

SPATIAL VARIATIONS OF PARTICULATE ORGANIC MATTER (POM)
COMPOSITION AND CONCENTRATIONS IN SURFACE WATERS AND
SEDIMENTS OF THE MERSIN BAY

A THESIS SUBMITTED TO
THE INSTITUTE OF MARINE SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

İSMAİL AKÇAY

IN PARTIAL FULLFILMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
OCEANOGRAPHY

SEPTEMBER 2015

Approval of the thesis:

**SPATIAL VARIATIONS OF PARTICULATE ORGANIC MATTER (POM)
COMPOSITION AND CONCENTRATIONS IN SURFACE WATERS AND
SEDIMENTS OF THE MERSIN BAY**

Submitted by **İSMAİL AKÇAY** in partial fulfillment of the requirements for the degree of **Master of Science in Department of Oceanography, Institute of Marine Sciences, Middle East Technical University** by,

Prof. Dr. Ahmet Erkan Kıdeys
Head of Institute, **Institute of Marine Sciences**

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

Prof. Dr. Süleyman Tuğrul
Supervisor, **Oceanography**

Examining Committee Members:

Prof. Dr. Süleyman Tuğrul
Oceanography Dept., METU

Prof. Dr. Zahit Uysal
Marine Biology and Fisheries Dept., METU

Assist. Prof. Dr. Nebil Yücel
Water Resources Management and Organization Dept.,
Iskenderun Technical University

Date: _____

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

Name, Last name : İsmail Akçay

Signature :

ABSTRACT

SPATIAL VARIATIONS OF PARTICULATE ORGANIC MATTER (POM) COMPOSITION AND CONCENTRATIONS IN SURFACE WATERS AND SEDIMENTS OF THE MERSIN BAY

Akçay, İsmail

M.Sc., Department of Oceanography

Supervisor: Prof. Dr. Süleyman Tuğrul

September 2015, 122 pages

Spatial and temporal variations of hydrophysical properties (temperature, salinity, density), eutrophication-related parameters (nutrients, Chl-*a*, dissolved oxygen) and particulate organic matter (POM) concentrations and composition (C/N/P) in water column and surface sediments were examined at 33 stations between April 2014 and February 2015 in Mersin Bay located at northeastern (NE) Mediterranean.

Regional and seasonal distributions of nutrients in the Mersin Bay are affected by human-induced pressures. Higher concentrations in polluted coastal waters enhanced biomass (in terms of Chl-*a*) and POM concentrations in both spring and winter. Particulate organic carbon (POC) concentrations exceeded 100 μM in the eutrophic coastal surface waters; similar patterns were also observed in particulate organic nitrogen (PON) and total particulate phosphorus (TPP) concentrations; bulk POM concentration decreased by at least 5-10 fold in less contaminated central bay waters of the bay.

However, POM content of surface sediments within the bay displayed different spatial patterns; higher concentrations of total organic carbon (TOC), total nitrogen (TN) and particulate organic phosphorus (POP) were observed in less polluted sites having muddy sediments on the bottom. Regression analysis of POM concentrations and grain-size distribution shows there is a significant and positive correlation between POM concentrations and mud content in Mersin Bay surface sediments located at NE Mediterranean.

Keywords: Mersin Bay, nutrients, POM, sediment.

ÖZ

MERSİN KÖRFEZİ YÜZEY SULARI VE SEDİMANLARINDA PARTİKÜL ORGANİK MADDE (POM) KOMPOZİSYONU VE KONSANTRASYONLARININ BÖLGESEL DEĞİŞİMİ

Akçay, İsmail

Yüksek Lisans, Oşinografi Bölümü

Tez Yöneticisi: Prof. Dr. Süleyman Tuğrul

Eylül 2015, 122 sayfa

Kuzeydoğu Akdeniz’de bulunan Mersin Körfezi’nde hidro-fiziksel (sıcaklık, tuzluluk, yoğunluk) özelliklerinin, ötrofikasyon-ilişkili parametrelerin (besin tuzları, klorofil-*a*, çözünmüş oksijen) ve partikül organik madde (POM) konsantrasyonlarının ve kompozisyonunun (C/N/P) bölgesel ve zamansal değişimi Nisan 2014-Şubat 2015 dönemleri arasında incelenmiştir.

Besin tuzlarının bölgesel ve mevsimsel dağılımları insan kaynaklı baskılardan etkilenmiştir. Kirli kıyısal alanda yüksek konsantrasyonlar biyokütle (klorofil-*a* bakımından) ve POM konsantrasyonlarını bahar ve kış döneminde artırmıştır. Partikül organik karbon (POC) konsantrasyonları ötrofik kıyı yüzey sularında 100 μM ’ı aşmıştır ve partikül organik azot (PON) ve toplam partikül fosfor (TPP) dağılımları benzer özellik göstermiştir; az kirli bölgelerde POM konsantrasyonlarında 5-10 katlık bir azalma gözlenmiştir.

Yüzey sedimanlarında, POM konsantrasyonları farklı özellik göstermiştir. Az kirli bölgelerde çamur içeriği fazla olan sedimanlarda yüksek toplam organik karbon (TOC), toplam azot (TN) ve partikül organik fosfor (POP) konsantrasyonları görülmüştür.

Mersin Körfezi yüzey sedimanlarında POM konsantrasyonları ve tane boyu dağılımı arasındaki regresyon analizi POM konsantrasyonu ve çamur içeriği arasında önemli ve pozitif bir ilişki olduğunu göstermektedir.

Anahtar Kelimeler: Mersin Körfezi, besin tuzları, POM, sediman.

To my family

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisor Prof. Dr. Süleyman Tuğrul for his valuable guidance, advice and criticism in my study.

I would like to thank Assist. Prof. Dr. Nebil Yücel for his valuable comments and suggestions.

I would also like to thank Prof. Dr. Zahit Uysal for his criticism to improve this study in scientific aspects.

I want to thank to my office-mate Pınar Külekçi for her endless support for this study and also special thanks to my friends Mehmet Durmaz, Melek Develi, Halil İpek, Ceyhun Demir, Önder Yıldırım, Mehmet Can Var and İlhan Bağ for mental support and special friendship.

I am grateful to our technical staff Şehmus Başduvar, Ramazan Ülger, Esabil Kakaç, Eren Dinçer, Merve Yeşildağ and Mehmet Durmaz for their kind assistance.

Finally, I am very grateful to my family for encouraging me within this study.

This study was supported by TUBITAK within 111G152 (Dredging Applications and Environmental Management of Dredged Material) project.

TABLE OF CONTENTS

ABSTRACT.....	iv
ÖZ	v
DEDICATION	vi
ACKNOWLEDGMENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xii
CHAPTER 1	1
INTRODUCTION	1
1.1. Distribution of Particulate Organic Matter (POM) in the Marine Environment.....	1
1.2. Oceanographic Properties of Northeastern Mediterranean	3
1.2.1. Hydrography and Circulation of the Northeastern Mediterranean.....	5
1.2.2. Principal Hydro-Chemical Properties of the Northeastern Mediterranean	6
1.2.3. Distribution of Inorganic Nutrients in the Northeastern Mediterranean	7
1.2.4. Distribution of Particulate Organic Matter (POM) in the Northeastern Mediterranean	8
1.2.5. Distributions of Total-N and Total-P in the Northeastern Mediterranean	9
1.3. Phosphorus Cycle.....	11
1.4. Composition of Sediments in the Marine Environment.....	13
1.4.1. Classification of Marine Sediments According to Their Grain-Size	14
1.4.2. Distribution of POM in the Surface Sediments of the Northeastern Mediterranean....	15
1.5. Previous Studies on POM Measurements in Surface Waters and Sediments of Cilician Basin of NE Mediterranean and Gaps in Regional POM Data.....	16
1.6. Aim and Objectives of the Study	20
CHAPTER 2	23
EXPERIMENTAL.....	23
2.1. Sampling Locations and Strategy	23
2.2. Measurements of Physical (Salinity, Temperature, Depth) Parameters.....	25
2.3. Measurements of Water Transparency	25
2.4. Sampling for Biochemical and Geochemical Parameters	26
2.4.1. Sampling for Dissolved Oxygen (DO).....	26

2.4.2. Sampling for Dissolved Inorganic Nutrients and Total Phosphorus (TP)	26
2.4.3. Sampling for Chl- <i>a</i>	27
2.4.4. Sampling for Total Suspended Solid	27
2.4.5. Sampling for Particulate Organic Matter (POM) in Seawater	27
2.4.6. Sampling for POM in Sediments	27
2.4.7. Sampling for Grain-Size Analysis	28
2.5. Analysis of Biochemical Parameters	28
2.5.1. Dissolved Oxygen Analysis	28
2.5.2. Dissolved Inorganic Nutrient Analysis	28
2.5.2.1. Dissolve Inorganic Phosphorus (PO ₄ -P) Analysis	28
2.5.2.2. Nitrate and Nitrite (NO ₃ +NO ₂ -N) Analysis	29
2.5.2.3. Nitrite (NO ₂ -N) Analysis	29
2.5.2.4. Ammonium (NH ₄ -N) Analysis	29
2.5.2.5. Reactive Silicate (Si(OH) ₄ -Si) Analysis	29
2.5.3. Total Phosphorus (TP) Analysis	30
2.5.4. Particulate Organic Matter (POM) Analysis.....	31
2.5.4.1. Particulate Organic Carbon (POC) and Nitrogen (PON) Analysis	31
2.5.4.2. Total Particulate Phosphorus (TPP) Analysis	32
2.5.5. Chlorophyll- <i>a</i> (Chl- <i>a</i>) Analysis	35
2.5.6. Particulate Organic Matter (POM) Analysis in Sediments	35
2.5.6.1. Total Organic Carbon (TOC) and Total Nitrogen (TN) Analysis.....	35
2.5.6.2. Total Particulate Phosphorus (TPP) and Particulate Organic Phosphorus (POP) Analysis in Sediments.....	36
2.5.7. Grain-Size Analysis in Sediments.....	39
CHAPTER 3	40
RESULTS	40
3.1. Spatial Variations of Hydrographic Parameters in Surface Waters of the Study Area...	40
3.2. Spatial Variations of Water Transparency in the Study Area	44

3.3. Spatial Variations of Nutrients, Dissolved Oxygen (DO) and Chl- <i>a</i> in Surface Waters of the Study Area.....	45
3.4. Spatial Variations of Particulate Organic Matter (POM) in Surface Waters of the Study Area.....	56
3.5. Spatial Variations of Total Carbon (TC), Particulate Phosphorus (TPP) and Nitrogen (TN) and Total Organic Carbon (TOC) and Particulate Organic Phosphorus (POP) in Surface Sediments of the Study Area.....	60
3.6. Grain-Size Distributions in Surface Sediments of the Study Area	65
CHAPTER 4	68
DISCUSSION.....	68
4.1. Spatio-Temporal Variations of Hydrographic Properties of the Mersin Bay	69
4.2. Spatio-Temporal Variations of Eutrophication Related BioChemical Parameters	71
4.2.1. Dissolved Inorganic Nutrients	71
4.2.2. Chlorophyll- <i>a</i> and Dissolved Oxygen (DO)	76
4.2.3. Particulate Organic Matter (POM).....	79
4.2.4. Ratios of Dissolved Inorganic Nutrients (N/P) and Molar Ratios (C/N/P) in Bulk POM	86
4.3. Spatio-Temporal Variations of POM Concentrations and Elemental Composition (C/N/P) in Surface Sediments of the Mersin Bay	94
4.3.1. Spatio-Temporal Comparison of POM in Surface Sediments	94
4.3.2. C/N/P Ratios in the Bay Sediments	100
CHAPTER 5	102
CONCLUSION.....	102
REFERENCES	106
APPENDICES	116
APPENDIX A. HYDROPHYSICAL AND BIOCHEMICAL PARAMETERS MEASURED IN SEAWATER.....	116
APPENDIX B. GEOCHEMICAL PARAMETERS MEASURED IN SURFACE SEDIMENTS	121

LIST OF TABLES

Table 1.1. The canonical definition of sediment grain-sizes (Wentworth, 1922).....	14
Table 2.1. Coordinates of the sampling stations visited in the study area of Mersin Bay	24
Table 2.2. Volume of stock inorganic phosphorus solution (50 μ M) added and measured absorbance values	34
Table 2.3. Extraction procedure for TPP and PIP analysis in sediments	36
Table 2.4. Volumes of the phosphate standard (50 μ M) added and the measure absorbance values	38
Table 2.5. Udden-Wentworth grain-size classification scheme (Wentworth, 1922)	39
Table 3.1. Average values and the range of hydrographic parameters measured in the coastal and central bay surface and near-bottom waters of the study area in April 2014.	43
Table 3.2. Grain-size results and TC, TOC, TN, TPP, PIP and POP concentrations and their molar ratios in surface sediments in April 2014 and February 2015	67
Table 4.1. POM concentrations and elemental compositions (C/N, N/P) in surface waters of the selected stations within the Mersin Bay in April 2014 and February 2015.	83
Table 4.2. POC, PON, TPP concentrations and its elemental compositions observed in NE Mediterranean.....	93

LIST OF FIGURES

Figure 1.1. Particulate Organic Matter (POM) cycle in marine environment (Herndl and Reinthaler, 2013).....	2
Figure 1.2. Surface circulation of Mediterranean Sea (Frangou <i>et al.</i> , 2010) and spatial distribution of surface chlorophyll- <i>a</i> concentration (mg/m^3) obtained by Satellite Modis Aqua in the Cilician basin of the NE Mediterranean in April 2015.....	4
Figure 1.3. General circulation of the NE Mediterranean (Collins and Banner, 1979).	5
Figure 1.4. Vertical profiles of Temperature and Salinity in the Cilician Basin of the Eastern Mediterranean for March 1991-March 1994 (Yılmaz and Tuğrul, 1998).....	6
Figure 1.5. Depth profiles of PO_4 and NO_3 in Rhodes cyclonic Gyre (Yılmaz and Tuğrul, 1998).	7
Figure 1.6. Depth profiles of PO_4 and TP from the data collected during expedition of RV Atlantis and RV Chain (Miller <i>et al.</i> , 1970 taken from Sert, 2010).....	10
Figure 1.7. Depth profiles of nitrate and DON in the NE Atlantic and in the NW Mediterranean (Aminot and K��rouel, 2004).....	10
Figure 1.8. Marine P cycle (Paytan and McLaughlin, 2007).	11
Figure 1.9. Typical distribution of SRP in the world’s major oceans: North Atlantic, North Pacific, Indian Ocean and Southern Ocean (Benitez-Nelson, 2000).	12
Figure 2.1. Sampling locations visited in Mersin bay in April 2014 and February 2015 (•).	23
Figure 2.2. 12-bottle Rosette System coupled on CTD probe.	26
Figure 2.3. Calibration curve for TP analysis prepared with digested MQ water.....	31
Figure 2.4. Calibration P-curve for TPP measurements, prepared by using standard-spiked and digested MQ (distilled de-ionized water, MQ) water with blank GF/F filters.....	33
Figure 2.5. Calibration curve of standard addition method for TPP analysis.	34
Figure 2.6. Weight optimization curve for TPP analysis in sediments.	37
Figure 2.7. Calibration curve of standard addition method for TPP analysis in sediments. ..	39
Figure 3.1. Surface distributions of temperature ($^{\circ}\text{C}$), salinity (psu) in the study area of Mersin Bay in April 2014.	41
Figure 3.2. Vertical profiles of temperature, salinity and density at selected stations in the inner bay (upper) and central bay (lower) in April 2014.	42
Figure 3.3. Surface distributions of temperature ($^{\circ}\text{C}$) and salinity (psu) in the study area of Mersin Bay in February 2015.	42
Figure 3.4. Vertical profiles of temperature, salinity and density at selected stations in the inner bay (upper) and central basin (lower) in February 2015.....	43
Figure 3.5. Distributions of SDD (m) and surface TSS (mg/L) concentrations in the study area of Mersin Bay in April 2014 (upper) and February 2015 (lower).....	45

Figure 3.6. Surface distributions of PO ₄ (μM) and TP (μM) concentrations in the study area of Mersin Bay in April 2014.....	46
Figure 3.7. Vertical profiles of PO ₄ and TP at selected stations in the inner bay (upper) and central bay (lower) in April 2014.....	47
Figure 3.8. Surface distributions of PO ₄ (μM) and TP (μM) concentrations in the study area of Mersin Bay in February 2015.....	47
Figure 3.9. Vertical profiles of PO ₄ and TP at selected stations in the inner bay (upper) and central bay (lower) in February 2015.....	48
Figure 3.10. Surface distributions of NO ₃ (μM), NH ₄ (μM) and DIN (μM) concentrations in the study area of Mersin Bay in April 2014.....	49
Figure 3.11. Vertical profiles of NO ₃ , NH ₄ and DIN at selected stations in the inner bay (upper) and central bay (lower) in April 2014.....	50
Figure 3.12. Surface distributions of NO ₃ (μM), NH ₄ (μM) and DIN (μM) concentrations in the study area of Mersin Bay in February 2015.....	51
Figure 3.13. Vertical profiles of NO ₃ , NH ₄ and DIN at selected stations in the inner bay (upper) and central bay (lower) in February 2015.....	51
Figure 3.14. Surface distribution of Si (μM) concentrations in the study area of Mersin Bay in April 2014 (left) and February 2015 (right).....	52
Figure 3.15. Surface distribution of DO, BOD ₅ (mg/L) and Chl- <i>a</i> (μg/L) concentrations in the study area of Mersin Bay in April 2014.....	53
Figure 3.16. Vertical profiles of DO and Chl- <i>a</i> at selected stations in the inner bay (upper) and central bay (lower) in April 2014.....	54
Figure 3.17. Surface distribution of DO, BOD ₅ (mg/L) and Chl- <i>a</i> (μg/L) concentrations in the study area of Mersin Bay in February 2015.....	55
Figure 3.18. Vertical profiles of DO and Chl- <i>a</i> at selected stations in the inner bay (upper) and central bay (lower) in February 2015.....	56
Figure 3.19. Surface distributions of POC (μM), PON (μM) and TPP (μM) concentrations in the study area of Mersin Bay in April 2014.....	57
Figure 3.20. Vertical profiles of POC, PON and TPP at selected stations in the inner bay (upper) and central bay (lower) in April 2014.....	58
Figure 3.21. Surface distributions of POC (μM), PON (μM) and TPP (μM) concentrations in the study area of Mersin Bay in February 2015.....	59
Figure 3.22. Vertical profiles of POC, PON and TPP at selected stations in the inner bay (upper) and central bay (lower) in February 2015.....	60
Figure 3.23. Distributions of TC (mg/g), TIC (mg/g) and TOC (mg/g) concentrations of surface sediments in the study area of Mersin Bay in April 2014.....	61

Figure 3.24. Distributions of TC (mg/g), TIC (mg/g) and TOC (mg/g) concentrations of surface sediments in the study area of Mersin Bay in February 2015.	62
Figure 3.25. Distributions of TN (mg/g) concentrations of surface sediments in the study area of Mersin Bay in April 2014 (left) and February 2015 (right).....	63
Figure 3.26. Distributions of TPP (mg/g), PIP (mg/g) and POP (mg/g) concentrations of surface sediments in the study area of Mersin Bay in April 2014.	64
Figure 3.27. Distributions of TPP (mg/g), PIP (mg/g) and POP (mg/g) concentrations of surface sediments in the study area of Mersin Bay in February 2015.	65
Figure 3.28. Grain-size distributions of surface sediments in the study area of Mersin Bay in April 2014.	66
Figure 3.29. Grain-size distributions of surface sediments in the study area of Mersin Bay in February 2015.	66
Figure 4.1. Surface distributions of temperature (°C), salinity (psu) and density (sigma-t) in Mersin bay in April 2009 (Sert, 2010) and 2014 (this study).	70
Figure 4.2. Surface distributions of PO ₄ (µM) and TP (µM) concentrations in the study area of Mersin Bay in April 2014 (upper) and February 2015 (lower).	72
Figure 4.3. Dissolved inorganic nutrients and Chl- <i>a</i> vs. salinity plot of the data measured from the study area of Mersin Bay in April 2014.	74
Figure 4.4. Dissolved inorganic nutrients and Chl- <i>a</i> vs. salinity plot of the data measured from the study area of Mersin Bay in February 2015.	74
Figure 4.5. Surface distributions of dissolved inorganic nutrients (µM), Chl- <i>a</i> (µg/L) and DO (mg/L) concentrations throughout the study area in winter period (Kaptan, 2013).....	75
Figure 4.6. Surface distributions of dissolved inorganic nutrients (µM), Chl- <i>a</i> (µg/L) and DO (mg/L) concentrations throughout the study area in spring period (Kaptan, 2013).....	76
Figure 4.7. Surface distributions of Chl- <i>a</i> and DO concentrations in Mersin bay in February 2009 (Sert, 2010).	78
Figure 4.8. Surface distributions of chl- <i>a</i> and DO concentrations in Mersin bay in April 2010 (Sert, 2010).	79
Figure 4.9. Correlations between nutrients (pressure parameter), Chl- <i>a</i> and POM (state parameters of eutrophication) concentrations in the study area of Mersin Bay.	81
Figure 4.10. Time series distribution of POC, PON, POP and PON/POP in northeastern Mediterranean between 2001-2003 (Doğan-Sağlamtimur, 2007).....	85
Figure 4.11. Surface current pattern of Mersin Bay in winter 2015 (left) and summer 2009 (right) (TUBITAK-DIPTAR 3 rd progress report, 2015).	87
Figure 4.12. Spatial distributions of NO ₃ /PO ₄ and DIN/PO ₄ molar ratios in surface waters of the study area in April 2014.....	87

Figure 4.13. Spatial distributions of NO_3/PO_4 and DIN/PO_4 molar ratios in surface waters of the study area in February 2015.....	88
Figure 4.14. NO_x and DIN vs. PO_4 plot of the data measured from the study area of Mersin Bay in the study period.	89
Figure 4.15. POC vs. PON and PON vs. TPP plot of the data measured from the study area of Mersin Bay in the study period.....	91
Figure 4.16. Spatial distributions of POC/PON and PON/TPP molar ratios in surface waters throughout the study area in April 2014 (upper) and February 2015.....	93
Figure 4.17. TPP vs. POP/TPP and TPP vs. POP plots of the sediment data obtained from the study area of Mersin Bay in spring (upper) and winter (lower).....	96
Figure 4.18. TOC vs. POP plot of the sediment data from the study area of Mersin Bay in spring and winter.....	97
Figure 4.19. TN/POP vs. TOC/TN plot of the sediment data from the study area of Mersin Bay in spring and winter.....	97
Figure 4.20. TOC , TPP and POP/TPP vs. mud content plots of the sediment data from the study area of Mersin Bay in the spring (upper) and in winter (lower).....	98
Figure 4.21. Grain-size distributions of surface sediments in the study area of Mersin Bay in April 2014 and February 2015.....	99
Figure 4.22. Spatial distributions of TOC/TN and TN/POP molar ratios of surface sediments in the study area of Mersin Bay in April 2014 (upper) and February 2015.....	101
Figure 5.1. Dissolved inorganic nutrients and $\text{Chl-}a$ vs. salinity plot of the data measured from the study area of Mersin Bay in April 2014.....	103
Figure 5.2. Dissolved inorganic nutrients and $\text{Chl-}a$ vs. salinity plot of the data measured from the study area of Mersin Bay in February 2015.....	103

CHAPTER 1

INTRODUCTION

1.1. Distribution of Particulate Organic Matter (POM) in the Marine Environment

Particulate organic matter (POM) in the oceans consists of living organisms and non-living (detrital) materials of different sizes and sinking rates (Chin *et al.*, 1998 and references therein; Volkman and Tanoue, 2002; Giani *et al.*, 2003). Bulk POM in the sea is mainly autochthonous origin from living organisms and physico-chemical transformations involving the colloidal organic compounds. However, Bulk POM in coastal waters fed by river discharges and human induced inputs (domestic + industrial and agricultural sources) may be composed of mainly autotrophic and partly allochthonous origin. Riverine inputs influence the coastal POM distributions with atmospheric inputs (dry + wet deposition) may contribute to the pool of bulk POM (Chin *et al.*, 1998 and references therein; Giani *et al.*, 2003), especially in oligotrophic seas such as the eastern Mediterranean (UNEP, 1989; Yılmaz and Tugrul, 1998; Kress and Herut, 2001; Krom *et al.*, 2004). POM in surface waters is not mainly composed of phytoplankton throughout the year; bacteria, microzooplankton, protozoa and detrital material constitute major fraction of the bulk POM when blooming is at minimal levels (Vostokov and Vedernikov, 1988; Polat *et al.*, 1998).

In the euphotic zone, CO₂ is fixed accompanied by sun light and POC is produced from inorganic constituents of seawater (nutrients). Between 1 and 40% of primary production is sinking below the euphotic zone and it exponentially attenuates to the base of the mesopelagic zone at around 1.000 m. In the water column, organic matter is remineralized, converting organic matter to CO₂. Therefore, only 1% of the surface production is buried in sea floor (Herndl and Reinthaler, 2013).

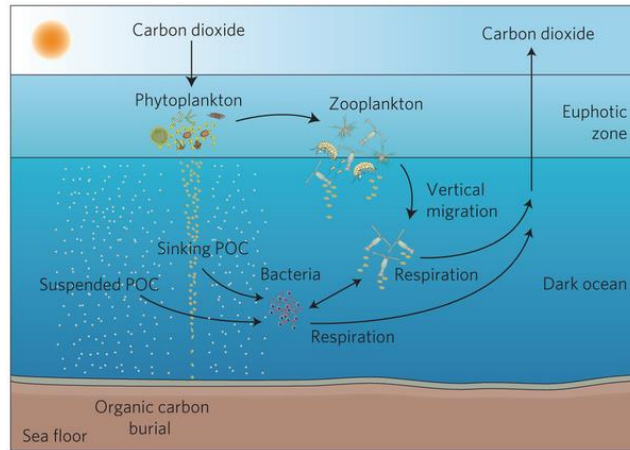


Figure 1.1. Particulate Organic Matter (POM) cycle in marine environment (Herndl and Reinthaler, 2013).

In this study, effects of dissolved inorganic nutrients loads originated from major rivers and wastewater discharged on POM production and its elemental composition (C/N/P) will be investigated in coastal ecosystem of the Mersin Bay located at northeastern (NE) Mediterranean having oligotrophic property. Moreover, the projections of high POM enhancement in surface sediments of the inner bay will also be determined. Regional variations of POM composition and concentrations in surface waters and sediments will be determined to assess the impacts of terrestrial inputs to oligotrophic NE Mediterranean.

Production, degradation and settling rates of POM in the euphotic zone fed by nutrient inputs from internal and external sources simply determine its abundance and composition in the water column of coastal and open seas (Tselepides *et al.*, 2000; Ediger *et al.*, 2005). Biochemical and physical processes dominating the POM distributions also lead to determine the concentrations of algal biomass (in terms of chlorophyll-*a*) in the euphotic zone, nutrients and dissolved oxygen in the entire water column from surface to deep waters of the oceans (Coban-Yıldız *et al.*, 2000).

Suspended (bulk) POM, also called seston in the marine environments, has relatively slow sinking rates (Çoban-Yıldız *et al.*, 2000; Doğan-Sağlamtimur, 2007; Erdoğan, 2014) and may be sampled by conventional Niskin bottles of different volumes during oceanographic studies

The elemental composition of (C/N/P ratio) of POM produced by photosynthesis in the sea under optimal growth conditions is expected to have a nearly invariant

chemical composition known as Redfield C/N/P ratio of 106/16/1 (Redfield *et al.*, 1963; Goldman *et al.*, 1979). However, abundance and elemental composition of bulk POM in the marine environment are controlled by complex physical and biochemical processes interacting in the upper layer as well as nutrient supplies from various sources (Tselepidis *et al.*, 2000; Ediger *et al.*, 2005).

POC concentrations in the western Mediterranean generally varied between 1.88 and 3.87 μM in the less productive open sea (Rabitti *et al.*, 1994) whilst in the more productive basins, POC concentrations reached to 9.0 μM due to higher nutrient supply from deep waters and land-based sources (Socal *et al.*, 1999). Expectedly, for the nitrogen component of the bulk POM, same regional and temporal trends appear with values ranging between 0.1 and 1.4 μM in the stratified period (Socal *et al.*, 1999; Doval *et al.*, 1999). Particulate matter profiles display coherent peaks with the deep chlorophyll maximum (DCM) zone constituting a remarkable fraction of total POM in the upper layer. The Levantine basin of the northeastern Mediterranean displayed pronounced spatial and temporal variability in the hydro-dynamical and biochemical properties from surface waters to at least 1000 m depth. Relatively high POC/PON and POC/Chl-*a* ratios in the NE Mediterranean indicate that POM pool composed mainly of detritus, bacteria and zooplankton (Ediger *et al.*, 2005). Limited POM data from the eastern Mediterranean indicates that the upper layer waters contain low concentrations of bulk POM (Abdel-Moati, 1990; Ediger *et al.*, 1999 referenced in Doğan-Sağlamtimur, 2007).

The Mersin Bay, fed by terrestrial inputs (rivers and wastewater discharges), is located on the wide shelf of NE Mediterranean having oligotrophic properties during the year. Since the present study aims to assess POM pool in the coastal bay waters, the basic oceanographic properties of the oligotrophic northeastern Mediterranean basin are introduced in this section to sound understand the variability in spatial distributions and elemental composition of bulk POM in the surface waters and surface sediments of the bay.

1.2. Oceanographic Properties of Northeastern Mediterranean

Mediterranean (Figure 1.2), the largest semi-enclosed sea among other European seas, is connected to the Oceans System by the Strait of Gibraltar and to the Red Sea through the Suez Canal (EEA, 1999) and the Black Sea by the Turkish Straits System

(EEA, 1999; Tuğrul *et al.*, 2002). The Mediterranean basin is divided into two sub-basins (Western and Eastern Mediterranean) by a relatively narrow opening between Tunisia and Sicily. These sub-basins have naturally different algal and animal communities due to direct effect of Atlantic inflow through the Gibraltar Strait and excess evaporation in the eastern basin (Karydis and Kitsiou, 2012).

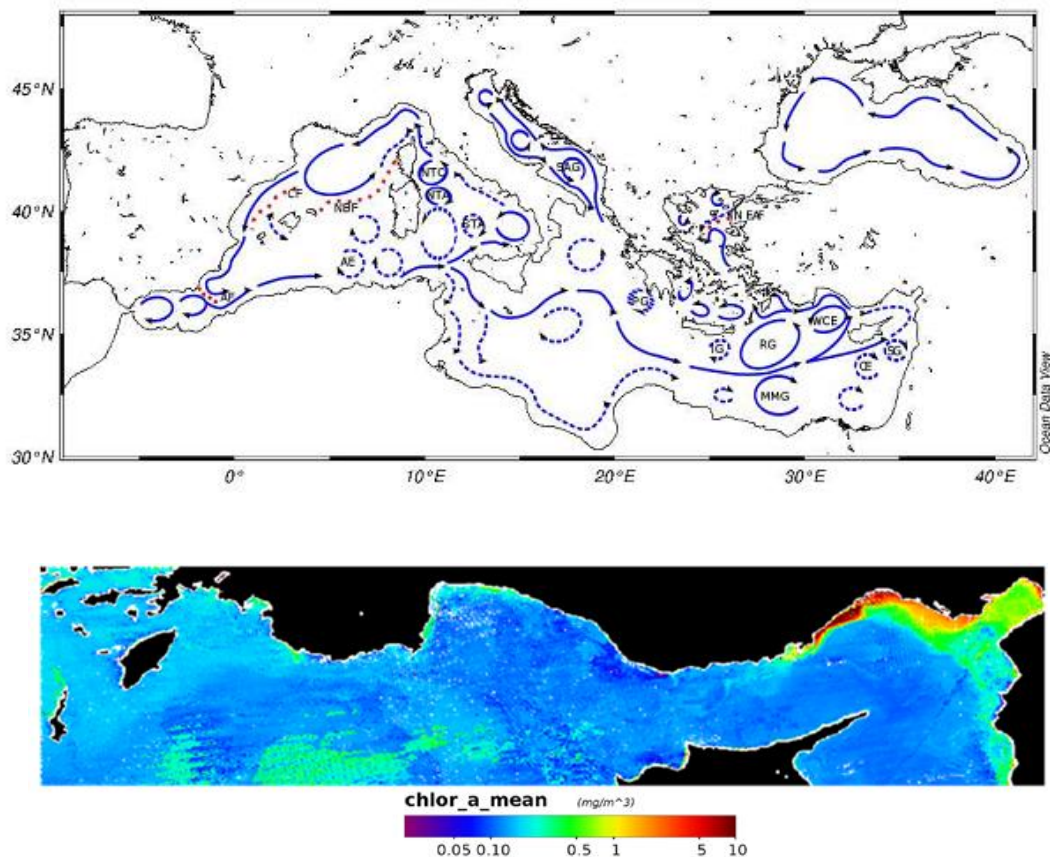


Figure 1.2. Surface circulation of Mediterranean Sea (Frangou *et al.*, 2010) and spatial distribution of surface chlorophyll-*a* concentration (mg/m^3) obtained by Satellite Modis Aqua in the Cilician basin of the NE Mediterranean in April 2015.

The Northeastern Mediterranean, a distinct example of oligotrophic seas, display three distinct regional behaviors which are the cyclonic Rhodes basin, the anti-cyclonic Cilician basin and transitional area (periphery and frontal regions) (Özsoy *et al.* 1991; Ediger *et al.*, 2005; POEM Group, 1992). Open surface layer of NE Mediterranean receives limited supply of nutrients both from internal and external sources (Ediger *et al.*, 2005; Yılmaz and Tuğrul, 1998; Béthoux *et al.*, 1992); low algal productivity in the euphotic zone of the basin is principally limited by low concentrations of phosphorus due to unusually high molar ratio of nitrate to

phosphate (NO_3/PO_4) in the deep water is $\sim 28:1$ (Krom *et al.*, 1991; Yılmaz and Tugrul, 1998; Kress and Herut, 2001) and in atmospheric wet + dry deposition and regional rivers waters (Koçak *et al.*, 2010).

1.2.1. Hydrography and Circulation of the Northeastern Mediterranean

The eastern Mediterranean is an open but isolated basin for global ocean circulation system (POEM group, 1992). General circulation system consists of three main elements that are Rhodes gyre, Mersa-Matruh gyre and Shikmona gyre (Figure 1.3) (Özsoy *et al.*, 1991; POEM group, 1992).

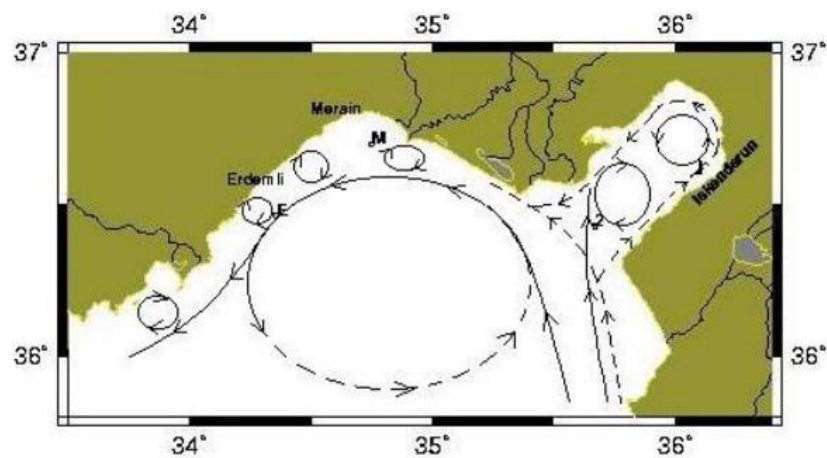


Figure 1.3. General circulation of the NE Mediterranean (Collins and Banner, 1979).

There are mainly four water masses in the water column of Levantine basin (Figure 1.4) based on climatological, salinity and water depth profiles (Hecht *et al.*, 1988; Kress and Herut, 2001; Özsoy *et al.*, 1991); Saltier Levantine surface waters occupy the upper layer; then less saline Atlantic water and Levantine intermediate water occupy the intermediate layer zone between the upper layer and the less saline, cooler Levantine deep water (Figure 1.4). The Atlantic water (AW) observed in the eastern Mediterranean, enters the basin through the straits of Gibraltar and passed through Sicily channel whose salinity and depth range increase as it flows eastward (Özsoy *et al.*, 1989). Although the formation mechanism of the LIW is not known exactly, generally, high evaporation in summer, winter cooling and vertical mixing of saline surface water result in the formation of LIW during winters (Özsoy *et al.*, 1993; Souvermezoglou and Krasakopoulou, 1999). Finally, these water masses reach intermediate depths in late-winter and early-spring period. The eastern Mediterranean deep water is originated from surface water of the Adriatic Sea

leaving the Adriatic as a bottom current through the Otranto channel (POEM group, 1992).

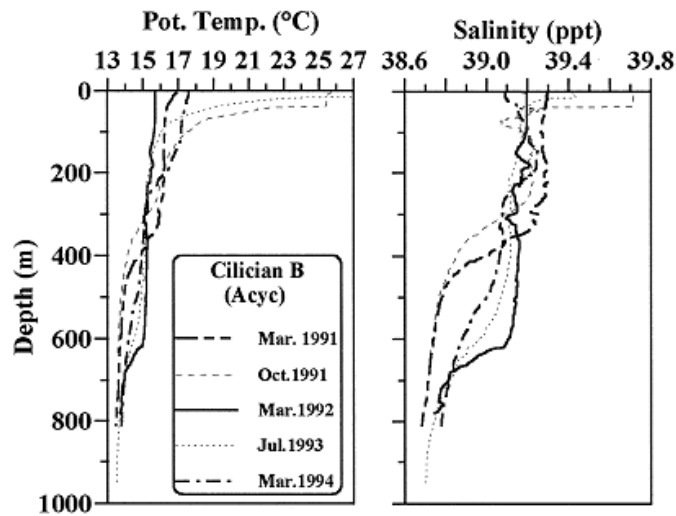


Figure 1.4. Vertical profiles of Temperature and Salinity in the Cilician Basin of the Eastern Mediterranean for March 1991-March 1994 (Yılmaz and Tuğrul, 1998).

1.2.2. Principal Hydro-Chemical Properties of the Northeastern Mediterranean

The Eastern Mediterranean is one of the world's oligotrophic seas due to limited nutrient supply to its surface waters from internal and external sources (UNEP, 1989; Yılmaz and Tuğrul, 1998; Kress and Herut, 2001; Krom *et al.*, 2004). Therefore, its surface layer waters are highly depleted in reactive inorganic nutrients for most of the year (Krom *et al.*, 2005). Recent studies conducted in NE Mediterranean revealed that the upper layer of the Rhodes cyclonic gyre is much more productive than the other sub-basins of Levantine Sea dominated by anticyclonic eddies and major current system (Ediger *et al.*, 2005; Yılmaz and Tuğrul, 1998). Remarkable spatial variations in the nutricline depth determine the supply of nutrients from the gradient zone to the overlying waters by physical processes. In open seas dominated by anticyclonic eddies, the nutricline is established at greater depths, much below the euphotic zone, which limits nutrient supply to the upper layer waters and thus algal production and bulk POM in the euphotic zone, as recently experienced in the Eastern Mediterranean (Ediger *et al.*, 2005; Krom *et al.*, 2005). In the nutrient-poor anticyclonic eddies, solar light can penetrate greater depths down to 100-150m, resulting in the formation of deep chl-*a* maximum (DCM) in the cooler waters below the seasonal thermocline. The DCM is principally is dominated by limited

nutrient inputs from intermediate depths and regeneration of suspended POM produced in the light-limited zone (Ediger *et al.*, 2005).

1.2.3. Distribution of Inorganic Nutrients in the Northeastern Mediterranean

Depth profiles of nutrients over Levantine basin of the eastern Mediterranean display different vertical features in the cyclonic Rhodes basin and anti-cyclonic Cilician basin and transitional areas of Levantine Sea (Özsoy *et al.*, 1991; Yılmaz and Tuğrul, 1998; Ediger *et al.*, 2005).

The surface concentrations of dissolved inorganic nutrients in the open sea are consistently low in the euphotic zone during spring-autumn period, increasing steadily within the pycnocline and reaching the peak values in the upper depths of Levantine deep waters (LDW) where the dissolved oxygen concentrations declined to the lowest levels. However, the nutrient maximum zone appears at much greater depths in the core of the Levantine anti-cyclonic gyres, where the nutricline is formed between 300-500 m (Yılmaz and Tuğrul, 1998). However, in the Rhodes cyclonic Gyre, the nutricline is formed at 75-100 m (Figure 1.5).

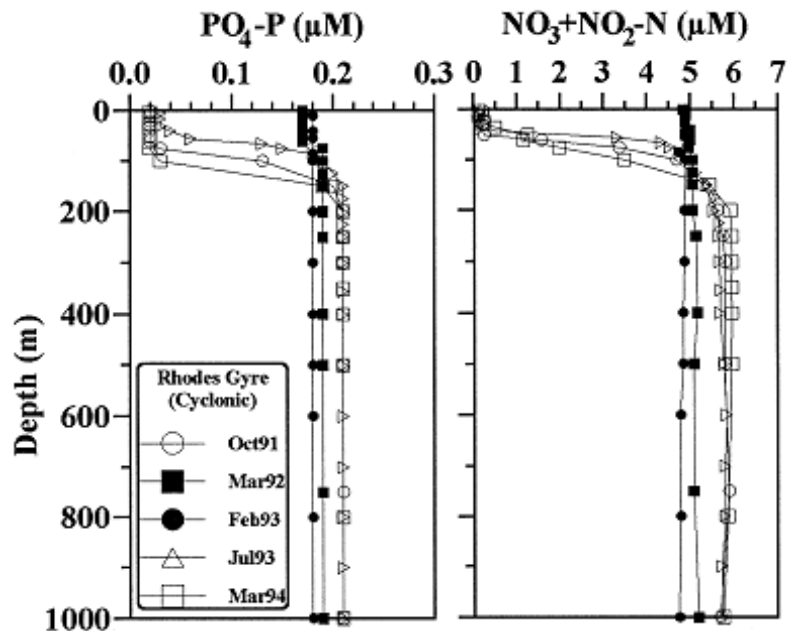


Figure 1.5. Depth profiles of PO_4 and NO_3 in Rhodes cyclonic Gyre (Yılmaz and Tuğrul, 1998).

Surface nutrient concentrations in the Cilician basin of Levantine Sea are as low as 0.02-0.03 μM for PO_4 and 0.1-0.3 μM for NO_3 for most of the year (Yılmaz and

Tuğrul, 1998; Sağlamtimur and Tuğrul, 2004). However, in winter, nutrient concentrations in the euphotic zone (EZ) of the Rhodes Cyclonic Gyre may increase markedly due to supply of nutrients from the nutricline zone by deep convective mixing and upwelling of LDW under severe winter conditions as experienced before (Ediger *et al.*, 2005); the near-surface concentrations were determined to range between 0.05-0.2 μM for PO_4 and 2-6 μM levels for NO_3 . N/P molar ratio in the upper layer varied between 5 and 20 during spring-autumn period when the phosphate concentration was as low as 0.02-0.03 μM (Yılmaz and Tuğrul, 1998). In P-depleted waters, weak acid soluble organic-P may cause positive interferences during reactive phosphate measurements by colorimetric method at low pH (~1.0) levels, which may increase N/P molar ratio in reactive phosphate-depleted surface waters. Higher N/P molar ratios varying at levels of 29-38 during summer-early autumn period have been obtained by more sensitive P-data of MAGIC method (Doğan-Sağlamtimur, 2007) in the shelf break waters of Cilician Basin, NE Mediterranean.

