81	7.41	0.14
	20	0.11	0.02	0.09			0.09	0.04	0.05	0.14	4.50	1.26		0.81	7.53	0.10
	30	0.12	0.02	0.10			0.09	0.04	0.06	0.15	4.50	1.23		0.79	7.40	0.13
	40	0.09	0.02	0.07			0.07	0.04	0.05	0.12	3.50	1.35		0.79	7.44	0.10
	50	0.11	0.02	0.09			0.08	0.04	0.05	0.13	4.00	1.16		0.79	7.39	0.11
	60	0.14	0.02	0.12			0.05	0.04	0.05	0.10	2.50	0.72		0.79	7.41	0.10
	75	0.13	0.02	0.11			0.08	0.04	0.10	0.18	4.00	1.42		0.82	7.32	0.10
	100	0.14	0.02	0.12			0.09	0.05	0.10	0.19	4.50	1.36		0.81	7.4	0.12

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
48	150	0.13	0.02	0.11			0.13	0.06	0.16	0.29	6.50	2.16		0.81	7.39	0.13
	200	0.15	0.02	0.13			0.39	0.09	0.20	0.59	19.50	4.05		1.00	7.39	
49	0		0.03				0.09	0.03	0.15	0.24	3.00			0.85	7.57	
50	0		0.03				0.08	0.03	0.11	0.19	2.67			0.79	7.41	
4. CRUISE - MARCH 2009																
1	0		0.11				3.36	0.24	0.29	3.65	30.55			4.68	7.63	0.21
2	0	0.09	0.02	0.07	2.22	1.07	1.02	0.15	0.13	1.15	51.00	13.29	25.65	1.68	7.71	0.10
	10	0.12	0.02	0.10	3.13	2.29	0.77	0.17	0.07	0.84	38.50	7.16	26.66	1.49	7.66	0.20
	19	0.11	0.02	0.09	4.20	3.54	0.62	0.19	0.04	0.66	31.00	6.20	39.45	1.37	7.66	0.21
3	0		0.03				1.11	0.17	0.06	1.17	37.00			1.55	7.68	0.21
4	0	0.12	0.02	0.10	7.13	6.24	0.78	0.15	0.11	0.89	39.00	7.21	57.79	0.97	7.60	0.25
	10	0.09	0.02	0.07	5.40	4.58	0.76	0.16	0.06	0.82	38.00	8.68	57.13	1.01	7.61	0.21
	20	0.11	0.02	0.09	5.45	4.58	0.64	0.14	0.23	0.87	32.00	7.98	50.00	1.04	7.65	0.17
	30	0.11	0.02	0.09	5.48	4.91	0.49	0.13	0.08	0.57	24.50	5.30	51.00	1.06	7.63	0.09
	40	0.08	0.02	0.06	5.17	4.24	0.62	0.17	0.31	0.93	31.00	11.13	61.86	1.26	7.61	0.16
	50	0.09	0.02	0.07	5.98	4.42	0.95	0.23	0.61	1.56	47.50	17.42	66.78	1.49	7.37	0.16
5	0		0.03				1.59	0.16	0.31	1.90	53.00			1.19	7.77	0.33
6	0	0.49	0.11	0.38			7.96	0.43	3.88	11.84	72.36	24.16		3.57	8.05	1.36
	7	0.42	0.11	0.31			6.42	0.40	2.57	8.99	58.36	21.40		2.56	7.47	1.40
7	0	0.35	0.08	0.27			3.45	0.28	0.43	3.88	43.13	11.09		2.77	7.91	0.89
	10	0.18	0.04	0.14			0.49	0.19	0.06	0.55	12.25	3.06		1.46	7.54	0.47
	16	0.19	0.05	0.14			0.53	0.19	0.06	0.59	10.60	3.11		1.51	7.48	0.39
10	0	0.14	0.02	0.12	5.22	3.56	1.46	0.14	0.20	1.66	73.00	11.59	36.44	1.12	7.71	0.31
	10	0.12	0.05	0.07	5.85	4.57	1.00	0.19	0.28	1.28	20.00	10.81	49.41	1.06	7.53	0.12
	20	0.12	0.02	0.10	5.84	4.73	0.90	0.18	0.21	1.11	45.00	9.25	48.67	1.05	7.37	0.19
	30	0.12	0.02	0.10	5.21	4.02	1.03	0.17	0.16	1.19	51.50	9.57	41.89	1.00	7.31	0.07
	40	0.12	0.02	0.10	5.38	4.13	1.04	0.20	0.21	1.25	52.00	10.30	44.32	1.12	7.32	0.04
	50	0.14	0.02	0.12	6.09	5.05	0.77	0.18	0.27	1.04	38.50	7.41	43.41	1.07	7.54	0.11
	70	0.33	0.03	0.30	9.44	7.81	0.84	0.21	0.79	1.63	28.00	4.98	28.84	1.37	7.55	0.10
11	0	1.14	0.49	0.65			4.85	0.64	15.74	20.59	9.90	18.06		4.66	7.43	1.03
	10	0.37	0.13	0.24			3.24	0.34	1.71	4.95	24.92	13.38		2.27	7.31	1.15
12	0	0.24	0.05	0.19			1.69	0.26	0.72	2.41	33.80	10.04		2.03	7.78	0.77
	10	0.09	0.04	0.05			0.47	0.18	0.40	0.87	11.75	9.67		1.41	7.55	0.19
	17	0.09	0.04	0.05			0.47	0.16	0.51	0.98	11.75	10.89		1.4	7.55	0.35
13	0	0.11	0.04	0.07			1.61	0.12	0.82	2.43	40.25	22.09		1.83	7.72	0.26
	10	0.07	0.03	0.04			0.72	0.10	0.81	1.53	24.00	21.86		1.21	7.61	0.30
	20	0.09	0.03	0.06			0.53	0.13	0.80	1.33	17.67	14.78		1.27	7.41	0.35
	30	0.09	0.04	0.05			0.48	0.13	0.81	1.29	12.00	14.33		1.28	7.45	0.41
14	0	0.19	0.03	0.16	6.54	4.00	1.24	0.30	1.30	2.54	41.33	13.16	33.88	1.46	7.60	0.24
	10	0.10	0.03	0.07	4.98	3.59	0.90	0.32	0.49	1.39	30.00	13.89	49.76	1.32	7.55	0.28
	20	0.09	0.02	0.07	5.17	3.91	0.67	0.35	0.59	1.26	33.50	13.41	55.03	1.22	7.47	0.20
	30	0.10	0.03	0.07	4.30	3.07	0.71	0.37	0.52	1.23	23.67	12.04	42.11	1.38	7.41	0.37
	40	0.11	0.03	0.08	5.05	3.75	0.69	0.40	0.61	1.30	23.00	11.57	44.95	1.38	7.44	0.42
16	0	0.35	0.09	0.26			4.84	0.37	1.35	6.19	53.78	17.69		2.67	7.85	1.90
	6	0.40	0.11	0.29			6.27	0.40	1.86	8.13	57.00	20.33		3.05	8.03	1.55
17	0	0.22	0.06	0.16			2.91	0.25	0.78	3.69	48.50	16.77		2.3	7.65	1.00
	14	0.14	0.05	0.09			1.16	0.21	0.69	1.85	23.20	13.21		1.61	7.53	1.18
18	0	0.21	0.07	0.14			2.75	0.16	1.09	3.84	39.29	18.29		2.79	7.99	0.80
	10	0.12	0.04	0.08			0.56	0.08	0.64	1.20	14.00	10.00		1.23	7.56	0.60
	18	0.11	0.04	0.07			0.54	0.09	0.74	1.28	13.50	11.64		1.3	7.47	0.33
21	0	0.25	0.11	0.14			3.43	0.32	0.94	4.37	31.18	17.48		2.04	8.05	1.19
	8	0.29	0.10	0.19			2.21	0.33	0.83	3.04	22.10	10.48		1.83	7.74	1.13
22	0	0.28	0.10	0.18			3.12	0.21	0.91	4.03	31.20	14.39		1.89	8.16	1.01
	10	0.32	0.10	0.22			1.79	0.16	0.89	2.68	17.90	8.38		1.66	7.78	0.89

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
27	1,5	0.24	0.07	0.17	10.06	4.09	3.76	0.20	2.21	5.97	53.71	25.31	42.64	4.34	8.59	0.32
	3	0.32	0.08	0.24	14.46	9.15	3.08	0.15	2.23	5.31	38.50	16.56	45.09	3.55	7.94	0.56
