ASSESSMENT OF THE TROPHIC STATUS OF THE MERSIN BAY WATERS, NORTHEASTERN MEDITERRANEAN

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ASSESSMENT OF THE TROPHIC STATUS OF THE MERSIN BAY WATERS, NORTHEASTERN MEDITERRANEAN

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ABSTRACT

ASSESSMENT OF THE TROPHIC STATUS OF THE MERSIN BAY WATERS, NORTHEASTERN MEDITERRANEAN

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Identifying the spatial and temporal variability of eutrophication related indicators such as Chlorophyll-*a* (Chl-*a*), oxygen saturation (DO%), dissolved inorganic nitrogen (DIN) and total phosphorus (TP), as a measure of the potential pressures and productivity, were measured within the Mersin Bay, a wide shelf region of the Cilician Basin located in the Northeastern Mediterranean Sea. This study aims to characterize the trophic status of the water masses in the eastern shelf waters of the bay fed by river discharges, through applying cluster analysis, TRIX (using DIN, TP, DO%, Chl-*a*) and UNTRIX index approaches, based on data collected seasonally in the eastern bay waters between September 2008 and February 2011.

Macro-nutrient (DIN, TP, Si) and Chl-*a* concentrations were found to be 10-fold high in the polluted shallow nearshore waters (<20 m in depth) compared to the offshore (>50 m) surface values. Cluster analysis of all the data highlighted the presence of three different trophic (eutrophic, mesotrophic and oligotrophic) region characteristics. The nearshore zone was assigned as “Eutrophic” whilst the offshore waters displayed “Oligotrophic” properties. Comparison of the TRIX, TRIX-IMS (modified TRIX with site-specific ‘a’ and ‘b’ coefficients) and UNTRIX classification approaches revealed that the original TRIX index was not efficient enough to demonstrate impacts of excessive nutrient loads on the oligotrophic waters whereas the TRIX-IMS and UNTRIX approaches categorized the inner bay water body to have “eutrophic” status compared to the “oligotrophic” waters of the outer bay.

Keywords: Eutrophication, TRIX, Trophic status, Eastern Mediterranean, Mersin Bay

ÖZ

KUZEYDOĞU AKDENİZ, MERSİN KÖRFEZ SULARININ TROFİK DURUMUNUN DEĞERLENDİRİLMESİ

Kaptan, Mehmet Salih
Yüksek Lisans, Kimyasal Oşinografi Bölümü
Tez Danışmanı: Prof. Dr. Süleyman Tuğrul

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Potansiyel baskı ve üretimin bir ölçüsü olarak Klorofil-*a* (Chl-*a*), çözünmüş oksijen doygunluğu (DO%), çözünmüş inorganik azot (DIN) ve toplam fosfor (TP) gibi ötrofikasyonla ilgili indikatörlerin bölgesel ve dönemsel değişimlerinin belirlenmesi için Kuzeydoğu Akdeniz Kilikya Baseninde bulunan Mersin Körfezi'nde ölçümler yapılmıştır. Bu çalışma Eylül 2008 ve Şubat 2011 arasında kalan dönemde mevsimsel olarak toplanan verilere kümeleme analizi, TRIX (DIN, TP, DO% ve Chl-*a* kullanılarak) ve UNTRIX indeks yaklaşımlarının uygulanmasıyla, nehir sularıyla beslenen Mersin Körfezi'nin doğu kıyı sularındaki su kütlelerinin trofik durumunu karakterize etmeyi amaçlar.

Makro besin tuzu (DIN, TP, Si) ve Chl-*a* konsantrasyonlarının, körfezin kirli sığ kıyı sularında (<20 m derinlik) açık yüzey sularına (>50 m) kıyasla 10 kat yüksek olduğu saptanmıştır. Tüm verilere uygulanan kümeleme analizi üç farklı trofik bölge (ötrofik, mesotrofik ve oligotrofik) özelliğinin varlığını ortaya çıkarmıştır. Sığ kıyısal bölge, "Ötrofik" olarak belirlenirken; açık bölge suları "Oligotrofik" özellik göstermiştir. TRIX, TRIX-IMS (bölgeye özel 'a' ve 'b' katsayıları ile modifiye edilmiş TRIX) ve UNTRIX sınıflandırmalarının karşılaştırması, orjinal TRIX indeksinin, oligotrofik sulara ulaşan besin tuzları fazlasının ötrofik etkisini göstermekte yeterince etkili olmadığını gösterirken; TRIX-IMS ve UNTRIX yaklaşımları iç körfezde yer alan su kütlesini, dış körfezde bulunan "oligotrofik" su kütlesine kıyasla "ötrofik" olarak kategorize etmiştir.

Anahtar Kelimeler: Ötrofikasyon, TRIX, Trofik durum, Doğu Akdeniz, Mersin Körfezi

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To My Family,

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INTRODUCTION

1.1 Aim of the Study

The salty Mediterranean sea is a unique example of the semi-enclosed basin, with a narrow connection to the Atlantic Ocean through the Strait of Gibraltar (Figure 1.1), the man-made connection to the Red Sea via the Suez Canal and the narrow Bosphorus Strait connecting it to the smaller enclosed Black Sea (Turley, 1999). The Eastern Mediterranean Sea is one of the most extreme oligotrophic seas in the world (Figure 1.1). Warm surface Atlantic water, already stripped of much of its nutrients by phytoplankton growth in the surface of the Atlantic flow through the narrow strait of Gibraltar and returns some 80-100 years later, having circulated the Mediterranean Basin in an anticlockwise direction. During its passage eastward, its nutrients are decreased even more by phytoplankton (Krom *et al*., 1991; Turley, 1999).

The Mediterranean Sea is characterized as Low Nutrient and Low Chlorophyll (LNLC). The average annual productivity in the Mediterranean Sea is half of the amount observed in the ultra-oligotrophic Sargasso Sea (Krom *et al*., 2004; Pitta *et al*., 2005). The eastern SeaWIFS satellite image (Figure 1.1) exhibits the clear low productivity of the Mediterranean Sea compared to the North Atlantic and Black Sea. Despite the low productivity in the Mediterranean Sea, a noticeable west to east gradient, with increasing oligotrophy from west to east can be seen clearly from the image (Turley, 1999).

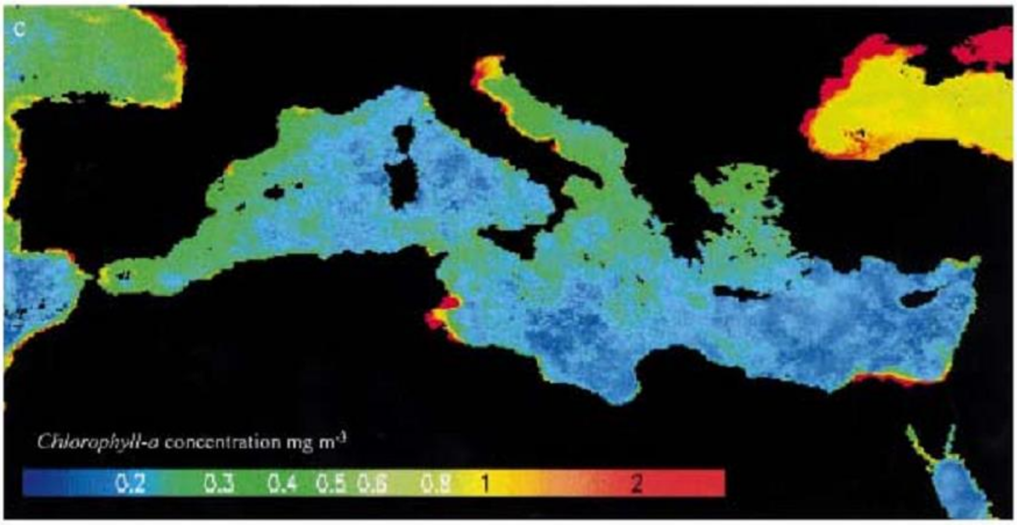

Figure 1.1. The Ocean color Sea-viewing Wide Field of View Sensor (SeaWiFS) image, estimates of phytoplankton concentration monthly composite during September 1997 (taken from Turley, 1999)

The Cilician Basin occupies the northeastern part of the eastern Mediterranean Levantine Basin between Cyprus and Turkey. This maritime ecosystem includes the wide continental shelf of the Bays of Mersin and İskenderun, adjoined by the wide Çukurova plain on land. The Cilician Basin joins to the Gulf of Antalya in the west, and the Lattakia Basin in the southeast. Smaller bays such as the Bays of Aydıncık, Akkuyu, Ovacık and Taşucu are lied along the narrower shelf part of the northern coast south of the Taurus mountain range.

The Cilician Basin coastal system embodies important natural resources of strategic importance, yet is presently experiencing rapid industrial growth and an explosive increase in population. Population expansion at the coast, increased industry, agriculture and tourism create significant environmental stresses on the coastal ecosystem. Present industrial activities cover chemical plants including steel, fertilizer, soda, glass, paper, textile, mechanical and energy production. Untreated or primary-treated municipal wastes from major towns of Mersin, Adana, Iskenderun and Antakya via Asi river are potential sources of marine pollution. Civilian and military marine transport linked to the harbours of Mersin, İskenderun and Taşucu, shipbuilding activities, oil storage and pipeline terminals at Yumurtalık and Ceyhan. Moreover, the major rivers of the region (Seyhan, Ceyhan, Berdan, Göksu and Lamas) display a crucial role in fertility of the wide shelf waters of Cilician basin (Kocak *et al.*, 2010).

Although the coastal upwelling systems constitute about 1% of the ocean surface they contribute almost half of the world's fisheries. This is the result of both high rates of new production and a short food chain in which much of the phytoplankton production is eaten by fish (Lavelle *et al.*, 2005 and references therein). Both natural and anthropogenic environmental changes are responsible for creating stresses on this sensitive marine ecosystem. Therefore, it is essential to assess the impact of such influence on marine environments in the Mediterranean considering trophic status. Supply of excess amount of nutrients into the surface waters of such fragile marine ecosystems may cause detrimental effect particularly on coastal areas receiving enormous amount of nutrients via man-made sources. Schematic illustration of excess amount of nutrient inputs to the marine ecosystems and its detrimental impacts are illustrated in Figure 1.2. As can be deduced from the diagram, such undesirable inputs may cause high concentrations of nutrients, uncommon algal blooms, and turbid waters, atypical distribution and occurrence of plants and animals and finally abnormal oxygen levels.

The present study aims to identify the spatial and temporal variability of eutrophication related indicators (Chl-*a*; as a proxy for phytoplankton biomass, O_2% (aD%O: Oxygen as absolute % deviation from saturation); as a measure of productivity or as a biotic component, dissolved inorganic nitrogen (DIN) and total phosphorus (TP); as a measure of the potential biomass or pressure factors) that influence trophic level in the

Cilician Basin of the Eastern Mediterranean. In addition, this study aims to define, for the first time the tropic status of the Mersin Bay on the Cilician Basin by applying the trophic index (TRIX), unscaled trophic index (UNTRIX), and Univariate statistical method and compare their drawbacks and affirmative peculiarities for each technique. Moreover, this work aims at calculating region-specific coefficients of the TRIX formula, which are crucial during the assessment of trophic status via the TRIX index approach suggested by Vollenweider et al. (1998). Data sets obtained in the eastern shelf waters of Mersin Bay were used to define the upper limits of concentrations for the "reference water body" in order to assess tropic status of the shallow water body of the bay having different biochemical properties.

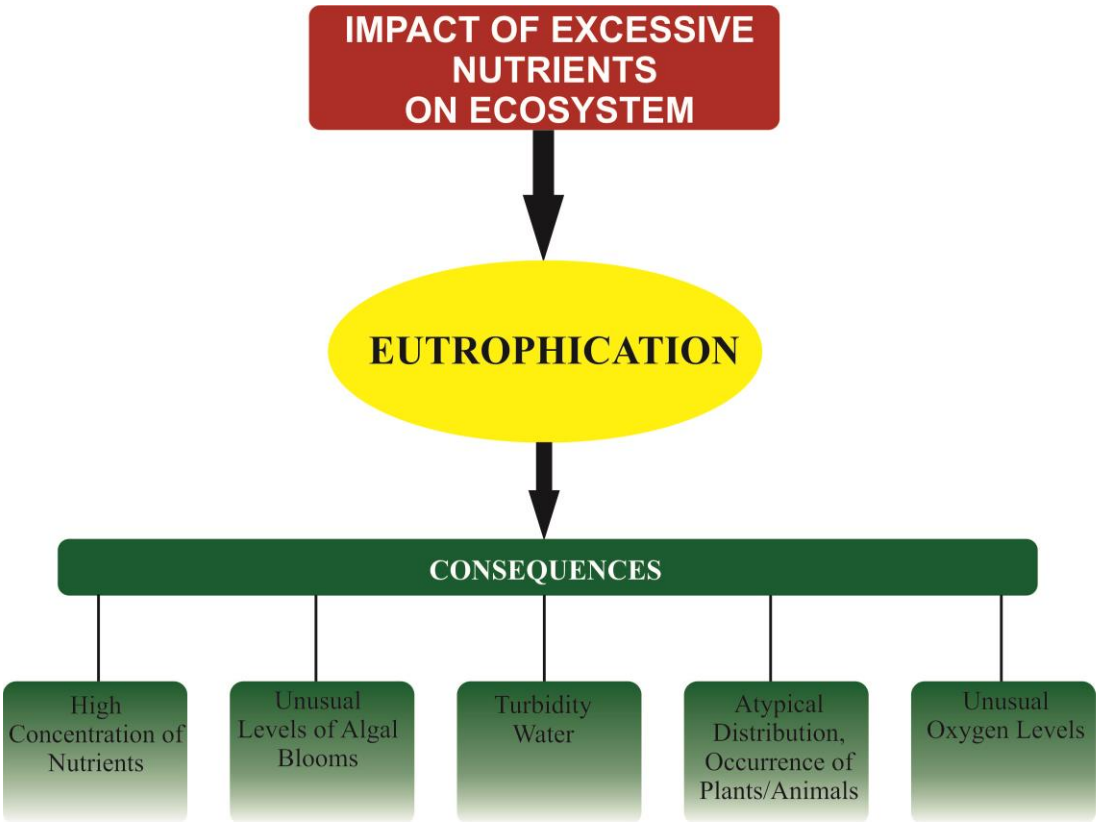

Figure 1.2. Schematic illustration of excess amount of nutrient inputs to the marine ecosystems and its detrimental impacts

1.2. General Characteristics of the Mediterranean Sea

The Mediterranean Sea is a semi-enclosed sea surrounded by three continents namely Europe to the north, Africa to the south and Asia to the east (see Figure 1.3). It is located half way between the temperate and subtropical zones. The Mediterranean Sea is connected to the Atlantic, the main entrance of the basin, through the Gibraltar Strait, to the

Red Sea through the man-made Suez Canal (1889) and to the Black Sea through the Turkish Straits Systems (Tuğrul *et al.*, 2002)

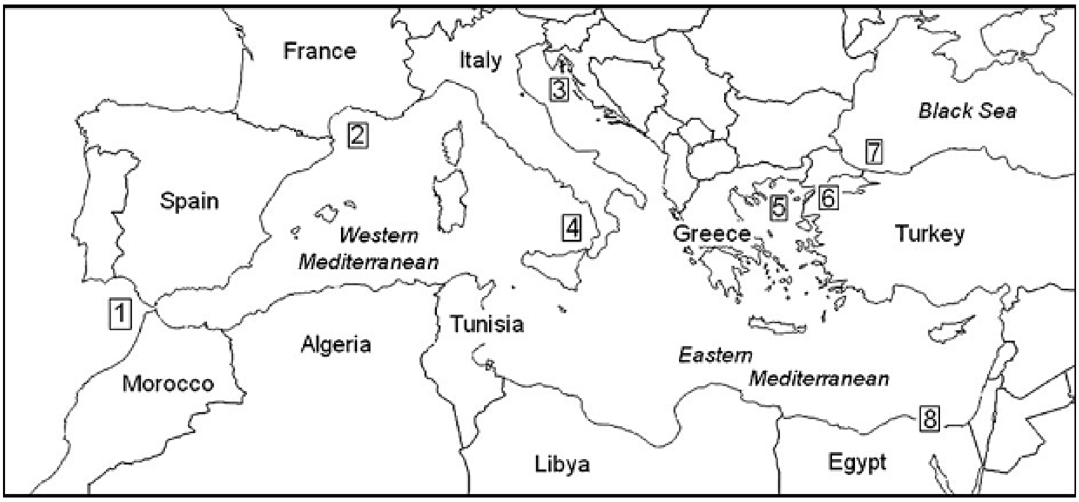

Figure 1.3. Morphological characteristics of the Mediterranean Sea: 1.Strait of Gibraltar, 2.Gulf of Lions, 3.Adriatic Sea, 4.Thyrrenian Sea, 5.Northern Aegean, 6.Straits of Dardanelles, 7.Straits of Bosporus, 8. Nile estuarine area (taken from Karydis and Kitsiou, 2012)

The Mediterranean Sea covers a surface area of about 2.5 x 10^6 km^2, nearly 1% of the world ocean and an average depth of 1,500 m. The basin is about 3800 km wide from west to east, whereas the distance from north to south changes with region. The widest part exists between France and Algeria about 900 km (EEA, 1999). The total length of the coastline is 46,000 km, however 40% of that is the length of islands' coastline (19,000km). 150 km wide narrow opening between Tunisia and Sicily divides the Mediterranean basin into two major sub-basins (east and west basins) (EEA, 1999). Each of those two sub-basins has different algal and animal communities, representing their characteristics. The Adriatic Sea and the Aegean Sea are semi enclosed extensions of the Eastern Mediterranean.

1.3. Hydrography and Circulation of the Mediterranean Sea

The general circulation of the Mediterranean Sea has been categorized into three major components; a) the large scale vertical circulation or thermohaline circulation, b) the sub-basin scale together with the Gibraltar-Atlantic water current system and c) the mesoscales (Pinardi *et al.,* 2005 and references therein). As stated by Pinardi et al. (2005) water loss is much higher than the water gains from precipitation and runoff in the Mediterranean. Furthermore, it has the negative net heat budget, therefore the vertical thermohaline circulation in the region is negative and anti-estuarine, with waters entering from the Atlantic at the surface and exiting the Mediterranean at depths (Pinardi *et al.*, 2005 and references therein). Based on Pinardi et al. (2005 and references therein) and Bergamasco and Malanotte-Rizolli (2010 and references therein), aforementioned circulations can be summarized as follow:

a) The large scale vertical circulation or thermohaline circulation: It is distinguished by multi-decadal time scales and water mass transformation processes that take place in the open ocean areas of the Northern Mediterranean (Pinardi *et al.*, 2005). Both intermediate deep and deep waters occur in the regions offshore the Gulf of Lions, the southern Adriatic and the northern Levantine. These occurrences are not only enforced by intense heat losses during the winter (February-March) but also affected by the presence of large scale cyclonic circulation driven by wind stress curl. Another source of deep waters for the Ionian Sea abyssal plains is Aegean Sea (Pinardi *et al.*, 2005). That event has occurred at the end of the eighties and the first half of nineties, however; it has propelled that the Aegean Sea has stopped the production of the deep waters (Pinardi *et al.*, 2005 and references therein).

b) The sub-basin scale together with the Gibraltar-Atlantic water current system: This circulation consists of several time scales and steady state components. The steady state ones include cyclonic and anticyclonic permanent gyres. These gyres are thermal fluxes and wind driven, superposed to and interacting with the Gibraltar inflow system. The large wind stress variability and inter annual variability cause seasonally varying amplitudes. The sub-basin scale cyclonic gyres imply that the upwelling motion prevails at their centers whereas the contrary occurs at their borders. It means that for permanent cyclonic gyre that has an impact on the continental slope and occasionally on the shelf, there is a downwelling tendency on the shelf. The theoretical studies of the wind driven circulation without Gibraltar inflow show that the time mean anticyclonic gyres of the circulation are remarkably varied by interaction with the Gibraltar-Atlantic flow system. It means that anticyclonic motion is limited to a narrow band encompassing the continental slope and shelves of the south-eastern Mediterranean or present in extended areas of the Algerian basin, the Sicily Strait and the southern Ionian Sea. These extended anticyclonic areas are generally occupied by non-permanent anticyclonic gyre structures or mesoscales. Thus the time mean circulation cause a weak down welling area. The Gibraltar forced flow field is composed of 3 main sub-basin current systems, especially the Algerian current in the western Mediterranean, the Atlantic-Ionian Stream in the Ionian Sea and the Mid-Mediterranean jet in the Levantine basin. In the eastern Mediterranean, on the right part of the Gibraltar-Atlantic Current system looking down-stream, in other words it follows the eastward direction, the general motion is anticyclonic: the anticyclonic Algerian current eddies, the Mersa-Matruh and Shikmona gyres. The presence of sub-basin scale structures, varying at inter-annual time scales, increases the anticyclonic tendency in the southern Mediterranean with regards to the steady state mean (Pinardi *et al.*, 2005 and references therein).

c) The mesoscales: The last group, the mesoscales, has been known with short time scale according to the thermohaline circulation and the subbasin scale. However it has large current amplitude and pervasive eddies in the basin. In the past, the mesoscales have been examined in several sub-regions (Pinardi *et al*., 2005 and references therein).

As it is depicted in Figure 1.4, the inflow of Atlantic surface water derives in a nearby region to the Gibraltar, the Alboran Sea. The Atlantic origin water drives the Gibraltar-Atlantic Current System/Atlantic Stream System (ASS) from the Alboran Sea to the North Levantine Sea. This current system forms the Atlantic-Ionian Stream (AIS) at the Strait of Sicily during its transport to the Levantine basin. While it travels across the second major basin, Eastern Mediterranean (EM), it occurs the Mid-Mediterranean Jet (MMJ), the main current in the EM. This eastward-flowing jet follows the path between the Rhodes gyre on the north and the Mersa-Matruh and the Shikmona gyres on the south. A branch of the MMJ combines with the Southern Levantine current to form the Asia Minor Current (AMC), westward-flowing current along the Turkish coast (POEM Group, 1992; Demirov and Pinardi, 2002; Pinardi *et al.*, 2005)

Figure 1.4. Schematic of the surface circulation from recent observational data and model simulations. Names of structures and currents are listed (taken from Pinardi *et al.*, 2005)

On the other hand, mean currents appear to have a relatively simple pattern, the actual time-dependent currents in any part of the eastern Mediterranean are far more complex, especially on the coastal regions. The shallow and wide shelf region adjacent to the Gulf of Iskenderun implies local characteristics of currents, and mixing and exchange mechanisms of the Gulf waters, which impact its biochemical structure and variability. The classical picture of surface circulation in the Gulf compiled from Collins and Banner (1979) based on ERTS imagery and Secchi Disc Depth (SDD) measurements and unpublished observations of IMS-METU in the region are schematized in Figure 1.5.

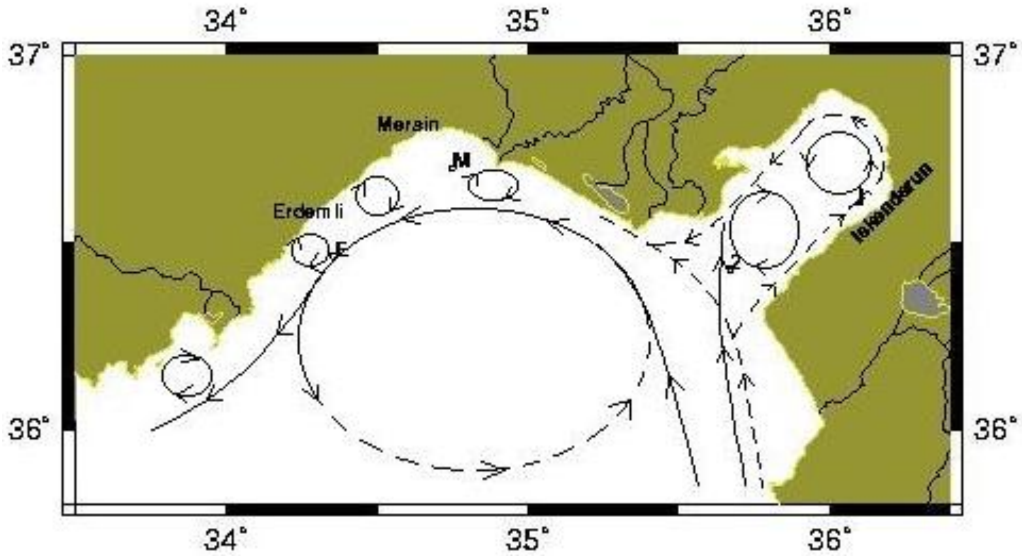

Figure 1.5. Schematic circulation in the Mersin and Iskenderun Bays (taken from Collins and Banner, 1979)

The general circulation of the EM is composed of dynamically interacting sub-basin scale eddies; the permanent cyclonic Rhodes gyre, with two eddy centers located at the deep basin south of Rhodes and the third one at the west of Cyprus; the anticyclonic Mersa-Matruh gyre, placed to the south of Rhodes gyre; and the anticyclonic Shikmona gyre, with three different centers and placed at the south of the Levantine basin (Özsoy *et al.*, 1991).

According to the salinity profiles, the water column of the Levantine Basin is separated four main water masses (Özsoy *et al.*, 1991). The surface water, called Levantine surface water (LSW), is identified with saline (>38.95) water, located between 0-40 m. Sank Atlantic water (AW) placed below LSW with the salinity ≤38.87. Levantine intermediate water (LIW) is existed with salinity about ≥38.94 and found between 200-310 m under the AW. Eastern Mediterranean deep water (EMDW) found at the bottom layer with the salinity of <38.74 below 700 m. According to the seasonal and regional conditions, these water masses can be found in different depths (Kress and Herut, 2001).

Atlantic water entering the Mediterranean Sea, Modified Atlantic Water (MAW), passes through the Sicily Channel into the EM. For the entire water column, it is characterized the water mass with a minimum salinity. When it moves eastwards the depth range increases until 200 m.

The formation mechanism and region of the LIW are not known exactly. Before 1992, according to the general aspects it was formed in a small region between Rhodes, Cyprus and South coast of Asia Minor, but now it is known that it forms over larger area, where the processes that include the gyres, such as Rhodes gyres, in place of limited regions (POEM Group, 1992). During the winter, vertical mixing and high evaporation rate of the Mediterranean causes cooling and salinity increase in surface waters, afterwards these water masses sinks (Özsoy *et al.*, 1993; Souvermozgolou and Krasakopolou, 1999) and reaches intermediate depths below the surface water in late winter and early spring period (Özsoy *et al.*, 1989). The LIW is existed and dispersed convectively to depths of a few hundred meters. Entire Mediterranean, especially the southern part of the Aegean Sea (Theocharis *et al.*, 1993), and the Atlantic Ocean has been affected by LIW as well as the Levantine basin.

The EM deep water, originated from the surface water of the Adriatic Sea, leaves the Adriatic as a bottom current through the Otronto Channel and flows along the western boundary of the Ionian Sea (POEM Group, 1992). 1500 km^3 of the surface water is transformed to deep water, below the 1,200 m depth, yearly in the Adriatic (EEA, 1999). Winter cooling in the Northern Adriatic causes high surface heat loss which results in the water sinking through the Southern Adriatic. That sinking water mass flow into Levantine basin.

1.4. Hydrochemistry of the Eastern Mediterranean

In the last few decades, various studies have been conducted to determine the hydrophysical and hydrochemical features in the Eastern Mediterranean. Especially the spatial and seasonal features have significance on both surface and vertical distributions of nutrients. In offshore areas of the EM has a very low nutrient concentration in the upper 100 m because of the limited terrestrial inputs. Under that layer (euphotic zone) nutrient concentrations rise with increasing depth until reaching deep waters where the concentrations get constant values.

Both in the Eastern and the Western Mediterranean nutrient concentrations in water column show seasonal variations as a result of two seasonal phenomena; stratification and winter mixing. From spring to autumn, stratification season, net input of particulate nutrient with unstable concentration has been observed from surface layer to nutrient-poor LIW.

Moreover, a slight increase in concentration of dissolved inorganic nutrient is expected to see in LIW (Yılmaz and Tuğrul, 1998).

In the EM, in winter, nutrient rich LDW mix with nutrient poor surface water in the cyclonic region. This mixing process makes nutrient concentration be available for primary production in the euphotic zone. However, in the anticyclonic regions, nutrient flux is very limited in winter time. In the same period, the nutricline can rise until the base of the euphotic zone and even reach to the surface in the core of the cyclone (Yılmaz and Tuğrul, 1998; Ediger *et al.*, 2005)

Dissolved oxygen and salinity show similar vertical distribution pattern in the EM. Dissolved oxygen concentrations vary between 250 and 300 μM levels with almost 100% saturation in the first 100 m depth however below the euphotic zone it tends to decrease until reaching constant deep water concentration (180-200 μM). While in cyclonic regions euphotic layer is about 75-85 m thick, its boundary can be reached at 110-120 m in anticyclonic regions. According to depth and location, dissolved oxygen concentrations similar to density profiles show variations in deep water which imply the rapid horizontal movement of deep water without creating any significant regional references (Oğuz and Tuğrul, 1998; Yılmaz and Tuğrul, 1998; Ediger *et al.*, 2005).

1.4.1. Distribution of TP and TN in the Eastern Mediterranean (EM)

Total nitrogen and phosphorus were mostly ignored in previous studies because of their high effort requirements. In the 60's, early basin scale TP observations in the EM were carried out during the cruise of RV Atlantis and RV Chain (Miller *et al.*, 1970). Even though being region limited around the Rhodes gyre and Antalya Bay, they gave basic information about TP distribution in the EM.

Although the EM is known with its highly oligotrophic character, primary production rate in coastal water increases with land-based nutrient fluxes. However their effect is limited in the offshore zone of the NE Mediterranean (Eker-Develi, 2004; Ediger *et al.*, 2005; Eker-Develi, 2006; Doğan-Sağlamtimur, 2007). Similar to other nutrients, high TP concentrations are observed in coastal waters. Land-based sources, *i.e.* rivers and domestic discharges, increase TP concentrations to the level of 1.5-2.0 μM in coastal areas (Doğan-Sağlamtimur, 2007).