1.2.4. Distribution of Particulate Organic Matter (POM) in the Northeastern Mediterranean

Bulk POM in the upper layer of marine environments is composed of living organisms and detrital materials of different sizes and settling rates. POM composition in the open sea is mainly autochthonous; however, the bulk POM pool in the coastal waters may contain allochthonous organic compounds introduced by terrestrial inputs. Atmospheric inputs (dry + wet deposition) influence both open and coastal systems, depending on the intensity of sources (Chin *et al.*, 1998 and references therein; Volkman and Tanoue, 2002 Giani *et al.*, 2003). Suspended POM in the upper layer waters of marine environments consists of phytoplankton, microzooplankton, aggregates of bacteria and detrital materials (Çoban-Yıldız *et al.*, 2000). In the coastal and open seas, the particulate organic matter of biogenic origin undergoes transformations and degradation both during settling and at the water sediment interface, which leads to nutrient regeneration and oxygen depletion in water column and water-sediment interface. Only a small fraction of POM sinking down the bottom is buried; the rest is utilized by benthic communities (Herndl and Reinthaler, 2013). The elemental composition of (C/N/P ratio) of POM produced by

photosynthesis in the sea under optimal nutritional conditions is expected to have a nearly invariant chemical composition known as the Redfield C/N/P ratio of 106/16/1 (Goldman *et al.*, 1979). This ratio, however, displays considerable regional variations, ranging between 10-20, due to changes in trophic status of water bodies and nutrient limitations during POM production (Goldman *et al.*, 1979; Sakshaug *et al.*, 1983; Çoban-Yıldız *et al.*, 2000). It appears that the abundance and chemical composition of bulk POM in the marine environment are determined by complex physical and biochemical processes interacting in the upper layer as well as rates of nutrient supplies from various sources (Tselepides *et al.*, 2000; Ediger *et al.*, 2005). Therefore, in the Mediterranean upper layer, higher concentrations of particulate matter were observed in more productive western regions and seasons (Socal *et al.*, 1999) and also coastal zone fed by nutrient-rich river discharges as experienced in the shelf waters of Cilician Basin, NE Mediterranean.

Bulk POC concentrations ranges between 2-5 μM in the less productive open sea of NE Mediterranean (Erdoğan, 2014), increasing markedly to 8-10 μM levels in the more productive western basin and coastal waters fed by terrestrial nutrient inputs (Socal *et al.*, 1999). In the less productive open sea, depth profiles of bulk POM display coherent peaks within the deep chlorophyll maximum (DCM) zone (Ediger *et al.*, 2005; Erdoğan, 2014). Relatively high POC/PON and POC/Chl-*a* ratios estimated from POM data sets indicate that POM pool has been dominated by detritus, bacteria and zooplankton in oligotrophic waters, indicating grazing effect of higher organisms on primary producers in the NE Mediterranean shelf and open waters (Ediger *et al.*, 2005; Doğan-Sağlamtimur, 2007; Erdoğan, 2014).

1.2.5. Distributions of Total-N and Total-P in the Northeastern Mediterranean

Challenges of accurate and sensitive measurements of TN and TP in seawater have limited to enhance systematic data sets especially in oligotrophic waters. Limited TP data were obtained the eastern Mediterranean during the cruise of RV Atlantis and RV Chain in the 1960's (Miller *et al.*, 1970), indicating very low levels of TP in the entire water column of the eastern Mediterranean (Figure 1.6). In the last decade, more TP data have been produced in the Cilician Basin of Levantine Sea (Sert 2010; Kaptan, 2013), being consistent with previous results from the open sea.

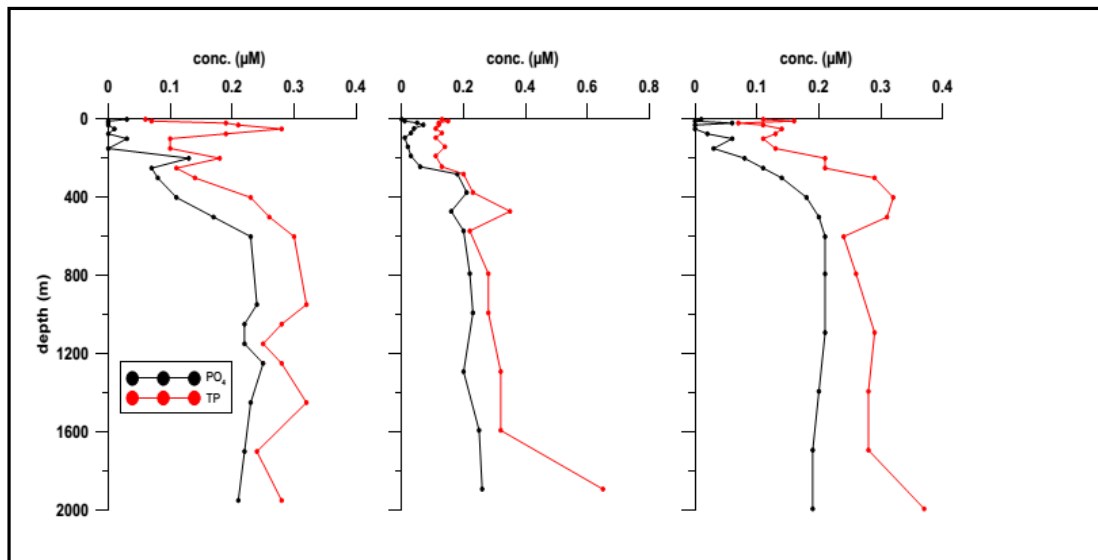


Figure 1.6. Depth profiles of PO_4 and TP from the data collected during expedition of RV Atlantis and RV Chain (Miller *et al.*, 1970 taken from Sert, 2010).

Total nitrogen data in the eastern Mediterranean are sparse due to the lack of studies. Limited measurements from Mersin Bay waters indicate that mean TN concentrations ranged locally between 4.82 and 8.19 μM , with higher values in river-fed near-shore zone (Sert, 2010). Krom *et al.* (2005) studied in the southern Cyprus warm eddy during CYPLOPS P-addition experiment and measured surface DON concentrations ranging from 4.5-11.5 μM in the upper 50 m depth to a constant value of ~ 2.0 μM below 350 m. The TN pool of the upper layer is dominated by organic-N whilst the nitrate constitutes a major fraction of TN in the deep waters having lower dissolved organic nitrogen (Figure 1.7).

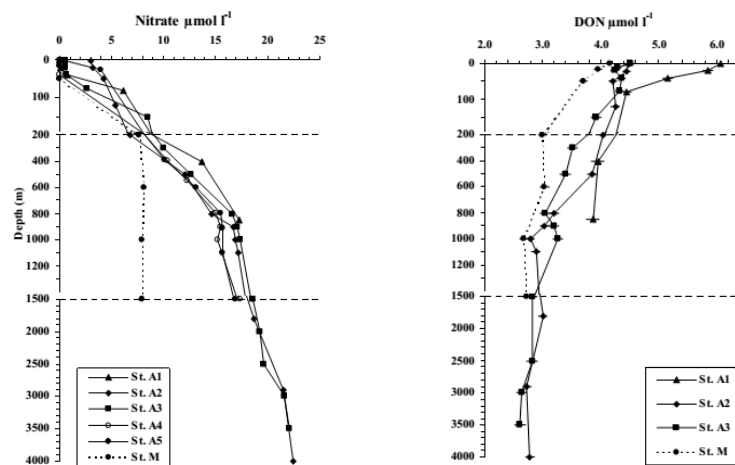


Figure 1.7. Depth profiles of nitrate and DON in the NE Atlantic and in the NW Mediterranean (Aminot and K rouel, 2004).

1.3. Phosphorus Cycle

TP pool in the marine environment is composed of inorganic and organic phosphorus compounds. As shown in Figure 1.8, TP pool of the upper layer is fed by inorganic and organic-P inputs from terrestrial sources, atmospheric precipitation and inorganic-P inputs from deeper layer waters by physical processes. Therefore, the productive upper layer concentrations of TP, organic and inorganic constituents of TP pool are determined by rates of P-inputs and removal by photosynthetic and heterotrophic activities and sinking of particulate-P (Butcher *et al.*, 1992; Paytan and McLaughlin, 2007).

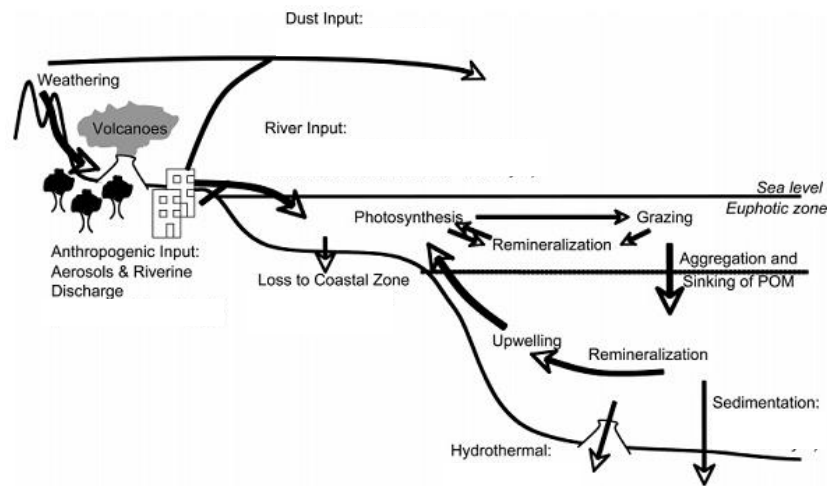


Figure 1.8. Marine P cycle (Paytan and McLaughlin, 2007).

Reactive PO_4 concentrations in the Levantine surface waters are high depleted, nearly detectable levels of 0.02-0.04 μM by the conventional method whilst TP concentrations are about 0.1-0.15 μM during the year (Yılmaz and Tuğrul, 1998; Doğan-Sağlamtimur, 2007; Sert, 2010). It appears that the TP pool is dominated by organic-P in the upper layer whereas the reactive phosphate is the major constituent of TP pool (see Figure 1.9) in the deep waters of marine environments (Butcher *et al.*, 1992; Paytan and McLaughlin, 2007). The majority of the ocean deep water is formed in the north Atlantic and slowly spreads to the south Atlantic, Indian and finally to the Pacific oceans. Due to continuous input of particulate P into the deep waters from surface layers, deep water PO_4 concentrations increase from north Atlantic to the Pacific Ocean (Butcher *et al.*, 1992).

Typical SRP Distributions in the Open Ocean

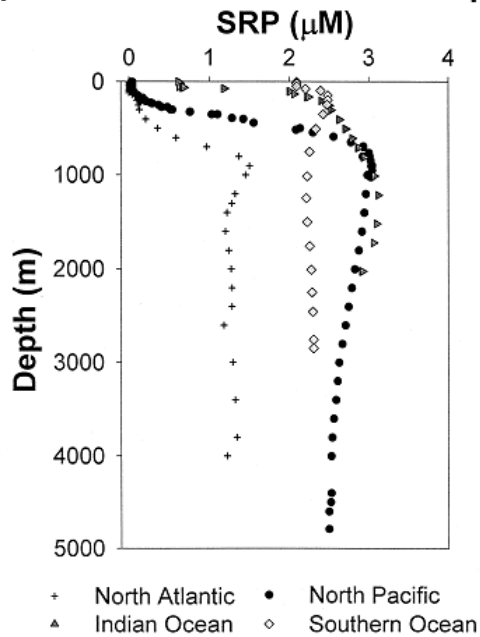


Figure 1.9. Typical distribution of SRP in the world's major oceans: North Atlantic, North Pacific, Indian Ocean and Southern Ocean (Benitez-Nelson, 2000).

In the productive upper layer of marine environments, organic phosphorus pool is dominated by dissolved organic compounds due to regenerative processes and accumulation of less reactive organic-P in the upper layer as the particulate-P sinks down below the productive upper layer (Sert, 2010). Inorganic-P contribution to TP pool increases significantly from oligotrophic open sea to the coastal waters receiving nutrient inputs from land-based sources (mainly rivers, domestic discharges and other external inputs). TP concentrations measured in the NE Mediterranean surface waters ranged from 0.10-0.12 μM in less productive offshore waters to 0.2-0.70 μM in river-fed coastal zone waters (Doğan-Sağlamtimur, 2007; Sert, 2010; Kaptan, 2013; Erdoğan, 2014). Contribution of particulate and dissolved organic-P increases to TP in the coastal waters due to enhanced algal productivity and bulk POM. For example, where reactive phosphate concentrations varied from 0.02-0.04 μM levels to 0.05-0.1 μM in the inner bay waters, much lower than TP, TP concentrations are dominated by organic-P compounds (Doğan-Sağlamtimur, 2007). Dissolved organic compounds including P constitute an important pool of reactive phosphorus especially in the EZ where dissolved organic phosphorus concentrations may exceed the dissolved inorganic phosphorus concentrations (Smith *et al.*, 1986; Karl and Yanagi, 1997). Although the chemical form of dissolved organic

phosphorus is not well known, it is reported that DOP pool is dominated by phosphate esters and phosphonates (Clark *et al.*, 1998).

Under the euphotic layer, however, TP concentrations tend to increase with depth until reaching a constant deep water values about 0.2-0.40 μM in the Levantine shelf and deep waters having 0.15-0.25 μM of reactive phosphate ions (Doğan-Sağlamtimur, 2007; Sert, 2010; Kaptan, 2013). Thermohaline stratification in the ocean system does not completely break down in the winter due to insufficient cooling of the upper layer waters other than in the polar region. More important source of P for the EZ are the major upwelling regions of the oceans and seas generally located adjacent to the western, subtropical continental margins and in equatorial divergence zones, cyclonic gyres in the Mediterranean Sea. Once P enters in the photic zone, it is readily incorporated into biogenic particles via photosynthetic activities of plants and some fraction of the biogenic material sinks. The majority of the particles decompose in the surface layer or in shallow sediments and the P is recycled directly back into the photic zone to be re-incorporated into biological particles. Only a small fraction of POM produced in the surface layers sinks into the deep ocean waters. Most of these particles eventually decompose and the recycled in the water column slowly. However, a very small fraction of these fast sinking particles is incorporated into the sediment (Butcher *et al.*, 1992). The buried P in the sediments is primarily organic P, apatitic P (including both authigenic apatite and fish debris), P associated with other mineral phases (primarily CaCO_3 and FeOOH) and P loosely sorbed onto other solid phases (Ruttenberg, 1993).

1.4. Composition of Sediments in the Marine Environment

Ocean sediments are heterogeneous with respect to their composition and also display an important degree of geographical variation. There are various types of sediments accumulated on the sea bottom, according to their origin and formation of the components:

Lithogenous sediments: They are transported and dispersed into the ocean as detrital particles either as terrigenous particles or as volcanic particles.

Biogenous sediments: They are directly produced by organisms or are formed by accumulation of skeletal fragments.

Hydrogenous or authigenic sediments: They precipitate directly out of solution as new formations or are formed de novo when the particles are in contact with the solution.

Cosmogenic sediments: They are particles and fragments of meteorites and are of secondary importance (Schulz and Zabel, 2006).

1.4.1. Classification of Marine Sediments According to Their Grain-Size

As yet, there is no general classification scheme applicable to marine sediments combining all characteristics for them. There are different schemes which are used in the classification of sediment types focusing either on origin, grain size distribution, chemical and mineralogical features of the sediment components, or the facial development of the sediments (Schulz and Zabel, 2006).

The most widely accepted and used grain size classification is that of Wentworth (1922) as shown in Table 1.1; gravel (> 2 mm), sand (1/16-2 mm), silt + clay (mud: < 1/16 mm) types of sediments.

Table 1.1. The canonical definition of sediment grain-sizes (Wentworth, 1922)

Millimeters (mm)	Micrometers (μm)	Phi (ϕ)	Wentworth size class
4096		-12.0	Boulder
256		-8.0	Cobble
64		-6.0	Pebble
4		-2.0	Granule
2.00		-1.0	Very coarse sand
1.00		0.0	Coarse sand
1/2	0.50	1.0	Medium sand
1/4	0.25	2.0	Fine sand
1/8	0.125	3.0	Very fine sand
1/16	0.0625	4.0	Coarse silt
1/32	0.031	5.0	Medium silt
1/64	0.0156	6.0	Fine silt
1/128	0.0078	7.0	Very fine silt
1/256	0.0039	8.0	Clay
0.00006	0.06	14.0	

Yemenicioğlu and Tunç (2013) stated that the gravel content of the sediments generally amounted to less than 1 % in the Mersin and Iskenderun bays. High amounts of gravel were found in the southern corner of the Iskenderun bay (35%) and in the western part of the Ceyhan river delta (23%) which involves mainly biogenic constituents. In the southern part of the Mersin Bay where water depth is between 50 and 100 m, the surface sediments are mainly composed of sand fraction

(55-80%) in which the sediments involve high amounts of biogenic remains. At most stations, fine sand fractions (125-250 μm) were the main component of the sandy fractions. Silt proportion of surface sediments in Mersin Bay generally ranges between 20 and 40%, depending on water depth. The dams on the Seyhan and Berdan rivers behave as a trap for the coarse grained sediments. Clay fraction is generally less than 35% in the shelf sediments and tends to increase from shelf to offshore due to the low sinking rate of clay.

1.4.2. Distribution of POM in the Surface Sediments of the Northeastern Mediterranean

Bottom sediments are major sites of detrital mineralization and nutrient recycling in aquatic ecosystems having oxic/anoxic conditions in sediment layer. Bulk organic detritus is defined as “the organic carbon lost by non-predatory process from any trophic level” (Fenchel and Blackburn, 1979 referenced in Nedwell, 1984). Major processes for the organic detritus formation in water column are ingestion, excretion, secretion, death and decay; phytoplankton (living POM) produces directly or indirectly detritus in water bodies via primary production, macrophyte primary production. In addition to internal sources, river inflows, waste discharges and surface runoff after heavy rains are terrestrial sources of particulate organic material transports from land to coastal waters (Nedwell, 1984). The origin of different form (apatite, non-apatite, inorganic, organic) of phosphorus in particulate phase can be either detrital or non-detrital (Williams *et al.*, 1976 referenced in Boston *et al.*, 2000) and detrital phosphorus constitute a small fraction of total P, 4-5% of TPP (Shackleton *et al.*, 1997).

An important proportion of pelagic primary production reaches the sea floor in continental margin environments (Jørgensen, 1983 referenced in Slomp, 1998). After mineralization of this organic matter in the sediment layer, dissolved PO_4 releases to the pore water which either escapes to the overlying water where it can become available for photosynthesis in shallow waters or is retained in the sediment especially under oxic conditions (Slomp, 1998).

Organic carbon levels of surface sediments of Cilician basin from Iskenderun to Mersin bay have been examined in recent decades. The TOC concentrations ranged from 0.9 to 14.3 mg/g dw (dry weight) in surface sediments, with the TN

concentrations varying between 0.12 and 1.6 mg/g dw where the grain-size distribution is dominated by fine grained particles, muddy content ranged from 2.6 to 96.6% (mean: 52.8%). The C/N ratios estimated from data ranged from 8.3-14.4 in the coastal sediments of Cilician Basin. (TUBITAK-DIPTAR 3rd progress report, 2015). However, data from polluted sites of Mersin inner bay sediments is very limited (Erdogan, 2014) and may be insufficient to assess the combined effect of nutrient influxes by domestic waste discharges and river inflows feeding the inner bay near-shore ecosystem of the Mersin city. Moreover, Erdoğan (2014) measured different forms of phosphorus in surface sediments of the Mersin bay. Total phosphorus concentrations range between 14.8 and 19.0 $\mu\text{mol/g}$ dw and tend to increase from coastal areas to open water sediments.

1.5. Previous Studies on POM Measurements in Surface Waters and Sediments of Cilician Basin of NE Mediterranean and Gaps in Regional POM Data

First studies on the oceanography of NE Mediterranean have been conducted during the POEM Program to understand the major current systems and sub-basin scale hydro-chemical properties of the large eastern Mediterranean Basin (Özsoy *et al.*, 1993). The initial results indicated the presence of complex circulations and basin-wide and mesoscale heterogeneity of the hydrographic properties in the entire water column. They also observed interannual variability of Levantine Intermediate Water (LIW) formation with the associated chemical properties in winter especially in anti-cyclonic eddies and along the coasts of northern Levantine basin (Özsoy *et al.*, 1993; Yılmaz and Tuğrul, 1998; Moutin and Prieur, 2012).

Nutrient chemistry and related parameters have been studied extensively since the late 1980's. Krom *et al.* (1991) presented nutrient data in the Levantine basin of the eastern Mediterranean. Their results indicated that nutrients were consistently depleted in the upper layer of 100-150m; the silicate concentration ranged 1-2 μM as the nitrate and phosphate concentrations were less than 0.5 μM and 0.05 μM , respectively, in the open sea surface layer. In the anticyclonic regions of the eastern basin, surface waters have very low and hardly detectable levels of phosphate in the summer-autumn period, ranging between <0.02 to 0.03 μM whereas the nitrate concentrations vary from 0.1-0.2 μM (summer-autumn value) to 0.5-0.8 μM in late autumn. Therefore, very low levels of phosphate in the upper layer waters challenges

the estimation of N/P ratio reliably and to assess which nutrient is primarily limits algal production in the open sea. However, experiments conducted in the last decade indicate the limiting role of phosphorus on primary productivity (Krom *et al.*, 1991; Yılmaz and Tuğrul, 1998; Doğan-Sağlamtimur, 2007; Tuğrul *et al.*, 2009; Sert, 2010; Erdoğan, 2014). High N/P ratios present in the Levantine deep waters (26-28), nitrate-laden river inputs and atmospheric deposition (wet + dry) strongly support the results of bio-assays indicating P-limited algal production in the eastern Mediterranean waters and coastal waters (Tufekci *et al.*, 2013).

Though the basic nutrient chemistry of the eastern Mediterranean have been documented extensively during the last two decades, limited data available on POM abundance and elemental composition of bulk POM in the eastern Mediterranean. First particulate data from the NE Levantine Sea was obtained by Ediger (1995), Çoban (1997), Çoban-Yıldız *et al.* (2000), Ediger *et al.* (2005), Doğan-Sağlamtimur (2007), Uysal *et al.* (2008) and Erdoğan (2014). Challenges in sampling, filtration on board and analysis on land resulted in limited POM studies in the region. The limited data indicated the ranges of POM (POC, PON, t-PP) distributions in the less productive sub-basin dominated by anti-cyclonic eddies and more productive waters of Rhodes Cyclonic Gyre (Ediger *et al.*, 2005) and Mersin Bay waters of Cilician Bay fed by the major regional rivers (Ceyhan, Seyhan and Göksu) and small creeks (Doğan-Sağlamtimur, 2007; Erdoğan, 2014). They determined spatial and seasonal variations of POM in the upper layer of 100-150 m of the NE Levantine Sea, spatio-temporal variations in the C/N/P ratio of POM in the studied sites and their correlations with bio-mass (in terms of Chl-*a*) in the upper layer. Ediger *et al.* (2005) have described vertical profiles of particulate organic matter and its relationship with chlorophyll-*a* in the upper layer of the northeastern Mediterranean Sea. They indicated that depth profiles for the bulk POM displayed a subsurface maximum and coincided with deep chlorophyll maximum (DCM) established near the base of the EZ of the Rhodes cyclone and its periphery where the nutricline was situated just below the EZ for most of the year.

However, limited POM data are present from the coastal waters of Mersin Bay receiving both domestic discharges and river inputs (Doğan-Sağlamtimur, 2007; Erdoğan, 2014). They observed remarkable variability in the concentrations and composition of bulk POM in the shelf waters having oligotrophic (low biomass, high

water transparency) and mesotrophic water (more productive, low SDD) properties. They also measured weak acid soluble fraction of total particulate-Phosphorus (t-PP) in POM to assess levels of organic-P in POM; their results indicate less acid soluble-P in the bulk POM content of offshore waters of the bay.

Çoban-Yıldız *et al.* (2000) have performed a comparable study on the abundance and elemental composition of POM in the interconnected basins: the Black, Marmara and Mediterranean Seas between 1990-1998 period. The main purpose of this study was to compare the C/N/P ratio of seston and understand factors controlling the seston composition, in near and offshore waters of the seas. For the Marmara Sea, average POC, PON, and PP concentrations in the EZ varied regionally and seasonally between 10-35 μM , 0.4-4.5 μM and 0.05-0.45 μM , respectively. Particulate concentrations in the Marmara Sea are mostly above the Black Sea value and much greater than those measured in the offshore waters of the NE Mediterranean whose near-shore data are comparable with the particulate concentrations of deep Black Sea. After they compared C/N/P ratios of seston, they suggested atmospheric and land-based phosphorus input affects the C/P and N/P ratios in the near-shore waters. They indicated that unlike the profiles for the Black and Marmara Seas, the particulate concentrations reached the peak values at the base of the EZ of the cyclonic regions of the NE Mediterranean when nutrients are depleted available for photosynthesis due to seasonal stratification. Thus, the input from nutricline depths enhanced shade-adapted algal production resulting in particulate and Chl-*a* maximum at the bottom of the EZ. The depth averaged concentrations were 1.44-5.18 μM for POC, 0.06-0.68 μM for PON and 0.01-0.037 μM for PP in the EZ of the Levantine basin in 1990-1998 period. Expectedly, depth averaged POC/PON and POC/PP ratios of seston in the EZ of the open Mediterranean Sea are mostly higher than classical Redfield ratios which are consistent with ratios for the Black and Marmara Seas. However, the PON/PP ratios were generally low although primary production in the Mediterranean Sea potentially limited by reactive phosphate due to high NO_3/PO_4 ratios of the water masses below the EZ (Yılmaz and Tuğrul, 1998). Moreover, although the NO_x/PO_4 ratios in the EZ may be as high as 38 when the water column is vertically mixed and nutrient concentrations are relatively high, the EZ NO_x/PO_4 ratios are low especially in the stratification period. Therefore, it is suggested that some fraction of PP measured in the surface water might be due to

non-biogenic, most probably atmospheric, origin reducing PON/PP ratio of seston (Çoban-Yıldız *et al.*, 2000).

Doğan-Sağlamimur (2007) has studied in NE Mediterranean and applied MAGIC method in order to obtain sensitive measurement for phosphorus fractions of TP pool. It was found that the dissolved P fractions (TDP), 56-97%, dominated the phosphorus pool. Moreover, dissolved organic phosphorus (DOP) was the major constituent of the TDP in the shelf water column. On the other hand, particulate organic phosphorus (POP) has a remarkable contribution to the particulate P pool. PON/POP (N/P) molar ratios mostly varied between 20-50 in the shelf which higher than classical Redfield ratio of 16/1. Therefore, it is suggested that primary production in the NE Mediterranean shelf waters is limited by phosphorus.

Sert (2010) has studied nutrient distributions in the Mersin Bay shelf waters between September 2008 and October 2009. According to this study, nutrient replete Seyhan and Berdan discharges markedly enhanced the nutrient concentrations and algal biomass (in terms of Chl-*a*) in the shallow zone where the depth < 15 m of the Mersin Bay. The mean concentrations of TN measured ranged spatially between 4.82 and 8.19 μM and the mean concentrations for TP varied between 0.20 and 0.70 μM . Higher concentrations were observed in near shore zone.

The geology and geochemistry of recent sediments from the NE Mediterranean basin have been studied extensively in recent years (Tunç, 2008; Yemenicioğlu and Tunç, 2013; Erdoğan, 2014; MEU, 2014; TUBITAK-DIPTAR 3rd progress report, 2015). Recent sediments represented a wide variety of sediment types (sandy to gravel to mud) and were generally characterized by their relatively high mud contents varying silt and clay fractions. Moreover, the organic carbon contents of the sediments with the exception of coastal sediments which are polluted by the water carried by rivers, mostly reflect the normal marine production of organic matter. Organic matter content of surface sediments in the Mersin Bay were also studied by Erdoğan (2014); TOC and TN concentrations were determined to range between 4.08-7.93 mg/g (dry weight) and 0.70-0.84 mg/g, respectively in the inner bay with higher values in the winter-spring period due to the inputs from major rivers. The C/N molar ratios calculated from sediment data ranged between 6.0-7.2 in spring period, consistent with C/N molar ratios of bulk POM in the water column. In the scope of pollution

program reported by Ministry of Environment and Urbanization (MEU) for the Mediterranean (TUBITAK-Mediterranean Pollution Monitoring Program), surface sediments were analyzed for the 10 stations from İskenderun Bay to Aegean Sea. Lower TOC concentrations were observed varying 1-8 mg/g (dry weight) displayed high variability in Mersin and İskenderun bays, relatively higher concentrations were observed in İskenderun inner bay. C/N molar ratios in surface sediments varied regionally between 8.3 and 14.4 due to highly variable POC, PON concentrations and grain-size distributions in surface sediments of the NE Mediterranean coastal zones (TUBITAK-DIPTAR 3rd progress report, 2015).

Since total particulate-P in bulk POM in sediment phase include both organic and inorganic forms, Eijsink *et al.* (1997) have performed sequential extraction techniques to determine soluble fraction of sedimentary phosphorus (the SEDEX method) in eastern Mediterranean sediments. They have observed a reasonable correlation between organic phosphorus and organic carbon and an average value of ~86 for organic C/P molar ratio in the oxic sediments and ~440 in the sapropel. More recently, Aydın *et al.* (2009) have studied inorganic and organic forms of phosphorus in surface sediments and seawater from NE Mediterranean Sea (Burclar Bay, Erdemli) in May 2007; they determined an average value about 4.36 µg P/g for organic-P in the surface sediment. Erdoğan (2014) studied in shelf waters and sediments in the NE Mediterranean (Mersin bay) during September 2008-November 2010. Close correlations were seen between the TP, DIN, and Chl-*a* concentrations and POM data in the coastal waters of Mersin Bay (Erdoğan, 2014), where the concentrations decreased markedly from the river-influenced zone to the offshore waters of the bay. Moreover, large variations were reported in TN/TPP molar ratio, ranging from 10 to 30 in bay waters, demanding further studies to sound understand such drastic spatio-temporal variations in POM content of surface sediments. However, there are no sufficient POM data available in highly polluted and less contaminated water columns of Mersin bay to assess the role of sinking particulate materials on sedimentary POM composition within bay.

1.6. Aim and Objectives of the Study

As emphasized above, studies on POM distributions in water and sediment phases are very limited in the NE Levantine Sea and its Cilician basin. In recent years, a few

studies have been conducted in the Mersin Bay waters to assess influences of river inputs on POM composition and concentrations in water and surface sediments of Mersin bay coastal waters renewed by oligotrophic waters of NE Levantine Sea.

However, POM data from the coastal area of Mersin Bay is very limited to assess variability in the elementary (C/N/P) composition of bulk POM in water and surface sediments due to nutrient and organic matter inputs by river + domestic wastewater discharges as compared to those of less effected central bay waters bay renewed by the oligotrophic waters of the NE Mediterranean by the major circulation system.

This study aims to contribute to better understanding and assessment of human-induced pressures on POM concentrations and composition of the inner bay ecosystem under more productive season by providing new data sets on POM and related bio-chemical parameters within the Mersin Bay. For this goal, chemical data on dissolved inorganic nutrient concentrations and algal biomass (in terms of Chl-*a*) in the inner and central bay waters were obtained and evaluated to assess influences of river + wastewater discharges on the distribution and composition of bulk POM in water and surface sediments of the hot points and less contaminated central bay ecosystem (Figure 2.1).

The main objectives of this study are:

- To produce reliable data sets for integrated evaluation of TP, mineral nutrients (N, P), POC and PON content of bulk POM to assess the trophic level of inner bay waters influenced by terrestrial inputs,
- To examine range of spatial variability in composition and concentrations of bulk POM in surface waters and sediments of the inner/central Mersin Bay ecosystem fed by inputs of nutrients and organic matter from terrestrial sources (rivers + wastewater discharges),
- To determine NO_3/PO_4 (N/P) molar ratios of the Mersin bay waters for understanding potential limiting nutrients during the study period,
- To determine levels of correlations between changes in biomass (Chl-*a*)-POM, nutrients-POM concentrations, and between N/P ratios of nutrients and POM in surface waters of more productive inner bay and less productive central bay waters renewed by oligotrophic waters of the NE Levantine upper layer waters.

- To determine correlations between the grain size distribution of the surface sediments and POM composition and concentrations in the inner and central bay sediments,
- To determine POC/PON/t-PP and weak soluble-PP/t-PP molar ratios of bulk POM to assess spatial variations of weak acid soluble fraction of particulate phosphorus (PP) in the bulk POM in water and buried in surface sediments under different nutritional conditions of the bay ecosystem.
- Finally, to compare limited POM data obtained in this study and previous works to assess influences of human-induced inputs on POM composition/content of the bay ecosystem refreshed by NE Levantine waters displaying oligotrophic properties.

CHAPTER 2

EXPERIMENTAL

2.1. Sampling Locations and Strategy

Pollution by shipping activities in the Harbor region, submarine discharges of partly treated domestic wastewaters of Mersin city and nutrient-laden river inflows to the coastal zone of the eastern Mersin Bay have been observed to modify the trophic status of Mersin Bay ecosystem (Kaptan, 2013). The major objectives of this study are to assess influences of natural + human-induced pressures on spatial distributions of dissolved inorganic nutrients, Chl-*a* and bulk POM concentrations composition in coastal waters and sediments of the eastern Mersin Bay fed by terrestrial inputs of organic/inorganic nutrients. For this goal, the inner part of the eastern Mersin Bay shown in Figure 2.1 were selected to collect water samples and sediments for analyses of nutrients, Chl-*a*, POM in wet (high flow period of rivers) and wet winter seasons. Seawater and sediment samples collected at the selected stations in April 2014 and February 2015 (Figure 2.1 and Table 2.1) were analyzed by following standard measurement methods as described below.

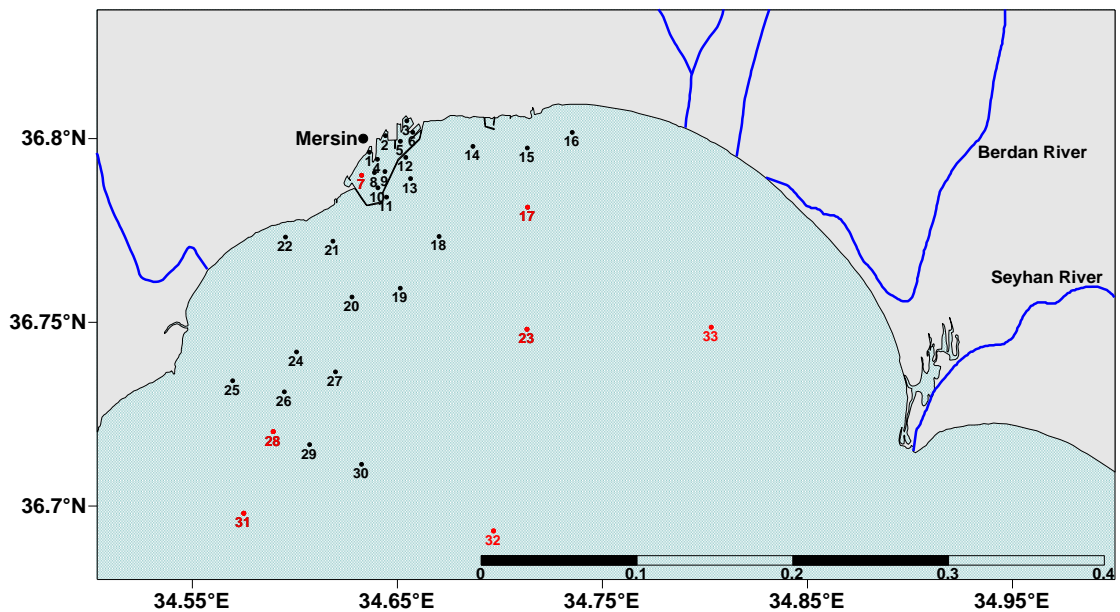


Figure 2.1. Sampling locations visited in Mersin bay in April 2014 and February 2015 (●).

Table 2.1. Coordinates of the sampling stations visited in the study area of Mersin Bay

Station	Latitude	Longitude
1	36° 47.777'	34° 38.180'
2	36° 48.048'	34° 38.651'
3	36° 48.290'	34° 39.275'
4	36° 47.662'	34° 38.415'
5	36° 47.956'	34° 39.087'
6	36° 48.103'	34° 39.450'
7	36° 47.401'	34° 37.954'
8	36° 47.446'	34° 38.329'
9	36° 47.462'	34° 38.635'
10	36° 47.197'	34° 38.430'
11	36° 47.044'	34° 38.683'
12	36° 47.693'	34° 39.245'
13	36° 47.347'	34° 39.385'
14	36° 47.873'	34° 41.210'
15	36° 47.847'	34° 42.802'
16	36° 48.101'	34° 44.117'
17	36° 46.880'	34° 42.811'
18	36° 46.402'	34° 40.220'
19	36° 45.557'	34° 39.084'
20	36° 45.413'	34° 37.671'
21	36° 46.325'	34° 37.113'
22	36° 46.392'	34° 35.725'
23	36° 44.887'	34° 42.792'
24	36° 44.516'	34° 36.048'
25	36° 44.046'	34° 34.179'
26	36° 43.865'	34° 35.691'
27	36° 44.191'	34° 37.188'
28	36° 43.215'	34° 35.366'
29	36° 43.003'	34° 36.431'
30	36° 42.681'	34° 37.951'
31	36° 41.882'	34° 34.505'
32	36° 41.594'	34° 41.813'
33	36° 44.920'	34° 48.184'

In April, seawater samples for nutrients and POM analyses were taken at 31 stations and in order to enhance wet period data sets, in February 2015, SW and sediment samples were also obtained at 7 stations. Field studies were carried out using R/V BILIM-2 of METU-IMS (Erdemli-Mersin).

The coordinates of sampling locations visited in the bay are given in Table 2.1. During the field surveys, physical parameters (salinity, temperature, depth) and water transparency measurements (Secchi Disc Depth (SDD)) were measured *in situ* on board R/V BILIM-2. For the measurements of chemical indicators of eutrophication and organic matter concentrations in the sea (nutrients, dissolved oxygen, Chl-*a*, suspended POM), water samples were taken at the selected depths (surface, intermediate depth and near-bottom waters) of the pre-determined stations (see Figure 2.1).

Surface sediments for TC, TN, TOC, TPP, POP analysis and grain-size measurements were sampled by a Grab Sampler.

2.2. Measurements of Physical (Salinity, Temperature, Depth) Parameters

During the field surveys, *in situ* hydrographic measurements of physical parameters were carried out by a SEABIRD model CTD probe coupled to a 12-plastic bottle (8L capacity) Rosette System for remote-controlled water sampling at selected depths of water column (Figure 2.2). CTD measurements were recorded in downcast and upcast; downcast data were used in plotting vertical profiles and surface distributions. The measurement ranges of conductivity (C) and temperature (T) are 0 to 9 S/m and -5 to +35 °C, respectively. The precisions of the CTD probe are ± 0.0005 S/m for conductivity and ± 0.005 °C for temperature (Sea-Bird Electronics booklet). Salinity (S) values were calculated automatically from *in situ* from conductivity and temperature measurements.

2.3. Measurements of Water Transparency

Secchi disc depth measurement is a simple tool to determine the euphotic zone thickness in aquatic environments and thus water transparency. During the day time, Secchi disc depth measurements were carried out in order to determine water transparency of the bay ecosystem.

2.4. Sampling for Biochemical and Geochemical Parameters

2.4.1. Sampling for Dissolved Oxygen (DO)

Water samples were taken from the selected stations and depths using 12-bottle Rosette System coupled on CTD probe (Figure 2.2). Subsamples for DO were taken into the Pyrex bottles with different volumes carefully and avoiding air bubbles from the samples by exceeding volume of the bottles as twice the volume while taking the samples from Niskin bottles. For this reason, transferring tube is squeezed during submerging into the bottle and taking out from the bottle while flowing and the transferring tube should be at the bottom of the Pyrex bottle. Then, manganese (II) chloride and alkaline potassium iodide were immediately added to the samples and shaken in order to let the reagents diffuse completely. Finally, samples were put in a dark place for at least 30 minutes so that the reaction will complete (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983; UNEP/MAP, 2005).



Figure 2.2. 12-bottle Rosette System coupled on CTD probe.

2.4.2. Sampling for Dissolved Inorganic Nutrients and Total Phosphorus (TP)

Seawater samples for inorganic nutrients (NO_3+NO_2 , NO_2 , NH_4 , Si and PO_4) were sub-sampled from Niskin bottles into 10 or 100ml polyethylene bottles (Kartell,

Italy) which are cleaned with 10% HCl and then rinsed with distilled-deionized water. Before sub-sampling of inorganic nutrients, polyethylene bottles are rinsed several times with the sample itself. If immediate measurements of inorganic nutrients are not possible, they are kept frozen at about -20 °C until analysis on board. In this study, seawater samples for inorganic nutrients were frozen occasionally when immediate analysis was not possible in 12 hours. Seawater samples for TP analysis taken in polyethylene bottles were frozen until analysis. It is important that the samples should be avoided contamination (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983; UNEP/MAP, 2005).

2.4.3. Sampling for Chl-*a*

Seawater samples collected by Niskin bottles were filtered and the filters were put in aluminum foil. Filtration of subsamples (0.5-1 L) on GF/F type filters should be performed under dim light. The filters were then kept frozen till the Chl-*a* measurements (UNEP/MAP, 2005; Wasmund *et al.*, 2006).

2.4.4. Sampling for Total Suspended Solid

Seawater samples (1.0 L) were filtered on Whatman GF/C filters (pore size: 1.2 µm) kept frozen until drying at the laboratory. It is important that salt particles should be removed from the filters by washing distilled water in order to make precise measurements.

2.4.5. Sampling for Particulate Organic Matter (POM) in Seawater

Nalgene bottles for sub-sampling were cleaned with dilute acid and washed with seawater before sub-sampling. Glass fiber filters (Whatman, GF/F type, pore size: 0.7 µm) were used to collect POM samples on pre-cleaned filters. Then they kept frozen within aluminum filters till the POM analysis at laboratory. GF/F filters should be combusted at 450 °C for 6-8 hours before particulate phosphorus analysis (Polat and Tuğrul, 1995).

2.4.6. Sampling for POM in Sediments

Surface sediments were taken by using a Van Veen grab type sampler at the selected stations: Subsamples from the upper surface layer (0-1.0 cm) were put on pre-cleaned aluminum foil; the folded subsamples were placed in nylon bags and then

kept frozen until analysis. Before sub-sampling, aluminum foils were combusted at 450 °C for 6-8 hours to remove organic contaminants on foil (UNEP/MAP, 2006).

2.4.7. Sampling for Grain-Size Analysis

Sufficient amounts of surface sediments (0.5-1 cm) were also taken into nylon bags and kept at room temperature until grain-size analysis.

2.5. Analysis of Biochemical Parameters

2.5.1. Dissolved Oxygen Analysis

Dissolved oxygen measurement in seawater was carried out by the automated Winkler titration method (Grasshoff *et al.*, 1983). The iodometric titration method is based on the oxidation of iodide ion to iodine by DO in seawater. Because dissolved oxygen in seawater does not directly oxidize the iodide ion to iodine, a manganese medium is used as a transfer medium for a multi-step oxidation (Grasshoff *et al.*, 1983). Finally, DO is measured by automated titration method by titration with 0.02 M sodium thiosulphate solution (UNEP/MAP, 2005).

2.5.2. Dissolved Inorganic Nutrient Analysis

A Bran Luebbe model four-channel autoanalyzer was used for the dissolved inorganic nutrients. Standard nutrient methods revised for autoanalyzer applications were performed for phosphate (Method No: G-175-96, MT 18), nitrate and nitrite (Method No: G-172-96, MT 19), nitrite (Method No: G-173-96, MT18), ammonia (Method No: G-171-96, MT 19) and silicate (Method No: G-177-96, MT 19).

2.5.2.1. Dissolve Inorganic Phosphorus (PO₄-P) Analysis

Colorimetric method developed for DIP analysis in water and seawater is based on the formation of a phosphomolybdate complex and its subsequent reduction to highly colored blue compounds (Strickland and Parsons, 1972). In order to obtain rapid color development and to prevent the interference of silicate, the final reaction pH \leq 1 and the molar ratio of sulphuric acid to molybdate in the mixed solution should be 230-330 (Grasshoff *et al.*, 1983). The wavelength of the detector is 880 nm and the detection limit of the automated method is nearly 0.015 μ g/L in the lower ranges (SEAL Analytical Booklet, Method No: G-175-96).

2.5.2.2. Nitrate and Nitrite (NO₃+NO₂-N) Analysis

Determination of nitrate and nitrite in the automated method is based on the procedure in which nitrate is reduced to nitrite by a copper-cadmium reductor column (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983; SEAL Analytical Booklet, Method No: G-172-96). Then, the nitrite reacts with sulfanilamide under acidic condition for the formation of a diazo compound. This compound then couples with N-1-naphthylethylene diamine dihydrochloride to form a purple azo dye which is determined at a wavelength of 550 nm. Detection limit for NO₃+NO₂-N analysis in the range of 0-4.0 µM is 0.02 µM (SEAL Analytical Booklet, Method No: G-172-96).

2.5.2.3. Nitrite (NO₂-N) Analysis

The automated method for the nitrite analysis was mentioned in section 2.5.2.2 as after reactions between nitrite and sulfanilamide under acidic conditions, a diazo compound is formed and this compound reacts with N-1-naphthylethylene diamine dihydrochloride to form a reddish-purple azo which is measured at 550 nm wavelength. Detection limit for NO₂-N analysis is 0.005 µM in the lowest range (SEAL Analytical Booklet, Method No: G-173-96).