	5	0.45	0.02	0.43	13.09	9.44	1.89	0.08	1.76	3.65	94.50	8.09	29.00	2.00	7.89	0.41
	10	0.36	0.02	0.34	6.55	3.62	1.30	0.07	1.63	2.93	65.00	8.25	18.45	1.62	7.79	0.40
	14	0.26	0.03	0.23	7.77	4.99	1.25	0.07	1.53	2.78	41.67	10.80	30.19	1.59	7.78	0.27
	24	0.22	0.04	0.18	10.05	7.57	0.86	0.08	1.62	2.48	21.50	11.19	45.35	1.39	7.64	0.36
28	0	0.10	0.03	0.07	6.64	5.93	0.57	0.30	0.14	0.71	19.00	7.32	68.44	1.05	7.40	0.07
	10	0.19	0.02	0.17	5.72	5.07	0.54	0.30	0.11	0.65	27.00	3.40	29.95	1.04	7.40	0.08
	20	0.13	0.03	0.10	5.82	5.20	0.50	0.31	0.12	0.62	16.67	4.86	45.59	1.08	7.43	0.08
	30	0.13	0.02	0.11	6.82	6.04	0.67	0.30	0.11	0.78	33.50	6.06	53.00	1.22	7.49	0.10
	40	0.12	0.02	0.10	5.22	4.22	0.89	0.35	0.11	1.00	44.50	8.59	44.84	1.32	7.49	0.20
	50	0.12	0.02	0.10	5.42	4.24	1.04	0.35	0.14	1.18	52.00	9.88	45.36	1.41	7.48	0.21
36	0	0.39	0.13	0.26	11.67	4.94	5.92	0.38	0.81	6.73	45.54	17.43	30.23	2.71	8.46	0.76
	8	0.32	0.14	0.18	10.01	5.30	4.24	0.38	0.47	4.71	30.29	14.88	31.62	1.95	8.07	1.12
38	0	0.42	0.16	0.26	15.04	5.99	8.26	0.68	0.79	9.05	51.63	21.77	36.18	5.36	8.66	0.94
	10	0.23	0.11	0.12	8.57	4.96	3.19	0.50	0.42	3.61	29.00	15.57	36.97	2.50	7.51	0.73
39	0	0.27	0.03	0.24	7.44	5.83	1.28	0.37	0.33	1.61	42.67	6.06	28.02	1.49	7.55	0.16
	10	0.13	0.02	0.11	6.94	5.49	1.20	0.35	0.25	1.45	60.00	11.01	52.68	1.48	7.54	0.28
	20	0.13	0.02	0.11	6.38	4.89	1.08	0.34	0.41	1.49	54.00	11.05	47.33	1.45	7.54	0.18
	25	0.15	0.03	0.12	5.96	4.17	1.18	0.39	0.61	1.79	39.33	11.61	38.65	1.46	7.57	0.20
40	0	0.13	0.03	0.10	5.03	4.29	0.49	0.16	0.25	0.74	16.33	5.66	38.48	1.10	7.65	0.14
	10	0.14	0.02	0.12	6.59	5.91	0.48	0.17	0.20	0.68	24.00	4.97	48.16	1.10	7.66	0.11
	20	0.11	0.02	0.09	5.19	4.34	0.50	0.18	0.35	0.85	25.00	7.57	46.20	1.10	7.62	0.11
	30	0.09	0.02	0.07	4.80	4.24	0.44	0.16	0.12	0.56	22.00	6.03	51.65	1.10	7.59	0.10
	40	0.08	0.02	0.06	4.88	4.13	0.44	0.18	0.31	0.75	22.00	9.04	58.80	1.07	7.66	0.12
	50	0.07	0.02	0.05	4.72	3.97	0.42	0.17	0.33	0.75	21.00	10.34	65.10	1.05	7.65	0.10
41	0	0.33	0.18	0.15	12.02	5.30	5.00	0.32	1.72	6.72	27.78	20.50	36.67	4.49	8.09	2.38
	13	0.25	0.17	0.08	7.81	3.77	2.25	0.23	1.79	4.04	13.24	16.28	31.47	2.51	7.61	1.66
42	0		0.10				3.80	0.22	1.85	5.65	38.00			4.09	8.00	0.98
43	0	0.20	0.11	0.09	7.66	3.49	2.06	0.12	2.11	4.17	18.73	21.05	38.66	2.37	7.81	0.62
	10	0.18	0.03	0.15	8.41	6.73	0.55	0.04	1.13	1.68	18.33	9.28	46.46	1.19	7.63	0.18
	20	0.16	0.03	0.13	9.39	7.79	0.52	0.04	1.08	1.60	17.33	9.98	58.56	1.16	7.65	0.21
44	0		0.02				0.36	0.06	0.93	1.29	18.00			1.20	7.65	0.16
45	0		0.02				0.54	0.05	1.13	1.67	27.00			1.19	7.59	0.09
46	0	0.16	0.02	0.14	6.12	5.22	0.56	0.15	0.34	0.90	28.00	5.48	37.28	1.05	7.66	0.12
	10	0.16	0.03	0.13	4.93	4.12	0.49	0.16	0.32	0.81	16.33	5.12	31.17	1.07	7.61	0.11
	20	0.13	0.02	0.11	4.34	3.59	0.44	0.16	0.31	0.75	22.00	5.64	32.63	1.03	7.46	0.04
	30	0.12	0.07	0.05	4.59	4.04	0.26	0.09	0.29	0.55	3.71	4.53	37.82	0.78	7.46	0.10
	40	0.06	0.02	0.04	4.43	3.85	0.31	0.13	0.27	0.58	15.50	9.11	69.57	1.00	7.44	0.14
	50	0.09	0.02	0.07	4.23	3.46	0.47	0.12	0.30	0.77	23.50	8.23	45.23	1.00	7.42	0.12
	75	0.09	0.02	0.07	4.30	3.13	0.80	0.19	0.37	1.17	40.00	13.21	48.56	1.07	7.33	0.15
	100	0.06	0.02	0.04	4.23	3.48	0.37	0.13	0.38	0.75	18.50	12.36	69.70	1.13	7.49	0.20
	125	0.08	0.02	0.06	5.40	4.35	0.46	0.17	0.59	1.05	23.00	12.56	64.61	1.16	7.65	0.30
47	0	0.09	0.03	0.06	5.22	4.34	0.65	0.14	0.23	0.88	21.67	10.28	61.01	0.83	7.65	0.22
	10	0.08	0.02	0.06	5.89	4.96	0.65	0.14	0.28	0.93	32.50	11.98	75.90	0.85	7.62	0.27
	20	0.09	0.03	0.06	5.16	4.31	0.66	0.14	0.19	0.85	22.00	10.00	60.71	0.95	7.50	0.20
	30	0.08	0.02	0.06	6.19	5.49	0.44	0.12	0.26	0.70	22.00	8.69	76.81	0.91	7.53	0.14
	40	0.19	0.02	0.17	6.21	5.62	0.35	0.13	0.24	0.59	17.50	3.06	32.17	0.91	7.50	0.09
	50	0.13	0.02	0.11	5.78	5.24	0.34	0.09	0.20	0.54	17.00	4.14	44.35	0.92	7.50	0.08
	75	0.13	0.02	0.11	5.60	4.99	0.33	0.09	0.28	0.61	16.50	4.84	44.44	0.98	7.50	0.11
	85	0.12	0.02	0.10	5.21	4.58	0.38	0.14	0.25	0.63	19.00	5.07	41.89	1.03	7.47	0.11
48	0	0.14	0.03	0.11	4.07	3.62	0.23	0.08	0.22	0.45	7.67	3.16	28.61	0.92	7.47	0.12
	10	0.15	0.03	0.12	3.73	3.42	0.23	0.09	0.08	0.31	7.67	2.09	25.16	1.07	7.47	0.13
	20	0.19	0.04	0.15	4.30	3.51	0.41	0.10	0.38	0.79	10.25	4.25	23.11	0.94	7.50	0.10

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
48	30	0.13	0.02	0.11	3.39	3.10	0.23	0.08	0.06	0.29	11.50	2.26	26.41	0.89	7.53	0.13
	40	0.13	0.02	0.11	4.45	3.95	0.31	0.10	0.19	0.50	15.50	3.96	35.22	0.90	7.46	0.14
	50	0.09	0.02	0.07	4.10	3.61	0.27	0.08	0.22	0.49	13.50	5.47	45.79	0.87	7.51	0.12
	75	0.14	0.02	0.12	4.73	4.35	0.23	0.08	0.15	0.38	11.50	2.63	32.79	0.87	7.46	0.12
	100	0.13	0.02	0.11	4.50	3.88	0.44	0.18	0.18	0.62	22.00	4.66	33.83	0.91	7.41	0.09