In surface water, TP concentrations tend to be higher than PO_4^{3-} concentration due to uptake by photosynthesis and accumulation in organic-P pool. While PO_4^{3-} content is depleted in the euphotic zone with the mean value of 0.02-0.03 μM, average TP concentrations are around 0.10-0.15 μM in open waters. Below the euphotic layer, TP concentrations rise with increasing depth until reaching the constant values of deep water (0.30-0.40 μM).

TN distribution is still questionary at regional scales in the EM because of the limited information in literature. Uncertainties in DON distributions are one of the reason of uncertainties in the TN pool in the EM. Nevertheless, the contribution of the land-based sources increase the dissolved inorganic nitrogen (DIN) concentrations, especially in the coastal zone of agricultural areas where ammonium concentrations may reach 4-5 μM levels. Thus, it has been expected to observe high TN concentrations in the coastal regions due to large contribution of organic and inorganic nitrogen compounds to the TN pool in the productive regions (Sert, 2010).

1.4.2. Distribution of Inorganic Nutrients in the Eastern Mediterranean (EM)

Hydrographically, Levantine basin of the EM, may separated into three different sub-basins; Rhodes cyclonic basin, Cilician anticyclonic basin and transitional areas (Özsoy *et al.,* 1991; Yılmaz and Tuğrul, 1998; Ediger *et al.,*2005). Various hydrophysical, spatial and seasonal features of these regions play an important role on nutrient concentrations in the water column. In cyclonic region, Rhodes cyclonic gyre, the nutricline represents a sharp incline under the euphotic zone. However, in severe winter conditions with strong vertical mixing it disappears. Under the euphotic layer inorganic nutrient concentrations are almost constant. In anticyclonic region, Cilician region, Levantine Deep Water (LDW) reaches at greater depths and nutricline, according to the location, occurs between 300-500 m depth (Yılmaz and Tuğrul, 1998).

Phosphate and nitrate concentrations are relatively low in the surface water of the EM. The average surface concentrations, except the coastal regions, are about 0.02-0.03 μM for phosphate and 0.1-0.3 μM for nitrate (Yılmaz and Tuğrul, 1998) for most of the year. In the Rhodes cyclonic gyre, nutrient concentrations are depleted during spring-autumn period in the euphotic layer (about 75-85 m). On the other hand, in winter season, nutrient concentrations in the EZ increase due to the upwelling of the LDW (Ediger *et al.,* 2005). Therefore, the concentrations rise to the levels of 0.2-0.3 μM for phosphate and 4-6 μM for nitrate, similar to the LDW content remaining almost constant with depth.

According to Yılmaz and Tuğrul (1998), the N/P molar ratios in the water column show significant variations with depth in the EM. It has been estimated to be as low as 5-20 in the surface water, with the assumption that PO_4^{3-} concentrations below the detection level (< 0.02 μM). In severe winters, the ratio is high (as 25-29) when the input from lower layers enriched the surface waters with high nutrient values (NO_3^-=4-6 μM; PO_4^{3-}=0.1-0.2 μM).

Below the euphotic zone, the N/P ratio exhibited atypical high values (40-120) at the top of the nutricline due to the shift between the onsets of the nitracline and phosphocline.

1.5. Human Pressures and Eutrophication

The EM is known with its oligotrophic properties. However, its NE coastal zones are influenced by the human activities, namely river discharges, agricultural runoff, urban sewage fall, industrial activity, fisheries and aquaculture, maritime traffic, urbanization and tourism (Saliot, 2005).

The population on the Mediterranean coastal zone has increased during the last 50 years. The estimated population was about 250 million in 1960 and then increased markedly to about 450 million in the late 1990. The population is expected to reach 570 million by 2025 around the Mediterranean coasts (Karydis and Kitsiou, 2012). The Mediterranean region is one of the most attractive tourist destinations of the world. According to the Blue plan in the Mediterranean, the number of tourists will raise from 135 million in 1990 to 235-353 million people in the year of 2025. The coastal tourism is heavily seasonal, reaching the peak points in summer months. There is a significant relationship between tourism and environment of degradation, such as land use, consumption of water resources, pollution and waste (Saliot, 2005).

Discharges via Rivers: The regional rivers play an important role in support the marine productivity in the Mediterranean Sea (Ludwig *et al.*, 2009). The high productivity is mainly observed in coastal waters influencing by fresh water inputs or discharges as demonstrated in Figure 1.6. The NE Cilician coastal waters are highly impacted by river discharges (Seyhan, Ceyhan, Göksu and Berdan). According to recent study in the region (Koçak *et al.,* 2010), the annual means of water discharge by Seyhan, Ceyhan, Göksu and Berdan rivers were found to be 168, 144, 45 and 6 m^3s^{-1}, respectively. Moreover, the authors have demonstrated that the discharges of these rivers show similar seasonality with highest chemical load during winter-spring period.

Agricultural Runoff: Agricultural applications of fertilizers constitute a non-point source of pollution. In addition to pesticides, heavy metals and pathogens, the runoff waters remove nutrients to finally the sea. It enriches nitrogen and phosphorus content of coastal system. Mediterranean agriculture is mostly intensive since about 1960 and the use of fertilizer has increased (Karydis and Kitsiou, 2012).

Urban Sewage Outfalls: Uncontrolled discharges into the sea cause deterioration of the quality of marine ecosystems, especially benthic communities, because of the releasing nutrients, organic and inorganic pollutants; toxic impacts on flora and fauna; and dispersion of pathogenic bacteria generating risks on human health. During rainy weather, direct discharges of urban storm water in the case of separate systems and the overflow from combined systems form urban waste waters (Saliot, 2005).

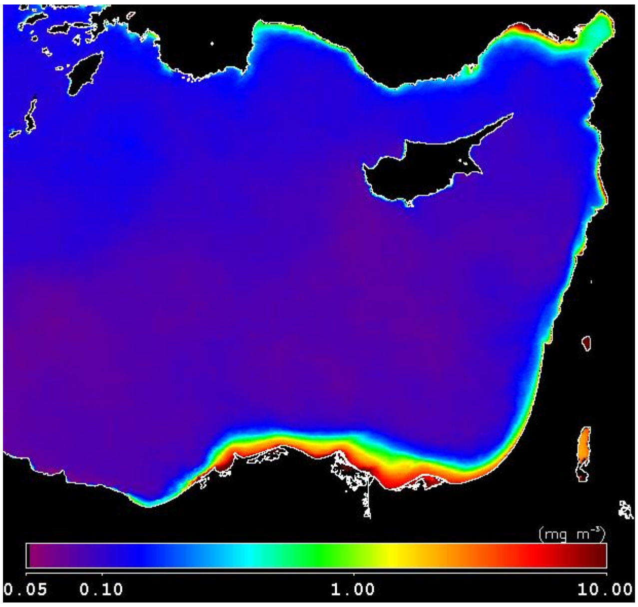

Figure 1.6. Annual average surface chlorophyll distribution in the Northern Levantine basin based on the MODIS satellite data for the year 2009 (courtesy of Hasan Örek)

Table 1.1. Annual averages of nutrient concentrations (µM) and discharges (m^3s^{-1}) for Seyhan, Ceyhan, Göksu, Berdan and Lamas rivers feeding the NE Mediterranean coast (taken from Koçak *et al.,* 2010)

River	Si_{diss}	PO_4^{3-}	NH_4^+	NO_3^-	Q
Seyhan	117	5.6	16	83	168
Ceyhan	161	1.9	19	105	144
Göksu	112	3.3	7	58	45
Berdan	91	4.8	34	85	6
Lamas	113	0.4	1	101	3

Industrial Activity: The heavy metal cycle of the Mediterranean is mostly influenced by mercury, zinc, lead and copper deposits from the Iberian Peninsula and copper deposits from Cyprus. Moreover, several oil and gas field has existed in Algeria, Egypt, Libya, Syria and Italy and also several refineries have been established all around the Mediterranean (Saliot, 2005).

Fisheries and aquacultures: Most of the fishery resources of the Mediterranean, *i.e.* demersal, small pelagic or large highly migratory species, are over-exploited. Aquaculture has an important impact on coastal benthic ecosystems. Several estimates of the loads of nutrients and organic carbon entering the marine environment have been made in intensive aquaculture. Phosphorus and nitrogen loads from semi-intensive aquaculture are 10% and 5% of those from intensive culture. Total input of phosphorus and nitrogen in 1990 was estimated to be 69 t and 630 t, while the figure for 2000; they increased up to 1500 t and 136000 t (assuming 12 kg phosphorus and 110 kg nitrogen output per ton of fish produced) for phosphorus and nitrogen (Saliot, 2005).

Maritime traffic: A comprehensive cargo analysis and forecast of the Mediterranean international seaborne trade flow have been carried out in the framework of the Mediterranean Action Plan (MAP) and performed by the Dutch Maritime Economics Research Centre for the year 1985. It was estimated that annually almost 220000 vessels of more than 100 t cross the Mediterranean, representing 20% of oil shipping and 30% of the total world merchant shipping (Saliot, 2005).

1.5.1. Eutrophication

There is no unique and universally accepted definition of marine eutrophication. The term of "*eutrophication*" is originated in Greek words, from "*eu*" means well and "*trope*" means nutrition. However, various definitions have been used to explain eutrophication in the last 50 years. For example, an excessive supply of nutrients is referred to as an eutrophication. The eutrophication as "an enrichment of water by nutrients especially compounds of nitrogen and phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms and the quality of the water concerned" (EU, Urban Wastewater Treatment Directive; UWWTD, C.E.C., 1991). The major consequences of eutrophication are algal scum, algal blooms (in other words "red tides"), enhanced benthic algal growth and, sometimes, a massive growth of submerged and floating macrophytes. Occasionally, these events are accompanied by bacterial blooms. During the summer period, at the end of the night, the increased consumption of dissolved oxygen in the water can induce the anaerobic conditions, causing the death of most of the animals living in the water and at the bottom (Saliot, 2005).

Assessing the risks and impacts of eutrophication in estuarine and coastal waters is one of the major issues in environmental management (Painting *et al*., 2005). In general, the ecological objectives related to eutrophication are: i) concentrations of nutrients close to natural levels, ii) natural distribution and occurrence of plants and animals, iii) natural levels of algal blooms, iv) natural oxygen levels and v) clear water (Andersen *et al.*, 2011). Therefore, various national and international authorities have taken legal and administrative measures to reduce eutrophication trends. In the Mediterranean region, policies on eutrophication can be divided in two groups: a) Mediterranean policies and b) European Union policies. The Mediterranean policies include Barcelona Convention (1978) and the Mediterranean Action Plan (1975). The EU policies on eutrophication are given in this present study as Shellfish Water Directive, Urban Waste Water Directive, Nitrates Directive, The Habitats Directive, The Water Framework Directive, Bathing Water Directive, and The Marine Strategy Framework Directive (Karydis and Kitsiou, 2012). Some of these directives (Karydis and Kitsiou, 2012): Urban Waste Water Directive (91/271/EEC) addresses removal of nitrate and phosphorus from waste water treatment facilities for cities with >10000 population (EEC, 1991a). Nitrates Directive (91/676/EEC) focuses the input of nitrogen compounds to marine ecosystem from agricultural sources. The Habitats Directive (92/43/EEC) focuses the concerning quality assurance of waters of high nature conservation values including nutrient control in municipal and industrial discharges (EEC, 1992). The Water Framework Directive (2000/60/EC) aims to provide "enhanced protection and improvement of the aquatic environment" (EC, 2000). Bathing Water Directive (2006/7/EC) focuses on the assessment of the bathing water quality and the protection of human health (EC, 2006). However it is indirectly related with eutrophication. The Marine Strategy Framework Directive (2008/56/EC) is aiming at monitoring and assessing ecosystem quality and requires from the Member States development of strategies and measures for "good" environmental status of marine waters (EC, 2008).

Table 1.2. The main legal framework for the Mediterranean environment (modified from Karydis and Kitsiou, 2012)

Legal document	**Date**	**Main objectives concerning eutrophication**	**Water quality assessment and measures to mitigate eutrophication**
The Mediterranean Action Plan (MAP)	1975	Sustainable management, reduction of pollutants, integrated approaches in coastal management	Monitoring of nutrients and chlorophylls
Barcelona Convention	1978	Pollution reduction in the Mediterranean, environmental protection, sustainable development	Reduction of nutrient fluxes from terrestrial sources
Shellfish Water Directive	1979	Coastal water quality protection for cultivation of shellfish	Measures to control eutrophication are a prerequisite for shellfish cultivation
Urban Waste Water Treatment Directive (UWWTD)	1991	Treatment and discharge of urban wastewater	Removal of phosphorus and/or nitrogen
Nitrates Directive	1991	To reduce nitrates from agricultural sources	Designation of vulnerable and sensitive areas, development of good agricultural practices
Habitats Directive	1992	Conservation of natural habitats	Monitoring and control on nutrients to mitigate stress to aquatic species
Water Framework Directive (WFD)	2000	Enhanced protection and improvement of the aquatic environment	Reference values for nutrients, eutrophication scales
Bathing Water Directive	2006	Good water quality for bathing and recreation	Close coordination with Urban Waste Water Directive and Nitrates Directive
Directive of European Marine Strategy (MSFD)	2008	Ecosystem quality, mitigation of eutrophication trends	Management of scientific information, environmental policy

1.5.2. Assessment of Trophic Status

From past to the present day, several indicators such as phosphorus, nitrogen, chlorophyl-*a* have been put forward to classify the trophic level of fresh water and coastal waters (Vollenweider *et al*., 1998; EEA, 1999). However, using quite a number of indicators caused some problems in assessing the trophic level. Especially, it was observed that some inconsistencies appeared in adopting methods and indexes that are regarded in the literature and used in classifying the coastal waters and determining the eutrophication (Nasrollahzadeh *et al.*, 2008; Primpas ve Karydis, 2010). Evaluating especially the effects and risk factors that are created by eutrophication in fresh water and coastal waters constitutes one of the fundamentals of environmental management policies (Painting *et al.*, 2005). It is difficult to determine a universally specific indicator or a scale while carrying our categorization studies because of the number of indicators used for assessment of eutrophication in various regions (Primpas and Karydis, 2010), and lack of procedures in practice. Considering that each study area has its own internal dynamics that are different from others, for example the difference in salinity, difference in availability of fresh water, huge differences between seasons, effects of man-made pollutants, and so on. It is evident that believing that one single indicator or index is sufficient to carry out practice will lead to failures.

Application of numerous parameters altogether is considered to be a realistic approach in water quality classification procedures. The application of the trophic index (TRIX) that was developed in accordance with this approach (Vollenweider *et al.*, 1998), offers some conveniences: (i) allowing evaluation of results with a single number and a scale ranging between 0 and 10; (ii) a multimetric index including 4 parameters associated to eutrophication. It is aimed to suppress the high and low values of the data set by putting log transformation into application for 4 parameters taking part in the TRIX algorithm (Primpas and Karydis, 2010 and references therein).

The TRIX has been widely applied by researchers in order to assess the trophic status of the coastal waters (Vollenweider *et al*., 1998; EEA, 2001; Moncheva *et al.*, 2002; UNEP, 2003; Giovanardi and Vollenweider, 2004; Vascetta *et al.*, 2004, 2008; Nasrollahzadeh *et al.*, 2008; Primpas and Karydis, 2010). The TRIX was used for the coastal areas of European Seas (Adriatic, Tyrrhenian, Baltic, Black Sea and North Sea) and the Mediterranean Sea to characterize their trophic status. The TRIX index between 0 and 10, covering a broad range of trophic level from oligotrophic to eutrophic, was first proposed by Italian research group in 1998 (Vollenweider *et al*.,1998). The TRIX index can be calculated as follow:

$$TRIX = \frac{\log(Chl-a*aD\%O*DIN*TP)-b}{a} \quad \ldots\ldots\ldots [1.1]$$

Chl-a = Chlorophyll-*a*, as µg /L,

aD%O = Oxygen as absolute % deviation from saturation; [abs | 100-%O |],

DIN = Dissolved inorganic nitrogen (NO_3-N+NO_2-N+NH_4-N), as µg/L

TP = Total phosphorus, as µg/L

b = -1.5

a = 1.2

Where ‘a’ and ‘b’ represent range log units and minimum log units, respectively, and these coefficients are derived from data set to normalize the TRIX ranging from 0 to 10, considering aforementioned parameters obtained during study period (for more details see Chapter 2.6). This research team combined four parameters namely, Chl-*a*; as a proxy for phytoplankton biomass, aD%O; as a measure of productivity or as a biotic component, DIN and TP; as a measure of the potential biomass or abiotic components for assessing the trophic condition in the coastal waters of North-Western Adriatic Sea.

Although, the TRIX is useful tool to classify tropic status of coastal waters, it has some draw backs. Primpas and Karydis (2010) have claimed that linking the number of variables such as causes (nutrients inputs) and effects (phytoplankton growth) are principal problems of the TRIX equation since interconnection introduces an artifact that may lead either to an overestimation or an underestimation. Thus, importance of high values taking part in data matrix is reduced in comparison with low values (Primpas and Karydis, 2010). As the scale of the TRIX application of which details and calculation balance are given above was developed for productive coastal waters, problems appeared when applications were carried out in different regions. Previously, while the applicability of the TRIX index into study regions was examined by carrying out comparisons (Nasrollahzadeh *et al.*, 2008; Primpas and Karydis, 2010), modification of the TRIX index study areas according to their biochemical features was suggested in order to come up with more precise identifications on the levels of trophic in the study areas. Moreover, without calculating ‘a’ and ‘b’ values from their data set, Pettine et al. (2007) have argued that the absolute trophic scale based on the TRIX index has a particular relevance for Italian coastal waters. According to this group, its application to other marine basins where maximum (derivation of a) and minimum (derivation of b) concentrations may show different ranges with respect to those of the northern Adriatic may be questioned. Hence these authors proposed the application of the UNTRIX instead of the TRIX. The proposed equation [1.2] is almost identical to the former except excluding ‘a’ and ‘b’ values for normalization.

$$UNTRIX = \log(Chl - a * aD\%O * DIN * TP) \dots\dots\dots [1.2]$$

The eutrophication status of the whole Baltic Sea is classified using related optical and biochemical indicators where information on the reference conditions and acceptable deviation from the reference conditions. The classification method is made by approach of the recently developed HELCOM Eutrophication Assessment Tool (HEAT). Some of the key assessment principles of the Water Framework Directive is used by the application of HEAT, for instance, the calculation of an Ecological Quality Ratio (EQR) and also the 'one out, all out' principle (Andersen *et al.*, 2011 and references therein). Therefore, HEAT combines both the principles of the HELCOM Baltic Sea Action Plan and the EU Water Framework Directive (Figure 1.7).

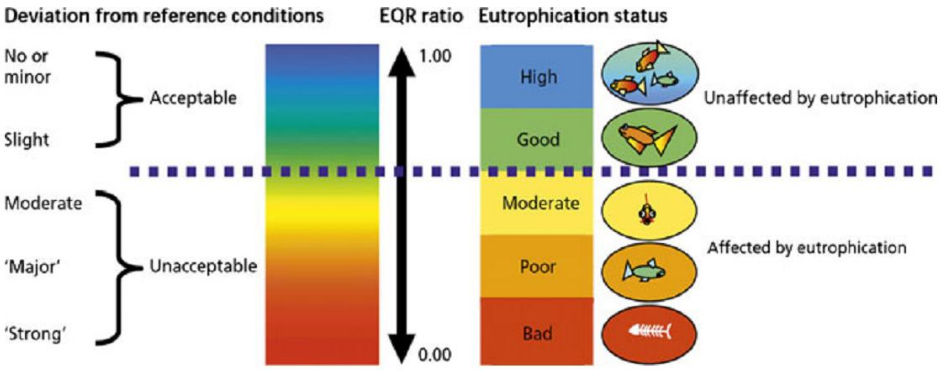

Figure 1.7. The key assessment principles used in the HEAT tool (taken from Andersen *et al.*, 2011)

CHAPTER II
MATERIALS and METHODS

2.1. Description of the Study Area

The study area (see Figure 2.1), located on the northeast coast of the Cilician Basin of the Eastern Mediterranean (EM), covers an area of about 1,150 km^2 between Göksu and Seyhan deltas. Its continental shelf is wider in the northeast and steeper in the southwest (Ediger *et al.,*1997) and extends from 36.35º to 36.9º E and 34.5º to 35.2º N. It is highly influenced by anthropogenic sources such as domestic water discharges, agricultural discharges, tourism and marine traffic. In fact, it is presently experiencing rapid industrial growth and an explosive increase in population. Population expansion at the coast, increased industry, agriculture and tourism create significant environmental stresses on the coastal system. Present industrial activities cover chemical plants including steel, fertilizer, soda, glass, paper, textile, mechanical and energy production. Untreated or primary-treated municipal wastes from major town of Mersin are potential sources of marine pollution. On the other hand, as a region of freshwater influence (ROFI), it is extremely impacted by riverine runoff from the rivers Seyhan, Ceyhan, Göksu, Berdan and Lamas. The total lengths of the main stem of Seyhan, Ceyhan, Göksu, Berdan and Lamas Rivers are 560, 509, 260, 124 and 130 km, with annual mean flow rates of 168, 144, 45, 6 and 3 m^3s^{-1}, respectively (Koçak *et al*., 2010).

Climatically, winter period in the region is characterized by generally warm and wet (from November to February) whereas the summer is described hot and dry (from June to September). The transitional seasons, spring and autumn, are generally short. The relatively longer spring season (from March to May) is characterized by unsettled winter-type weather associated with the occurrence of North African cyclones; otherwise it shows similarity to summer. Autumn usually lasts only one month (October) and is characterized by an abrupt change from the summer to the unsettled weather of winter (Özsoy *et al.*, 1981).

In the Cilician basin, 12 field surveys were performed seasonally in the period between September 2008 and February 2011. Data were collected by R/V-Bilim-2 from 50 stations located in the Mersin Bay of the Cilician basin during the studied period; in winter: January, February, March 2009, February 2010 and February 2011, in summer: September 2008, August 2009 and July 2010, in fall: October 2009 and November 2010 and in spring: April 2009 and April 2010. In the present study both surface and water column were sampled, however only the data of surface water were used to assess the trophic status of the region. The depth ranges of the stations are given in Figure 2.1. (0-10m: red, 0-20m: green, 0-50m: blue, 0-100m: black, 0-150m: magenta)

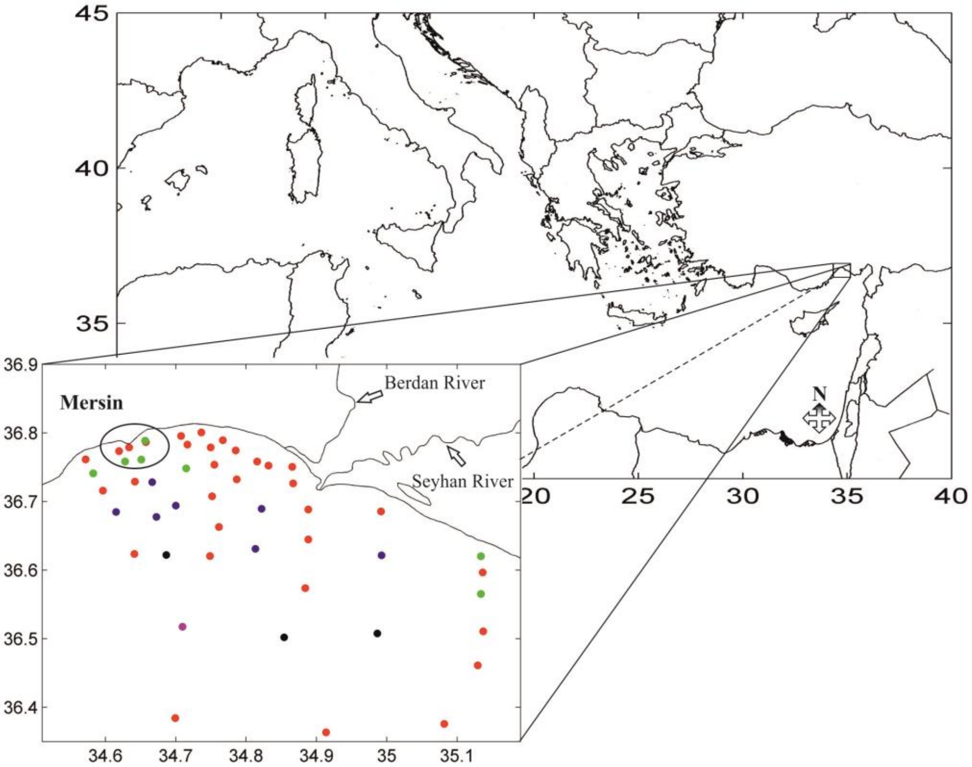

Figure 2.1. Locations of the study area (Mersin Bay) and oceanographic stations used in the Cilician Basin of the Northeastern Mediterranean during the present study

2.2. Preparation of the Chemical Reagents

(a) Reagents for Nitrate (NO_3^-) and Nitrite (NO_2^-)

Synthetic seawater: 35 g of sodium chloride and 0.2 g of sodium hydrogen carbonate were dissolved in 800 mL of DDW (distilled de-ionized water) and diluted to 1 liter with DDW.

System wash solution: 6 mL of Brij-35 was added to 1 liter of DDW.

Ammonium chloride: 10 g of ammonium chloride was dissolved in about 900 mL of DDW and the pH was adjusted to 8.5 ± 0.1 with ammonium solution (25%). After diluting it to 1 L with DDW, 0.5 mL of Brij-35 was added to per liter and mixed thoroughly.

Color reagent: 700 mL of DDW was added to 100 mL of concentrated phosphoric acid and 10 g of sulfanilamide. After dissolving completely, 0.5 g of N-1-naphthylethylenediamine dihydrochloride was added and diluted to 1 L with DDW.

Stock copper sulphate solution (2%) for Cd column: 2 g of copper sulfate was dissolved in about 60 mL of DDW and diluted to 100 mL with DDW.

6 N Hydrochloric acid: 495 mL of hydrochloric acid is cautiously and slowly added to about 400 mL of DDW. After cooling it down to room temperature, it is diluted to 1 L with DDW.

Stock standard nitrite (5000 µM): 0.345 g of sodium nitrite is dissolved in DDW. After diluting it to1 L, it is stored in dark bottle.

Stock standard nitrate (5000 µM): 0.505 g of potassium nitrate is dissolved in DDW. After diluting to 1 L, stored it in a dark bottle.

Color reagent for only nitrite: 10 g of sulfanilamide is dissolved in 750 mL of DDW and 100 mL concentrated phosphoric acid solution. After adding 0.5 g of N-1-naphthylethylenediamine dihydrochloride, it is diluted to 1 L with DDW. 4 mL of Brij-35 is added in the last step.

Stock standard nitrite (5000 µM), 0.345 g of sodium nitrite is dissolved in DDW. After diluting it to 1 L, it is stored in dark bottle.

(b) Reagents for Ammonium (NH_4^+)

Artificial seawater: 31 g of sodium chloride was dissolved in about 900 mL of DDW and diluted to 1 L with DDW.

Systems wash solution (30%): DDW with 2 mL/L Brij-35 was used as a solution.

Complexing reagent: 30 g of EDTA, 120 g of tri-sodium citrate dehydrate and 0.5 g of sodium nitroprusside were dissolved in 800 mL of DDW and diluted to 1 L with DDW. Then 3 mL of Brij-35 was added.

Salicylate, dichloro isocyanuric acid (DCI): 3.5 g of sodium hydroxides was completely dissolved in 80 mL of DDW. After adding 0.2 g of dicholoroisocyanuric acid sodium salt dehydrate solution was diluted to 100 mL with DDW.

Salicylate: 300 g of sodium salicylate was dissolved in 800 mL of DDW and diluted to 1 L with DDW.

Phenate reagent and Dicholoro isocyanuric acid: 1 g of dicholoroisocyanuric acid sodium salt dehydrate was dissolved in 80 mL of DDW. It was diluted to 100 mL with DDW .

Phenol: 36 g of sodium hydroxide and 50 g of phenol were dissolved in 800 mL of DDW. Then solution was diluted to 1 L with DDW.

Stock standard of ammonium (5000 µM): 0.330 g of ammonium sulfate was dissolved in about 600 mL of DDW and diluted to 1 L with DDW.

(c) Reagents for Phosphate (PO_4^{3-})

Synthetic seawater: 35 g of sodium chloride and 0.2 g of sodium hydrogen carbonate was dissolved in about 800 mL of DDW and diluted to 1 liter with DDW.

System wash solution: DDW containing 8 g/L sodium dodecyl sulphate (SDS) was used as a solution.

Stock antimony potassium tartrate: 2.3 g of antimony potassium tartrate was dissolved in 80 mL of DDW and diluted to 100 mL with DDW.

Ammonium molybdate: 64 mL of concentrated sulfuric acid was carefully added to 500 mL of DDW. After cooling the solution, 6 g of ammonium molybdate was dissolved and 22 mL of stock antimony potassium tartrate was added. At the end entire solution was diluted to 1 L with DDW.

Ascorbic acid: 8 g of ascorbic acid was dissolved in 600 mL of DDW. Then 45 mL of acetone and 8 g of sodium dodecyl sulfate were added and solution diluted to 1 L.

Sodium hydroxide: 4.6 g of sodium hydroxide was dissolved in about 600 mL of DDW. After cooling down to the room temperature, it was diluted to 1 L.

Stock standard phosphate: 0.68045 g of potassium dihydrogen phosphate was dissolved in DDW. After diluting to 1 L, stored it in a dark bottle.

(d) Reagents for Total Phosphorus (TP)

Ascorbic acid: 10 g of ascorbic acid was dissolved in 50 mL of DDW and diluted to 100 mL by adding 50 mL of 4.5 M sulphuric acid solution.

Mix reagent: 12.5 g of ammonium molybdate was dissolved in 125 mL of DDW and added in 350 mL of 4.5 M sulfuric acid solution. 5 g of potassium antimony tartarate was dissolved in 20 mL of DDW. After mixing two solutions, final volume was completed to 1 L.