2.5.2.4. Ammonium (NH₄-N) Analysis

The automated method for ammonia analysis is based on the Berthelot reaction in which a blue-green colored complex is formed measured at 660 nm. It is essential to use a complexing agent in order to prevent the precipitation of calcium and magnesium hydroxides (SEAL Analytical Booklet, Method No: G-171-96).

2.5.2.5. Reactive Silicate (Si(OH)₄-Si) Analysis

The automated method for determination of dissolved inorganic silicate is based on the reduction of silicomolybdate in acidic solution to molybdenum blue by ascorbic acid. In order to prevent/minimize the interference of phosphates, oxalic acid is added to the sample stream before addition of ascorbic acid (SEAL Analytical Booklet, Method No: G-177-96; Grasshoff *et al.*, 1983). Working wavelength for dissolved inorganic silicate is 820 nm. Detection limit of the automated method for inorganic silicate is 0.05 µM in the lowest range (SEAL Analytical Booklet, Method No: G-177-96).

2.5.3. Total Phosphorus (TP) Analysis

For total phosphorus analysis, persulfate digestion method was used in which potassium peroxydisulfate is an oxidizing agent (Menzel and Corwin, 1965). After digestion and extraction of dissolved inorganic phosphorus from dissolved and particulate organic phosphorus (Doğan-Sağlamtimur, 2007), DIP was measured colorimetrically by the conventional ascorbic acid method at 880 nm wavelength (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983). The procedure of TP analysis is as follow:

- a) 45 mL of thawed seawater samples is added into pre-digested Teflon capped bottles.
- b) 5 mL of oxidizing agent is added (10 g of potassium peroxydisulphate is dissolved in 100 mL MQ water).
- c) The sample bottles are placed into the autoclave and heated until about 100 °C temperature and 2 atm pressure and the autoclave is cooled about 1 hour.
- d) After cooling, discharging valve of the autoclave is opened in order to make inner pressure of the autoclave zero.
- e) The caps of the digested samples are opened and let the samples cool until they reach to room temperature.
- f) After reaching to room temperature, pH of the samples is adjusted to 8.0 by using 4.0 M NaOH (80 g of NaOH is dissolved in 500 mL of MQ water). The indicator for checking basicity is phenolphthalein (2.5 g of phenolphthalein is dissolved in 250 mL 95% ethyl alcohol and 250 mL MQ water is added to this solution).
- g) After pH control, 1 mL of ascorbic acid (10 g of ascorbic acid is dissolved in 50 mL MQ water and 50 mL of 4.5 M H₂SO₄ (250 mL H₂SO₄ dissolved in 750 mL MQ water) is added to this solution and let the solution mixed.
- h) 1 mL of mixed reagent (25 g of ammonium molybdate dissolved in 250 mL of MQ water and 700 mL of 4.5 M H₂SO₄ is added to this solution. 1 g of potassium antimony tartrate is dissolved in 40 mL MQ water and added to the previous solution. Final volume of the solution is completed to 1.0 L) is added to the samples and the reaction is completed in about 10 minutes.
- i) After 10 minutes, samples are measured at 880 nm with 5 cm cell and the measurements should be completed within 30 minutes.

- j) The calibration standards are in the range of 0.2-1.0 μM prepared with digested MQ water.

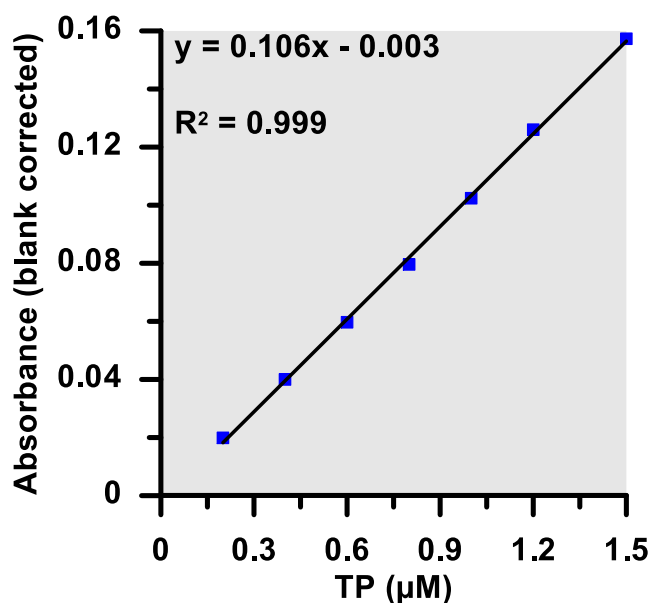


Figure 2.3. Calibration curve for TP analysis prepared with digested MQ water.

TP concentrations of the samples are calculated from the calibration curve (Figure 2.3).

$$\text{TP } (\mu\text{M}) = \frac{a-b}{m} * C$$

Where;

a = absorbance (sample) – absorbance (blank)

b = intercept of the calibration curve

m = slope of the calibration curve

C = dilution factor

2.5.4. Particulate Organic Matter (POM) Analysis

2.5.4.1. Particulate Organic Carbon (POC) and Nitrogen (PON) Analysis

Frozen filter samples for POC and PON are dried at about 50 °C overnight. If the filters are 47 mm size, the filters are cut and the weight of each piece should be noted. Then, the filters are placed in a desiccator which contains stock HCl solution so that the filters are treated with HCl fume to remove all inorganic forms of carbon

(carbonates). After removing inorganic carbon from filters into solution, the carbonate-free filters are dried again. Each filter sample is then placed into the tin foil and capsuled by a special apparatus (hydraulic press). Finally, samples are measured by High Temperature Dry Combustion Method, using a Vario El Cube Elementar Model CHN analyzer. Calibration standards at low concentrations are prepared from acetanilide which contains 71.09% C and 10.36% N. Generally, 4 calibration standards are measured to calculate POC and PON concentrations of filters as described in Polat and Tuğrul (1995) and Çoban-Yıldız (2000).

2.5.4.2. Total Particulate Phosphorus (TPP) Analysis

Filters for TPP analysis are dried at 50 °C and then combusted at 450 °C for 3 hours in order to convert/oxidize all organic forms of phosphorus into inorganic phosphorus (Polat and Tuğrul, 1995; Doğan-Sağlamtimur, 2007; Erdoğan, 2014). Combusted filters are placed into the Teflon capped pre-digested bottles and 45 mL of distilled de-ionized (ultra poor) water is added into the bottles. Then, 5 mL of oxidizing agent (10 g of potassium peroxydisulfate is dissolved in 100 mL MQ water) is added to the samples. After digesting by autoclaving, the oxidized samples are allowed to cool to room temperature. Then, supernatant of the digested solution is taken into a 50-ml syringe coupled disposable filter (Minisart NY 25) whose pore size is 0.45 µm. Then, as described in section 2.5.3 [f, g, h, i, j], manual colorimetric method of DIP is followed to measure the concentration of phosphorus in the digested and filtered samples at 880 nm.

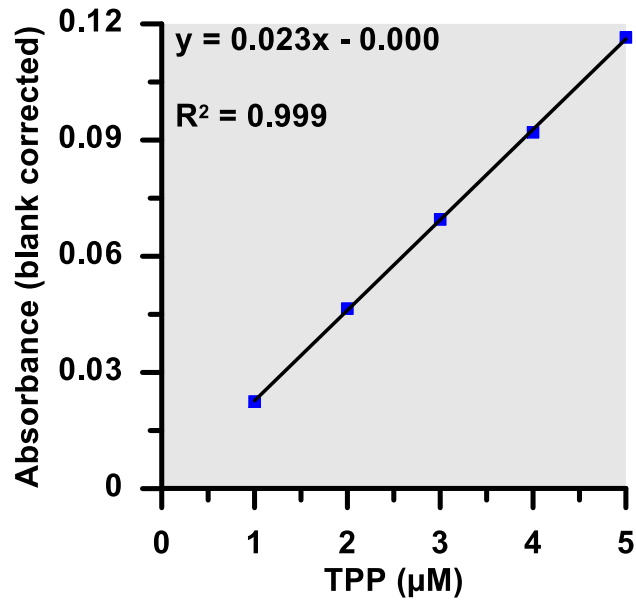


Figure 2.4. Calibration P-curve for TPP measurements, prepared by using standard-spiked and digested MQ (distilled de-ionized water, MQ) water with blank GF/F filters.

TPP concentrations of the seawater samples are calculated by using the formula given below using absorbance measurement values of samples, blank and the slope of the calibration curve (Figure 2.4):

$$\text{TPP } (\mu\text{M}) = \frac{a-b}{m} * \frac{c}{v} * \frac{w(t)}{w(1)}$$

Where;

a = absorbance (sample) – absorbance (blank)

b = intercept of the calibration curve

c = final volume of the sample (for this study, 50 mL)

m = slope of the calibration curve

v = volume of the seawater filtered

$w(t)$ = total weight of the filter

$w(1)$ = weight of the cut-filter

For this study, Quality Control/Assurance studies were performed for TPP analysis in order to increase the accuracy and precision of method. Standard addition experiments were also performed to calculate recoveries of the standards from the

solutions digested with GF/F filters, compared to direct colorimetric measurements of the same standards. For this experiment, seawater samples were obtained from METU-IMS harbor and 500 mL of the samples were filtered on GF/F filters to concentrate TPP on filter. After digesting filters by combustion at 450 °C for 3 hours, samples are put in Teflon capped pre-digested bottles and stock inorganic phosphorus (50 µM) was added into the samples with different volumes (Table 2.2).

Table 2.2. Volume of stock inorganic phosphorus solution (50 µM) added and measured absorbance values

Sample	Volume filtered (mL)	Volume added (mL)	Absorbance (blank corrected)
1	500	0	0.027
2	500	0.25	0.033
3	500	0.5	0.039
4	500	0.75	0.045
5	500	1.00	0.050

After the final volume of solution is adjusted to 50 mL, the procedure described in section 2.5.4.2 was performed and phosphorus concentrations in seawater were calculated from the calibration curve slope determined by the standard addition method (Figure 2.5). Absorbance of the blank was as low as 0.001.

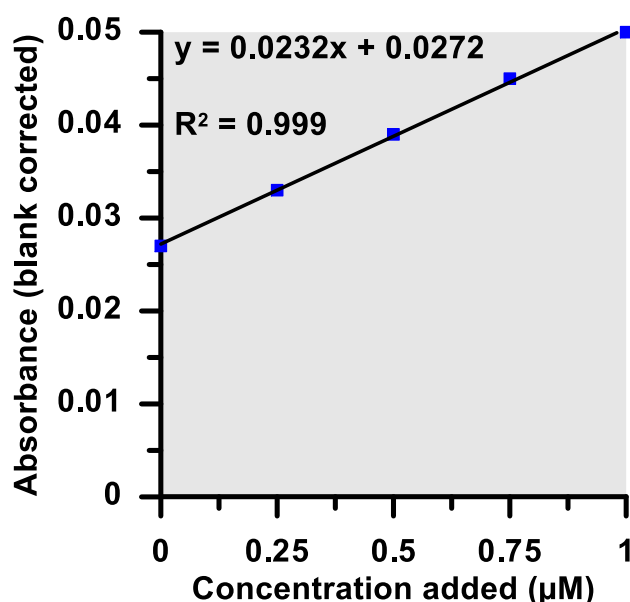


Figure 2.5. Calibration curve of standard addition method for TPP analysis.

By using calibration curve for TPP analysis (Figure 2.4), TPP concentration in the METU IMS harbor was calculated as 0.118 μM which is termed as measured value. TPP concentration calculated from standard addition curve (Figure 2.5) was 0.117 which is denoted as calculated value. Therefore, % recovery was calculated by using the following equation:

$$\% \text{ recovery} = \frac{\text{calculated value}}{\text{measured value}} * 100$$

The % recovery of TPP from digested filter samples was estimated as ~99.0%, showing that the dry oxidation + wet extraction method of filters is adequate for quantitative measurement of TPP in seawater at low concentrations recorded in NE Mediterranean.

2.5.5. Chlorophyll-*a* (Chl-*a*) Analysis

Chlorophyll-*a* measurements were performed by the conventional spectrofluorometric method after digestion of filters (Strickland and Parsons, 1972; UNEP/MAP, 2005). The filter samples are placed in the tubes and extracted by 90% acetone (vol/vol). The extracted samples are kept in the refrigerator for one day. It is important that the samples are kept in dark. Finally, after centrifuging the samples at 6000 rounds per minute (rpm) for 5 minutes, Chl-*a* measurements are taken by a HITACHI model F-2500 Fluorescence Spectrophotometer. The excitation wavelength is 420 nm and the emission wavelength is 669 nm.

2.5.6. Particulate Organic Matter (POM) Analysis in Sediments

2.5.6.1. Total Organic Carbon (TOC) and Total Nitrogen (TN) Analysis

As already discussed in section 2.5.4.1, TOC and TN measurements in sediments are also performed by the Vario El Cube Elementar Model CHN analyzer with dry oxidation method (Grasshoff *et al.*, 1983; UNEP/MAP, 2006). Sediment samples for the TC, TOC and TN measurements were initially freeze-dried. Dry sediments were then powdered and sieved on 63 μm pore size for the homogenization of the samples. For TOC analysis, nearly 30 mg of dry and homogeneous sediment samples were put into the silver cups (pre-combusted at 400 $^{\circ}\text{C}$ for 6 hours). Then, 10 μL of distilled water is added into each silver cup to wet the samples. After distilled water addition, 10 μL of 20 % HCl (vol/vol) was added to remove inorganic carbon from the

sediment samples. The HCl additions were continued until all the inorganic carbon was removed in the form of CO₂. Then, the samples were dried at 60-70 °C for one day. After drying the sediment samples, silver cups were compacted and put into autosampler of the CHN analyzer (Nieuwenhuize *et al.*, 1994). TC and TN analyses in sediments were performed by the same method as for the TOC analysis, but without acid addition and the weighed sediment samples were put in tin cups and compacted to place in autosampler of the CHN analyzer. TC, TN and TOC concentrations in sediments were determined quantitatively by using working standards prepared by acetanilide (71.09% C, 10.36% N).

2.5.6.2. Total Particulate Phosphorus (TPP) and Particulate Organic Phosphorus (POP) Analysis in Sediments

In this study, total particulate phosphorus (TPP) and inorganic phosphorus (PIP) concentrations were determined by the methods described in Berner and Rao (1994) and Fang *et al.* (2007).

Table 2.3. Extraction procedure for TPP and PIP analysis in sediments

Sample	Chemical Treatment	Phase Extracted
30 mg	1.0 M HCl, 24 h	PIP
30 mg	Combust at 550 °C for 3 h, 1.0 M HCl, 24 h	TPP

For the analysis of TPP in sediments, 30 mg of freeze-dried and homogeneous sediment samples are weighed and put into pre-combusted aluminum cups. Then, they are combusted in a muffle furnace at 550 °C for 3 hours in order to convert organic forms of phosphorus into inorganic form and they are placed in Teflon capped bottles. 25 mL of 1.0 M of HCl is added into each bottle for the extraction of phosphorus. After waiting 24 hours, the supernatant solution is removed by using single use syringe filter (Minisart NY 25) whose pore size is 0.45 µm. When pH is stabilized between 7.5-8.0 with 4.0 M NaOH, final solution is adjusted to 50 mL (Ruttenberg, 1992; Fang *et al.*, 2007). Finally, the conventional colorimetric phosphate method was applied as discussed in section 2.5.3 (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983).

The measurements of particulate inorganic phosphorus (PIP), assuming that weak acid soluble fraction of phosphorus in sediment is mainly inorganic phosphorus compounds and merely small fraction of organic-P dissolved in weak acid solution, were carried out to determine POP concentrations in surface sediments of the Mersin bay (Erdoğan, 2014). For PIP analysis in sediment, 30 mg of sediment samples are weighed and put into the Teflon capped bottles and 25 mL of 1.0 M HCl was added to each sample and kept at room temperature for 24 hours. Then, the dissolved-P in the acidic solution is filtered; after pH adjustment, PIP concentrations of the filtered samples were measured by the conventional colorimetric method (Strickland and Parsons, 1972; Grasshoff *et al.*, 1983).

Before starting the analysis of TPP and PIP, optimization experiments were performed to determine optimum sediment weight for phosphorus measurements in sediments. For this purpose, a surface sediment sample from the Mersin Bay was used for TPP measurements; the weights of the sediment sample varied between 20 and 100 mg and the curve plotted by weight against absorbance (blank corrected) showed both the consistency of the different-weight TPP analysis and the homogeneity of the sediment samples (Figure 2.6). Moreover, since there was no deviation from the weight-optimization curve at high weight values, the optimum sediment weight for the TPP analysis was determined between 10 and 100 mg and 30 mg of sediment samples were weighed for TPP and PIP analysis for this study.

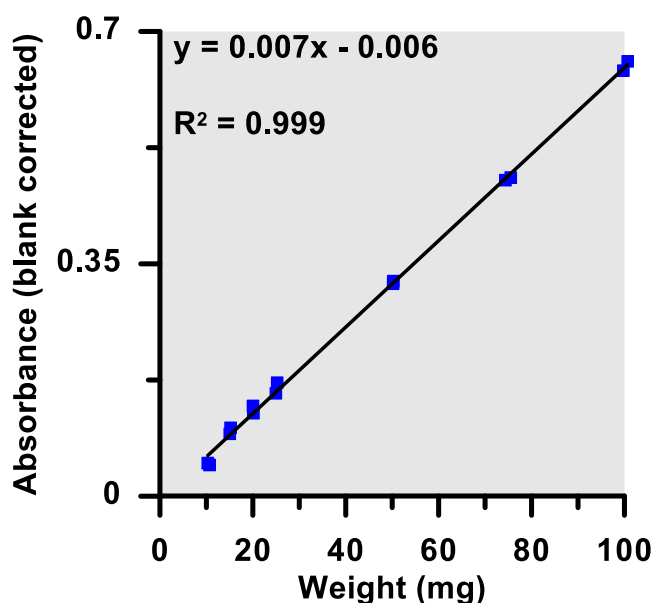


Figure 2.6. Weight optimization curve for TPP analysis in sediments.

After determining optimum weight of the sediment for TPP analysis, standard addition experiments were also conducted in order to determine the accuracy of the results. For this purpose, 30 mg of sediments were weighed from the same sediment sample into the aluminum cup and they are combusted at 550 °C for 3 hours. Then, different volumes of the intermediate phosphate standard (50 µM) were added to the replicate (almost same weight) sediment samples (Table 2.4) so as to get a standard addition calibration graph (Figure 2.7).

Table 2.4. Volumes of the phosphate standard (50 µM) added and the measure absorbance values

Sample	Volume added (mL)	Absorbance (blank corrected)
1	0.0	0.197
2	1.0	0.221
3	2.0	0.241
4	3.0	0.261
5	4.0	0.285
6	5.0	0.307

TPP concentration was determined as 0.015 mmol P/g sediment (dw) and termed as “calculated value”. The TPP concentration determined by calibration curve was 0.016 and termed as “measured value”. The percent recovery was therefore calculated by dividing calculated value by measured value as 94 % for the analysis of TPP in sediments.

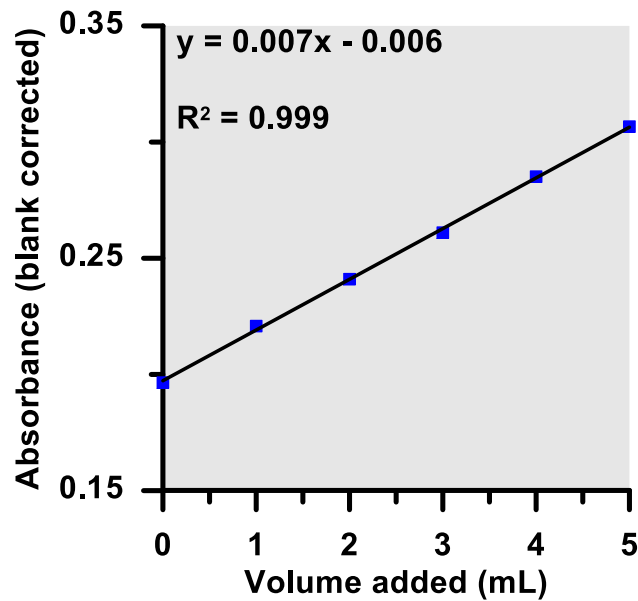


Figure 2.7. Calibration curve of standard addition method for TPP analysis in sediments.

2.5.7. Grain-Size Analysis in Sediments

In this study, grain-size analysis was performed by using Mastersizer Model instrument with sieving and pipetting methods. The grain-size distribution in surface sediments is classified according to four groups which are gravel (> 2mm), sand (2-0.063 mm), silt (0.063-0.0039 mm) and clay (<0.0039 mm) (Table 2.5).

Table 2.5. Udden-Wentworth grain-size classification scheme (Wentworth, 1922)

Millimeters (mm)	Micrometers (μm)	Phi (φ)	Wentworth size class
4096		-12.0	Boulder
256	-----	-8.0	Cobble
64	-----	-6.0	Pebble
4	-----	-2.0	Granule
2.00		-1.0	
1.00	-----	0.0	Very coarse sand
1/2	0.50 500	1.0	Coarse sand
1/4	0.25 250	2.0	Medium sand
1/8	0.125 125	3.0	Fine sand
1/16	0.0625 63	4.0	Very fine sand
1/32	0.031 31	5.0	Coarse silt
1/64	0.0156 15.6	6.0	Medium silt
1/128	0.0078 7.8	7.0	Fine silt
1/256	0.0039 3.9	8.0	Very fine silt
0.00006	0.06	14.0	Clay

CHAPTER 3

RESULTS

The main objective of the study is to assess effects of human-induced pressures and nutrient-laden river discharges on the spatial and temporal variations of the eutrophication-related bio-chemical parameters in the oligotrophic shelf waters of NE Mediterranean. For this goal, concentrations of dissolved inorganic nutrients, chl-*a* (algal biomass indicator) and particulate organic matter (POM) concentrations and its elemental composition (C/N/P ratio) in surface waters and sediments were measured at the hot points and less contaminated sites of the Mersin bay (Figure 2.1 and Table 2.1), located in the wide shelf zone of Cilician basin, NE Mediterranean, in the periods of April 2014 and February 2015.

The spring data represent the biochemical properties of the Mersin Bay the water quality/trophic status of the bay ecosystem during the high-flow period of the major rivers feeding the bay ecosystem. The February-2015 (winter) data represent the trophic status (eutrophication-related properties) of the well mixed upper layer waters during the rainy (wet) winter period when the conditions for photosynthesis are not sufficient to consume all DIN supplied to the inner bay by terrestrial inputs. In the first section, the results of hydrographic, secchi disc depth (SDD) and total suspended solid (TSS) measurements, dissolved inorganic nutrients, N/P ratios, concentrations and elemental composition (C/N/P ratio) of particulate organic matter (POM) determined in seawater and surface sediments, and grain-size analysis of sediments have been evaluated.

3.1. Spatial Variations of Hydrographic Parameters in Surface Waters of the Study Area

Hydrographic (salinity, temperature, water density) parameters were measured *in situ* in water column at 31 stations in April 2014 and only 7 stations in February 2015.

In April 2014, surface distribution of salinity values in the studied site varied from 38.0 in the river-fed coastal waters to 39.2 in central basin (depth>20 m), in the western part of the study area (Figure 3.1). Surface temperature values varied regionally between 19.5-22.3 °C, with warmer surface waters observed in coastal area. Surface density values, ranging between 26.5 and 28.1, naturally displayed

similar regional distributions, decreasing in the less saline and warmer coastal waters of the bay (Table 3.1).

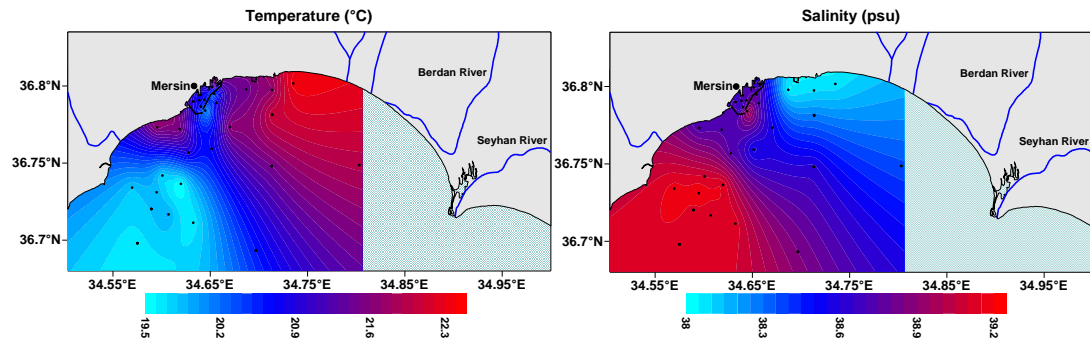


Figure 3.1. Surface distributions of temperature ($^{\circ}\text{C}$), salinity (psu) in the study area of Mersin Bay in April 2014.

Vertical distributions of hydrographic parameters (S, T, sigma-t) are depicted in Figure 3.2. Surface temperature values in the bay ranged regionally from 19.5 to 22.3 $^{\circ}\text{C}$ whilst the near-bottom values varied locally between 18.3 and 21.6 $^{\circ}\text{C}$ in April 2014, with higher values in the river-fed, less saline waters. Since the inner bay waters are highly influenced by river discharges in the study area, the surface salinity was naturally lower in the Berdan delta region, with the values of 38.0-38.5 in the shallow zone (depth<20 m) and then increasing to 39.2 levels off the Berdan delta (Figure 3.1). In the spring, the near-bottom salinity values slightly increased to 38.5-39.2 levels, exhibiting similar spatial distributions as in the surface layer and reaching levels of 39.3 in the central bay bottom waters. Density values calculated from T, S values naturally exhibited spatial features similar to those of T, S distributions; greater density values, ranging from 27.0 to 28.1, were observed in near-bottom waters of the study area. Observation of similar surface and bottom distributions in the bay clearly indicate the intrusion of high saline offshore waters up to coastal waters off the Mersin Harbor (Figure 3.1). Typical depth profiles of hydrographic parameters depicted in Figure 3.2 show small increases in salinity below the surface mixed layer whilst the temperature profiles displayed an opposite feature. In April 2014, the depth profiles of salinity and temperature displayed a weak vertically stratified water masses. In the productive inner bay, less saline water masses occupied the mixed upper layer (2-5 m) (depth<20 m) and displayed a density gradient, increasing density in near-bottom waters. A weak seasonal stratification was also observed in central basin (Figure 3.2) where depth ranged

from 20 to 40 m. Less saline water masses occupied in the upper 15 m (salinity ~39.1 and density ~28.1). Moreover, higher temperature values were observed in upper 15 m, coinciding with lower density values in the central basin. Ranges of hydrographic measurements in the studied area are summarized in Table 3.1.

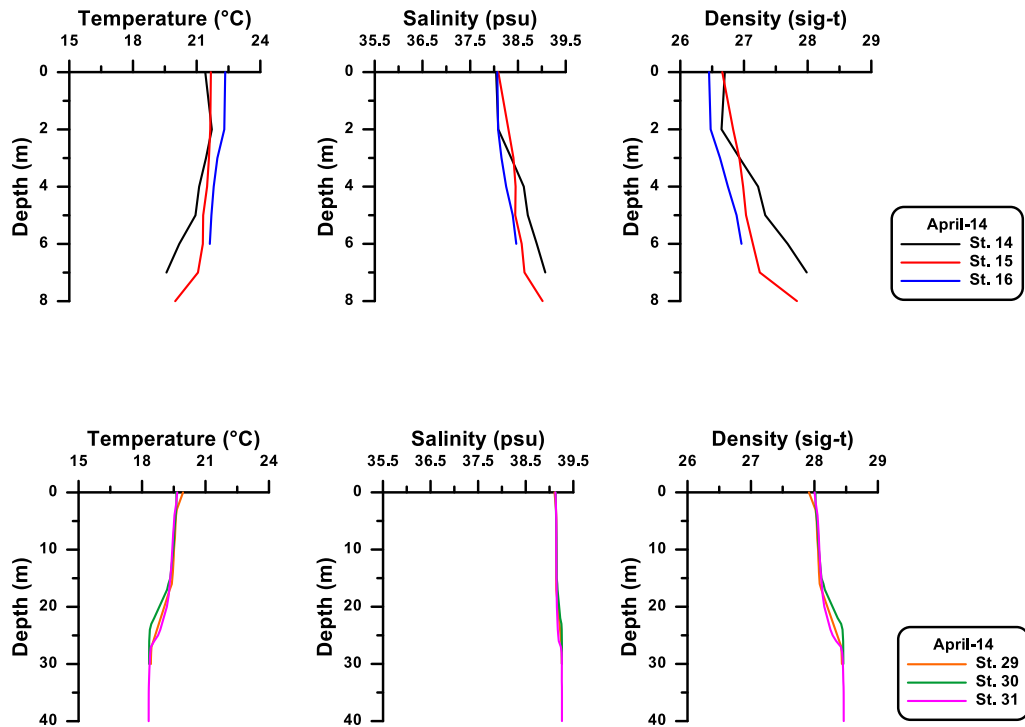


Figure 3.2. Vertical profiles of temperature, salinity and density at selected stations in the inner bay (upper) and central bay (lower) in April 2014.

Surface distributions of hydrographic parameters (temperature, salinity and density) measured in February 2015, are depicted in Figure 3.3. Surface temperature varied locally between 14.5 and 17.6 °C with lower temperature values observed in river-fed zone. Surface salinity distributions were similar to temperature distributions, increasing from 36.1 in the near-shore to 39.1 in the central bay.

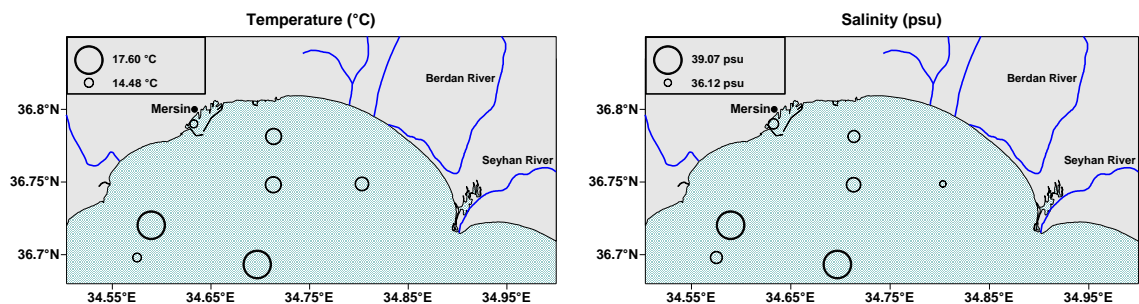


Figure 3.3. Surface distributions of temperature (°C) and salinity (psu) in the study area of Mersin Bay in February 2015.

Depth profiles of temperature, salinity and density in February 2015 are depicted in Figure 3.4, showing almost similar depth distributions in the near-shore zone. Expectedly, more saline and denser water masses occupied the layer below 5-10 m depth in coastal waters. However, vertically uniform depth profiles were observed at central basin with higher values compared to coastal waters (T~17, S~39, D~28.5).

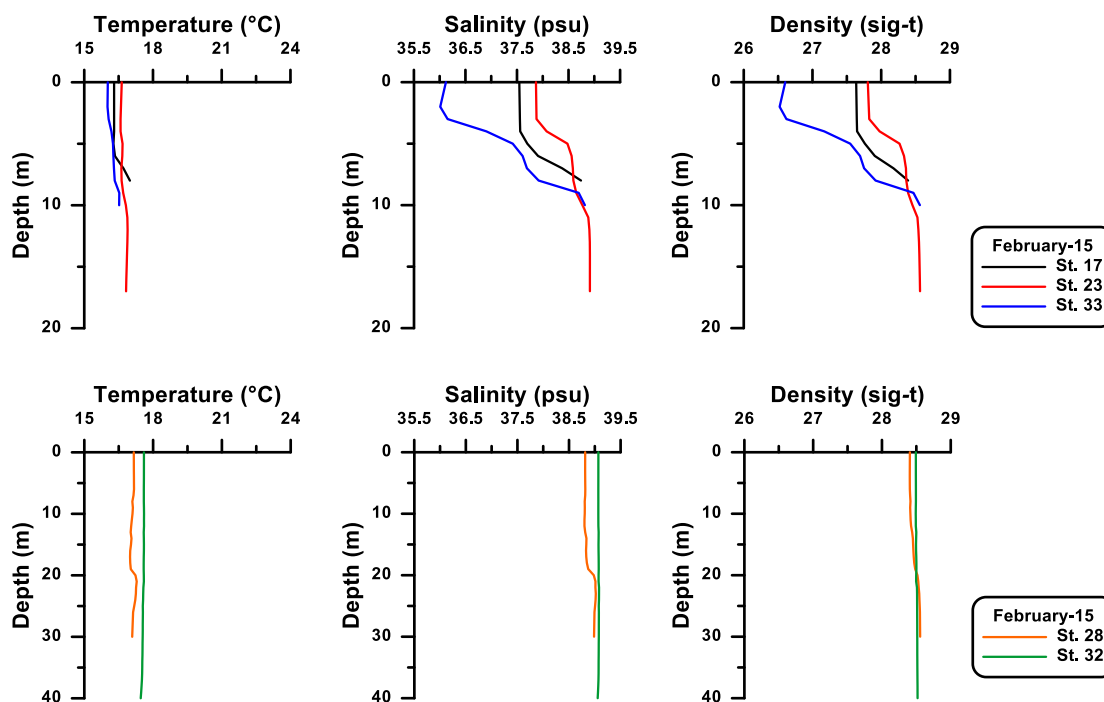


Figure 3.4. Vertical profiles of temperature, salinity and density at selected stations in the inner bay (upper) and central basin (lower) in February 2015.

Table 3.1. Average values and the range of hydrographic parameters measured in the coastal and central bay surface and near-bottom waters of the study area in April 2014.

Layer	Coastal area (depth < 20 m)			Central basin (depth > 20 m)		
	Temperature (°C) (Range)	Salinity (psu) (Range)	Density (sigma-t) (Range)	Temperature (°C) (Range)	Salinity (psu) (Range)	Density (sigma-t) (Range)
Surface	21.1	38.6	27.2	19.7	39.1	28.0
	(19.9-22.3)	(38.0-39.0)	(26.5-27.9)	(19.5-19.9)	(39.1-39.2)	(27.9-28.1)
Near-bottom	21.0	38.9	27.8	18.7	39.2	28.3
	(18.7-21.6)	(38.5-39.2)	(27.0-28.3)	(18.3-19.1)	(39.1-39.3)	(28.2-28.5)

3.2. Spatial Variations of Water Transparency in the Study Area

Water transparency is dominated by particulate organic/inorganic matter and dissolved/colloidal organic chemicals in aquatic environments. Development of eutrophic conditions in the coastal water fed by discharges of nutrient-laden wastewaters and river waters with large amount of suspended matter during wet period drastically limits light penetration in the near-surface waters. The measurement of secchi disc depth (SDD) is a common tool to determine the thickness of lighted upper layer (about 2.5-3.0 x SDD) in the sea. In April 2014, for this goal, SDD and total suspended solid (TSS) measurements were conducted to realize the influence of terrestrial inputs on the water transparency within the studied area of Mersin Bay; the results are depicted in Figure 3.5.

In April, the SDD varied between 7 and 20 m in the central bay waters (total depth: 20-40 m); however, it declined drastically to levels of 1-3 m meters in the shallow coastal zone between the Mersin harbor to Berdan River delta, due to large volumes of river inflows and wastewater discharges of Mersin city.

Expectedly, these coastal surface waters also contain greater concentrations of TSS, ranging between 10.3-30.7 mg/L in the coastal zone (depth<20 m) and then decreased to 6.3-17.0 mg/L levels in the central basin waters. Maximum TSS concentrations were observed in the near-shore waters around the Mersin harbor, where SDD was as low as 1-2 m in April 2014. Briefly, water transparency decreased about at least 5-10 fold in the polluted near-shore and Mersin Harbor waters. Similar spatial variations were also observed in the TSS concentrations of the near-bottom waters in the study area, ranging from 31.9 mg/L around the harbor to 8.0-10 mg/L in the central basin.

SDD values varied regionally between 1.5 and 11.0 m in February 2015 and lower values observed in the points highly influenced by the river inflows having large loads of suspended matter and nutrients enhancing POM production in the shallow coastal waters of the bay (Figure 3.5).

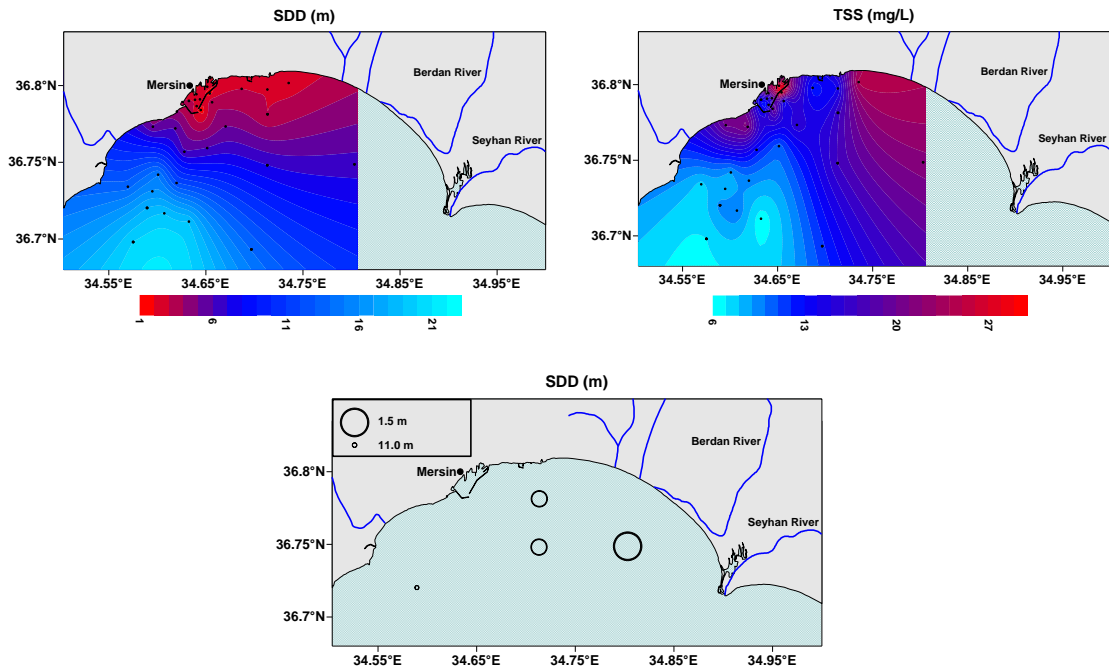


Figure 3.5. Distributions of SDD (m) and surface TSS (mg/L) concentrations in the study area of Mersin Bay in April 2014 (upper) and February 2015 (lower).

3.3. Spatial Variations of Nutrients, Dissolved Oxygen (DO) and Chl-*a* in Surface Waters of the Study Area

The chemical data obtained in April 2014 represent the condition of more productive spring period within the bay due to enhanced nutrient inputs by the regional rivers with the maximum volume fluxes in spring period. As clearly shown from the surface distributions of biochemical data in the studied area (Figure 3.6-18), higher concentrations of nutrient and Chl-*a* (living phytoplankton biomass indicator) were consistently observed in the shallow coastal waters fed by nutrient-laden river inflows and domestic water discharges.

Surface distributions of PO₄ and TP concentrations in April 2014 displayed regional variations (Figure 3.6); the TP (total of organic + inorganic-P) increased from 0.11 μM in the phosphorus-depleted central basin to 0.74 μM in the polluted coastal waters due to terrestrial inputs. However, spatial variability in the surface PO₄ values was less pronounced, ranging merely between 0.02-0.06 μM in the central bay waters and rising to 0.1-0.2 μM levels in the polluted waters of the inner bay. Briefly, the surface distributions of PO₄ and TP displayed similar spatial patterns in the Mersin

Bay, enhancing by 5 to 10 fold in the polluted near-shore waters as compared to the P-depleted central basin waters of the bay (depth>20 m).

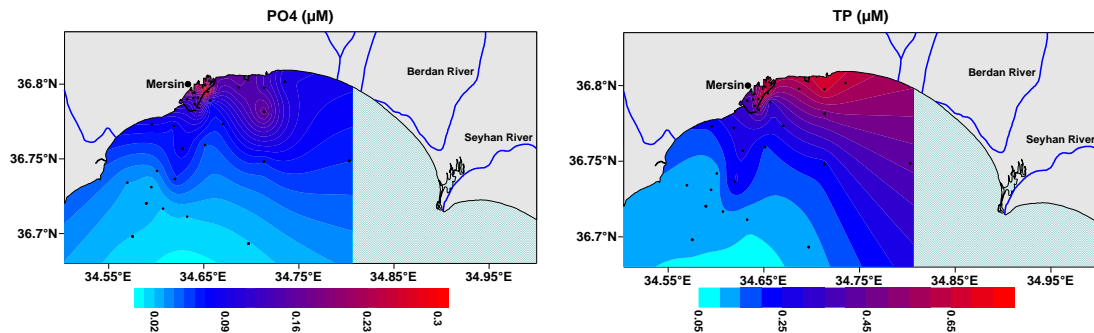


Figure 3.6. Surface distributions of PO₄ (µM) and TP (µM) concentrations in the study area of Mersin Bay in April 2014.

Depth distributions of PO₄ and TP in the bay waters are illustrated in Figure 3.7, showing that water column PO₄ concentrations were almost similar in the near-shore waters in April 2014. However, the near-bottom values of PO₄ and TP in the bay decreased from the polluted coastal zone to the central bay as recorded in their surface distributions in the spring period (Figure 3.6). Near-bottom TP values were as high as 0.5-1.1 µM in the shallow coastal hot points (depth<20 m) and then declined to 0.13-0.40 µM levels in the central bay (depth<50 m) in April 2014.

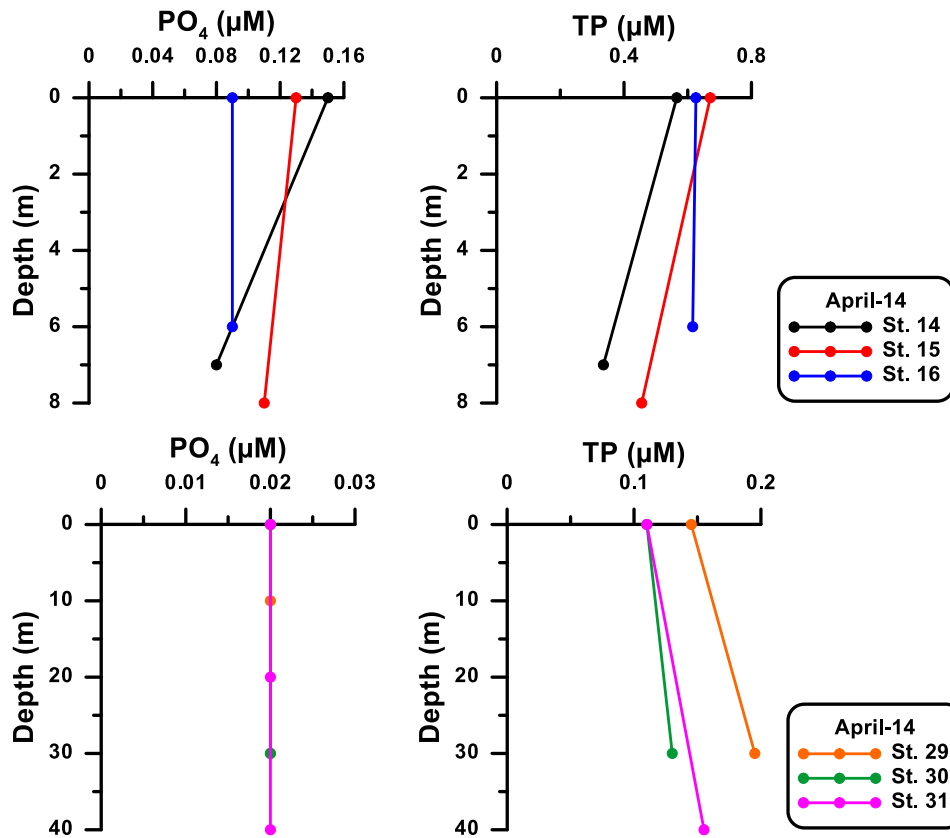


Figure 3.7. Vertical profiles of PO_4 and TP at selected stations in the inner bay (upper) and central bay (lower) in April 2014.