	125	0.13	0.02	0.11	4.25	3.48	0.55	0.18	0.22	0.77	27.50	6.05	33.37	0.97	7.35	0.06
	150	0.14	0.02	0.12	4.41	3.53	0.61	0.20	0.27	0.88	30.50	6.47	32.43	1.01	7.31	0.03
	200	0.15	0.02	0.13	5.92	5.37	0.31	0.07	0.24	0.55	15.50	3.79	40.76	1.12	7.56	0.08
49	0		0.03				0.45	0.15	0.42	0.87	15.00			0.95	7.54	0.09
50	0		0.02				0.40	0.16	0.20	0.60	20.00			0.92	7.47	0.09
5. CRUISE - APRIL 2009																
1	0		0.05				0.65	0.08	0.69	1.34	13.00			1.43	7.82	
2	0	0.11	0.03	0.08	4.65	4.20	0.14	0.03	0.31	0.45	4.67	4.10	42.33	0.69	7.98	0.51
	10	0.07	0.03	0.04	7.48	7.06	0.12	0.03	0.30	0.42	4.00	5.93	105.58	0.64	7.95	0.30
	19	0.13	0.02	0.11	9.27	8.24	0.11	0.06	0.92	1.03	5.50	7.88	70.93	1.02	7.99	0.35
3	0		0.02				0.09	0.05	0.19	0.28	4.50			0.71	7.98	
4	0	0.10	0.03	0.07	9.39	9.08	0.13	0.04	0.18	0.31	4.33	3.24	97.98	0.67	8.10	0.62
	10	0.07	0.03	0.04	6.10	5.80	0.09	0.03	0.21	0.30	3.00	4.01	81.57	0.66	8.12	0.61
	20	0.08	0.03	0.05	6.21	5.90	0.06	0.02	0.25	0.31	2.00	3.70	74.07	0.67	8.04	0.53
	30	0.10	0.02	0.08	5.78	5.26	0.49	0.12	0.03	0.52	24.50	4.99	55.70	1.25	7.43	0.77
	50	0.10	0.02	0.08	5.05	4.13	0.77	0.24	0.15	0.92	38.50	9.60	52.74	1.45	7.57	0.75
5	0		0.03				0.20	0.07	0.04	0.24	6.67			1.04	8.26	
6	0	0.41	0.12	0.29			4.06	0.21	1.69	5.75	33.83	14.02		3.51	7.38	1.01
	9,5	0.33	0.11	0.22			2.29	0.16	1.59	3.88	20.82	11.94		2.34	7.36	0.85
7	0	0.30	0.05	0.25			2.62	0.14	0.31	2.93	52.40	9.77		2.31	8.18	1.01
	10	0.11	0.02	0.09			0.20	0.04	0.10	0.30	10.00	2.68		0.68	7.85	0.25
	16	0.11	0.03	0.08			0.08	0.04	0.05	0.13	2.67	1.20		0.74	7.84	0.21
8	0		0.03				0.11	0.04	0.26	0.37	3.67			0.63	7.95	0.12
9	0		0.03				0.09	0.03	0.20	0.29	3.00			0.94	8.17	
10	0	0.17	0.05	0.12	8.21	8.00	0.14	0.07	0.07	0.21	2.80	1.21	47.29	0.93	8.17	0.79
	10	0.06	0.02	0.04	4.00	3.71	0.19	0.05	0.10	0.29	9.50	4.69	64.66	1.01	8.04	0.53
	20	0.05	0.02	0.03	4.35	4.20	0.06	0.04	0.09	0.15	3.00	3.01	87.28	1.39	8.04	0.22
	30	0.07	0.03	0.04	3.83	3.60	0.09	0.04	0.14	0.23	3.00	3.44	57.29	1.68	8.24	0.43
	40	0.05	0.02	0.03	4.26	3.20	1.00	0.38	0.06	1.06	50.00	21.25	85.40	2.28	7.41	0.44
	50	0.07	0.03	0.04	4.93	3.57	1.28	0.47	0.08	1.36	42.67	18.67	67.65	2.26	7.22	0.71
	70	0.07	0.04	0.03	4.70	2.23	2.16	0.74	0.31	2.47	54.00	36.40	69.24	2.42	7.02	0.60
11	0	0.37	0.07	0.30			3.01	0.19	2.01	5.02	43.00	13.57		3.44	8.06	0.79
	10	0.26	0.07	0.19			0.57	0.11	1.07	1.64	8.14	6.24		1.22	7.43	0.67
12	0	0.29	0.10	0.19			1.77	0.19	0.36	2.13	17.70	7.34		1.84	8.42	0.98
	10	0.30	0.14	0.16			0.38	0.14	0.45	0.83	2.71	2.80		1.25	8.03	0.78
	14	0.27	0.08	0.19			0.14	0.12	0.41	0.55	1.75	2.05		0.96	7.74	0.37
13	0	0.20	0.04	0.16			0.28	0.04	0.23	0.51	7.00	2.56		2.21	8.59	0.56
	10	0.14	0.05	0.09			0.14	0.02	0.19	0.33	2.80	2.44		1.21	8.12	0.40
	20	0.12	0.04	0.08			0.11	0.02	0.10	0.21	2.75	1.72		0.94	7.85	0.34
	28	0.07	0.05	0.02			0.16	0.03	0.29	0.45	3.20	6.72		0.75	7.91	0.24
14	0	0.15	0.04	0.11	8.16	7.81	0.14	0.05	0.21	0.35	3.50	2.31	53.78	2.46	8.38	1.10
	10	0.08	0.05	0.03	5.33	5.15	0.06	0.04	0.12	0.18	1.20	2.34	69.42	1.48	8.11	0.57
	20	0.07	0.04	0.03	4.92	4.71	0.06	0.03	0.15	0.21	1.50	3.01	70.44	1.10	8.08	0.53
	30	0.08	0.02	0.06	5.09	4.86	0.05	0.02	0.18	0.23	2.50	2.80	62.07	1.03	7.77	0.65
	42	0.08	0.03	0.05	4.89	3.76	0.94	0.26	0.19	1.13	31.33	13.64	58.99	1.77	7.09	1.31
15	0		0.05				0.52	0.09	0.34	0.86	10.40			2.77	8.61	
16	0	0.39	0.11	0.28			5.19	0.32	0.85	6.04	47.18	15.33		9.03	8.20	1.55
	7	0.25	0.09	0.16			1.13	0.20	0.55	1.68	12.56	6.75		2.44	8.44	1.00
17	0	0.36	0.08	0.28			2.60	0.25	0.37	2.97	32.50	8.20		1.55	8.55	1.46

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
17	12	0.24	0.09	0.15			0.21	0.17	0.31	0.52	2.33	2.20		1.76	7.56	0.50
18	0	0.47	0.07	0.40			2.20	0.26	0.48	2.68	31.43	5.67		7.4	8.86	1.06
	10	0.28	0.05	0.23			0.18	0.14	0.15	0.33	3.60	1.20		1.07	7.99	0.44
	19	0.26	0.06	0.20			0.21	0.16	0.17	0.38	3.50	1.46		1.38	7.95	0.26
19	0		0.08				0.86	0.10	0.84	1.70	10.75			5.25	9.52	1.01
20	0		0.05				0.89	0.12	0.23	1.12	17.80			4.64	8.79	
21	0	0.29	0.08	0.21			1.50	0.19	0.62	2.12	18.75	7.31		6.38	8.62	1.33
	7	0.44	0.06	0.38			0.76	0.17	0.30	1.06	12.67	2.41		3.29	8.54	1.36
22	0	0.47	0.07	0.40			2.39	0.24	0.39	2.78	34.14	5.90		6.87	8.82	1.14
	10	0.29	0.05	0.24			0.27	0.17	0.29	0.56	5.40	1.90		1.95	8.28	0.47
23	0		0.31				4.11	0.26	1.10	5.21	13.26			14.78	9.70	
24	0		0.19				2.80	0.19	1.23	4.03	14.74			9.98	9.73	
25	0		0.09				1.31	0.13	0.85	2.16	14.56			6.50	9.49	1.19
26	0		0.07				0.74	0.10	0.70	1.44	10.57			4.15	9	
27	0	0.10	0.08	0.02	7.03	6.36	0.45	0.03	0.22	0.67	5.63	6.58	69.09	1.07	7.95	0.80
	5	0.10	0.05	0.05	7.93	7.52	0.24	0.02	0.17	0.41	4.80	3.95	76.42	0.61	8.12	0.65
	10	0.11	0.04	0.07	5.48	5.20	0.22	0.02	0.06	0.28	5.50	2.59	50.73	0.60	7.99	0.35