Oxidant: 42 g of potassium peroxydisulfate and 84 g of disodium tetraborate were dissolved in 100 mL of DDW and then it was diluted to 700 mL.

(e) Reagents for Silicate

Synthetic Seawater: 35 g of sodium chloride and 0.2 g of sodium hydrogen carbonate were dissolved in about 800 mL of DDW and diluted to 1 L with DDW.

System wash solution: DDW containing 2 g/L SDS is used as a solution.

Ammonium molybdate: 15 g of ammonium molybdate was dissolved in about 800 mL of DDW. Then sequentially 4.2 mL of sulfuric acid and 5 g of SDS were added. Finally, the solution was diluted to 1 L.

Oxalic Acid: 95 g of oxalic acid was dissolved in 800 mL and diluted to 1 L of DDW.

Ascorbic acid: 50 g of ascorbic acid was dissolved in 700 mL of DDW and diluted to 1 L with DDW.

Stock standard Silicate (5000 μM): 1.0 g of sodium meta-silicate nonahydrate was dissolved in 800 mL of DDW and diluted to 1 L.

2.3. Sampling

Samples were obtained using a Sea-Bird Model 9 CTD profiling system coupled to a General Oceanics rosette sampler having 12 Nansen bottles of 5 L volume. The CTD+the rosette system were operated using a Lebus hydrographic winch with a 2000 m cable. CTD probe system are composed of conductivity, external temperature, fluorescence, dissolved oxygen sensors and with an internal pressure sensor. The sample bottles on the Rosette system were closed through commands issued from the deck-unit through a conductive cable. The cable allowed both for trapping the bottles and for the real time display of CTD data in areas of interest in the water column. After obtaining samples from the pre-defined depths, sub-samples were taken according to the required volume of each parameter to be measured. In the first step, 100 mL sample was taken for dissolved oxygen analysis before it interacts with air. Then, parallel samples were taken for TP (100 mLx2) and nutrient (15 mLx2) analysis. While dissolved inorganic nutrient sample measurements were generally carried out onboard as soon as possible after the sampling, TP and particulate matter samples were kept frozen (-18ºC) without adding any chemicals to preserve until analysis. Chlorophyll-*a* (Chl-*a*) samples (1-2 L of seawater) were taken into Nalgene containers. For Chl-*a* measurements, 1-2 L of seawater were filtered through the 47 mm GF/F filters and kept frozen until analysis. Biochemical parameters including inorganic nutrients (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} and Si), particulate organic carbon and nitrogen (POC, PON), Chl-*a*, pH and dissolved oxygen measurements were performed on board or at the laboratory of METU-IMS on Erdemli Campus.

2.4. Measurements and Instruments

Summary of measured parameters and applied techniques were given in Table 2.1. Inorganic nutrients (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} and Si), TP, Chl-*a* and DO were analyzed by applying AutoAnalyzer, Spectrophotometer, Fluorometer and Oxygenmeter, respectively.

Table 2.1. Parameters and their measurement instruments

Instrument	Parameter	Method
Auto Analyzer	NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-}	Colorimetric
Spectrometer	TP	Colorimetric
Fluorometer	Chl-*a*	Fluorometric
Oxygenmeter	DO	Titrimetric

2.4.1. AutoAnalyzer

AutoAnalyzer (AA) is an automated multi-channel nutrient analyzer using a special flow technique named "continuous flow analysis (CFA)" or more correctly "segmented flow analysis (SFA)". The instrument was invented in 1957 by Leonard Skeggs, PhD and Jack Whitehead's Technicon Corporation commercialized it. The clinical analysis was the first applications; however methods for industrial analysis soon followed. In 1987, the Technicon Industrial division was bought by Bran Luebbe. SEAL Analytical now own&manufactures the AutoAnalyzer brand with service and support for the AutoAnalyzer.

The AutoAnalyzer is an automated device used in measuring the nutrient concentration, *i.e.* PO_4^{3-}, NO_3^-+NO_2^-, NO_2^-, NH_4^+ and Si analysis via standard procedures (Bran+Luebbe, 2008a, b, c, d, e and references therein). A basic Autoanalyzer system consists of an a) autosampler, b) a peristaltic pump, c) a chemistry manifold, d) a detector and e) data acquisition software.

a) Autosampler: It has 40 tube capacity and includes tube slots to place the samples. Each sample tube has 15 mL volume which is enough for measuring 3 parameters (PO_4^{3-}, NO_3^- +NO_2^-, Si). Sampler section is connected to computer with interconnection cable to enter information about operation.

b) Pump: It works as a kind of vacuum. After taking samples with plastic hose/tube, it mixes reagents and provides a constant flow in glass tubes. Specific tubing systems, with an exact volume and diameter, take samples and reagents from sampler in a different rate which is specific for each parameter. Pump also supplies precise air bubble injection for having constant and balanced flow. According to the parameter, each system has different colors to make easy to recognize.

c) Manifold: It includes glass tubing systems which are chemically inert and allow for easy visual check of operation for each parameter (PO_4^{3-}, NO_2^- +NO_3^-, NO_2^-, Si and NH_4^+). Besides tubing systems, it has circular spires with 5, 10 or 20 curves. Samples and reagents enter the manifold through the spires with the help of pump. The flows in glass tubings and spires must be operated constant and steady rate. After mixing samples and reagents, solution is transferred to heating bath to break organic particles with heat (37 ℃).

d) Detector: Measurements of each parameter are achieved by using different wavelengths. The colorimeter consists of four filters with specific wavelengths 880 nm, 550 nm, 550 nm, 820 nm and 660 nm for PO_4^{3-}, NO_2^-+NO_3^-, NO_2^-, Si and NH_4^+, respectively. The transfer of information from colorimeter to computer is accomplished by interconnection cable. Perfomance specifications is given in Table 2.2.

The determination of dissolved reactive phosphate (DRP), orthophosphate, (PO_4^{3-}) is based on the colorimetric measurement in which a blue color is formed by the reaction of orthophosphate, antimony ion and molybdate ion. This reaction followed by reduction with ascorbic acid in acidic medium (pH <1). The reduced blue phospho-molybdenum complex is read at 880 nm. The optimum value determined by Riley and Yang coincidences with the [H^+]:[Mo] ratio in the reaction mixture.

Table 2.2. Performance specifications of AutoAnalyzer application

	Ammonia	**Nitrate&Nitrite**	**Silicate**	**Phosphate**	**Nitrite**
Sampling Tube	yel-yel	yel-yel	yel-yel	blu/blu	blu/blu
Sampling Rate	60/h	60/h	60/h	60/h	60/h
Sample Wash Ratio	04:01	04:01	04:01	04:01	04:01
Sensivity	0.06	0.44-0.48	0.36-0.44	0.40-0.44	0.07
Reagent Absorbance	0.02-0.04	0.01-0.03	0.01-0.03	0.02-0.04	0.01
Coefficient of Variation	0.30	0.21	0.05	0.02	0.20
Correlation Coefficient	0.999	0.9999	0.999	0.9999	1
Detection Limit (µmol/L)	0.04	0.015	0.03	0.024	0.003

The nitrate and nitrite (NO_2^-+NO_3^-) determination is based on the reduction of nitrate to nitrite that is used the copper-cadmium reductor column. Then the nitrite reacts with sulphanilamide to form a diazo compound under acidic conditions. This compound then couples with N-(1-naphthyl)ethylenediamine dihydrochloride to form a purple azo dye. The concentration of oxidizing and reducing agents and interfering some (*i.e.* iron, copper, mercury and other metals) metal ions can make interference effect. When they reach sufficient concentration, metal ions may cause a positive error, *i.e.* divalent copper and divalent mercury may form colored complex ions having adsorption bands in the range of color measurement. Moreover, significant quantities of sulfate, sulfide and/or organic matter may cause interference effect on the performance of the copper-cadmium reductor column and hence such samples should be pre-treated before analysis. The method is also applicable to persulfate digested samples.

For the determination of nitrite, diazo compounds form as a result of the reaction between nitrite ion and sulfanilamide under acidic conditions. This compound then couples with N-(1-naphthyl)ethylenediamine dihydrochloride to form a reddish-purple azo dye.

The measurement of soluble silicates (Si) is based on the reduction of silico-molybdate to molybdenum blue by ascorbic acid in acidic solution. To minimize interference from phosphates, oxalic acid is introduced into the sample stream, before the addition of ascorbic acid.

Ammonium (NH_4^+) determination method utilizes the Berthelot reaction, in which a formation of blue-green colored complex is measured at 660 nm. The use of a complexing agent prevents the precipitation of calcium and magnesium hydroxides. Sodium nitroprusside is used for enhancing the sensitivity.

During the cleaning procedure, vessels were not contacted by any detergent. To avoid particular matter accumulation, HCl acid (10%) was passed through system after each measurement. If there is any irregularity in the flow of bubbles during the measurement, NaOH (1M) is passed along the system for 15 minutes.

2.4.2 Spectrophotometer (Varian Cary 100)

A spectrophotometer is a photometer that can measure intensity as a function of the light source wavelength. The spectrophotometers are used in various scientific fields, such as chemistry, biochemistry, physics, materials science and molecular biology.

The Varian Cary 100, a cost-effective UV-visible spectrophotometer, has a versatile set of accessories containing liquid and solid sample holders, multicell holders, temperature control, diffuse reflectance, specular reflectance, and also fiber optics. It is controlled by the Cary WinUV, Windows-based, software. With its modular design the Cary WinUV makes the functionality easy to upgrade, if your requirements change. WinUV software provides a wide range of applications, *i.e.* Analysis, Bio and Pharma, via a simple interface. The Cary 100 has a double beam design that compares the light intensity between two light paths, one includes a reference sample and the other contains the test sample. The bandwidth of Cary 100 ranges between 0.2 and 0.4 nm. The light source is Tungsten or Deuterium.

In oligotrophic waters of the Mediterranean, TP has a low concentration which is hard to precise. On account of that low precision, measurement with autoanalyser was not preferred as a determination method for phosphorus analysis. Spectrophotometric manual analysis method was used rather than automated analysis.

Procedure for the manual method:

a) Ascorbic acid solution: 10 g of ascorbic acid was dissolved in 50 mL of DDW and diluted to 100 mL by 4.5 M sulfuric acid solution. The solution, with yellowish color, is stable for one week in dark colored glass bottle and it should not be used when its color get lost.

b) Mix reagent solution: 12.5 g of ammonium molybdate was dissolved in 125 mL of DDW and added in 350 mL of 4.5 M sulfuric acid solution. 5 g of potassium antimony tartarate was dissolved in 20 mL of DDW. Both of them were shaken vigorously to obtain well mixed solution. Final solution is stable for few months in glass bottle.

c) Standards and samples: A set including phosphate standards (0.2-1 μM) and blanks were prepared. 1 mL of ascorbic acid solution is added into both samples and standards. After a couple of minutes, 1 mL of mix reagent was added. The entire reaction completes in 8 minutes. Measurement of samples and standards were accomplished at 880 nm wavelength with spectrophotometer by using 5 cm quartz cuvette.

For total phosphorus analysis, pre-cleaned Teflon caped bottles were filled with HCl (10%) and heated to 200℃ for 90 minutes. Then they were rinsed and filled with double distilled water (DDW) and subjected to autoclave process, at least two times.

2.4.3 Fluorescence (Spectro Fluorometer F-2500)

Fluorometer is applied to measure parameters of fluorescence, the emission of light by a substance. After excitation by a certain spectrum of light, fluorescence intensity and wavelength distribution of emission spectrum are used to identify the presence and the amount of specific molecules in a medium. It is applied in various scientific fields *i.e.* life sciences, biotechnology, education, quality control, new materials and other basic scientific researches.

The F-2500 Fluorescence Spectrophotometer has the widest range of fluorescence applications with a resolution of 2.5 nm, scan speeds of up to 3000 nm/min and comprehensive data processing functions for photometry, wavelength scanning and time scanning. 150 W Xenon lamb is used as a light source in the instrument. The F-2500 Fluorescence Spectrophotometer can be used to measure sample with 220 to 730 nm wavelength range.

This conventional fluorometric method was applied to determine the chlorophyll-*a* concentration (Grasshoff *et al.*, 1983). Acetone was added for extraction of frozen samples and they were 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.

2.4.4. Dissolved Oxygen by Winkler Method

The Winkler (Grasshoff *et al.,* 1983) titration is an elegant method for determining the oxygen content in water. Oxygen amount of water is measured as a result of redox and iodometric processes. The reaction between manganese (II) chloride and NaOH forms Mn (III) hydroxides. After being dissolved in acid, in the presence of iodide ions, Mn (III) is reduced to Mn (II). The amount of iodine, equivalent to the oxygen, is released and can be titrated with thiosulphate. The automated method of Winkler titration was used in this study (Grasshoff *et al.*, 1983).

2.5. Application of Statistical Techniques

2.5.1. Cluster Analysis

Cluster analysis (CA) is the statistical method of partitioning a sample into homogeneous classes to produce an operational classification. In other words, it is an exploratory data analysis tool for organizing observed data into meaningful taxonomies, groups, or clusters, which maximizes the similarity of cases within each cluster while maximizing the dissimilarity between groups that are initially unknown.

Although many books are published on clustering techniques, there are still some controversies about the efficiency of clustering methods in ecological and environmental applications. The main reasons of these controversies are: (*a*) criteria of selecting similarity measures, or distance measures, (*b*) The selection of clustering algorithms and (*c*) “structure” of ecological data (Kitsiou and Karydis, 2011).

In the study, Euclidean Distance was chosen as the distance measurement method. It was pointed out the suitability of abiotic variables characterizing eutrophication such as water transparency, nutrient concentrations, Chl-*a* values and phytoplankton cell number (Kitsiou and Karydis, 2011). Ward linkage was used as Average Linkage Clustering Method (UPGMA). It was found as the best successful agglomerative algorithm in discriminating tributaries and the best resolution in discriminating sampling sites of different trophic status (Kitsiou and Karydis, 2011).

2.5.2. Handling of Data

In 1980, Hawkins defined outliers as “an observation which deviates so much from other observations as to arouse suspicions that it was generated by a different mechanism”. This deviation from average may plays a misleading role in establishing relations for distribution that summarizes the real data set of variables (Ignatiades *et al*., 1992 and references therein). Because of that reason, it is generally advised that to get rid of the outliers before applying any statistical behavior (Kitsiou and Karydis, 2011 and references therein). In the present study, removed outlier values were determined by using frequency distribution and multivariate statistics. The distributions of variables have shown significant overlapping between three data sets due to seasonal fluctuations. The temporal fluctuations in physical factors have an important role in limiting and controlling the biological response to nutrient enrichment (Painting *et al.*, 2005). It was understood that the seasonality was one of the main reason of extreme atypical values of each variables that could affect the statistical properties of the data sets. To deal with that extreme values, the values out of the data between 10% and 90% of each parameter (TP, DIN, aD%O and Chl-*a*) were excluded. Thus, according to the raw data, the new data set is more representative for eutrophic, mesotrophic and oligotrophic water types.

2.5.3. Application of Kruskall-Wallis test

The Kruskall-Wallis (K-W) test is a non-parametric statistical tool to compare three or more samples and it explores the null hypothesis that the different samples in the comparison were strained from the same distribution. Thus, K-W test was applied in order to assess for the presence of significant difference in measured parameters categorized by cluster analysis.

2.6. Trophic Index (TRIX)

A Trophic index (TRIX), defined as a linear combination of the logarithms of four state variables (Chl-*a*, oxygen as absolute [%] deviation from saturation (aD%O), dissolved nitrogen (DIN), total phosphorus (TP) was proposed by Volleinweider et al. (1998) to characterize the trophic conditions of coastal marine environments.

$$TRIX = (\log(Chl - a * aD\%O * DIN * TP) - b)/a \quad \ldots\ldots\ldots [2.1]$$

Chl-*a* = Chlorophyll-*a* , as μg/L;
aD%O = Oxygen as absolute % deviation from saturation; [abs | 100-%O |]
DIN = Dissolved inorganic nitrogen (NO_3-N+NO_2-N+NH_4-N), as μg/L
TP = Total phosphorus, as μg/L
b = -1.5
a = 1.2

'b' and 'a' are scale factors based on the data set concerning the Northern Adriatic Sea. However, its application to the other regions may be questioned because of the different concentration limits with respect to the Northern Adriatic (Pettine *et al.,* 2007). According to the minimum and maximum values of each parameters, the scaling factors "a" and "b" must be recalculated to be reasonable/meaningful for the study area.

So that Pettine et al. (2007) proposed a TRIX-derived index, unscaled TRIX (UNTRIX), which is given by:

$$UNTRIX = \log(Chl - a * aD\%O * DIN * TP) \ldots\ldots\ldots [2.2]$$

One method for assessing the trophic status by using the UNTRIX is TQR_{TRIX} trophic index. This index is calculated by the ratio between the median UNTRIX value in the reference site and the 75th percentile of the UNTRIX in an impacted site, according to:

$$TQRTRIX = 50th\ of\ UNTRIXref/75th\ of\ UNTRIXsite \ldots\ldots\ldots [2.3]$$

The range of this ratio varies from 0 to 1; the higher value of the ratio, the more similar is the site to the reference. The proposed trophic scale of the TQR_{TRIX} (Pettine *et al.*, 2007) is given in Table 2.3 below:

Table 2.3. TQR_{TRIX} trophic scale

TQR_{TRIX} value	Trophic classification
0.00-0.29	Bad
0.30-0.49	Poor
0.50-0.69	Moderate
0.70-0.84	Good
0.85-1.00	High

2.7. Quality Assurance

The accuracy of the autoanalyzer and spectrophotometer measurements was continuously verified by using the certified reference material prepared by QUASIMEME (Quality Assurance of Information in Marine Environmental monitoring). QUASIMEME was founded in 1992. It has been coordinated by QUASIMEME project office at Wageningen University and Research Centre (Alterra DLO) in Netherlands. QUASIMEME is part of WEPAL (Wageningen Evaluating Programmes for Analytical Laboratories) accredited for the organization of Inter-laboratory Studies by the Dutch Accreditation Council RvA, since 2011.

QUASIMEME has many collaborators who prepare and provide test materials for determining the laboratory performance. The sea water has been used as a test material for nutrient analysis. This material is collected from Eastern Atlantic Ocean. After the sea water is filtered to remove bacteria and other particles, it is dispensed into appropriate bottles. The test materials for Chl-*a* are prepared from algae cultures and sub-sampled onto Whatman GF/F, 47 mm filter paper and frozen in liquid nitrogen.

During this study obtained results from the analysis of the certified reference material are given with total error values and Z scores values in Table 2.4. The results generally are consistent with QUASIMEME. Although the results for NH_4^+ were questionable at some points, they were generally satisfactory.

Table 2.4. Concentrations along with their Z scores of macro nutrients and total phosphorus measured in inter-comparison for simulated sea water

	NO_2^-	NH_4^+	PO_4^{3-}	TN	TP	Chl-*a*
Mean	1.54 0.01 0.66	3.44 0.10 1.91	1.24 0.02 0.46	21.70 4.45 9.95	1.30 0.07 0.48	16.85
Assigned Value	1.50 0.02 0.62	4.21 0.20 1.89	1.25 0.04 0.50	19.57 4.93 9.52	1.31 0.13 0.58	14.28
Total Error	0.10 0.01 0.04	0.30 0.08 0.16	0.10 0.03 0.06	1.42 0.87 0.82	0.10 0.04 0.06	1.81
Z Scores	0.50 -1.10 0.90	-2.50 -1.40 0.10	-0.10 -0.60 -0.70	1.50 -0.60 0.50	-0.10 -1.40 -1.70	1.40

TP, PO_4^{3-}, NO_2^-, NH_4^+, TN = µM
Chl-*a* = µg/L

CHAPTER III
RESULTS AND DISCUSSION

3.1. Spatial and Temporal Variations of Biochemical Parameters of Raw Data Set

Previous studies conducted in the Mediterranean Sea have demonstrated that inshore and offshore waters have different physical (S and T), chemical (macro nutrients) and biological (Chl-*a*) properties (Ignatiades *et al*., 1992; Pettine *et al*., 2007; Yucel-Gier *et al*., 2011). For example, from 5 to 10 fold increases were recorded in biomass (Chl-*a*), PO_4^{3-} and NO_3^- values from offshore to inshore waters of Saronikos Gulf (Ignatiades *et al*., 1992). Similar spatial trends were observed in the Izmir Bay (Yucel-Gier *et al*., 2011), Caspian (Nasrollahzadeh *et al*., 2008), Adriatic, Tyrrhenian, Baltic, Black and Northern Seas (Pettine *et al*., 2007 and references therein).

The spatial variations of aforementioned parameters (nutrients, Chl-*a*, dissolved oxygen and physical parameters) in the study area are depicted in Figures 3.1-3.8. The seasonal mean values for each station were obtained from long term surveys conducted between September 2008 and February 2011 and plotted as contour diagrams using MatLab programme. It is apparent that all parameters indicate large spatial variabilities, exceeding 10-fold decreases from inshore to offshore waters throughout the study period. Taking into account the surface distribution diagrams the following general conclusions can be reached:

a) Macro-nutrients: In general, macro-nutrients have their higher concentrations in coastal waters, reaching peak values at hot spots (waste water discharge points and river delta) in the Mersin Bay (Figure 3.1 to Figure 3.4). Lower concentrations of macro-nutrients were observed in the offshore waters of the Mersin Bay due to the limited inputs from anthropogenic and fresh water sources to oligotrophic waters of the NE Mediterranean.

In the Mersin bay, the peak values of ammonium concentrations, exceeding 15 µM, were detected at some hot points in winter, whereas the rest of the NH_4^+ data were below 8.5 µM in the polluted nearshore zone during the studied period. The offshore NH_4^+ values were found to be as low as 0.1 µM during the year, consistent with low nitrate and phosphate values.

Surface nutrient concentrations showed remarkable increases in winter (Figure 3.1) e.g. the January 2009, February 2009-2010-2011 and March 2009 values were relatively high in the shallow waters of the bay (<50 m) due to increasing riverine inputs and effective winter mixing. The dissolved reactive phosphate (DRP, PO_4^{3-}) concentrations generally ranged between 0.04 and 0.3 µM in the shallow coastal region, decreasing to 0.02 µM levels in the offshore waters of the bay. However, in March-2009, which represents wet period of late-winter and early-spring, it reached 0.5 µM levels in the river-fed nearshore waters (S=38‰). Concentrations of nitrate (NO_3^- and NO_2^-) varied locally from 0.23 to 13 µM in the bay, where the ammonium (NH_4^+) generally ranged between 0.15 and 8 µM. The surface TP and DIN (NO_3^- and NH_4^+) concentrations regionally ranged between 0.04-1.2 µM and 0.4-20 µM in winter. The highest DIN concentration was as high as 44 µM at hot points. The N/P ratio generally ranged from 3.67 to 170 in the bay; however, it reached the peak value of 409 in February 2010 at the hot points. The silicate concentrations locally varied from 0.66 µM in the offshore water to 10 µM in the bay with the higher values in the river-fed coastal zone.

In spring (April 2009 and 2010), nutrient concentrations were markedly high in the coastal waters between the Mersin Harbor and Seyhan Delta, exhibiting the similar spatial distributions to those observed in winter (Figure 3.2). Especially, the nutrient discharges of Seyhan and Berdan rivers highly influenced the surface concentrations due to their increased loads of river flows in spring. The surface TP concentrations exceeded 0.6 µM levels at the hot points in the nearshore waters (<20m) while it declined to 0.05 µM levels in the offshore waters. The TP reached the peak value of 1.2 µM in the nearshore zone fed by wastewater discharges. The surface nitrate concentrations varied regionally from 0.06 µM in the offshore to 5.8 µM in the inshore zone. The DRP concentrations showed a similar spatial pattern with the TP, exceeding 0.3 µM in the inshore and declined to 0.02 µM in the offshore surface waters. The DIN concentrations ranged between 0.15-1.15 µM in the offshore zone, rising to the levels of 0.5-6.75 µM in the river-fed coastal zone. Ammonium concentrations ranged regionally between 0.06-2.01. The spring N/P (DIN/DRP) ratio generally varied between 4.5 and 50 in the inshore water, decreasing to the levels of 1.2-20 in the offshore surface water. However, a peak value of 72 was determined at the hot point where DIN was 5 µM. The spring ratios were locally lower than the winter ones.

Summer field surveys were conducted in early September 2008, August 2009 and July 2010; the surface nutrient distributions are depicted in Figure 3.3. In summer, surface nutrient concentrations were relatively low, except ammonia in the near-shore zone. The summer TP concentrations varied between 0.05 µM and 1 µM, reaching the peak values in the polluted near-shore waters having high NH_4^+ concentrations. The DRP and DIN concentrations ranged between 0.02-0.26 µM and 0.2-6.62 µM, respectively, in inshore waters fed by terrestrial inputs. The concentrations varied between 0.02-0.06 µM for DRP and 0.1-1 µM for DIN in nutrient poor offshore surface waters. In general, N/P molar ratios varied spatially between 6-90 in the near-shore zone and 4-40 in the offshore water. The Si concentrations were markedly high in the river-fed coastal waters, reaching 7.8 µM and declined to 0.7-1 µM levels in the offshore water.

In autumn, two cruises were held in October 2009 and November 2010 (Figure 3.4). DRP concentrations were observed to range between 0.1-0.21 μM in coastal sites (<20m), declining to 0.02-0.08 μM in the open water. Nitrate concentrations ranged locally from 0.06-0.21 μM in the salty offshore to 0.05-8.34 μM in the near-shore zone water. The ammonium showed regional variations from offshore (0.05 μM) to polluted near-shore zone (4.9 μM). The DIN concentrations ranged between 0.15 μM and 8 μM from the offshore to the inshore zone, with the extreme values exceeding 13 μM in the point close to the river mouth. The N/P ratios were expectedly high (100-110) in the nitrate-rich nearshore waters.

b) Dissolved oxygen and Chl-a: The dissolved oxygen (DO) concentration in seawater is controlled by interacting physical and biogeochemical processes as well as related factors such as the inputs of terrestrial organic matter, atmospheric input of O_2, salinity, temperature and nutrients which affect photosynthetic production (Grasshoff *et al.*, 1983). In winter, as a result of insufficient light intensity and nutrient inputs from external and internal sources to the euphotic zone, primary productivity decreases (Yılmaz and Tuğrul, 1998; Pettine *et al.*, 2007) and this situation leads enhanced DO concentration in the euphotic zone.

In winter, DO concentrations were high in river-fed inshore waters, ranging from 7.22-9.96 mg/L, decreasing to the levels of 7.22-8.82 mg/L in the offshore water of the bay. Chl-*a* concentrations also showed a similar spatial pattern with DO, increasing from 0.05 μg/L in the offshore to 6.7 μg/L in the coastal zone.

In spring the concentrations of DO exceeded 9.5 mg/L in the river-fed coastal waters and decreased to 7.5-8 mg/L in the offshore. The surface Chl-*a* values varied regionally between 0.02 and 2.25 μg/L, consistent with spatial pattern, of the surface nutrients distributions in the Cilician basin. Higher values were recorded in the nutrient rich nearshore waters.

In summer, DO concentrations decreased to 6.2 mg/L levels in the more saline offshore surface waters whilst it was markedly high in the DIN-loaded coastal zone. Surface Chl-*a* concentrations varied regionally between 0.02 and 3.2 μg/L, reaching the peak values in the river-fed coastal waters. Similarly, DO concentrations in the surface waters of the bay ranged from 5.7 to 8.0 mg/L (Figures 3.1-3.4).