In February 2015, surface distributions of PO_4 and TP are depicted in Figure 3.8. TP concentrations varied between 0.19 and 0.56 μM in the eutrophic coastal waters and decreased to 0.11-0.27 μM levels in less polluted central bay surface waters. Surface PO_4 concentrations displayed similar but less pronounced spatial distribution, ranging locally from 0.03 to 0.15 μM , with maximum values in the river-fed and wastewater polluted coastal zone of the bay.

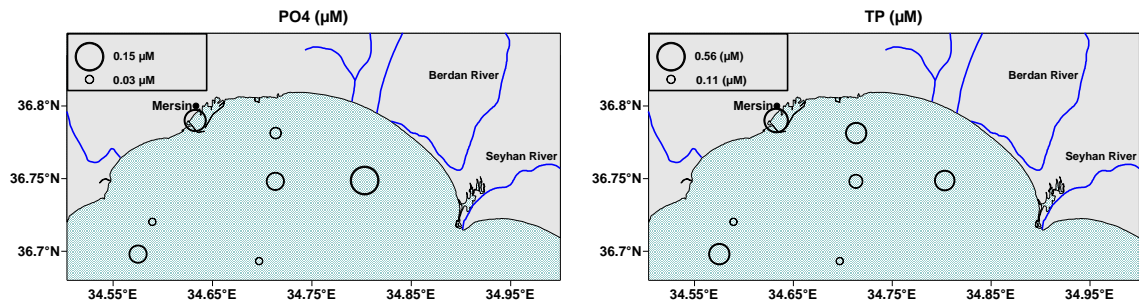


Figure 3.8. Surface distributions of PO_4 (μM) and TP (μM) concentrations in the study area of Mersin Bay in February 2015.

Depth profiles of PO_4 and TP in February 2015 are shown in Figure 3.9. Higher PO_4 and TP concentrations were observed in surface waters of the polluted coastal zone; however, vertically uniform profiles with lower concentrations were observed in the central bay. PO_4 and TP concentrations varied locally between 0.03 and 0.07 μM , and between 0.11 and 0.27 μM , respectively. In the shallow coastal zone, surface waters are impacted by human-induced pressures, PO_4 concentrations ranged between 0.07-0.15 μM in surface waters, declining slightly to 0.09 μM levels in near-bottom waters. TP concentrations in the near-shore zone varied from 0.2 to 0.6 μM .

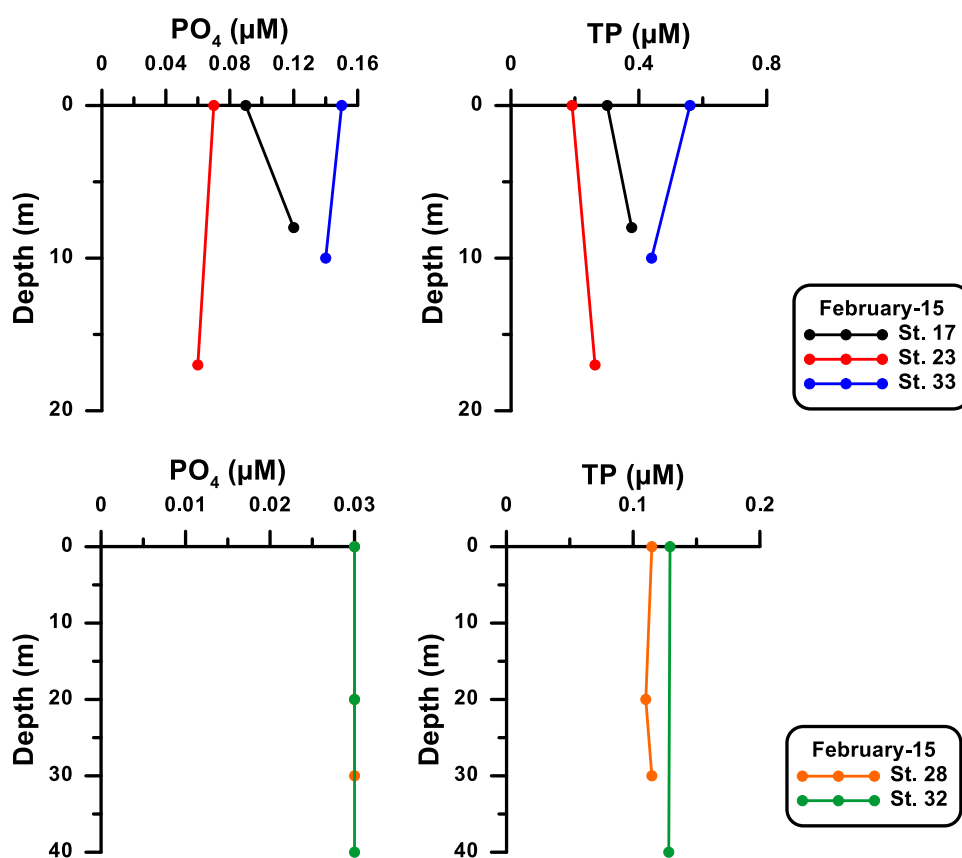


Figure 3.9. Vertical profiles of PO_4 and TP at selected stations in the inner bay (upper) and central bay (lower) in February 2015.

In April 2014, surface distributions of NO_3 (referred to $\text{NO}_3 + \text{NO}_2$), NH_4 and DIN in the bay waters displayed similar spatial changes as that of PO_4 and TP. Maximum NO_3 , NH_4 and DIN concentrations were naturally observed in the polluted near-shore waters receiving terrestrial nutrient inputs. Surface distributions of NO_3 , NH_4 and DIN (Figure 3.10) clearly showed drastic increases in DIN concentrations, reaching levels of 10-16 μM in the shallow coastal zone from Mersin Harbor to Berdan River

delta due to large amounts of nutrient inputs by domestic wastewaters and river discharges. Since the major source of NH_4 is domestic wastewaters, the highest NH_4 values were recorded at one of the hot points polluted by wastewater discharges of Mersin city, where the concentrations of nitrate and ammonia were measured as high as 50-60 μM in April 2014. These polluted waters were diluted in the coastal zone by at least 10-fold (Figure 3.10); NO_3 concentrations decreased apparently to levels of 0.05-0.3 μM in the central bay (depth > 20 m), reaching levels of 2-10 μM in the shallow coastal waters (Figure 3.10). Expectedly, the lowest ammonium concentrations were determined in the less contaminated central bay waters (0.07-0.38 μM) where the lowest NO_3 values were recorded and then increased to levels of 3-5 μM levels in the near-shore waters (depth < 20 m). Dissolved inorganic nitrogen (DIN: nitrate + nitrite + ammonium) concentrations displayed similar regional distributions, enhancing markedly in the shallow near-shore waters of the inner bay. Surface DIN concentrations reached 10-16 μM levels in the coastal hot points and then declined to 0.2-0.5 μM in the central bay waters having the low concentrations of nitrate and ammonia, indicating at least 3 to 5 fold decreases in the less contaminated sites of the bay.

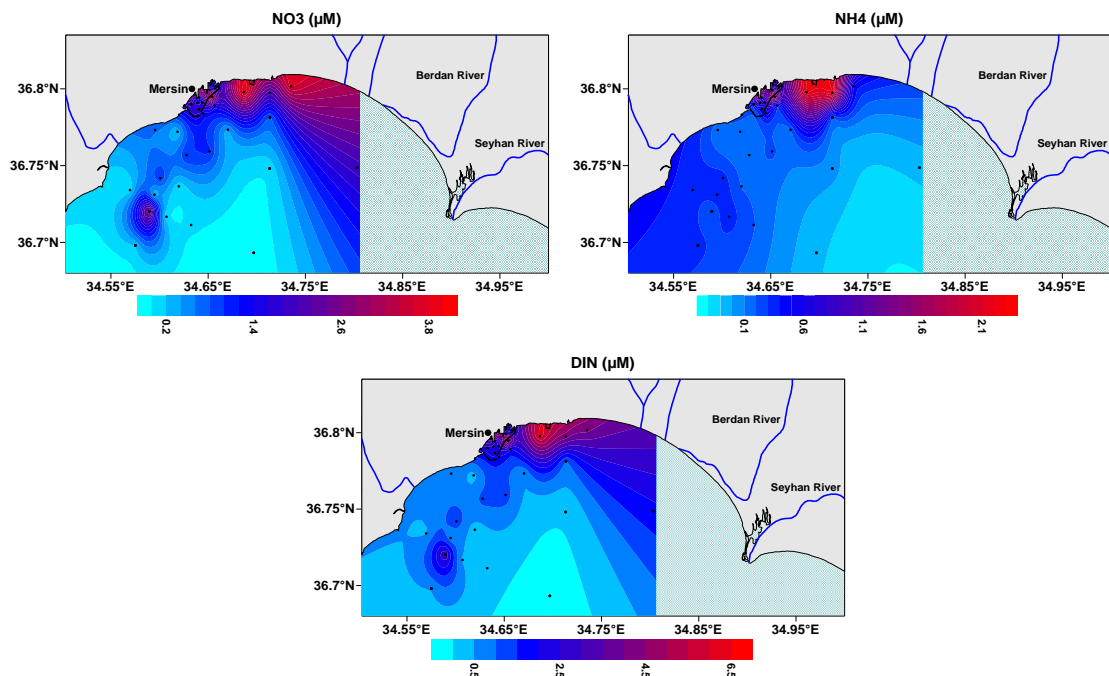


Figure 3.10. Surface distributions of NO_3 (μM), NH_4 (μM) and DIN (μM) concentrations in the study area of Mersin Bay in April 2014.

In April 2014, concentrations of NO_3 , NH_4 and DIN in the near-bottom waters ranged between 0.06-5, 0.10-2.22 and 0.19-7.22 μM , respectively, lower than the surface values in the polluted locations (Figure 3.11). In the central bay waters, the nitrate profiles displayed an apparent increasing trend in the near-bottom waters.

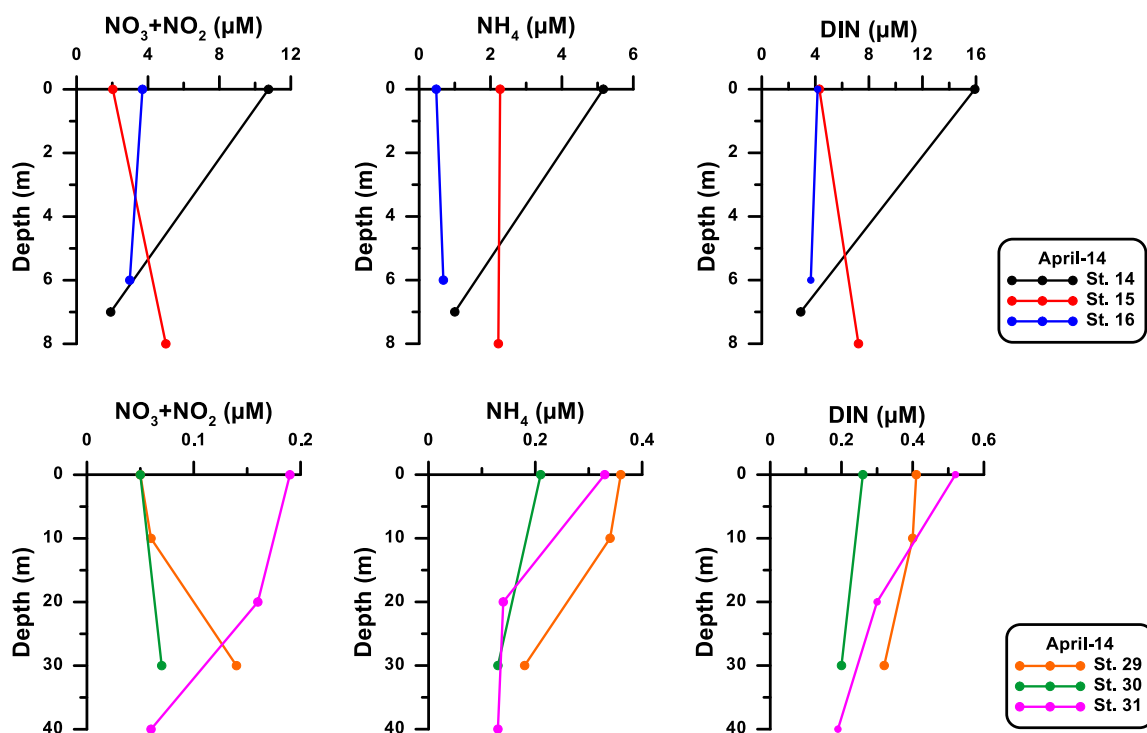


Figure 3.11. Vertical profiles of NO_3 , NH_4 and DIN at selected stations in the inner bay (upper) and central bay (lower) in April 2014.

Surface distributions of NO_3 ($\text{NO}_3 + \text{NO}_2$), NH_4 and DIN (sum of nitrate + nitrite + ammonium) in February 2015 were similar to the winter PO_4 and TP distributions, but the spatial variability was much greater due to DIN-laden river and domestic water discharges to the inner bay. Maximum NO_3 , NH_4 and DIN concentrations were observed in river-fed zone and city harbor as 13.7, 2.7 and 16.3 μM , respectively (Figure 3.12). Lower concentrations were observed in surface waters of the less contaminated sites of the central bay, with nitrate values of 0.65 to 1.78 μM and NH_4 : 0.10-0.50 μM levels. The NH_4 increased markedly to 1.0-3.0 μM levels in the polluted coastal waters of the bay. Thus, the surface DIN varied locally between 1.2-1.9 μM in the central bay and enhanced in the coastal hot points (10-16.3 μM). Comparison of spatial DIN data indicates 10-20 fold increase in NO_3 , NH_4 concentrations from the central bay surface waters to the hot points on the coastal zone located between Mersin harbor and Berdan River delta.

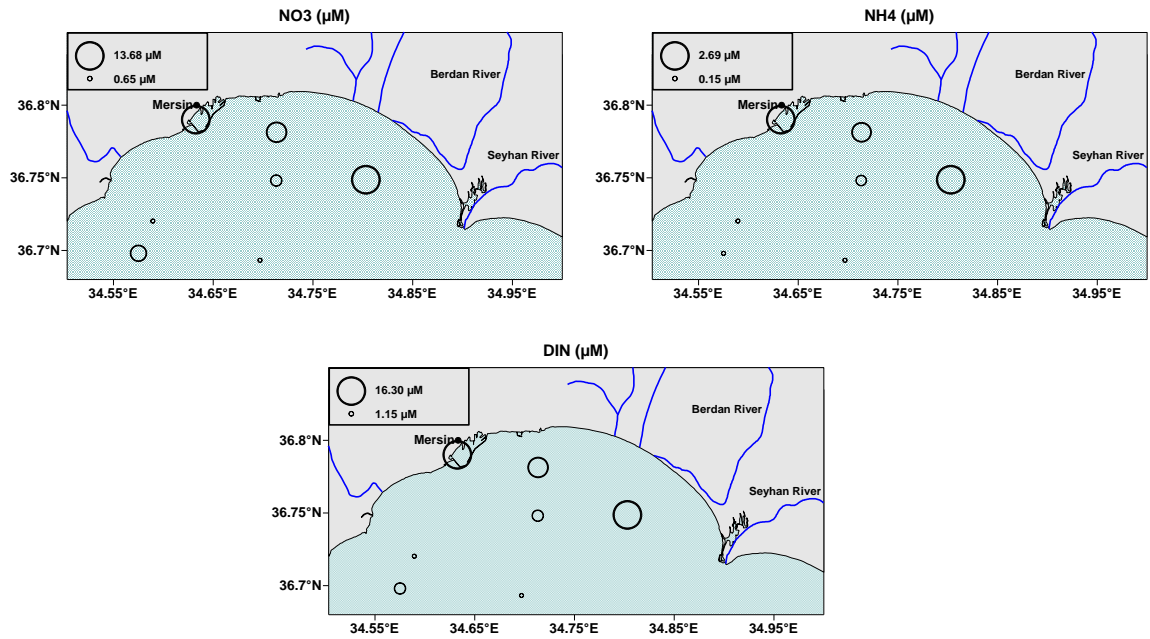


Figure 3.12. Surface distributions of NO_3 (μM), NH_4 (μM) and DIN (μM) concentrations in the study area of Mersin Bay in February 2015.

In winter 2015, depth distributions of NO_3 , NH_4 and DIN are depicted in Figure 3.13. Higher surface concentrations were observed in near-shore zone due to terrestrial inputs. The concentrations were much lower in the central basin and displayed almost vertically uniform depth profiles due to effective vertical mixing of the water column in winter.

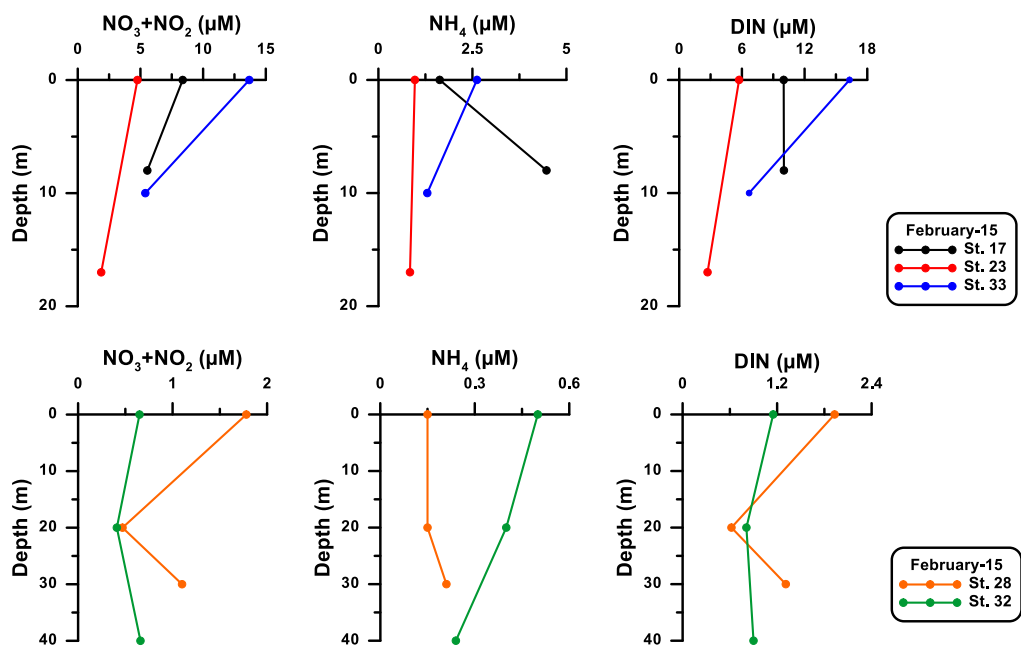


Figure 3.13. Vertical profiles of NO_3 , NH_4 and DIN at selected stations in the inner bay (upper) and central bay (lower) in February 2015.

In April 2014, surface distribution of silicate (Si) displayed similar pattern to that of NO_3 due to Si-laden fresh water inputs to the coastal zone of the bay (Figure 3.14). Surface Si concentrations were as high as 3-6 μM in less saline coastal waters, then decreasing to 1-2 μM levels in the central bay.

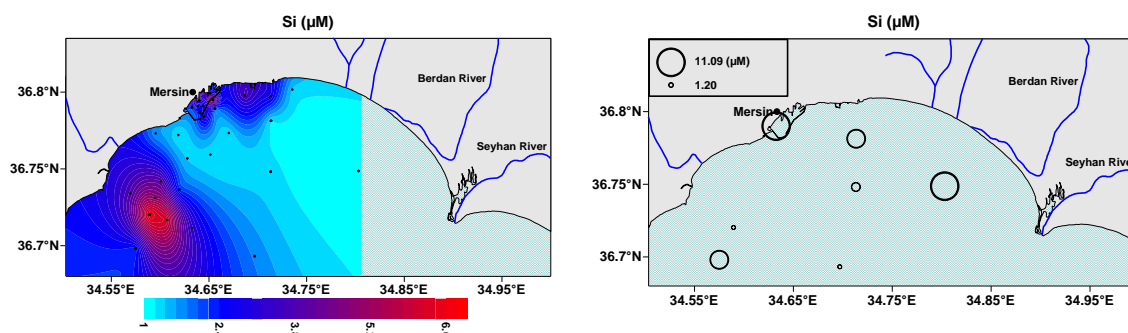


Figure 3.14. Surface distribution of Si (μM) concentrations in the study area of Mersin Bay in April 2014 (left) and February 2015 (right).

In February 2015, surface Si concentrations regionally varied locally from 1.2 in the central bay waters to 11 μM in the river-fed coastal zone of the bay, exhibiting nitrate-like spatial variations within the bay (Figure 3.14)

Concentrations of dissolved oxygen (DO) in surface waters in spring period are depicted in Figure 3.15 for April 2014 period. In nutrient-replete, less saline coastal surface waters, the DO varied between 7.1 and 8.9 mg/L and then declined slightly to 7.7-7.8 mg/L levels in the central bay waters. The near-bottom DO values in April 2014 ranged between 7.0 and 8.7, indicating almost saturated levels of DO in the bottom waters of the bay in April 2014.

Biochemical oxygen demand (BOD_5) measurements were also performed in order to assess the spatial variation of slowly sinking biodegradable organic materials in the bay waters (Figure 3.15). BOD_5 concentrations ranged from 0.35 to 1.12 mg/L in the central basin of the bay with limited effect of land-based sources and then increased to 2.0-2.7 mg/L levels in the domestic wastewater and river-fed coastal zone waters of the bay.

Surface chlorophyll-*a* (Chl-*a*) distributions in April 2014 in the study area were expectedly higher in the nutrient-replete coastal waters of the bay (Figure 3.15). The surface Chl-*a* concentrations declined apparently from 0.62-4.40 $\mu\text{g/L}$ levels in the

more productive coastal zone to 0.08-0.34 $\mu\text{g/L}$ in the less contaminated waters of the bay.

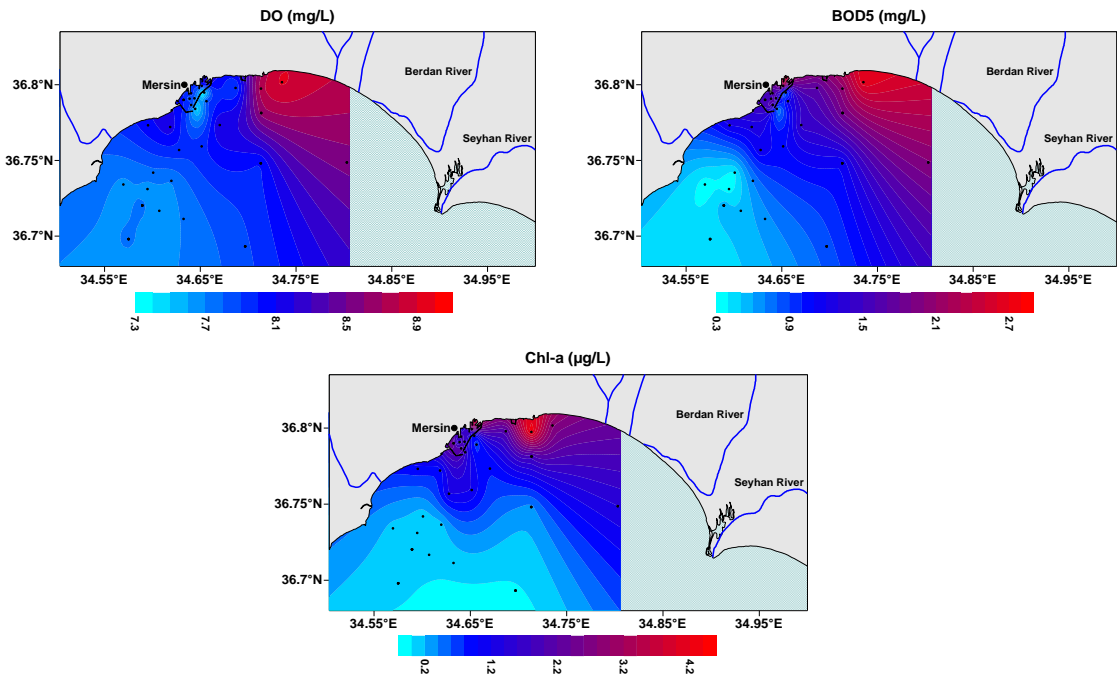


Figure 3.15. Surface distribution of DO, BOD₅ (mg/L) and Chl-*a* ($\mu\text{g/L}$) concentrations in the study area of Mersin Bay in April 2014.

The depth profiles of DO and Chl-*a* in April 2014 are shown in Figure 3.16; the concentrations of DO and Chl-*a* were higher in surface waters of the polluted near-shore waters. DO concentrations ranged between 7.0-8.7 mg/L in near-bottom waters of the studied area. Chl-*a* concentrations varied from 0.08 to 4.40 $\mu\text{g/L}$ in the study area, with the highest value in the nutrient-rich coastal waters. DO concentrations increased from 7.0-7.83 mg/L in near-bottom waters of the central bay to 6.99-8.7 mg/L levels in polluted coastal waters. Chl-*a* concentrations in near-bottom waters of the less polluted sites of the bay varied between 0.06-0.67 $\mu\text{g/L}$ and increased markedly to 0.54-3.72 $\mu\text{g/L}$ levels in productive near-shore waters.

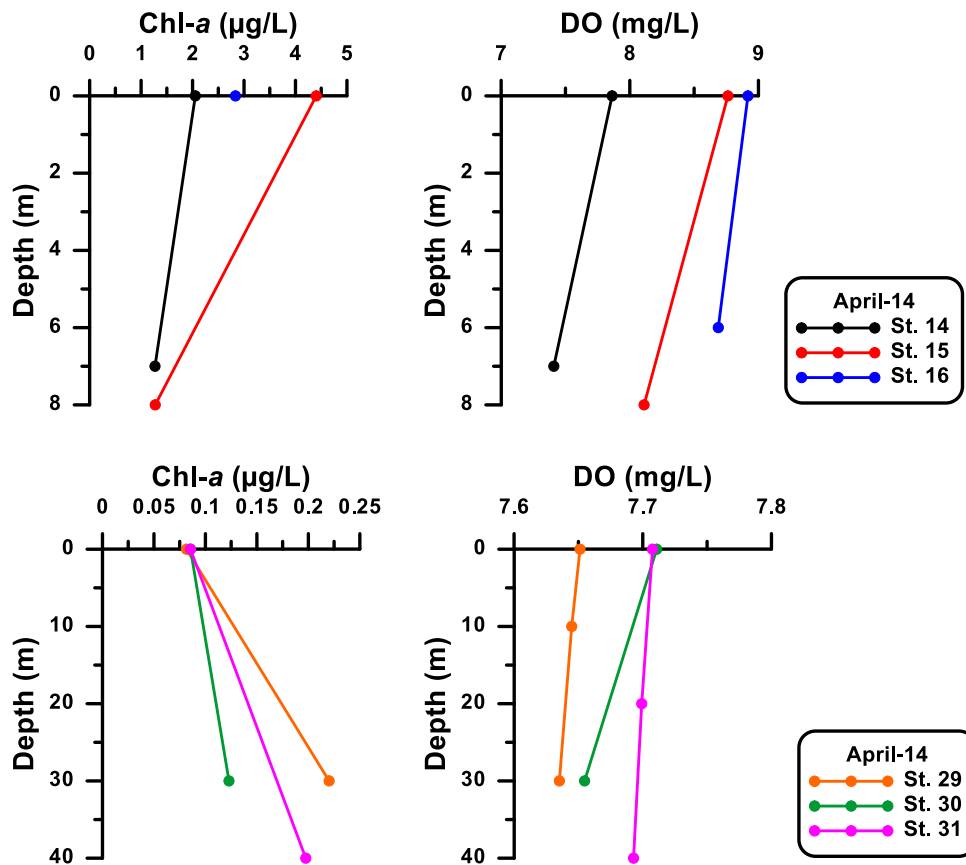


Figure 3.16. Vertical profiles of DO and Chl-*a* at selected stations in the inner bay (upper) and central bay (lower) in April 2014.

In February 2015, Chl-*a* concentrations in surface waters of the study area displayed similar pattern to that of DO distribution. Chl-*a* concentrations ranged between 0.14-0.7 µg/L in the central bay (depth>20 m) and increased to 1.0 -2.0 µg/L levels in the eutrophic coastal waters fed by terrestrial nutrient inputs (Figure 3.17). Surface DO concentrations varied regionally between 7.63 and 8.84 mg/L; higher concentrations were observed in productive and nutrient replete river-fed, less saline coastal waters. BOD₅ distributions in surface waters were similar to Chl-*a* pattern, with lower values (0.4-0.6 mg/L) in the less contaminated sites of the bay and increased to 0.8-1.0 mg/L levels in the eutrophic (rich in organic matter and nutrients) near-shore waters (Figure 3.17).

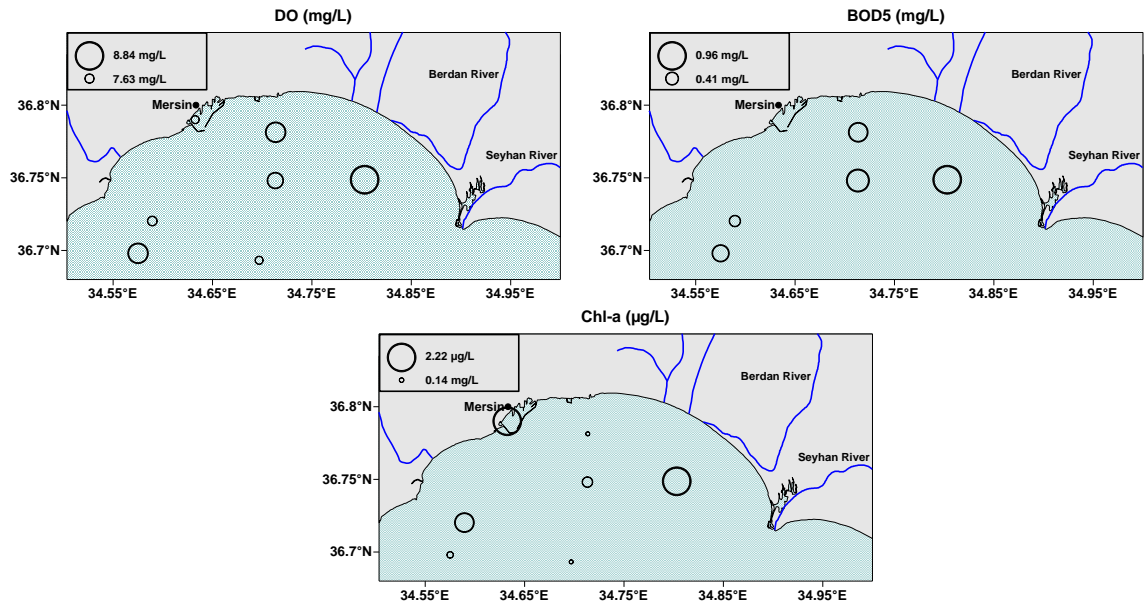


Figure 3.17. Surface distribution of DO, BOD₅ (mg/L) and Chl-*a* (µg/L) concentrations in the study area of Mersin Bay in February 2015.

Depth profiles of Chl-*a* and DO were very similar vertical features in central bay in winter period, decreasing from the surface layer to the near-bottom waters (Figure 3.18). Chl-*a* concentrations varied from 0.14-2.22 µg/L levels in the surface layer to 0.24-0.45 µg/L in the near-bottom waters of the less contaminated sites (Figure 3.18). The Chl-*a* values reached 1.0-2.0 µg/L levels in the productive coastal waters of the bay. DO concentrations were about 8.84 mg/L in the surface waters at St.33 (depth: 10m) and then decreased slightly to 7.75 mg/L in the near bottom waters indicating well-oxygenated water column within the bay in winter.

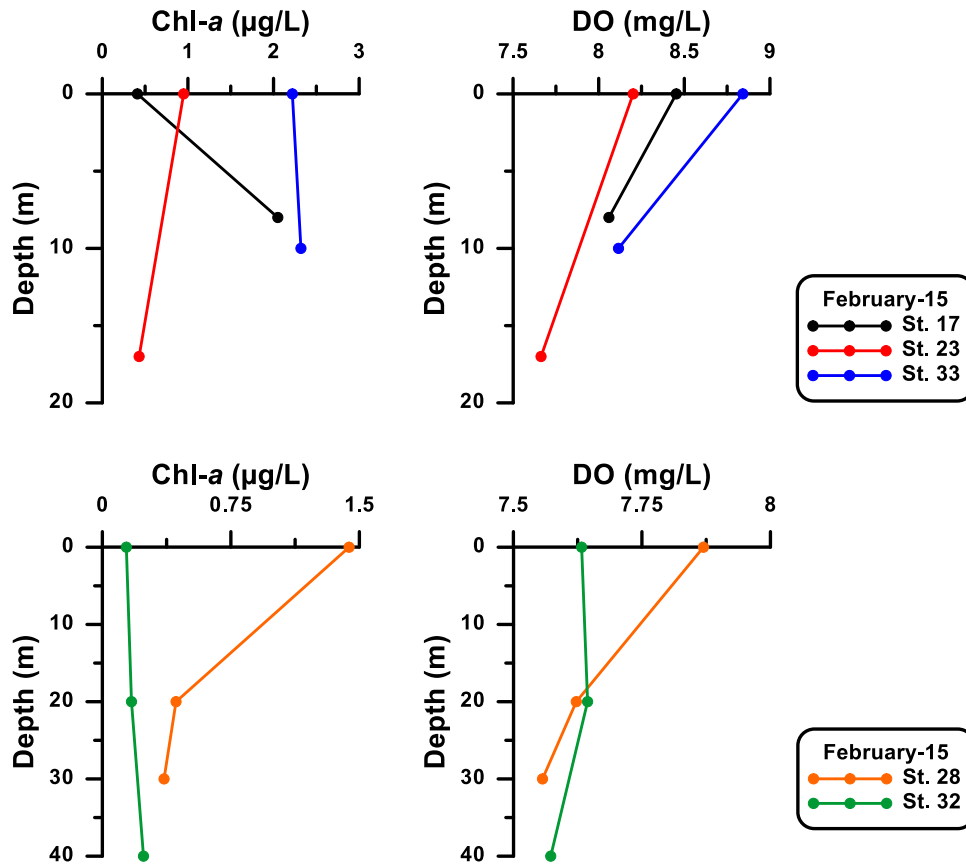


Figure 3.18. Vertical profiles of DO and Chl-*a* at selected stations in the inner bay (upper) and central bay (lower) in February 2015.

3.4. Spatial Variations of Particulate Organic Matter (POM) in Surface Waters of the Study Area

This study mainly aims to understand influences of terrestrial chemical inputs on enhancement and elemental composition of bulk POM in water column and surface sediments on the continental shelf of NE Mediterranean having oligotrophic properties. For this goal, POM and related biochemical data were obtained from highly influenced (productive) and less influenced sites of the Mersin Bay. All POM results in 2014 and 2015 have been evaluated to assess influences of terrestrial (wastewater + river discharges) inputs on POM enhancement and composition in mesotrophic/eutrophic and oligotrophic sites of Mersin Bay.

In April 2014, POM data were obtained at 23 stations in the productive coastal zone and 8 stations in the central bay (depth > 20 m) waters (see Figure 2.1). The results clearly show marked enhancement of POC in the coastal waters, reaching levels of

77-107 μM in surface waters of the river-fed coastal zone (Figure 3.19). The background concentrations of 3-15 μM were recorded in less productive central bay waters having low biomass (Chl-*a*) concentrations. Surface PON concentrations in the study area expectedly exhibited similar regional distributions, reaching the maximum level (12.9 μM) at St.6 in the highly productive coastal waters (Figure 3.19) and then declining markedly to 0.56-2.48 μM levels in the central bay waters.

TPP (total particulate-P) concentrations of bulk POM in the surface bay waters displayed nearly similar regional distributions, with higher concentrations (>0.45 μM) in the shallow coastal waters between Mersin harbor and Berdan River delta (Figure 3.19). Surface TPP values decreased markedly to 0.025-0.058 μM levels in the western part of bay (depth >20 m) receiving less nutrient inputs compared to the hot points at the near-shore zone.

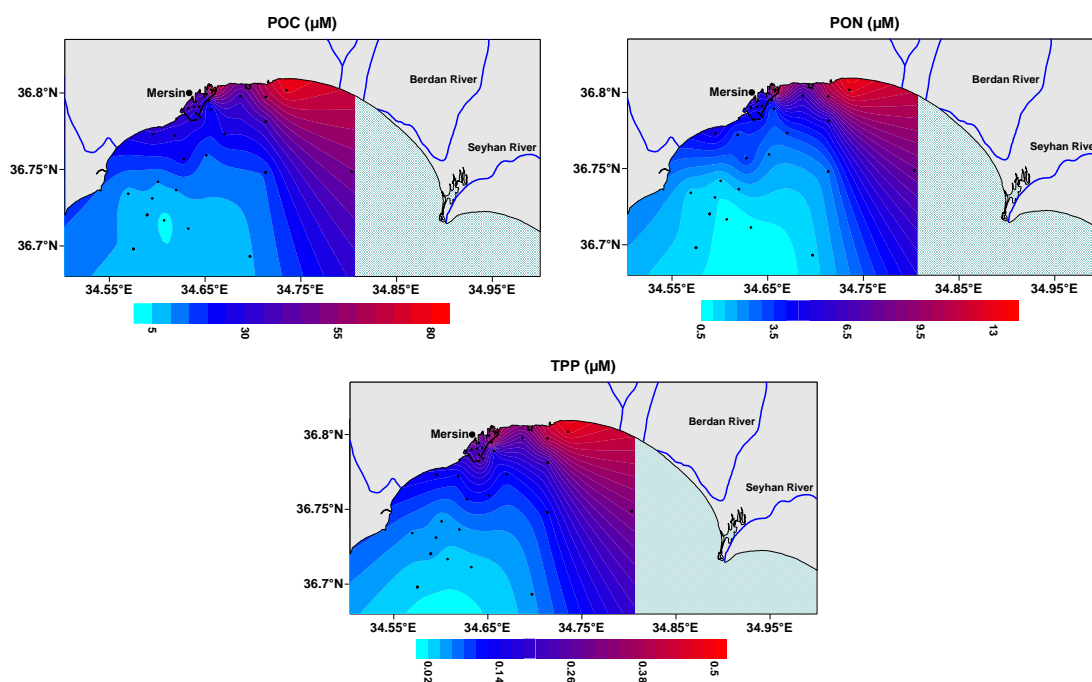


Figure 3.19. Surface distributions of POC (μM), PON (μM) and TPP (μM) concentrations in the study area of Mersin Bay in April 2014.

Depth profiles of POC, PON and TPP shown in Figure 3.20 were expectedly similar to vertical profiles of Chl-*a*. Lower concentrations of bulk POM were measured in near-bottom waters of the eutrophic/mesotrophic inner bay. In the POM depleted central bay waters receiving less inputs from land-based sources (Figure 3.20), the concentration slightly enhanced in the near-bottom waters (depth $>20\text{m}$). POC, PON and TPP concentrations of bulk POM in near-surface and bottom waters of the bay

displayed similar regional distributions in April 2014. The POC exceeding 70 μM in the river-fed coastal zone, declined by about 5-fold to 14-15 μM levels in the less contaminated central bay water column. Similar spatial variations were also observed in PON concentrations, decreasing from 8-10 μM levels at the hot points to 1-2 μM in near-bottom waters occupying the western part of central basin (Figure 3.20). TPP concentrations also displayed similar spatial variations, ranging from 0.03 μM in the central bay near-bottom waters to 0.42 μM in productive waters of the hot points receiving terrestrial inputs of inorganic nutrients and organic pollutants.

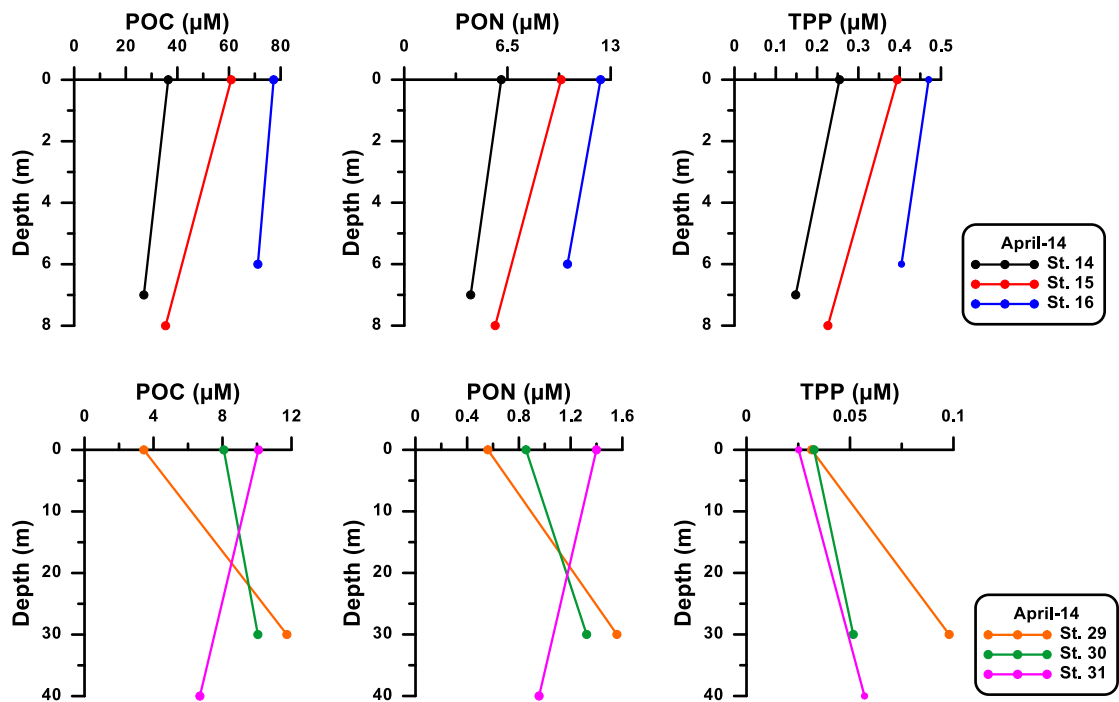


Figure 3.20. Vertical profiles of POC, PON and TPP at selected stations in the inner bay (upper) and central bay (lower) in April 2014.

In February 2015, POC enhancement was clearly seen in the productive coastal waters especially in the river-fed zone. The POC varied between 5.72 and 12.5 μM levels in the less contaminated locations and exceeded 40.0 μM in surface waters of the polluted sites. Similar spatial variations were seen in PON and TPP data. The PON concentrations ranged from 1.8 to 5.9 μM in hot points and declined to 1.0-1.5 μM levels in the less productive sites of the inner bay. TPP concentrations in the study area varied locally between 0.026 and 0.37 μM ; the peak value was measured as St.33 located between Mersin Harbor and Berdan River mouth (Figure 3.21).

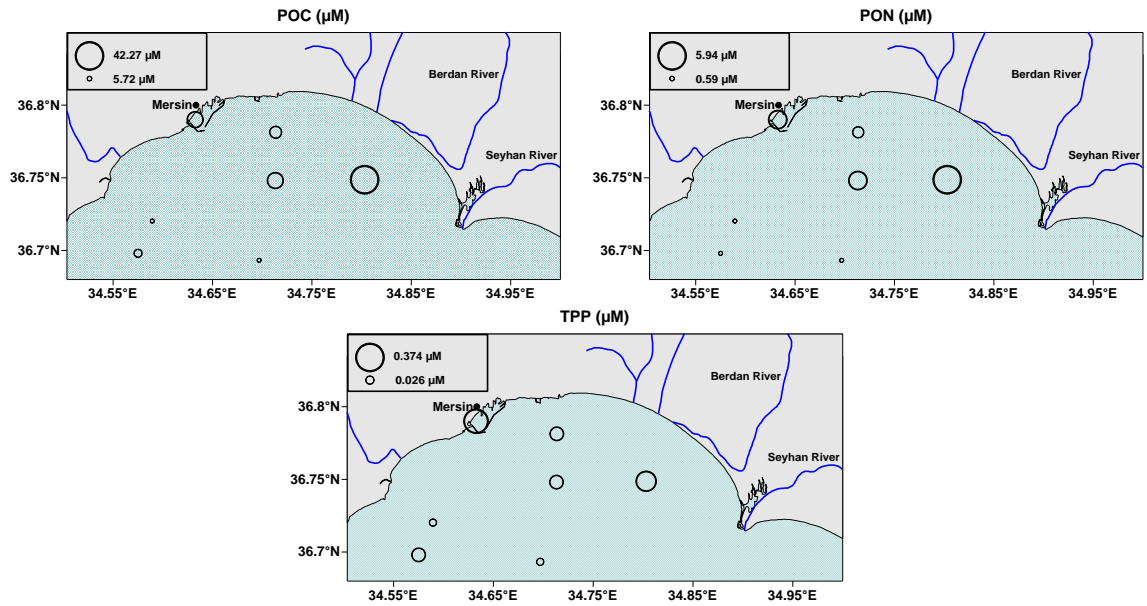


Figure 3.21. Surface distributions of POC (μM), PON (μM) and TPP (μM) concentrations in the study area of Mersin Bay in February 2015.