	15	0.10	0.04	0.06	5.18	4.81	0.24	0.02	0.13	0.37	6.00	3.59	50.26	0.65	8.25	0.41
	25	0.12	0.06	0.06	5.57	4.72	0.52	0.09	0.33	0.85	8.67	6.93	45.41	1.09	7.42	0.93
28	0	0.17	0.02	0.15	7.96	6.81	0.96	0.10	0.19	1.15	48.00	6.78	46.93	1.91	8.04	0.98
	10	0.08	0.03	0.05	6.40	5.85	0.31	0.06	0.24	0.55	10.33	6.64	77.23	1.89	8.08	0.57
	20	0.05	0.02	0.03	4.88	4.67	0.07	0.03	0.14	0.21	3.50	3.83	88.93	1.90	7.68	0.09
	30	0.05	0.03	0.02	4.58	4.21	0.10	0.03	0.27	0.37	3.33	7.57	93.68	1.77	7.61	0.18
	40	0.09	0.03	0.06	4.84	3.41	1.11	0.44	0.32	1.43	37.00	15.75	53.31	1.13	7.21	0.83
	50	0.09	0.05	0.04	4.93	3.43	1.17	0.43	0.33	1.50	23.40	15.82	51.98	2.79	7.25	0.66
29	0		0.05				0.24	0.03	0.21	0.45	4.80			1.04	8.20	0.19
30	0	0.11	0.03	0.08	6.16	5.83	0.17	0.03	0.16	0.33	5.67	3.00	56.01	0.74	7.71	
31	0		0.16				3.19	0.22	1.12	4.31	19.94			11.21	9.33	
32	0		0.12				2.19	0.17	0.86	3.05	18.25			8.31	9.14	0.89
33	0	0.46	0.12	0.34	18.43	13.96	3.25	0.20	1.22	4.47	27.08	9.70	39.97	9.30	9.08	1.47
	8	0.32	0.20	0.12	11.04	11.04	0.71	0.19	1.24		3.55	0.00	34.80	3.03	7.41	0.58
34	0	0.39	0.08	0.31	15.58	11.19	3.29	0.20	1.10	4.39	41.13	11.34	40.25	9.07	9.04	1.08
	8	0.19	0.07	0.12	8.69	8.69	0.61	0.10	1.02		8.71	0.00	45.11	2.08	8.09	0.44
35	0		0.11				0.92	0.05	0.32	1.24	8.36			1.57	8.19	0.41
36	0		0.19				4.34	0.28	1.61	5.95	22.84			11.63	8.93	2.25
37	0		0.10				0.95	0.13	1.11	2.06	9.50			4.05	8.54	
38	0	0.13	0.06	0.07	7.78	6.65	0.86	0.05	0.27	1.13	14.33	8.58	59.08	2.07	8.07	0.23
	10	0.16	0.05	0.11	7.70	6.85	0.62	0.11	0.23	0.85	12.40	5.39	48.84	1.35	7.52	0.64
39	0	0.11	0.03	0.08	6.98	6.21	0.54	0.03	0.23	0.77	18.00	6.95	63.02	1.12	8.04	0.30
	10	0.09	0.03	0.06	6.42	5.70	0.42	0.07	0.30	0.72	14.00	7.84	69.90	0.64	8.07	0.24
	24	0.11	0.06	0.05	4.94	3.74	0.83	0.10	0.37	1.20	13.83	11.03	45.40	1.28	7.62	0.46
40	0	0.12	0.03	0.09	8.63	8.47	0.10	0.02	0.06	0.16	3.33	1.35	73.06	0.73	7.62	0.10
	10	0.08	0.03	0.05	4.84	4.71	0.07	0.03	0.06	0.13	2.33	1.60	59.42	0.72	7.62	0.05
	20	0.08	0.03	0.05	4.04	3.93	0.06	0.03	0.05	0.11	2.00	1.38	50.87	0.84	7.89	0.05
	30	0.06	0.02	0.04	4.16	4.00	0.09	0.03	0.07	0.16	4.50	2.86	74.28	0.92	7.68	0.05
	40	0.07	0.03	0.04	4.98	4.87	0.06	0.03	0.05	0.11	2.00	1.57	70.88	1.03	7.55	0.15
	56	0.08	0.03	0.05	5.29	5.04	0.13	0.05	0.12	0.25	4.33	3.27	69.27	1.33	7.50	0.25
41	0		0.03				0.66	0.07	0.44	1.10	22.00			2.10	7.97	0.40
42	0		0.06				0.09	0.02	0.21	0.30	1.50			1.27	7.95	
43	0	0.11	0.04	0.07	10.03	9.70	0.20	0.02	0.13	0.33	5.00	2.90	88.19	0.86	7.82	0.28
	10	0.09	0.04	0.05	4.94	4.51	0.20	0.03	0.23	0.43	5.00	4.90	56.23	0.87	8.01	0.23
	19	0.15	0.07	0.08	7.80	7.20	0.46	0.10	0.14	0.60	6.57	4.01	52.13	1.55	7.84	0.40
44	0		0.04				0.22	0.04	0.17	0.39	5.50			0.81	7.76	
45	0		0.16				0.13	0.06	0.06	0.19	0.81			0.70	8.01	

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
47	0	0.05	0.04	0.01	4.54	3.93	0.09	0.03	0.52	0.61	2.25	11.09	82.57	1.48	7.78	0.26
	10	0.07	0.03	0.04	4.99	4.74	0.07	0.02	0.18	0.25	2.33	3.41	68.06	1.11	7.92	0.23
	20	0.08	0.03	0.05	4.42	4.00	0.14	0.02	0.28	0.42	4.67	5.50	57.88	1.24	7.76	0.18
	30	0.06	0.02	0.04	4.27	3.99	0.08	0.02	0.20	0.28	4.00	4.51	68.75	1.94	7.70	0.13
	50	0.05	0.04	0.01	3.80	3.44	0.10	0.03	0.26	0.36	2.50	6.55	69.11	1.95	7.58	0.28
	80	0.07	0.04	0.03	4.95	3.21	1.54	0.42	0.20	1.74	38.50	26.29	74.79	2.33	7.29	0.56
48	0	0.07	0.04	0.03	3.36	2.90	0.12	0.02	0.34	0.46	3.00	7.08	51.69	1.53	7.68	0.06
	5	0.06	0.03	0.03	4.09	3.67	0.10	0.03	0.32	0.42	3.33	6.99	68.08	1.11	7.68	0.06
	10	0.05	0.03	0.02	4.75	4.40	0.09	0.03	0.26	0.35	3.00	6.73	91.35	1.17	7.66	0.05
	20	0.06	0.04	0.02	4.78	4.40	0.14	0.04	0.24	0.38	3.50	6.43	80.94	1.37	7.63	0.10
	35	0.05	0.03	0.02	4.57	4.23	0.13	0.04	0.21	0.34	4.33	6.30	84.68	1.56	7.66	0.21
	65	0.06	0.03	0.03	5.14	4.47	0.45	0.15	0.22	0.67	15.00	11.75	90.18	1.72	7.46	0.09
	75	0.06	0.05	0.01	3.98	3.08	0.52	0.14	0.38	0.90	10.40	14.52	64.19	1.87	7.34	0.02
	100	0.06	0.04	0.02	3.34	2.10	0.80	0.18	0.44	1.24	20.00	20.67	55.67	1.74	7.42	0.09
	150	0.06	0.05	0.01	3.57	2.35	0.79	0.11	0.43	1.22	15.80	19.06	55.78	2.22	7.56	0.17
	200	0.08	0.07	0.01	3.50	1.57	1.34	0.05	0.59	1.93	19.14	24.13	43.75	2.64	7.10	0.25
49	0		0.03				0.09	0.02	0.05	0.14	3.00			1.16	7.52	
50	0		0.04				0.06	0.03	0.08	0.14	1.50			0.75	7.76	
6. CRUISE - AUGUST 2009																
1	0		0.06				0.25	0.13	0.49	0.74	4.17			1.33	6.71	
2	0	0.14	0.08	0.06	6.51	5.94	0.10	0.07	0.47	0.57	1.25	3.97	45.34	1.11	6.79	0.35
	10	0.13	0.05	0.08	4.39	4.24	0.06	0.04	0.09	0.15	1.20	1.14	33.26	2.17	6.35	0.25
	19	0.12	0.11	0.01	4.70	3.61	0.31	0.12	0.78	1.09	2.82	9.08	39.19	3.04	6.04	0.21
3	0		0.07				0.15	0.10	1.42	1.57	2.14			1.11	6.68	
4	0	0.05	0.03	0.02	4.19	2.85	0.12	0.05	1.22	1.34	4.00	29.78	93.06	0.76	6.40	0.12
	10	0.09	0.03	0.06	4.01	2.28	0.14	0.06	1.59	1.73	4.67	19.60	45.41	0.75	6.38	0.06