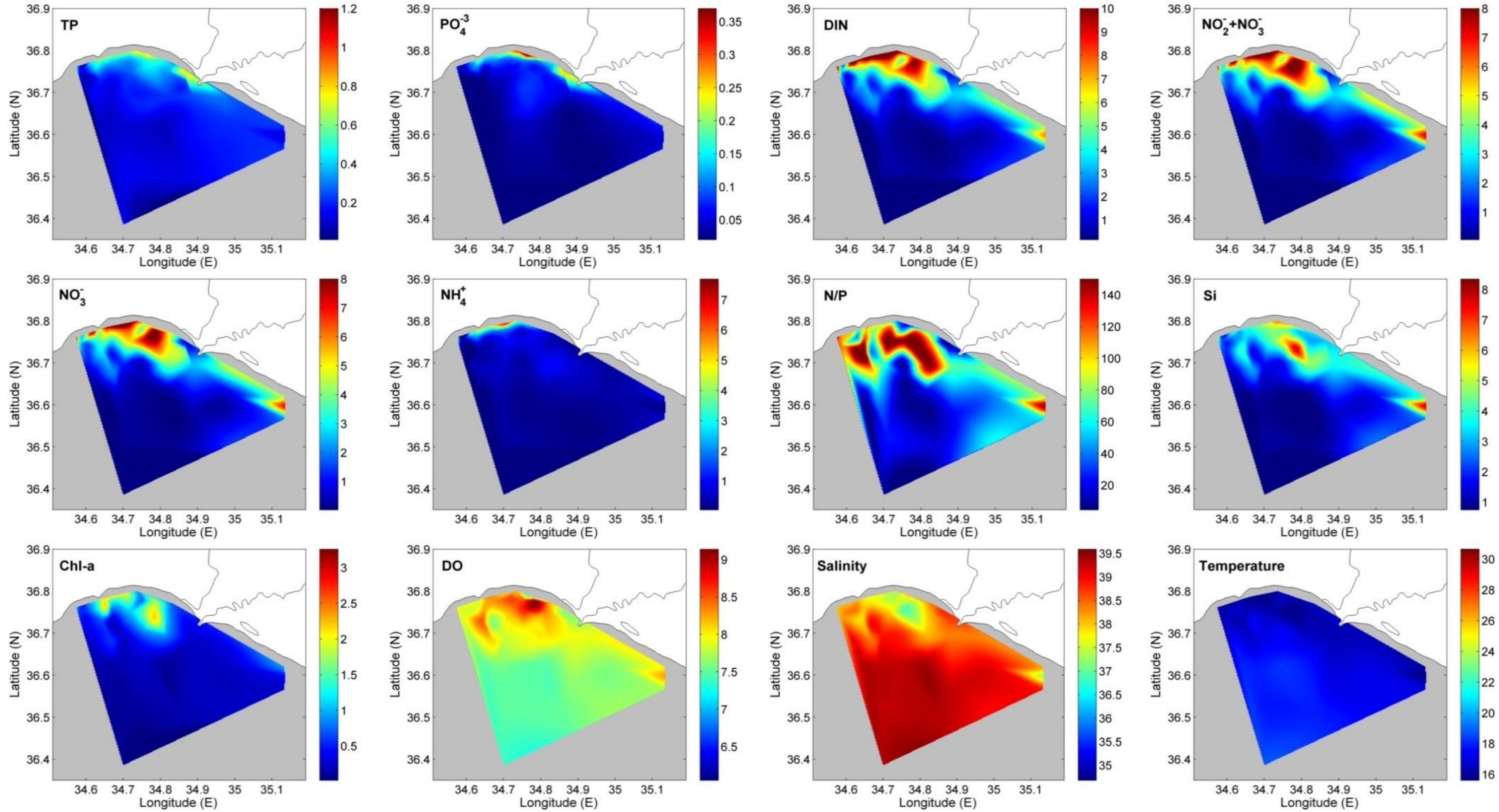

Figure 3.1. Surface distribution of winter season

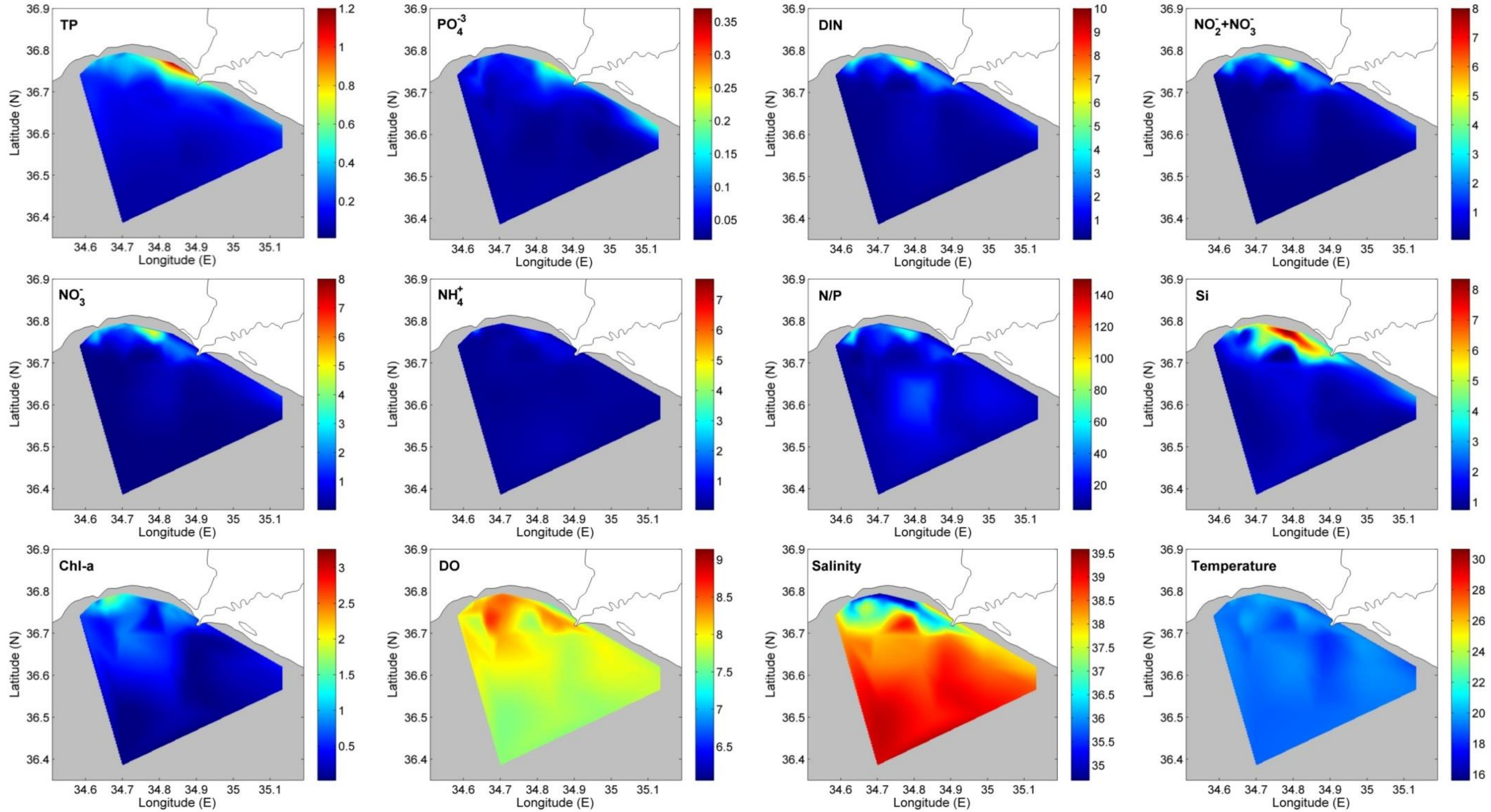

Figure 3.2. Surface distribution of spring season

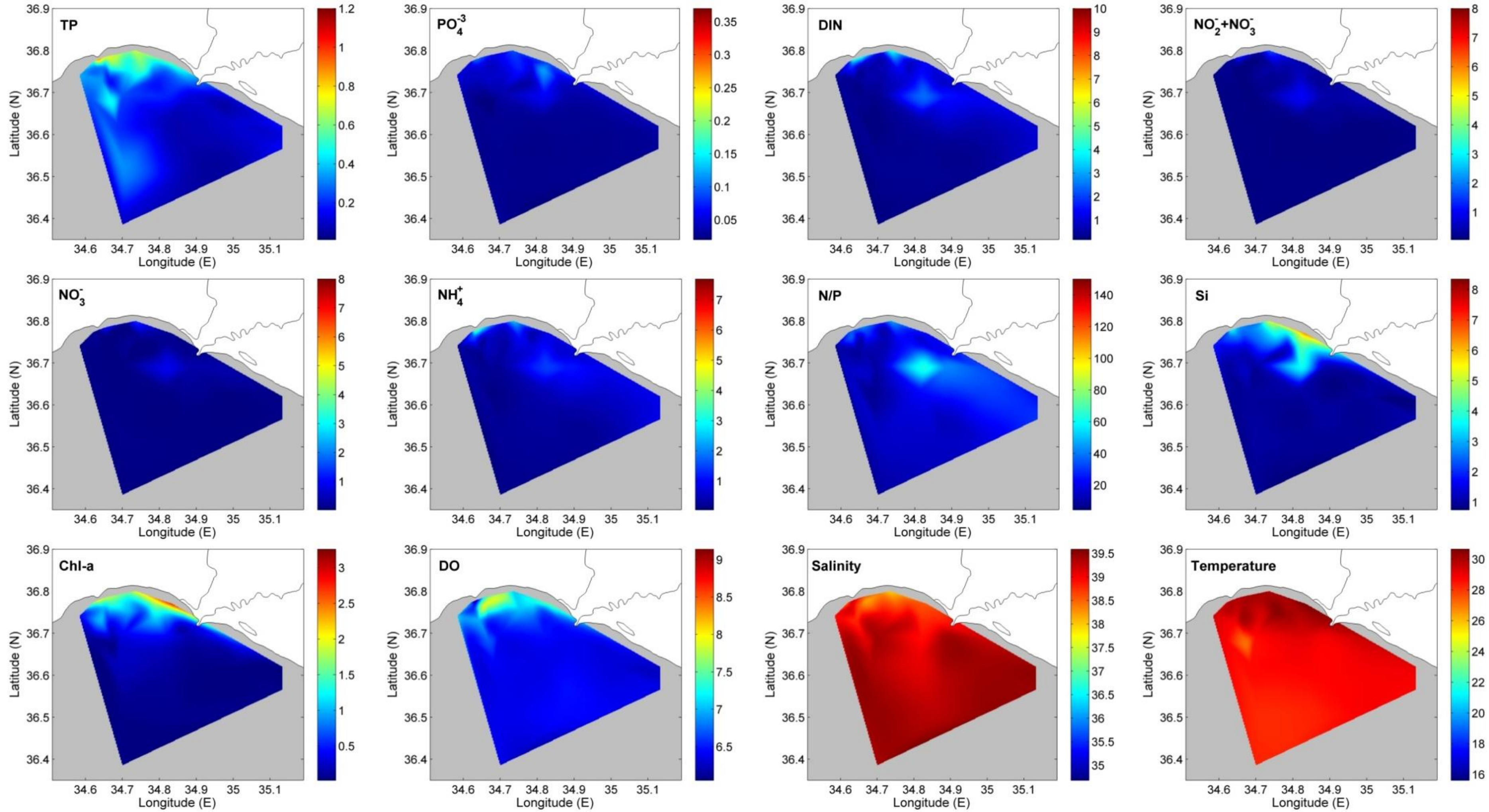

Figure 3.3. Surface distribution of summer season

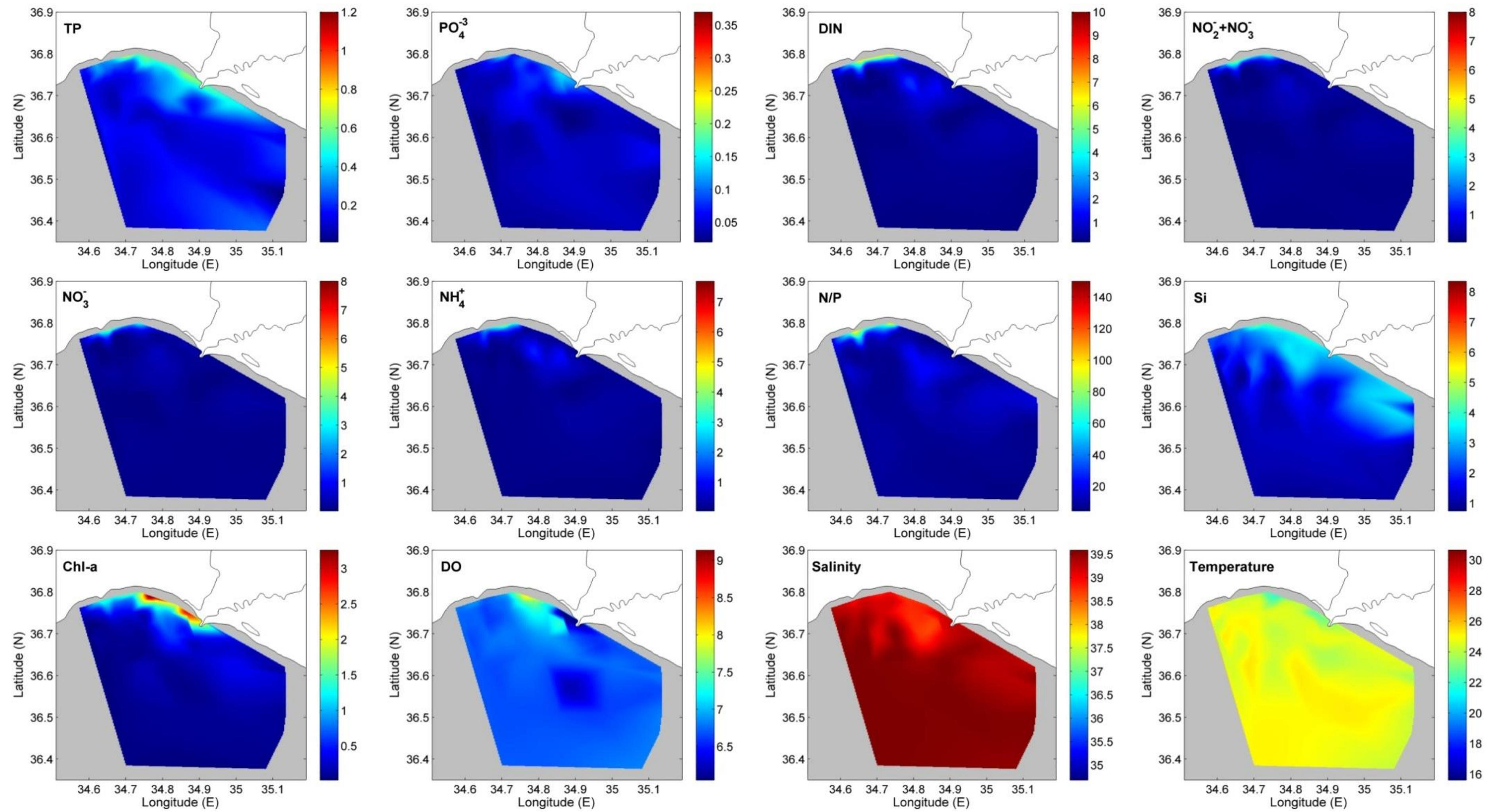

Figure 3.4. Surface distribution of autumn season

3.2. Spatial and Temporal Variations of Biochemical Parameters of Weighted Data Set

a) Macro-nutrients: In winter (Figure 3.5), surface DRP concentration varied from 0.1-0.37 µM in the nearshore zone to 0.02-0.04 µM level in the offshore waters. TP concentrations generally ranged between 0.19 and 0.76 µM in the coastal region, decreasing to 0.05-0.19 µM range in the offshore. The nitrate (in fact, NO_3^-+NO_2^-) and DIN (NO_3^-+NO_2+NH_4^+) concentrations ranged between 1-8 µM and 1.2-10 µM, respectively, in the inshore waters; they varied between 0.06-0.57 µM for nitrate and 0.22-0.71 µM for DIN in the nutrient poor offshore surface waters. Ammonium concentrations in open waters ranged between 0.06-0.46 µM, increasing to the levels of 0.27-4.80 µM in the nearshore zone. The winter N/P molar ratio spatially changed between 4.2 and 140 generally in the near-shore zone and 8.75-29 in the offshore water.

In spring, depicted in Figure 3.6, the surface TP concentrations ranged between 0.23 and 0.61 µM in the nearshore waters (<20m) whereas it declined to 0.06-0.08 µM levels in offshore waters. DRP concentration was very close to the detection limit of the method (0.02 µM) in the offshore water and increased to the levels of 0.04-0.12 µM in the nearshore waters. The concentration of DIN in coastal water was generally in the range of 0.7-6.34 µM, decreasing to 0.23-0.39 µM levels in the offshore water. Concentrations of nitrate, varied locally from 0.41-5.19 µM in river-fed nearshore water to the levels of 0.09 and 0.13 µM in open water while the ammonium generally ranged between 0.19 and 2 µM in coastal water and declined to 0.11-0.28 µM levels in the offshore zone. The N/P molar ratio varied from 11.7-71.7 range in the nearshore zone to 7.7-16.5 levels in the offshore waters. Silicate concentrations reached its peak values (8-9 µM range) at hot points in the inshore zone and declined to the levels of 0.96-1.10 µM in the offshore surface waters of the bay.

In summer, seasonal variations of surface nutrients are depicted in Figure 3.7. TP concentrations ranged between 0.3 and 0.6 µM in the nearshore zone, decreasing to the levels of 0.06-0.2 µM in the offshore zone. The summer DIN concentrations were less than the spring values (0.54-4.69 µM) in the inshore zone due to rapid consumption of limited inputs in the shallow waters. The offshore DIN values ranged between 0.07-0.14 µM in the nutrient poor offshore water. The concentration of DRP changed from 0.04-0.11 µM in the coastal zone (<50m) and decreased to 0.02-0.04 µM levels in the offshore. The ammonium generally ranged between 0.18 and 0.30 µM in the coastal water, declining slightly to 0.11-0.28 µM levels in the offshore zone. The N/P molar ratios varied spatially between 8.4 and 78.4 in the shallower coastal zone and from 10 to 20.5 in the offshore water. The summer silicate concentrations varied between 0.7 and 1.5 µM level in the offshore surface waters, exceeding 5.0 µM in the near-shore waters.

In autumn, DRP concentrations were measured in the range of 0.04-0.17 µM in the inshore waters, declining slightly to 0.02-0.04 µM in the open water. TP concentrations varied between 0.23 and 0.63 µM in the nearshore zone, whereas the offshore values ranged locally between 0.07 and 0.15 µM. DIN concentrations were as low as 0.2 µM in the offshore, increasing to the levels of 5.0-7.7 µM at hot points. Nitrate concentrations ranged locally from 0.06-0.46 µM in the salty offshore water to 0.5-5.1 µM in the near-shore zone. Ammonium values also showed regional variations from 0.06-0.34 µM in the offshore to the polluted near-shore zone levels of 0.5-3.67 µM. N/P molar ratios exceeded 80 at the nitrate-rich hot points on the coastal zone, decreasing to 5-20 levels in the offshore surface waters. Silicate concentrations were as low as 0.9-1.0 µM in the offshore surface waters, reaching 4.5 µM in the river-fed coastal surface waters (Figure 3.8).

b) Dissolved oxygen and Chl-a: DO concentrations in winter were highly variable in the terrestrial based inshore waters, ranging from 7.22-9.21 mg/L, while it declined to 7.28-7.65 mg/L levels in the offshore surface waters. Chl-*a* concentrations increased from 0.06-0.23 µg/L in the offshore to 0.37-2.47 µg/L in the coastal waters. In spring, the concentrations of DO were around 7.38 and 9.08 mg/L levels in polluted inshore waters and decreased to 7.57-7.86 mg/L in the offshore waters. The surface Chl-*a* values varied regionally between 0.56 and 1.76 µg/L in the coastal waters and decreased to 0.04-0.16 µg/L levels in the Mersin Bay. In summer, inshore water DO concentrations ranged between 6.16-7.20 mg/L, and then it decreased to 6.22-6.62 mg/L levels in the offshore waters. Surface Chl-*a* concentrations, varying locally from 0.03 to 1.84 µg/L towards the coastal zone. In autumn, DO varied between 6.05-7.50 µg/L in the coastal waters and in offshore water it decreased to 6.50-6.87 µg/L level. Chl-*a* concentration ranged between 0.04 and 0.18 µg/L in the offshore zone and varied locally in the coastal waters in the range between 0.36 and 2.83 µg/L.

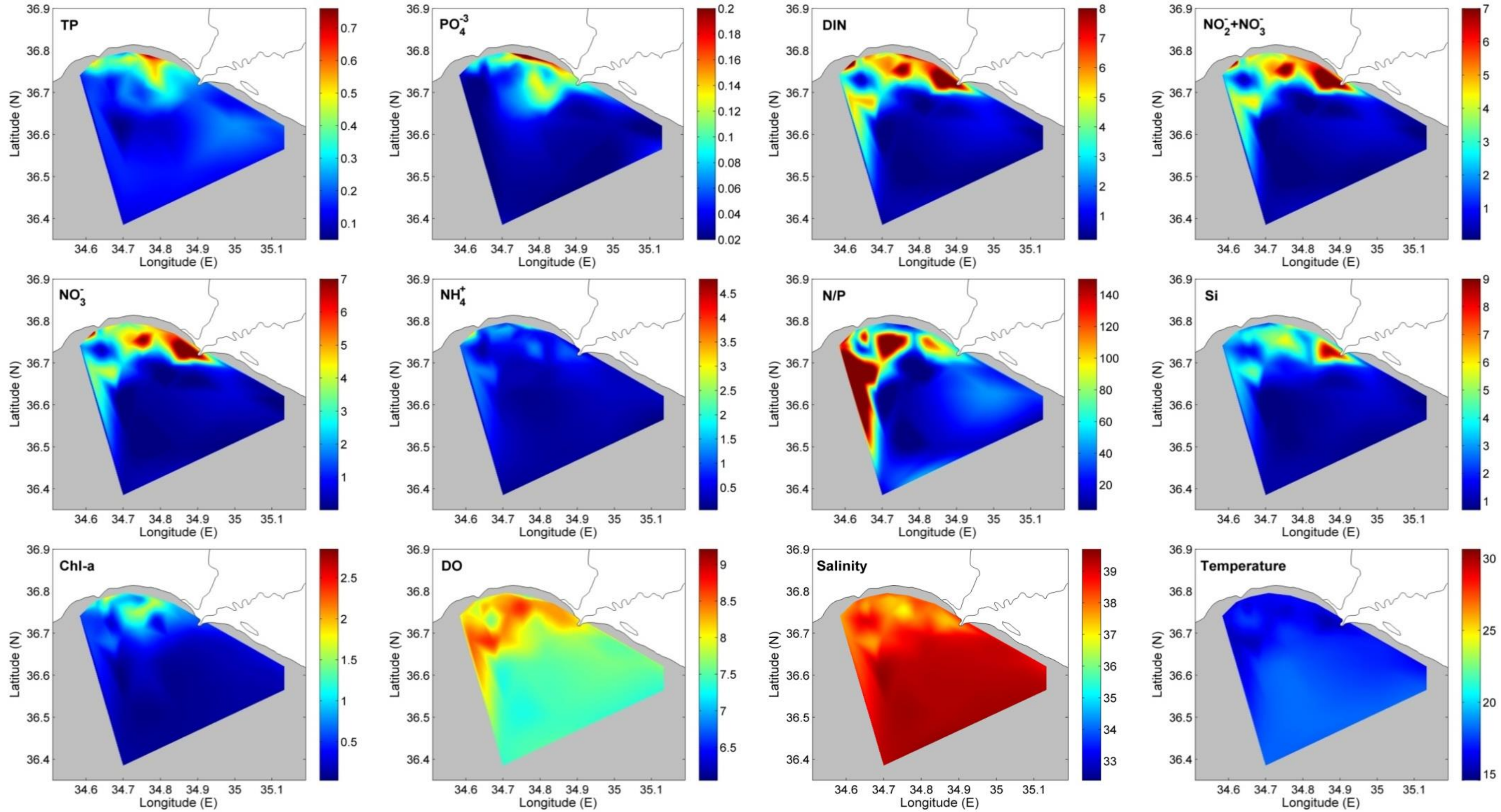

Figure 3.5. Surface distribution of winter season (weighted data between 10-90 %)

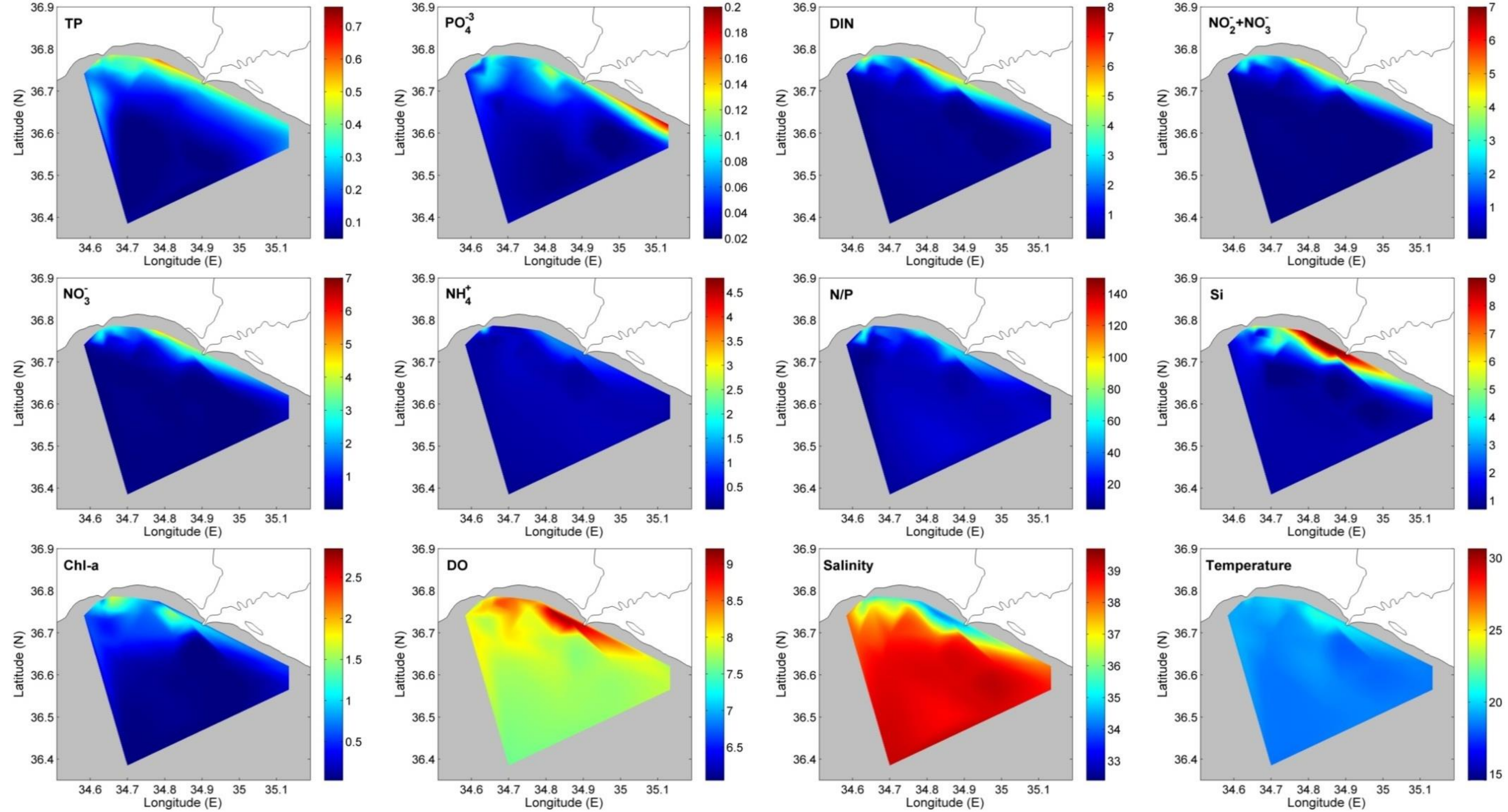

Figure 3.6. Surface distribution of spring season (weighted data between 10-90 %)

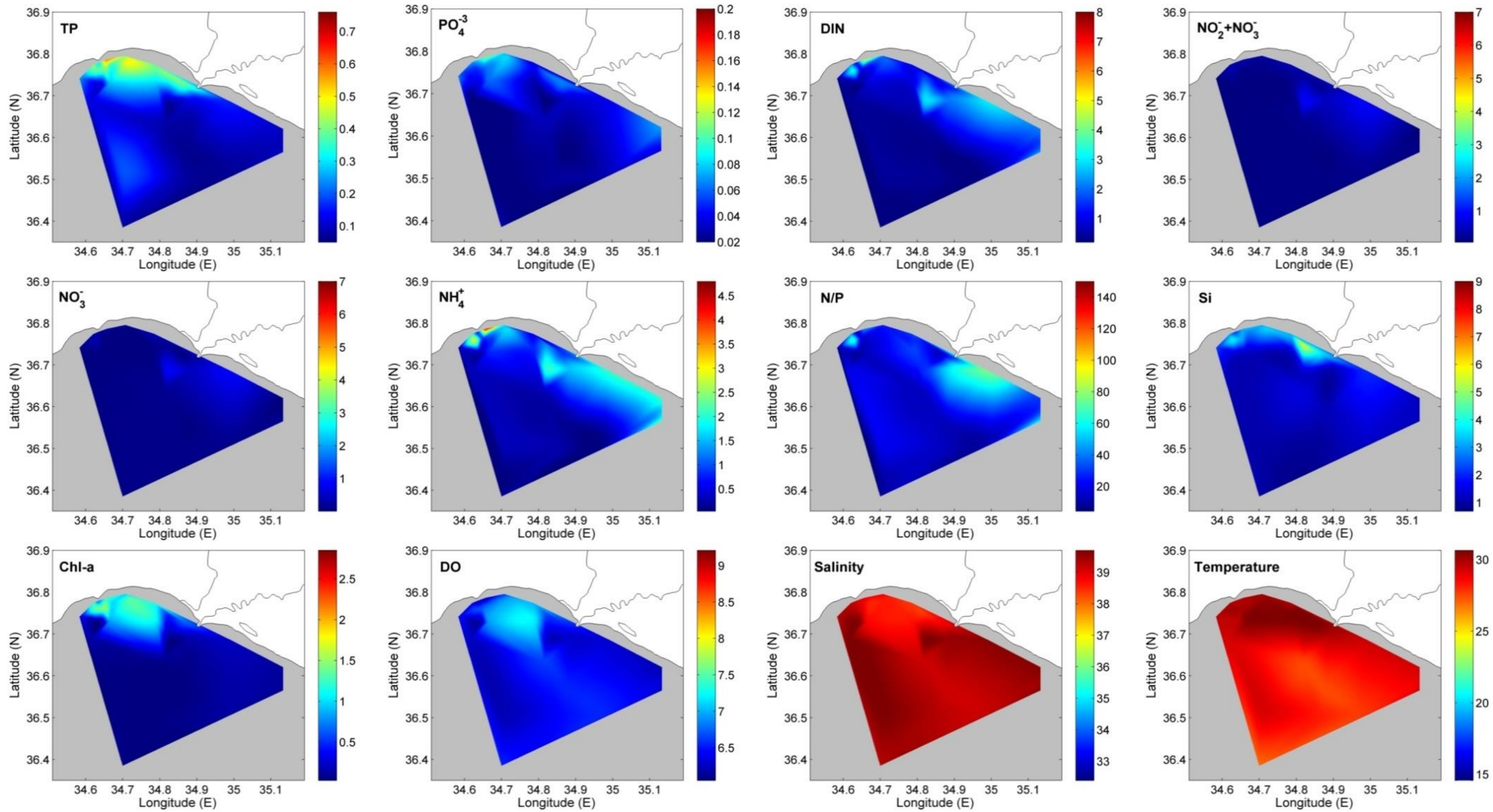

Figure 3.7. Surface distribution of summer season (weighted data between 10-90 %)