In February, depth profiles of POC, PON and TPP in the inner bay were similar to the *Chl-a* vertical distributions; higher concentrations were observed in the productive surface waters of the inner bay. POC concentrations were recorded to range between 20-45 μM in surface waters of the coastal waters (depth < 20m) and decreased to levels of 10-25 μM in near-bottom waters. PON concentrations in surface waters exceeded 5.0 μM at the coastal locations and declined to 1.0 μM levels in near-bottom waters (Figure 3.22). Similar changes were observed in the depth profiles of TPP; decreasing from 0.2-0.4 μM in surface waters to 0.1 μM levels in bottom waters. In the central bay, POC and PON concentrations increased with depth (Figure 3.22) whilst variability in TPP distribution was much less pronounced.

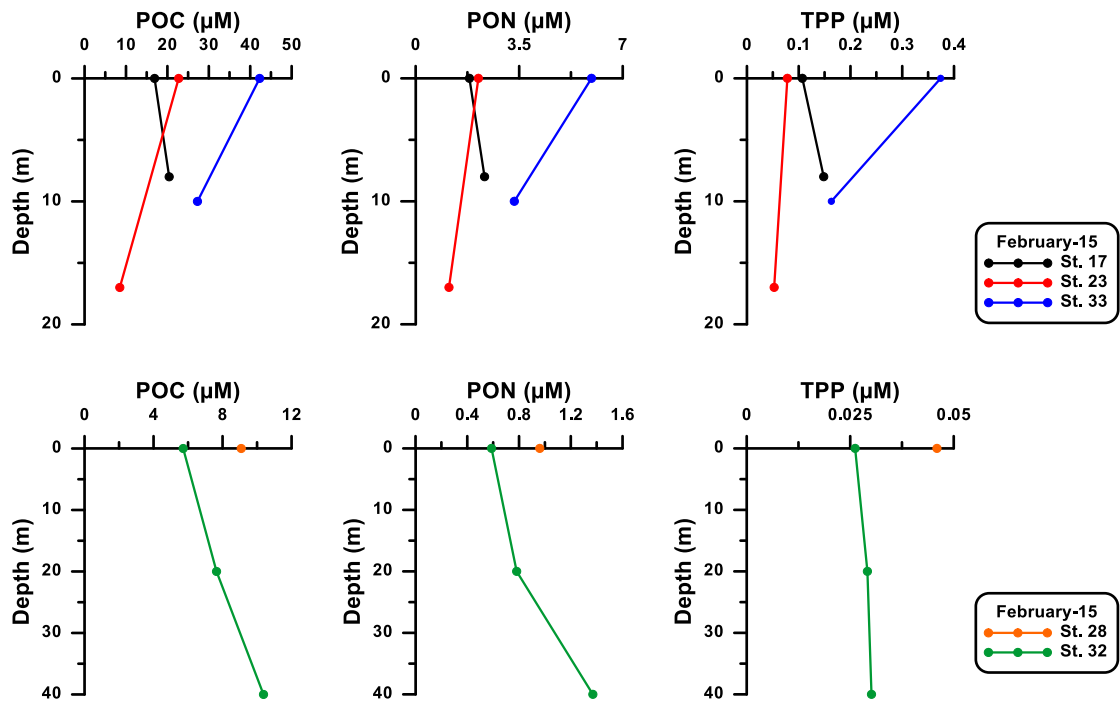


Figure 3.22. Vertical profiles of POC, PON and TPP at selected stations in the inner bay (upper) and central bay (lower) in February 2015.

3.5. Spatial Variations of Total Carbon (TC), Particulate Phosphorus (TPP) and Nitrogen (TN) and Total Organic Carbon (TOC) and Particulate Organic Phosphorus (POP) in Surface Sediments of the Study Area

In this study, total carbon (TC), particulate phosphorus (TPP) and nitrogen (TN) and total organic carbon (TOC) and particulate organic phosphorus (POP) measurements were also performed in surface sediments of the bay. Sediment samples were collected at the locations from more productive coastal zone and less productive central bay where nutrients and bulk POM data were obtained by bottle casts. All data sets on nutrients, biomass (in terms of Chl-*a*) results in seawater and POM data in sediment and seawater compiled in Appendix A and B are evaluated together in the next chapter to assess correlations between pressures (land-based nutrient inputs) and state parameters (biomass and POM increases and composition) in water and sediment phases of the eutrophic and mesotrophic/oligotrophic sites of the bay. In April 2014, total carbon (TC: organic + inorganic) concentrations varied locally between 38.5 and 112.5 mg/g (dry weight) in surface sediments of the study area with maximum concentrations observed in polluted inner bay especially in city harbor and its surrounding. TC concentrations in surface sediments ranged merely

between 38.5 and 47.7 mg/g in the central bay, increasing levels of 74-113 mg/g in the shallow harbor region (Figure 3.23). Local variations in TIC (TC - TOC) content of surface sediments (29.1-110 mg/g) were well-pronounced; the TC-rich sediment samples from the Mersin harbor region have higher TIC concentrations (70-110 mg/g) due to transports of terrestrial inorganic particles by the small creeks in the region and heavy surface runoff during rainy period transports. Currents and wave actions help organic rich suspended mater transport deeper part (offshore) of the bay whilst POM-poor sandy particles accumulates on the bottom of near-shore zone. The result of TOC enriched in muddy sediments displayed weak spatial patterns, depending influences of terrestrial inputs, POM production and currents in the study area; the higher values ranging between 6.4-7.5 mg/g were recorded in surface sediments of the central bay where POM-rich particles carried by surface currents and settled down in the region. TOC concentrations in the surface sediments of the near-shore zone varied from 2.0 mg/g at St.22 to 23.4 mg/g at St.1 polluted by terrestrial POM inputs.

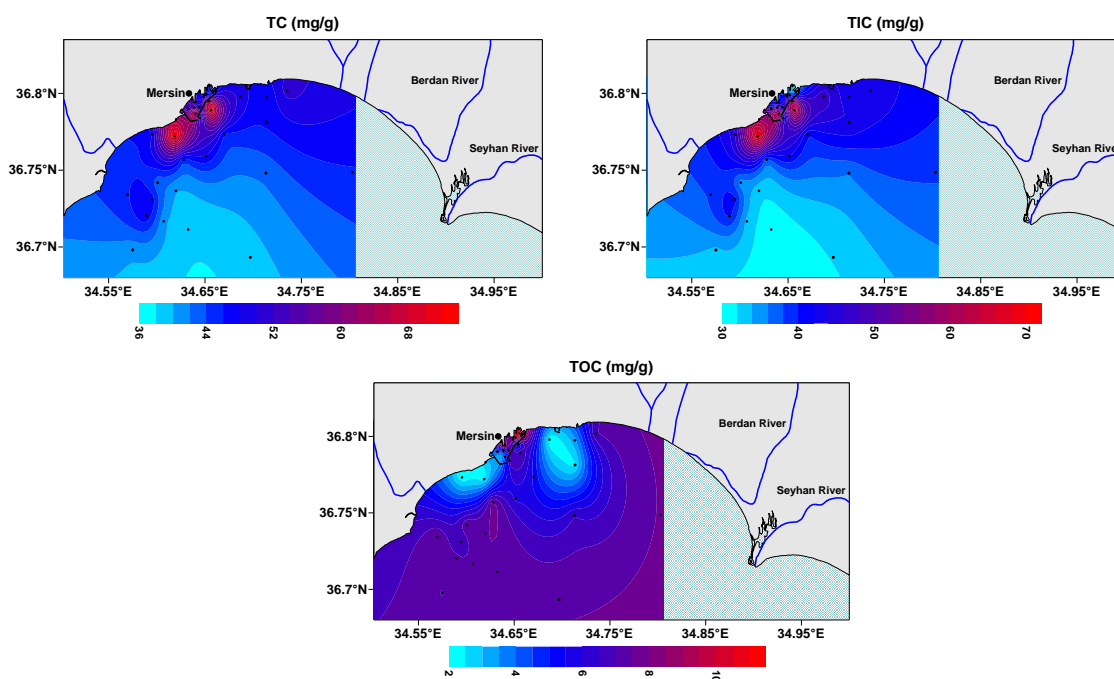


Figure 3.23. Distributions of TC (mg/g), TIC (mg/g) and TOC (mg/g) concentrations of surface sediments in the study area of Mersin Bay in April 2014.

In February 2015, TIC-dominated TC concentrations in surface sediments displayed less pronounced spatial variations in the studied area of the bay. TC concentrations of the surface sediments varied between 34.1 and 49.0 mg/g in the studied locations;

higher TC values were measured in sandy sediments of the shallow coastal zone especially in city harbor and its surrounding as observed in spring period (Figure 3.24). TIC distributions in surface sediments naturally displayed similar pattern, with values varying between 30-35 mg/g in the studied sites. On the other hand, organic carbon content of surface sediments in the samples displayed different spatial pattern as compared to the TIC-dominated TC distributions. Expectedly, locally polluted sediments within the Mersin harbor, surface sediments of the near-shore zone contained less organic carbon (3-6 mg/g; 10-15% of TC) as compared to those measured in the deeper region of the bay (6.8-9.1 mg/g; 15-20% of TC) receiving slowly sinking more organic rich particles from productive coastal zone by surface currents.

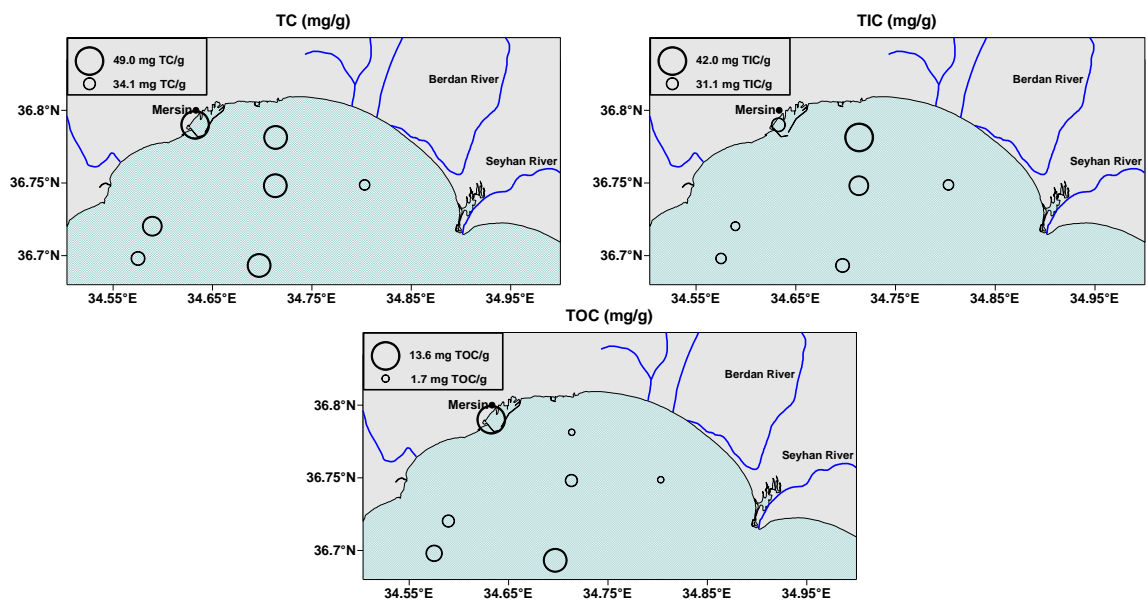


Figure 3.24. Distributions of TC (mg/g), TIC (mg/g) and TOC (mg/g) concentrations of surface sediments in the study area of Mersin Bay in February 2015.

Regional variations of total nitrogen in surface sediments of the bay in April 2014 were very similar to that of TOC (Figure 3.25). TN concentrations varied between 0.62 and 0.82 mg/g in the central bay and then decreased to 0.5-0.6 mg/g in the coastal sediments having greater fractions of sandy materials.

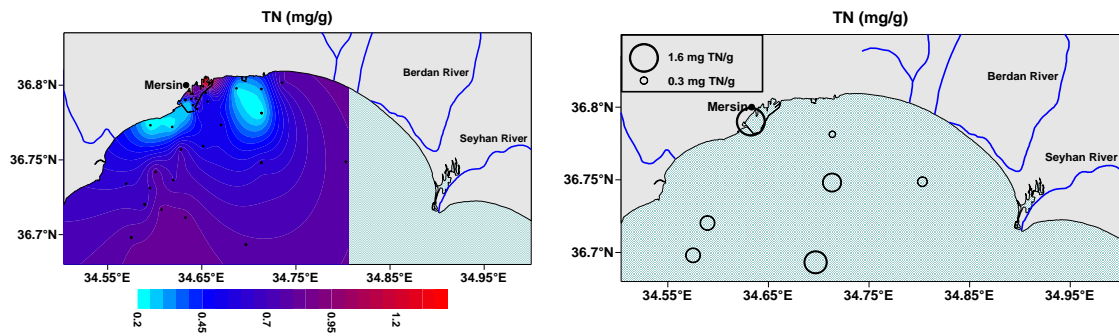


Figure 3.25. Distributions of TN (mg/g) concentrations of surface sediments in the study area of Mersin Bay in April 2014 (left) and February 2015 (right).

In February 2015, TN concentrations in surface sediments were similar to those measured in the spring 2014 samples; TN concentrations ranged locally from 0.3 to 1.6 mg/g in the study area with lower values in the coastal zone having less fine particles as compared to sandy materials-dominated surface sediments (Figure 3.25). However, maximum TN concentration was recorded within the city harbor sediments polluted by wastewater, surface runoff and organic compound discharges from shipping activities within the harbor.

Spatial distribution of total particulate phosphorus (TPP: sum of particulate organic + inorganic-P) concentrations in surface sediment samples displayed a gradually increasing trend from coastal zone to the central bay (Figure 3.26). TPP concentrations were as low as 0.22 mg/g in the coastal sediments and then increased to 0.50 mg/g in the central bay sediments mainly composed of fine-grained particles. Regional distributions of POP in surface sediments displayed similar pattern to that of TPP values; POP concentrations varied locally between 0.01-0.11 mg/g in the studied area of the bay, exhibiting greater variation in the coastal zone sediments of different grain size composition (Figure 3.26). Similar spatial variations were observed in PIP concentrations (calculated from TPP-POP difference), increasing from 0.37 mg/g levels in the near-shore sediments to 0.45-0.50 mg/g in the central bay. The lowest values of TPP and POP in sediment samples were recorded on the near-shore zone between Mersin Harbor and west coast of the city whilst their concentrations increased by about 2-4 fold in the central bay sediments (Figure 3.26).

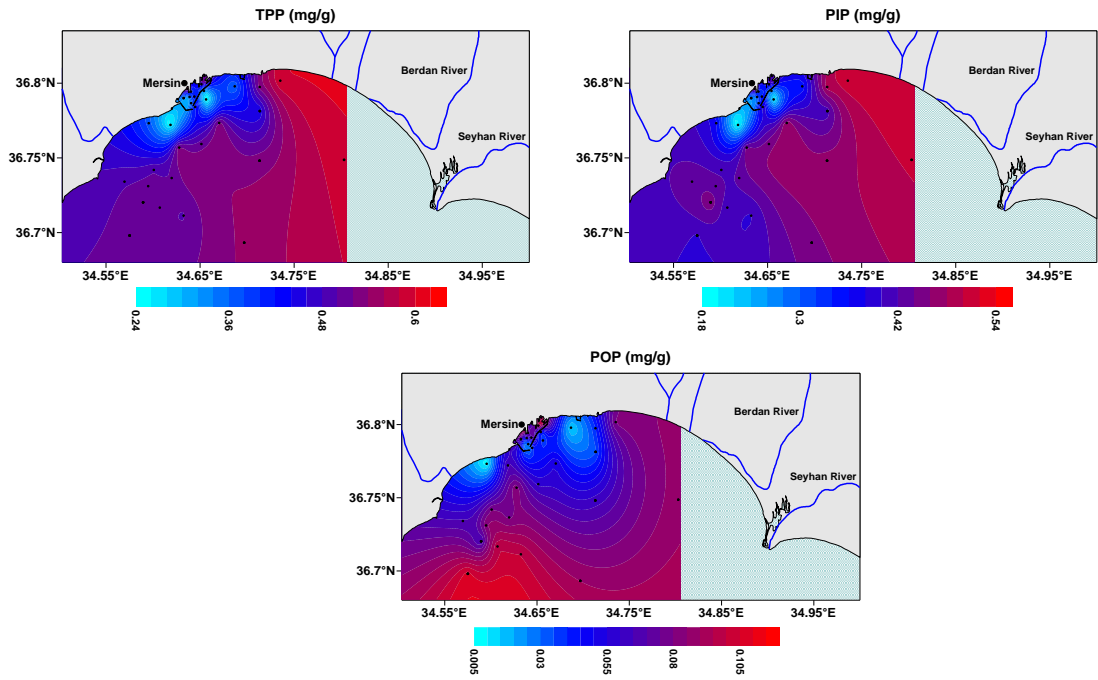


Figure 3.26. Distributions of TPP (mg/g), PIP (mg/g) and POP (mg/g) concentrations of surface sediments in the study area of Mersin Bay in April 2014.

In February 2015, spatial variations of TPP and PIP concentrations in surface sediments were not well pronounced in the study area (Figure 3.27). TPP concentrations varied locally between 0.37 and 0.56 mg/g with the maximum value within the Mersin Harbor. PIP concentrations ranged between 0.24-0.43 mg/g; reaching maximum levels in the coastal site receiving large amounts of inorganic particles by Berdan and Seyhan River inflow. In the studied area, POP contents of surface sediments were relatively low, varying merely from 0.07 mg/g in the PIP-rich coastal sediments between Mersin harbor and Berdan Rivers to 0.14 mg/g in the central bay muddy sediments with higher POC concentrations. However, the maximum POP value was determined in polluted Mersin Harbor sediments receiving organic pollutants from shipping activities in the harbor and possibly discharges of untreated organic-rich wastewater (Fig. 3.27).

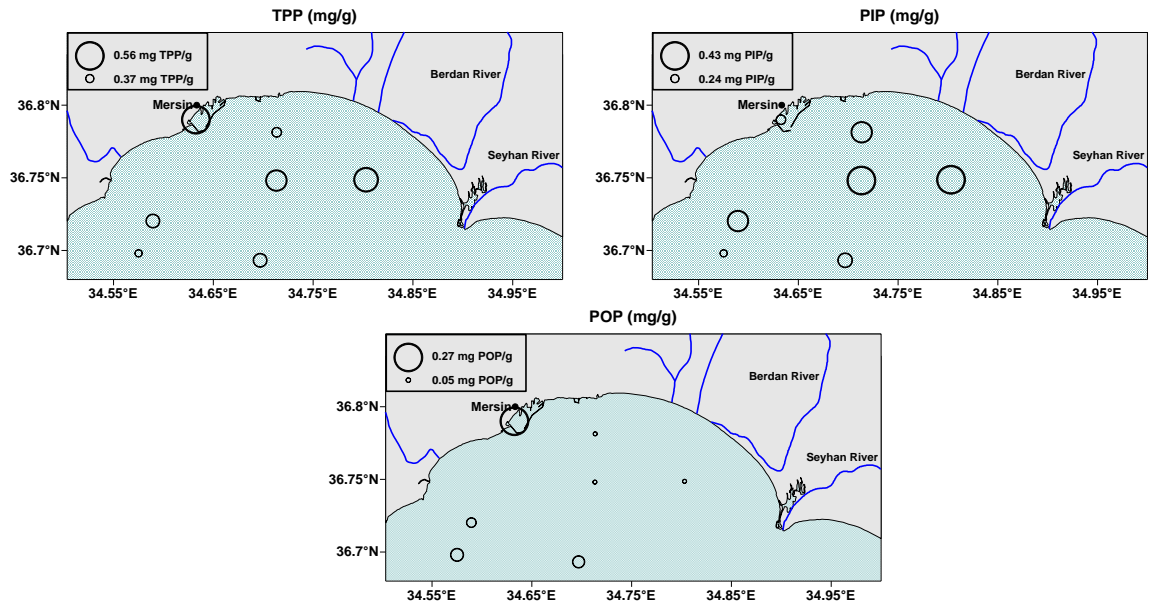


Figure 3.27. Distributions of TPP (mg/g), PIP (mg/g) and POP (mg/g) concentrations of surface sediments in the study area of Mersin Bay in February 2015.

3.6. Grain-Size Distributions in Surface Sediments of the Study Area

Grain-size analyses of the sediment samples were also performed to determine regional distribution of sedimentary texture within the bay and to examine correlations between the geochemical properties of surface sediments at the visited locations of Mersin Bay. The grain-size composition analyses and the geochemical data in surface sediments of the bay are compiled in Table 3.2; the grain-size data clearly show that in spring, the near-shore surface sediments were mainly composed of sandy + gravel (large size) materials with 33-97% levels, reaching the peak in sample from the point near the Mersin Harbor entrance, influenced directly solid materials carried by fresh water inflows and removal (suspension) of small size materials from sediment phase by waves especially in winter-spring period. However, small-size (silt + clay) materials are carried by large rivers to the bay reach as far as the bay offshore zone and dominate the composition of the surface sediments of the central bay (>20 m) with 54-72% of small particle (<63 μm) as illustrated in Figure 3.28.

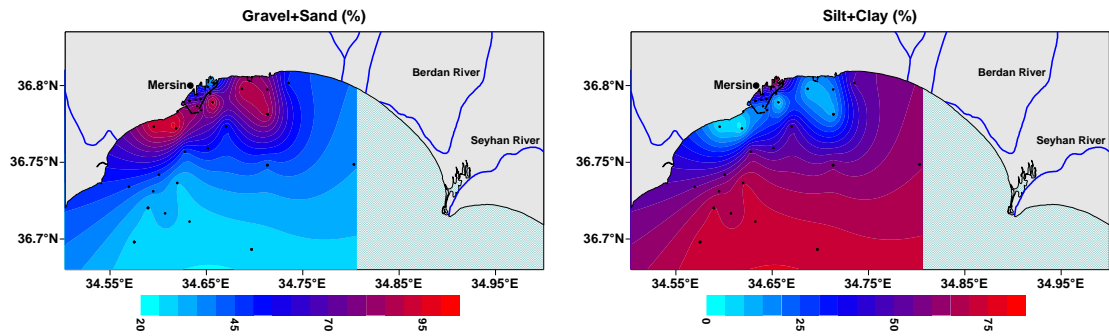


Figure 3.28. Grain-size distributions of surface sediments in the study area of Mersin Bay in April 2014.

In February 2015, coarse-grained particles were also dominated in the coastal surface sediments of the bay, varying between 32-87% and declined to 13% in the central bay surface sediments having over 70% muddy materials carried by regional rivers (Figure 3.29).

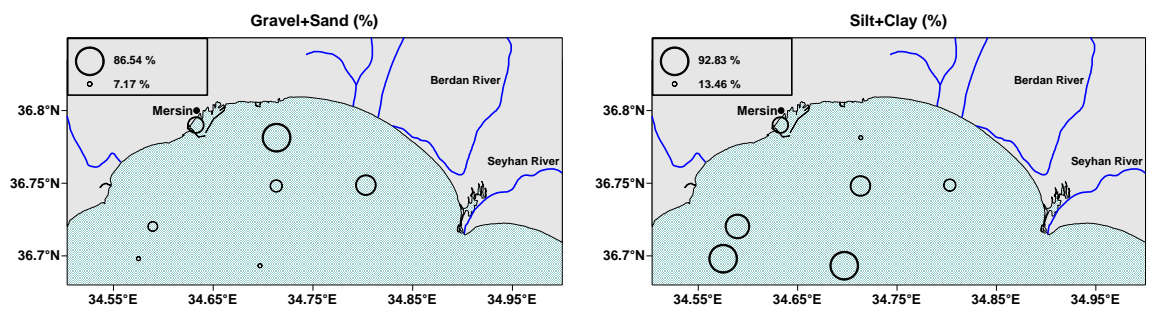


Figure 3.29. Grain-size distributions of surface sediments in the study area of Mersin Bay in February 2015.

Table 3.2. Grain-size results and TC, TOC, TN, TPP, PIP and POP concentrations and their molar ratios in surface sediments in April 2014 and February 2015

APRIL 2014																	
Station	TC (mg/g)	TC (mmol/g)	TOC (mg/g)	TOC (mmol/g)	TN (mg/g)	TN (mmol/g)	TC/TN (molar)	TOC/TN (molar)	TPP (mg/g)	TPP (mmol/g)	PIP (mg/g)	PIP (mmol/g)	POP (mg/g)	POP (µmol/g)	TN/POP (molar)	Silt+Clay	Gravel+Sand
1	57.6	4.80	23.4	1.95	2.39	0.17	28.2	11.4	0.63	0.020	0.52	0.017	0.11	3.39	50.2	60.2	39.8
2	46.7	3.89	5.2	0.43	0.57	0.04	95.3	10.6	0.39	0.012	0.34	0.011	0.05	1.59	25.7	53.9	46.1
3	48.2	4.01	14.3	1.19	1.39	0.10	40.4	11.9	0.50	0.016	0.41	0.013	0.09	2.78	35.8	66.4	33.6
4	51.5	4.29	8.8	0.73	0.83	0.05	82.8	14.1	0.36	0.012	0.30	0.010	0.06	2.09	21.5	29.8	70.2
5	45.2	3.77	10.7	0.89	1.22	0.09	43.1	10.2	0.52	0.017	0.41	0.013	0.10	3.32	26.3	62.3	37.7
6	41.2	3.43	12.1	1.01	1.29	0.09	37.2	10.9	0.52	0.017	0.42	0.014	0.10	3.30	27.9	67.0	33.0
7	51.3	4.27	4.1	0.34	0.36	0.03	164.7	13.2	0.33	0.011	0.26	0.008	0.07	2.31	11.2	31.9	68.1
8	54.3	4.52	4.4	0.37	0.40	0.03	157.9	12.9	0.30	0.010	0.26	0.008	0.04	1.18	24.4	39.2	60.8
9	48.8	4.07	7.7	0.64	0.83	0.06	68.9	10.8	0.48	0.015	0.39	0.012	0.09	2.91	20.3	38.1	61.9
10	74.4	6.19	3.3	0.28	0.27	0.02	316.2	14.1	0.31	0.010	0.30	0.010	0.01	0.33	60.1	8.9	91.1
11	46.9	3.91	6.9	0.58	0.60	0.04	91.8	13.6	0.46	0.015	0.42	0.014	0.04	1.29	28.5	28.2	71.8
12	66.4	5.53	3.9	0.32	0.41	0.03	190.0	11.0	0.29	0.009	0.26	0.008	0.03	0.96	19.2	20.8	79.3
13	73.8	6.15	7.1	0.59	0.49	0.04	141.6	13.6	0.22	0.007	0.18	0.006	0.04	1.17	18.3	3.2	96.8
14	49.6	4.13	2.1	0.17	0.24	0.02	239.9	10.1	0.36	0.012	0.35	0.011	0.01	0.43	40.0	10.4	89.6
15	45.9	3.82	3.3	0.28	0.31	0.02	170.4	12.3	0.53	0.017	0.49	0.016	0.04	1.27	17.7	18.2	81.8
16	50.9	4.24	7.0	0.58	0.74	0.05	79.8	10.9	0.60	0.019	0.52	0.017	0.08	2.62	20.2	51.2	48.8
17	46.4	3.87	2.3	0.20	0.20	0.01	272.8	13.8	0.44	0.014	0.41	0.013	0.03	1.09	13.1	12.4	87.6
18	45.5	3.78	5.5	0.45	0.55	0.04	96.2	11.5	0.53	0.017	0.48	0.015	0.06	1.79	22.0	50.8	49.2
19	48.2	4.01	5.9	0.49	0.53	0.04	106.1	12.9	0.51	0.016	0.45	0.014	0.06	1.89	20.1	46.5	53.5
20	44.5	3.70	7.7	0.64	0.72	0.05	72.3	12.5	0.53	0.017	0.45	0.014	0.08	2.70	19.0	55.6	44.4
21	112.5	9.36	2.1	0.18	0.22	0.02	592.4	11.2	0.24	0.008	0.17	0.006	0.07	2.13	7.4	2.6	97.4
22	47.5	3.95	2.0	0.17	0.19	0.01	291.3	12.3	0.37	0.012	0.37	0.012	0.01	0.16	82.9	5.1	94.9
23	42.6	3.55	6.5	0.54	0.62	0.04	80.0	12.2	0.53	0.017	0.47	0.015	0.06	2.01	22.1	58.9	41.1
24	42.6	3.55	7.5	0.63	0.80	0.06	62.3	11.0	0.50	0.016	0.42	0.013	0.08	2.57	22.1	53.7	46.3
25	45.8	3.82	7.5	0.63	0.64	0.05	82.9	13.6	0.50	0.016	0.43	0.014	0.07	2.13	21.6	54.3	45.7
26	47.3	3.94	6.4	0.53	0.70	0.05	79.3	10.7	0.51	0.016	0.42	0.014	0.08	2.73	18.2	63.8	36.2
27	40.2	3.34	7.4	0.62	0.69	0.05	67.9	12.6	0.50	0.016	0.42	0.014	0.08	2.52	19.6	70.2	29.8
28	47.7	3.97	7.2	0.60	0.67	0.05	82.7	12.4	0.52	0.017	0.46	0.015	0.06	2.04	23.6	70.6	29.4
29	40.7	3.39	7.2	0.60	0.81	0.06	58.3	10.3	0.51	0.016	0.41	0.013	0.10	3.20	18.2	65.9	34.1
30	38.5	3.21	7.5	0.62	0.82	0.06	54.7	10.6	0.50	0.016	0.40	0.013	0.10	3.22	18.2	70.9	29.1
31	40.6	3.38	7.0	0.58	0.79	0.06	59.8	10.3	0.51	0.016	0.40	0.013	0.11	3.47	16.3	71.8	28.2
FEBRUARY 2015																	
Station	TC (mg/g)	TC (mmol/g)	TOC (mg/g)	TOC (mmol/g)	TN (mg/g)	TN (mmol/g)	TC/TN (molar)	TOC/TN (molar)	TPP (mg/g)	TPP (mmol/g)	PIP (mg/g)	PIP (mmol/g)	POP (mg/g)	POP (µmol/g)	TN/POP (molar)	Silt+Clay	Gravel+Sand
7	49.0	4.08	13.6	1.14	1.6	0.11	36.5	10.2	0.56	0.018	0.29	0.009	0.27	8.84	12.7	55.3	44.7
17	43.7	3.64	1.7	0.14	0.3	0.02	172.0	6.6	0.41	0.013	0.36	0.012	0.05	1.62	13.1	13.5	86.5
23	42.8	3.56	6.4	0.53	1.0	0.07	48.7	7.2	0.49	0.016	0.41	0.013	0.08	2.63	27.8	67.6	32.4
28	40.7	3.39	6.8	0.57	0.9	0.06	53.0	8.8	0.48	0.015	0.37	0.012	0.11	3.55	18.0	80.0	20.0
31	39.6	3.30	7.9	0.66	1.0	0.07	47.7	9.6	0.37	0.012	0.24	0.008	0.13	4.19	16.5	92.8	7.2
32	44.2	3.68	9.1	0.76	1.3	0.09	40.5	8.4	0.47	0.015	0.31	0.010	0.17	5.34	17.0	88.2	11.8
33	34.1	2.84	3.0	0.25	0.5	0.04	75.6	6.6	0.51	0.016	0.43	0.014	0.08	2.62	14.4	42.7	57.3

CHAPTER 4

DISCUSSION

Particulate organic matter (POM) in the seawater is composed of living organisms and detrital materials of different sizes, undergoing transformation in the upper layer (Giani *et al.*, 2003); only a small fraction of POM reaches the sediment phase in deep seas (Bernier, 1982). However, in the wide shelf basins such as the Cilician basin of NE Mediterranean fed by nutrient-laden river inflows, more productive coastal waters are rich in bulk POM (Doğan-Sağlamtimur, 2007; Erdoğan, 2014). POM accumulated on surface sediments is degraded (oxidized) by aerobic zoo-benthos and microbial activities; then, only a small fraction of POM is buried into the seafloor (Bernier, 1982). Studies on the geochemical composition of marine sediments provide valuable information about grain-size distributions, influences of enhanced POM fluxes on the POM content and composition of buried sediments on the shelf and further understanding of the carbon, nitrogen and phosphorus cycles in the marine environment (Bartholini *et al.*, 2008). Moreover, measurements of human-induced organic and metal pollutants in sediment phase are widely used to assess impacts of human pressures on coastal ecosystem by developing site-specific pollution indices for the coastal marine environments (Tuğrul *et al.*, 2009; MEU, 2014).

Recent oceanographic data obtained in the Cilician basin of NE Mediterranean indicate marked spatio-temporal variations in the bio-chemical properties of Mersin Bay located on the wide shelf zone of Cilician basin (Tuğrul *et al.*, 2004; Doğan-Sağlamtimur, 2007; Sert, 2010; Kaptan, 2013). The inner and central waters are renewed at different rates by oligotrophic waters of NE Mediterranean open waters. Offshore waters displayed distinct circulation patterns compared to coastal waters and the residence time was calculated as 1.6 years meaning water masses recycling fast and new available nutrients entered through the boundaries (Yumruktepe, 2011). The coastal waters of the bay have been mainly fueled by nutrient-laden wastewater discharges and regional rivers (Kocak *et al.*, 2010). However, chemical data on POM within the shallower part of Mersin Bay are very limited for a detailed examination of the influences of terrestrial (natural and anthropogenic) nutrient inputs on POM distribution in waters and surface sediment phases of the inner and central bay ecosystem.

The sub-marine discharges of partly treated wastewaters of Mersin city and regional rivers (small creeks in wet winter-spring period and Berdan, Seyhan rivers during the year with the enhanced chemical loads in wet winter and spring months) have highly influenced the coastal water ecosystem between the Mersin city and Seyhan River delta. In this study, hydro-chemical data collected from highly/less influenced sites of the bay have been examined to assess impacts of terrestrial nutrient and organic matter inputs on the spatial distributions and elemental composition (C/N/P) of bulk POM in the coastal waters and surface sediments of the Mersin Bay.

4.1. Spatio-Temporal Variations of Hydrographic Properties of the Mersin Bay

The hydrographic properties of the Mersin Bay is highly influenced by seasonally varying inflows leading to remarkable seasonal and spatial variability in salinity and temperature distributions within the bay (Figure 3.1-3.4). In spring period, freshwater inflows reduced the surface water salinity of the coastal zone (depth<20 m); the river effect declined markedly in the central and offshore zones of the bay where the surface salinity exceeded 39.0. However, surface temperature values within the bay displayed an opposite spatial pattern, with warmer waters in the polluted coastal zone. Similar surface salinity and temperature distributions were reported previously in the bay for the spring period (Sert, 2010; Kaptan, 2013; Erdoğan, 2014).

In the shallow coastal zone, the less saline, warmer surface waters were separated from the saltier near-bottom waters by a seasonal density gradient. Apparent differences observed between the salinity values of coastal and central bay near-bottom water values indicate that renewal rate of coastal bottom waters by the saltier central bay waters is still not sufficient to compensate the dilution by vertical mixing that weakens in the spring period.

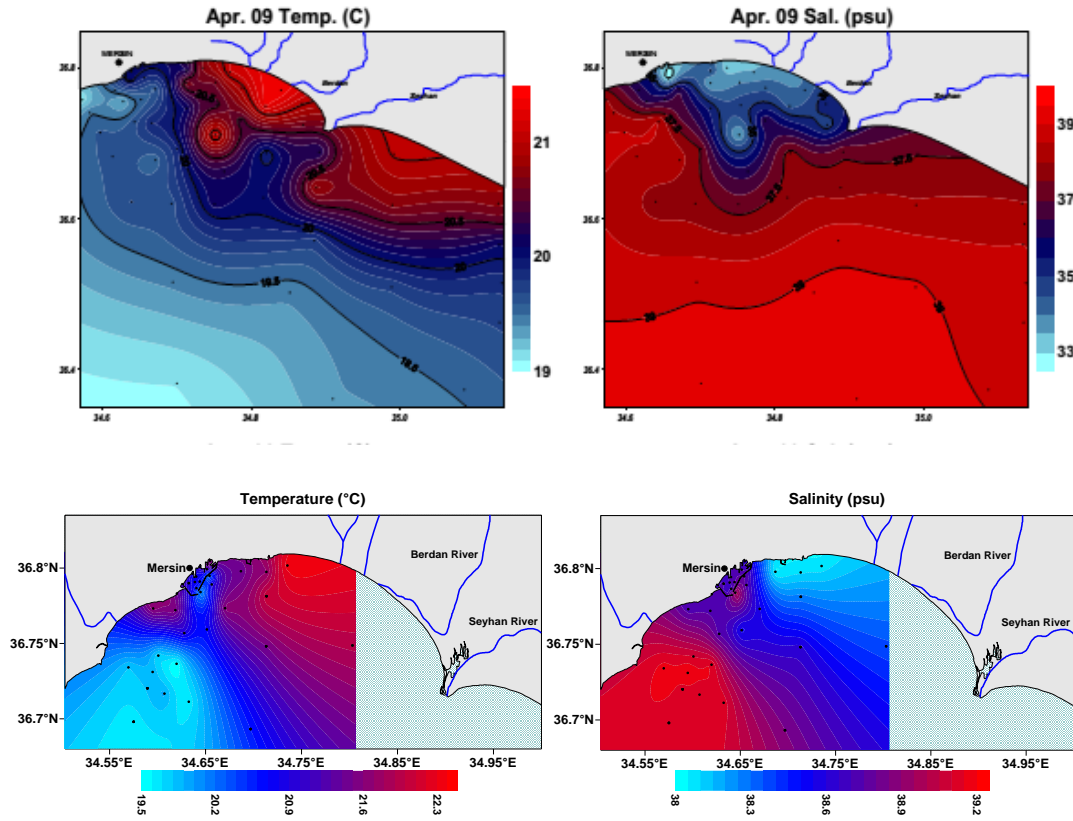


Figure 4.1. Surface distributions of temperature ($^{\circ}\text{C}$), salinity (psu) and density ($\sigma\text{-t}$) in Mersin bay in April 2009 (Sert, 2010) and 2014 (this study).

In winter 2015, spatial variations of salinity and density displayed similar patterns to those observed in April 2014. On the contrary to surface temperature distribution in spring period (Figure 3.1), surface temperature values were higher in surface waters of the less contaminated sites of the bay in winter period (Figure 3.3).

Effects of river discharges and winter cooling on the bay ecosystem have been discussed in previous studies in detail (Sert, 2010; Erdoğan, 2014). Similar spatial and seasonal features have been recorded in the studied area of the bay. In February 2015, representing winter period, hydrographic properties of the bay water differ from the spring features; surface water temperature decreased by about $13\text{ }^{\circ}\text{C}$ from summer to winter period throughout the bay (Sert, 2010). However, in winter, near-surface temperature values displayed local changes from $14.5\text{ }^{\circ}\text{C}$ in the less saline coastal waters to $17.6\text{ }^{\circ}\text{C}$ in the central bay (see Figure 3.3). Similar spatial changes were observed in surface salinity values of the bay due to large fresh water inputs to the eastern part of the bay. Briefly, the increased river discharges influences the coastal and central parts of the bay, depending on rates of vertical mixing processes

and currents in the region. These factors expectedly dominate the distributions of biochemical parameters fueled by terrestrial inputs (rivers, surface runoff, wastewater discharges) to the bay waters as briefly discussed below.

4.2. Spatio-Temporal Variations of Eutrophication Related BioChemical Parameters

4.2.1. Dissolved Inorganic Nutrients

Although eastern Mediterranean is one of the world's oligotrophic seas due to limited nutrient inputs to its surface waters (Krom *et al.*, 1991; Krom *et al.*, 1993; Yılmaz and Tugrul, 1998), its coastal ecosystem is highly fueled by nutrient inputs from land-based sources, mainly by river inputs and wastewater discharges (Krom *et al.*, 1991; Doğan-Sağlamtimur, 2007; Erdoğan, 2014). Coastal waters of the Mersin Bay located on the wide shelf zone of Cilician basin have higher nutrient concentrations compared to the central bay waters. The peak values of nutrients were recorded in the near-shore waters, highly influenced by both river inputs and wastewater discharges. The largest concentration gradients were observed in DIN from near-shore zone to the central bay due to DIN-rich discharges of rivers and domestic wastewaters. In April, maximum values of NO_3 , NH_4 were determined as 67 and 58 μM , respectively, whilst the PO_4 was nearly 0.34 μM in the hot points of the shallow coastal zone between Mersin Harbor and Berdan River delta. The background values of PO_4 were observed in the salty central bay waters of the visited area as 0.02-0.06 μM .

In February 2015, expectedly, similar spatial distributions were observed in the visited locations of the eastern bay influenced by river inflows and polluted by partially treated wastewater discharges of Mersin city, where PO_4 , NO_3 and NH_4 concentrations were recorded as 0.15, 13.68 and 2.62 μM , respectively. Higher concentrations of ammonia were recorded at limited hot points within the Mersin Harbor and near-shore waters receiving wastewater discharges as emphasized in recent studies (Sert, 2010; MEU, 2014).

Spatial variations of PO_4 and TP were less pronounced as compared to the surface nitrate distribution in the study area (Figure 4.2), due to low concentrations of P compounds in external sources. Phosphorus concentrations in winter period enhanced by 5-10 fold in the coastal surface waters due to river waters. Surface PO_4

concentrations varied between 0.03-0.15 μM in the bay. Figure 4.2 demonstrate that seasonal variations appeared to be very low in the surface water PO_4 concentrations of the central basin (depth>20 m). In recent studies, similar PO_4 concentrations were reported ranging between 0.02-0.30 μM with lower concentrations observed in offshore surface waters (Kaptan, 2013).

TP concentrations also displayed similar spatio-temporal variations in the bay; with higher values in the coastal surface waters ranging from 0.20 to 0.74 μM in spring period and the coastal water values in winter decreased slightly to 0.50 μM levels due to intensive mixing in water column.

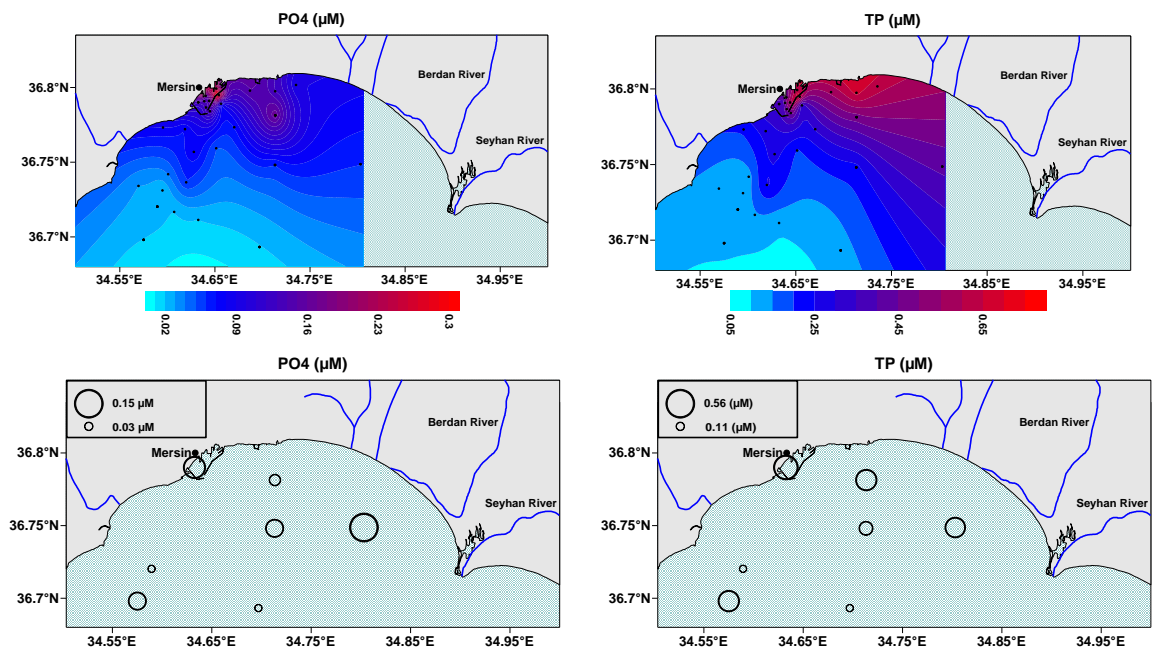


Figure 4.2. Surface distributions of PO_4 (μM) and TP (μM) concentrations in the study area of Mersin Bay in April 2014 (upper) and February 2015 (lower).