	20	0.09	0.02	0.07	4.29	2.81	0.12	0.06	1.36	1.48	6.00	16.41	47.55	0.85	6.39	0.11
	30	0.08	0.03	0.05	4.22	2.71	0.12	0.06	1.39	1.51	4.00	19.71	55.06	1.17	6.43	0.06
	49	0.08	0.06	0.02	4.72	2.75	0.18	0.10	1.79	1.97	3.00	23.90	57.24	1.87	6.25	0.07
5	0		0.03				0.06	0.05	0.05	0.11	2.00			0.82	6.31	
6	0	0.33	0.09	0.24			0.28	0.14	0.48	0.76	3.11	2.30		1.39	6.40	0.57
	10	0.30	0.14	0.16			1.07	0.30	1.51	2.58	7.64	8.49		4.05	5.41	0.42
7	0	0.23	0.05	0.18			0.12	0.10	0.18	0.30	2.40	1.29		0.99	6.46	0.46
	10	0.25	0.03	0.22			0.10	0.07	0.22	0.32	3.33	1.29		2.46	6.00	0.14
	17	0.28	0.14	0.14			0.56	0.20	1.03	1.59	4.00	5.72		4.75	5.47	0.45
8	0	0.27	0.05	0.22			0.07	0.04	1.28	1.35	1.40	4.93		0.88	6.95	
9	0		0.04				0.11	0.06	1.09	1.20	2.75			0.81	6.49	
10	0	0.05	0.03	0.02	3.33	3.19	0.07	0.05	0.07	0.14	2.33	2.72	64.74	0.76	6.31	0.49
	10	0.06	0.02	0.04	4.33	4.18	0.06	0.05	0.09	0.15	3.00	2.38	68.65	0.78	6.33	0.06
	20	0.07	0.02	0.05	3.53	3.36	0.09	0.07	0.08	0.17	4.50	2.40	49.86	0.79	6.39	0.04
	30	0.06	0.03	0.03	3.47	3.32	0.09	0.08	0.06	0.15	3.00	2.49	57.68	0.77	6.44	0.04
	50	0.05	0.03	0.02	3.33	3.16	0.10	0.07	0.07	0.17	3.33	3.51	68.63	0.88	6.50	0.02
	70	0.07	0.05	0.02	3.85	2.72	0.33	0.23	0.80	1.13	6.60	15.74	53.66	1.07	7.52	0.07
11	0	0.31	0.08	0.23			0.39	0.19	0.86	1.25	4.88	3.99		2.21	6.17	0.70
	10	0.37	0.17	0.20			1.12	0.40	2.75	3.87	6.59	10.40		5.81	5.06	0.69
12	0	0.32	0.06	0.26			0.18	0.14	0.65	0.83	3.00	2.59		2.18	6.77	1.27
	10	0.18	0.05	0.13			0.23	0.22	0.81	1.04	4.60	5.65		1.71	6.42	2.40
	17	0.23	0.08	0.15			0.37	0.20	1.49	1.86	4.63	8.27		3.8	5.71	1.21
13	0	0.27	0.06	0.21			0.06	0.04	0.77	0.83	1.00	3.10		1.22	6.93	0.80
	10	0.21	0.04	0.17			0.05	0.03	0.93	0.98	1.25	4.67		1.58	6.47	
	20	0.15	0.04	0.11			0.09	0.04	0.82	0.91	2.25	6.11		1.9	6.02	0.92
	27	0.13	0.05	0.08			0.17	0.07	1.27	1.44	3.40	11.16		2.3	6.03	0.51
14	0	0.07	0.05	0.02	3.49	2.94	0.12	0.03	0.43	0.55	2.40	8.22	52.18	0.89	6.31	0.13
	10	0.09	0.04	0.05	3.91	3.26	0.09	0.03	0.56	0.65	2.25	7.47	44.94	0.89	6.31	0.06

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
14	20	0.07	0.05	0.02	3.40	2.73	0.10	0.02	0.57	0.67	2.00	8.97	45.51	0.94	6.39	0.03
	30	0.10	0.05	0.05	4.49	3.49	0.10	0.04	0.90	1.00	2.00	9.73	43.67	1.42	6.36	0.25
	41	0.14	0.07	0.07	5.19	3.92	0.24	0.09	1.03	1.27	3.43	8.79	35.90	2.14	6.14	0.24
15	0		0.05				0.13	0.11	0.76	0.89	2.60			0.74	6.32	
16	0	0.59	0.11	0.48			0.45	0.23	4.24	4.69	4.09	8.00		3.18	6.16	1.26
	7	0.57	0.15	0.42			0.71	0.30	5.01	5.72	4.73	9.98		4.15	5.93	0.97
17	0	0.35	0.07	0.28			0.17	0.15	1.22	1.39	2.43	3.98		2.65	6.74	1.00
	13	0.40	0.05	0.35			0.16	0.13	1.41	1.57	3.20	3.96		1.78	6.43	0.82
18	0	0.61	0.09	0.52			0.68	0.22	0.64	1.32	7.56	2.15		3.89	7.74	2.11
	10	0.28	0.06	0.22			0.05	0.03	0.43	0.48	0.83	1.74		1.15	6.82	0.45
	18	0.34	0.13	0.21			0.39	0.26	1.41	1.80	3.00	5.31		4.67	5.76	
19	0		0.07				0.16	0.05	0.78	0.94	2.29			1.14	6.50	
20	0		0.03				0.14	0.10	0.33	0.47	4.67			0.73	6.27	
21	0	0.42	0.08	0.34			0.38	0.17	1.76	2.14	4.75	5.07		3.22	6.58	0.95
	7	0.42	0.09	0.33			0.38	0.19	1.85	2.23	4.22	5.33		3.31	6.69	1.77
22	0	0.50	0.08	0.42			0.23	0.21	1.68	1.91	2.88	3.84		3.39	6.95	1.32
	10	0.21	0.14	0.07			0.41	0.31	1.85	2.26	2.93	10.71		4.32	5.89	0.58
24	0		0.07				0.15	0.09	1.05	1.20	2.14			3.45	7.64	
25	0	0.32	0.04	0.28	8.91	7.82	0.24	0.12	0.85	1.09	6.00	3.39	27.68	2.52	7.19	1.16
26	0	0.29	0.03	0.26	7.88	6.94	0.16	0.08	0.78	0.94	5.33	3.20	26.82	1.35	7.20	1.10
27	0	0.44	0.13	0.31	9.09	5.16	1.92	0.31	2.01	3.93	14.77	8.98	20.79	8.08	6.47	0.82
	3	0.20	0.06	0.14	6.52	6.18	0.18	0.07	0.16	0.34	3.00	1.74	33.26	2.58	6.44	0.43
	5	0.10	0.05	0.05	5.46	5.05	0.10	0.04	0.31	0.41	2.00	4.06	54.14	1.60	6.39	0.36
	8	0.07	0.06	0.01	5.21	5.02	0.08	0.04	0.11	0.19	1.33	2.54	69.76	0.91	6.33	0.26
	14	0.06	0.03	0.03	4.62	4.49	0.06	0.02	0.07	0.13	2.00	2.03	72.17	1.05	6.26	0.09
	20	0.07	0.03	0.04	4.35	4.17	0.07	0.04	0.11	0.18	2.33	2.58	62.31	1.48	6.17	0.20
	30	0.12	0.09	0.03	5.65	4.12	0.38	0.16	1.15	1.53	4.22	13.19	48.69	3.22	5.78	0.51
28	0	0.05	0.03	0.02	4.13	3.38	0.13	0.08	0.62	0.75	4.33	15.16	83.55	0.83	6.27	0.33
	10	0.08	0.03	0.05	3.52	2.61	0.14	0.10	0.77	0.91	4.67	11.04	42.64	0.83	6.30	0.03
	20	0.08	0.02	0.06	3.20	2.13	0.14	0.11	0.93	1.07	7.00	13.29	39.79	0.81	6.31	0.02
	30	0.07	0.03	0.04	3.15	2.29	0.16	0.12	0.70	0.86	5.33	12.85	47.05	0.75	6.39	0.03
	50	0.11	0.05	0.06	3.80	2.12	0.48	0.19	1.20	1.68	9.60	15.60	35.34	2.65	5.98	0.05
29	0		0.05				0.09	0.02	0.39	0.48	1.80			0.92	6.37	
30	0	0.06	0.03	0.03	4.04	3.53	0.06	0.03	0.45	0.51	2.00	8.22	65.07	0.85	6.38	0.02
31	0		0.06				2.32	0.43	3.08	5.40	38.67			7.81	7.73	
32	0	0.39	0.04	0.35	8.09	7.07	0.21	0.10	0.81	1.02	5.25	2.58	20.48	3.69	7.11	1.52