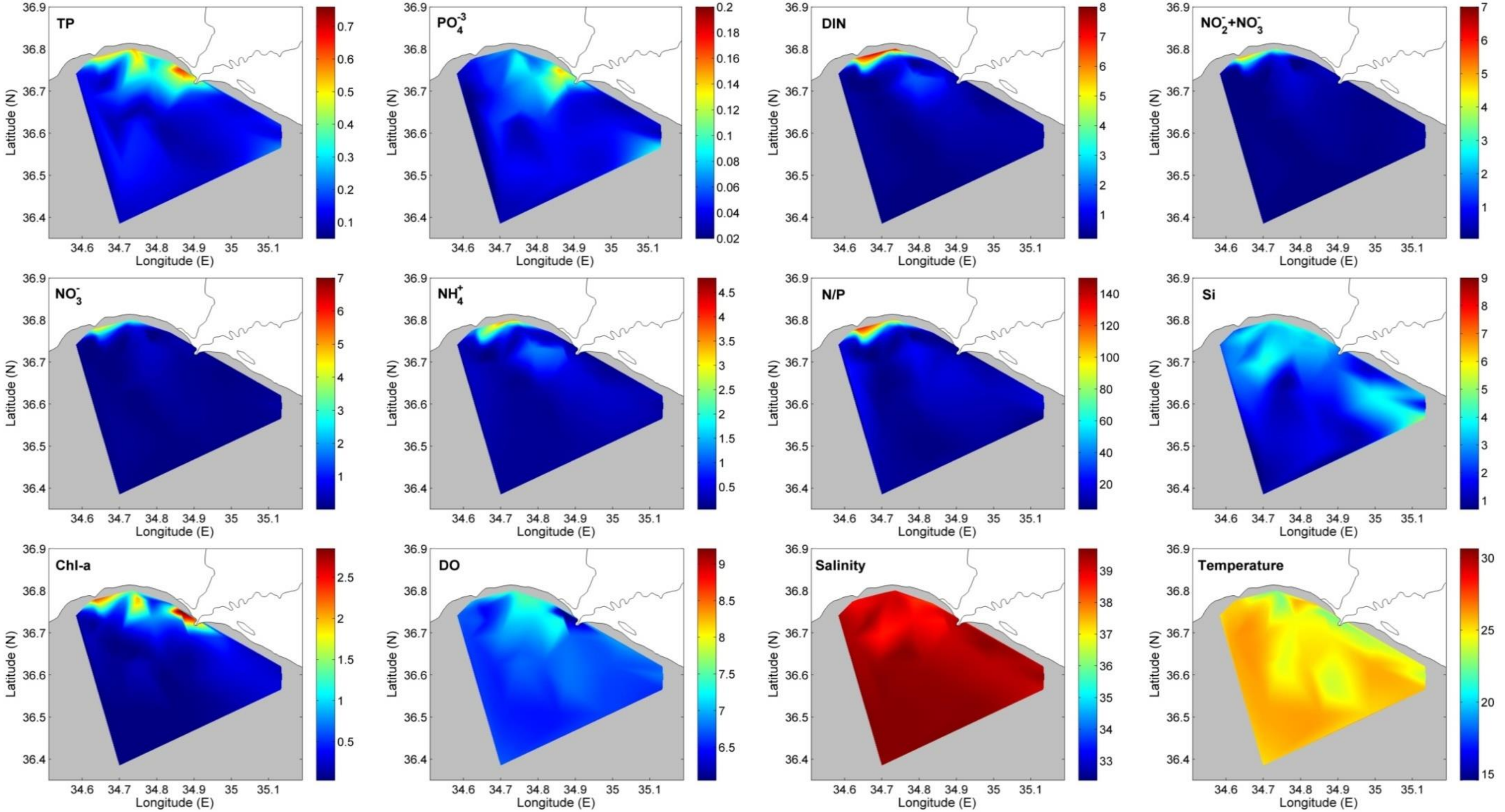

Figure 3.8. Surface distribution of autumn season (weighted data between 10-90 %)

3.3. Classification of Trophic Status According to Eutrophication Indicators

Cluster analysis is a statistical tool that allows one to group observations from a data set into clusters of similar points. Therefore, in the study this statistical approach is used to reduce cases (in other words stations), to characterize possible common vicinities. Thus, a total of 50 stations in the bay were classified according to the surface water of concentrations of TP, DIN, Chl-*a* and oxygen saturation % (aD%O: absolute % deviation from saturation), SDD (Secchi disk depth) and salinity values of each station. During the application of this technique, Ward's method and Euclidean distance were utilized to classify study area. Figure 3.9 shows a hierarchical tree plot (dendogram) obtained from cluster analysis for the Northeastern Cilician Basin of the Eastern Mediterranean. As can be seen from dendogram, three main groups were extracted from cluster analysis. Two main groups (M and O) were found to be joined to each other at the similarity level of 70% whereas group E was found distinctly different (dissimilar at the value of 0) than remain two groups (M and O). Group E was mainly consisted of stations located at inshore waters (Mersin Bay and river mouths, see Figure 3.10). Thus this group was assigned as Eutrophic (E) owning to its nutrient composition, Chl-*a*, aD%O, SDD and salinity peculiarities (Table 3.1a and Table 3.1b). On the other hand, group M was highly loaded with stations situated at water masses between inshore and offshore water types and it can be characterized as transitional zone and mesotrophic (M) respect to nutrient and Chl-*a* concentrations along with corresponding aD%O, SDD and salinity values (see Table 3.1a and Table 3.1b). The last group (O) was particularly incorporated with stations placed at open or offshore waters and it might be categorized as oligotrophic (O) since it has lowest values of trophic status indicators (see Table 3.1a and Table 3.1b). As a result of the cluster analysis 42% (21 stations), 34% (17 stations) and 24% (12 stations) of the 50 stations were determined as eutrophic, mesotrophic and oligotrophic stations, respectively.

Locations of the grouped stations according to cluster analysis in the region are given (red=Eutrophic, green=Mesotrophic, blue=Oligotrophic) in Figure 3.10. It is clearly visible that the effects of the river in the region are limited to interior bay rather than affecting the whole area.

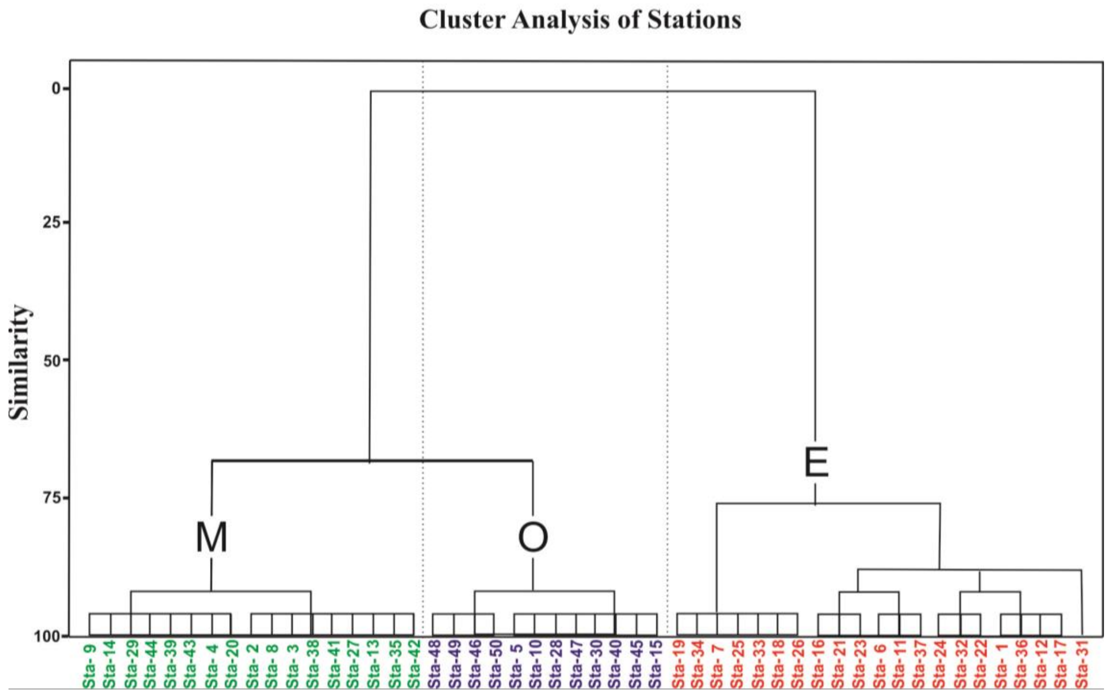

Figure 3.9. Dendogram for cluster analyses of 50 stations applying their TP, DIN, Chl-*a*, aD%O, SDD and salinity values. Linkage rule: Ward's method, Distance measure: Euclidean, E: Eutrophic, M: Mesotrophic, O: Oligotrophic

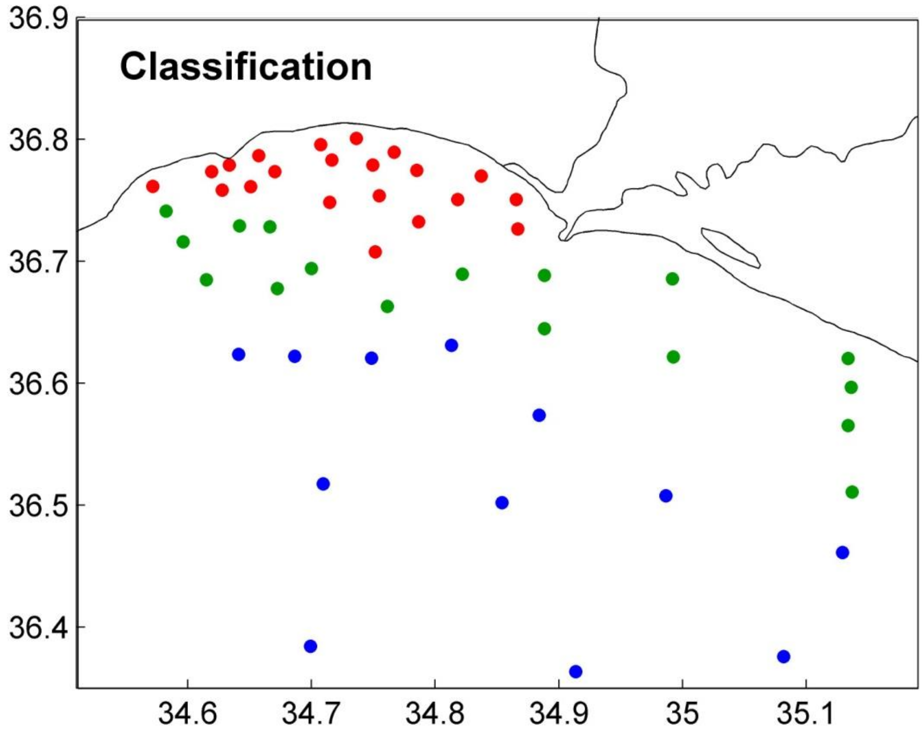

Figure 3.10. Locations of classified stations in the Mersin Bay according to cluster analysis using TP, DIN, Chl-*a*, aD%O, SDD and Salinity. Eutrophic (red), Mesotrophic (green) and Oligotrophic (blue) water bodies

Table 3.1a. Raw data sets of Eutrophic, Mesotrophic and Oligotrophic water masses of the Cilician Basin

Eu	**TP**	**PO_4^{3-}**	**DIN**	**NO_2^-+NO_3^-**	**NO_2^-**	**NO_3^-**	**NH_4^+**	**Chl-*a***	**aD%O**	**DO (%)**	**DO**	**SDD**	**DIN/PO_4^{3-}**	**Si**
Min	0.08	0.02	0.27	0.06	0.02	0.02	0.13	0.11	0.09	87.88	6.05	1.00	4.21	0.80
Max	1.47	0.49	44.06	21.30	1.86	19.44	22.76	6.69	66.14	166.14	10.27	12.00	528.00	14.20
Ave	0.45	0.10	4.83	3.24	0.28	2.96	1.60	1.31	9.48	108.86	7.66	3.42	56.19	3.73
Stdev	0.23	0.07	5.74	4.02	0.25	3.82	2.53	1.11	9.64	10.22	0.86	1.71	71.63	2.16
N	168	168	168	168	168	168	168	168	168	168	168	168	168	168
Meso	**TP**	**PO_4^{3-}**	**DIN**	**NO_2^-+NO_3^-**	**NO_2^-**	**NO_3^-**	**NH_4^+**	**Chl-*a***	**aD%O**	**DO (%)**	**DO**	**SDD**	**DIN/PO_4^{3-}**	**Si**
Min	0.04	0.02	0.17	0.05	0.01	0.01	0.04	0.02	0.004	95.18	6.18	1.50	4.63	0.66
Max	0.83	0.19	10.60	10.22	0.69	9.67	2.38	2.80	34.55	134.55	8.93	18.00	519.00	11.14
Ave	0.20	0.05	1.73	1.24	0.12	1.12	0.49	0.37	5.19	104.99	7.32	6.58	43.49	2.23
Stdev	0.13	0.03	2.45	2.24	0.14	2.13	0.57	0.41	6.20	6.37	0.74	3.09	71.08	1.88
N	130	130	130	130	130	130	130	130	130	130	130	130	130	130
Oligo	**TP**	**PO_4^{3-}**	**DIN**	**NO_2^-+NO_3^-**	**NO_2^-**	**NO_3^-**	**NH_4^+**	**Chl-*a***	**aD%O**	**DO (%)**	**DO**	**SDD**	**DIN/PO_4^{3-}**	**Si**
Min	0.01	0.02	0.11	0.05	0.02	0.02	0.05	0.001	0.04	87.90	5.66	6.00	3.67	0.69
Max	0.48	0.08	6.57	6.31	0.30	6.05	1.00	0.98	21.15	121.15	8.20	29.00	219.00	8.45
Ave	0.12	0.03	0.50	0.29	0.06	0.23	0.22	0.14	4.17	103.64	7.13	17.24	18.81	1.16
Stdev	0.08	0.01	0.75	0.73	0.06	0.69	0.17	0.16	5.72	6.07	0.58	5.46	26.92	0.89
N	80	80	80	80	80	80	80	80	80	80	80	80	80	80

TP, PO_4^{3-}, DIN, NO_2^-+NO_3^-, NO_2^-, NO_3^-, NH_4^+, Si concentrations = μM

Chlorophyll-*a* (Chl-*a*) = μg/L

Dissolved Oxygen (DO) = mg/L

DO (%) = Deviation from saturation value

aD%O = Oxygen as absolute % deviation from saturation

Secchi Disc Depth (SDD) = meter (m)

Table 3.1b. Weighted data sets between 10% and 90% of Eutrophic, Mesotrophic and Oligotrophic water masses of the Cilician Basin

Eu (10-90)	**TP**	**PO_4^{3-}**	**DIN**	**$NO_2^-+NO_3^-$**	**NO_2^-**	**NO_3^-**	**NH_4^+**	**Chl-*a***	**aD%O**	**DO (%)**	**DO**	**SDD**	**DIN/PO_4^{3-}**	**Si**
Min	0.19	0.02	0.54	0.09	0.03	0.02	0.19	0.36	1.00	87.88	6.05	1.00	4.21	1.35
Max	0.76	0.37	12.81	11.93	0.69	11.27	4.80	2.83	19.19	119.19	9.21	6.00	528.00	9.30
Ave	0.40	0.09	3.99	2.83	0.24	2.59	1.16	1.14	8.90	108.25	7.69	3.29	57.91	3.91
Stdev	0.12	0.05	3.10	2.79	0.15	2.67	0.99	0.54	4.83	5.87	0.81	1.01	73.74	1.91
N	86	86	86	86	86	86	86	86	86	86	86	86	86	86
Meso (10-90)	**TP**	**PO_4^{3-}**	**DIN**	**$NO_2^-+NO_3^-$**	**NO_2^-**	**NO_3^-**	**NH_4^+**	**Chl-*a***	**aD%O**	**DO (%)**	**DO**	**SDD**	**DIN/PO_4^{3-}**	**Si**
Min	0.09	0.02	0.28	0.06	0.02	0.01	0.04	0.08	0.55	95.18	6.18	3.00	4.63	0.69
Max	0.36	0.19	5.55	4.72	0.69	4.05	2.38	0.80	15.01	115.01	8.82	11.00	269.00	5.24
Ave	0.18	0.05	1.27	0.72	0.10	0.62	0.54	0.32	4.11	103.81	7.29	6.39	36.28	2.02
Stdev	0.07	0.03	1.37	1.09	0.14	0.97	0.59	0.19	3.93	4.23	0.71	2.41	51.55	1.13
N	59	59	59	59	59	59	59	59	59	59	59	59	59	59
Oligo (10-90)	**TP**	**PO_4^{3-}**	**DIN**	**$NO_2^-+NO_3^-$**	**NO_2^-**	**NO_3^-**	**NH_4^+**	**Chl-*a***	**aD%O**	**DO (%)**	**DO**	**SDD**	**DIN/PO_4^{3-}**	**Si**
Min	0.05	0.02	0.20	0.06	0.02	0.03	0.06	0.04	0.55	98.48	6.22	8.00	5.00	0.69
Max	0.20	0.08	0.71	0.57	0.30	0.41	0.46	0.23	13.57	113.57	7.86	29.00	29.00	2.60
Ave	0.10	0.03	0.36	0.16	0.05	0.11	0.21	0.09	2.30	101.91	7.07	17.79	12.60	1.12
Stdev	0.04	0.01	0.12	0.12	0.05	0.09	0.09	0.05	2.41	2.74	0.51	5.55	5.26	0.39
N	37	37	37	37	37	37	37	37	37	37	37	37	37	37

TP, PO_4^{3-}, DIN, $NO_2^-+NO_3^-$, NO_2^-, NO_3^-, NH_4^+, Si concentrations = µM
Chlorophyll-*a* (Chl-*a*) = µg/L
Dissolved Oxygen (DO) = mg/L
DO (%) = Deviation from saturation value
aD%O = Oxygen as absolute % deviation from saturation
Secchi Disc Depth (SDD) = meter (m)

Table 3.1a and Table 3.1b demonstrates the statistical summary of raw data before (a) and after (b) of the exclusion of outliers for three distinct water masses namely: eutrophic, mesotrophic and oligotrophic. The table are also included average arithmetic means for (TP, DIN, Chl-*a*, aD%O) along with corresponding standard deviations, minimum and maximum values in the selected sites. It is clear from the table that, the values for measured parameters were related to the origin of the water masses with an apparent tendency of gradual increase from oligotrophic to eutrophic for nutrients, Chl-*a*, aD%O and steady decrease in SDD and salinity from the oligotrophic offshore to the eutrophic coastal zone. Moreover, Kruskal-Wallis (K-S) test was applied in order to explore for the presence of significant difference in nutrient composition, Chl-*a*, aD%O, SDD and salinity. In terms of aforementioned parameters, the K-W test for raw and weighted data showed that there was a statistically significant ($p<0.001$) difference in eutrophic, mesotrophic and oligotrophic water types. As an example, the box-plot diagrams are presented in Figure 3.11 for weighted data set. For instance, the arithmetic mean TP concentration in the eutrophic water type (0.40 μM) was almost 2 and 4 times higher than those observed for mesotrophic (0.18 μM) and oligotrophic (0.10 μM) water types, respectively. The mean DIN value in the eutrophic waters (3.99 μM) was found to be 3 to 10 time higher compared to concentrations detected in the mesotrophic (1.27 μM) and the oligotrophic (0.36 μM) water bodies. Expectedly, similar trends appeared in Chl-*a* and aD%O, with average values decreasing in the order eutrophic>mesotrophic>oligotrophic. The mean value of Chl-*a* for the eutrophic sites (1.14 μg/l) was found around 2 times higher than that of the mesotrophic waters (0.32 μg/l) whereas ten-fold decrease in the concentration of Chl-*a* was monitored from the inshore to the offshore water bodies (0.09 μg/l). The calculated mean aD%O value for the oligotrophic water type (2.3) was found substantial lower (~2 to ~4 times, respectively) than those observed for the mesotrophic (4.11) and the eutrophic water bodies (8.9).

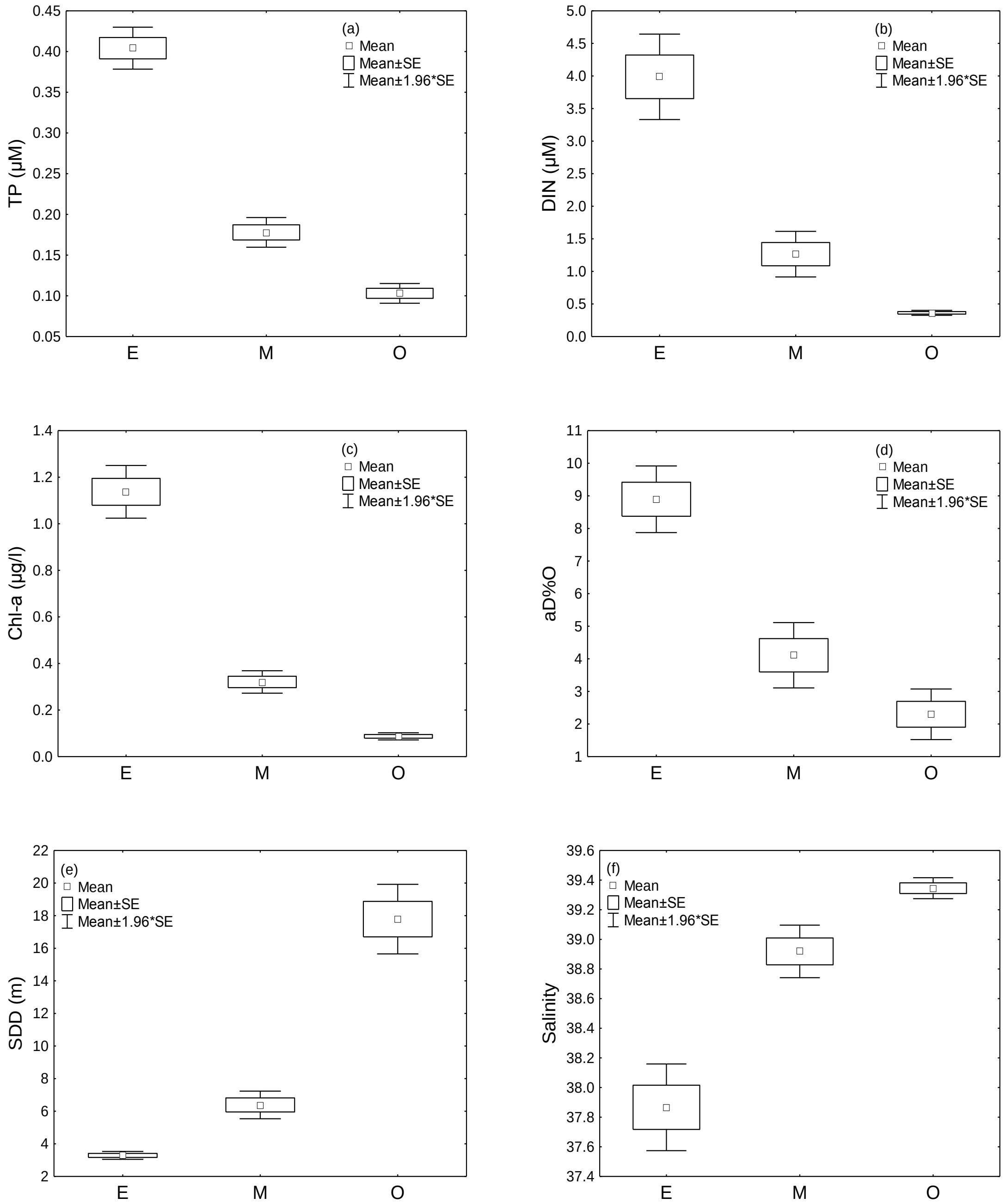

Figure 3.11. Box-plot diagrams for weighted data set; (a) TP, (b) DIN, (c) Chl-*a*, (d) aD%O, (e) SDD, (f) Salinity

After the removal of inconsistent values from data sets (those standing out of 10-90%), the nutrient frequency distribution profiles drawn are given in Figure 3.12. Especially, tendency of frequency distribution of DIN and nitrate parameters to right, is an indication that there is a need for data transformation in order to approach to normal distribution. As for transformation method, logarithmic transformation was applied and the results found to be sufficient. Frequency distributions of the transformed data sets are given in Figure 3.13.

Frequency distribution profiles, and mean values (μ) and standard deviation (σ) values of parameters were used as a basis to point out interpretations. Mean (μ) and standard deviation (σ) values of logarithmic transformation parameters were used to determine the concentration scales of nutrients after back-transformation. In scales, (μ) has been referred as origin, and +σ was referred as increase in the scale (see Table 3.2).

Average TP concentration (0.39 μM) in the eutrophic waters is 4 times more than the average TP concentration (0.10 μM) in the oligotrophic waters, and 2 times more than concentration (0.165 μM) in the mesotrophic surface waters in the central bay. When DIN concentration is considered, the average concentration for the eutrophic waters (2.9 μM) is about 4 times greater than that for the mesotrophic waters (0.84 μM), and 8.5 folds the oligotrophic value (0.34 μM).

According to eutrophication evaluation study in the Mersin Bay; the frequency distribution of normalized nutrient can be used to assess water quality of the NE Mediterranean and long-term changes in the marine ecosystem. The data range of nutrients that are produced in statistical terms represent the "typical" structure of the eastern Mediterranean which is characterized with low phosphate concentrations. Also, water masses that get richer with various nutrient sources might lead to a universal method of application through the use of this kind of classification (Ignatiades *et al.*, 1992).

Table 3.2. Computation of the ranges on the basis of mean (μ) and standard deviation (σ) of each nutrient for the different water types

Water Types	Nutrient	(μ)	(σ)	μ and μ+σ range	μ+σ and μ+2σ range	μ+2σ and μ+3σ range
Eutrophic	TP	0.39	0.13	0.39-0.52	0.52-0.65	0.65-0.79
	DIN	2.88	0.37	2.88-3.25	3.25-3.62	3.62-3.99
	Chl-*a*	1.02	0.20	1.02-1.22	1.22-1.43	1.43-1.63
Mesotrophic	TP	0.17	0.17	0.17-0.33	0.33-0.50	0.50-0.67
	DIN	0.84	0.37	0.84-1.21	1.21-1.58	1.58-1.95
	Chl-*a*	0.27	0.29	0.27-0.55	0.55-0.84	0.84-1.13
Oligotrophic	TP	0.10	0.15	0.10-0.25	0.25-0.40	0.40-0.55
	DIN	0.34	0.14	0.34-0.48	0.48-0.62	0.62-0.76
	Chl-*a*	0.07	0.22	0.07-0.29	0.29-0.51	0.51-0.73

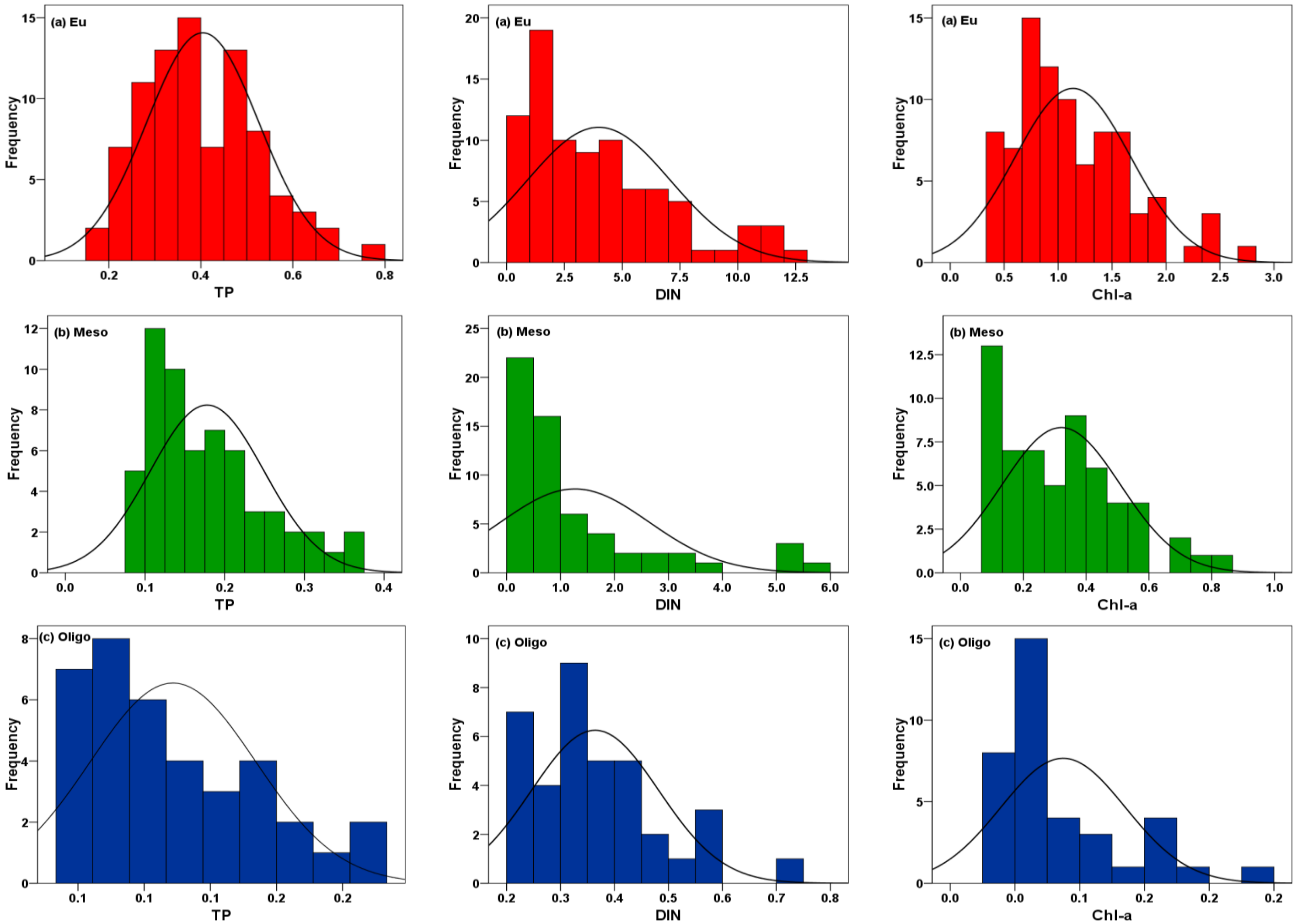

Figure 3.12. Nutrient frequency distributions of the raw data (after exclusion of outliers)