Spatial variations of NO_3 , NH_4 and DIN in the bay were well pronounced in both spring and winter periods (Figure 3.10 and 12); in April 2014, the nitrate concentrations enhanced from 0.05-2.88 μM to 5-10 μM levels in the river-fed coastal waters. The higher NH_4 values were recorded in the limited hot points and within the Mersin Harbor polluted by wastewater discharges. In February 2015, when fresh water inputs at higher rates in the regional rivers and wind-induced currents are intensive in the region, the river discharges influenced larger areas within the bay (see Figure 3.12); DIN concentrations increased to levels of 5.73-

16.30 μM in the river-fed coastal waters and then decreased to levels of 1.1-2.0 μM in the less influenced central bay waters.

Spatial variability of Si concentration was apparent from coastal to central bay waters of the bay due to Si-laden River water inflows. In April, the coastal Si values ranged between 2.0-6.7 μM and decreased to levels of 1.3-2.0 μM in deeper part of the central bay waters. In winter, however, high-Si waters occupied greater area in the bay due to increased Si inputs by rivers and transport of Si-enriched water by intensive winter circulations within the bay. In the river-fed coastal surface waters, the Si exceeded 6.5 μM in spring and 11.0 μM in winter. Not unexpectedly, temporal and spatial variation of Si and NO_3 concentrations displayed similar patterns within bay as reported previously (Doğan-Sağlamtimur, 2007; Sert, 2010).

Surface water distributions of dissolved inorganic nutrients in the coastal zone of the bay displayed weak correlation within the salinity gradient zone in spring (Figure 4.3), due to fast uptake of nutrients by photosynthetic organism. However, the correlations are strong under winter conditions when the dilution rate exceeded the uptake rate of nutrients (Figure 4.4). In spring, the concentrations displayed partly linear decreasing trend in the coastal waters of 38-38.8 salinity values and then reached the open sea properties in the central basin waters with salinity values of 39.1-39.2 (Figure 4.3) as reported in recent studies (Sert, 2010; Kaptan, 2013; Erdoğan, 2014). In winter, the linear decrease became much more pronounced in the salinity gradient zone though the data were obtained in limited area of the bay (Figure 4.4). When salinity values reached open sea properties, concentrations of dissolved inorganic nutrients decreased markedly to their central bay values due to dilution of nutrient-laden river inflows in the coastal zone of the bay as clearly shown in previous studies (Figure 4.5).

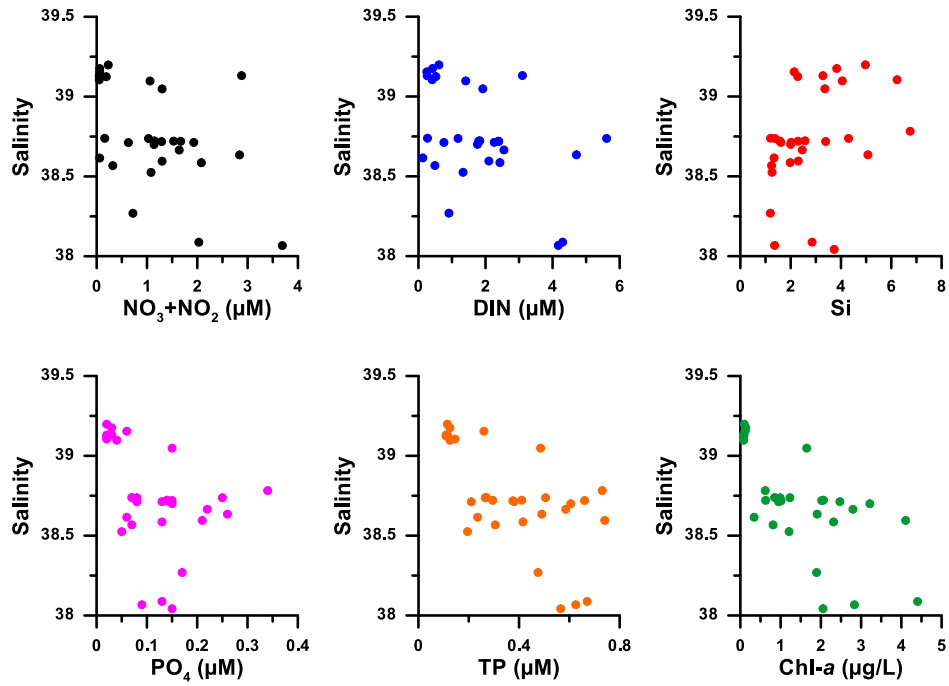


Figure 4.3. Dissolved inorganic nutrients and Chl-*a* vs. salinity plot of the data measured from the study area of Mersin Bay in April 2014.

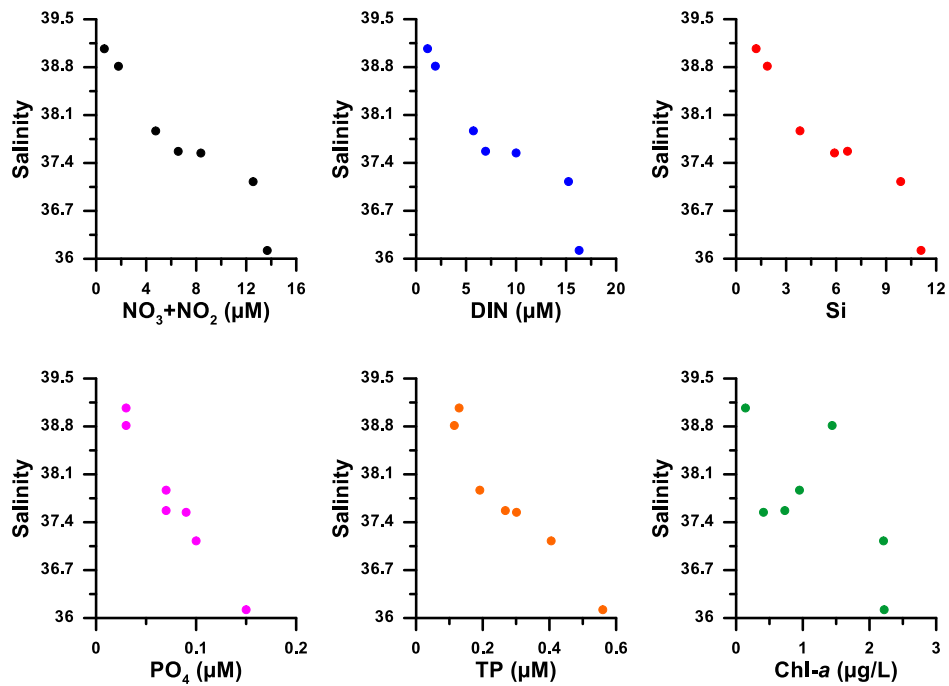


Figure 4.4. Dissolved inorganic nutrients and Chl-*a* vs. salinity plot of the data measured from the study area of Mersin Bay in February 2015.

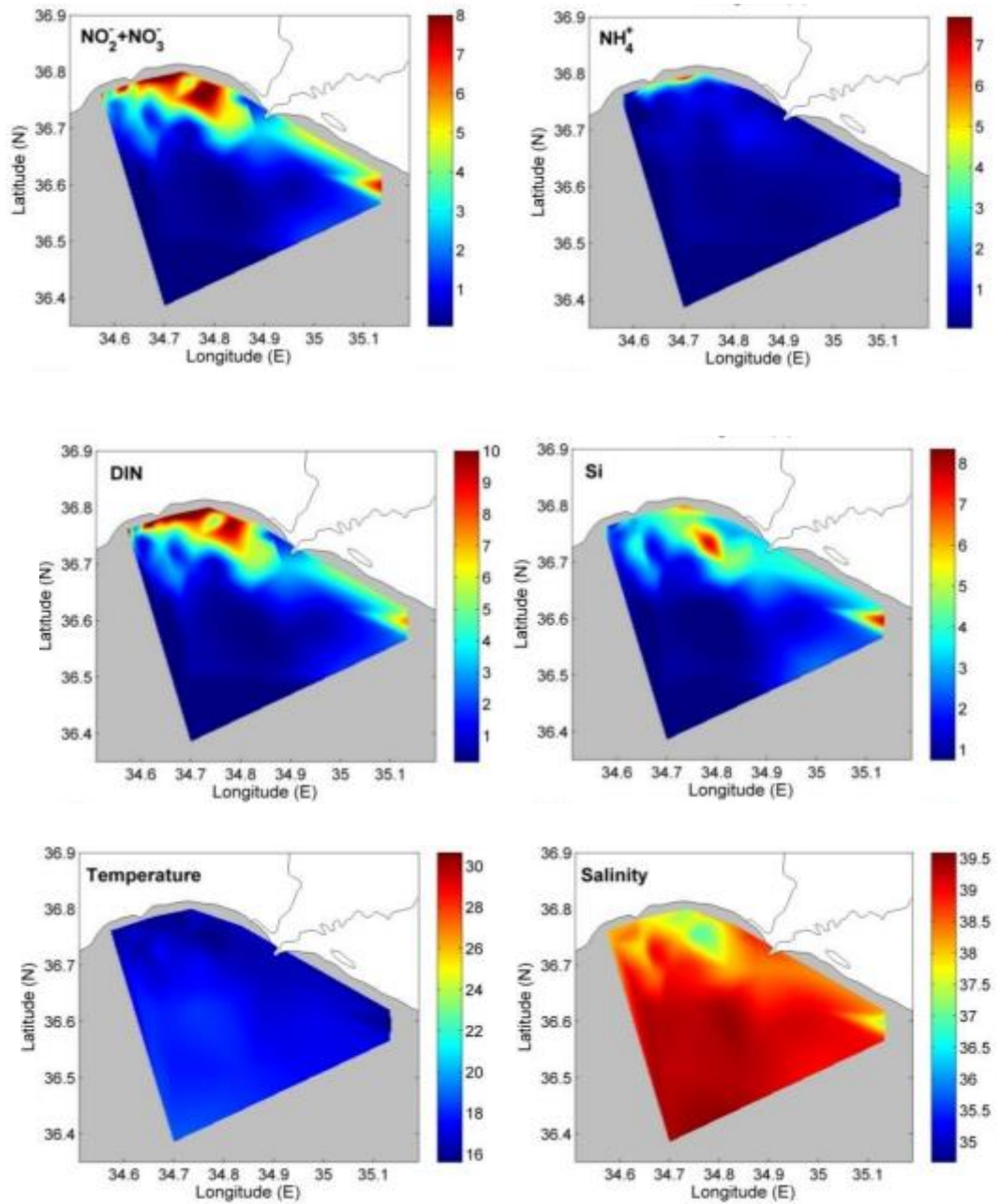


Figure 4.5. Surface distributions of dissolved inorganic nutrients (μM), Chl-*a* ($\mu\text{g/L}$) and DO (mg/L) concentrations throughout the study area in winter period (Kaptan, 2013).

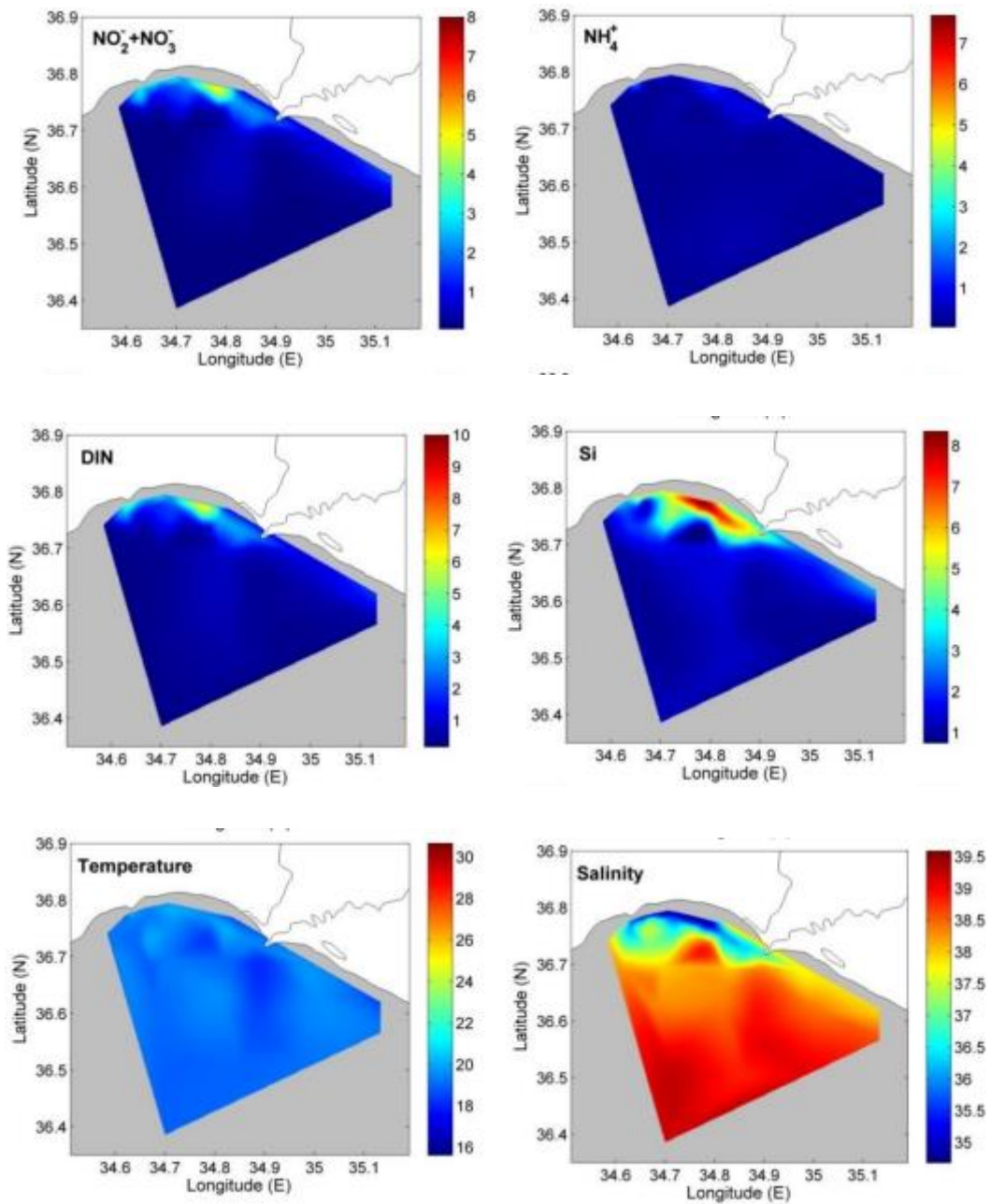


Figure 4.6. Surface distributions of dissolved inorganic nutrients (μM), Chl-*a* ($\mu\text{g/L}$) and DO (mg/L) concentrations throughout the study area in spring period (Kaptan, 2013).

4.2.2. Chlorophyll-*a* and Dissolved Oxygen (DO)

Phytoplankton biomass (in terms of Chl-*a*) concentrations enhanced in the eutrophic inner bay waters fed by nutrient-rich river inflows and wastewater discharges (Figure 3.15 and 3.17), showing similar spatial patterns reported in recent studies (Sert, 2010; Kaptan, 2013; Erdoğan, 2014). However, during the dry summer-autumn

period when nutrient inputs by the regional rivers decline, algal biomass-enriched waters are limited to the near-shore zone with a total depth of less than >15-20 m, depending on surface salinity distributions (salinity gradient zone) in the study area. In highly productive coastal zone of the bay, the enhanced turbidity and organic matter in surface waters deteriorate water quality and thus reduce water transparency drastically. These changes in water quality highly limit solar light penetration to greater depths, leading to have very low SDD values (2-4 m) and limit algal production the upper 5-10 m in the near-shore waters of the bay; the SDD declines drastically to 1-2 m within Mersin Harbor and hot points (wastewater discharge zone and river-fed zone) in the near-shore.

Spatial variations of Chl-*a* concentrations decreased by 3 to 15 fold from river-fed coastal waters to the less polluted sites of the bay (see Figure 3.15 and 17). The spatio-temporal variations of algal biomass, in terms of surface Chl-*a* concentrations, were expectedly well pronounced in the bay due to apparent changes in volume fluxes of nutrient-replete rivers inflows feeding the bay ecosystem.

In spring 2014 and winter 2015, the coastal Chl-*a* values ranged between 0.62-4.40, and 0.41-2.22 µg/L, respectively with higher Chl-*a* values in spring. In the central bay, surface Chl-*a* values changed locally between 0.08-0.34 µg/L in spring and 0.14 to 1.44 µg/L in winter. Surface Chl-*a* distributions in Figure 3.15 and 3.17 show that nutrient-inputs by the regional rivers markedly influenced the inner bay ecosystem and enhanced algal biomass in the coastal ecosystem (depth < 20 m). Salinity-dependent Chl-*a* changes in surface waters of the bay in Figure 4.3-4 indicate that the natural offshore values of Chl-*a* were reached in the water body with $S > 39$, where the total depth > 20 m in the central bay.

Spatial and temporal variations of DO in the surface waters are dominated by primary production, salinity, temperature and wind-induced vertical mixing of surface water layer over the sea. Therefore, enhancement of algal biomass, cooling of water and lower salinity lead to increase DO in the euphotic zone. However, increased wind speed and vertical mixing remove excess oxygen from the near-surface waters. When these factors are considered in the bay, DO concentrations are expected to increase from spring (higher temperature) to winter (lower temperature)

and decrease from coastal (more productive) to central bay waters (lower algal biomass) of the bay as also observed in previous studies in the bay (Figures 4.7-4.8).

Surface DO concentrations in productive coastal waters were measured in the range of 7.1-8.9 mg/L in spring, increasing slightly to levels of 7.6-8.8 mg/L in February 2015. Similar temporal variations were also observed in the central bay (less productive and saltier) waters of the bay, varying between 7.65-8.0 mg/L in spring and 7.6-8.4 mg/L in winter.

Slowly sinking biodegradable organic matter (bulk POM) concentrations (determined in terms of BOD₅) displayed similar pattern to Chl-*a* distributions; higher concentrations were observed more productive waters in spring. BOD₅ concentrations in coastal surface waters varied between 0.47 and 2.67 mg/L in April, declining to 0.75-0.96 mg/L levels in February. In conclusion, distributions of nutrients, surface Chl-*a* and BOD₅ displayed similar spatial distributions due to biomass-dominated bulk POM pool in the marine environments. Their concentrations enhanced markedly in highly productive coastal bay ecosystem fed by large amount of nutrients carried by rivers and wastewater discharges as observed in previous studies conducted in the bay (Sert 2010; Kaptan, 2013; Erdoğan, 2014).

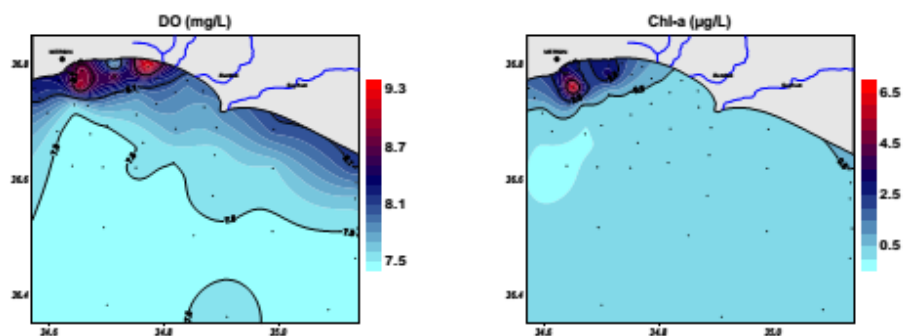


Figure 4.7. Surface distributions of Chl-*a* and DO concentrations in Mersin bay in February 2009 (Sert, 2010).

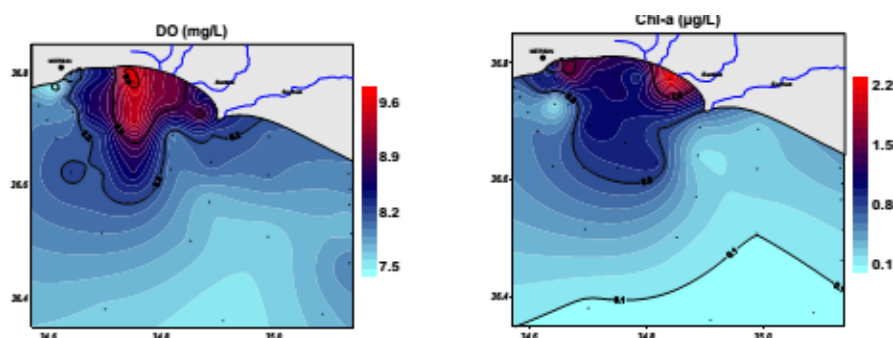


Figure 4.8. Surface distributions of chl-*a* and DO concentrations in Mersin bay in April 2010 (Sert, 2010).

4.2.3. Particulate Organic Matter (POM)

Spatial distributions of bulk POM (POC, PON, TPP) concentrations and its elemental composition (C/N/P ratio) in the marine environment are controlled by various interacting factors (Tselepidis *et al.*, 2000; Ediger *et al.*, 2005). The concentrations of slowly sinking POM in the euphotic zone of the bay are principally determined by nutrient inputs from external sources. Seasonally varying inputs of nutrients from internal source (sediment phase) in the shallow zone of the bay are also expected to contribute bulk POM pool during the year with increasing rates in winter by intensive vertical mixing. Since the upper layer of the NE Mediterranean is poor in nutrients (Krom *et al.*, 1991; Krom *et al.*, 1993; Yılmaz and Tuğrul, 1998), internal nutrient inputs by lateral intrusion of water masses from the open sea have limited contribution to POM pool; the inputs from the cool near-bottom waters increase by vertical mixing of the upper layer water column during winter period.

Close examination of bulk POM data from the studied area of the bay clearly show the dominating role of terrestrial nutrient inputs on the POM pool of Mersin Bay (Figures 3.19-22). In spring, POM concentrations enhanced about 6-fold from the central bay (POC: 3.4-10.2 μM) to the eutrophic inner bay waters (POC: 14.5-107 μM) fueled mainly by Seyhan and Berdan river inflows and domestic wastewater discharges to the near-shore zone between Mersin Harbor and Berdan River delta. However, the maximum POM values in the surface waters, exceeding 100 μM , were recorded in Mersin Harbor waters having limited exchanges with the coastal waters of the bay.

In winter, surface POC concentrations varied between 16.9 and 42.3 μM in the coastal waters and then declined the background levels of 5.7-12.5 μM in the central bay waters.

The spatial distribution of PON in the studied area was very similar to that appeared in POM, with the C/N ratios of 7.1-10.7. The PON values varied locally between 0.56-12.89 μM in April, exhibiting less spatial variability (0.59-5.94 μM) in February. The coastal water concentrations ranged between 2.4-12.9 μM in April, greater than the winter PON values (1.8-5.9 μM). Seasonal changes in the PON values of the central bay waters were less pronounced due to decreasing pressure of river inputs on the POM pool of the central bay ecosystem. The peak values were recorded at St.16 located at the hot points fed by the river inputs (see Figure 3.19). The lowest POM concentration was measured the salty central bay waters ($S > 39$) receiving limited nutrient inputs from land-based sources in spring. In winter, maximum concentrations of POM were recorded at St.33 ($S: 34.8$) influenced directly by Seyhan and Berdan river inflows, whereas the minimum POM concentration was determined at St.32 located in the central bay ($S = 39.1$ and depth: 40 m).

Regional variations of TPP (sum of organic + inorganic-P) concentration measured in the surface waters displayed were much pronounced than those observed in POC and PON. The TPP varied from 0.025 in the central bay to 0.470 μM at hot points of the coastal zone in spring. The highest concentration was recorded at St.16 where the POM reached the peak levels due to river inputs. TPP concentrations varied locally between 0.025 and 0.470 μM in April 2014 and declined to 0.026-0.374 μM levels at the sampling points visited in February 2015. POM and TPP values were always higher in the more productive surface waters as compared the water column concentrations. Minimum TPP concentrations expectedly appeared at the POM-depleted central bay waters ($S > 39.0$). Not unexpectedly, close correlations were determined between spatial distributions of nutrients (pressure parameter), Chl-*a* and POM (state parameters of eutrophication) concentrations within bay; their concentrations enhanced in the less saline near-shore zone waters fed by nutrient inputs from external sources (Figure 4.9).

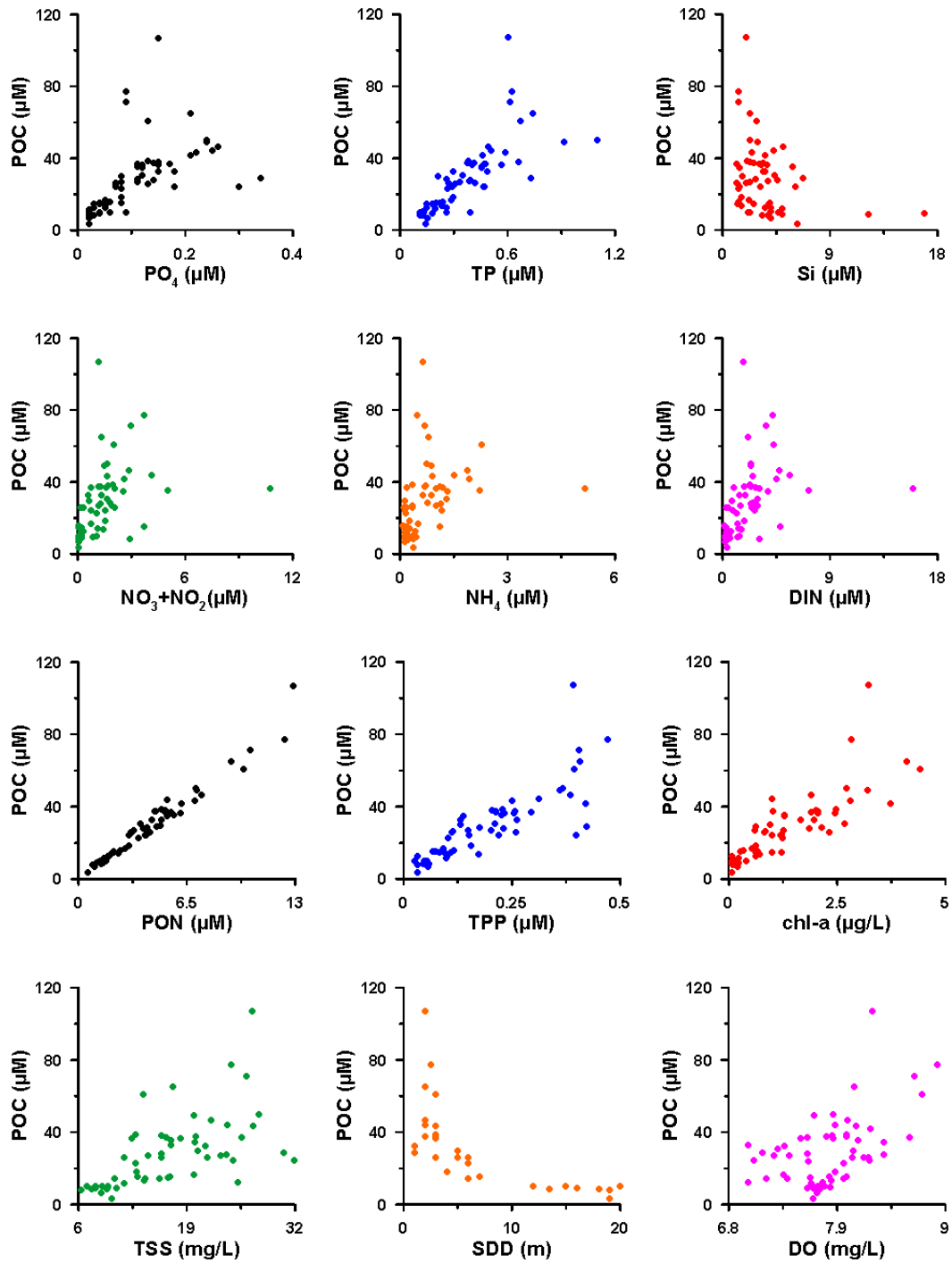


Figure 4.9. Correlations between nutrients (pressure parameter), Chl-*a* and POM (state parameters of eutrophication) concentrations in the study area of Mersin Bay.

Limited POM data obtained recently in Mersin Bay are compiled in Table 4.1. Seasonal POM data collected by Erdoğan (2014) between 2008-2010 displayed similar spatio-temporal variations within the bay; bulk POC concentrations varied locally between 40 and 50 μM in the shallow coastal waters of the eastern part of the bay and then declined to 2-5 μM levels in the offshore waters of the bay receiving

limited terrestrial inputs of nutrients and organic matter by the regional river inflows. These POC values are consistent with the results of the present study. According to the data of Erdogan (2014), seasonal POC and PON concentrations ranged between 4-40 μM , 0.4-3.9 μM , respectively in the eastern part of the bay. In spring, the coastal POM concentrations increased to levels of 22.6-63.0 μM for POC, 3.37-7.72 μM for PON and 0.2-0.350 μM for TPP, exhibiting 5-10 fold enhancements compared to the offshore values. Erdogan (2014) also observed a close correlation between the POC and Chl-*a* concentration changes, enhancing in the coastal waters with the POC/Chl-*a* ratio of 310 in spring-autumn.

Table 4.1. POM concentrations and elemental compositions (C/N, N/P) in surface waters of the selected stations within the Mersin Bay in April 2014 and February 2015.

April 2014						
Region	Station	POC (μM)	PON (μM)	TPP (μM)	POC/PON	PON/TPP
<i>Coastal Surface Waters</i>	1	46.63	7.36	0.385	6.3	19.1
	2	44.10	5.30	0.312	8.3	17.0
	3	65.09	9.16	0.406	7.1	22.5
	4	37.58	4.58	0.256	8.2	17.9
	5	43.26	7.00	0.249	6.2	28.1
	6	107.03	12.89	0.391	8.3	33.0
	7	38.68	4.97	0.229	7.8	21.7
	8	37.51	4.65	0.214	8.1	21.8
	9	38.15	5.22	0.205	7.3	25.4
	10	26.07	4.29	0.259	6.1	16.6
	11	32.66	4.42	0.262	7.4	16.9
	12	28.78	4.67	0.422	6.2	11.1
	13	18.32	3.04	0.156	6.0	19.5
	14	36.44	6.11	0.254	6.0	24.0
	15	60.84	9.88	0.394	6.2	25.1
	16	77.30	12.37	0.470	6.3	26.3
	17	37.06	5.22	0.214	7.1	24.4
	18	26.00	3.15	0.112	8.3	28.2
	19	14.47	2.36	0.109	6.1	21.7
	20	22.90	3.60	0.103	6.4	35.0
	21	26.12	3.21	0.114	8.1	28.1
	22	29.81	4.89	0.131	6.1	37.2
	23	15.68	2.48	0.115	6.3	21.6
<i>Central Bay Surface Waters</i>	24	10.16	1.36	0.048	7.5	28.4
	25	8.47	1.34	0.058	6.3	23.1
	26	9.00	1.07	0.056	8.4	19.2
	27	10.02	1.63	0.055	6.2	29.6
	28	8.59	1.38	0.045	6.2	30.5
	29	3.44	0.56	0.031	6.1	17.8
	30	8.08	0.85	0.033	9.4	26.2
31	10.08	1.40	0.025	7.2	55.6	
February 2015						
Region	Station	POC (μM)	PON (μM)	TPP (μM)	POC/PON	PON/TPP
<i>Coastal Surface Waters</i>	7	26.27	2.86	0.250	9.2	11.4
	17	16.90	1.82	0.107	9.3	17.0
	23	22.72	2.12	0.078	10.7	27.1
	33	42.27	5.94	0.374	7.1	15.9
<i>Central Bay Surface Waters</i>	28	9.08	0.96	0.046	9.5	20.9
	31	12.47	1.33	0.109	9.4	12.3
	32	5.72	0.59	0.026	9.7	22.4

A similar study has been conducted by Doğan Sağlamtimur (2007) in the western shelf zone of the bay, Cilician basin of NE Mediterranean; the surface POM data in the area of the Lamas River mouth (Erdemli) displayed remarkable spatial and temporal variations (Figure 4.10). For example, the offshore waters were depleted in POM (POC: 2.07-18.07 μM) in dry season, due to limited influences of terrestrial inputs on the regional POM pool. The POC concentrations of the coastal surface waters varied markedly with season, ranging in the range of 1.9-114 μM in the coastal waters fed by Lamas River inflow having small volume (and thus nutrient) fluxes as compared to the nutrient loads of Seyhan and Goksu Rivers (Koçak *et al.*, 2010). Comparison of the POM data from western shelf zone (Figure 4.10) and the present results from the eastern bay waters reveals that surface PON concentrations exhibited similar spatial and temporal variations, ranging between 0.11 and 9.99 μM . Since the offshore waters of the bay display oligotrophic properties (low nutrients, low algal biomass), surface POM concentrations exhibit significant increases from the open sea to the eutrophic/mesotrophic coastal zone of the area; maximum concentrations were observed in near-shore waters in late winter-spring period when river inputs reached the maximum level and highly influenced larger sites of the shelf zone where the surface salinity decreased to 37-38 levels (Doğan-Sağlamtimur, 2007) as observed in the eastern part of bay. Similarly, the concentrations of POM markedly were enhanced in highly productive spring period especially in late March-May period when the terrestrial inputs are at maximum levels and a weak thermal stratification in the surface layer is formed in the near surface waters. This feature prevents dilution of the nutrient-enriched upper layer waters by deeper waters via vertical mixing processes and results in enhancement of bulk POM in the near surface layer throughout the bay. Similar POM concentrations were also obtained in this study, higher concentrations were observed in coastal surface waters. POM concentrations varied regionally and seasonally between 3.4 and 107 μM for POC, 0.56-12.89 μM for PON and 0.025-0.470 μM for TPP in surface waters of the bay.

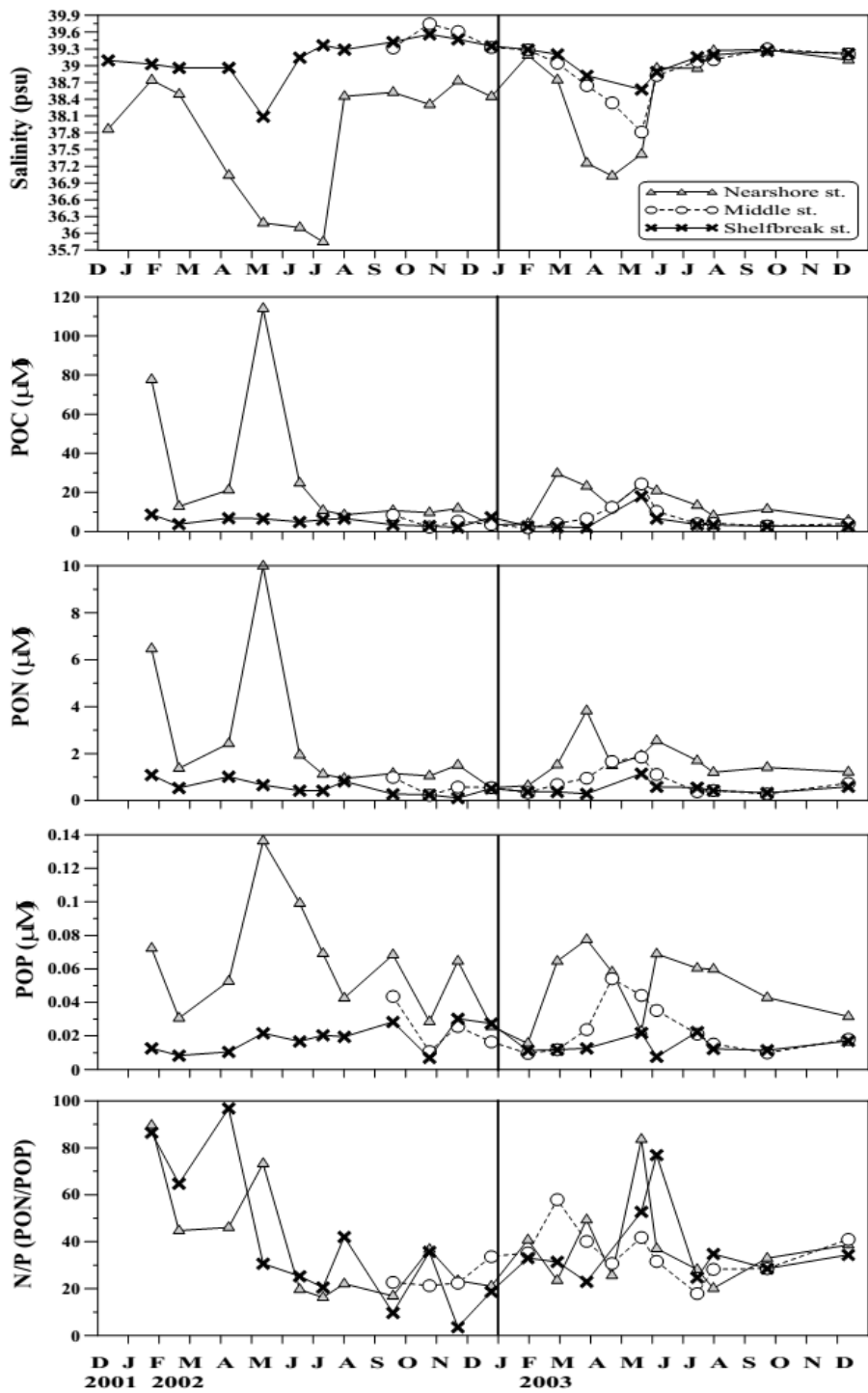


Figure 4.10. Time series distribution of POC, PON, POP and PON/POP in northeastern Mediterranean between 2001-2003 (Doğan-Sağlamtimur, 2007).

4.2.4. Ratios of Dissolved Inorganic Nutrients (N/P) and Molar Ratios (C/N/P) in Bulk POM

For better understanding of elemental composition (C/N/P ratio) of bulk POM in the bay waters influenced by terrestrial inputs, spatial and temporal variations of nitrate/phosphate (N/P) and POC/Chl-*a* ratios in the same environment should be examined in detail. The spatial variation of N/P molar ratios, calculated from NO_x (NO₃+NO₂) and PO₄ data obtained in April 2014 are displayed in Figure 4.12. In order to evaluate regional variations in the study area more precisely, very high N/P ratios, exceeding 100-150 in the nitrate-rich near-shore waters (S<38.5) fed by the wastewater discharges, were not used in the plot of surface N/P distributions; however, these high ratios determined at the hot points are presented in Appendix A. The surface distribution of N/P ratio of nutrients in more saline waters (S>38.5) are displayed in Figure 4.12. The presence of the nitrate-laden coastal waters with higher N/P ratios (>20) during the year strongly suggests P-limited living POM (primary) production via photosynthesis as previously determined in bio-assay study of Tufekci *et al.* (2013). However, the N/P ratio decreased markedly to 1-12 levels in the central bay waters where the river influence remained at minimal levels. It should be noted that the reactive phosphate measured in seawater by colorimetric method (final solution pH≈1) at levels of 0.02-0.05 μM levels may have positive interference from labile organic-P compounds soluble at low pH levels (Doğan-Sağlamtimur and Tugrul, 2004). Therefore, relatively low N/P ratios (<10) estimated for PO₄-depleted central bay waters of the bay may have been underestimated as emphasized previously by Doğan-Sağlamtimur (2007) who measured lower concentrations of dissolved PO₄ ions in seawater by more sensitive co-precipitation (MAGIC method), leading to increases in N/P ratio.

Since the central bay waters were also depleted in ammonia (0.1-0.3 μM range) and nitrate, the DIN/PO₄ ratio displayed similar decreasing patterns towards the central bay, declining below 5, indicating PO₄ depleted and thus potentially P-limited algal production in the central bay waters of the bay as experienced in the eastern Mediterranean ecosystem (Doğan-Sağlamtimur, 2007; Erdoğan, 2014). Higher N/P ratios obtained in the western part of the studied area may be resulted from regional circulations carrying river fed surface waters to this site (see Figure 4.11) for regional current system in the region.

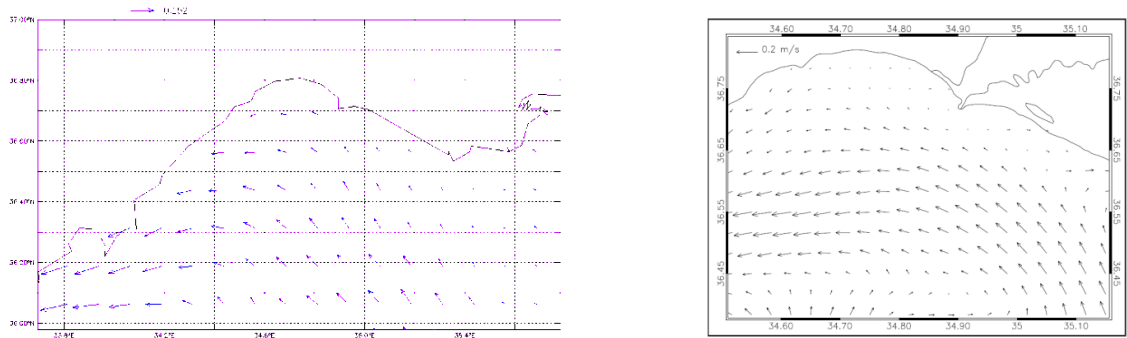


Figure 4.11. Surface current pattern of Mersin Bay in winter 2015 (left) and summer 2009 (right) (TUBITAK-DIPTAR 3rd progress report, 2015).

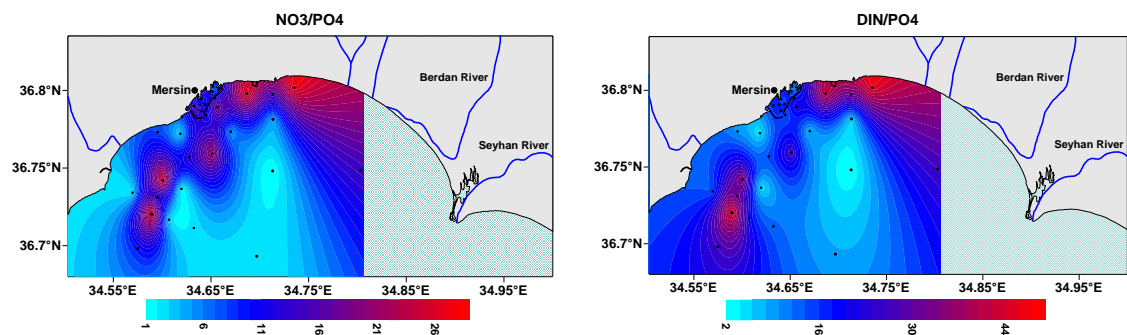


Figure 4.12. Spatial distributions of NO_3/PO_4 and DIN/PO_4 molar ratios in surface waters of the study area in April 2014.

In February, limited number of stations were visited for chemical measurements in the bay and the N/P molar ratios obtained from the nutrient data are depicted in Figure 4.13, exhibiting similar spatial variations to those observed in April 2014. NO_3/PO_4 molar ratios in coastal surface waters varied between 68 and 125 and declined to 21-93 levels in less contaminated sites of the bay. DIN/PO_4 ratios showed similar regional variations, higher values were recorded at hot points especially in city harbor and river-fed zone of the bay.

Due to nitrogen-rich inputs from land-based sources and atmospheric inputs with high N/P molar ratios (Kocak *et al.*, 2010) in the NE Mediterranean region, the N/P molar ratios of nutrients were markedly higher in February than the ratios calculated for the April period due to higher consumption rates of excess nutrients in spring period as compared to winter period.

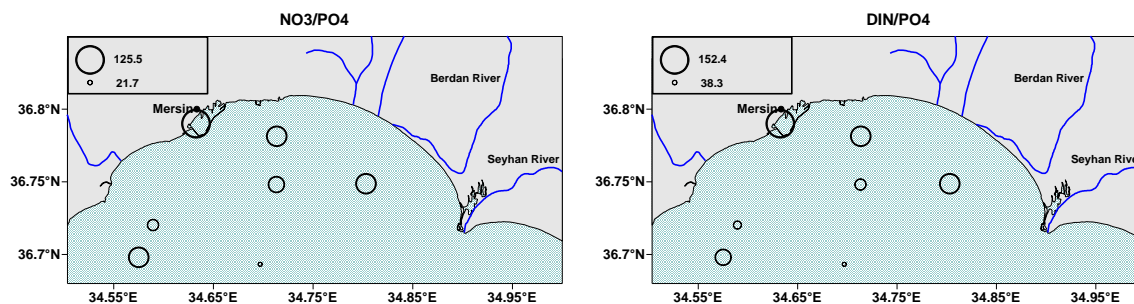


Figure 4.13. Spatial distributions of NO_3/PO_4 and DIN/PO_4 molar ratios in surface waters of the study area in February 2015.