33	0	0.40	0.06	0.34	11.62	10.14	0.27	0.17	1.21	1.48	4.50	3.68	28.86	5.49	6.71	0.55
	9	0.56	0.17	0.39	12.21	8.73	0.71	0.48	2.77	3.48	4.18	6.18	21.67	9.26	4.94	1.52
34	0	0.43	0.07	0.36	11.89	10.31	0.22	0.19	1.36	1.58	3.14	3.69	27.74	4.25	6.68	0.82
	8	0.45	0.08	0.37	10.99	9.15	0.36	0.20	1.48	1.84	4.50	4.11	24.53	4.28	6.53	1.13
35	0	0.12	0.02	0.10	5.79	4.80	0.15	0.07	0.84	0.99	7.50	8.10	47.37	1.03	6.38	0.21
36	0	0.48	0.05	0.43	15.18	13.15	0.41	0.16	1.62	2.03	8.20	4.19	31.36	7.21	7.37	1.53
37	0		0.08				0.23	0.14	1.41	1.64	2.88			6.41	6.84	
38	0	0.12	0.06	0.06	6.29	5.86	0.11	0.09	0.32	0.43	1.83	3.70	54.12	1.17	6.61	1.28
	10	0.09	0.04	0.05	5.02	4.61	0.12	0.08	0.29	0.41	3.00	4.58	56.15	1.11	6.38	0.29
39	0	0.07	0.03	0.04	5.20	5.03	0.05	0.02	0.12	0.17	1.67	2.47	75.41	0.90	6.27	0.03
	10	0.06	0.04	0.02	5.09	4.93	0.09	0.05	0.07	0.16	2.25	2.83	90.06	0.96	6.30	0.09
	20	0.12	0.09	0.03	4.95	4.64	0.12	0.10	0.19	0.31	1.33	2.58	41.17	1.78	6.16	0.41
	25	0.14	0.12	0.02	8.99	8.54	0.16	0.14	0.29	0.45	1.33	3.13	62.45	1.92	6.17	0.21
40	0	0.05	0.03	0.02	4.55	4.04	0.08	0.05	0.43	0.51	2.67	11.02	98.26	0.76	6.33	0.05
	10	0.05	0.03	0.02	5.59	5.17	0.07	0.06	0.35	0.42	2.33	8.01	106.66	0.81	6.35	0.05
	20	0.05	0.02	0.03	5.67	5.20	0.06	0.04	0.41	0.47	3.00	9.22	111.21	0.54	6.38	0.05
	30	0.05	0.03	0.02	4.78	4.31	0.08	0.07	0.39	0.47	2.67	8.79	89.42	0.69	6.39	0.06
	50	0.09	0.02	0.07	5.30	4.66	0.17	0.12	0.47	0.64	8.50	7.50	62.06	1.07	6.84	0.25

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
40	56	0.08	0.02	0.06	6.33	5.49	0.22	0.14	0.62	0.84	11.00	11.04	83.16	1.16	6.87	0.24
41	0	0.06	0.03	0.03	3.98	3.44	0.11	0.07	0.43	0.54	3.67	8.47	62.50	1.06	6.30	0.05
42	0		0.02				0.10	0.04	0.34		5.00			0.81	6.25	
43	0	0.23	0.02	0.21	6.66	6.24	0.09	0.06	0.33	0.42	4.50	1.81	28.68	0.82	6.27	0.02
	10	0.13	0.02	0.11	3.88	3.28	0.11	0.07	0.49	0.60	5.50	4.45	28.82	0.87	6.30	0.03
	19	0.14	0.10	0.04	3.69	3.03	0.14	0.12	0.52	0.66	1.40	4.62	25.80	1.16	6.31	0.02
44	0		0.04				0.07	0.03	0.76	0.83	1.75			0.93	6.36	
45	0		0.04				0.07	0.04	0.70	0.77	1.75			0.83	6.32	
46	0		0.02				0.06	0.02	0.23	0.29	3.00			0.71	6.29	
47	0	0.10	0.02	0.08	4.73	4.00	0.07	0.03	0.66	0.73	3.50	7.63	49.51	0.69	6.31	0.07
	10	0.07	0.02	0.05	4.26	3.41	0.08	0.04	0.77	0.85	4.00	12.34	61.83	0.68	6.41	0.08
	20	0.13	0.02	0.11	4.11	3.42	0.08	0.04	0.61	0.69	4.00	5.50	32.76	0.73	6.38	0.09
	30	0.11	0.02	0.09	3.30	2.59	0.09	0.04	0.62	0.71	4.50	6.64	30.90	0.72	6.41	0.15
	50	0.09	0.02	0.07	3.29	2.56	0.10	0.06	0.63	0.73	5.00	8.16	36.76	0.97	6.84	0.57
	82	0.08	0.03	0.05	4.45	3.50	0.18	0.10	0.77	0.95	6.00	11.69	54.82	0.61	7.59	0.17
48	1	0.10	0.03	0.07	3.70	2.70	0.08	0.04	0.92	1.00	2.67	9.53	35.23	0.83	6.26	0.03
	3	0.10	0.03	0.07	3.83	2.83	0.08	0.03	0.92	1.00	2.67	10.46	40.03	0.83	6.34	0.02
	7	0.10	0.03	0.07	3.51	2.28	0.09	0.06	1.14	1.23	3.00	11.73	33.44	0.97	5.70	0.02
	20	0.11	0.03	0.08	3.73	2.62	0.09	0.06	1.02	1.11	3.00	10.37	34.90	0.82	6.42	0.03
	35	0.12	0.04	0.08	3.80	2.51	0.08	0.05	1.21	1.29	2.00	10.91	32.17	1.52	6.73	0.25
	45	0.11	0.03	0.08	3.20	1.75	0.20	0.08	1.25	1.45	6.67	13.56	29.92	1.19	7.46	0.14
	75	0.08	0.02	0.06	3.10	1.96	0.15	0.06	0.99	1.14	7.50	13.69	37.24	0.82	7.74	0.12
	90	0.07	0.03	0.04	3.37	2.01	0.16	0.08	1.20	1.36	5.33	18.37	45.48	0.96	7.60	0.12
	150	0.07	0.03	0.04	3.38	2.32	0.15	0.08	0.91	1.06	5.00	14.32	45.59	0.84	7.23	0.03
	200	0.10	0.05	0.05	3.64	2.01	0.59	0.07	1.04	1.63	11.80	16.69	37.27	1.43	7.00	0.02
49	0		0.03				0.06	0.03	0.81	0.87	2.00			0.80	6.28	
50	0		0.04				0.06	0.03	1.01	1.07	1.50			0.74	6.32	
7. CRUISE - OCTOBER 2009																
1	0		0.03				0.05	0.02	0.29	0.34	1.67			3.15	6.87	
2	0	0.21	0.03	0.18	6.45	5.78	0.27	0.07	0.40	0.67	9.00	3.24	31.19	3.17	6.68	0.35
	10	0.19	0.02	0.17	6.04	5.45	0.20	0.06	0.39	0.59	10.00	3.05	31.27	3.08	6.64	0.38
	19	0.21	0.06	0.15	7.08	5.59	0.65	0.16	0.84	1.49	10.83	7.14	33.90	3.64	6.30	0.36
3	0		0.02				0.24	0.10	0.47	0.71	12.00			2.73	6.54	
4	0	0.14	0.02	0.12	4.87	4.40	0.12	0.02	0.35	0.47	6.00	3.43	35.55	2.75	6.61	0.18
	10	0.17	0.03	0.14	5.22	4.62	0.23	0.03	0.37	0.60	7.67	3.61	31.42	2.45	6.54	0.18
	20	0.11	0.03	0.08	4.64	4.17	0.10	0.02	0.37	0.47	3.33	4.28	42.31	2.10	6.55	0.13
	35	0.15	0.03	0.12	4.18	3.44	0.30	0.14	0.44	0.74	10.00	4.98	28.11	2.16	6.45	0.17
	48	0.12	0.02	0.10	6.48	3.77	2.22	0.42	0.49	2.71	111.00	22.15	53.00	6.13	6.24	0.23
5	0		0.04				0.08	0.02	0.21	0.29	2.00			1.76	6.57	
6	0	0.448	0.05	0.40			3.40	0.31	1.45	4.85	68.00	10.83		2.44	7.05	1.89
	10	0.404	0.05	0.35			3.28	0.32	1.54	4.82	65.60	11.93		2.67	6.82	1.75
7	0	0.231	0.04	0.19			0.64	0.10	0.66	1.30	16.00	5.63		3.34	6.69	0.83
	10	0.256	0.06	0.20			0.79	0.15	0.90	1.69	13.17	6.60		3.84	6.47	0.71