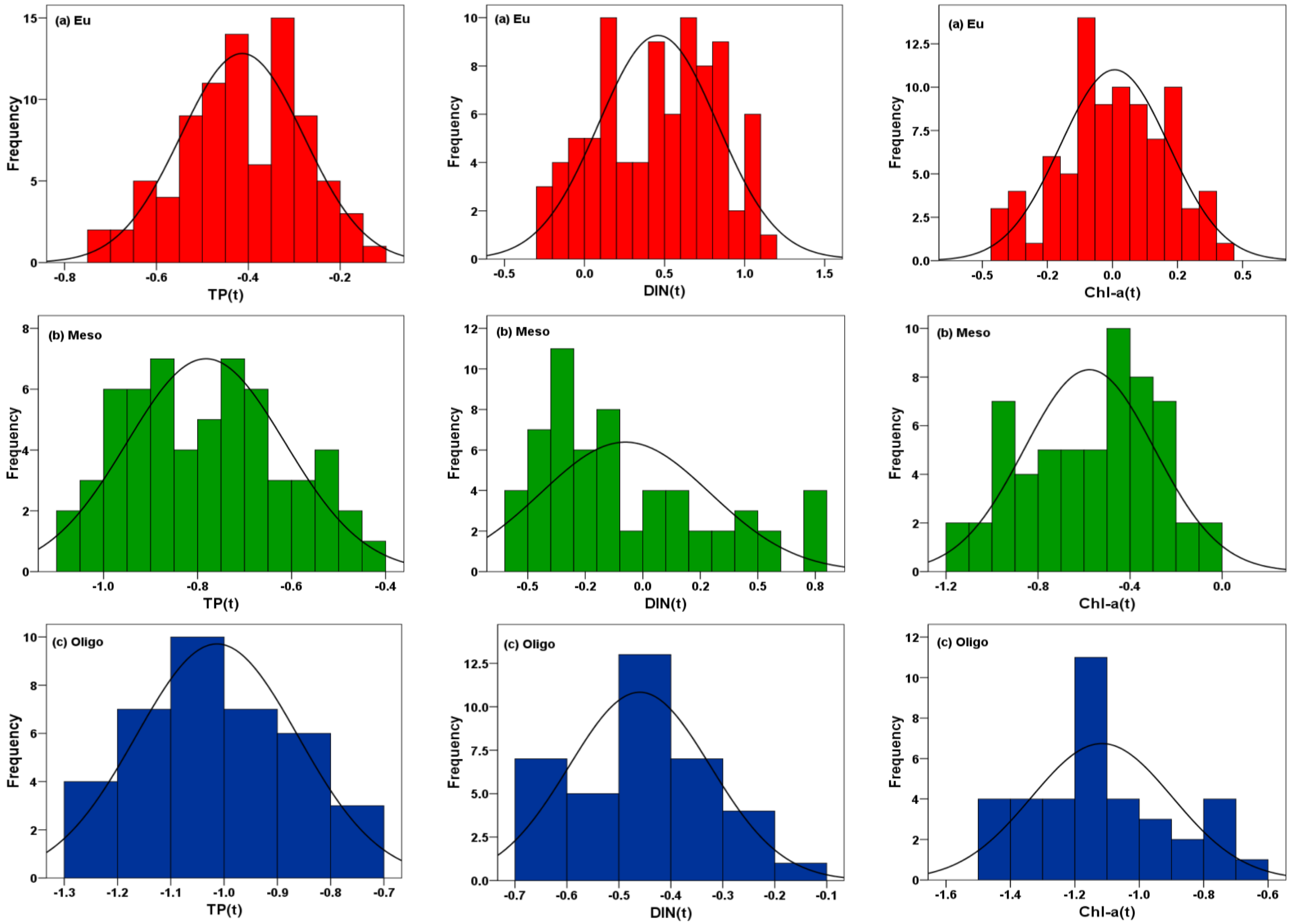

Figure 3.13. Nutrient frequency distributions of transformed data (after log-transformation)

3.4. Assessment of TRIX-based Trophic Index (TRIX-IMS)

In the last 30 years, different indicators have been developed by several authors for the classification of trophic status of the freshwater and coastal water systems, based on the phosphorus, nitrogen and also Chl-*a* concentrations (Vollenweider *et al.*, 1998; EEA, 2001; Nasrollahzadeh *et al.*, 2008 and references therein). Although the general concept of eutrophication emphasizes the relationship between nutrient input and ecosystem response in terms of the growth of phytoplankton and higher forms of plant life, this relationship varies depending on many parameters. The temporal variability of physical factors plays a critical role in controlling the biological response to nutrient enrichment. Moreover, spatial variability also plays an important role both alongshore and from inshore to offshore waters. For example, nutrient inputs and biological responses in coastal waters which are not strongly influenced by river run-off or point sources are likely to be different from those in coastal waters adjacent to river mouths or sewage outlets (Painting *et al.*, 2005). These kind of regional differences and the usage of different indicators cause some inconsistencies in adopting methods and assessing the trophic level. It is evident that assuming the presence of universally specific indicator or scale and/or believing that one single indicator or index is sufficient to carry out practice will lead to failure.

In developing the trophic index (TRIX) the following principles are highly expected to provide: (i) the component variables of the index should be meaningful with respect to both production and production dynamics; (ii) they should cover main causal factors; (iii) they should be routine measurements in most marine surveys (Vollenweider *et al*., 1998). The TRIX developed by Vollenweider et al. (1998) aggregates nutrients as a pressure, Chl-*a* (indicator of biomass) as a biological response and oxygen as an environmental disturbance in the water quality (Pettine *et al.*, 2007). As mentioned in chapter 1.5, the TRIX index includes 4 eutrophication related parameters and assesses the results with a single number, ranging between 0-10. These two pecularities make the TRIX more useful in quantifying environmental quality (Primpas and Karydis, 2010). Putting log transformation into application for 4 parameters suppresses the high and low values of the data set and reduces the importance of high values compared to the smaller values (Primpas and Karydis, 2010 and references therein). As the scale of TRIX application of which details and calculation balance are given in the previous chapter was developed for productive coastal waters, problems appeared when the TRIX-based classification was applied in different regions. Previously, while the applicability of the TRIX index into different study regions was examined by carrying out comparisons (Nasrollahzadeh *et al.*, 2008; Primpas and Karydis, 2010), adaptation of the TRIX index according to the biochemical features of study regions was needed in order to come up with more precise identification of trophic levels of different areas. For example, principle bio-chemical features of the Eastern Mediterranean open waters are very different from those of the Adriatic Sea. The oligotrophic peculiarity of the North Adriatic (TP=0.29 μM, DIN=4.5 μM, Chl-*a*=1.7 μg/L) (Vollenweider *et al.*, 1998) is quite different from both those of the Aegean (DIN=1.56 μM, Chl-*a*=0.1μg/L) (Primpas and Karydis, 2010) and the NE Mediterranean Sea (TP=0.10 μM, DIN=0.36 μM, Chl-*a*=0.09 μg/L). Thus, considering the physical and biochemical features of the coastal areas regarded as polluted (eutrophic) and of the basic features of the Eastern Mediterranean, a study was carried out by using the outcomes obtained throughout seasonal measurements between 2008-2011 in the Mersin Bay (at about 50 stations) in order to adopt the conventional TRIX-equation for the Eastern Mediterranean.

For the each parameter, the upper and lower limits of parameters can be defined according to the data distribution (Table 3.3). In the previous studies, some scientists used the mean±2.5 standard deviation ranges in order to define the maximum and minimum values (Vollenweider *et al.*, 1998, Pettine *et al.*, 2007, Nasrollahzadeh *et al.*, 2008). However, in the present study the data set between 10% and 90% were chosen to focus on the sites from highly impacted to slightly impacted (outside the highly polluted hot points) but still keeping its oligotrophic properties compared to the open sea. Therefore, it is desired to exclude extreme values that rarely occur in the hot points. In that way, it is aimed to reduce the risk of having a large statistical range (Vollenweider *et al.*, 1998).

$$TRIX = [\log(Chl - a * aD\%O * DIN * TP) - b]/a$$

Chl-*a* = Chlorophyll-*a*, as μg /L;
aD%O = Oxygen as absolute % deviation from saturation; [abs│100-%O│]
DIN = Dissolved inorganic nitrogen (NO_3-N+NO_2-N+NH_4-N), as μg/L
TP = Total phosphorus, as μg/L
“a” and “b” = site specific coefficient

The presence of decreasing trends, in Table 3.3, were determined in terms of TP, DIN, Chl-*a* and aD%O from the nearshore water to the offshore water. The average TP (0.4 μM) and aD%O (8.9) values in the eutrophic water body were about 2 times and 4 times greater than those in the mesotrophic (TP=0.18 μM and aD%O= 4.11) and oligotrophic (TP=0.1 μM and aD%O= 2.3) water bodies. The mean value of DIN concentration (3.99 μM) in the eutrophic water body was 3 times higher than that in the mesotrophic (1.27 μM) and 10-folds the oligotrophic (0.36 μM) water bodies. The biomass indicator, Chl-*a* concentration, in the eutrophic water (1.14 μg/L) was 4 times and 13 times higher than that in the mesotrophic (0.32 μg/L) and oligotrophic (0.09 μg/L) water bodies.

Table 3.3. Raw (original) data set of the Mersin Bay obtained 2008-2011 and statistical summary table belonging to processed data set of which 10-90 % has been considered

a) Raw data from three standard sets of data					b) Data between 10% and 90% of raw data				
Variables	Max	Min	Mean	Std. Dev	Variables	Max	Min	Mean	Std. Dev
Eutrophic Water Body (N=168)					Eutrophic Water Body (N=86)				
TP (μM)	1.47	0.08	0.45	0.23	TP (μM)	0.76	0.19	0.4	0.12
DIN (μM)	44.06	0.27	4.83	5.74	DIN (μM)	12.81	0.54	3.99	3.1
Chl-*a* (μg/L)	6.69	0.11	1.31	1.11	Chl-*a* (μg/L)	2.83	0.36	1.14	0.54
aD%O	66.14	0.09	9.48	9.64	aD%O	19.19	1	8.9	4.83
Mesotrophic Water Body (N=130)					Mesotrophic Water Body (N=59)				
TP (μM)	0.83	0.04	0.2	0.13	TP (μM)	0.36	0.09	0.18	0.07
DIN (μM)	10.6	0.17	1.73	2.45	DIN (μM)	5.55	0.28	1.27	1.37
Chl-*a* (μg/L)	2.8	0.02	0.37	0.41	Chl-*a* (μg/L)	0.8	0.08	0.32	0.19
aD%O	34.5	0.004	5.2	6.2	aD%O	15.01	0.55	4.11	3.93
Oligotrophic Water Body (N=80)					Oligotrophic Water Body (N=37)				
TP (μM)	0.48	0.01	0.12	0.08	TP (μM)	0.19	0.05	0.1	0.04
DIN (μM)	6.57	0.11	0.5	0.75	DIN (μM)	0.71	0.20	0.36	0.12
Chl-*a* (μg/L)	0.98	0.001	0.14	0.16	Chl-*a* (μg/L)	0.23	0.04	0.09	0.05
aD%O	21.15	0.04	4.17	5.72	aD%O	13.6	0.55	2.3	2.41

In the Mersin Bay, the ranges of four eutrophication related variables, in Table 3.4, during the study period were determined to be 0.04-2.83 μg/L, 0.55-19.19, 0.2-12.81 μM and 0.05-0.76 μM for Chl-*a*, aD%O, DIN and TP, respectively. After determining the lower and the upper limits of each parameter, minimum and the maximum logarithmic units were calculated (the units of DIN and TP should be turned from μM to μg/L). The ranges of logarithmic units were divided to 10 to fixing the number of the classes. The sum of the minimum logarithmic units and sum of the step ranges that is divided to 10 were used as a "b" and "a" coefficients. These coefficients were calculated as -1.049 and 0.641, specific to the Cilician Basin.

Table 3.4. Definition of the proposed trophic index: lower and upper limits, and range within which the trophic index is defined (TRIX-IMS) for the NE Mediterranean

Parameters	Min log units	Max log units	Range of log units	Step range/ 10
1.Chlorophyll-*a*	– 1.456 (0.035)	0.452 (2.832)	1.908	0.191
2. aD%O abs[100-%O]	– 0.264 (0.545)	1.283 (19.19)	1.547	0.154
3.Dissolved Inorganic Nitrogen [N(NO_3^-+NO_2^-+NH_4^+)]	0.447 (2.8)	2.253 (179.34)	1.806	0.181
4.Total Phosphorus [TP]	0.224 (1.674)	1.374 (23.684)	1.150	0.115
Sum of logs of the parameters	– 1.049	5.362	6.411	0.641

$$\boldsymbol{TRIX-IMS} = (\log\,(Chl-a * aD\%O * DIN * TP) - (-1.05))/0.64$$

Frequency distributions of the TRIX-IMS variable values determined for the eutrophic, mesotrophic and oligotrophic sites of the Mersin Bay on the shelf zone of the Cilician Basin (Figure 3.14). It was determined each display apparent peak and the value of 7.2 (E), 4.2 (M) and 2.1 (O) that separated from each other.

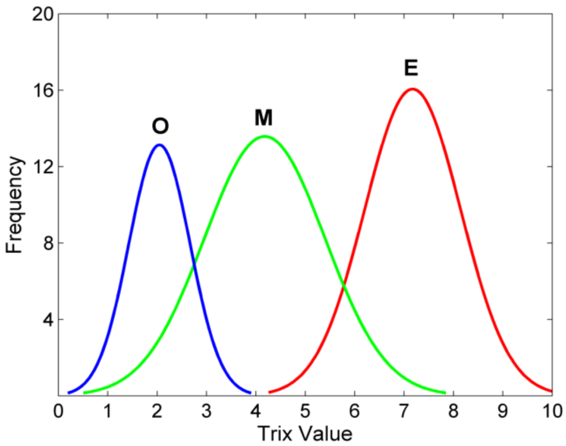

Figure 3.14. Frequency distribution of the TRIX-IMS values from the three standard sets of data), O-oligotrophic, M-mesotrophic, E-eutrophic water mass

It should be noted that the TRIX-IMS scale with different constant values derived from the Mersin Bay data set in the present study is the first application to the NE Mediterranean coastal waters. It seems possible to produce a more reliable and applicable trophic index scale provided that the systematic of data set are increased in the region. The TRIX parameters of TP, DIN, Chl-*a* and aD%O, were measured seasonally between 2008 and 2011. The seasonal and 4-year averages of the TRIX-IMS values are depicted in Figure 3.15. TRIX-IMS values in the inshore waters of the bay are strongly increases with terrestrial inputs. In the oligotrophic offshore waters the TRIX-IMS values were less than 3, whereas the TRIX-IMS range were generally over 5 in the eutrophic coastal waters. The scale ranges show gradual regional increases from 0.5-3.9 in the oligotrophic zone to 4.9-9.1 in the eutrophic zone. Although the seasonal ranges do not show significant differences, seasonal average values vary between 4.3 and 5.6 in the whole area. The surface TRIX-IMS values, in winter, ranged between 5.7 and 9.1 in the nearshore waters (<20m) whereas they decreased to 1.3-2.6 levels in the open waters (>50m). The values of spring varied locally from 6.4-8.5 in the river-fed nearshore (<20m in depth) water to the levels of 1.3-3.2 in the offshore water (>50m) while the values of summer changed between 4.9 and 7.7 in the coastal water and declined to 1.9-2.6 levels in the offshore zone. The surface TRIX-IMS values in autumn varied between 5.3 and 8.4 in the nearshore waters, declining to the levels of 0.5-2.7 in the oligotrophic open waters (>50m in depths).

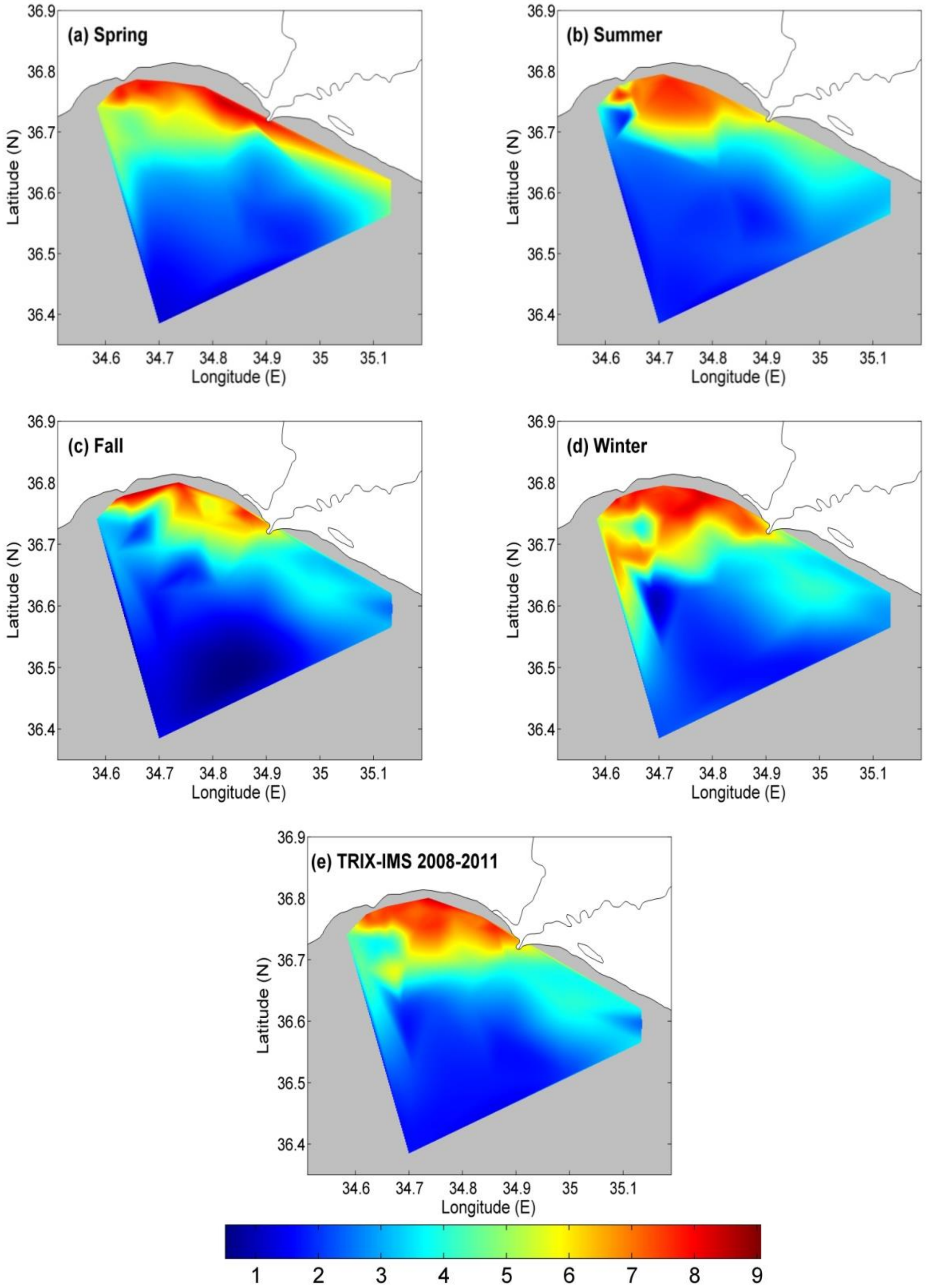

Figure 3.15. TRIX-IMS distribution in the Cilician Basin surface waters: (a) Spring, (b) Summer, (c) Fall, (d) Winter, (e) 4-year mean of the TRIX-IMS between September 2008-February 2011

3.5. Unscaled Trophic Index (UNTRIX)

In the application of the Water Framework Directive (WFD), the selection of reference sites is important for attaining a final classification of trophic status, since a large natural variability characterizes marine-coastal waters as a function of their specific trophic dynamics. The application of the WFD for the region of Roskilde Fjord in Denmark, has obviously shown that local reference conditions highly influence the ecological status classification, as they result from standard representative for undisturbed conditions in that area and related acceptable deviations (Pettine *et al.*, 2007 and references therein). This undisturbed condition varies from one region to another due to the difference in internal dynamics. For this goal, reference stations (Sta 28, 39 and 41) were chosen in the outer bay (depth>40m), according to its basic biochemical and spatial specifications. The trophic status of this water body has a tendency from oligotrophic to mesotrophic characters with small deviations from its oligotrophic properties.

The UNTRIX-based classification procedure, TQR_{TRIX} do not completely follow the approach suggested by the WFD, based on separate assessment of biological and physicochemical quality elements and *ex-post* aggregation of results (Pettine *et al.*, 2007).

The scale of TQR_{TRIX} the ratio, between the median UNTRIX value in the reference site and the 75th percentile of the UNTRIX in an impacted site was calculated in the Mersin Bay. According to this ratio, quality of the water body is classified as bad, poor, moderate, good and high status with decreasing productivity properties of the water body. The calculated TQR_{TRIX} values change between 0.00 and 0.29 in very productive region namely dystrophic area, also known as ‘Bad’ status and vary between 0.30 and 0.49 in the eutrophic inshore waters of the bay with ‘Poor’ status whereas they vary between 0.50 and 0.69 in the mesotrophic waters, ‘Moderate’, of the transition area. The TQR_{TRIX} ratio ranges between 0.70 and 0.84 in the oligotrophic waters, ‘Good’, while the ratio higher than 0.85 can be characterized as ultraoligotrophic system classified as ‘High’. The trophic state classification of the stations in the bay according to the TQR_{TRIX} is depicted in Figure 3.16. The TQR_{TRIX} trophic scale ranges between 0.30 and 6.52 for the Cilician Basin. The values, which are higher than 1 are already classified as “High” or ultra-oligotrophic status.

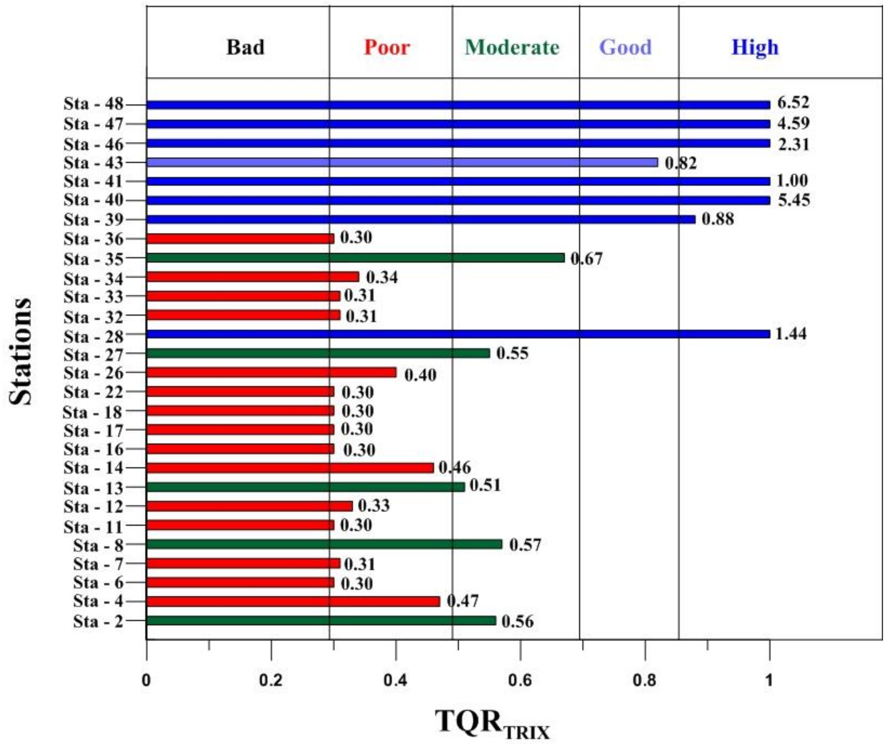

Figure 3.16. UNTRIX-based classification TQR_{TRIX} trophic scale

3.6. Comparison of Trophic Index (TRIX) and Unscaled Trophic Index (UNTRIX) Classification

By the end of the 20th Century, the term of eutrophication had acquired a scientific and legal denotation, which in Europe was enshrined in several European Directives, a decision by the European Court of Justice in 2004; and OSPAR's 1998 definition: "Eutrophication means the enrichment of water by nutrients causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned, and therefore refers to the undesirable effects resulting from anthropogenic enrichment by nutrients ..." (Ferreira *et al.*, 2011 and references therein). Eutrophic regions are generally characterized with: (a) increasing nutrient concentration, primary production and biomass of algae by about 10-fold; (b) decreasing oxygen concentration by some 10% in the bottom water and water transparency by at least 5-fold and also; (c) drastic changes in biodiversity.

For our study area, especially in the shallow nearshore zone of the Mersin Bay, enhanced nutrient concentrations, increased primary production and reduced water transparency by 5-10 fold have been clearly observed due to direct impacts of riverine and domestic inputs. Moreover, the geographical structure of the Mersin Bay simplifies the exchange of water bodies between inshore and offshore zones. However, the inner bay is isolated from the general circulation pattern of the NE Mediterranean and this limits the nutrient exchange between coastal and open waters. Although the biodiversity change is not significant in the river-fed nearshore zone where harmful algal blooms rarely occur, the trophic status of inshore bay tends to alter from mesotrophic status to eutrophic status, when the open water is assumed to be oligotrophic during the late spring-autumn period when a seasonal thermohaline stratification develops in the near-surface waters, which limits ventilation of near-bottom waters and exchanges of waters with the open sea by wind-induced circulations.

According to the trophic index (TRIX) as proposed by Vollenweider et al. (1998) and the corresponding status (Nasrollahzadeh *et al.*, 2008 and references therein), the TRIX ranges vary between 4.5 and 6 in the eutrophic nearshore waters (<20m in depth) fed by terrestrial inputs and then declines to <2 in the offshore waters. The TRIX index changes in the bay waters are closely correlated with the nutrients, Chl-*a*, DO, TP and negatively correlated with SDD (water transparency).

The TRIX ranges of different water masses in the bay, and comparison of the TRIX scale suggested for the Mersin Bay with the scales developed for the Italian and Aegean coastal waters are depicted in Table 3.5. According to the scale, developed for Italian coastal waters, the original TRIX is consistently high (>5) in the nearshore waters of the Mersin Bay during the year whereas the TRIX estimates is below 3 for the oligotrophic offshore water, declining to <2 in the open sea having ultra-oligotrophic characters. The high values of the TRIX index indicate the tendency to the development of eutrophic conditions in the bay nearshore waters compared to the water quality of the oligotrophic open waters of the region.

The large ranges of the eutrophication related bio-optical and bio-chemical parameters in space and time appear to limit the application of the original TRIX formula to different coastal regions having different reference conditions. It has to be discussed extensively that if the upper and lower limits proposed by Vollenweider *et al.* (1998) are an acceptable assumption for monitoring and assessing the trophic state of the entire European coastal and marine waters. For increasing the sensitivity of the TRIX, probably the ranges have to be redefined for different regions (EEA, 2001) having different reference conditions. This can be managed by re-calculating the constants of the TRIX formula to use 0-10 scale in scaling the trophic status of the interested region compared to its reference point.

According to the scales of the TRIX-IMS that were calculated from the eutrophication parameters measured in the Mersin Bay in the period of 2008-2011: the TRIX-IMS scale adopted in the NE Mediterranean changes between 6.0 and 8.0 in the eutrophic inshore waters of the bay whereas it varies between 3.0 and 6.0 in the mesotrophic waters of the central bay. The TRIX-IMS estimates range between 1.5 and 3.0 in the Cilician oligotrophic waters while the values below 1.5 can be characterized as ultraoligotrophic system of the NE Mediterranean. The mesotrophic site with wide trophic range values is a transition zone between eutrophic and oligotrophic waters. Therefore, it can be divided into two sub-regions, the shallower part has a tendency to shift to eutrophic conditions whilst the deeper part (>30m) occasionally show tendency to oligotrophy when the circulation is limited in the region.

The applications of the TRIX index in the Adriatic, western Aegean Sea and Mersin Bay by different groups (Pettine *et al.*, 2007) and group from Greece (Primpas and Karydis, 2010) are complied in Table 5.3, showing mean values, standart deviation values and data range for different water bodies of the western and eastern Mediterranean. The TRIX-IMS ranges in the Mersin Bay is also included in the table to compare with the TRIX ranges for similar water bodies.

Table 3.5. Ranges of the TRIX Index based on values from the three standard sets of data

AREA	Adriatic Sea	Aegean Sea	Mersin Bay	NE Mediterranean Sea (Present Study) TRIX-IMS Scale			
Water Type	TRIX Scale[a]	TRIX Scale[b]	TRIX Scale[c]	Mean Value	Std. Dev.	Range	Proposed Scale
Ultra Oligotro.	<2.0	<1.6	<2.0				<1.5
Oligotrophic	2.0-4.0	1.6-2.8	2.0-3.0	2.1	0.6	1.5-2.7	1.5-3.0
Mesotrophic	4.0-6.0	2.8-4.0	3.0-4.0	4.2	1.2	3.0-5.4	3.0-6.0
Eutrophic	6.0-8.0	4.0-5.3	4.0-5.0	7.2	1.0	6.2-8.2	6.0-8.0
Dystrophic	8.0<	5.3	5.0-6.0				8.0<

[a] Pettine *et al*., (2007)
[b] Primpas and Karydis (2010)
[c] Present Study

According to the modified TRIX index (TRIX-IMS), adopted for the Cilician Basin, and the TQR_{TRIX}, the trophic conditions of the bay bodies correspond to poor, moderate, good and high status. Approximately 5%, 41%, 33% and 21% of the stations in the bay (42 stations) were characterized as dystrophic, eutrophic, mesotrophic and oligotrophic waters based on the TRIX-IMS index scaling. Using the TQR_{TRIX}, proposed by Pettine et al. (2007), 54%, 18%, 3% and 25% of the stations (28 stations) were classified to have eutrophic, mesotrophic, oligotrophic and ultraoligotrophic properties.