N/P molar ratios calculated from the present nitrate and phosphate data were highly variable ranging between 2 and 370 in coastal waters of the bay (depth < 20 m); the ratios were much greater in the river-influenced sites than the classical Redfield Ratio of 16; however, they are very consistent with the high ratios of the coastal waters given in previous studies (Doğan-Sağlamtimur, 2007; Sert, 2010; Kaptan, 2013; Erdoğan, 2014).

Put simply, since the regional rivers are carrying relatively large amount of DIN to PO_4 (Koçak *et al.*, 2010), markedly high N/P molar ratios of surface waters have been determined consistently in the coastal zone fed by river and domestic water discharges (Tuğrul *et al.*, 2009; Kaptan, 2013; Erdoğan, 2014).

The N/P molar ratio calculated from regression analysis of NO_x vs. PO_4 using the data obtained from river-fed sites during in this study is nearly 17, excluding high PO_4 data in hot points receiving wastewater. The high N/P ratio indicates that nitrate ions remain excess in the river-fed coastal waters of Mersin Bay as reactive phosphate ions have been consumed down to hardly detectable levels ($< 0.03 \mu\text{M}$) implying potentially P-limited algal production in the bay ecosystem (Figure 4.14). However, in the hot points polluted by partly treated domestic wastewaters, phosphorus pollution enhanced TP and PO_4 concentrations, reducing the DIN/PO_4 ratio to 10-20 range suggesting that both of N, P may be limiting factors; their concentrations declined to the threshold levels for new production.

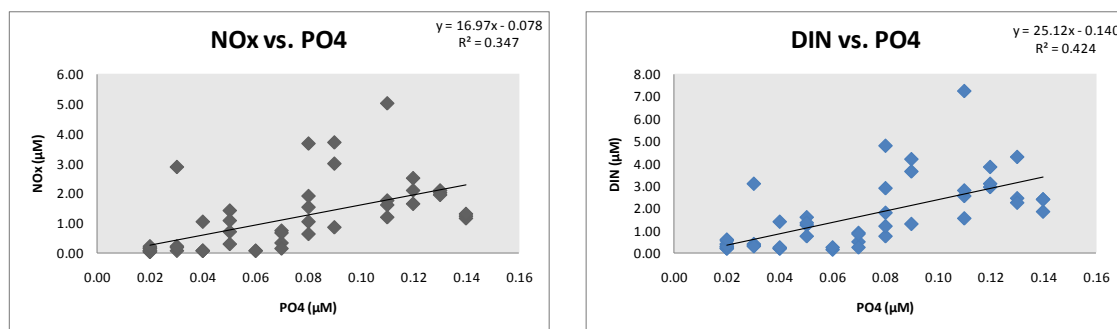


Figure 4.14. NO_x and DIN vs. PO₄ plot of the data measured from the study area of Mersin Bay in the study period.

In conclusion, consistently high N/P ratios determined in the bay waters are the results of excess inputs of DIN (mainly in nitrate form) by river inflows and direct atmospheric precipitations and surface runoff in the region (Koçak *et al.*, 2010).

The observations of high N/P ratios during the year in the P-depleted coastal waters indicate P-limited primary production as recently reported in the bio-assay study of Tufekci *et al.* (2013). In addition to nitrate-laden terrestrial inputs in the NE Mediterranean coastal waters, upwelling of the Levantine deep waters to near-surface layer fuels the upper layer ecosystem with high N/P ratios (26-28) as previously reported in Yılmaz and Tugrul (1998), Krom *et al.* (1991) and Ediger *et al.* (1999). Therefore, in the eastern Mediterranean open sea, primary production has been observed to be limited primarily by phosphorus for most of the year (Thingstad *et al.*, 2005). These findings lead to suggest that production by bio-mediated processes and enrichment of bio-degradable POM in the bay water occur with higher N/P ratios exceeding the classical Redfield ratio.

In April 2014, the N/P molar ratios of dissolved inorganic nutrients data show drastic regional variations in the Mersin bay with markedly high ratios in the coastal surface waters (Figures 4.12-13). However, POC/PON (C/N) and PON/TPP (N/P) molar ratios in bulk POM in the ambient waters show less pronounced spatial changes in the bay (Figure 4.16). The C/N ratios in bulk POM varied locally between 6.0 and 9.5 in the studied site; the higher C/N and C/P ratios were determined in selectively POC-enriched POM due to presumably enrichment of less labile organic matter (more resistant to biomediated oxidation) in the POM pool at the sampling point of the central bay (St. 30). At this location, the surface nitrate was as low as 0.05 µM and thus the Chl-*a* concentration (living biomass indicator) was nearly 0.09 µg/L,

leading to very high POC/Chl-*a* ratio (1134). The inner bay mean value of the POC/PON ratios (nearly 7.0) is slightly greater than the classical Redfield ratio of 6.63 strongly suggesting that no apparent N-limitation exists on POM production in the P-depleted waters of Mersin Bay ecosystem. The present C/N ratios obtained in more productive season are higher than of the ratios of POM collected in less productive summer-autumn period (Erdogan, 2014). A similar study has conducted in NE Mediterranean between 1990-1998 by Çoban-Yıldız *et al.* (2000). The depth averaged concentrations were 1.44-5.18 μM for POC, 0.06-0.68 μM for PON and 0.01-0.037 μM for PP in the EZ of the Levantine basin and depth averaged POC/PON and POC/PP ratios of seston in the EZ of the open Mediterranean Sea are mostly higher than classical Redfield ratios.

However, the surface N/P molar ratios of the PON and TPP concentrations of bulk POM in the bay were highly variable, ranging locally from 11.1 in the TPP-enriched POM samples at St.12 to 55.6 at St.31 in the studied site of the bay (Figure 4.16); the mean value of PON/TPP is as high as 25 (n:38) and markedly higher than the Redfield Ratio of 16.

In spring, the higher C/N ratios in bulk POM was determined in particulate samples collected at St.30 where the surface water was depleted in nutrients, with very low NO_3/PO_4 ratio (2.5); but the PON/TPP molar ratio and POC/Chl-*a* ratio (in weight) values were markedly high, reaching levels of 26 and 1130, respectively. The lower N/P ratios in selectively TPP-enriched POM were collected at St.12 in spring where POC and Chl-*a* concentrations were 28.8 μM and 0.62 $\mu\text{g/L}$ respectively, leading to a POC/chl-*a* ratio of 559 in bulk POM (with the C/N ratio of 6.17).

In winter, the POC/PON molar ratios ranged between 7.1-10.7 in the study area. The higher ratio was recorded at St.23 (coastal) with the high values of NO_3/PO_4 (68), PON/TPP (27) and POC/Chl-*a* ratios (287). These findings indicate the limited contribution of new-produced, labile organic carbon in the bulk POM. In winter, TPP-enriched POM was obtained at St.7 located within the polluted Mersin Harbor, with POC concentration as 26.3 μM , Chl-*a* concentration as 2.21 $\mu\text{g/L}$, and POC/Chl-*a* ratio as 143 showing impact of particulate phosphorus on algal production.

The ratios (C/N/P) derived from slopes of regression analyses of the POM data within the bay indicates no apparent significant N-deficiency in the composition of bulk POM enhanced in the surface waters of the coastal bay (Figure 4.15). Higher POC/PON ratios determined in POM of some locations having low concentrations of POM or receiving selectively organic-C rich POM inputs by river discharges.

However, the PON/TPP ratios of POM were highly variable, increasing markedly in the P-depleted coastal waters (PO_4 : 0.05-0.34 μM , TP: 0.20-0.74 μM ; NO_3 : 0.16-10.75 μM) where salinity ranged seasonally between 38 and 38.9 and POC concentrations varied spatially between 14-107 μM . The PON/TPP ratio estimated from the regression analysis of POM data (Figure 4.15) was nearly 21 and greater than the classical Redfield Ratio (16) of the average POM in the oceans. It can be concluded that the less saline, POM-rich coastal waters of the bay fed by DIN-laden freshwater discharges was relatively enriched in organic-C, N compounds as compared to its phosphorus content leading to higher PON/TPP ratios.

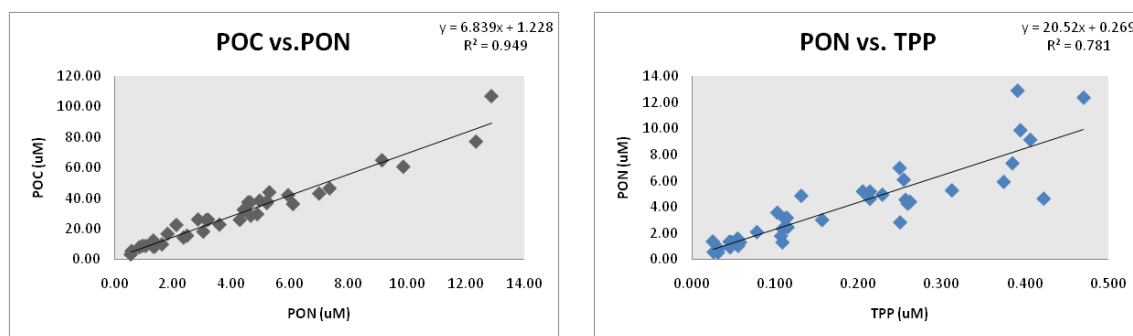


Figure 4.15. POC vs. PON and PON vs. TPP plot of the data measured from the study area of Mersin Bay in the study period.

Elemental compositions of the bulk POM displayed similar spatial variability in February 2015; no significant changes were observed in the POC/PON ratio, ranging between 7.1 and 10.7. However, the PON/TPP molar ratio varied from 11.4 at St.7 to 27.1 at St.23 in the studied sites of the bay.

The surface POC and PON concentrations display similar spatial and temporal variations over the bay, leading to limited changes in C/N ratios (mostly between 7-10) as previously reported (Erdoğan, 2014). The C/N ratio of POM in the bay are similar to those reported from NE and western Mediterranean as stated in Table 4.2. The ratios determined from the regression analysis are nearly similarly to the

Redfield Ratio of biogenic POM (C/N: 6.63) (Figure 4.15). However, the PON/TPP molar ratios are much more variable than the C/N ratios in the bulk POM collected in P-deficient waters of NE Mediterranean suggesting the selective enrichment of nitrogenous organic matter in POM pool. Low PON/TPP ratios determined in particulate samples most probably originate from inorganic-P adsorbed on small-sized particulate matter collected on filters. During wet period, regional rivers carry large amounts of P-adsorbed inorganic particulate matter to the coastal waters. These particulates are collected on filters and P analysis by wet method measure the total organic and inorganic P in particulate matter. Recent studies indicate that the contributions of inorganic P is apparent in the river fed coastal waters of NE Mediterranean (Doğan-Sağlamtimur, 2007; Erdoğan, 2014). In conclusion, inorganic particulate-P inputs to the total particulate P pool of the bay have made the N/P ratio more variable than the C/N ratio of bulk POM in the coastal bay especially during high flow periods of the regional rivers.

Sensitive phosphorus measurements by MAGIC method showed POP has remarkable contribution to the particulate P pool in NE Mediterranean. N/P molar ratios calculated in POM data varied between 20-50 in the shelf waters suggesting primary production in NE Mediterranean shelf waters is limited by phosphorus. The higher PON/TPP ratios (20.5 and 25) estimated from regression analysis and the average of all POM data are greater than the classical Redfield ratio strongly suggesting P-limited primary production in the Mersin bay and NE Mediterranean coastal waters as experienced in other studies (Doğan-Sağlamtimur, 2007; Tufekçi *et al.*, 2013; Erdoğan, 2014).

Table 4.2. POC, PON, TPP concentrations and its elemental compositions observed in NE Mediterranean

Region	POC (μM)	PON (μM)	TPP (μM)	C/N	N/P	Reference
Mersin Bay coastal surface waters	14.47-107.03	1.82-12.89	0.078-0.470	5.96-10.7	11.1-37.2	This study
Mersin Bay central basin surface waters	3.44-15.68	0.56-2.48	0.025-0.115	6.14-9.7	12.3-55.6	This study
Mersin Bay coastal surface waters	22.6-63.3	3.37-7.72	0.2-0.4	6.68-8.45		Erdoğan, 2014
Mersin Bay offshore surface waters	2.33-5.24	0.29-0.59	0.02-0.04	7.09-10.1	10-50	Erdoğan, 2014
Mediterranean Sea surface waters-December 2001-2003	1.9-114	0.11-10	0.029-0.191	4.7-19.6	8.9-56.2	Doğan-Sağlamtimur, 2007
Anticyclonic Cilician Basin-October 1991 (average)	2.7 ± 1.61	0.20 ± 0.03		14 ± 8.0		Ediger <i>et al.</i> , 2005
Anticyclonic Cilician Basin-March 1992 (average)	1.8 ± 0.61	0.25 ± 0.08		7.0 ± 1.2		Ediger <i>et al.</i> , 2005

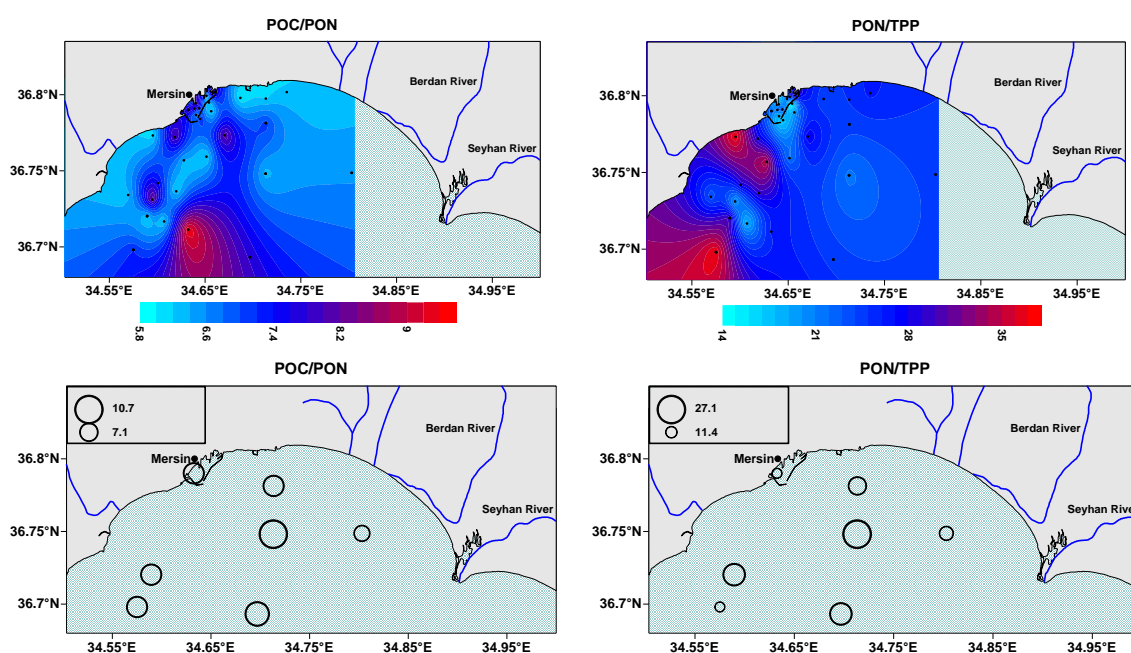


Figure 4.16. Spatial distributions of POC/PON and PON/TPP molar ratios in surface waters throughout the study area in April 2014 (upper) and February 2015.

4.3. Spatio-Temporal Variations of POM Concentrations and Elemental Composition (C/N/P) in Surface Sediments of the Mersin Bay

4.3.1. Spatio-Temporal Comparison of POM in Surface Sediments

In order to realize the reflection of POM composition and abundance in water column to the POM buried in sediment phase, the concentrations of TC, TOC, TN, TPP, PIP and POP (TPP-PIP) were measured in surface sediment samples taken at the POM stations visited in the near-shore zone and deeper part of the Mersin inner bay. The TC content of surface sediments in spring-2014 varied markedly between 38.5 and 112.5 mg/g (dry weight) in the April samples and from 34.1 to 49 mg/g in the samples collected in February 2015 (Figures 3.23-24). Grain-size distributions of surface sediments displayed high variability, depending on the depth and distance to the terrestrial sources carrying solid materials to the bay. In addition to external sources of particles, physical processes (waves and current systems) in the region are also other important factors controlling grain-size distributions of surface sediments accumulated on the shelf (Yemenicioğlu and Tunç, 2013). Higher TC values were determined at St.21 (1.5 km to coastline), indicating increased inputs of carbonate-rich materials by creeks and surface runoff. Low TC values were determined in the surface sediment of St.30 (8.3 km to the coastline and 8.5 km to the creeks, southwestern side of the bay) composed of small-sized (muddy) materials.

TOC concentrations of surface sediments showed significant regional variations, ranging from 2.01 mg/g at St.22 to 23.4 mg/g at St.1 (inside the city harbor) in April 2014 (Figure 3.23). The TN content of surface sediments varied between 0.19-2.39 mg/g, exhibiting similar spatio-temporal changes as experienced in recent studies (Erdoğan, 2014). Higher TOC and TN concentrations were expectedly observed at the same locations; the peak values of where POC, PON and Chl-*a* concentrations were determined as 46.6 µM, 7.4 µM and 1.91 µg/L, respectively. Lower POM concentrations were recorded in surface sediments of St. 22, where POM concentrations in surface waters were 29.8 µM for POC, 4.9 µM for PON and Chl-*a* concentration as 0.95 µM in spring. However, in winter, both TOC-TN high and low sediments were observed inside the city harbor and St.17, respectively where the concentrations of bulk POM and Chl-*a* concentrations did not show significant spatial variations indicating limited effect of bulk POM on the POM enhancement in

sediment phase. Decreased primary production under severe winter conditions and transport of both inorganic and organic (bulk POM) particles by surface currents from the coastal region to the offshore are the major factors for the enrichment of POM in the central bay surface sediments composed of small (muddy) particles.

The concentrations TPP (organic + inorganic-P=POP + PIP) in surface sediments varied locally from 0.22 mg/g (dry weight) at St.13 to 0.63 mg/g at St.1. POP measured in surface sediments of the inner bay ranged between 0.01-0.11 mg/g. Similar TPP and POP concentrations were also recorded in previous studies (Aydın *et al.*, 2009; Erdoğan, 2014); TPP concentrations varied between 206.24 and 210.18 µg/g whilst POP ranged 2.85-5.87 µg/g in surface sediments of the Burclar Bay (Erdemli, Mersin) (Aydın *et al.*, 2009).

Regression analysis of TPP vs. POP/TPP ratio indicates a weak correlation (R^2 : 0.05, see Figure 4.17), indicating that the ratio values were highly variable at similar TPP values; nevertheless, the average ratio was about 0.15 for the region. On the other hand, the plot of TPP vs. POP concentrations depicted in Figure 4.17 indicates a close correlation (R^2 : 0.38); The POP/TPP ratio derived from the regression analysis is estimated as 0.17, nearly similar to the average (0.15) of all POP data. It appears that the POP constituted about 15-20 % of the TPP content of the surface sediments in spring. There e exists a close correlation ($R^2 = 0.479$) between TOC and POP concentrations in the surface sediments (Figure 4.18). Regression analyses of TN/POP vs. TOC/TN ratios in Figure 4.19 shows that organic-P compounds in POM are more labile than particulate organic-N, buried in surface sediments, leading less variable C/N ratios but much variable TN/POP ratios in the surface sediments of the bay. The C/N and N/P ratios derived from the slope of regression analysis are 10.4 and 16.5, respectively. Though C/N molar ratio from regression analysis is higher than Redfield Ratio of 6.63, N/P molar ratio in surface sediments is very close to Redfield ratio of 16 due to enhancement of organic phosphorus in sediment phase.

Preservation rate of phosphorus in sediments depend on nature of phosphorus from sediment/water interface, sedimentation rate, bioturbation, bottom current and oxygen concentrations in bottom waters and diagenetic processes such as formation of phosphorus-bearing mineral. Due to changes in these state parameters, burial rate of phosphorus may vary according to depositional environment (Cha *et al.*, 2005;

Aviles *et al.*, 2006). In winter, intensive vertical mixing of coastal waters is expected to leach more labile forms of inorganic-P compounds from surface sediments as the new production of POM contributes to POP sedimentation on the bottom, leading to increase POP% in TPP (higher TOP/TPP ratio) in surface sediments (Figure 4.17). Changes in grain size distributions also influence TOC, TPP concentrations and POP/TPP in surface sediments. In spring, higher organic carbon and total phosphorus concentrations were observed in small-sized sediment samples in the study area with organic phosphorus content as ~14 % (Mud: 2.6-72 %). However, in winter time when small-sized particles increased from spring to winter, organic phosphorus concentration was about 27% indicating role of grain-size distribution on organic phosphorus distribution in the bay (Figure 4.20).

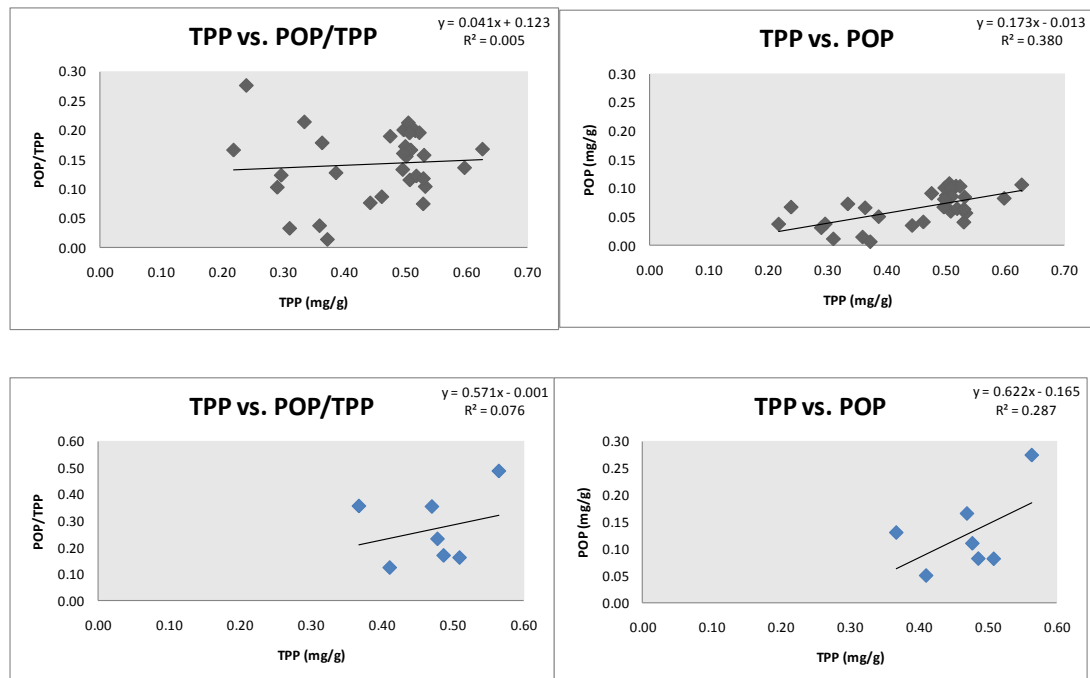


Figure 4.17. TPP vs. POP/TPP and TPP vs. POP plots of the sediment data obtained from the study area of Mersin Bay in spring (upper) and winter (lower).

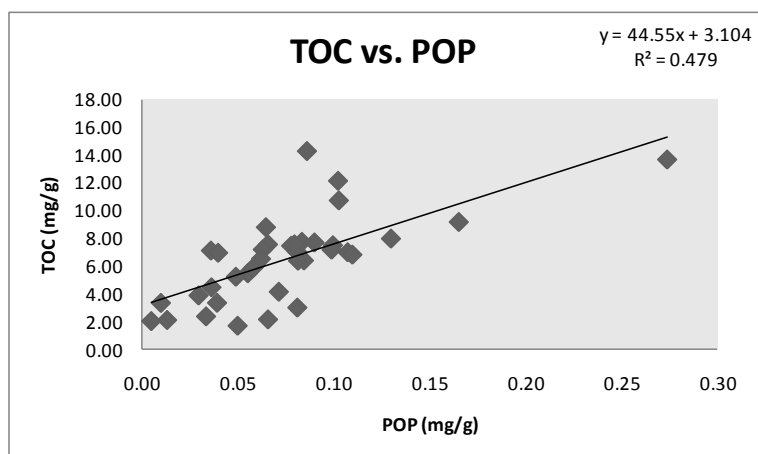


Figure 4.18. TOC vs. POP plot of the sediment data from the study area of Mersin Bay in spring and winter.

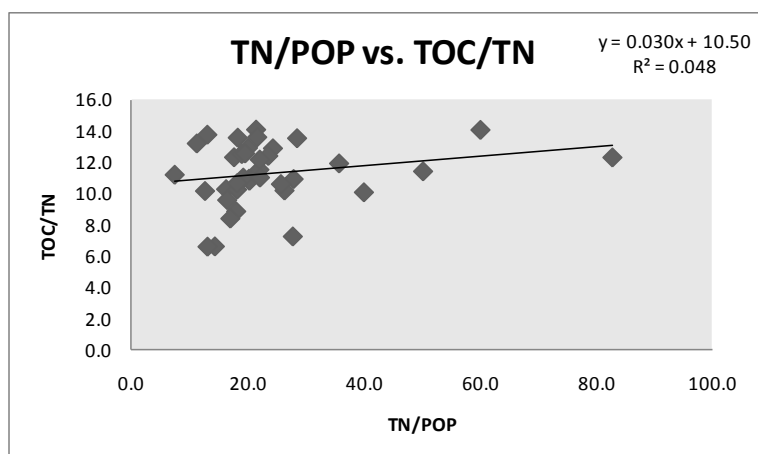


Figure 4.19. TN/POP vs. TOC/TN plot of the sediment data from the study area of Mersin Bay in spring and winter.

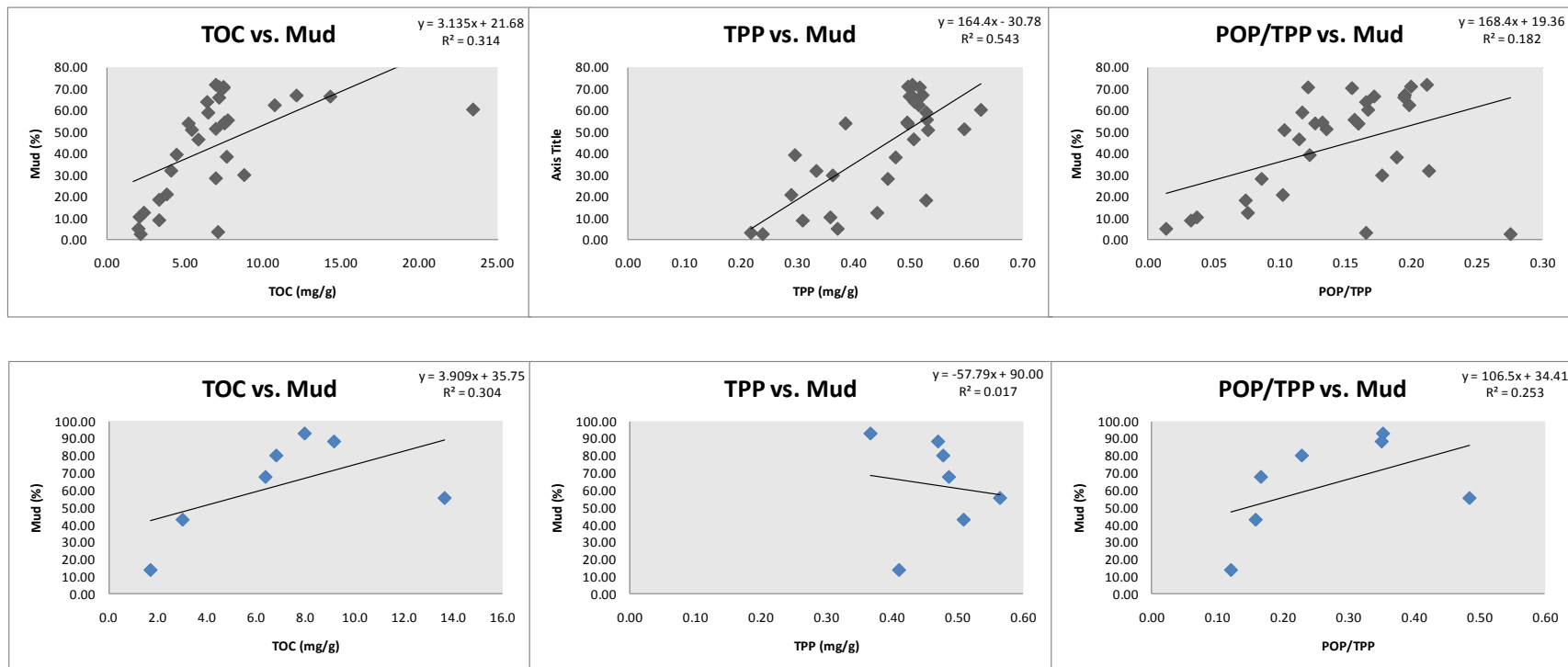


Figure 4.20. TOC, TPP and POP/TPP vs. mud content plots of the sediment data from the study area of Mersin Bay in the spring (upper) and in winter (lower).

Decreasing vertical mixing from winter to spring-autumn period reduce removal of inorganic-P from sediment phase whilst the increased aerobic bacterial activities in water-sediments enhance removal of more labile (P-rich) organic matter in surface sediments. Changing rates of these processes in different seasons principally determine POP concentrations and POP/TPP ratios in water column and surface sediments of the coastal marine environments. Combined effects of these processes appear to reduce POP concentrations in surface sediments of the bay in spring and the POP/TPP ratio mostly to 0.1-0.2 levels in spring, indicating inorganic-P dominated TPP pool in coastal surface sediments of the bay.

Organic carbon distributions depend on complex interactions of biogenic, terrigenous, hydrodynamic and anthropogenic factors (Yemenicioğlu and Tunç, 2013). Higher TOC concentrations were observed in surface sediments of the less polluted sites of the bay though peak values were observed in city harbor as also observed previously by Erdoğan (2014).

POM vs. grain-size changes depicted in Figure 4.20 indicates close correlations in spring; the POM concentrations enhanced in sediment phase with increasing mud% in spring. Winter data are not enough to examine POM vs. grain size correlations (Figure 4.20).

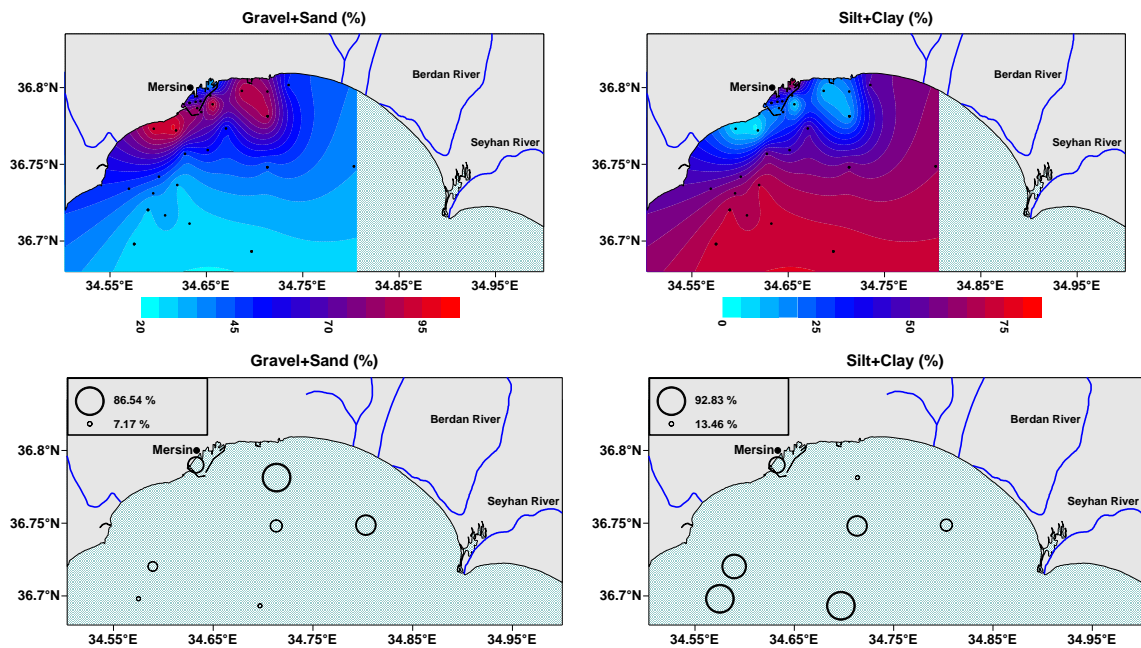


Figure 4.21. Grain-size distributions of surface sediments in the study area of Mersin Bay in April 2014 and February 2015.

4.3.2. C/N/P Ratios in the Bay Sediments

TOC/TN molar ratios in coastal surface sediments of the bay did not show significant spatial change in surface sediments of the Mersin bay as observed in the C/N ratio of bulk POM in surface waters of the bay (Figure 4.22) though higher values ranging between 10-14 were observed locally in coastal surface sediment in spring period.

The TOC/TN molar ratios in surface sediments varied regionally between 10.1 and 14.1 in spring; limited winter data indicate detectable decreases in the ratio to levels of 6.6-10.2 due presumably to selective removal/leaching of organic-C rich fraction of POM from the sediment phase to water column.

TOC/TN molar ratios in surface sediments are also higher than C/N molar ratios in the bulk POM in surface waters and near-bottom waters of the bay. C/N elemental ratios of the phytoplankton biomass in the oceanic system may vary from 6-8 to 5-15 (Giani *et al.*, 2003) and sinks down to depths with regionally and seasonally varying C/N/P ratios. It should be noted that the bulk POM in water phase has low sinking rates whereas the POM measured in surface sediments most probably originates from fast sinking POM with slightly different composition. However, the origins of sinking POM are similar and can be decomposed by bacterial processes in water column and in sediment phase. The older POM buried in sediment phase are expected to have been degraded more with greater loss from more labile N-rich organic fraction of POM, increasing POC/TN ratio in sediments (Clavier *et al.*, 1995). Previous sediment data obtained in Mersin bay showed C/N molar ratio varied regionally and seasonally between 6.3 and 11.4 with slightly higher values observed in the summer period (Erdoğan, 2014).

The spring TN/POP molar ratios in sediments of the bay displayed remarkable spatial variations (7.4-83) with higher values observed in polluted coastal area receiving high DIN-loaded terrestrial inputs (Figure 4.22). However, regional variations of the ratio in winter were less pronounced, ranging between 13 and 28 in the study area. Similar seasonal changes were also observed in PON/TPP molar ratios in bulk POM in water column. Similar regional variations of N/P molar ratios in surface sediments were also observed by Erdoğan (2014) varying between 7 and 12.7. Lower N/P molar ratios in sediments might be due to enhancement of organic phosphorus in central bay and the seasonal change in N/P molar ratio (decreasing

from spring to winter) coincided with increase in mud content in surface sediments suggesting role of fine-grained organic matter carrying sediments in the bay.

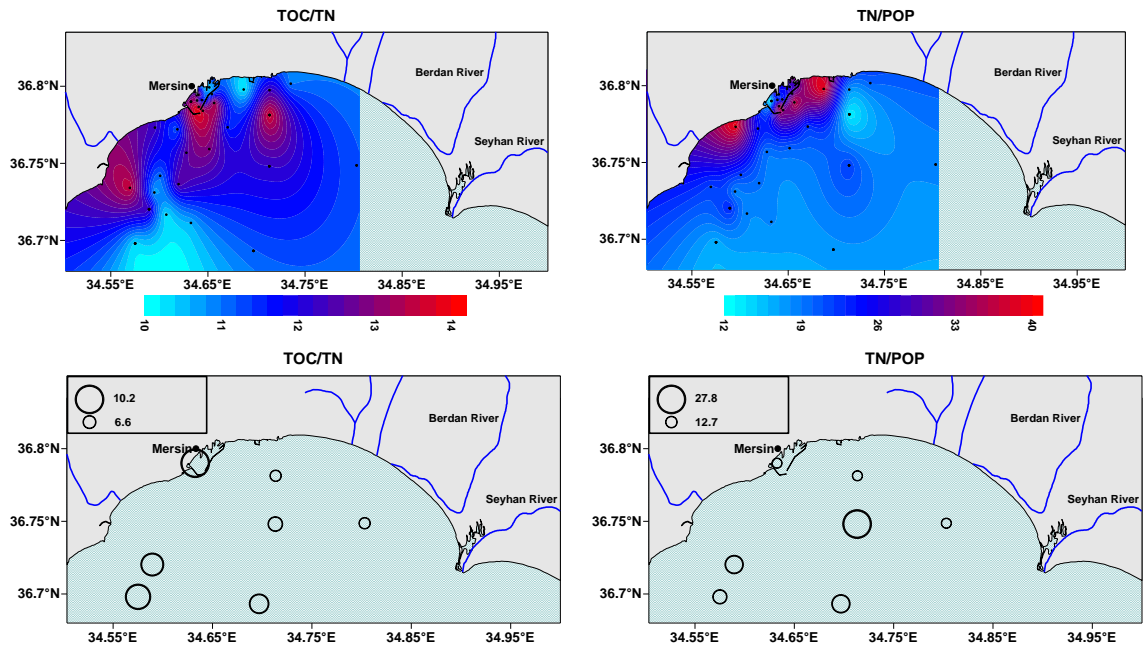


Figure 4.22. Spatial distributions of TOC/TN and TN/POP molar ratios of surface sediments in the study area of Mersin Bay in April 2014 (upper) and February 2015.

CHAPTER 5

CONCLUSION

The study aims to further understand factors dominating spatial distributions and elemental composition (C/N/P) of bulk POM in coastal waters and surface sediments of the Mersin inner bay ecosystem fueled by nutrient and organic matter inputs from the regional rivers and domestic wastewater discharges of Mersin city.

For this goal, POM data in seawater and sediment phases, physical (temperature, salinity, density) and eutrophication-related parameters (dissolved inorganic nutrients, Chl-*a* and DO) measured within the bay in April 2014 and February 2015 are examined in this study to assess spatio-temporal variations and correlations between the bio-chemical parameters.

Terrestrial inputs enhance the concentrations of both nutrients, algal bio-mass (in terms of Chl-*a*) and bulk POM by at least 5-10 fold in the coastal surface waters fed by river and wastewater discharges. The largest concentration increases were DIN concentrations due to PO₄-depleted but nitrate-laden freshwater inflows during the year. DIN concentrations increase from 0.13-3.10 μM levels in the least affected central bay waters (salinity ≥ 39.0) to 5-10 μM levels in the less saline near-shore waters (S < 38.5). Naturally, similar spatial changes appear in Chl-*a* concentrations (indicator of algal biomass) in the surface waters of the bay, enhancing by at least 10-fold from 0.08-0.14 μg/L to 1.84 μg/L levels in the nitrate rich but PO₄ depleted coastal waters of the inner bay. Higher nutrient concentrations with high algal biomass (in terms of Chl-*a*) are consistent with those previously observed in the coastal area of the Mersin bay affected by land-based sources (Tugrul *et al.*, 2004; Doğan-Sağlamtimur, 2007; Sert, 2010; Kaptan, 2013, Erdoğan, 2014).

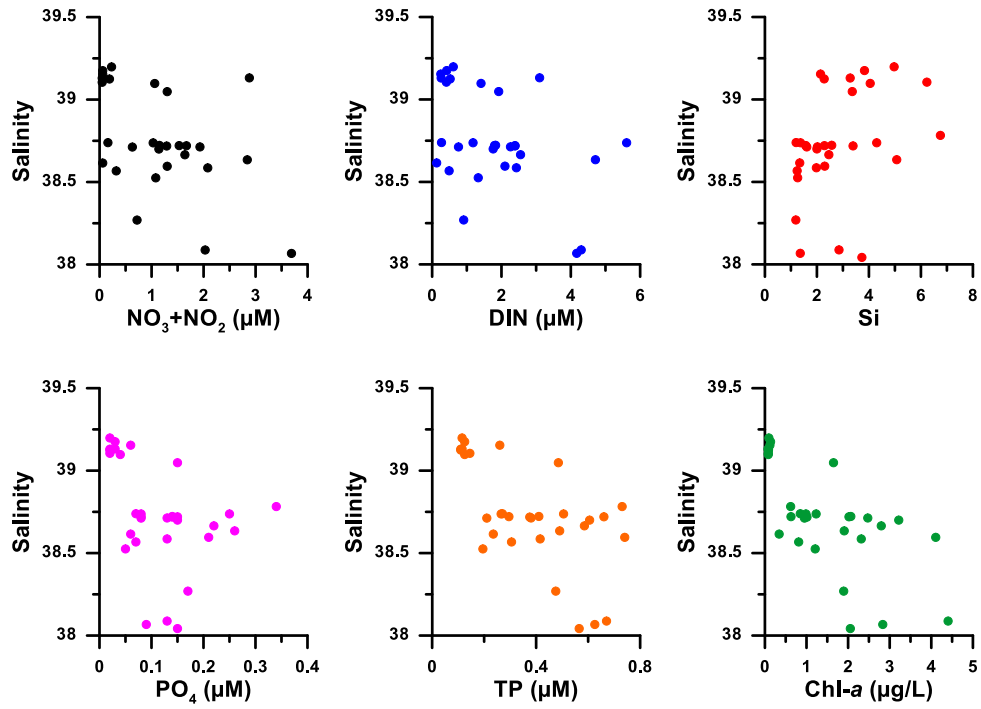


Figure 5.1. Dissolved inorganic nutrients and Chl-*a* vs. salinity plot of the data measured from the study area of Mersin Bay in April 2014.

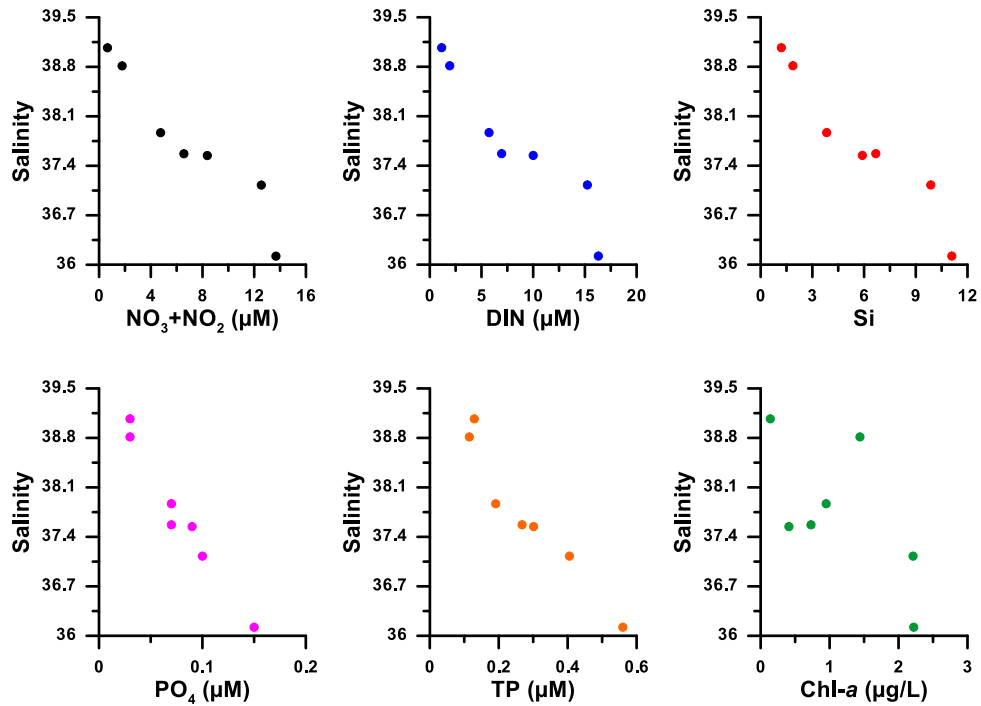


Figure 5.2. Dissolved inorganic nutrients and Chl-*a* vs. salinity plot of the data measured from the study area of Mersin Bay in February 2015.

High N/P molar ratios in both sources (rivers and atmospheric precipitation) and near-shore waters fed by terrestrial nutrient inputs indicate potentially P-limited POM production via photosynthesis.

Large nutrient inputs with high N/P ratios have enhanced production of biogenic POM and thus bulk POM and Chl-*a* (algal biomass) concentrations in the coastal waters by at least 10-fold as compared the central bay values (salinity \geq 39.0).