	14	0.277	0.10	0.18			0.22	0.22	1.08	1.30	2.20	4.69		4.22	6.32	0.51
8	0	0.121	0.04	0.08			0.06	0.02	0.25	0.31	1.50	2.56		2.96	6.66	0.18
9	0		0.03				0.14	0.06	0.37	0.51	4.67			3.58	6.76	
10	0	0.09	0.05	0.04	3.97	3.65	0.09	0.02	0.23	0.32	1.80	3.66	45.40	2.11	6.55	0.09
	10	0.06	0.03	0.03	4.26	3.96	0.07	0.03	0.23	0.30	2.33	5.24	74.35	2.04	6.53	0.06
	20	0.07	0.03	0.04	4.08	3.73	0.08	0.02	0.27	0.35	2.67	5.08	59.12	1.87	6.54	0.09
	30	0.10	0.02	0.08	4.03	3.65	0.09	0.04	0.29	0.38	4.50	3.84	40.65	1.64	6.65	0.09
	50	0.12	0.02	0.10	3.93	3.58	0.09	0.04	0.26	0.35	4.50	2.92	32.75	1.09	7.64	0.16
	68	0.14	0.03	0.11	4.02	3.26	0.45	0.27	0.31	0.76	15.00	5.51	29.14	1.52	7.35	0.10
11	0	0.517	0.05	0.47			5.01	0.42	1.35	6.36	100.20	12.30		2.25	7.02	2.34
	10	0.422	0.06	0.36			4.15	0.41	0.20	4.35	69.17	10.30		3.2	6.60	1.24

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (µM)	DIP (µM)	DOP (µM)	TN (µM)	DON (µM)	NO3 (µM)	NO2 (µM)	NH4 (µM)	DIN (µM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (µM)	DO (mg/L)	chl-a (µg/L)
12	0	0.325	0.05	0.28			2.23	0.29	2.20	4.43	44.60	13.63		3.75	6.49	1.49
	10	0.327	0.02	0.31			1.26	0.17	1.48	2.74	63.00	8.38		3.57	6.49	0.99
	17	0.262	0.03	0.23			0.48	0.12	1.27	1.75	16.00	6.68		3.24	6.46	0.38
13	0	0.090	0.05	0.04			0.18	0.02	0.10	0.28	3.60	3.11		2.46	6.50	0.30
	10	0.091	0.04	0.05			0.08	0.03	0.15	0.23	2.00	2.53		2.47	6.49	0.25
	20	0.091	0.06	0.03			0.16	0.06	0.17	0.33	2.67	3.63		2.52	6.43	0.35
	30	0.298	0.16	0.14			0.53	0.27	0.21	0.74	3.31	2.48		3.11	6.24	0.31
14	0	0.21	0.05	0.16	6.33	5.99	0.10	0.05	0.24	0.34	2.00	1.64	30.63	3.98	6.89	0.13
	10	0.11	0.04	0.07	4.82	4.40	0.11	0.03	0.31	0.42	2.75	3.80	43.52	2.99	6.63	0.60
	20	0.12	0.03	0.09	4.25	3.98	0.06	0.02	0.21	0.27	2.00	2.24	35.31	2.08	6.55	0.18
	35	0.13	0.05	0.08	4.97	4.17	0.49	0.23	0.31	0.80	9.80	6.15	38.18	2.33	6.46	0.27
	40	0.15	0.12	0.03	5.62	3.46	1.74	0.88	0.42	2.16	14.50	14.17	36.85	3.96	6.16	0.42
15	0		0.02				0.10	0.07	0.29	0.39	5.00			2.43	6.59	
16	0	0.496	0.09	0.41			8.34	0.57	4.91	13.25	92.67	26.71		4.05	6.71	2.21
	6	0.445	0.08	0.37			9.34	0.56	5.06	14.40	116.75	32.36		4.06	6.70	2.50
17	0	0.160	0.05	0.11			0.55	0.19	1.06	1.61	11.00	10.06		3.43	6.63	0.85
	14	0.252	0.11	0.14			0.75	0.31	1.44	2.19	6.82	8.69		4.24	6.22	0.59
18	0	0.134	0.02	0.11			0.06	0.02	0.21	0.27	3.00	2.01		3.66	6.76	0.32
	10	0.104	0.02	0.08			0.05	0.02	0.20	0.25	2.50	2.40		3.11	6.63	0.26
	17	0.215	0.07	0.15			0.11	0.03	0.23	0.34	1.57	1.58		3.08	6.61	0.49
19	0		0.08				0.14	0.03	0.52	0.66	1.75			4.41	7.36	
20	0		0.02				0.08	0.06	0.10	0.18	4.00			3.28	6.61	
21	0	0.876	0.21	0.67			1.94	0.45	4.71	6.65	9.24	7.59		5.17	6.43	1.53
	8	0.723	0.39	0.33			2.83	0.63	5.76	8.59	7.26	11.88		7.66	5.21	1.35
22		0.284	0.06	0.22			0.44	0.20	1.30	1.74	7.33	6.13		3.93	6.67	0.92
		0.307	0.08	0.23			0.47	0.22	1.35	1.82	5.88	5.93		4.14	6.55	0.95
24	0		0.06				0.08	0.02	0.67	0.75	1.33			3.82	7.18	
25	0	0.24	0.07	0.17	7.68	7.17	0.06	0.02	0.45	0.51	0.86	2.12	31.91	4.06	7.39	0.25
26	0	0.28	0.07	0.21	9.07	8.42	0.20	0.09	0.45	0.65	2.86	2.32	32.32	4.12	7.39	0.70
27	0	0.48	0.05	0.43	11.03	9.07	0.86	0.21	1.10	1.96	17.20	4.10	23.10	5.33	7.14	0.99
	3	0.39	0.05	0.34	9.80	7.78	0.80	0.21	1.22	2.02	16.00	5.16	25.05	4.97	7.11	0.84
	5	0.32	0.04	0.28	8.22	6.57	0.60	0.22	1.05	1.65	15.00	5.13	25.57	4.56	7.10	0.83
	10	0.18	0.02	0.16	4.29	3.25	0.19	0.14	0.85	1.04	9.50	5.76	23.77	2.45	6.51	0.11
	15	0.14	0.02	0.12	4.20	3.13	0.17	0.13	0.90	1.07	8.50	7.55	29.63	1.89	6.54	0.07
	20	0.17	0.02	0.15	3.80	2.80	0.16	0.14	0.84	1.00	8.00	5.95	22.63	1.88	6.51	0.08
	25	0.17	0.03	0.14	4.25	3.43	0.16	0.15	0.66	0.82	5.33	4.83	25.02	1.91	6.49	0.11
	30	0.16	0.03	0.13	4.56	3.41	0.22	0.17	0.93	1.15	7.33	7.40	29.35	1.95	6.54	0.14
28	0	0.10	0.02	0.08	4.64	4.23	0.09	0.06	0.32	0.41	4.50	4.18	47.34	2.60	6.62	0.11
	10	0.11	0.02	0.09	5.30	4.89	0.09	0.06	0.32	0.41	4.50	3.73	48.18	1.96	6.55	0.07
	20	0.08	0.02	0.06	4.56	4.04	0.10	0.07	0.42	0.52	5.00	6.87	60.20	1.67	6.53	0.07
	30	0.07	0.02	0.05	4.42	4.03	0.08	0.06	0.31	0.39	4.00	5.29	59.91	1.64	6.53	0.06
	50	0.10	0.03	0.07	4.31	3.56	0.29	0.18	0.46	0.75	9.67	7.88	45.28	2.00	7.55	0.23
29	0		0.02				0.13	0.07	0.68	0.81	6.50			1.76	6.48	
30	0	0.13	0.05	0.08	3.89	3.44	0.08	0.02	0.37	0.45	1.60	3.43	29.69	1.47	5.66	0.03
31	0		0.08				0.61	0.16	1.14	1.75	7.63			3.03	7.52	
32	0	0.28	0.06	0.22	7.31	6.71	0.09	0.03	0.51	0.60	1.50	2.12	25.87	3.77	7.43	0.44
33	0	0.27	0.08	0.19	6.65	5.90	0.19	0.08	0.56	0.75	2.38	2.76	24.46	4.08	7.25	0.36
	10	0.37	0.13	0.24	7.43	6.18	0.49	0.24	0.76	1.25	3.77	3.38	20.07	5.20	6.55	0.31
34	0	0.36	0.07	0.29	8.65	7.70	0.27	0.13	0.68	0.95	3.86	2.66	24.21	3.75	7.50	0.64
	8	0.44	0.16	0.28	9.16	6.27	1.63	0.67	1.26	2.89	10.19	6.59	20.87	7.07	5.61	0.42