A total of 28 stations in the bay were commonly evaluated in terms of applicability of both TQR_{TRIX} and TRIX-IMS. It was observed that the grouping of stations with the TQR_{TRIX} were generally compatible to the TRIX-IMS results. According to these two methods, 64% of the stations were determined to be in the same trophic level while the rest of the stations were classified in different status. If a data point get close to threshold value between two different trophic status levels may create some problems during the evaluation. For example; in the evaluation of stations according to the TRIX-IMS, 2 stations were very close to the limit value between oligotrophic and ultraoligotrophic properties. Therefore, a shift of stations 28, 40, 46, 47 and 48 (>50m) from ultraoligotrophic group to oligotrophic level; a shift of stations 39 and 41 from ultraoligotrophic to mesotrophic group; a shift of station 43 from oligotrophic level to mesotrophic level and also a shift of stations 4 and 14 (20m-50m) from eutrophic to mesotrophic were observed from the TQR_{TRIX} to the TRIX-IMS.

For the cases of eutrophic and mesotrophic status, the results of the both method were 64.3% consistent with each other. For nutrient poor waters, oligotrophic and ultra-oligotrophic waters, the similarity ratio of stations decreased. In other words, main difference was seen in less impacted offshore stations. Stations 28, 39, 40, 43, 46, 47, 48 (>20m) and 41 (5m-10m) gave slight better trophic status results (ultra-oligotrophic status) with the TQR_{TRIX}. The stations influenced by fresh water input, including 26, 32, 33, 34 and 36 (<20m) were classified to have poor status, or eutrophic status, by both the TQR_{TRIX} and the TRIX-IMS trophic scales.

According to Table 3.6, the sensitivity of both TRIX and TQR_{TRIX} shows differences from the nearshore to the offshore waters. In European coastal waters having comparable properties of reference (oligotrophic) conditions, the TRIX has a high potential application to assess the trophic status of coastal waters. However, its sensitivity decreases in the oligotrophic marine environments, demanding a modification in TRIX formula by re-calculating its two constants, ‘a’ and ‘b’ coefficients based on long-term data from the oligotrophic coastal seas.

Table 3.6. Comparison of the TRIX, UNTRIX and TRIX-IMS classifications in the Mersin Bay water bodies

		TROPHIC STATUS		
STATION NUMBER	**CLUSTER ANALYSIS**	**TRIX[a]**	**UNTRIX[b]**	**TRIX-IMS[c]**
Sta 2	M	O	M	M
Sta 4	M	O	E	M
Sta 6	E	M	E	E
Sta 7	E	M	E	E
Sta 8	M	O	M	M
Sta 11	E	M	E	E
Sta 12	E	M	E	E
Sta 13	M	O	M	M
Sta 14	M	O	E	M
Sta 16	E	M	E	E
Sta 17	E	M	E	E
Sta 18	E	M	E	E
Sta 22	E	M	E	E
Sta 26	E	O	E	E
Sta 27	M	O	M	M
Sta 28	O	UO	UO	O
Sta 32	E	M	E	E
Sta 33	E	M	E	E
Sta 34	E	O	E	E
Sta 35	M	O	M	M
Sta 36	E	M	E	E
Sta 39	M	O	UO	M
Sta 40	O	UO	UO	O
Sta 41	M	O	UO	M
Sta 43	M	O	O	M
Sta 46	O	UO	UO	O
Sta 47	O	UO	UO	O
Sta 48	O	UO	UO	O

(a) Vollenweider *et al*., (1998)
(b) Pettine *et al*., (2007)
(c) Present study

CHAPTER IV
CONCLUSIONS

Surface distributions of eutrophication related bio-chemical parameters display remarkable regional variations in the Mersin Bay of the Cilician Basin. Concentrations of macro-nutrients show about 10-fold increases from the oligotrophic offshore waters to the polluted inshore zone. Especially, TP and DIN are markedly high at the hot points of Mersin Bay due to riverine and waste water discharges. The offshore concentrations of TP, DRP and DIN ranged between 0.05-0.2 μM for TP, 0.02-0.08 μM for DRP and 0.2-0.7 μM for DIN; variations of Chl-*a* concentrations (biomass indicator) are consistent with the changes in nutrient concentrations, significantly increasing from offshore (0.04 μg/L) to the polluted inshore waters (2.83 μg/L). Extremely high values of nutrients and biomass measured at a few hot points fed by riverine and wastewater inputs were excluded before assessing the trophic status of the nearshore water body in the bay.

Surface distributions and cluster analysis of TP, DIN, Chl-*a*, aD%O, SDD and Salinity parameters at about 50 stations in the bay highlighted three distinct trophic regions (Table 4.1). The water body in the inner bay can be classified as eutrophic with high nutrient concentrations (0.45 μM for TP and 4.83 μM for DIN concentrations), Chl-*a* (1.31 μg/L), aD%O (9.48), low SDD (3.42 m) and lower salinity (38.01 ‰) peculiarities between the Mersin Harbour and Seyhan River Delta. The water body between the inshore (20m) and the offshore (>50m) water types, is characterized as mesotrophic having related low nutrients (TP=0.20 μM and DIN=1.73 μM) and Chl-*a* concentrations (0.32 μg/l), aD%O (5.19), and higher SDD (6.58 m) and salinity (38.95 ‰) values than the inshore waters. The offshore waters is categorized as oligotrophic with very low values of trophic status indicators (TP=0.12 μM and DIN=0.50 μM, Chl-*a*=0.14 μg/L), and higher SDD (~17 m) and salinity (39.35 ‰) values. The Kruskall-Wallis tests for raw and weighted data demonstrate that there exist statistically significant ($p<0.001$) differences in eutrophic, mesotrophic and oligotrophic water types. The average values of TP, DIN, Chl-*a* and aD%O show 2-times and 4-times decreasing trend in the order eutrophic>mesotrophic>oligotrophic whilst contrasting tendencies were detected for SDD and Salinity parameters with values increasing in the order of eutrophic<mesotrophic<oligotrophic.

The results of the TRIX, TRIX-IMS and UNTRIX applications in the Mersin Bay, depicted in Table 4.1, indicate that these approaches allow us to assess the trophic status of the North Eastern Mediterranean. The TRIX procedure enables to classify three different water bodies of the Mersin Bay, namely mesotrophic inner bay, oligotrophic middle bay and ultra-oligotrophic open sea with the average TRIX values of 4.35, 2.84 and 1.48.

Considering trophic status categories obtained from the TRIX, we may suggest that this approach is not powerful enough to show impact of excessive nutrient loads on the oligotrophic waters of the NE Mediterranean. However, the modified TRIX (TRIX-IMS) and UNTRIX approaches enable to assess the trophic status of the NE Mediterranean shelf waters fed by land-based inputs. The TRIX-IMS application in the Mersin Bay permits us to classify coastal waters as Dystrophic (8.26 with average value), Eutrophic (7.21), Mesotrophic (4.35) and Oligotrophic (2.07) whereas the UNTRIX classification method permits us to define Eutrophic, Mesotrophic, Oligotrophic and Ultra-Oligotrophic water bodies with the values of TQR_{TRIX} 0.34, 0.57, 0.82 and 3.17 in the Mersin Bay of the NE Mediterranean.

For regional applications of the TRIX in the coastal regions of oligotrophic seas, the constant coefficients of ‘a’ and ‘b’ values in the TRIX equation needs to be redefined. However, there is no need to use any coefficients to calculate the UNTRIX since the equation deliberately ignores such values to achieve the UN-Scaled TRIX because the data sets are compared to the reference point in the offshore.

Comparison of the trophic status of different water bodies, which were obtained by the TRIX, TRIX-IMS and UNTRIX methods (Table 4.1) exhibits a good agreement between the results of the TRIX-IMS and UNTRIX classifications. For example, about 64% of the total data in the bay yielded similar trophic status. The remaining stations were mainly characterized as “Oligotrophic” by the TRIX-IMS and “Ultra-oligotrophic” by the UNTRIX, due to sensitivity of the TRIX-IMS and UNTRIX equations in the offshore waters. The use of constant coefficients, “a” and “b” makes trophic index equation more sensitive to pressures and impacts on the coastal ecosystem. Therefore, the UNTRIX approach leaded to underestimation of assessments for lower trophic status while the scale approaches ‘zero’. It should be noted that the TRIX approach developed for the Adriatic Sea (more productive seas) (Vollenweider *et al.*, 1998) underestimates the trophic status of the coastal waters of the NE Mediterranean having oligotrophic properties. However, it permits global comparison of the trophic status of coastal waters impacted by land-based inputs.

In conclusion, oligotrophy of the NE Mediterranean limits direct application of trophic scales developed for much more productive marine environments. Trophic classification of coastal waters fed by land-based inputs should be done with respect to reference points of the areas with different biochemical properties varying in space and time.

Table 4.1. Comparison of the average values of eutrophication related parameters TP, DIN, Chl-*a*, aD%O, SDD and Salinity in the Mersin surface waters for 2008-2011 period

		Cluster Analysis	TRIX	TRIX-IMS	UNTRIX
TP (µM)	**E**	0.45 ± 0.23		0.41 ± 0.08	0.37 ± 0.09
	M	0.2 ± 0.13	0.45 ± 0.12	0.18 ± 0.02	0.17 ± 0.02
	O	0.12 ± 0.08	0.20 ± 0.07	0.10 ± 0.03	0.15 ± 0.05
		Cluster Analysis	**TRIX**	**TRIX-IMS**	**UNTRIX**
DIN (µM)	**E**	4.83 ± 5.74		3.81 ± 1.38	3.56 ± 1.3
	M	1.73 ± 2.45	4.41 ± 1.81	1.34 ± 0.59	1.14 ± 0.39
	O	0.50 ± 0.75	1.51 ± 0.75	0.37 ± 0.09	0.62 ± 0.37
		Cluster Analysis	**TRIX**	**TRIX-IMS**	**UNTRIX**
aD%O	**E**	9.48 ± 9.64		9.15 ± 1.61	8.69 ± 1.80
	M	5.19 ± 6.20	8.82 ± 2.0	4.34 ± 2.08	4.34 ± 1.30
	O	4.17 ± 5.72	4.90 ± 2.47	1.93 ± 1.17	2.44 ± 1.34
		Cluster Analysis	**TRIX**	**TRIX-IMS**	**UNTRIX**
Chl-*a* (µg/L)	**E**	1.31 ± 1.11		1.23 ± 0.47	0.99 ± 0.34
	M	0.37 ± 0.41	1.30 ± 0.44	0.37 ± 0.18	0.34 ± 0.08
	O	0.14 ± 0.16	0.41 ± 0.21	0.11 ± 0.07	0.13 ± 0.08
		Cluster Analysis	**TRIX**	**TRIX-IMS**	**UNTRIX**
SDD (m)	**E**	3.42 ± 1.71		3.23 ± 0.63	3.75 ± 1.20
	M	6.58 ± 3.09	3.03 ± 0.71	6.03 ± 1.25	6.17 ± 1.28
	O	17.24 ± 5.46	5.72 ± 0.46	17.64 ± 3.91	13.81 ± 1.66
		Cluster Analysis	**TRIX**	**TRIX-IMS**	**UNTRIX**
Salinity (‰)	**E**	38.01 ± 0.45		37.92 ± 0.58	37.90 ± 0.51
	M	38.95 ± 0.37	37.95 ± 0.61	38.93 ± 0.40	38.93 ± 0.30
	O	39.35 ± 0.15	38.80 ± 0.46	39.27 ± 0.10	39.27 ± 0.17

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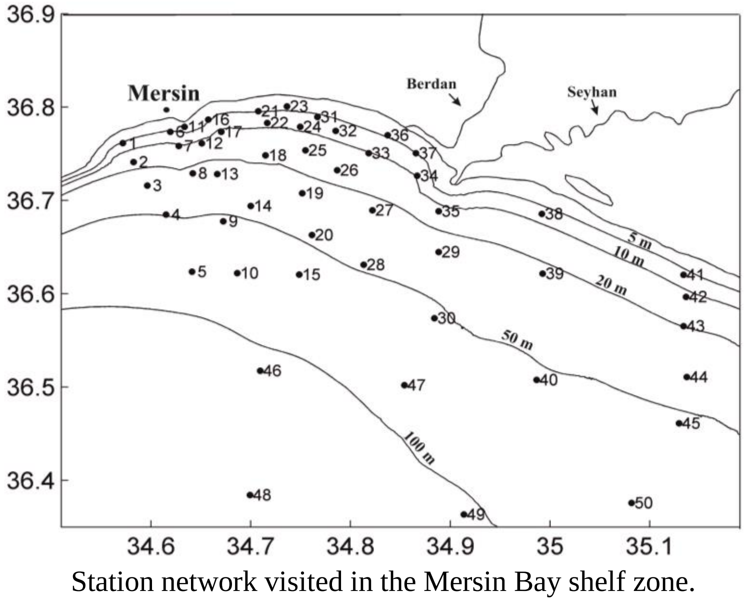
APPENDIX

APPENDIX A

Coordinates of the sampling locations visited in the Mersin Bay

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



Station network visited in the Mersin Bay shelf zone.

APPENDIX B

Sta	TP	PO_4^{3-}	NO_3^-+NO_2^-	DIN	Si	DIN/PO_4^{3-}	DO	DO (%)	Chl-*a*	SDD	T	Salinity
No	(µM)	(µM)	(µM)	(µM)	(µM)		(mg/L)		(µg/L)	(m)	(°C)	(‰)
1. Cruise September 2008												
2	0.353	0.06	0.11	0.48	3.54	8.00	6.19	101.3	0.40	5.0	29.59	39.40
4	0.121	0.02	0.07	0.38	1.18	19.00	6.25	101.9	0.14	9.0	29.26	39.70
6	0.500	0.05	0.37	3.92	4.23	78.40	6.25	103.4	1.84	4.5	30.25	39.46
7	0.376	0.05	0.34	3.11	3.65	62.20	6.65	109.7	1.35	5.0	30.11	39.32
8	0.124	0.04	0.08	0.35	1.37	8.75	6.18	101.4	0.08	10.0	29.67	39.66
10	0.098	0.02	0.06	0.16	0.97	8.00	6.25	101.8	0.06	20.0	29.18	39.78
11	1.470	0.12	0.27	6.89	4.97	57.42	6.07	99.9	3.28	3.0	30.03	39.21
12	0.471	0.06	0.10	1.04	4.01	17.33	6.73	111.0	1.66	3.5	30.17	39.24
13	0.069	0.03	0.06	0.26	1.21	8.67	6.19	101.4	0.10	7.0	29.54	39.66
14	0.217	0.02	0.11	0.19	0.97	9.50	6.24	101.8	0.06	8.5	29.27	39.69
16	1.112	0.11	3.50	6.73	3.92	61.18	7.20	119.2	4.20	2.5	30.35	39.29
17	0.800	0.02	0.22	1.32	3.67	66.00	6.62	109.5	2.33	3.0	30.29	39.31
18	0.159	0.03	0.10	0.34	2.17	11.33	6.33	104.0	0.43	6.0	29.81	39.54
21	0.624	0.06	0.63	0.83	3.93	13.83	7.73	128.1	2.11	3.0	30.40	39.25
22	0.438	0.07	0.24	0.45	5.16	6.43	7.21	118.9	1.74	3.0	30.21	39.00
23	0.560	0.08	2.70	3.05	4.36	38.13	7.73	128.0	3.46	2.0	30.14	39.13
25	0.745	0.10	0.47	1.51	3.55	15.10	6.79	111.9	0.25		30.06	39.26
26	0.118	0.05	0.45	1.20	1.42	24.00	6.23	101.8	0.99		29.40	39.67
27	0.089	0.02	0.89	2.90	1.50	145.00	6.29	103.2	0.11	5.0	29.67	39.68
28	0.119	0.02	0.07	0.82	0.82	41.00	6.18	100.7	0.03		29.18	39.74
32	0.659	0.12	0.51	0.80	5.42	6.67	7.62	125.7	3.32	2.0	30.30	38.90
33	0.327	0.26	0.91	2.17	6.24	8.35	6.38	105.8	2.97	2.0	30.65	38.76
34	0.335	0.06	0.15	0.54	2.93	9.00	6.46	106.5	0.44		30.03	39.51
35	0.138	0.05	0.90	3.18	1.19	63.60	6.19	101.2	0.11	6.0	29.44	39.68
36	0.685	0.14	0.45	0.86	5.92	6.14	7.78	129.0	4.19	2.0	30.61	38.85
38	0.158	0.04	0.95	3.03	2.05	75.75	6.31	103.1	0.23	5.0	29.43	39.60
39	0.157	0.02	0.06	1.55	1.03	77.50	6.23	101.5	0.06	8.5	29.21	39.67
40	0.045	0.02	0.10	0.67	0.73	33.50	6.35	103.1	0.00		28.97	39.80
41	0.102	0.07	0.06	2.13	1.23	30.43	6.21	101.4	0.10	5.0	29.34	39.65
43	0.114	0.04	0.15	2.53	1.15	63.25	6.25	101.9	0.08	7.0	29.26	39.66
46	0.195	0.02	0.09	0.41	1.02	20.50	6.22	101.3	0.03	21.0	29.21	39.70
2. Cruise January 2009												
4	0.277	0.02	0.06	0.49	0.66	24.50	7.33	99.5	0.18	13.0	18.72	39.44
6	0.460	0.21	8.92	14.11	3.85	67.19	7.26	95.8	0.37	4.0	17.27	39.18
7	0.140	0.02	0.12	0.40	0.80	20.00	7.45	100.7	0.23	8.0	18.46	39.44
10	0.161	0.02	0.15	0.95	0.81	47.50	7.50	102.2	0.10	12.0	18.91	39.44
11	0.420	0.13	2.41	3.70	1.58	28.46	7.22	95.0	0.43	3.0	17.16	39.04
12	0.160	0.04	0.28	0.44	0.86	11.00	7.36	99.5	0.13	11.5	18.46	39.45
13	0.090	0.02	0.10	0.47	0.80	23.50	7.37	99.4	0.10	4.0	18.32	39.44
14	0.201	0.02	0.08	0.61	0.81	30.50	7.39	99.7	0.12		18.35	39.43
16	0.550	0.24	5.08	11.82	2.26	49.25	7.48	99.4	0.24	3.0	17.60	39.24
17	0.370	0.18	2.36	5.58	1.81	31.00	7.33	97.5	0.44	4.0	17.67	39.30
18	0.090	0.04	0.37	1.32	0.82	33.00	7.52	100.4	0.28	6.0	17.79	39.43
21	0.740	0.40	21.30	44.06	4.42	110.15	7.25	93.9	0.51	2.0	16.37	39.02
22	0.110	0.15	5.74	11.96	3.31	79.73	7.66	99.3	0.49	3.5	16.37	39.13
27	0.081	0.04	0.24	0.34	0.94	8.50	7.49	99.6	0.08	6.0	17.59	39.43
28	0.048	0.03	0.21	1.21	0.89	40.33	7.48	100.1	0.20	13.0	17.95	39.47
36	0.146	0.06	1.75	3.31	1.41	55.17	7.53	100.2	0.20		17.69	39.31
38	0.138	0.06	1.18	1.54	1.79	25.67	7.58	99.3	0.32	5.0	16.95	39.08
39	0.131	0.06	1.08	1.12	1.68	18.67	7.58	100.0	0.15	6.0	17.28	39.13
40	0.139	0.02	0.06	0.29	0.76	14.50	7.31	99.2	0.07		18.67	39.44

Sta	TP	PO_4^{3-}	$NO_3^-+NO_2^-$	DIN	Si	DIN/PO_4^{3-}	DO	DO (%)	Chl-*a*	SDD	T	Salinity
No	(µM)	(µM)	(µM)	(µM)	(µM)		(mg/L)		(µg/L)	(m)	(°C)	(‰)
41	0.210	0.02	0.24	0.63	0.81	31.50	7.67	99.4	0.36	4.0	16.44	38.81
43	0.149	0.05	0.37	0.41	0.96	8.20	7.37	98.7	0.17	10.0	18.02	39.34
47	0.121	0.02	0.13	0.38	0.74	19.00	7.28	99.5	0.07		19.04	39.42
48	0.209	0.02	0.13	0.37	0.79	18.50	7.22	99.4	0.08		19.45	39.48
3. Cruise February 2009												
2	0.231	0.05	8.91	10.60	4.02	212.00	8.17	103.1	1.19		15.33	38.00
4	0.054	0.03	0.26	0.64	0.82	21.33	7.53	99.5	0.14		17.30	39.40
6	0.480	0.10	9.34	10.92	3.09	109.20	8.35	103.3	2.47	4.0	14.57	37.33
7	0.780	0.26	9.62	13.78	3.92	53.00	8.29	103.4	2.73	3.0	14.83	37.82
10	0.054	0.03	0.16	0.48	0.73	16.00	7.46	99.3	0.07	21.0	17.64	39.41
11	0.510	0.09	11.69	13.44	3.40	149.33	8.51	105.4	3.61	3.0	14.59	37.42
12	0.450	0.10	14.39	17.10	3.64	171.00	9.03	112.0	6.69	3.5	14.65	37.49
13	0.200	0.06	3.43	3.93	2.23	65.50	7.75	100.7	0.24	7.0	16.64	38.63
14	0.049	0.02	0.18	0.47	0.76	23.50	7.51	99.6	0.14	18.0	17.50	39.39
16	1.000	0.15	11.35	15.87	1.83	105.80	8.87	109.7	2.56	3.0	14.45	37.71
17	0.450	0.11	12.42	15.51	1.83	141.00	8.77	108.5	2.27	3.0	14.51	37.50
18	0.370	0.08	11.23	13.03	5.19	162.88	8.02	101.8	0.51	5.5	15.75	37.74
21	0.650	0.15	8.89	14.82	2.94	98.80	7.66	96.6	2.78	2.5	15.25	38.28
22	0.480	0.11	10.08	11.28	3.10	102.55	8.79	109.0	3.46	3.0	14.86	36.82
26	0.164	0.08	7.17	8.11	3.86	101.38	7.9	101.6	0.35		16.26	38.17
27	0.222	0.06	4.86	7.15	3.56	119.17	7.76	100.2	0.11	7.0	16.38	38.40
28	0.106	0.03	0.06	0.11	0.84	3.67	7.50	99.6	0.11	16.0	17.54	39.42
30	0.071	0.02	0.06	0.13	0.83	6.50	7.57	100.1	0.15		17.31	39.39
33	0.192	0.07	6.66	7.36	3.63	105.14	7.92	101.8	0.49		16.16	38.49
34	0.092	0.06	3.13	3.77	2.49	62.83	7.76	99.9	0.27		16.12	38.81
35	0.104	0.04	0.99	1.29	1.22	32.25	7.75	101.3	0.11		16.79	39.23
36	0.179	0.08	5.23	5.86	3.35	73.25	7.92	101.8	0.20		16.12	38.57
38	0.149	0.05	8.19	8.50	4.64	170.00	8.06	102.7	0.40		15.75	38.33
39	0.108	0.02	0.79	1.28	1.18	64.00	7.58	99.1	0.19	9.0	16.78	39.25
40	0.122	0.02	0.12	0.22	0.82	11.00	7.47	99.4	0.17		17.64	39.42
41	0.129	0.05	7.65	8.52	4.76	170.40	8.11	102.8	0.53		15.63	37.86
43	0.041	0.04	0.43	0.81	0.99	20.25	7.67	100.3	0.15		16.77	39.29
46	0.135	0.02	0.12	0.58	0.80	29.00	7.43	99.1	0.10		17.77	39.43
47	0.188	0.02	0.14	0.22	0.86	11.00	7.45	99.0	0.09		17.58	39.42
48	0.109	0.03	0.11	0.16	0.81	5.33	7.42	99.2	0.15	21.0	20.78	39.28
4. Cruise March 2009												
2	0.087	0.02	1.02	1.15	1.68	57.50	7.71	116.5	0.10		16.92	39.27
4	0.123	0.02	0.78	0.89	0.97	44.50	7.60	115.4	0.25		17.39	39.25
6	0.490	0.11	7.96	11.84	3.57	107.64	8.05	112.9	1.36	2.5	16.73	38.07
7	0.350	0.08	3.45	3.88	2.77	48.50	7.91	113.3	0.89	3.5	16.52	38.17
10	0.143	0.02	1.46	1.66	1.12	83.00	7.71	116.2	0.31		17.19	39.12
11	1.140	0.49	4.85	20.59	4.66	42.02	7.43	108.2	1.03	2.5	16.68	38.01
12	0.240	0.05	1.69	2.41	2.03	48.20	7.78	110.9	0.77	4.0	16.35	38.32
13	0.110	0.04	1.61	2.43	1.83	60.75	7.72	112.0	0.26	8.0	16.95	38.71
14	0.193	0.03	1.24	2.54	1.46	84.67	7.60	115.7	0.24		17.26	39.22
16	0.350	0.09	4.84	6.19	2.67	68.78	7.85	107.4	1.90	2.5	16.45	37.90
17	0.220	0.06	2.91	3.69	2.3	61.50	7.65	108.8	1.00	4.0	16.39	38.24
18	0.210	0.07	2.75	3.84	2.79	54.86	7.99	112.8	0.80	2.5	16.70	38.36
21	0.250	0.11	3.43	4.37	2.04	39.73	8.05	108.9	1.19	2.0	16.53	38.19
22	0.280	0.10	3.12	4.03	1.89	40.30	8.16	108.1	1.01	2.5	16.53	37.95
27	0.236	0.07	3.76	5.97	4.34	85.29	8.59	120.9	0.32	5.0	17.32	37.33
28	0.097	0.03	0.57	0.71	1.05	23.67	7.40	113.6	0.07	29.0	17.60	39.38
36	0.386	0.13	5.92	6.73	2.71	51.77	8.46	110.2	0.76	1.5	16.82	38.08
38	0.416	0.16	8.26	9.05	5.36	56.56	8.66	109.7	0.94	2.0	16.80	37.29
39	0.266	0.03	1.28	1.61	1.49	53.67	7.55	113.2	0.16		17.07	39.25
40	0.131	0.03	0.49	0.74	1.10	24.67	7.65	116.9	0.14		17.15	39.36
41	0.328	0.18	5.00	6.72	4.49	37.33	8.09	113.8	2.38	1.5	16.72	38.08

Sta	TP	PO_4^{3-}	$NO_3^-+NO_2^-$	DIN	Si	DIN/PO_4^{3-}	DO	DO (%)	Chl-*a*	SDD	T	Salinity
No	(µM)	(µM)	(µM)	(µM)	(µM)		(mg/L)		(µg/L)	(m)	(°C)	(‰)
43	0.198	0.11	2.06	4.17	2.37	37.91	7.81	120.0	0.62	3.0	16.80	39.09
46	0.164	0.02	0.56	0.90	1.05	45.00	7.66	117.4	0.12		17.39	39.21
47	0.086	0.03	0.65	0.88	0.83	29.33	7.65	116.2	0.22		17.30	39.27
48	0.142	0.03	0.23	0.45	0.92	15.00	7.47	117.1	0.12		17.70	39.36
5. Cruise April 2009												
2	0.110	0.03	0.14	0.45	0.69	15.00	7.98	111.3	0.51		19.49	37.86
4	0.096	0.03	0.13	0.31	0.67	10.33	8.10	117.0	0.62		19.64	38.37
6	0.410	0.12	4.06	5.75	3.51	47.92	7.38	108.8	1.01	3.0	19.34	36.09
7	0.300	0.05	2.62	2.93	2.31	58.60	8.18	117.8	1.01	4.0	19.28	36.21
10	0.174	0.05	0.14	0.21	0.93	4.20	8.17	117.3	0.79	6.0	19.66	37.81
11	0.370	0.07	3.01	5.02	3.44	71.71	8.06	112.1	0.79	2.5	20.06	35.60
12	0.290	0.10	1.77	2.13	1.84	21.30	8.42	117.8	0.98	3.5	19.53	36.27
13	0.199	0.04	0.28	0.51	2.21	12.75	8.59	118.1	0.56	3.5	19.91	37.21
14	0.152	0.04	0.14	0.35	2.46	8.75	8.38	120.9	1.10		19.87	37.50
16	0.394	0.11	5.19	6.04	9.03	54.91	8.20	113.7	1.55	2.5	19.92	32.39
17	0.362	0.08	2.60	2.97	1.55	37.13	8.55	115.9	1.46	3.5	19.57	36.58
18	0.473	0.07	2.20	2.68	7.4	38.29	8.86	116.3	1.06	3.0	20.10	35.36
21	0.290	0.08	1.50	2.12	6.38	26.50	8.62	119.6	1.33	3.0	20.17	34.68
22	0.471	0.07	2.39	2.78	6.87	39.71	8.82	116.5	1.14	3.0	20.69	33.32
27	0.102	0.08	0.45	0.67	1.07	8.38	7.95	115.0	0.80	5.0	19.91	37.77
28	0.170	0.02	0.96	1.15	1.91	57.50	8.04	118.3	0.98	8.0	20.08	37.77
33	0.461	0.12	3.25	4.47	9.30	37.25	9.08	118.8	1.47		21.32	34.27
34	0.387	0.08	3.29	4.39	9.07	54.88	9.04	116.9	1.08		20.64	34.58
38	0.132	0.06	0.86	1.13	2.07	18.83	8.07	121.0	0.23	4.5	21.02	37.48
39	0.111	0.03	0.54	0.77	1.12	25.67	8.04	120.8	0.30	5.0	20.74	38.05
40	0.118	0.03	0.10	0.16	0.73	5.33	7.62	120.6	0.10		19.73	39.06
43	0.114	0.04	0.20	0.33	0.86	8.25	7.82	118.1	0.28	9.0	20.10	38.51
47	0.055	0.04	0.09	0.61	1.48	15.25	7.78	118.7	0.26	13.0	19.43	38.91
48	0.045	0.04	0.12	0.36	1.53	9.00	7.68	121.2	0.06		19.43	39.12
6. Cruise August 2009												
2	0.144	0.08	0.10	0.37	1.11	4.63	6.79	111.29	0.35		29.83	38.97
4	0.045	0.03	0.12	0.34	0.76	11.33	6.40	104.98	0.12		29.72	39.40
6	0.331	0.09	0.28	0.76	1.39	8.44	6.40	104.67	0.57	4.5	29.66	39.03
7	0.232	0.05	0.12	0.30	0.99	6.00	6.46	105.54	0.46		29.64	39.02
10	0.051	0.03	0.07	0.14	0.76	4.67	6.31	102.79	0.49	22.0	29.39	39.06
11	0.313	0.08	0.39	1.25	2.21	15.63	6.17	101.05	0.70	3.5	29.74	39.07
12	0.321	0.06	0.18	0.83	2.18	13.83	6.77	110.72	1.27	4.5	29.79	38.71
13	0.268	0.06	0.06	0.83	1.22	13.83	6.93	114.60	0.80	4.0	30.52	38.80
14	0.067	0.05	0.12	0.55	0.89	11.00	6.31	103.19	0.13	11.0	29.51	39.45
16	0.586	0.11	0.45	4.69	3.18	42.64	6.16	101.07	1.26	2.5	29.86	38.97
17	0.349	0.07	0.17	1.39	2.65	19.86	6.74	110.34	1.00	3.5	29.90	38.56
18	0.614	0.09	0.68	1.32	3.89	14.67	7.74	128.23	2.11	3.0	30.83	38.16
21	0.422	0.08	0.38	2.14	3.22	26.75	6.58	108.14	0.95	3.5	30.08	38.87
22	0.498	0.08	0.23	1.91	3.39	23.88	6.95	114.36	1.32	3.0	30.26	38.61
25	0.322	0.04	0.24	1.09	2.52	27.25	7.19	119.31	1.16	3.0	30.87	38.26
26	0.294	0.03	0.16	0.94	1.35	31.33	7.20	119.19	1.10	3.0	30.58	38.65
27	0.437	0.13	1.92	3.93	8.08	30.23	6.47	106.04	0.82	3.0	30.13	38.10
28	0.049	0.03	0.13	0.45	0.83	15.00	6.27	102.40	0.33	13.0	29.86	38.35
30	0.062	0.03	0.06	0.38	0.85	12.67	6.38	104.85	0.02	16.0	29.88	39.48
32	0.395	0.04	0.21	1.02	3.69	25.50	7.11	118.28	1.52	3.5	30.96	38.48
33	0.403	0.06	0.27	1.48	5.49	24.67	6.71	111.58	0.55	2.5	30.97	38.36
34	0.429	0.07	0.22	1.58	4.25	22.57	6.68	111.32	0.82		31.17	38.17
35	0.122	0.02	0.15	0.99	1.03	49.50	6.38	104.76	0.21		29.82	39.36
36	0.484	0.05	0.41	2.03	7.21	40.60	7.37	121.93	1.53	2.5	30.70	38.19
38	0.116	0.06	0.11	0.43	1.17	7.17	6.61	109.99	1.28		30.76	39.04
39	0.069	0.03	0.05	0.17	0.90	5.67	6.27	103.10	0.03	8.0	29.90	39.49
40	0.046	0.03	0.08	0.21	0.76	7.00	6.33	103.78	0.05	12.0	29.68	39.48