Excess DIN inputs to the shallow shelf waters partly modified the elemental composition (C/N/P molar ratios) of bulk POM filtered from the coastal surface waters of Mersin Bay. The C/N ratio calculated from individual POM data ranged between 6.0-9.45 in April 2014 and 7.1-10.7 in February 2015. Biochemically less labile POM inputs by the regional rivers slightly lead to increase POC/PON ratio in slowly sinking POM sampled from the bay coastal waters in wet winter period. Though POM concentrations were variable with region, no significant spatial changes appeared in C/N molar ratios of bulk POM in surface waters of the study area.

However, the C/N ratio estimated from POC versus PON regression is nearly slightly higher than the classical Redfield Ratio (6.63) due to selective degradation of more labile organic-N compounds in bulk POM filtered from the near-surface waters. On the other hand, PON/TPP ratios calculated from POM data are more variable (11.1-55.6) in the coastal waters due to transport of non-biogenic inorganic P compounds by river discharges. These compounds with low sinking rates associated to suspended particulate-P (organic + inorganic) pool of the coastal ecosystem. The N/P ratio of bulk POM has been observed to be less variable (18-31) in the central bay waters as reported previously by Doğan-Sağlamtimur (2007). The N/P ratio derived from the regression analysis of the POM data obtained in P-depleted bay waters (having high DIN/PO₄ ratio) is nearly 20.5, greater than the Redfield Ratio (16). Higher PON/TPP were obtained in P-limited coastal waters due most probably to enhanced rates of POM production (higher POM concentrations) with higher N/P ratios and then selectively fast decomposition organic phosphorus in bulk POM pool as compared to organic-N compounds. High N/P molar ratios of nutrients in both surface water and POM strongly suggest P-limited algal production in the Mersin Bay, supporting previous bio-assay results.

There exists a strong correlation between mud content and organic matter (C, N, P) concentrations of the bay surface sediments; higher organic matter concentrations in mud-rich sediments exceed the POM content of the sandy coastal sediments.

No significant changes have been observed in the elemental composition of organic matter buried in sediment phase of the bay ecosystem. The C/N ratio of POM in the bay surface sediments varied between 6.6-14.1, slightly greater than the ratios (6.0-10.7) in bulk POM filtered from surface waters of the region. However, TN/TPP ratios in the bay surface sediments were highly variable (1.0-8.4) and much lower than the ratio in bulk POM filtered from the water column. Total particulate-P compounds measured water and sediment phases are composed of both biogenic organic and inorganic-P of terrestrial origin whereas the particulate N is composed of totally organic-N compounds of biogenic origin. These factors appear to produce remarkable variability in POC/PON/TPP ratios of suspended particles filtered from water and in sediment phase. New studies on C, N, P cycles in the eutrophic/oligotrophic marine environments are needed to further understand processes controlling the composition of slowly sinking particles and surface sediments in the marine environment, especially in the enclosed seas having distinctly different biochemical properties.

REFERENCES

- Abdel-Moati, A.R. 1990. Particulate organic matter in the subsurface chlorophyll maximum layer of the Southeastern Mediterranean. *Oceanologica Acta*, 13, 307-315.
- Aminot, A., Kerouel, R., 2004. Dissolved organic carbon, nitrogen and phosphorus in the N-E Atlantic and the N-W Mediterranean with particular reference to non-refractory fractions and degradation. *Deep-Sea Res. I* 51, 1975-1999.
- Aviles, A., Rodero, J., Amores, V., Vicente, I., Rodriguez, M.I., Niell, F.X. 2006. Factors controlling phosphorus speciation in a Mediterranean basin (River Guadalfeo, Spain), *J. Hydrol.* 331, 396–408.
- Aydın, I., Aydın, F., Saydut, A., Hamamcı, C. 2009. A sequential extraction to determine the distribution of phosphorus in the seawater and marine surface sediment. *Journal of Hazardous Materials* 168, 664–669.
- Bartholini, G., Spagnoli, F., Dinelli, E., Giordano, P. 2008. *Estuarine, Coastal and Shelf Science*, 80- 1, 21-30.
- Benitez-Nelson, C.R., Karl, D.M. 2000. Phosphorus cycling in the North Pacific subtropical gyre using cosmogenic ³²P and ³³P. *Limnology and Oceanography*, 47, 762-770.
- Berner, R.A. 1982. Burial of organic carbon and pyrite sulfur in the modern ocean: Its geochemical and environmental significance. *American Journal of Science*, 282, 451-473.
- Berner, R.A., Rao, J.L. 1994. Phosphorus in sediments of the Amazon River and estuary: Implications for the global flux of phosphorus to the sea. *Geochimica Cosmochimica Acta*, 58, 2333-2340.
- Béthoux, J.P., Morin, P., Madec, C., Gentili, B. 1992. Phosphorus and nitrogen behaviour in the Mediterranean Sea. *Deep-Sea Research*, 39 (9), 1641-1654.
- Boston, V., Dominic, J., Bostina, M. and Pardos, M. 2000. Forms of particulate phosphorus in suspension and in bottom sediment in the Danube Delta, *Lakes Reserv Res Manag*, 5, 105–110.

Butcher, S.S., Charlson, R.J., Orians, G.H., Wolfe, G.V., 1992. Global biogeochemical cycles. Unites States Edition published by Academic Press INC. San Diego. pp. 301-317.

Cha, H.J., Lee, C.B., Kim, B.S., Choi, M.S., Ruttenberg, K.C. 2005. Early diagenetic redistribution and burial of phosphorus in the sediments of the south western East Sea (Japan Sea), *Marine Geol.* 216, 127–143.

Chin, W-C, M.V. Orellana & P. Verdrugo, 1998. Spontaneous assembly of marine dissolved organic matter into polymer gels. *Nature* 391: 568-572.

Clark, L.L., Ingall, E.D., Benner, R. 1998. Marine phosphorus is selectively remineralized. *Nature*, 393, 426.

Collins, M.B., and Banner, F.T., 1979. Secchi disc depths, suspensions and circulation, northeastern Mediterranean Sea. *Marine Geology*, 31,1-2, 39-46.

Çoban, Y. 1997. The abundance and elemental composition of suspended organic matter in the Turkish Seas (Black, Marmara and Eastern Mediterranean). M.S. Thesis, Institute of Marine Sciences, Middle East Technical University, Mersin, Turkey, 187 pp.

Çoban-Yıldız, Y., Tuğrul, S., Ediger, D., Yılmaz, A., Polat, S.Ç. 2000. A comparative study on the abundance and elemental composition of POM in three interconnected basins: the Black, the Marmara and the Mediterranean Seas. *Mediterranean Marine Science*, 1/1, 51-63.

Doğan-Sağlamtimur, N. 2007. Seasonal variations of particulate and dissolved fractions of phosphorus and related hydrochemical parameters in the Northeastern Mediterranean shelf zone. Ph.D. Thesis, Institute of Marine Sciences, Middle East Technical University, Mersin, Turkey, 260 pp.

Doğan-Sağlamtimur, N., Tuğrul, S. 2004. Effect of Riverine Nutrients on Coastal Water Ecosystems: A Case Study from the Northeastern Mediterranean Shelf., 13, 11b, Sp. Iss., 1288-1294.. "Fresenius Environ. Bulletin", 13, p.1288-1294.

Doval, M.D., Perez, F.F., Berdalet, E. 1999. Dissolved and particulate organic carbon and nitrogen in the Northwestern Mediterranean. *Deep-Sea Research I*, 46, 511-527.

Ediger, D. 1995. Interrelationship among primary production, chlorophyll and environmental conditions in the North Levantine Basin. Ph.D. Thesis, Institute of Marine Sciences, Middle East Technical University, Mersin, Turkey, 178 pp.

Ediger, D., Tuğrul, S., Polat, Ç.S., Yılmaz, A., Salihoğlu, İ. 1999. Abundance and elemental composition of particulate matter in the upper layer of Northeastern Mediterranean, In: *The Eastern Mediterranean as a Laboratory Basin for the Assessment of Contrasting Ecosystems* (Malanotte-Rizzoli, P., Eremeev V.N., eds.). Kluwer Academic Publishers, Netherlands, pp. 241 -266.

Ediger, D., Tuğrul, S., Yılmaz, A. 2005. Vertical profiles of particulate organic matter and its relationship with chlorophyll-a in the upper layer of the NE Mediterranean Sea. *Journal of Marine Systems*, 55, 311-326.

EEA. 1999. State and pressures of the marine and coastal Mediterranean environment. Copenhagen: European Environment Agency.

Eijssink, L.M., Krom, M.D., de Lange, G.J. 1997. The use of sequential extraction techniques for sedimentary phosphorus in eastern Mediterranean sediments. *Marine Geology* 139, 147-155.

Erdoğan, E. 2014. Distribution of particulate organic matter, its elemental composition (C/N/P) and variation with environmental factors in the shelf waters and sediments in the northeastern Mediterranean (Mersin Bay). Ph.D. Thesis, Institute of Graduate School Of Natural And Applied Sciences, Mersin University, Turkey, 150 pp.

Fang, T.-H., Chen, J.-L., Huh, C.-A. 2007. Sedimentary phosphorus species and sedimentation flux in the East China Sea. *Continental Shelf Research* 27, 1465-1476.

Frangou, S., Christaki, U., Mazzocchi, M.G., Montresor, M., Riberra d' Alcalá, M., Vaque, D., Zingone, A. 2010. Plankton in the open Mediterranean Sea: a review. *Biogeosciences*, 7, 1543–1586.

- Giani, M., Savelli, F, Boldrin, A. 2003. Temporal variability of particulate organic carbon, nitrogen and phosphorus in the Northern Adriatic Sea. *Hydrobiologia*, 494, 319-325.
- Goldman, J.C., McCarthy, J.J., Peavey, D.G., 1979. Growth rate influence on the chemical composition of phytoplankton in oceanic waters. *Nature*, 279, 210-215.
- Grasshoff, K., Erhardt, M. and Kremling, K. 1983. Determination of nutrients. In: *Methods of Seawater Analysis* (2nd ed.), Verlag Chemie GmbH, Weinheim, Germany, pp. 125-188.
- Hecht, A., Pinardi, N., Robinson, A.R. 1988. Currents, Water Masses, Eddies and Jets in the Mediterranean Levantine Basin. *Journal of Physical Oceanography*, 18, 1320-1353.
- Herndl, G.J., Reinthaler, T. 2013. Microbial control of the dark end of the biological pump. *Nature Geoscience* 6, 718–724.
- Kaptan, M.S., 2013. Assessment of the trophic status of the Mersin bay waters, northeastern Mediterranean. M.Sc. Thesis, Institute of Marine Sciences, Middle East Technical University, Mersin, Turkey, 81 pp.
- Karl, D.M., Yanagi, K. 1997. Partial characterization of the dissolved organic phosphorus pool in the oligotrophic North Pacific Ocean. *Limnology and Oceanography*, 42, 1398-1405.
- Karydis, M., Kitsiou, D. 2012. Eutrophication and environmental policy in the Mediterranean Sea: a review. *Environ Monit Assess*, 184:4931–4984.
- Koçak, M., Kubilay, N., Tuğrul, S., Mihalopoulos, N. 2010. Atmospheric nutrient inputs to the northern levantine basin from a long-term observation: sources and comparison with riverine inputs. *Biogeosciences*, 7, 12, 4037-4050.
- Kress, N., Herut, B. 2001. Spatial and seasonal evolution of dissolved oxygen and nutrients in the Southern Levantine Basin (Eastern Mediterranean Sea). Chemical characterization of the water masses and inferences on the N:P ratios. *Deep-Sea Research I*, 48, 2347-2372.

Krom, M.D., Brenner, S., Israilov, L., Krumpal, B. 1991. Dissolved nutrients, preformed nutrients and calculated elemental ratios in the South-East Mediterranean Sea. *Oceanologica Acta*, 14, 2, 189-194.

Krom, M.D., Groom, S., Zohary, T. 2003. The Eastern Mediterranean. In: *The Biogeochemistry of Marine Systems* (Black, K.D., Shimmield, G.B., eds.), Blackwell Publishing, Oxford, pp. 91 -126.

Krom, M.D., Woodward, E.M.S., Herut, B., Kress, N., Carbo, P., Mantoura, R.F.C., Spyrès, G., Thingstad, T.F. 2005. Nutrient cycling in the south east Levantine basin of the eastern Mediterranean: Results from a phosphorus starved system. *Deep-Sea Research II*, 52, 2879-2896.

Menzel, D.W., Corwin, N. 1965. The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation. *Limnology and Oceanography*, 10, 280-282.

Miller, A.R., Tchernia, P., Charnock, H., McGill, D.A., Atlantis (Research vessel), Chain (Research vessel). 1970. *Mediterranean Sea atlas of temperature, salinity, oxygen profiles and data from cruises of R. V. Atlantis and R. V. Chain*, by A. R. Miller, P. Tchernia [and] H. Charnock. With, *Distribution of nutrient chemical properties*, by D. A. McGill, Woods Hole Oceanographic Institution, Woods Hole, Mass.

Ministry of Environment and Urbanization. 2014. TUBITAK Project No: 5148704 (Mediterranean Pollution Monitoring Program), Final report.

Moutin, T. and Prieur, L. 2012. Influence of anticyclonic eddies on the Biogeochemistry from the Oligotrophic to the Ultraoligotrophic Mediterranean (BOUM cruise), *Biogeosciences*, 9, 3827-3855.

Nedweil, D.B., 1984. The input and mineralization of organic carbon in anaerobic aquatic sediments. *Adv. Microb. Ecol.*, 10: 93-131.

Nieuwenhuize, J., Maas, Y. E. M., Middelburg, J. J. 1994. Rapid analysis of organic carbon and nitrogen in particulate materials. *Marine Chemistry*, 45, 217-224.

- Özsoy, E., Hecht, A., Ünlüata, Ü. 1989. Circulation and hydrography of the Levantine Basin. Results of POEM coordinated experiments 1985-1986. *Prog. Oceanogr.*, 22, 125-170.
- Özsoy, E., Hecht, A., Ünlüata, Ü., Brenner, S., Oguz, T., Bishop, J., Latif, M.A., Rosentraub, Z. 1991. A review of the Levantine Basin circulation and its variability during 1985-1988. *Dynamics of Atmosphere and Oceans*, 15, 421-456.
- Özsoy, E., Hecht, A., Ünlüata, Ü., Brenner, S., Sur, H.İ., Bishop, J., Latif, M.A., Rosentraub, Z., Oğuz, T. 1993. A synthesis of the Levantine Basin circulation and hydrography, 1985-1990. *Deep-Sea Research II*, 40, 6, 1075-1119.
- Paytan, A., McLaughlin, K. 2007. The Oceanic phosphorus cycle. *Chem. Rev.* , 107, 563–576.
- POEM Group. 1992. General circulation of the Eastern Mediterranean. *EarthScience Reviews*, 32, 285-309.
- Polat, S.Ç., Tuğrul, S. 1995. Nutrient and organic carbon exchanges between the Black and Marmara Seas through the Bosphorus Strait. *Continental Shelf Research*, 15, 1115-1132.
- Polat, S.Ç., Tuğrul, S., Çoban, Y., Basturk, O., Salihoglu, I. 1998. Elemental composition of seston and nutrient dynamics in the Sea of Marmara. *Hydrobiologia*, 363, 157-167.
- Rabitti, S., Bianchi, F., Boldrin, A., Daros, L., Socal, G., Totti, C. 1994. Particulate matter and phytoplankton in the Ionian Sea. *Oceanologica Acta*, 17 (3), 297-307.
- Redfield, A.C., Ketchum, B.H., Richards, F.A. 1963. The influence of organisms on the composition of sea water, *The Sea, Ideas and Observations on Progress in the Study of the Seas* (Hill, M.N., ed.), Interscience Publishers, New York, 2, pp. 26-77.
- Ruttenberg, K.C. 1993. Reassessment of the oceanic residence time of phosphorus. *Chem. Geol.* 107, 405-409.
- Sakshaug, E., Andersen, K., Mykkestad, S., Olsen, Y., 1983. Nutrient status of phytoplankton communities in Norwegian waters (marine, brackish, fresh) as revealed by their composition. *J. Plankton Res.*, 5, 175-196.

SBE - Sea-Bird Electronics Booklet

Schulz, H.D., Zabel, M. 2006. Marine geochemistry. 2nd revised, updated and extended edition. Springer Berlin Heidelberg New York. pp. 1-25.

SEAL Analytical Booklet, AutoAnalyzer Applications, Method No: G-171-96 Rev. 15.

SEAL Analytical Booklet, AutoAnalyzer Applications, Method No: G-172-96 Rev. 17.

SEAL Analytical Booklet, AutoAnalyzer Applications, Method No: G-173-96 Rev. 10.

SEAL Analytical Booklet, AutoAnalyzer Applications, Method No: G-175-96 Rev. 15.

SEAL Analytical Booklet, AutoAnalyzer Applications, Method No: G-177-96 Rev. 11.

Sert, M.F. 2010. Determination of total nitrogen and total phosphorus in the northeastern Mediterranean water column. M.Sc. Thesis, Institute of Marine Sciences, Middle East Technical University, Mersin, Turkey, 110 pp.

Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. 1997. Proceedings of the Ocean Drilling Program, Scientific Results, 154, 475-481.

Slomp, C.P., Malschaert, F.P., Raaphorst, W.V. 1998. The role of adsorption in sediment-water exchange of phosphate in North Sea continental margin sediments. *Limnol. Oceanogr.*, 43(5), 832-846.

Smith, S.V., Kimmerer, J., Walsh, T.W. 1986. Vertical flux and biochemical turnover regulate nutrient limitation of net organic production in the North Pacific Gyre. *Limnology and Oceanography*, 31, 161 -167.

Socal, G., Boldrin, A., Bianchi, F., Civitarese, A., Rabitti, S., Totti, C., Turchetto, M. 1999. Nutrient, particulate matter and phytoplankton variability in the photic layer of the Otranto strait. *Journal of Marine Systems*, 20, 381-398.

Souvermezoglou, E. and Krasakopoulou, E. 1999. The effect of physical processes on the distribution of nutrients and oxygen in the NW Levantine Sea. In: MalanotteRizzoli, P., Eremeev, V.N. Editors, 1999. Proceedings of NATO Advanced Research Workshop: the Eastern Mediterranean as a laboratory basin for the assessment of contrasting ecosystems. NATO ARW Series, Vol. 51 Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 225-240.

Strickland, J.D.H., Parsons, T.R. 1972. A Practical Handbook of Seawater Analysis, 2nd edition. Bulletin of the Fisheries Research Board of Canada, No. 167, 310 pp.

Thingstad, T.F., Krom, M.D., Mantoura, R.F.C., Flaten, G.A.F., Groom, S., Herut, B., Kress, N., Law, C.S., Pasternak, A., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., Tselepidis, A., Wassmann, P., Woodward, E.M.S., Riser, C.W., Zodiatis, G., Zohary, T. 2005. Nature of phosphorus limitation in the ultraoligotrophic eastern Mediterranean, *Science*, 309 (5737), 1068-1071.

Tselepidis, A., Zervakis, V., Polychronaki, T., Donavaro, R., Chronis, G., 2000. Distribution of nutrients and particulate organic matter in relation to the prevailing hydrographic features of the Cretan Sea (NE Mediterranean). *Progress in Oceanography*, 46, 113-142.

TUBITAK Project No: 111G152 (Dredging Applications and Environmental Management of Dredged Material), 3rd Progress Report, 2015 (in Turkish).

Tuğrul, S., Beşiktepe, T., Salihoğlu, İ. 2002. Nutrient Exchange fluxes between the Aegean and Black Seas through the Marmara Sea. *Mediterranean Marine Science*, 3/13 33-42.

Tuğrul, S., Ediger, D., Doğan-Sağlamtimur, N. and Yılmaz, D. 2004. TUBITAK, Project No: YDABAG-102Y057, 108 pp (in Turkish).

Tuğrul, S., Küçüksezgin, F., Yemenicioğlu, S., Uysal, Z. 2009. Med Pol Phase IV long term biomonitoring, trend and compliance monitoring program in coastal areas from Aegean, Northeastern Mediterranean and eutrophication in Mersin bay 2009 final report. Republic of Turkey Ministry of Environment and Forestry. 211 pp.

- Tunç, Ş.Ç. 2008. Geology and geochemistry of recent sediments from the Northeastern Mediterranean Basin. M.Sc. Thesis, Institute of Marine Sciences, Middle East Technical University, Mersin, Turkey, 127 pp.
- Tüfekçi, V., Kuzyaka, E., Tüfekçi, H., Avaz, G., Günay, A.S., Tuğrul, S. 2013. Determination of limited nutrients in the Turkish coastal waters of the Mediterranean and Aegean Seas. *J. Black Sea/Mediterranean Environment* Vol. 19, No. 3: 299-311.
- UNEP, 1989: State of the Mediterranean Marine Environment. MAP Technical Series No. 28, UNEP, Athens.
- UNEP/MAP, 2005: Sampling and analysis techniques for the eutrophication monitoring strategy of MED POL, MAP Technical Reports Series No. 163, Athens.
- UNEP/MAP, 2006: methods for sediment sampling and analysis, Review Meeting of MED POL - Phase III Monitoring Activities, Athens.
- Uysal, Z. Latif, M.A. Özsoy, E. Tuğrul, S. Kubilay, N. Beşiktepe, Ş.T. Yemenicioğlu, S. Mutlu, E. Ediger, D., Beşiktepe, Ş., Ediger, V., Ak Örek, Y., Örek, H., Demirel, M., Tunç, Ş.Ç. and Terbiyik, T. 2008. The Scientific and Technical Research Council of Turkey TUBITAK Project No: 104Y277, 523 pp (in Turkish).
- Volkman, J. K., Tanoue, E. 2002. Chemical and biological studies of particulate organic matter in the ocean. *Journal of Oceanography*, Vol. 58, pp. 265-279.
- Vostokov, S.V., Vedernikov, V.I. 1988. Living and non-living particulate organic matter in the euphotic zone of the epipelagic ecosystem. *Oceanology*, 28, 100-105.
- Wasmund N., Topp I., Schories D., 2006, Optimising the storage and extraction of chlorophyll samples, *OCEANOLOGIA*, 48 (1), pp. 125–144.
- Wentworth, C.W. 1922. The canonical definition of sediment grain sizes as defined by geologist Chester K. Wentworth in a 1922 article in *The Journal of Geology*: "A Scale of Grade and Class Terms for Clastic Sediments".
- Yemenicioğlu, S., Tunç, Ş.Ç. 2013. Geology and Geochemistry of Recent Sediments from the Mediterranean Sea: Sediment Texture of Northeastern Mediterranean Basin. *Open Journal of Geology*, 3, 371-378.

Yılmaz, A., Tuğrul, S. 1998. The effect of cold- and warm- core eddies on the distribution and stoichiometry of dissolved nutrients in the northeastern Mediterranean. *Journal of Marine Systems*, 16, 253-268.

Yumruktepe, Ç. 2011. Investigation of primary production and nutrient cycles in the Cilician Basin. M.S. in Physical Oceanography. M.Sc. Thesis, Institute of Marine Sciences, Middle East Technical University, Mersin, Turkey, 94 pp.

APPENDICES

APPENDIX A. HYDROPHYSICAL AND BIOCHEMICAL PARAMETERS MEASURED IN SEAWATER

APRIL 2014																		
St.	Depth (m)	Temp. (°C)	Salinity	Density	TP (µM)	PO ₄ (µM)	NO ₃ +NO ₂ (µM)	NO ₂ (µM)	Si (µM)	NH ₄ (µM)	DO (mg/L)	BOD ₅ (mg/L)	Chl-a (µg/L)	TSS (mg/L)	TPP (µM)	PON (µM)	POC (µM)	SDD (m)
13	0	20.9	38.7	27.4	0.30	0.08	1.53	0.16	1.57	0.27	7.88	1.21	0.63	13.00	0.156	3.04	18.32	4
	5	20.5	38.8	27.5	0.23	0.05	1.43	0.14	1.59	0.16	7.84		0.72	13.86	0.174	1.85	13.44	
14	0	21.4	38.0	26.7	0.57	0.15	10.75	0.49	3.73	5.16	7.86	1.69	2.05	12.38	0.254	6.11	36.44	3
	7	19.6	39.1	28.0	0.34	0.08	1.91	0.18	2.32	1.00	7.41		1.27	14.35	0.148	4.18	27.00	
15	0	21.7	38.1	26.7	0.67	0.13	2.03	0.24	2.85	2.27	8.76	2.05	4.40	13.76	0.394	9.88	60.84	3
	8	20.0	39.0	27.8	0.46	0.11	5.00	0.79	5.83	2.22	8.11		1.27	17.06	0.226	5.73	35.42	
16	0	22.3	38.1	26.5	0.63	0.09	3.69	0.13	1.36	0.48	8.92	2.67	2.83	24.35	0.470	12.37	77.30	3
	6	21.6	38.5	27.0	0.62	0.09	2.98	0.16	1.32	0.68	8.69			26.15	0.404	10.28	71.18	
18	0	21.7	38.6	27.0	0.31	0.07	0.32	0.12	1.24	0.17	8.21	1.44	0.81	16.00	0.112	3.15	26.00	5
	13	19.0	39.2	28.2	0.29	0.05	0.71	0.18	2.20	0.51	7.35		0.54	19.85	0.091	2.79	16.76	
17	0	22.1	38.3	26.7	0.48	0.17	0.72	0.09	1.19	0.19	8.64	1.90	1.89	16.52	0.214	5.22	37.06	3
	11	19.4	39.1	28.1	0.46	0.12	2.51	0.19	1.44	1.32	8.37		1.27	19.99	0.137	5.31	34.78	
23	0	21.5	38.6	27.1	0.24	0.06	0.06	0.02	1.34	0.07	8.00	1.12	0.34	17.03	0.115	2.48	15.68	7
	20	18.8	39.2	28.3	0.26	0.05	0.31	0.06	4.03	0.42	7.00		0.63		0.100	1.78	12.42	
21	0	21.6	38.7	27.2	0.27	0.07	0.16	0.03	1.20	0.11	8.17	1.24	0.85	21.49	0.114	3.21	26.12	6
	9	20.5	38.8	27.5	0.29	0.07	0.74	0.09	1.42	0.13	8.23		0.99	24.58	0.152	3.02	24.38	

St.	Depth (m)	Temp. (°C)	Salinity	Density	TP (µM)	PO ₄ (µM)	NO ₃ +NO ₂ (µM)	NO ₂ (µM)	Si (µM)	NH ₄ (µM)	DO (mg/L)	BOD ₅ (mg/L)	Chl-a (µg/L)	TSS (mg/L)	TPP (µM)	PON (µM)	POC (µM)	SDD (m)
22	0	21.7	38.7	27.1	0.21	0.08	0.63	0.06	1.61	0.13	8.06	1.21	0.95	20.31	0.131	4.89	29.81	5
	7	21.3	38.8	27.3	0.19	0.07	0.66	0.05	1.76	0.17	8.11							
20	0	20.9	38.7	27.4	0.27	0.08	1.03	0.12	1.37	0.15	7.96	1.20	1.23	12.82	0.103	3.60	22.90	6
	17	18.7	39.2	28.3	0.15	0.04	0.06	0.02	2.64	0.15	7.39		1.00	13.99	0.084	2.40	14.64	
19	0	20.7	38.5	27.3	0.20	0.05	1.08	0.18	1.26	0.25	7.97	1.08	1.21	10.34	0.109	2.36	14.47	6
	18	18.8	39.2	28.3	0.18	0.03	0.23	0.08	3.84	0.10	7.18		0.63	15.78	0.094	2.07	14.59	
10	0	20.7	38.6	27.3	0.42	0.13	2.08	0.18	1.98	0.35	8.06	1.87	2.32	11.50	0.259	4.29	26.07	3
	11	19.3	39.1	28.1	0.30	0.18	0.57	0.06	3.54	0.86	6.99		1.97	17.10	0.132	4.97	32.87	
7	0	20.9	38.7	27.3	0.38	0.13	1.93	0.10	2.02	0.33	8.00		2.47	12.89	0.229	4.97	38.68	3
	9	19.3	39.1	28.1	0.26	0.11	1.77	0.10	2.79	0.76	7.60		2.15	15.98	0.176	4.13	28.35	
4	0	20.6	38.7	27.4	0.41	0.14	1.15	0.12	2.57	0.68	7.99		2.07	20.03	0.256	4.58	37.58	2
	11	20.2	38.9	27.7	0.39	0.14	1.25	0.10	4.62	1.13	8.37		1.86	23.79	0.230	3.90	27.86	
1	0	20.9	38.6	27.3	0.49	0.26	2.84	0.28	5.07	1.87	8.00		1.91	21.86	0.385	7.36	46.63	2
	7	21.0	38.7	27.3	0.46	0.21	2.59	0.23	3.56	1.92	8.24		3.72		0.420	6.17	41.77	
8	0	20.7	38.7	27.4	0.38	0.14	1.29	0.18	3.39	1.10	7.79	1.43	1.01		0.214	4.65	37.51	3
	9	19.7	39.0	27.9	0.35	0.12	1.63	0.15	4.36	1.30	7.30		2.66		0.211	3.73	30.63	
9	0	20.8	38.7	27.4	0.66	0.15	1.67	0.15	2.29	0.72	7.85	1.70	2.02	15.99	0.205	5.22	38.15	3
	9	20.5	38.9	27.6	0.40	0.12	2.08	0.15	3.20	1.00	7.53		2.46	18.26	0.234	5.52	36.40	
3	0	21.7	38.6	27.0	0.74	0.21	1.30	0.16	2.30	0.80	8.07	2.67	4.11	17.31	0.406	9.16	65.09	2
	8	20.7	38.8	27.5	0.92	0.24	1.46	0.16	2.88	0.88	7.67		3.19	19.90	0.361	7.10	49.21	

St.	Depth (m)	Temp. (°C)	Salinity	Density	TP (µM)	PO ₄ (µM)	NO ₃ +NO ₂ (µM)	NO ₂ (µM)	Si (µM)	NH ₄ (µM)	DO (mg/L)	BOD ₅ (mg/L)	Chl-a (µg/L)	TSS (mg/L)	TPP (µM)	PON (µM)	POC (µM)	SDD (m)
5	0	21.3	38.7	27.2	0.59	0.22	1.64	0.15	2.46	0.91	8.10	2.34	2.80	26.92	0.249	7.00	43.26	3
	12	20.3	38.9	27.7	0.47	0.18	1.51	0.16	3.14	1.17	7.60		1.19		0.219	4.02	24.18	
6	0	21.3	38.7	27.2	0.61	0.15	1.14	0.17	2.00	0.62	8.26	2.08	3.22	26.90	0.391	12.89	107.03	2
	11	21.1	38.8	27.4	1.10	0.24	1.63	0.19	2.32	0.75	7.86		2.71	27.60	0.367	7.04	50.11	
2	0	21.1	38.7	27.3	0.51	0.25	4.10	0.24	4.30	1.51	7.88	1.80	0.99	23.84	0.312	5.30	44.10	2
	12	20.8	38.8	27.5	0.47	0.11	1.59	0.17	3.05	1.19	7.60		2.03	25.64	0.295	5.56	37.02	
11	0	19.9	39.0	27.9	0.49	0.15	1.30	0.19	3.36	0.62	7.37	0.63	1.65	21.24	0.262	4.42	32.66	1
	13	18.8	39.2	28.3	0.39	0.11	1.18	0.11	3.80	0.34	7.26		0.60	23.01	0.202	3.31	27.11	
12	0	19.9	38.8	27.7	0.73	0.34	67.70	0.64	6.75	58.24	7.14	0.47	0.62	30.65	0.422	4.67	28.78	1
	8	19.5	39.0	27.9	0.47	0.30	52.18	0.53	6.13	47.03	7.05		1.22	31.90	0.399	4.04	24.28	
27	0	19.5	39.2	28.1	0.26	0.06	0.06	0.02	2.14	0.19	7.70		0.12	9.51	0.055	1.63	10.02	12
	24	18.5	39.3	28.4	0.18	0.04	0.06	0.02	16.88	0.13	7.60		0.23	10.60	0.055	1.49	9.15	
30	0	19.6	39.1	28.0	0.11	0.02	0.05	0.02	3.28	0.21	7.71		0.09	6.33	0.033	0.85	8.08	19
	30	18.3	39.3	28.5	0.13	0.02	0.07	0.02	4.68	0.13	7.65		0.12	8.08	0.052	1.32	10.05	
31	0	19.7	39.1	28.0	0.11	0.02	0.19	0.06	2.28	0.33	7.71		0.09	6.96	0.025	1.40	10.08	20
	20	19.2	39.2	28.2		0.02	0.16	0.05	2.85	0.14	7.70							
	40	18.3	39.3	28.5	0.16	0.02	0.06	0.02	4.05	0.13	7.69		0.20	8.71	0.057	0.96	6.69	
29	0	19.9	39.1	27.9	0.15	0.02	0.05	0.02	6.23	0.36	7.65		0.08	10.05	0.031	0.56	3.44	19
	10	19.5	39.1	28.1		0.02	0.06	0.02	6.03	0.34	7.64							
	30	18.4	39.3	28.4	0.20	0.02	0.14	0.03	5.01	0.18	7.64		0.22	11.45	0.098	1.56	11.73	
25	0	19.8	39.2	28.0	0.13	0.03	0.06	0.02	3.83	0.36	7.67	0.35	0.14	7.63	0.058	1.34	8.47	14
	19	19.1	39.1	28.2	0.22	0.04	0.06	0.02	3.97	0.18	7.82		0.26	13.09	0.074	2.11	15.32	

St.	Depth (m)	Temp. (°C)	Salinity	Density	TP (µM)	PO ₄ (µM)	NO ₃ +NO ₂ (µM)	NO ₂ (µM)	Si (µM)	NH ₄ (µM)	DO (mg/L)	BOD ₅ (mg/L)	Chl-a (µg/L)	TSS (mg/L)	TPP (µM)	PON (µM)	POC (µM)	SDD (m)
28	0	19.8	39.1	28.0	0.12	0.03	2.88	0.32	12.24	0.22	7.72	0.56	0.08	9.42	0.045	1.38	8.59	18
	25	19.1	39.2	28.2	0.15	0.03	0.19	0.09	3.57	0.13	7.75		0.06	25.09	0.031	1.75	12.36	
26	0	19.9	39.2	28.0	0.12	0.02	0.23	0.06	4.97	0.38	7.66	0.35	0.10	8.07	0.056	1.07	9.00	16
	22	19.0	39.1	28.2	0.39	0.09	0.84	0.09		0.45	7.83		0.40	9.53	0.051	1.16	9.69	
24	0	19.7	39.1	28.0	0.13	0.04	1.06	0.29	4.05	0.35	7.77	0.38	0.08	8.88	0.048	1.36	10.16	15
	21	19.1	39.2	28.2	0.20	0.08	3.68	0.37	56.39	1.12	7.63		0.67	16.78	0.067	2.10	15.02	
FEBRUARY 2015																		
St.	Depth (m)	Temp. (°C)	Salinity	Density	TP (µM)	PO ₄ (µM)	NO ₃ +NO ₂ (µM)	NO ₂ (µM)	Si (µM)	NH ₄ (µM)	DO (mg/L)	BOD ₅ (mg/L)	Chl-a (µg/L)	TSS (mg/L)	TPP (µM)	PON (µM)	POC (µM)	SDD (m)
31	0	15.1	37.6	27.9	0.27	0.07	6.56	0.48	6.68	0.39	8.38	0.61	0.73	19.98	0.109	1.33	12.47	
	20	16.6	38.8	28.5	0.15	0.03	1.82	0.16	2.40	0.19	7.65	0.27	0.33	20.97	0.076	1.14	7.79	
	36	16.4	38.8	28.6	0.17	0.03	1.93	0.11	2.26	0.17	7.52	0.07	0.45	20.70	0.061	0.48	3.19	
28	0	17.2	38.8	28.4	0.11	0.03	1.78	0.17	1.87	0.15	7.87	0.41	1.44		0.046	0.96	9.08	11
	20	17.2	39.0	28.5	0.11	0.03	0.47	0.11	1.48	0.15	7.62		0.43					
	27	17.1	39.0	28.6	0.11	0.03	1.10	0.15	1.61	0.21	7.56		0.36					
32	0	17.6	39.1	28.5	0.13	0.03	0.65	0.02	1.20	0.50	7.63		0.14		0.026	0.59	5.72	
	20	17.6	39.1	28.5		0.03	0.41	0.03	1.13	0.40	7.64		0.17		0.029	0.78	7.65	
	40	17.5	39.1	28.5		0.03	0.66	0.02	1.13	0.24	7.57		0.24		0.030	1.37	10.37	
7	0	14.5	37.1	27.7	0.41	0.10	12.55	0.56	9.87	2.69	7.65		2.21		0.250	2.86	26.27	

St.	Depth (m)	Temp. (°C)	Salinity	Density	TP (µM)	PO ₄ (µM)	NO ₃ +NO ₂ (µM)	NO ₂ (µM)	Si (µM)	NH ₄ (µM)	DO (mg/L)	BOD ₅ (mg/L)	Chl-a (µg/L)	TSS (mg/L)	TPP (µM)	PON (µM)	POC (µM)	SDD (m)	
33	0	16.0	36.1	26.6	0.42	0.15	13.68	0.64	11.09	2.62	8.84	0.96	2.22		0.374	5.94	42.27	1.5	
	10	16.5	38.8	28.6	0.44	0.14	5.39	0.47	4.12	1.30	8.12		2.32		0.163	3.34	27.26		
23	0	16.6	37.9	27.8	0.19	0.07	4.76	0.33	3.83	0.97	8.20	0.82	0.95		0.078	2.12	22.72	3.5	
	17	16.8	38.9	28.6	0.26	0.06	1.87	0.30	2.21	0.84	7.66		0.43		0.053	1.13	8.50		
17	0	16.3	37.5	27.6	0.30	0.09	8.37	0.52	5.90	1.63	8.45	0.75	0.41		0.107	1.82	16.90	3.5	
	8	17.0	38.7	28.4	0.38	0.12	5.55	0.54	4.80	4.47	8.06		2.05		0.148	2.33	20.43		

APPENDIX B. GEOCHEMICAL PARAMETERS MEASURED IN SURFACE SEDIMENTS

St.	TC (mg/g)	TOC (mg/g)	TC (mmol/g)	TOC (mmol/g)	TN (mg/g)	TN (mmol/g)	TPP (mg/g)	PIP (mg/g)	POP (µg/g)	TPP (mmol/g)	PIP (mmol/g)	POP (µmol/g)	Coarse >63 µm	Mud <63 µm
13	73.84	7.09	6.15	0.59	0.30	0.02	0.22	0.18	36.13	0.007	0.006	1.17	96.79	3.21
14	49.58	2.08	4.13	0.17	0.24	0.02	0.36	0.35	13.31	0.012	0.011	0.43	89.63	10.37
15	45.91	3.32	3.82	0.28	0.31	0.02	0.53	0.49	39.34	0.017	0.016	1.27	81.77	18.23
16	50.89	6.98	4.24	0.58	0.74	0.05	0.60	0.52	81.22	0.019	0.017	2.62	48.80	51.20
18	45.46	5.45	3.78	0.45	0.55	0.04	0.53	0.48	55.34	0.017	0.015	1.79	49.23	50.77
17	46.43	2.34	3.87	0.20	0.20	0.01	0.44	0.41	33.61	0.014	0.013	1.09	87.56	12.44
23	42.61	6.49	3.55	0.54	0.62	0.04	0.53	0.47	62.23	0.017	0.015	2.01	41.05	58.95
21	112.46	2.13	9.36	0.18	0.22	0.02	0.24	0.17	65.88	0.008	0.006	2.13	97.40	2.60
22	47.47	2.01	3.95	0.17	0.19	0.01	0.37	0.37	5.07	0.012	0.012	0.16	94.94	5.06
20	44.46	7.71	3.70	0.64	0.72	0.05	0.53	0.45	83.53	0.017	0.014	2.70	44.44	55.56
19	48.18	5.87	4.01	0.49	0.53	0.04	0.51	0.45	58.41	0.016	0.014	1.89	53.52	46.48
27	40.15	7.43	3.34	0.62	0.69	0.05	0.50	0.42	77.93	0.016	0.014	2.52	29.79	70.21
30	38.53	7.47	3.21	0.62	0.82	0.06	0.50	0.40	99.68	0.016	0.013	3.22	29.08	70.92
31	40.56	6.97	3.38	0.58	0.79	0.06	0.51	0.40	107.35	0.016	0.013	3.47	28.23	71.77
29	40.69	7.15	3.39	0.60	0.81	0.06	0.51	0.41	98.97	0.016	0.013	3.20	34.09	65.91
25	45.83	7.53	3.82	0.63	0.64	0.05	0.50	0.43	65.86	0.016	0.014	2.13	45.69	54.31
28	47.73	7.16	3.97	0.60	0.67	0.05	0.52	0.46	63.16	0.017	0.015	2.04	29.42	70.58
26	47.34	6.37	3.94	0.53	0.70	0.05	0.51	0.42	84.59	0.016	0.014	2.73	36.23	63.77
24	42.61	7.53	3.55	0.63	0.80	0.06	0.50	0.42	79.66	0.016	0.013	2.57	46.25	53.75
10	74.37	3.31	6.19	0.28	0.27	0.02	0.31	0.30	10.09	0.010	0.010	0.33	91.13	8.87
7	51.32	4.12	4.27	0.34	0.36	0.03	0.33	0.26	71.51	0.011	0.008	2.31	68.13	31.87
4	51.47	8.77	4.29	0.73	0.63	0.04	0.36	0.30	64.78	0.012	0.010	2.09	70.20	29.80
1	57.65	23.39	4.80	1.95	2.39	0.17	0.63	0.52	105.12	0.020	0.017	3.39	39.85	60.15
8	54.32	4.44	4.52	0.37	0.40	0.03	0.30	0.26	36.42	0.010	0.008	1.18	60.79	39.21
9	48.83	7.67	4.07	0.64	0.83	0.06	0.48	0.39	90.08	0.015	0.012	2.91	61.86	38.14
3	48.22	14.26	4.01	1.19	1.39	0.10	0.50	0.41	86.16	0.016	0.013	2.78	33.63	66.37
5	45.25	10.70	3.77	0.89	1.22	0.09	0.52	0.41	102.76	0.017	0.013	3.32	37.67	62.33

St.	TC (mg/g)	TOC (mg/g)	TC (mmol/g)	TOC (mmol/g)	TN (mg/g)	TN (mmol/g)	TPP (mg/g)	PIP (mg/g)	POP (µg/g)	TPP (mmol/g)	PIP (mmol/g)	POP (µmol/g)	Coarse >63 µm	Mud <63 µm
6	41.19	12.11	3.43	1.01	1.29	0.09	0.52	0.42	102.36	0.017	0.014	3.30	33.01	66.99
2	46.74	5.20	3.89	0.43	0.57	0.04	0.39	0.34	49.14	0.012	0.011	1.59	46.13	53.87
11	46.91	6.93	3.91	0.58	0.51	0.04	0.46	0.42	39.89	0.015	0.014	1.29	71.82	28.18
13	66.39	3.85	5.53	0.32	0.26	0.02	0.29	0.26	29.70	0.009	0.008	0.96	79.25	20.75
FEBRUARY 2015														
St.	TC (mg/g)	TOC (mg/g)	TC (mmol/g)	TOC (mmol/g)	TN (mg/g)	TN (mmol/g)	TPP (mg/g)	PIP (mg/g)	POP (µg/g)	TPP (mmol/g)	PIP (mmol/g)	POP (µmol/g)	Coarse >63 µm	Mud <63 µm
31	39.62	7.95	3.30	0.66	0.97	0.07	0.37	0.24	129.93	0.012	0.008	4.19	7.17	92.83
28	40.72	6.79	3.39	0.57	0.89	0.06	0.48	0.37	109.83	0.015	0.012	3.55	19.99	80.01
32	44.17	9.15	3.68	0.76	1.27	0.09	0.47	0.31	165.25	0.015	0.010	5.34	11.82	88.18
7	48.98	13.65	4.08	1.14	1.57	0.11	0.56	0.29	273.78	0.018	0.009	8.84	44.72	55.28
33	34.13	2.98	2.84	0.25	0.53	0.04	0.51	0.43	81.15	0.016	0.014	2.62	57.30	42.70
23	42.76	6.35	3.56	0.53	1.02	0.07	0.49	0.41	81.50	0.016	0.013	2.63	32.44	67.56
17	43.66	1.67	3.64	0.14	0.30	0.02	0.41	0.36	50.04	0.013	0.012	1.62	86.54	13.46