35	0	0.20	0.05	0.15	5.27	4.24	0.24	0.13	0.79	1.03	4.80	5.28	26.99	3.45	6.66	0.36
36	0	0.37	0.08	0.29	9.25	7.95	0.59	0.14	0.71	1.30	7.38	3.49	24.81	4.43	7.41	0.60
37	0		0.08				0.49	0.18	0.67	1.16	6.13			4.68	7.16	
38	0	0.83	0.07	0.76	12.15	11.63	0.26	0.13	0.26	0.52	3.71	0.63	14.71	4.69	6.42	0.29

APPENDIX A. CONTINUED

St. no	Dep. (m)	TP (μM)	DIP (μM)	DOP (μM)	TN (μM)	DON (μM)	NO3 (μM)	NO2 (μM)	NH4 (μM)	DIN (μM)	NO3/ PO4	DIN/ TP	TN/ TP	Si (μM)	DO (mg/L)	chl-a (μg/L)
38	10	0.44	0.08	0.36	14.30	13.76	0.34	0.16	0.20	0.54	4.25	1.24	32.82	4.84	6.24	0.22
39	0	0.13	0.04	0.09	4.89	4.38	0.13	0.05	0.38	0.51	3.25	3.99	38.24	3.79	6.67	0.31
	10	0.17	0.05	0.12	4.12	3.60	0.16	0.08	0.36	0.52	3.20	3.04	24.05	4.30	6.58	0.29
	20	0.17	0.13	0.04	4.13	3.39	0.40	0.17	0.34	0.74	3.08	4.35	24.29	3.58	6.17	0.21
	26	0.18	0.09	0.09	4.11	3.52	0.27	0.12	0.32	0.59	3.00	3.25	22.60	3.03	6.31	0.09
40	0	0.11	0.04	0.07	4.28	3.87	0.07	0.03	0.34	0.41	1.75	3.64	38.03	1.76	6.53	0.05
	10	0.10	0.03	0.07	3.83	3.40	0.06	0.03	0.37	0.43	2.00	4.34	38.66	1.75	6.52	0.05
	20	0.07	0.03	0.04	3.83	3.46	0.07	0.03	0.30	0.37	2.33	5.27	54.55	1.82	6.51	0.08
	30	0.09	0.03	0.06	3.19	2.68	0.10	0.03	0.41	0.51	3.33	5.76	36.05	1.83	6.50	0.07
	50	0.08	0.02	0.06	3.03	2.34	0.13	0.05	0.56	0.69	6.50	8.75	38.42	1.28	7.62	0.12
	68	0.09	0.03	0.06	3.08	1.89	0.54	0.15	0.65	1.19	18.00	13.75	35.58	2.34	7.27	0.11
41	0	0.17	0.05	0.12	5.53	4.94	0.27	0.11	0.32	0.59	5.40	3.39	31.78	5.24	6.67	0.12
42	0		0.05				0.22	0.10	0.45	0.67	4.40			5.14	6.66	
43	0	0.23	0.09	0.14	7.00	6.51	0.27	0.11	0.22	0.49	3.00	2.10	29.95	5.09	6.57	0.32
	10	0.20	0.07	0.13	8.06	7.63	0.27	0.11	0.16	0.43	3.86	2.15	40.29	5.09	6.58	0.32
	20	0.19	0.10	0.09	5.13	4.61	0.31	0.16	0.21	0.52	3.10	2.70	26.64	4.87	6.44	0.30
44	0		0.06				0.14	0.03	0.29	0.43	2.33			2.44	6.60	
45	0		0.05				0.11	0.03	0.23	0.34	2.20			1.78	6.57	
46	0	0.15	0.04	0.11	4.13	3.80	0.16	0.02	0.17	0.33	4.00	2.14	26.84	1.35	6.52	0.04
	10	0.16	0.04	0.12	3.70	3.50	0.12	0.03	0.08	0.20	3.00	1.22	22.50	1.32	6.52	0.06
	20	0.15	0.04	0.11	3.93	3.69	0.09	0.04	0.15	0.24	2.25	1.57	25.70	1.34	6.54	0.03
	30	0.12	0.04	0.08	3.58	3.41	0.08	0.03	0.09	0.17	2.00	1.39	29.31	1.28	6.54	0.05
	50	0.11	0.05	0.06	3.68	3.31	0.08	0.03	0.29	0.37	1.60	3.40	33.86	0.90	7.91	0.03
	80	0.12	0.05	0.07	3.45	2.53	0.76	0.17	0.16	0.92	15.20	7.91	29.64	1.67	7.20	0.08
	100	0.11	0.04	0.07	3.23	2.46	0.68	0.07	0.09	0.77	17.00	6.90	28.95	1.29	7.12	0.05
	125	0.19	0.07	0.12	6.22	4.41	1.65	0.10	0.16	1.81	23.57	9.36	32.16	2.23	6.75	0.03
47	0	0.11	0.04	0.07	3.14	2.94	0.06	0.02	0.14	0.20	1.50	1.84	28.91	1.61	6.50	0.04
	10	0.12	0.04	0.08	3.21	3.04	0.07	0.02	0.10	0.17	1.75	1.44	27.12	1.62	6.51	0.03
	20	0.13	0.04	0.09	2.93	2.70	0.09	0.03	0.14	0.23	2.25	1.78	22.69	1.63	6.55	0.03
	30	0.11	0.03	0.08	3.77	3.54	0.08	0.02	0.15	0.23	2.67	2.09	34.24	1.61	6.54	0.04
	50	0.12	0.03	0.09			0.09	0.03	0.17	0.26	3.00	2.17		0.94	7.86	0.02
	80	0.20	0.06	0.14	3.84	2.67	1.02	0.34	0.15	1.17	17.00	5.77	18.93	1.98	7.06	0.05
48	0	0.13	0.03	0.10	3.72	3.46	0.09	0.02	0.17	0.26	3.00	2.08	29.72	1.08	6.57	0.04
	5	0.09	0.03	0.06	3.47	3.13	0.07	0.04	0.27	0.34	2.33	3.61	36.78	1.08	6.54	0.03
	10	0.09	0.03	0.06	3.60	3.36	0.08	0.03	0.16	0.24	2.67	2.57	38.59	1.07	6.54	0.06
	20	0.15	0.03	0.12	3.48	3.17	0.07	0.03	0.24	0.31	2.33	2.13	23.93	1.05	6.54	0.03
	30	0.14	0.03	0.11	2.90	2.72	0.06	0.03	0.12	0.18	2.00	1.26	20.24	0.94	6.94	0.05
	50	0.06	0.02	0.04	3.03	2.56	0.07	0.05	0.40	0.47	3.50	7.64	49.14	0.92	7.84	0.05
	75	0.07	0.03	0.04	3.54	2.76	0.52	0.18	0.26	0.78	17.33	10.81	49.10	1.46	7.30	0.16
	100	0.10	0.02	0.08	2.93	2.38	0.39	0.14	0.16	0.55	19.50	5.78	30.81	0.94	7.22	0.05
	150	0.10	0.03	0.07	3.08	1.88	1.09	0.07	0.11	1.20	36.33	11.45	29.41	1.21	7.01	0.02
	200	0.11	0.03	0.08	3.67	1.42	2.06	0.07	0.19	2.25	68.67	19.66	32.03	1.81	6.89	0.00
49	0		0.05				0.07	0.03	0.08	0.15	1.40			1.80	6.58	
50	0		0.05				0.10	0.02	0.17	0.27	2.00			1.37	6.56	

APPENDIX B. CONCENTRATIONS USED IN SURFACE DISTRIBUTION PLOTS OF NUTRIENTS

Cruise	**St.**	**Dep.**	**DIP**	**NO3**	**NH4**	**DIN**
date	**no.**	**m**	**µM**	**µM**	**µM**	**µM**
Sep. 08	11	0			4.00	4.00
	16	0		1.00		4.00
	23	0		1.00		
Jan. 09	6	0		6.00		11.19
	21	0	0.25	6.00	7.00	13.00
	23	0			7.00	13.00
Mar. 09	11	0	0.15		4.00	8.85
Apr. 09	23	0	0.20			
Aug. 09	27	0		0.90		
	31	0		1.00		
Oct. 09	6	0		1.00		2.45
	11	0		1.00		2.35
	12	0		1.00	2.00	3.00
	16	0		1.00	2.00	3.00
	21	0		1.00	2.00	3.00

APPENDIX C. CORRECTION FACTORS USED FOR TOTAL NITROGEN MEASUREMENTS

Cruise date	data set	Blank (µM)	Correction factor
Sep. 08	1	0.86	0.8
	2	0.92	0.8
Jan. 09	1	0.95	0.9
	2	0.95	0.8
Feb. 09	1	0.93	0.9
	2	0.94	0.9
Mar. 09	1	0.84	0.8
	2	0.90	0.8
Apr. 09	1	0.88	0.8
	2	0.95	0.8
Oct. 09	1	0.85	0.8
	2	0.90	0.8