Sta	TP	PO_4^{3-}	$NO_3^-+NO_2^-$	DIN	Si	DIN/PO_4^{3-}	DO	DO (%)	Chl-*a*	SDD	T	Salinity
No	**(µM)**	**(µM)**	**(µM)**	**(µM)**	**(µM)**		**(mg/L)**		**(µg/L)**	**(m)**	**(°C)**	**(‰)**
41	0.064	0.03	0.11	0.54	1.06	18.00	6.30	104.17	0.05		30.20	39.47
43	0.232	0.02	0.09	0.22	0.82	11.00	6.27	102.62	0.02		29.56	39.46
47	0.096	0.02	0.07	0.33	0.69	16.50	6.31	102.77	0.07	17.0	29.24	39.47
48	0.105	0.03	0.08	0.20	0.83	6.67	6.26	102.50	0.03	19.0	29.64	39.45
7. Cruise October 2009												
2	0.21	0.03	0.27	0.67	3.17	22.33	6.68	102.9	0.35		25.92	39.24
4	0.14	0.02	0.12	0.47	2.75	23.50	6.61	102.0	0.18		25.99	39.39
6	0.448	0.05	3.40	4.85	2.44	97.00	7.05	107.3	1.89	5.5	25.34	38.79
7	0.231	0.04	0.64	1.30	3.34	32.50	6.69	102.0	0.83	4.0	25.40	38.91
8	0.121	0.04	0.06	0.31	2.96	7.75	6.66	102.6	0.18	11.0	25.93	39.19
10	0.09	0.05	0.09	0.32	2.11	6.40	6.55	101.3	0.09	15.0	26.08	39.55
11	0.517	0.05	5.01	6.36	2.25	127.20	7.02	106.6	2.34	4.0	25.24	38.77
12	0.325	0.05	2.23	4.43	3.75	88.60	6.49	98.7	1.49	4.0	25.26	38.91
13	0.090	0.05	0.18	0.28	2.46	5.60	6.50	100.7	0.30	11.0	26.17	39.47
14	0.21	0.05	0.10	0.34	3.98	6.80	6.89	105.6	0.13		25.80	38.65
16	0.496	0.09	8.34	13.25	4.05	147.22	6.71	101.9	2.21	2.5	25.22	38.80
17	0.160	0.05	0.55	1.61	3.43	32.20	6.63	100.9	0.85	4.0	25.33	38.93
18	0.134	0.02	0.06	0.27	3.66	13.50	6.76	103.6	0.32	8.0	25.77	38.81
21	0.876	0.21	1.94	6.65	5.17	31.67	6.43	97.6	1.53	3.0	25.28	38.59
22	0.284	0.06	0.44	1.74	3.93	29.00	6.67	101.6	0.92	6.0	25.42	38.73
25	0.24	0.07	0.06	0.51	4.06	7.29	7.39	112.9	0.25	7.0	25.74	38.36
26	0.28	0.07	0.20	0.65	4.12	9.29	7.39	112.6	0.70		25.66	38.14
27	0.48	0.05	0.86	1.96	5.33	39.20	7.14	107.5	0.99	4.5	25.02	37.93
28	0.10	0.02	0.09	0.41	2.60	20.50	6.62	102.3	0.11	16.0	26.06	39.35
30	0.13	0.05	0.08	0.45	1.47	9.00	5.66	87.9	0.03	21.0	26.28	39.62
32	0.28	0.06	0.09	0.60	3.77	10.00	7.43	113.6	0.44	6.0	25.70	38.53
33	0.27	0.08	0.19	0.75	4.08	9.38	7.25	110.6	0.36		25.67	38.32
34	0.36	0.07	0.27	0.95	3.75	13.57	7.50	113.9	0.64		25.44	38.21
35	0.20	0.05	0.24	1.03	3.45	20.60	6.66	102.2	0.36		25.81	38.87
36	0.37	0.08	0.59	1.30	4.43	16.25	7.41	113.0	0.60		25.67	38.25
38	0.83	0.07	0.26	0.52	4.69	7.43	6.42	98.8	0.29		25.84	39.24
39	0.13	0.04	0.13	0.51	3.79	12.75	6.67	102.6	0.31	6.5	25.83	39.28
40	0.11	0.04	0.07	0.41	1.76	10.25	6.53	101.2	0.05	18.0	26.15	39.57
41	0.17	0.05	0.27	0.59	5.24	11.80	6.67	101.9	0.12		25.53	39.00
43	0.23	0.09	0.27	0.49	5.09	5.44	6.57	100.6	0.32		25.61	39.13
46	0.15	0.04	0.16	0.33	1.35	8.25	6.52	100.8	0.04		25.99	39.63
47	0.11	0.04	0.06	0.20	1.61	5.00	6.50	100.5	0.04		26.05	39.61
48	0.13	0.03	0.09	0.26	1.08	8.67	6.57	101.7	0.04	28.5	26.09	39.64
8. Cruise February 2010												
2	0.17	0.03	3.31	5.22	3.99	174.00	8.11	100.85	0.57		15.27	36.02
4	0.19	0.02	4.08	5.38	3.74	269.00	8.54	108.09	0.56		15.57	37.91
8	0.191	0.02	6.16	6.74	6.36	337.00	8.93	111.25	0.86		15.13	36.76
9	0.139	0.03	4.45	5.55	4.64	185.00	8.69	109.69	0.69		15.52	37.63
10	0.06	0.02	1.14	1.43	1.75	71.50	7.73	101.70	0.23	13.0	17.22	39.08
12	0.347	0.02	5.84	6.36	6.06	318.00	8.74	108.75	1.80		15.11	36.60
14	0.21	0.03	4.72	5.08	3.46	169.33	8.82	110.68	0.43	5.5	15.21	37.67
16	0.522	0.08	16.0	22.8	5.98	285.00	8.90	111.04	4.50		15.18	36.82
17	0.375	0.08	7.56	8.11	7.91	101.38	9.00	112.05	1.35		15.24	36.29
18	0.228	0.02	10.05	10.6	7.68	528.00	9.21	114.46	2.41	4.0	15.10	36.44
21	0.730	0.15	16.7	20.3	10.53	135.20	9.38	116.24	4.87	3.0	15.31	35.30
22	0.411	0.04	12.7	13.5	9.18	337.00	9.63	119.53	2.61	4.0	15.18	35.98
25	0.32	0.05	11.9	12.8	7.11	256.20	9.13	113.96	2.32	4.0	15.35	36.35
26	0.37	0.03	9.96	10.1	14.2	336.33	8.58	106.28	5.63	4.0	15.12	35.85
27	0.21	0.02	10.2	10.4	11.1	519.00	8.65	107.56	2.80	4.5	15.10	36.54
28	0.08	0.04	0.47	0.53	1.22	13.25	7.65	101.25	0.16	17.0	17.50	39.19
30	0.23	0.02	0.60	0.70	1.63	35.00	7.68	100.78	0.28	19.0	17.08	39.07
32	0.43	0.07	12.9	14.4		205.43	9.96	124.62	1.91	2.0	15.39	36.61

Sta	TP	PO_4^{3-}	$NO_3^-+NO_2^-$	DIN	Si	DIN/PO_4^{3-}	DO	DO (%)	Chl-*a*	SDD	T	Salinity
No	**(µM)**	**(µM)**	**(µM)**	**(µM)**	**(µM)**		**(mg/L)**		**(µg/L)**	**(m)**	**(°C)**	**(‰)**
33	0.30	0.04	9.29	9.83		245.75	9.04	113.02	1.79	4.0	15.30	36.76
34	0.28	0.11	9.17	10.2	8.83	92.82	8.28	104.01	0.62	4.5	15.34	37.42
35	0.33	0.05	6.14	7.03	7.18	140.60	8.28	103.89	0.38		15.32	37.29
36	0.28	0.08	10.25	11.47	6.07	143.38	9.17	115.33	1.44	4.0	15.52	37.05
38	0.27	0.05	7.03	7.26	7.27	145.20	8.10	101.53	0.81	7.0	15.23	37.41
39	0.18	0.03	1.24	1.73	2.28	57.67	7.75	100.23	0.65	11.0	16.52	38.44
40	0.20	0.03	6.31	6.57	8.45	219.00	8.20	103.93	0.62	12.0	15.85	37.26
41	0.21	0.06	6.68	6.85	6.13	114.17	8.26	104.31	0.61	5.0	15.48	37.85
42	0.103	0.05	7.43	7.57	7.91	151.40	8.28	104.50	0.43	6.5	15.62	37.28
43	0.08	0.04	8.08	8.20	8.02	205.00	8.21	103.84	0.30	12.0	15.73	37.31
46	0.09	0.03	0.11	0.20	0.99	6.67	7.54	100.35	0.12		17.78	39.20
47	0.11	0.02	0.38	0.45	1.22	22.50	7.60	100.28	0.42	16.0	17.34	39.17
48	0.20	0.03	0.08	0.21	0.94	7.00	7.49	99.81	0.19	20.0	17.84	39.23
9. Cruise April 2010												
2	0.303	0.06	0.33	0.62	1.66	10.33	7.89	106.4	0.70		18.83	38.17
4	0.292	0.05	0.08	0.28	1.39	5.60	8.05	109.6	0.56	4.0	19.32	38.21
6	0.545	0.12	1.18	1.46	3.4	12.17	8.03	108.4	1.32		19.04	37.71
8	0.192	0.08	0.43	0.64	2.06	8.00	7.80	95.2	0.46	3.0	19.03	
9	0.136	0.03	0.08	0.34	1.17	11.33	7.94	107.3	0.47		18.88	38.33
10	0.060	0.03	0.13	0.37	1.03	12.33	7.77	104.6	0.16	15.0	18.47	38.93
12	0.381	0.07	0.63	0.82	1.93	11.71	8.04	108.4	1.59		18.91	37.93
14	0.143	0.04	0.12	0.47	0.80	11.75	8.09	109.0	0.53	9.0	18.69	38.48
16	0.523	0.11	1.4	1.67	3.66	15.18	7.71	104.3	1.76		19.16	37.63
17	0.369	0.07	0.34	0.47	1.24	6.71	8.15	110.2	1.49	8.0	19.08	37.78
18	0.233	0.04	0.41	0.70	1.91	17.50	7.81	105.5	0.57	4.0	18.88	38.26
21	0.486	0.11	2.73	3.38	3.53	30.73	7.92	100.3	1.59	2.0	19.34	
22	0.369	0.07	2.03	2.25	3.40	32.14	8.09	109.9	1.09	2.0	19.41	37.65
25	0.328	0.07	1.13	1.48	3.95	21.14	8.00	107.9	0.71	3.5	19.06	37.54
26	0.219	0.07	0.56	0.82	1.2	11.71	7.70	103.4	0.26	3.0	18.40	38.72
27	0.220	0.05	0.85	1.21	2.6	24.20	7.79	103.9	0.24	8.0	18.17	38.39
28	0.083	0.03	0.09	0.37	0.96	12.33	7.86	106.8	0.11	10.0	18.99	38.99
30	0.060	0.03	0.11	0.39	0.96	13.00	7.73	104.4	0.05	11.0	18.63	39.03
32	0.610	0.10	5.11	6.34	8.35	63.40	8.07	108.3	0.56	2.0	19.64	34.80
33	0.804	0.18	1.46	1.86	4.81	10.33	7.52	100.9	0.33	1.5	18.68	37.82
34	0.606	0.14	0.89	1.29	2.38	9.21	7.54	100.7	0.39	1.5	18.32	38.18
35	0.236	0.05	0.42	0.66	1.65	13.20	7.80	104.1	0.11	4.0	18.17	38.39
36	1.214	0.26	0.69	1.16	3.82	4.46	7.34	98.4	1.15	1.2	18.45	38.29
38	0.527	0.11	0.94	1.27	2.46	11.55	7.67	102.3	0.24		18.27	38.09
39	0.192	0.03	0.13	0.42	1.39	14.00	7.82	104.8	0.13		18.28	38.81
40	0.075	0.03	0.09	0.37	1.10	12.33	7.69	103.8	0.04	14.0	18.60	39.06
41	0.362	0.19	1.70	1.98	3.14	10.42	7.72	103.3	0.53		18.48	37.93
43	0.252	0.05	0.56	0.76	1.20	15.20	7.82	105.0	0.25	3.0	18.43	38.62
46	0.069	0.03	0.10	0.35	0.90	11.67	7.62	103.5	0.02		18.88	39.21
47	0.064	0.02	0.09	0.33	1.02	16.50	7.70	103.6	0.07		18.48	38.80
48	0.069	0.03	0.12	0.23	0.97	7.67	7.57	101.8	0.05	24.0	18.35	39.18
10. Cruise July 2010												
2	0.632	0.04	0.22	0.48	1.26	12.00	8.43	134.5	0.70		28.63	38.11
4	0.594	0.04	0.13	0.48	1.17	12.00	6.69	105.8	0.06		27.69	39.11
6	0.799	0.05	0.16	0.37	1.14	7.40	7.91	125.0	3.01	1.2	28.35	37.14
8	0.542	0.04	0.17	0.36	1.32	9.00	7.73	122.6	1.93	2.0	28.33	37.92
9	0.459	0.02	0.09	0.30	1.23	15.00	6.67	104.5	0.07		27.16	39.14
10	0.480	0.03	0.15	0.28	1.12	9.33	6.64	104.6	0.05	20.0	27.47	39.22
12	0.203	0.04	0.15	0.42	1.27	10.50	9.84	157.8	0.19		29.02	37.83
14	0.466	0.03	0.07	0.30	1.22	10.00	6.67	104.8	0.85		27.32	39.07
16	0.509	0.05	0.25	1.29	1.42	25.80	8.20	131.9	0.19	2.5	29.19	37.86
17	0.820	0.05	0.12	0.37	1.08	7.40	10.27	166.1	1.11	2.0	29.91	36.85
18	0.517	0.03	0.09	0.28	1.38	9.33	6.54	103.1	0.32	12.0	27.50	39.17

Sta	TP	PO_4^{3-}	$NO_3^-+NO_2^-$	DIN	Si	DIN/PO_4^{3-}	DO	DO (%)	Chl-*a*	SDD	T	Salinity
No	**(µM)**	**(µM)**	**(µM)**	**(µM)**	**(µM)**		**(mg/L)**		**(µg/L)**	**(m)**	**(°C)**	**(‰)**
21	0.762	0.05	0.40	1.90	1.39	38.00	8.66	139.7	1.81	2.0	29.68	36.94
22	0.609	0.05	0.16	0.39	1.04	7.80	8.74	141.2	0.68	3.0	29.51	37.81
23	0.836	0.10	0.56	5.29	6.12	52.90	6.46	104.3	0.54	2.0	29.77	36.80
27	0.050	0.03	0.12	0.35	1.30	11.67	6.61	104.4	0.15	6.0	27.70	38.99
28	0.080	0.03	0.14	0.41	1.46	13.67	6.62	104.4	0.07	25.0	27.54	39.15
30	0.062	0.02	0.10	0.32	1.13	16.00	6.54	103.1	0.05		27.51	39.13
32	0.383	0.03	0.90	1.22	2.60	40.67	6.96	111.2	0.79	3.0	28.61	38.38
33	0.093	0.03	0.26	0.51	1.69	17.00	6.80	108.6	0.25	5.0	28.38	38.90
34	0.082	0.02	0.43	0.66	2.41	33.00	6.57	105.4	0.11	5.0	28.68	38.88
35	0.074	0.03	0.09	0.32	1.10	10.67	6.63	104.5	0.19		27.45	39.21
38	0.071	0.03	0.21	0.44	1.81	14.67	6.59	105.2	0.39		28.36	38.99
39	0.075	0.03	0.10	0.24	0.96	8.00	6.49	102.5	0.05		27.64	39.16
40	0.065	0.03	0.13	0.31	1.26	10.33	6.54	103.6	0.12	15.0	27.78	39.17
41	0.401	0.02	0.15	0.42	1.36	21.00	6.49	102.7	0.06		27.73	39.20
43	0.156	0.03	0.18	0.46	1.37	15.33	6.59	103.8	0.04		27.43	39.25
46	0.440	0.03	0.12	0.25	0.95	8.33	6.53	102.4	0.08	21.0	27.16	39.24
47	0.065	0.03	0.14	0.35	1.11	11.67	6.57	103.3	0.05	20.5	27.34	39.16
48	0.076	0.03	0.11	0.30	1.10	10.00	6.54	102.2	0.07	18.0	26.95	39.31
11. Cruise November 2010												
1	0.274	0.06	0.35	0.59	1.99	9.83	6.81	101.0	0.21		23.79	39.53
2	0.091	0.04	0.41	0.57	1.40	14.25	6.82	101.7	0.09		24.04	39.53
3	0.133	0.04	0.30	0.46	1.17	11.50	6.73	100.8	0.03		24.27	39.57
4	0.128	0.05	0.31	0.45	0.87	9.00	6.67	100.2	0.04		24.43	39.60
5	0.168	0.02	0.07	0.18	1.13	9.00	6.68	100.4	0.03	15.0	24.46	39.59
6	0.281	0.06	1.08	1.64	1.88	27.33	6.73	99.6	0.33		23.63	39.51
7	0.413	0.05	0.29	0.64	1.19	12.80	6.79	101.0	0.21		23.91	39.53
8	0.107	0.03	0.08	0.17	0.91	5.67	6.78	101.3	0.07		24.17	39.55
9	0.068	0.04	0.27	0.40	0.92	10.00	6.77	101.6	0.06		24.36	39.58
10	0.200	0.02	0.05	0.15	1.12	7.50	6.76	101.8	0.05	25.0	24.57	39.58
11	0.131	0.06	2.38	3.43	2.61	57.17	6.66	97.7	0.29		23.16	39.23
12	0.192	0.05	0.43	0.75	1.35	15.00	6.78	100.7	0.31		23.83	39.52
13	0.109	0.02	0.10	0.23	1.09	11.50	6.73	100.3	0.17		24.03	39.53
14	0.089	0.06	0.30	0.46	1.07	7.67	6.69	100.3	0.07		24.33	39.58
15	0.151	0.03	0.08	0.22	1.08	7.33	6.74	100.9	0.18		24.26	39.56
16	0.304	0.07	0.57	0.94	1.70	13.43	6.71	99.5	0.46		23.73	39.53
17	0.410	0.08	0.64	1.26	1.57	15.75	6.79	100.5	0.73		23.59	39.49
18	0.185	0.06	0.22	0.45	1.36	7.50	6.73	99.8	0.38	5.0	23.69	39.55
19	0.203	0.07	0.38	0.53	1.56	7.57	6.82	101.8	0.15	5.5	24.08	39.54
20	0.086	0.06	0.32	0.47	1.01	7.83	6.75	101.2	0.08	9.0	24.35	39.58
21	0.519	0.07	3.75	7.29	3.88	104.14	7.49	108.4	1.65	3.0	22.51	39.07
22	0.304	0.06	1.45	3.06	2.50	51.00	7.09	104.3	0.86	3.0	23.26	39.47
23	0.576	0.07	4.04	7.71	4.46	110.14	7.46	107.7	1.42	2.5	22.37	38.93
24	0.507	0.09	0.94	1.42	3.37	15.78	7.41	107.6	1.97	2.5	22.61	39.13
25	0.258	0.08	0.61	1.40	1.91	17.50	6.77	99.7	0.51	5.0	23.32	39.52
26	0.325	0.09	1.09	3.02	2.57	33.56	6.86	101.0	0.85	4.0	23.32	39.47
27	0.213	0.03	0.10	0.20	1.10	6.67	6.68	99.5	0.19	10.5	23.96	39.54
28	0.085	0.08	0.46	0.58	1.08	7.25	6.81	102.1	0.10	8.0	24.33	39.58
29	0.161	0.02	0.08	0.17	1.30	8.50	6.78	100.8	0.23		23.83	39.52
30	0.081	0.04	0.21	0.44	1.38	11.00	6.77	100.7	0.07	10.0	23.88	39.55
31	0.561	0.10	1.71	2.24	4.04	22.40	8.01	115.2	3.26	3.0	22.23	38.75
32	0.604	0.07	0.41	0.56	3.02	8.00	7.68	111.6	3.17	4.0	22.72	39.04
33	0.478	0.08	0.43	0.62	2.66	7.75	7.15	104.7	1.66	3.0	23.05	39.28
34	0.535	0.17	0.36	1.69	2.75	9.94	6.97	102.5	0.81	4.0	23.32	39.23
35	0.167	0.04	0.26	0.49	1.36	12.25	6.84	101.5	0.35		23.74	39.52
36	0.598	0.14	0.86	1.33	3.92	9.50	7.29	106.0	3.22	2.5	22.73	39.07
37	0.633	0.14	0.52	0.83	3.63	5.93	6.05	87.9	2.83	2.5	22.67	39.07
38	0.130	0.03	0.16	0.31	1.28	10.33	6.89	102.0	0.40		23.59	39.54

Sta	TP	PO_4^{3-}	$NO_3^-+NO_2^-$	DIN	Si	DIN/PO_4^{3-}	DO	DO (%)	Chl-*a*	SDD	T	Salinity
No	(µM)	(µM)	(µM)	(µM)	(µM)		(mg/L)		(µg/L)	(m)	(°C)	(‰)
39	0.187	0.04	0.54	0.71	2.49	17.75	6.82	99.5	0.44	5.0	22.81	39.38
40	0.102	0.04	0.16	0.24	0.89	6.00	6.73	100.8	0.17		24.28	39.58
41	0.184	0.03	0.36	0.75	1.79	25.00	6.84	100.9	0.29		23.42	39.46
42	0.116	0.03	0.29	0.48	1.47	16.00	6.79	100.6	0.24		23.63	39.54
43	0.204	0.03	0.14	0.25	1.09	8.33	6.75	100.5	0.09		23.96	39.57
44	0.165	0.03	0.13	0.19	0.98	6.33	6.81	101.7	0.08		24.14	39.55
45	0.008	0.03	0.12	0.19	0.97	6.33	6.81	101.9	0.09		24.25	39.57
46	0.037	0.03	0.20	0.30	1.04	10.00	6.81	101.6	0.08	27.0	24.06	39.54
47	0.245	0.05	0.21	0.41	0.89	8.20	6.80	101.5	0.14	17.0	24.09	39.55
48	0.067	0.03	0.15	0.21	0.96	7.00	6.87	102.4	0.05	21.0	24.02	39.53
50	0.281	0.04	0.15	0.20	1.01	5.00	6.83	102.1	0.05		24.18	39.51
12. Cruise February 2011												
1	0.676	0.12	10.09	17.78	6.99	148.17	8.22	105.8	1.37		16.44	37.90
2	0.160	0.04	0.85	1.23	1.46	30.75	7.71	102.4	0.54		17.71	39.06
4	0.091	0.02	0.18	0.26	0.87	13.00	7.47	100.2	0.34		18.18	39.29
5	0.096	0.02	0.19	0.24	0.77	12.00	7.49	100.0	0.17	21.00	17.95	39.27
6	0.663	0.11	6.64	11.44	4.91	104.00	8.19	105.6	0.37		16.55	37.91
7	0.447	0.08	2.78	5.10	3.79	63.75	7.81	102.2	0.85		17.28	38.14
8	0.188	0.02	0.37	0.53	1.70	26.50	8.04	106.1	0.49		17.40	38.97
9	0.090	0.02	0.13	0.23	0.94	11.50	7.46	100.2	0.42		18.21	39.30
10	0.096	0.02	0.19	0.30	0.74	15.00	7.47	100.1	0.11	24.00	18.13	39.27
11	0.507	0.07	3.50	4.81	4.60	68.71	8.47	108.4	1.61		16.32	37.40
12	0.458	0.06	2.48	2.93	4.23	48.83	8.24	106.6	1.09		16.68	37.99
13	0.158	0.03	0.23	0.32	1.58	10.67	7.65	101.3	0.41	7.00	17.54	39.05
14	0.237	0.08	0.67	1.01	1.77	12.63	7.91	104.2	0.46	4.00	17.40	38.80
15	0.100	0.04	0.23	0.35	0.75	8.75	7.51	100.7	0.23	22.00	18.18	39.28
16	0.887	0.18	7.34	11.52	8.59	64.00	8.69	110.1	2.06		16.08	36.47
17	0.562	0.08	2.60	3.45	4.30	43.13	8.63	111.1	0.96		16.48	37.81
18	0.399	0.06	2.35	2.90	4.06	48.33	8.22	106.2	1.05	3.00	16.56	38.06
19	0.191	0.08	1.08	1.41	2.15	17.63	7.98	105.0	0.89	4.00	17.31	38.64
20	0.195	0.07	0.49	0.76	1.59	10.86	7.85	103.8	0.40	5.00	17.53	38.93
21	0.874	0.30	7.59	11.7	6.44	39.10	8.30	106.5	0.90	2.00	16.46	37.22
22	0.662	0.16	5.50	7.47	6.49	46.69	8.50	108.3	0.74	2.00	16.27	36.86
23	0.818	0.31	8.31	12.56	6.59	40.52	8.28	106.1	0.90	1.50	16.48	37.23
24	0.464	0.12	4.33	5.08	4.55	42.33	8.51	109.5	0.76	2.50	16.59	37.53
25	0.492	0.10	3.25	4.08	4.53	40.80	8.16	104.5	0.84	3.00	16.29	37.57
26	0.491	0.13	2.83	4.07	4.64	31.31	7.85	101.2	0.38	2.50	16.51	37.90
27	0.306	0.12	0.34	0.64	2.42	5.33	7.70	101.0	0.38		17.09	39.05
28	0.137	0.04	0.23	0.46	0.74	11.50	7.51	100.7	0.07	13.00	18.11	39.29
31	0.764	0.37	5.26	7.81	5.69	21.11	7.39	95.6	1.32	1.50	16.69	37.95
32	0.581	0.14	4.85	5.57	3.33	39.79	8.31	107.7	1.64	2.00	16.66	38.26
33	0.539	0.12	0.95	1.23	2.55	10.25	7.93	104.1	0.73	2.00	17.21	38.60
34	0.385	0.09	0.35	0.60	1.38	6.67	7.78	102.5	0.22	1.50	17.28	39.22
35	0.297	0.04	0.72	1.54	2.30	38.50	7.78	101.9	0.35		17.15	38.68
36	0.618	0.33	1.12	1.39	3.29	4.21	7.43	97.7	0.79	1.00	17.27	38.81
37	0.771	0.26	1.28	1.54	3.26	5.92	7.60	98.8	0.54	1.00	16.70	38.78
38	0.370	0.05	0.26	0.41	1.65	8.20	7.64	101.2	0.16		17.46	39.26
39	0.336	0.03	0.17	0.35	1.41	11.67	7.66	101.8	0.15		17.66	39.25
40	0.322	0.03	0.71	0.82	1.43	27.33	7.76	103.4	0.17	6.50	17.78	39.31
43	0.571	0.03	0.21	0.37	1.33	12.33	7.59	100.9	0.08		17.68	39.29
46	0.179	0.03	0.29	0.55	1.10	18.33	7.34	98.5	0.07	18.00	18.17	39.29
47	0.135	0.03	0.11	0.27	1.16	9.00	7.57	101.2	0.06	12.50	17.99	39.29
48	0.103	0.03	0.23	0.32	0.95	10.67	7.37	98.8	0.13	23.00	18.17	39.28